

AN INVESTIGATION OF THE SYNTHESIS
OF SULFUR YLIDS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY

Robert Lee Burns

1966



This is to certify that the

thesis entitled

*An Investigation of the Synthesis
of Sulfur Ylids*

presented by

Robert L. Burns

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Robert D. Schuetz
Major professor

Date *2-22-67*

**AN INVESTIGATION OF THE SYNTHESIS
OF SULFUR YLIDS**

By

Robert Lee Burns

AN ABSTRACT

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

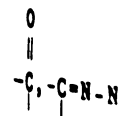
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Department of Chemistry

1966

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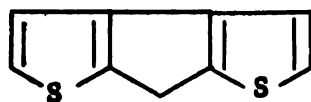
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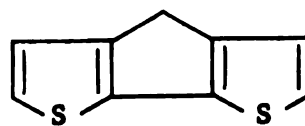
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ABSTRACT

The purpose of this investigation was the preparation of new sulfur ylids. Methods were developed to obtain cyclic dithiophenes of type I and type II.

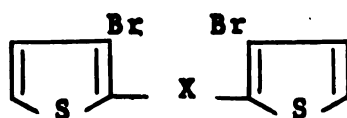
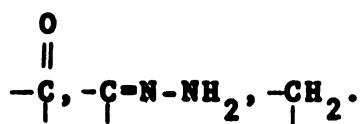


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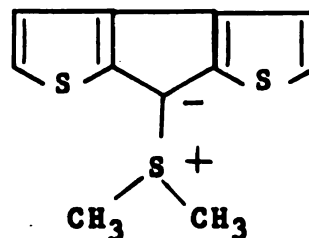


(II)

In the course of this study the preparation of 3-bromo- and 3,4-dibromothiophene was improved and methods were developed to obtain compounds of type IV where $X = \text{HC}-\text{OH}$,



(IV)



(III)

Contrary to reports (1), it was shown that some thienyl ketones can be reduced via a Wolff Kishner reduction to the corresponding dithienyl methane.

Various new N,N-dimethylcarboxamides of thiophene were prepared and treated with thienyllithium compounds. Substituted carboxamides were found to be unreactive while unsubstituted carboxamides produced ketones in high yield.

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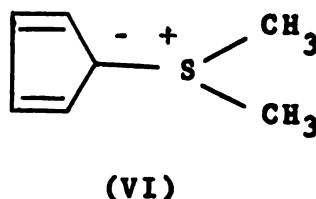
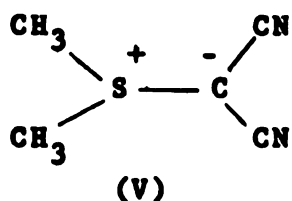
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Compound (I) was converted to the corresponding ylid (III) via the dimethyl sulfonium salt according to the method of Ingold and Jessop (2). The ylid was found to be unstable and decomposed after several minutes. The method of preparing sulfur ylids from sulfonium salts was expanded to include the preparation of dimethylsulfonium dicyanomethylide (V) and 5-dimethylsulfonium cyclopentadienylide (VI).



The preparation of dimethylsulfonium dicyanomethylide (V) was improved by effecting the dehydration of dimethylsulfoxide and malonylnitrile. This ylid decomposed by cleavage of the ylid bond, giving :C(CN)_2 and dimethyl sulfide. However, attempts to trap the carbene were unsuccessful.

The reverse process, the addition of carbenes to sulfides was suggested by the work of Speziale and Seyferth in 1960. They observed the interaction of phosphines with carbenes produced phosphinemethylenes. The extension of this work to include sulfides proved to be unsuccessful.

1. N. Lofgren and C. Tegner, *Acta Chem. Scand.*, 6, 1020 (1952).
2. C. Ingold and J. Jessop, *J. Chem. Sec.*, 713 (1930).

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ACKNOWLEDGEMENT

The author wishes to express his sincerest appreciation to Professor Robert D. Schuetz, research director and valued friend, whose enduring patience and guiding hand have been a prime factor in the success of this work as well as in his graduate studies.

Special gratitude is extended to his parents Mr. and Mrs. Robert C. Burns for their financial assistance and encouraging advice during the years of his education.

Most of all, the author expresses his appreciation to his wife, Judith, for her patience and understanding during the course of this investigation.

Finally, I wish to acknowledge the help and encouragement given me by the General Electric Company during the months required to write this thesis. I am indebted to the typist, Mrs. Carmella Ciaranello who spent numerous hours to convert this thesis into its present form.

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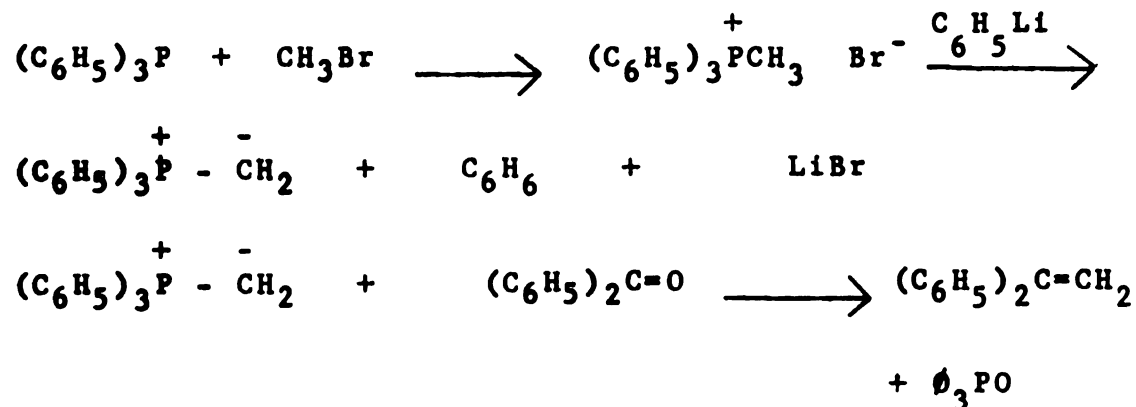
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INTRODUCTION AND HISTORICAL

While the reaction of phosphorus ylids with carbonyl compounds was discovered almost a half century ago by Staudinger and Meyer (Ref. 1) it is only within the last few years that its full potential and scope have been realized. Wittig and Schollkopf in 1954 (Ref. 2) showed that alkylidene- and arylidenetriphenyl- phosphoranes (*) react with carbonyl compounds to form an olefin, in which the carbonyl oxygen is replaced by a methylene group. Since that time numerous preparations and reactions of these ylids have been reported (Ref. 3). The process known as the Wittig reaction, is illustrated by,



Triphenylphosphine is allowed to react with methyl bromide to give triphenylmethylphosphonium bromide. Treatment of this salt with phenyllithium yields an alkylidenephosphine (an ylid) which on interaction with benzophenone forms 1,1-diphenylethylene and triphenylphosphine oxide.

(*) For nomenclature of these compounds see Ramires and Dershowitz, J. Org. Chem. 22, 41, (1957).

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(b) R

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An alkylidenetriphenylphosphorane may be represented as a resonance hybrid of contributing structures 1a and 1b, with a relative large contribution from the dipolar structure 1a (Ref.4).

Reaction of the ylid with a carbonyl compound involves attack by the nucleophilic carbon of the phosphorane on the carbonyl group and elimination of triphenylphosphine oxide, via a four membered cyclic transition state. The position of the double bond is never in doubt, even when it occupies an energetically unfavorable position.

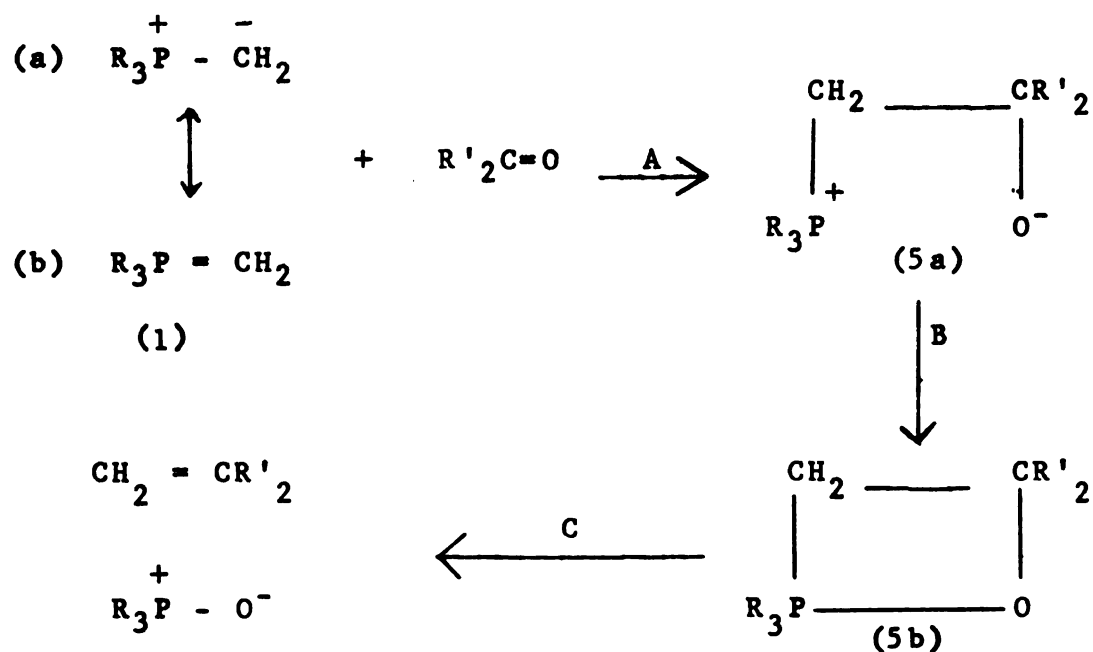


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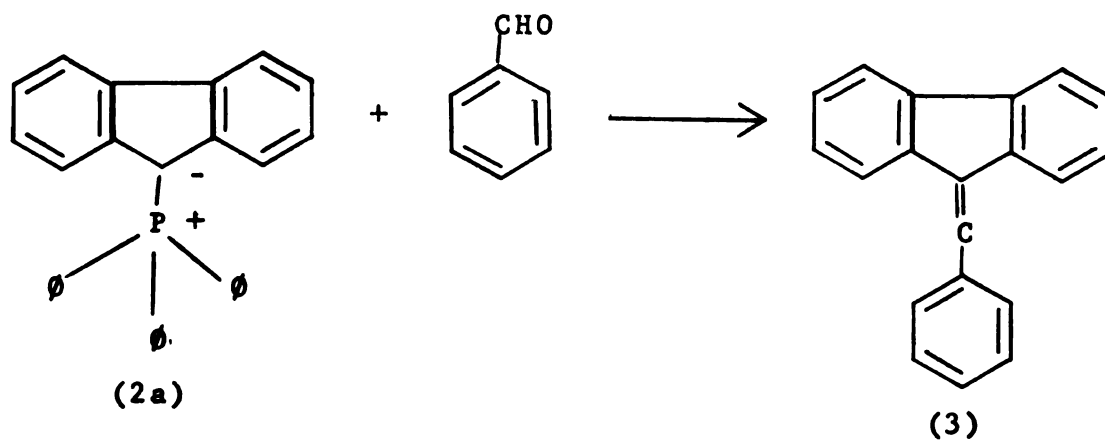
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As is apparent from the currently accepted mechanism (Ref. 5,6,7), (Chart 1) several factors control the success or failure of the three step Wittig reaction.

Step A, involving the attack of an anionic center at a carbonyl carbon, must be controlled in part by the polarity of the carbonyl group, and aldehydes would be expected to be more reactive than ketone. In fact, acetone, dimethylacetonedicarboxylate, cyclohexanone and fluorenone all failed to react with the triphenylphosphoniumfluorenylide (2a) whereas benzaldehyde reacted in high yield to give benzalfluorene (3) (Ref.8). Alkyl triphenylphosphinemethylenes (4b) fail to distinguish between and react equally well with both aldehydes and ketones (Ref. 9).

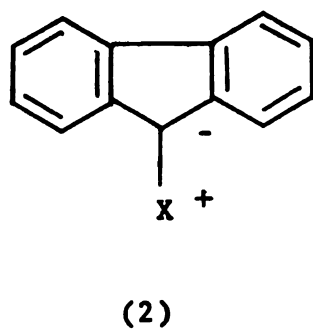
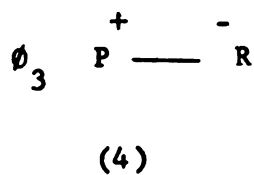
Thus, the reaction is facilitated by a highly polarized carbonyl group as demonstrated by the ease of reaction of triphenyl-phosphoniumfluorenylide (2a) with substituted benzaldehydes (Ref. 8). The triphenylphosphonium ylid (2a) exhibited selective reactivity with the aromatic carbonyl compounds in Table 1 since substitution by a group which increases the polarization of the benzaldehyde carbonyl group (e.g. nitro) facilitated the reaction (Ref. 8,10).

CHART 2

(4a) R = cyclopentadienyl

(4b) R = CH_2 (4c) R = $\text{CH}-\text{C}_6\text{H}_5$ (4d) R = $\text{CH}-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ (4e) R = $\text{CH}-\text{C}(=\text{O})-\text{O}-\text{Pr}$

(2a) R = fluorenyl

(2a) X = $\text{C}_6\text{H}_5_3\text{P}$ (2b) X = $(\text{CH}_3)_3\text{P}$ (2c) X = $(n\text{-Bu})_3\text{P}$ (2d) X = $\text{C}_6\text{H}_5_3\text{As}$ (2e) X = $(\text{CH}_3)_3\text{S}$

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Tri-*n*-butylphosphoniumfluorenylide (2c) reacted equally well with all substituted benzaldehydes but did show selectivity in reaction with a series of less polarized carbonyls. Thus, the trialkylphosphonium ylid is more reactive than its triphenyl analog (Ref.10).

The carbanion character of the attacking ylid should also affect Step A. Tending to decrease this character, and hence the ease of attack at the carbonyl group, will be resonance interaction ($p - p\pi$) with groups attached to the carbanion which delocalize the negative charge. In agreement with this postulate, Ramirez (Ref.11) reported that triphenylphosphoniumcyclopentadienyldide (4a), a stable and high melting solid, failed to react with aldehydes or ketones in the usual manner and it also resisted alkaline hydrolysis. The resonance stabilization afforded by delocalization of the electrons in the carbon 2p-orbital throughout the cyclopentadienyl ring together with the usual overlap with a 3d-orbital of phosphorus (Ref.24, 25) may account for this unusual stability.

The chemistry of fluorene is similar to that of cyclopentadiene but the former is considerably less reactive. In many cases this is due to a decreased tendency for electron delocalization in the fluorenyl anion compared to that in the cyclopentadienyl anion.

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TABLE 1Reaction of Ylids with Aromatic Carbonyl Compounds

% yield of olefin with

<u>Carbonyl Compound</u>	<u>Triphenyl Ylid (2a)</u>	<u>Tri-n-butyl Ylid(2c)</u>
<u>Aldehydes</u>		
p-nitrobenzaldehyde	96	99
p-chlorobenzaldehyde	93	96
benzaldehyde	84	96
p-anisaldehyde	37	94
p-dimethylaminobenzaldehyde	0	94
<u>Ketones</u>		
m-nitroacetophenone		67
p-nitroacetophenone		60
p-chloroacetophenone		9
acetophenone		0

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An examination of the chemistry of (2a) the fluorenyl derivative, compared to that of (4a) the cyclopentadienyl derivative, reflects this difference (Ref.8). Triphenylphosphoniumfluorenylide (2a) is thus intermediate in reactivity between the alkyl (4b) and cyclopentadienyl (4a) derivatives (Ref.8). It may be concluded that the π -orbitals of the fluorenyl portion of the molecule compete favorably with the 3d-orbital of phosphorus for the available electron pair in the carbon 2p-orbital and such interaction affords added stability to the molecule. It is also evident that the effect of the electronic structure of the phosphinemethylene (in terms of the degree of localization of charge at the attacking carbon) on the reaction is also in accord with the proposed reaction mechanism. Triphenylphosphinebenzoylmethylene (4d) (Ref.26). and triphenylphosphinecarbethoxymethylene (4e)(Ref.27,28)reacted with benzaldehyde but failed to react with cyclohexanone in the usual manner. In both examples there is an available "electron sink" to compete with the 3d-orbital of phosphorus for the electron pair on carbon, thereby increasing the stability and decreasing the reactivity of these reagents.

These results verify that the particular groups attached to the carbanion will decrease the reactivity of the ylid in proportion to their electron withdrawing power.

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The extent of (2p - 3d) d-orbital resonance (i.e. the contribution of structure 1b to the resonance hybrid) between the carbanion and the phosphorus atom should also affect the carbanion character of the ylid. The less the contribution of form 1b to the resonance hybrid the greater should be the reactivity of the ylid (i.e. the more reactive and less stable reagent should possess the largest dipole character; the largest concentration of negative charge on the carbon next to phosphorus). The degree of d-orbital resonance hinges upon a large formal positive charge on the phosphorus atom (Ref.12) and it is apparent that substituents (R in 4 p. 4) can therefore effect the extent of such resonance through electronic interaction with the phosphorus atom. Jaffe (Ref.13,14), Rao et al. (Ref.15), and Mann (Ref.16), have shown that there are no resonance interactions between benzenoid rings and tetravalent phosphorus atoms. As a result, any interaction affecting the degree of positive charge on phosphorus must be of an inductive type. It is to be expected that the larger the -I (electron withdrawing) effect of the phosphorus substituents the greater should be the operation of d-orbital resonance in the ylid.

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This expectation is verified by four illustrations from the literature. Chatt et al. (Ref.17), recently reported that in planar complexes of the type trans-(L, piperidine PtCl₂), a larger ligand field splitting (a measure of the extent of d-orbital resonance between the metal atom and phosphorus) is shown for L = P(OCH₃)₃ than for L = P(CH₃)₃, as was expected on the basis of a larger -I effect for the methoxyl group. Earlier, Chatt and Williams (Ref.18), showed, via the "trans effect", that the π -bonding ability of trivalent phosphorus decreased in the order PF₃ > PCl₃ > P(OCH₃)₃ > P(CH₃)₃, which is the same as the order of decreasing inductive electron withdrawing (-I) effect of the substituents. More recently, Meriwether and Fiene, (Ref.19), using infrared spectra studies on nickeldicarbonyl-diphosphines, determined the order PCl₃ > P(OEt)₃ > P(C₆H₅)₃ > P(C₄H₉)₃ for decreasing participation in d-orbital resonance. Similar conclusions have been reached by Wilkinson et. al. (Ref.20), from an examination of the infrared spectra of compounds of type L₃Mo(CO)₃ where L = ligand group.

Phenyl substituents in phosphonium ylids (1, p2 R = phenyl) would be expected to increase the formal positive charge on phosphorus via a -I effect (Ref.21). and therefore permit a large contribution of form 1a to the resonance hybrid. On the other hand alkyl substituents would be

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expected to decrease the contribution of form 1a by a + I effect. As a result trialkylphosphonium ylids (2c, p4) would be expected to be more reactive than triphenylphosphonium ylids (p4) and therefore undertake step A with greater ease.

Additional evidence bearing on this expectation are provided by an examination of the pKa's of the conjugate acids of several onium fluorenylide reported in Table 2.

Table 2 pKa of Fluorenyl Ylid Conjugate Acids (Ref. 10)

<u>Fluorenylide</u>	<u>pKa</u>
triphenylphosphonium (2a)	7.5
triphenylarsonium (2d)	7.8
tri-n-butylphosphonium (2c)	8.0
dimethylsulfonium (2e)	7.3

It is to be expected that the greater the contribution of form 1b (d-orbital resonance) to the resonance hybrid the more acidic will be the conjugate acid. Therefore, the more acidic conjugate acid should afford the least reactive ylid. This is in fact the case as the acidity of the fluorenylide conjugate acids decrease in the order dimethylsulfonium (2e) > triphenylphosphonium (2a) > triphenylarsonium (2d) > tri-n-butylphosphonium (2c) but the reactivity decreases in the opposite order.

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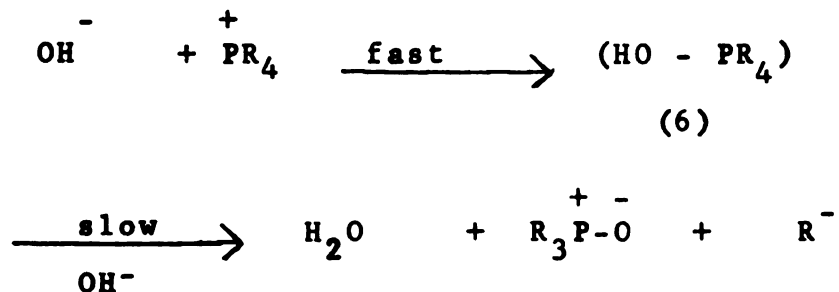
(Ref. 22, 10). Hence a measurement of the pK_a value allows a prediction of the expected reactivity of an ylid.

The higher stability of the triphenylphosphonium ylid (p4) compared to that of the trialkylphosphonium ylids (2c p4) toward hydrolysis is also consistent with a higher degree of d-orbital resonance in the former.

The factors affecting the ease with which step B occurs have not been determined. Levisales (Ref. 3) and Wittig (Ref. 2), explain the reported failure of trimethylphosphonium ylid (2b p4) to undergo a Wittig reaction by failure of (5a, p2) (R = alkyl) to form a pentacovalent intermediate (5b, p2) by way of step B, due to the electron donating inductive effect of alkyl groups inhibiting the attack of the oxyanion on phosphorus. In view of the recent report (Ref. 23) on the kinetics of the reaction of quaternary phosphonium salts with hydroxide ion in which the first step (fast) was the attack of hydroxide ion on the salt to form a pentacovalent intermediate (6 p12), Johnson (Ref. 10) suggests that it is unlikely that the similar conversion of (5a) into (5b p2) (step B) controls the success of the Wittig reaction, regardless of the nature of the phosphorus substituents whether they be alkyl or phenyl.

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Little is known regarding the factors affecting step C, p2 of the reaction. Johnson (Ref. 10), considers this step to be similar to the slow step of the hydroxide decomposition of phosphonium salts (Ref. 23), in which the pentacovalent intermediate (6) undergoes an electron shift and loss of a hydrocarbon group with its electrons. The ease of departure of the hydrocarbon group paralleled its stability as an anion. The same electron shift takes place in step C of the Wittig reaction and if the same effect is operative, that is the electron withdrawing ability of the group CR'_2 , and this controls the decomposition of (5b p2), two intermediates differing only in the nature of the group R should decompose at nearly the same rate. Apparently this is not the case for there are differences in the reaction rates of the ylids (2a p4) (triphenyl) and (2c p4) (tri-n-butyl) with p-dimethylaminobenzaldehyde. (Ref. 10).



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It is apparent that the course of the Wittig reaction and the relative ease with which various ylids and carbonyl compounds react can best be accounted for on the basis of the initial condensation (step A) being rate controlling. Steric effects, if important, may result in step B becoming rate controlling. However, in all cases to date steric effects have been found not important. Undoubtedly a specially designed example in which it is sterically impossible or highly unfavorable to bring the phosphonium and oxyanion groups together could be found and would permit isolation of an intermediate (5a, p2). Thus, the Wittig reaction will probably evolve as another case where either electrical or steric effects may be of major importance, depending on the reactants involved.

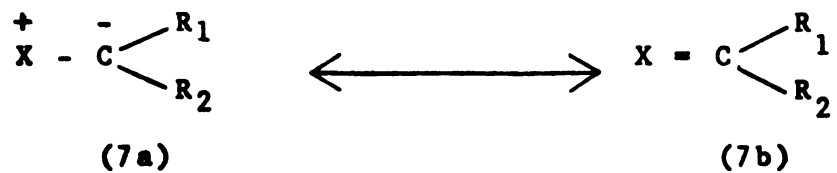
The Wittig reaction is known to fail unless the hetero atom (X) is capable of stabilizing the adjacent negative charge above and beyond coulombic interaction, in addition to any delocalization afforded by the groups R_1 and R_2 (Ref.29).

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Since the bulk of this stabilization is derived from valence shell expansion of the hetero atom (Ref. 10,2,3) via resonance from 7b, any other atom X capable of behaving likewise should yield an ylid capable of undergoing a Wittig reaction.

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Thus, it became obvious that ylids containing hetero atoms other than phosphorus should be capable of existence. The major requirement appeared to be the ability of the hetero atom to stabilize the ylid carbanion, usually by overlap of the free electron pair with the vacant, low energy d-orbitals of the hetero atom. In instances where this was not possible, such as many nitrogen ylids (Ref.30), the substances were capable of only fleeting existence.

In more recent years Johnson (Ref. 22) and Wittig (Ref.31), have investigated the chemistry of ylids containing group V hetero atoms other than phosphorus. It was thought feasible that sulfur should behave similar to phosphorus in the formation of ylids since sulfur has been shown to be capable of expanding its octet to a decet. Doering and Hoffmann (Ref.32) observed that in deuterium exchange experiments with trimethylsulfonium and tetramethylphosphonium salts the heats of activation were lowered from the expected values (calculated on the basis of coulombic interactions) by 17.2 and 15.4 kcal. respectively. This lowering was ascribed to resonance stabilization of an ylid type intermediate through the use of 3d-orbitals in each case. In a less precise but analogous manner they indicated that in proceeding down the group V elements, the

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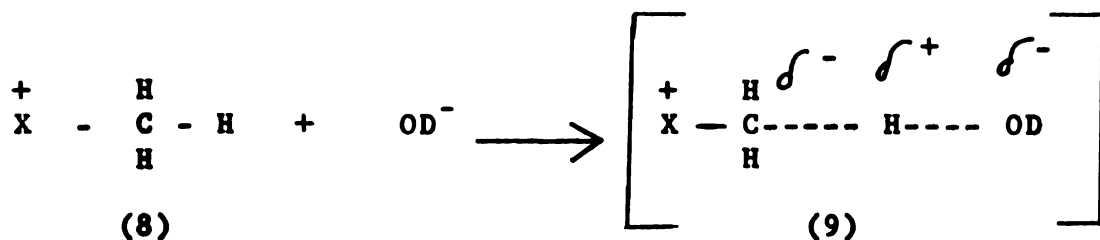
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contribution of d-orbital resonance should remain nearly constant, the rate of exchange decreasing in proportion to and due solely to the increase in bond distance.

The removal of a proton through a transition state such as (9) would be promoted in part by the electrostatic stabilization of the carbanion by X^+ and, for the second row elements, in part by resonance interaction involving acceptance of electrons by the sulfur or phosphorus through utilization of 3d-orbitals.



The total stabilization should be larger for the second row elements, which can expand their valence shell to accept a pair of electrons in addition to stabilizing the carbanion by electrostatic interaction.

TABLE 3Deuterioxide Catalyzed Deuterium Exchange
of Methyl "Onium" Salts (Ref. 4)

<u>Compound</u>	<u>% Exchange</u>
$\text{Me}_4\text{N}^+ \text{I}^-$	1.13*
$\text{Me}_4\text{P}^+ \text{I}^-$	73.90
$\text{Me}_4\text{As}^+ \text{I}^-$	7.44
$\text{Me}_4\text{Sb}^+ \text{I}^-$	0.78
$\text{Me}_3\text{S}^+ \text{I}^-$	98.00
$\text{Me}_3\text{Se}^+ \text{I}^-$	13.20
$\text{Me}_3\text{Te}^+ \text{I}^-$	3.99

*Run at a much higher temperature and a longer period of time.

There are numerous other examples of the ability of sulfur to stabilize adjacent carbanion centers in reaction intermediates through octet expansion (Ref. 4,33). Ultraviolet and infrared spectroscopic studies have provided additional evidence of this phenomenon (Ref. 33, 34, 35, 36, 37). Therefore, a sulfur group appears to fulfill the electronic requirements for participation in a Wittig type reaction.

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The study of sulfur ylids began in 1930 with the preparation of dimethylsulfoniumfluorenylide (2e p4) by Ingold and Jessop (Ref. 38). This relatively unstable, yellow compound was prepared by treating the sulfonium salt of dimethyl sulfide and 9-bromofluorene with sodium hydroxide, ammonium hydroxide or barium hydroxide. The ylid was insoluble in water and ether but soluble in benzene and hydrochloric acid, which converted it to the original sulfonium salt. 9-Fluorenyldimethylsulfonium bromide was decomposed with hot water to give 9-fluorenyl alcohol and when treated with aqueous sodium picrate yielded 9-fluorenyldimethylsulfonium picrate. Pyrolysis of the ylid produced gaseous dimethyl sulfide and a red amorphous product from which fluorene could be distilled.

The dipole moment of the ylid (2e) is reported to be 6.2D. (Ref. 39), which is significantly lower than those of other fluorenylides. The hydrobromide of the ylid (2e p20) had a pK_a of 7.3 (Ref.10). From a study of the pK 's of the fluorenylide hydrobromides Johnson (Ref.10) has shown the sulfur ylid (2e p20) to be the least basic, and suggested that the tetravalent form (2e' p20), the result of octet expansion with its accompanying resonance stabilization, makes a greater contribution to the structure of the resonance hybrid of

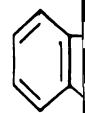
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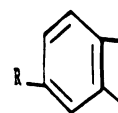
the sulfur ylid (2e p20) than in the case of the other ylids. This was further substantiated by examination of the dipole moment which was significantly lower than those of the other fluorenylides. However, the larger numerical value of the dipole moment was interpreted by Price and Oae (Ref. 4) to indicate that the contribution of the structure (2e' p20), the tetravalent form, is small and that the compound is primarily dipolar in character (2e p20).

In 1935 Hughes and Kuriyan (Ref. 40) attempted to stabilize the ylid (2e p20) by introducing nitro groups in the fluorenyl portion of the molecule. One nitro group stabilized the ylid to the extent that the purple compound (10a p20) could be kept for several days without decomposition. The introduction of two nitro groups into 9-bromofluorene inhibited sulfonium salt formation with dimethyl sulfide. 9-Fluorenyl-dimethyl-sulfonium picrate, however on direct nitration and treatment with base gave a 2,7-dinitro sulfur ylid (10b p20). This ylid was found to be stable at ordinary temperatures. Upon heating in nitromethane, these ylids (10 p20) decomposed rapidly to give the corresponding nitro-bisdiphenylene-ethylene (11 p20)



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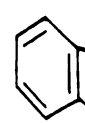
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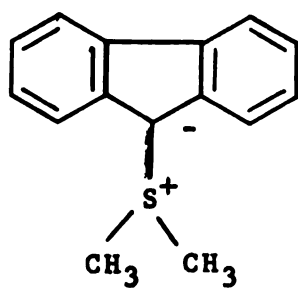
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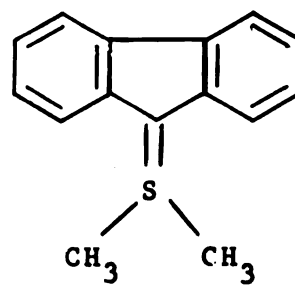
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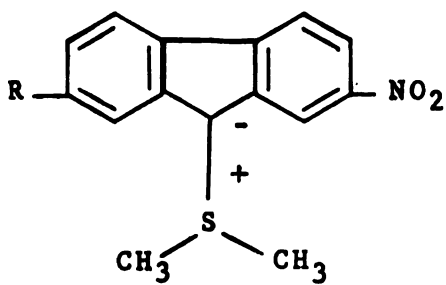
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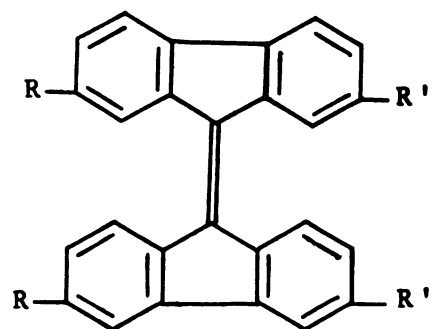
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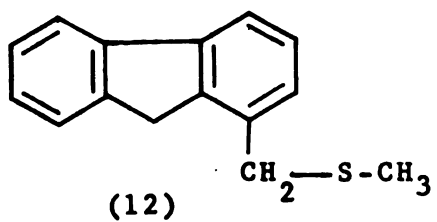
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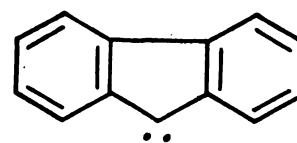
(10a) R=H

(10b) R=NO₂(11a) R=H, R'=NO₂(11b) R=R'=NO₂

(11c) R-R'=H



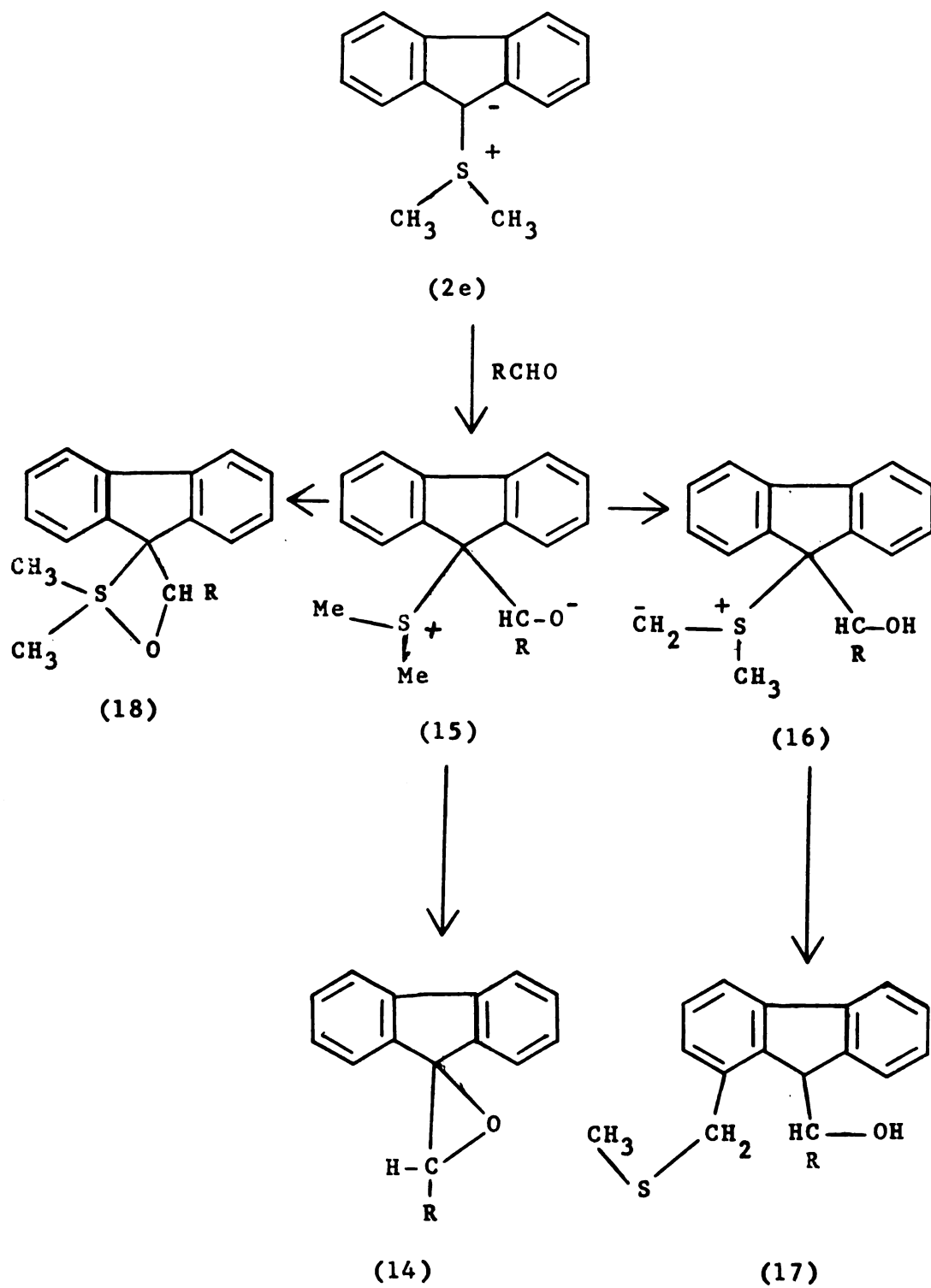
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In 1961 Johnson (Ref.29) reopened the study of sulfur ylids through his investigation of ylids containing hetero atoms other than phosphorus. Base catalyzed hydrolysis of (2e p20) failed to afford fluorene as had the other fluorenylides, but its hydrobromide was readily hydrolyzed to fluorenol in warm water, a reaction that failed with the other ylids. Extended treatment of the ylid (2e p20) with a methanolic sodium hydroxide solution gave 1-methylthiomethylfluorene (12 p20), the result of an internal anionic Sommelet rearrangement. Chromatography of the ylid (2e p20) on neutral or slightly basic alumina afforded difluorenylidene (11c p20) and fluorenone. This transformation likely occurred by decomposition of the ylid to dimethyl sulfide and the methylene derivative (13 p20); the later then dimerized to difluorenylidene or reacted with oxygen to form fluorenone (Ref.41). Franzen (Ref.42) has recently postulated the analogous decomposition of 9-trimethylammonium fluorenylide into the carbene (13p20) followed by its subsequent reaction with other amines. The coupling of carbenes with nucleophiles to form ylids, the reverse of the above decomposition, has been reported recently (Ref. 43, 44).

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The reaction between the sulfur ylid (2e p22) and benzaldehydes (Ref. 29) did not give benzalfluorenes as expected from the work with phosphorus and arsenic ylids, instead benzalfluorene oxides (14 p22) and phenyl-9-(1-methylthiomethyl)-fluorenylcarbinols (17 p22) were formed. The mechanism shown in Chart 4 was proposed to account for the observed products and, according to Johnson and LaCount, was based on the relative carbonyl reactivity sequence, analogous with other sulfonium salts displacements, and the analogy with the known Sommelet rearrangement of the original ylid.

Since all ylids are nucleophiles of varying strength, it was expected that the sulfur ylids would undergo at least the first step of the Wittig reaction, i.e, the attack of the ylid carbanion on the carbonyl carbon to form a betaine intermediate (15 p22). The two mechanism apparently diverge in the second step. Two explanations are possible. In spite of the greater ability of sulfur over phosphorus to stabilize an adjacent negative charge by valence shell expansion (Ref. 32), sulfur is apparently less able to form a formally bonded intermediate of highly covalency, at least to the extent required in the Wittig reaction. Thus, the oxyanion (15 p22) failed to attack the tervalent sulfur to form the required intermediate (18 p22). The greater electron withdrawing

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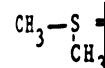
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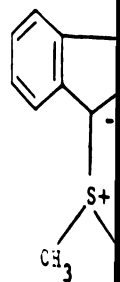
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power of the dimethylsulfonium group over the tri-substituted phosphorus group would be expected to facilitate the displacement of the dimethylsulfonium group from the C-9 carbon of fluorene. Johnson, has shown, for example, that dimethylfluorenylsulfonium bromide is hydrolyzed to fluorenol in aqueous solution whereas triphenyl- or trimethylfluorenylphosphonium bromides are inert under these conditions (Ref.29) There exists an additional example of this phenomenon in the early work of Ingold and co-workers (Ref.45) wherein they found that phosphonium salts, when treated with sodium hydroxide, afforded a phosphine oxide and a hydrocarbon via direct attack of hydroxide ion on the phosphorus atom to form a pentacovalent intermediate. This mechanism has recently been supported by Van der Werf, et. al. (Ref.46). On the other hand, sulfonium salts under the same conditions gave either an alcohol or olefin together with a thioether. In each instance, the hydroxide ion did not attack the sulfur atom but rather an adjacent carbon. Thus, tervalent sulfur is not attacked by an anionic reagent as is tetravalent phosphorus and arsenic.

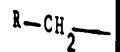
Bond energy differences between phosphine oxides and sulfoxides are the fundamental reason behind the change in mechanism in going from phosphorus to sulfur



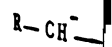
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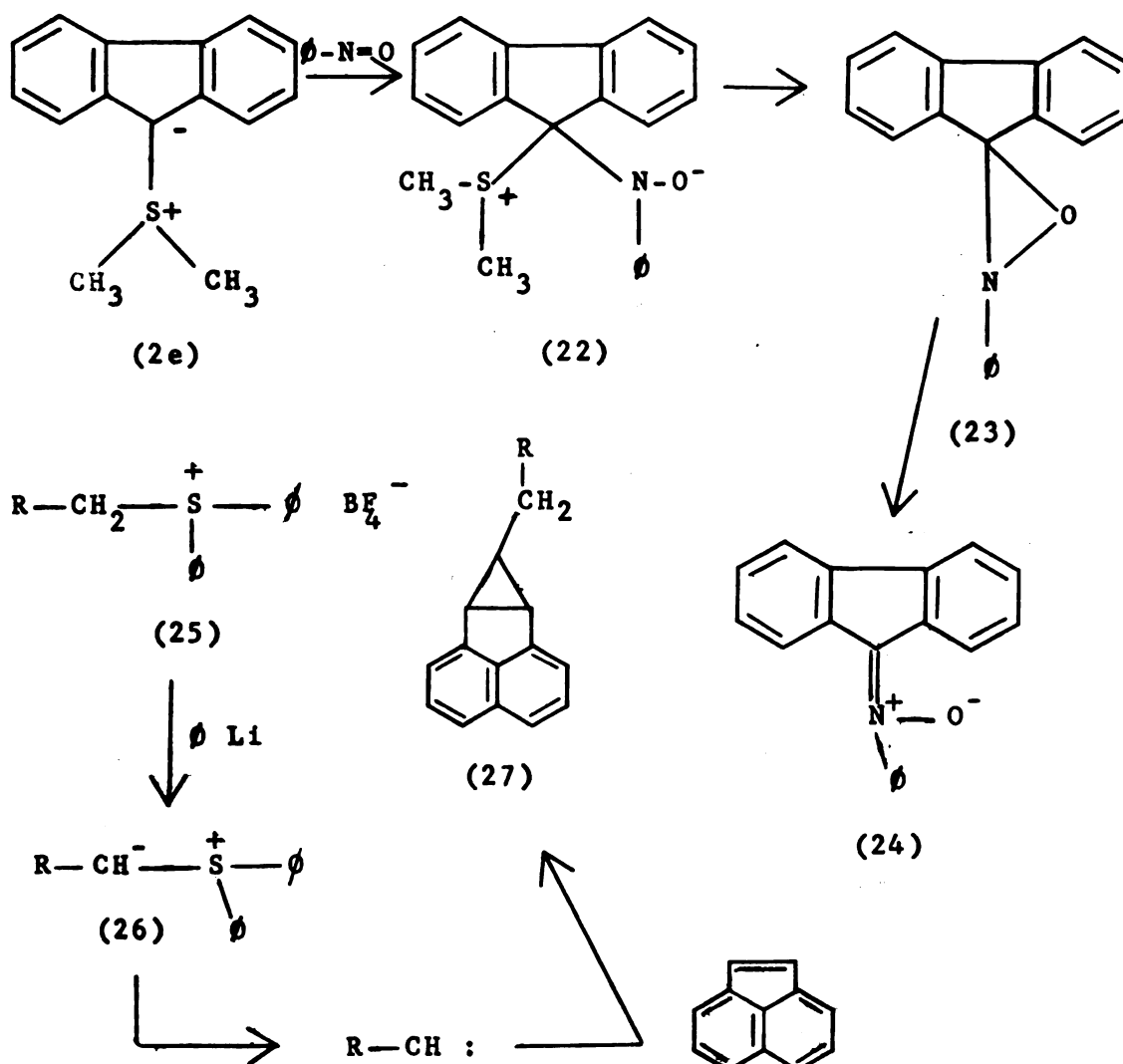
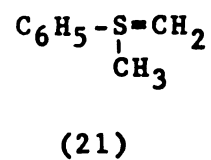
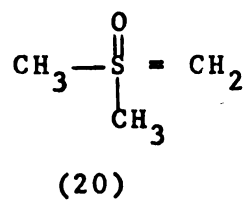
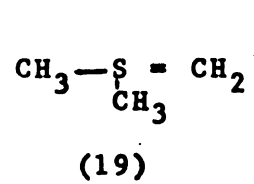
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and their respective reactions with carbonyl compounds. Thus, epoxide formation, rather than olefin formation as in the Wittig reaction, was not wholly unexpected on the basis of the differences in bond dissociation energies of dimethylsulfoxide (89 kcal/mole) (Ref. 47) and triphenylphosphine oxide (128 kcal/mole) (Ref.48) and the known reluctance of hydroxide to attack trivalent sulfur but not tetravalent phosphorus (Ref.45).

On the basis of this work Johnson et. al. (Ref.49) predicted that most, if not all, sulfonium ylids would form epoxides upon reaction with aldehydes and ketones. This expectation has been verified in the much later work reported by Corey, et. al., with dimethylsulfonium methyllide (19 p25) (Ref. 51) and dimethylsulfoxonium methyllide (20 p25) (Ref. 50) and the more recent reports by Franzen and co-workers using phenylmethylsulfonium methyllide (21 p25) (Ref.52, 53)

The other product (17 p22) obtained in the Wittig type reaction with benzaldehydes was accounted for by an intramolecular proton transfer in (15 p22) to form a new intermediate ylid (16 p22). This transformation should be quite facile since the sulfonium group is an excellent proton labilizing group and the oxyanion is a sufficiently strong base (Ref.33). The intermediate (16 p22) is then converted into the observed alcohol

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(17 p22) by a Sommelet rearrangement analogous to that occurring with the ylid itself (Ref. 5, 4).

By analogy with its reaction with benzaldehydes Johnson (Ref. 55) expected the sulfur ylid (2e p25) to react with nitrosobenzene to give the oxazirane (23 p25). However, this was not the case and a nitron (24 p25) was formed. Due to the facile rearrangement of N-phenyl oxaziranes (Ref. 57), Johnson concluded that the oxazirane (23 p25) was in fact the initial product of the ylid reaction but that it had isomerized to the nitron under the reaction conditions. This sequence of reactions is presented in Chart 5 p25.

It was conceivable that the sulfur ylids were first decomposed to a carbene which then reacted with nitrosobenzene to form the nitron rather than the oxazirane. Franzen (Ref. 56) has shown that nitrogen ylids can be decomposed to carbenes and several of the by-products from the reaction of the sulfur ylid (2e) with carbonyl compounds were best accounted for by decomposition of (2e p25) to the fluorenyl carbene (13 p20) (Ref. 29). More recent work (Ref. 57) has demonstrated that other sulfur ylids can be decomposed under mild conditions to carbenes which can in turn be trapped with acenaphthylene. Benzyl diphenylsulfonium tetrafluoroborate (25a p25)

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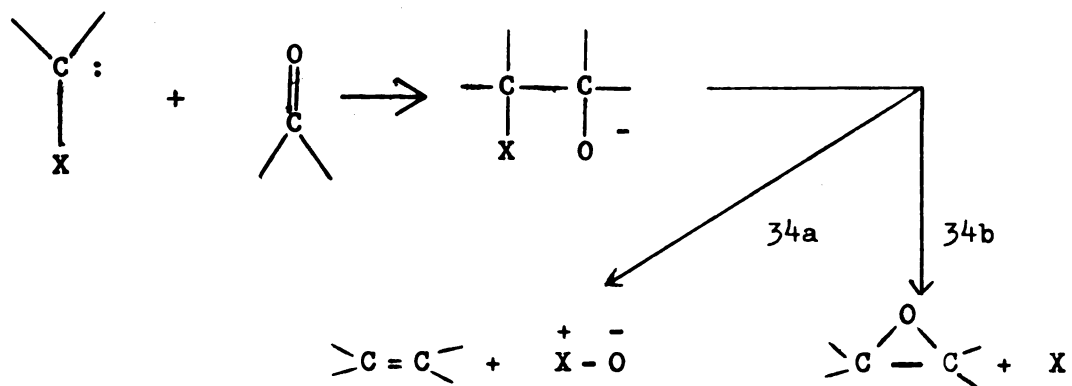
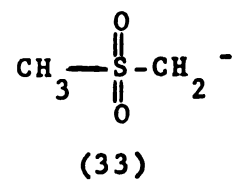
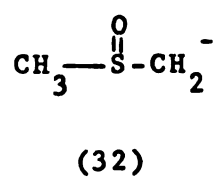
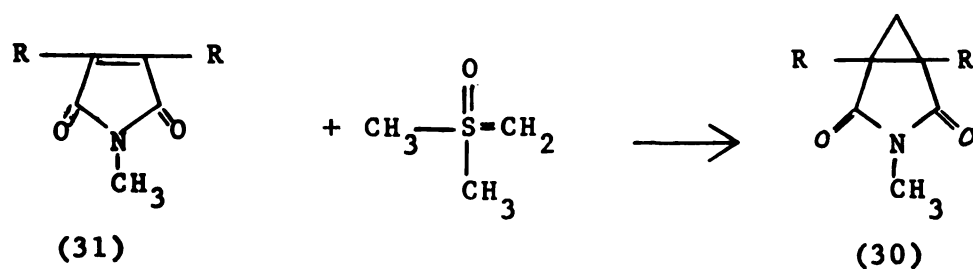
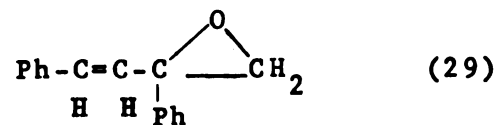
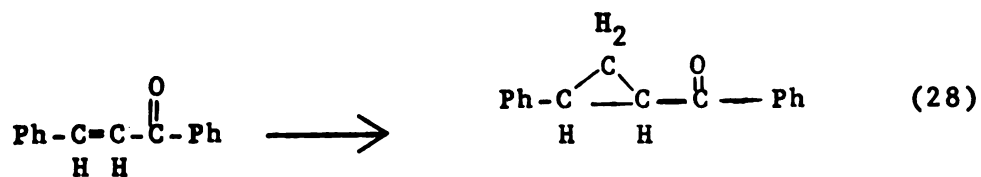
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was treated with n-butyl lithium to form the ylid (26a p25) which then reacted with acenaphthylene to form the adduct (27a p25).

Franzen and co-workers have reported a similar reaction with n-butyldiphenylsulfonium tetrafluoroborate (25b p25) (Ref. 58). However, all attempts to trap the carbene with cyclohexane were unsuccessful. Rotherberg and Thornton (Ref.59, 60, 61) have shown that decomposition of p-nitrobenzyldimethylsulfonium tosylate in aqueous sodium hydroxide does not proceed by way of the carbanion mechanism but most likely proceeds via a carbene intermediate. Elimination reactions of the ylid, and their reaction mechanisms under the influence of strong base have been reviewed (Ref. 79).

Several years ago Corey and Chayovsky described the reaction of dimethyloxosulfonium methylide (20 p25) with certain carbonyl compounds to give oxiranes by methylene transfer and also observed that conjugated carbonyl compounds which are receptive to a Michael condensation reaction afford cyclopropyl derivatives instead of oxiranes with this reagent (Ref. 50, 51). More recently Corey and co-workers reported that the more reactive dimethylsulfonium methylide (19 p 25) could also be used for oxirane synthesis from aldehydes and ketones and that this was the preferred course of methylene

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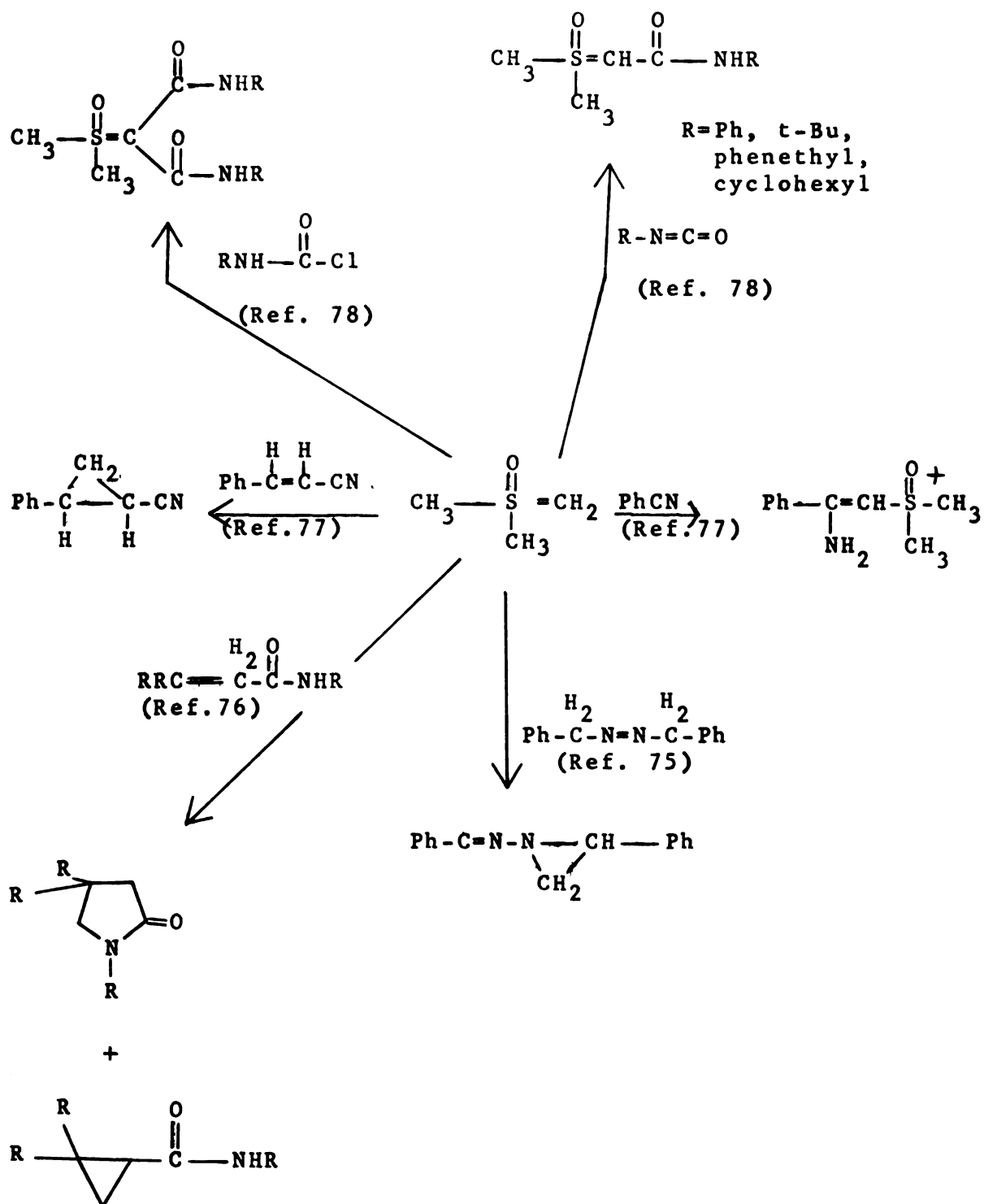
transfer even with Michael acceptors which gave cyclopropanes with (20 p25) (Ref.51, 62). Conflicting with this was the work of Franzen and Driessen (Ref. 52) who reported that the ylid (20 p25) and phenylmethylsulfonium methylide (21 p25) converted benzalacetophenone to the corresponding cyclopropane (28 p29). However, Corey and Chaykovsky have repeated this work and found that the oxirane (29 p29) was the only product and not the cyclopropane derivative (Ref. 64).

Synthetic application of dimethylsulfoxonium methylide was reported by Izzo who prepared some aryl cyclopropanedicarboximides (30 p29) from arylmaleimides (31 p29) (Ref.65).

Metzger and co-workers (Ref. 75, 76, 77, 78) have treated dimethylsulfoxonium methylide (20 p31) with nitriles, isocyanates, carbamoyl chlorides, and azo compounds to produce some rather exotic compounds as indicated in Chart 7 p31.

Simultaneously Corey and Chaykovsky (Ref. 63) and Walling and Boblyky (Ref. 66) have indicated that both the methylsulphinyl carbanion (32 p29) and the methylsulphonyl carbanion (33 p29) reacted with benzophenone to form a mixture of mainly diphenylmethane, 1,1-diphenylethylene, and diphenylacetaldehyde.

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Diphenylmethane was shown to have been formed from 1,1-diphenylethylene; however an explanation for the formation of diphenylacetaldehyde is lacking. The acetaldehyde was thought to have arisen via rearrangement of 1,1-diphenylethylene oxide, the supposed original product formed by path (34b p29). However, Cope and co-workers (Ref. 67) have shown this rearrangement fails to proceed in basic media.

Recently Johnson undertook a search for other groups which were capable of acting as leaving groups in the Wittig synthesis of olefins (path 34a p29) or in the synthesis of epoxides (path 34b p29). The phenylsulphonyl group was used due to the availability of sulphones and their ability to follow either (path 34a p29) leaving as the benzenesulphonate ion, or (path 34b p29) leaving as the benzenesulphinate ion. 9-Phenylsulphonyl-fluorene (35 p33) was quantitatively converted to its stable anion (36 p33) with strong base; treatment with nitrosobenzene afforded N-phenyl-fluorenone ketoxime (38 p33) as indicated in Chart 8 p33 (Ref. 68). By analogy to the behavior of the sulphur ylid, 9-dimethyl-sulfonium fluorenylide (2e p25) in its reaction with nitrosobenzene, the initial product from the above reaction is probably the oxazirane (37 p33). The latter has been shown to rapidly rearrange to the nitrone

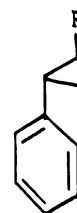
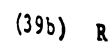
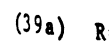
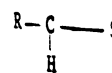
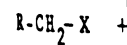
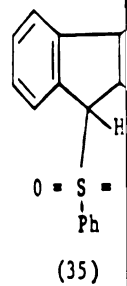
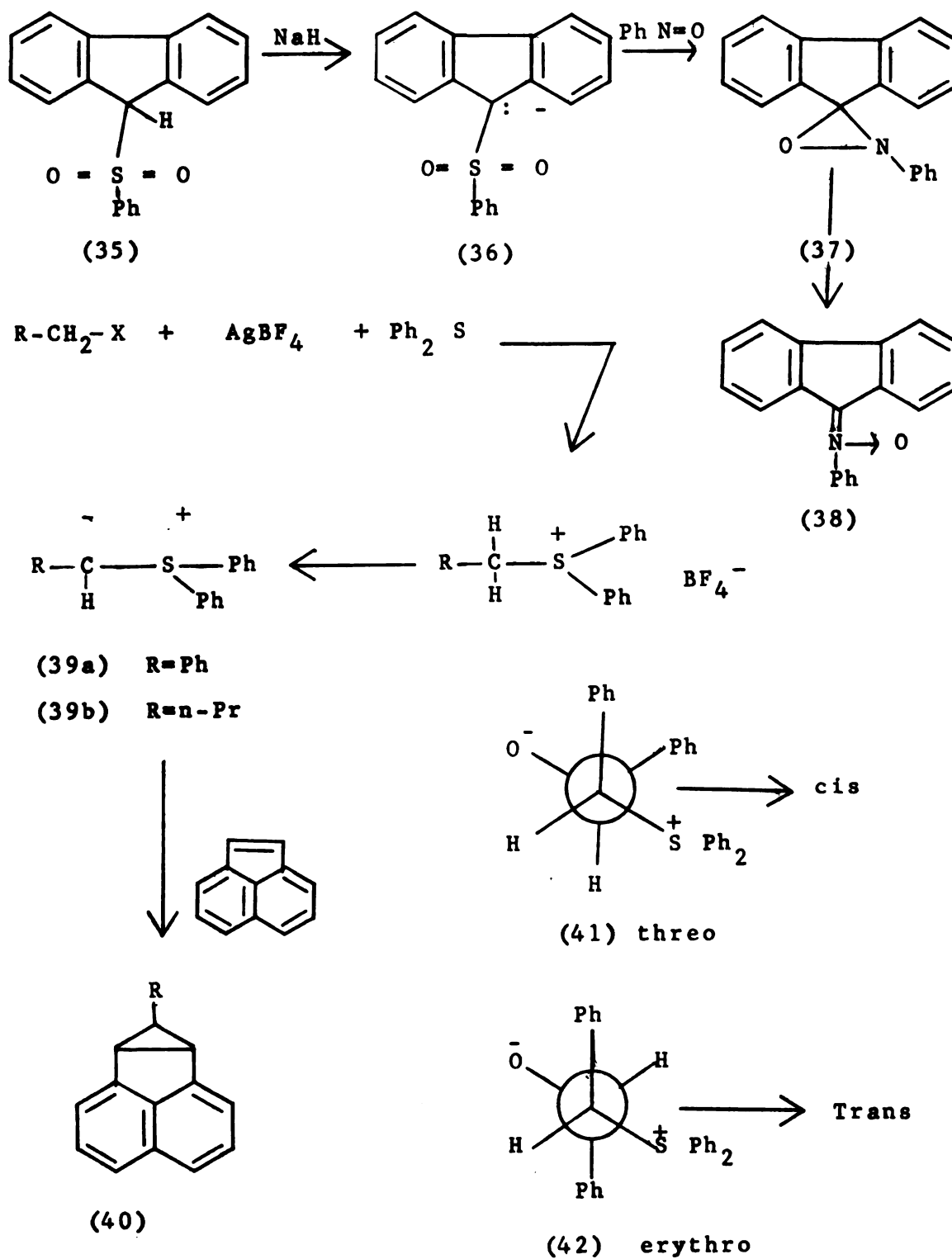


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(38 p33) (Ref. 70). Thus, in this instance the sulphonyl group must have been ejected through (path 34b p29) in a non-oxidized state, i.e., as the benzenesulphinate ion. Apparently the sulphonyl ylids can be made to follow either path (34a p29), forming an olefin, or path (34b p29), forming an epoxide.

For Johnson and his collaborators to develop their original reaction between sulfonium ylids and carbonyl compounds into one of practical value for the synthesis of epoxides, two modifications would be required. First, the reactivity of the ylid would have to be increased since the fluorenylide (2e p25) reacted only with benzaldehydes carrying electron withdrawing groups. Thus, they prepared and studied the reactions of sulfonium ylids carrying a benzyl or a butyl group, both of which have been shown to be more reactive than the corresponding fluorenylide. The second major requirement for a useful synthetic procedure would be prevention of the formation of the rearranged alcohol (17 p22) and analogous substances. If the mechanism developed is correct, replacement of the methyl groups on sulfur by groups with no alpha hydrogen should prevent the Sommelet rearrangement. Thus Johnson chose to study the chemistry of diphenylsulfonium benzylide (39a p33) and diphenylsulfonium butylide (39b p33) (Ref. 49).

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Both ylids can be decomposed into diphenyl sulfide and carbenes which were trapped with acenaphthylene. Setting the ylid (39a p33) aside at -40° afforded cis and trans stilbene, while treating it with substituted benzaldehydes gave the corresponding substituted stilbene oxide as expected. Diphenylsulfonium butylide (39b p33) also reacted with carbonyl compounds to afford epoxides and it was noted that in every case the resulting stilbene oxides were of the trans configuration. The stereochemistry of the ylid reaction with carbonyl compounds is accounted for by the above mechanism; the initial step, attack of the ylid on the carbonyl carbon, the second step, a typical SN-2 backside displacement of the sulfonium group by the oxyanion involving the two configurations (41 p33) and (42 p33). The threo form (41 p33) would be expected to have a higher energy barrier for completion of the second step than would the erythro form (42 p33). If the second step in the reaction were reversible, only the erythro form would then be converted to product, while the threo form would revert to starting materials. Speziale and Bissing (Ref.69) have shown that in the reaction between phosphonium ylids and carbonyl compounds, formation of an analogous betaine intermediate, is reversible. Such may

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also be the case for the sulfonium benzylide (39a p33) and may therefore account for the stereoselective formation of the trans stilbene oxide. Thus, the reaction between sulfonium ylids and carbonyl compounds has some potential as a general and stereoselective synthesis of epoxides.

Lillya and Miller (Ref. 142, 152) have very recently prepared stable bis (dialkylsulfonium) methylides (43, p37) from the corresponding methylene-bis (dialkylsulfonium)difluoroborates with one equivalent of potassium hydroxide in methanol. They represent the first case of an isolable sulfonium ylid in which the negative charge is stabilized only by sulfonium groups.

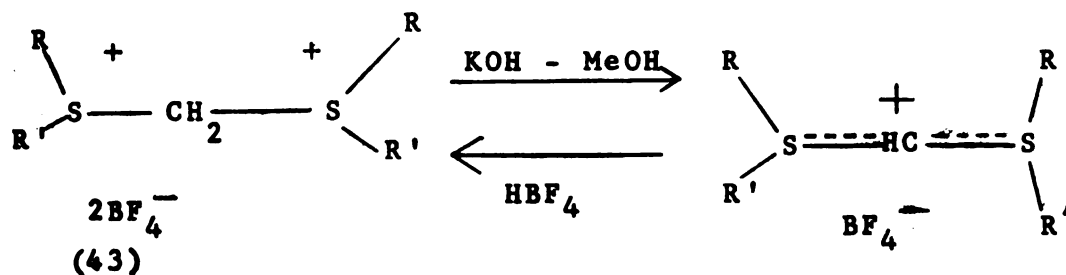
Within the past several months dimethylsulfonium-phenacylide (44 p37) has been prepared by B.M. Trost (Ref. 143) by treating the corresponding sulfonium salt with a 10% aqueous sodium hydroxide solution. The chemistry of ylid (44 p37) is summarized in Chart 9 p37.

Suld and Price (Ref. 150) recently have described an interesting series of aromatic sulfonium ylids. They found that treatment of 2,4,6-triphenylthiopyrylium perchlorate with phenyllithium afforded a violet, amorphous substance which was formulated as 1,2,4,6-tetraphenylthiabenzene (46 p37). The thiabenzene could be kept under nitrogen for a week but the color

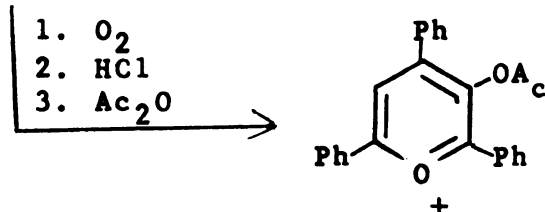
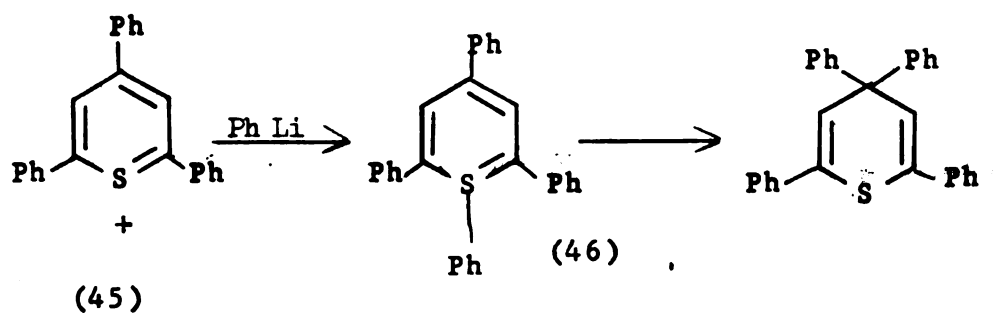
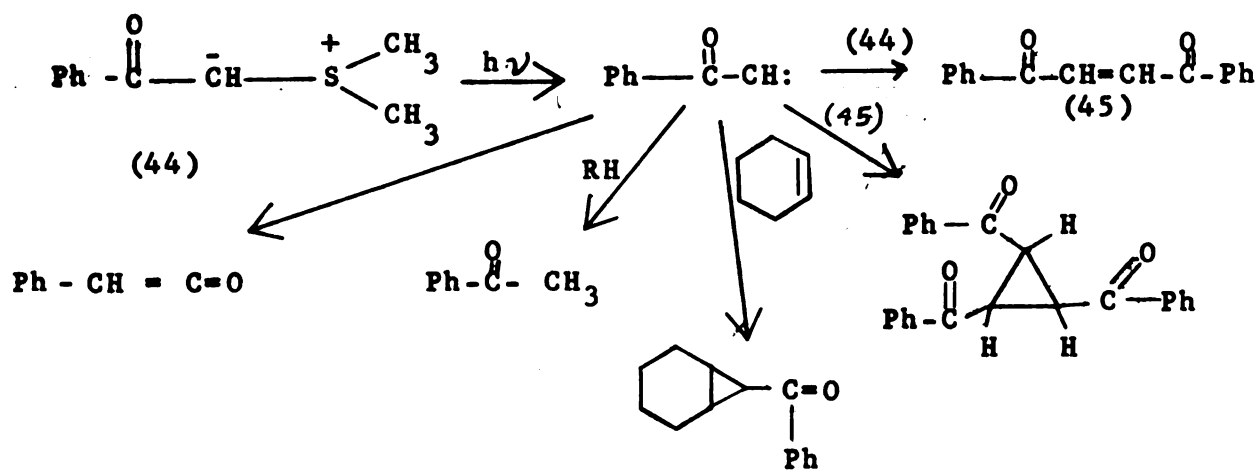
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CHART 9

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slowly faded and 2,4,4,6-tetraphenylthiapyran could be isolated. When the thiabenzene (46 p37) was treated with oxygen a peroxide was formed but addition of hydrogen chloride liberated phenylmercaptan and a zwitterion, the later being converted to 3-acetoxy-2,4,6-triphenylpyrylium perchlorate by acetylation. The isolation of phenylmercaptan indicated that one of the phenyl groups in the thiabenzene, presumably that from the phenyllithium, must have been attached to sulfur or must have migrated to it during the oxidation procedure.

More recently Price and coworkers (Ref. 172) have reported the preparation of four new thiabenzene derivatives, 1-phenyl-1-thianaphthalene, 2-phenyl-2-thianaphthalene, 10-phenyl-10-thianaphthalene and 9,10-diphenyl-10-thianaphthalene, all of which were prepared from the corresponding thiapyrylium perchlorates by treatment with phenyllithium. These systems all were more stable than the initially reported thiabenzene (46 p37). All were red-brown solids, capable of isolation and purification, and were stable to oxygen and even to boiling acetic acid solution.

The dipole moments of all four of the thiabenzene derivatives have been measured and were between 1.5 and 1.9 D. This is far less than the values of near 7 D reported for other ylids. (Ref. 173) and indicates a high degree of covalent

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character for these compounds. The NMR spectra of the thiabenzene derivatives showed only aromatic-type hydrogens with adsorption centered near 3.0 τ . In view of the chemical stability and the above physical properties, it is apparent that while these compounds might be represented as resonance hybrids of at least two important contributing structures, the covalent form certainly must be the most important (45 p37). Therefore, while these compounds are, in a formal sense, sulfonium ylids their properties are considerably different from the usual sulfonium ylid and they are best considered as a separate and unique class of compounds. These cyclic sulfonium ylids appear to be somewhat more stable than the similar cyclic phosphonium ylids reported by Markl (Ref. 174).

Price (Ref. 172) has accounted for the remarkable stability of the bicyclic and tricyclic derivatives of thiabenzene by proposing that the sulfur atom uses a 3p-z-orbital for overlap with the 2p-orbitals of the adjacent carbon atoms in the formation of the cyclic conjugated system. The unshared pair on sulfur would be promoted to a 3d-orbital. The σ bond skeleton was assumed to be the

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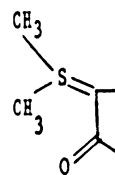
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result of trigonal hybridization. It also was proposed that the monocyclic derivative (46 p37) used p^3 - orbitals for σ skeleton in order to reduce the steric hindrance between the 1,2- and 6-phenyl groups and that this then requires the use of 3d-orbitals for overlap with the carbon 2p-orbitals to form the cyclic conjugated system, the result being a less stable aromatic system.

Isolable carbonyl stabilized sulfonium ylids were unknown until very recently and were thus studied in situ (Ref. 145, 146). The treatment of sulfonium salts with sodium hydroxide in the presence of Schiff bases to yield β -anilinocinnamamides and esters has been presumed to involve sulfonium ylids (48, 49 p41).

The isolation of 3-dimethylsulfuranylidene-2,4,5-pyrrolidine-trione (47 p41), after treatment of carbanoyl-methyl dimethyl sulfonium chloride with sodium methoxide and diethyl oxalate, affords one example of stabilization by two carbonyl groups (Ref. 144, 149). N,N-Diethyl (dimethylsulfuranylidene) acetamide (48 p41), and ethyl (dimethylsulfuranylidene)acetate (49 p41) react normally with Schiff bases and aldehydes to produce intermediate betaines which subsequently lead to products. However, attempts to carry out similar reactions with the corresponding aryl ketones failed (Ref. 144).



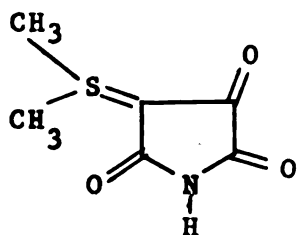
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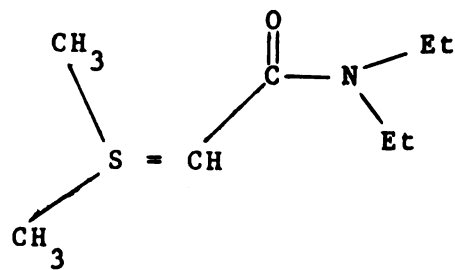


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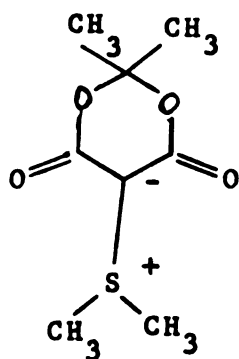


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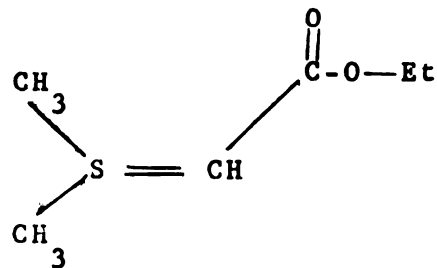
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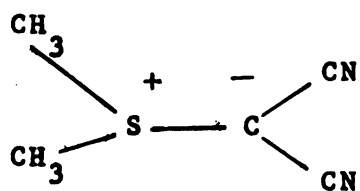
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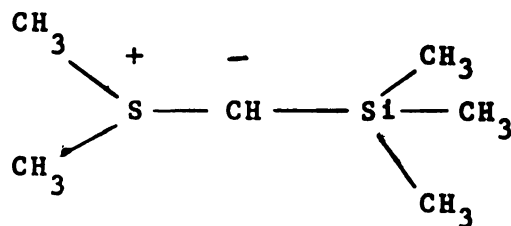
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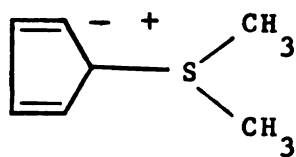
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Since the original manuscript was completed, activity in sulfur ylid research has increased leading to the isolation and characterization of several new sulfur ylids. Hochrainer and Wessely (Ref. 153) isolated the cyclic bis-ester ylid (50, p41) from reaction of methyl sulfoxide with the corresponding bromide. Linn et al. (Ref.154) and Middleton et al. (Ref. 155) both have reported obtaining dimethylsulfonium dicyanomethylide (51, p41) from the reaction of methyl sulfide with tetracyanoethylene oxide or with bromomalononitrile. Use of the former procedure with a variety of different sulfides afforded a series of dialkylsulfonium dicyanomethylides, all of which were isolated and characterized. These sulfonium ylids had dipole moments in the range of 7.0-8.1 D. They would not react with carbonyl compounds and were stable to hydrogen peroxide, water, weak acids, and weak bases. Miller (Ref. 156) had reported the preparation of the liquid trimethylsilylmethylenedimethylsulfurane (52, p41) by way of the sulfonium salt. Behringer and Scheidl (Ref.157) have isolated 5-dimethylsulfonium cyclopentadienylide (53,p41) This ylid underwent electrophilic substitution reactions and had a dipole moment of 5.7 D, considerably smaller than the 6.99 D moment reported for the phosphonium cyclopentadienylide (Ref.158).

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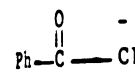
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Johnson and Amel (Ref.159) have prepared and characterized phenacylidenedimethylsulfurane (54,.p44) This ylid reacted with either its conjugate acid or with phenacyl bromide to afford tribenzoylcyclopropane, apparently by an alkylation-elimination-addition mechanism. The decomposition of the phenacyl ylid (54,p 44) afforded the same cyclopropane, probably via a carbenoid mechanism. Benzoylation of (54,.p44) with benzoic anhydride or with benzoyl chloride resulted in C-benzoylation or O-benzoylation, respectively. The ylid would form an oxirane (55,.p44), although in low yield, upon reaction with p-nitrobenzaldehyde. This is contrary to the behavior of the analogous phenacylidenesulfurane (59,.p44) as reported by Nozaki et. al. (Ref. 170).

Cook et. al. (Ref.160) have provided additional examples verifying Corey and Chaykovsky's (Ref.171) conclusions that dimethylsulfonium methylide usually attacks a cycloalkanone at an axial position while dimethylsulfoxonium methylid (20 p,25) attacks at an equatorial position. Konig, Metzger and Seelert (Ref. 161,162,163) have published full details of their study of the reactions of (20, p25) with conjugated olefins, nitriles and acylating agents.



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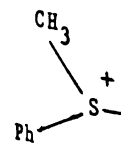
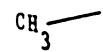
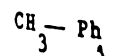
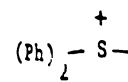
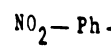
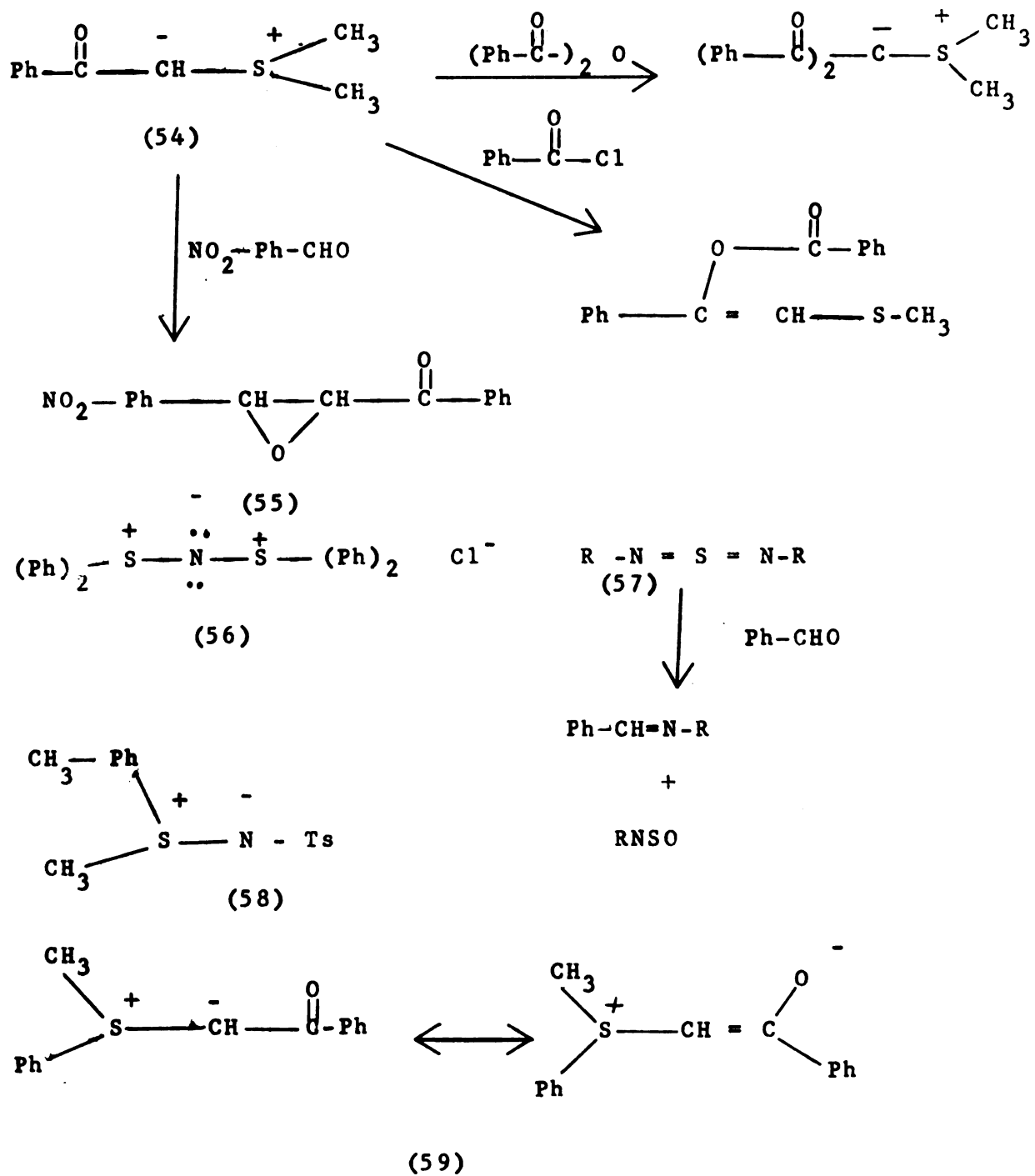


CHART 11

Additional information pertaining to the chemistry of iminosulfuranes also has been reported. Appel and Buchler (Ref.164) have prepared the bisimine (56, p44) from phenyl sulfide and nitrogen trichloride. Clemens et al. (Ref. 165, 166) have shown that the dialkyl sulfur diimines (57,p44) have ylidic character since they were found to react with benzaldehyde to afford Schiff bases, presumably via a betaine intermediate as for the Wittig reaction (57,p44). The diimines also reacted with isocyanates and isothiocyanates, again by nitrogen attack on carbon. The ylidic character of N-sulfinylaniline was demonstrated again (Ref.167) by its reaction with nitrosyl perchlorate to afford benzenediazonium perchlorate, a reaction very similar to that between iminophosphoranes and nitrosyl chloride as reported by Zimmer and Singh (Ref.168).

Day and Cram (Ref.169) have prepared optically active N-tosyliminomethyl-p-tolylsulfurane (58, p44) either from optically active p-tolylmethylsulfoxide and p-toluenesulfonamide or from the same sulfoxide and N-sulfinyl-p-toluenesulfonamide. Both preparative reactions took place with inversion of the sulfur configuration. Hydrolysis of (58,p44) with methanolic potassium hydroxide to regenerate the sulfoxide and p-toluenesulfonamide also took place with inversion of

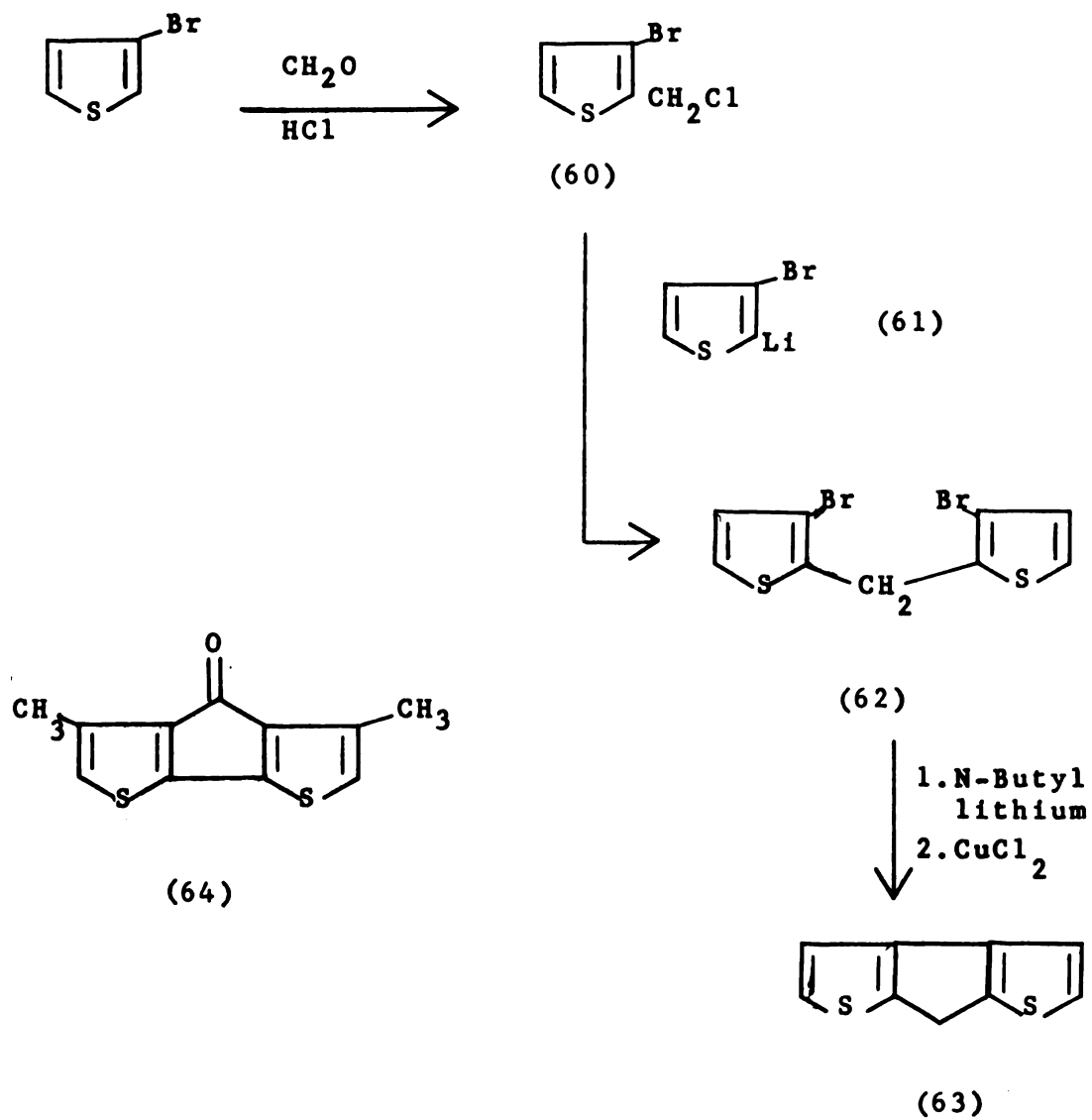
configuration.

The initial preparation of a thiophene analogue of fluorene, a cyclopenta (1,2:4,3) dithiophene, was reported in 1963 by Poirier (Ref. 71) . 2,5-Diisopropylidene cyclopentanone, prepared from the condensation of two molecules of acetone with cyclopentanone, was heated to 200°C with sulfur to give (64, p47) in a very low yield. Recent attempts to repeat this ring closure have been unsuccessful (Ref. 80).

One of the most direct routes, viz., via chloromethylation of 3,3'-dithienyl afforded only polymeric material (Ref. 73).

Gronowitz (Ref. 84) attempted to prepare these compounds several years ago but was unsuccessful.

Very recently, Wynberg prepared cyclopenta (1,2-b : 4,3-b') dithiophene (63, p47) by the sequence shown in Chart 12, p47. Chloromethylation of 3-bromothiophene gave 3-bromo-2-thienylchloride (60, p47) which was allowed to react with 3-bromo-2-thienyllithium (61, p47) to afford 3,3'-dibromo-2,2'-dithienylmethane (62, p47) in 16% yield. The compound (62, p47) was converted to its dilithium derivative and the latter underwent ring closure by oxidation with cupric chloride to give the condensed thiophene (63, p47). However, the overall yield of this sequence is poor (Ref.72).

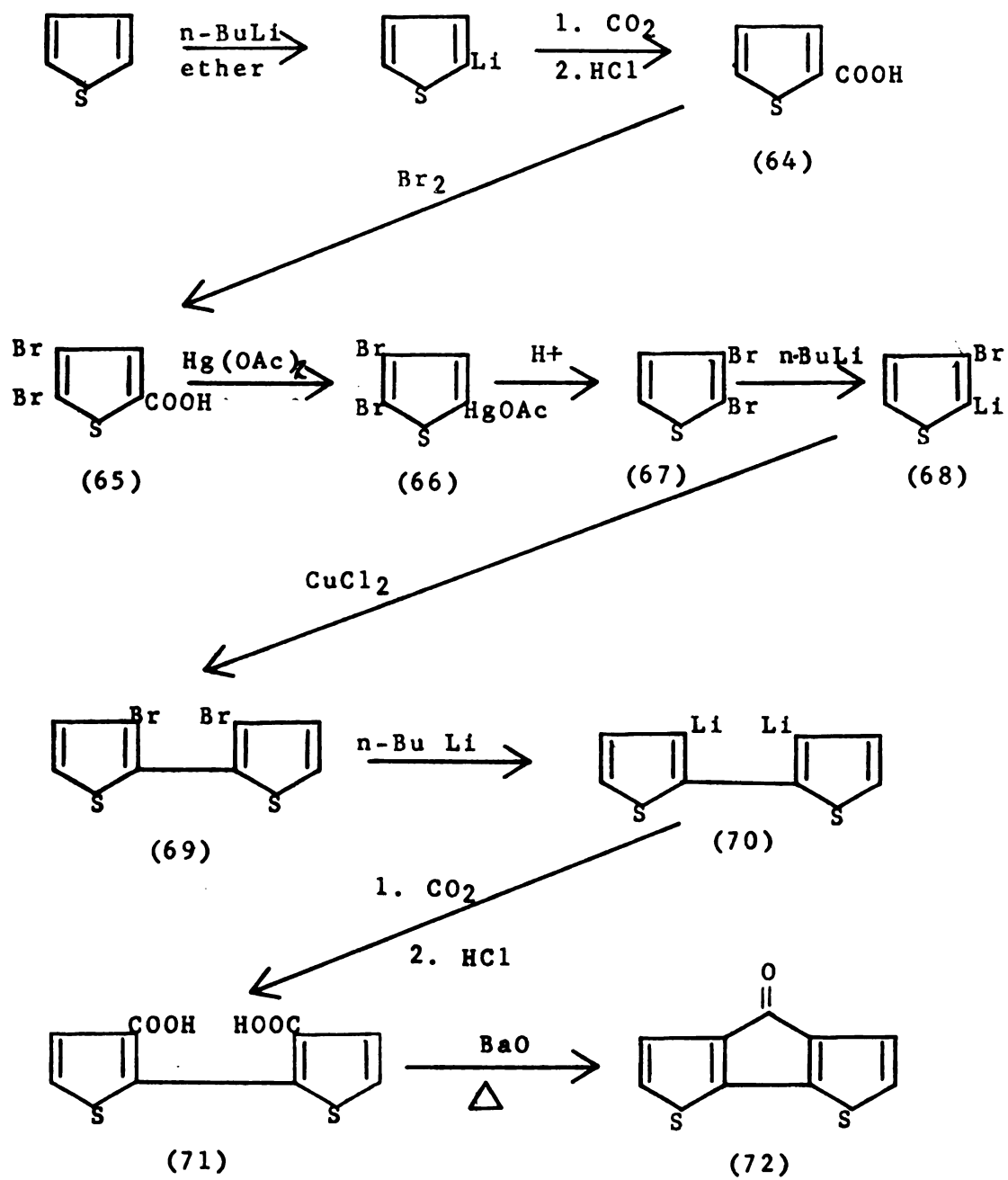
CHART 12

DISCUSSION

In an attempt to gain a synthetic entry to the cyclopentadithiophene sulfur ylid system, the first effort of this study centered around the preparation of cyclopentadithiophene. Previous attempts to prepare compounds of this type have met with failure (Ref. 81,82). However, in the past year Wynberg (Ref. 83) reported the successful preparation of cyclopenta (1,2-b:4,3-b') dithiophene, (63 p47) but the synthetic procedure did not permit its extension to obtaining the other five possible isomers of this general class.

The initial work reported here involved an attempt to convert 3,3'-di-carboxy-2,2-dithienyl by pyrolysis of its barium salt to the corresponding ketone (72 p49) as shown on Chart 13 p49.

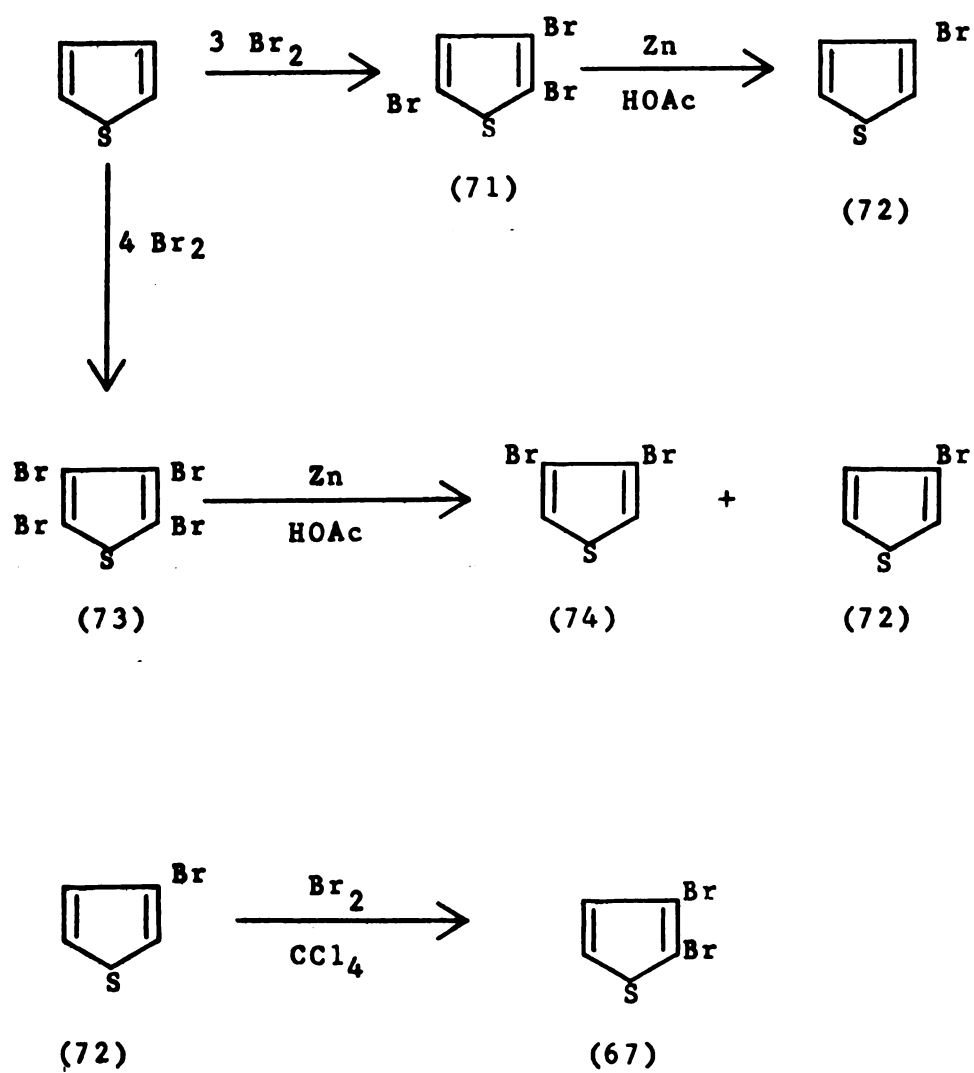
A thiophene-ether solution was added to n-butyl-lithium at -10°, and the mixture was allowed to warm to its reflux temperature to force the evolution of the butane formed in the hydrogen-metal exchange. The mixture was poured over a dry ice-ether slurry, and hydrolysis gave 2-thiophene carboxylic acid (64 p49) in an 83% yield. The acid was directly brominated to the 2,3-dibromo-5-thiophene carboxylic acid (65 p49) The crude acid was decarboxylated via the 2,3-dibromo-5-mercuriacetate derivative (66 p49) to obtain a 85% yield of pure 2,3-dibromothiophene (67 p49)

CHART 13

This rather lengthy and time-consuming procedure was discarded when Gronowitz (Ref. 84) reported that 2,3-dibromothiophene could be prepared in nearly quantitative yield through the bromination of 3-bromothiophene.

The procedure proposed by Taft (Ref. 85) for the preparation of 2,3-dibromothiophene by the selective reduction of 2,3,5-tribromothiophene with zinc and acetic acid has been shown to be incorrect. Infrared and N.M.R. spectra of the reduction products indicated a mixture of the 2,3 and 2,4 dibromoisomers.

3-Bromothiophene (72 p51) was synthesized in a two step conversion starting with the bromination of thiophene using a three molar excess quantity of bromine. The crude 2,3,5-tribromothiophene (71 p51) was refluxed with a suspension of zinc dust in acetic acid for 19 hours. After exhaustive steam distillation of the reaction mixture using a Barret tube, a 41% yield of 3-bromothiophene (72 p51) was obtained. A later modification involved the direct bromination of thiophene to tetrabromothiophene (73 p51) and its subsequent reduction by zinc-acetic acid to a mixture of 3,4-dibromothiophene (74 p51) and 3-bromothiophene (72 p51) in nearly quantitative yield.

CHART 14

Several preparations of 2,3-dibromothiophene (67 p51) according to the Gronowitz procedure (Ref. 84) by the bromination of 3-bromothiophene with a molar ratio of bromine in carbon tetrachloride at room temperature gave better than 95% yields.

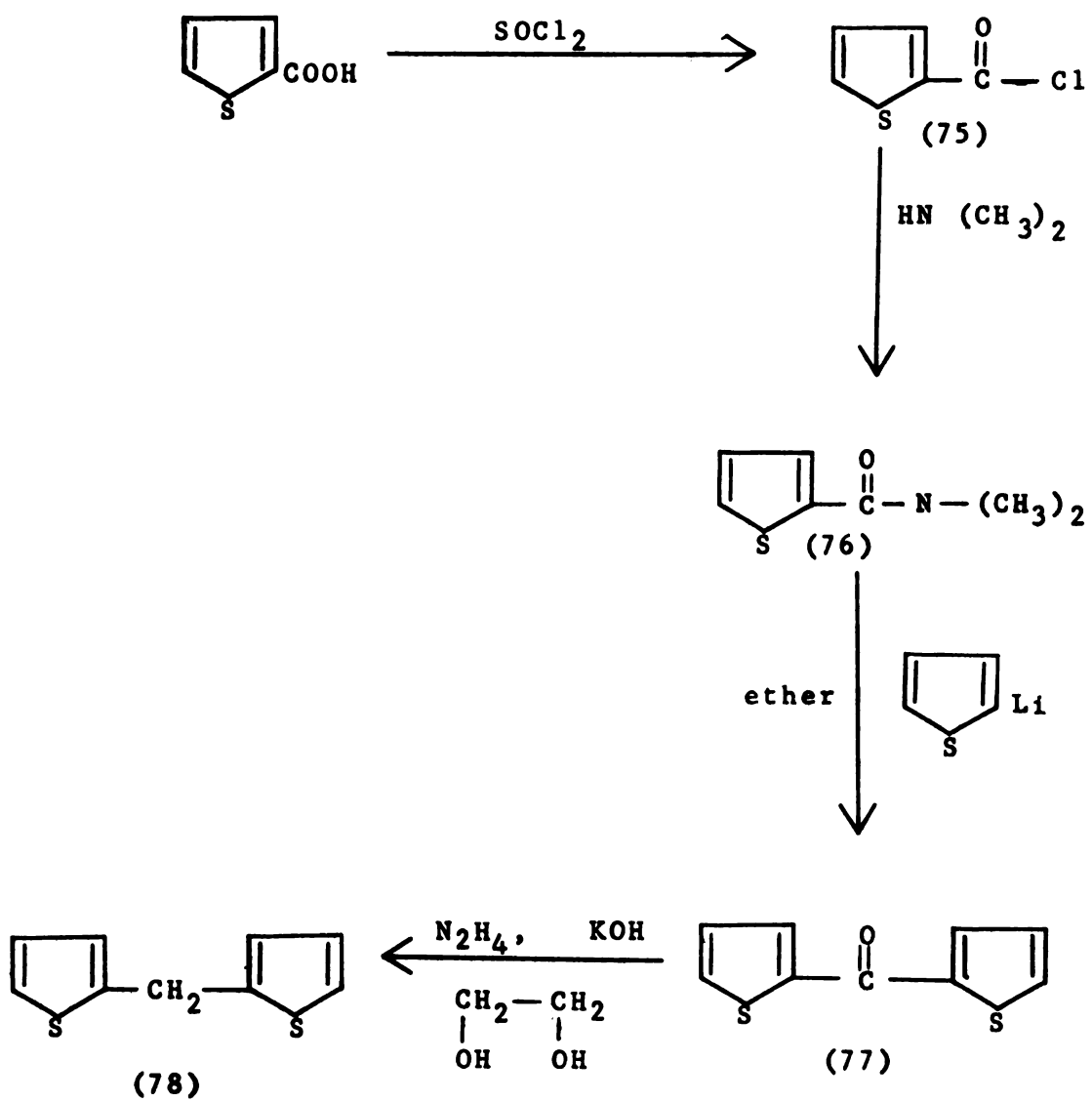
3-Bromo-2-thienyllithium was prepared by the halogen-metal interaction between 2,3-dibromothiophene and n-butyllithium in anhydrous ether at -70° (Ref. 86). Subsequent oxidative coupling with anhydrous Copper (II) chloride at -70° gave 3,3'-dibromo-2,2'-bithienyl in 51% yield according to the Gronowitz procedure (Ref. 86). The dibromo compound was treated with a two mole equivalent of n-butyllithium at -70° . The mixture was poured over a dry ice-ether slurry and hydrolyzed to give 3,3'-dicarboxy-2,2'-bithienyl in 44% yield.

Although the pyrolysis of dicarboxylic acid salts to ketones is a well known reaction (Ref. 87), several attempts to achieve the condensation by pyrolysis of the diacid (71) with BaO under varied conditions failed. At this juncture in the study due to the possibility of an alternate procedure this method was set aside.

The methods of Taft (Ref. 85), Gronowitz (Ref. 84), and Nord (Ref. 88) were then used in an attempt to prepare di-2-thienyl methane via the N,N-dimethylthiophene carboxamide (Chart 15, p54).

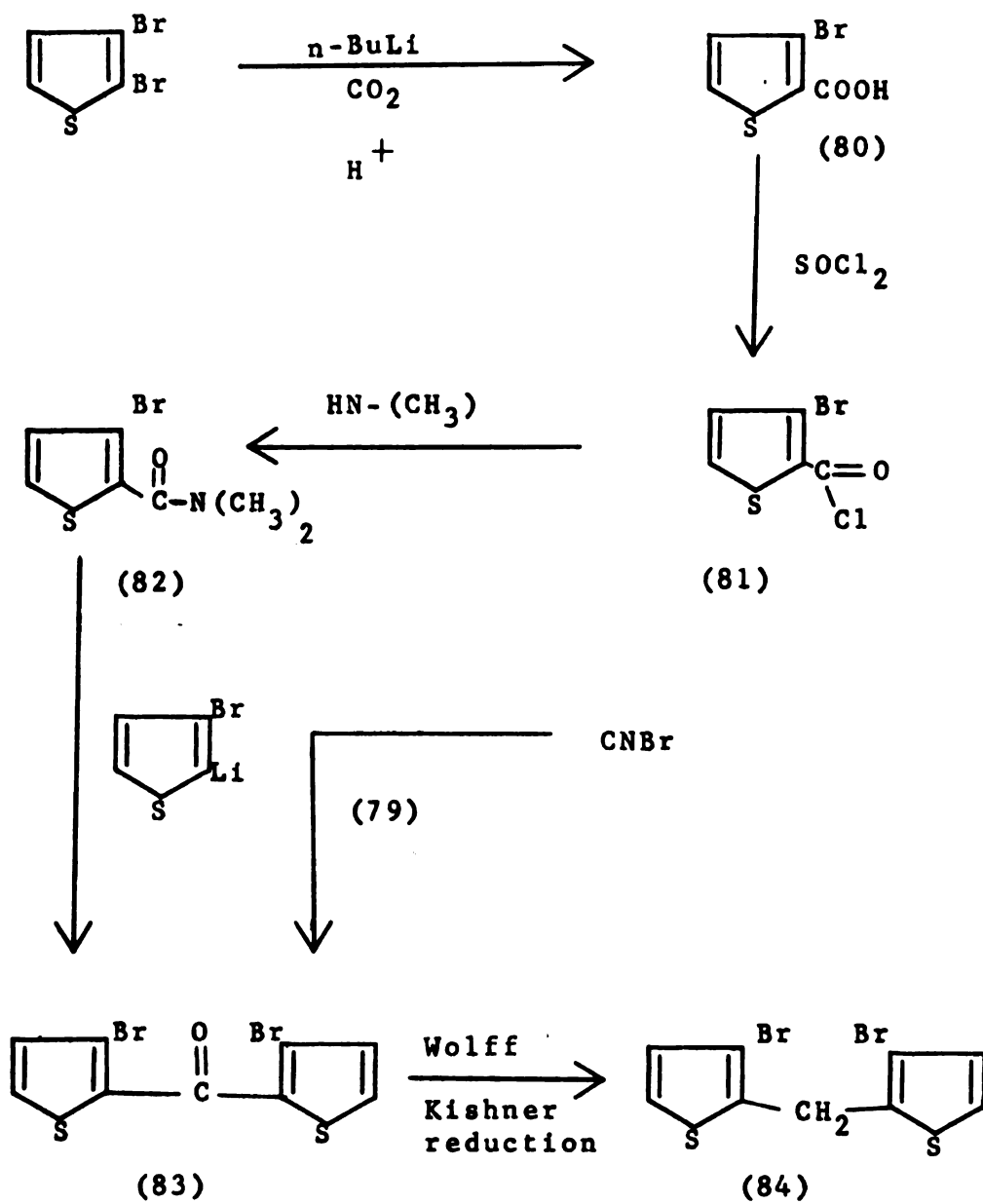
Crude 2-thiophenecarboxylic acid was treated with thionyl chloride to give an 89% yield of 2-thienoyl chloride (75 p54). Treatment of the acid chloride in ether solution with gaseous dimethylamine under rapid stirring and cooling produced a 68% of N,N-dimethyl-2-thiophene carboxamide (76 p54). A light yellow solid formed when an equimolar amount of the amide was added to a rapidly stirred ether solution of 2-thienyllithium cooled to -70°C . The slurry, on warming to room temperature, was hydrolyzed with a saturated ammonium chloride solution. Distillation at reduced pressure led to a 58% yield of di-2-thienyl ketone (77 p54). Contrary to the report of Lofgren and Tegner (Ref. 103) the di-2-thienyl ketone was successfully reduced via a Wolff-Kishner reduction (Ref. 88) to di-2-thienyl methane (78 p54) in an 86% yield.

Initial attempts to prepare di-3-bromo-2-thienyl ketone (82 p54), which was to be subsequently reduced and coupled to give a cyclopentadithiophene, centered around the Thomas-Coudere procedure (Ref. 90). In this procedure cyanogen bromide was treated with 3-bromo-2-thienyl-

CHART 15

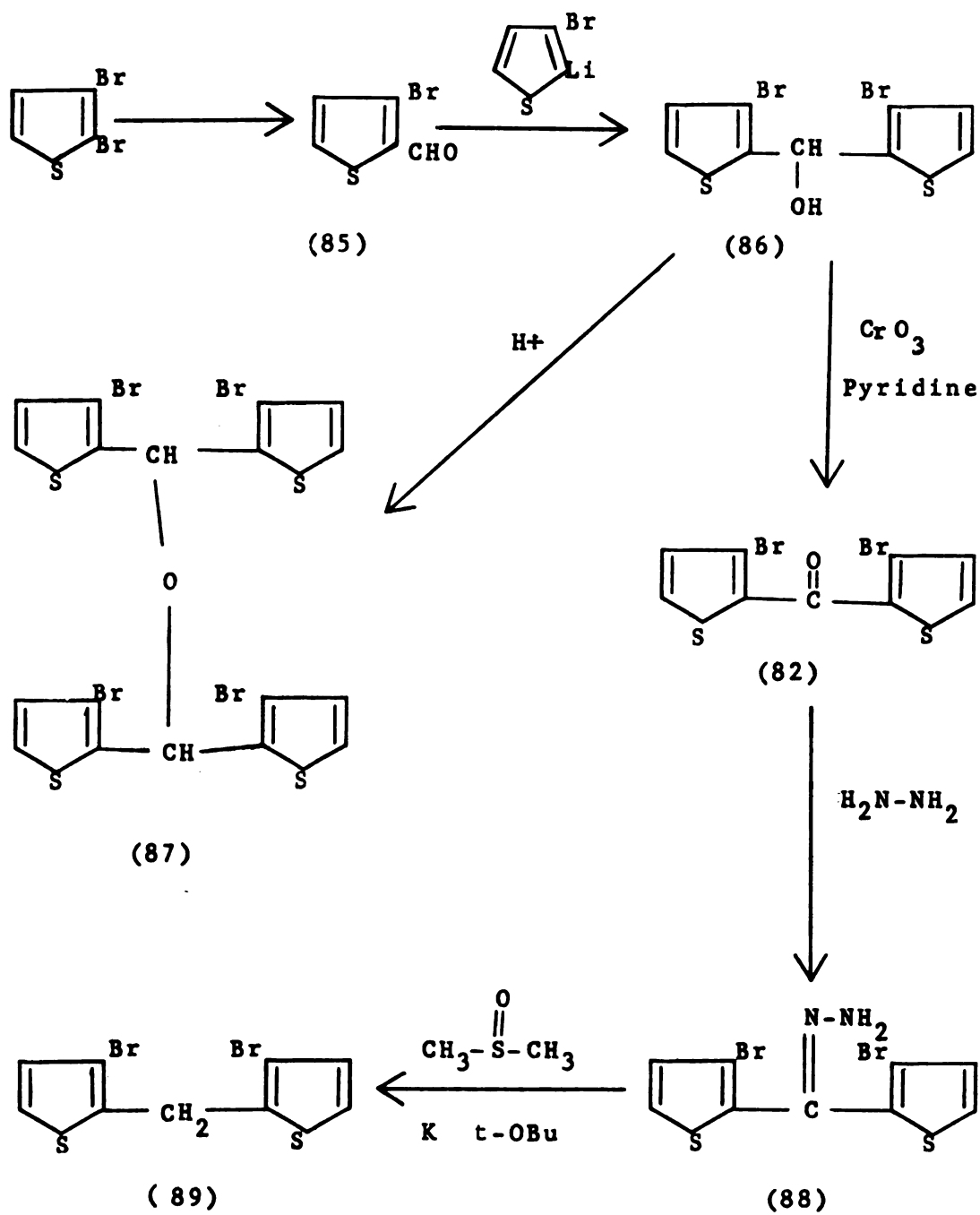
lithium at -70° in ether solution (79 p56). However, infrared analysis of the reaction mixture indicated the absence of a ketone.

A new route (Chart 16 p56) was proposed for the formation of the ketone. The reaction between 2,3-dibromothiophene and n-butyllithium at -70° , followed by carbonation with a dry ice-ether slurry, and hydrolysis afforded 3-bromo-2-thiophene carboxylic acid (80 p56). Treatment of this acid in turn with thionyl chloride (81 p56) followed by dimethyl amine gave 3-bromo-N,N-dimethylthiophenecarboxamide (82 p56) in an over-all yield of 47% from 2,3-dibromothiophene. An ether solution of the N,N—dimethylcarboxamide was then treated with an equimolar quantity of 3-bromo-2-thienyllithium in anticipation of obtaining the required ketone (83 p56). This reaction failed to give isolable products. A similar sequence of reactions was followed with 3,4-dibromothiophene as the starting dibromothiophene.

CHART 16

A final sequence of reactions did lead to the successful preparation of the ketone and involved the route described in Chart 17 p58. Attempts to prepare 3-bromo-2-thiophene carboxaldehyde (85 p58) according to the Nishimura procedure (Ref. 92) by the formulation of 3-bromothiophene with dimethylformamide and phosphorus oxychloride gave a low yield of the aldehyde. This method was discarded in favor of the procedure recently reported by Gronowitz (Ref. 93) which involved the treatment of dimethylformamide with a thienyllithium salt. An equimolar amount of N,N-dimethylformamide was added at -25° to a stirred ethereal solution of 3-bromo-2-thienyllithium. Hydrolysis of the resulting slurry gave on distillation an 81% yield of 3-bromo-2-thiophene carboxaldehyde (85 p58).

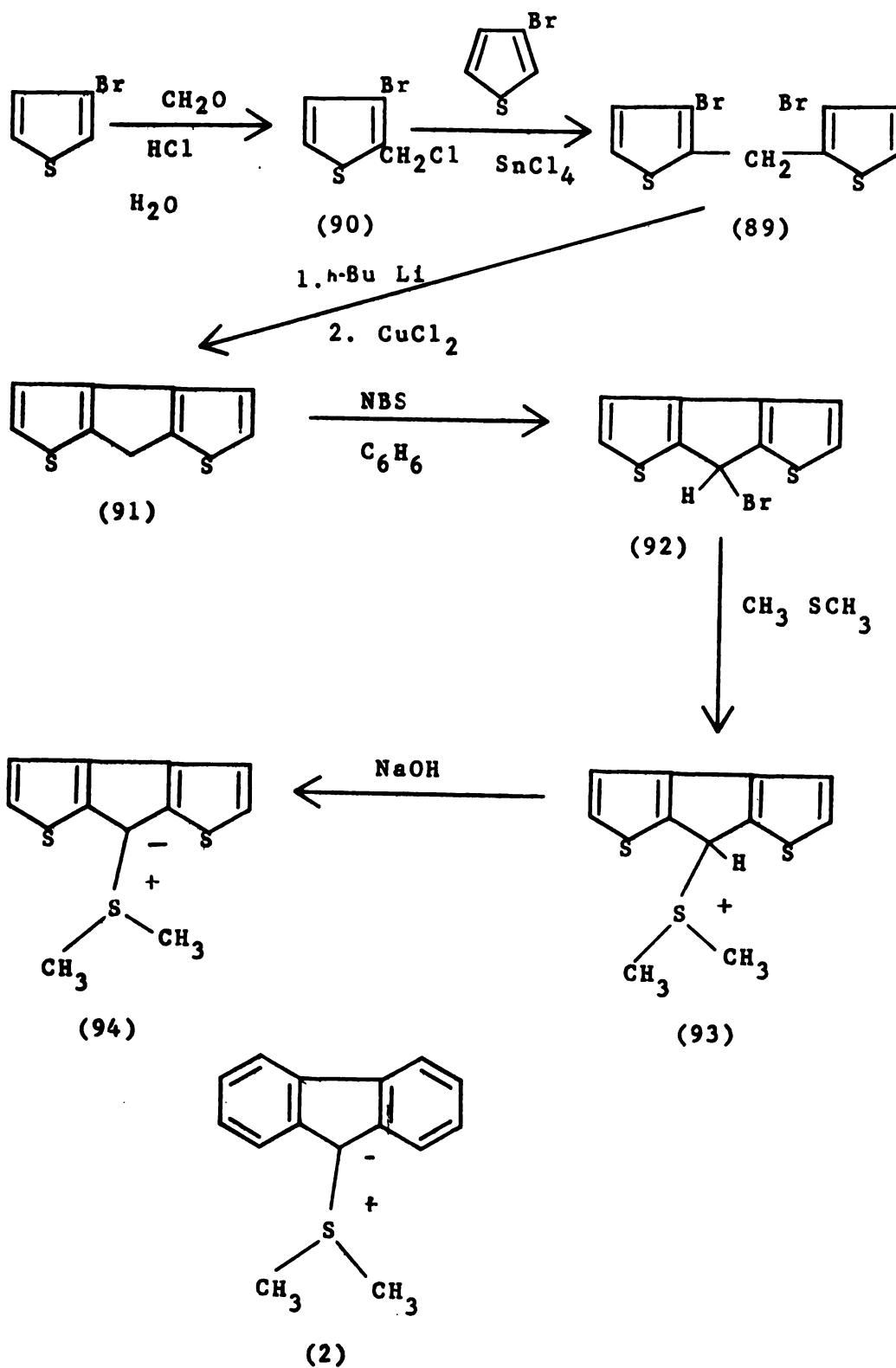
Gronowitz (Ref. 91) has recently shown that thienyllithium reagents added rapidly to the carbonyl group of aldehydes. This led to the treatment of 3-bromo-2-thiophene carboxaldehyde with 3-bromo-2-thienyllithium at -70° in ether solution. The product obtained was a mixture of the brominated dithienyl carbinol (86 p58) and its bis-(dithienylmethyl) ether (87 p58). The dithienyl carbinol (86 p58) was found to be unstable. It turned a dark blue-black color upon exposure to the atmosphere at room temperature, although it was found to be stable under nitrogen in the cold.

CHART 17

The pronounced tendency toward ether formation of thienyl carbinols has previously been noted by Goldfarb (Ref. 94). Heat, slightly acidic conditions or prolonged standing (in contact with air) readily converted the carbinol to the corresponding ether. Basic oxidation of the brominated dithienyl carbinol (86 p58) with the CrO_3 -pyridine complex gave the desired ketone in 60% yield.

Initial attempts at reduction of the ketone under Wolff Kishner conditions (Ref. 88) led to degradation of the compound as indicated by the formation of H_2S . The ketone (82 p58) was readily converted to the corresponding hydrozone (88 p58) by refluxing it for two hours in ethanol with hydrazine hydrate and barium oxide. The hydrazone (88 p58) was then reduced, according to a modified room temperature Wolff Kishner reduction procedure (Ref. 95) yielding 3,3'-dibromo-2,2'-dithienyl methane (89 p58) in 20% yield.

The preparation of 3-bromo-2-thienyl chloride reported recently by Wynberg (Ref. 83) provided a more direct synthesis of di-3-bromo-2-thienyl methane (89 p60). The 3-bromo-2-thienyl chloride (90 p60) was prepared by the chloromethylation of 3-bromothiophene with formaldehyde and hydrogen chloride in aqueous solution. After fractionation under reduced pressure, an 85% yield of the desired product was obtained.

CHART 18

The alkylation of 3-bromothiophene with 3-bromo-2-thenyl chloride (90p60) in carbon disulfide with a stannic chloride catalysis provided a convenient synthesis of 3,3'-dibromo-2,2'-dithienylmethane (89 p60).

An equimolar amount of 3-bromo-2-thenyl chloride (90 p60) in carbon disulfide was added drop-wise during 24 hours to a carbon disulfide solution of 3-bromothiophene containing a catalytic quantity of stannic chloride. Fractionation of the residue gave a 62% yield of 3,3'-dibromo-2,2'-dithienyl methane. This product was shown to be identical to that prepared previously by Wynberg (Ref. 83), by comparison of the N.M.R. spectra.

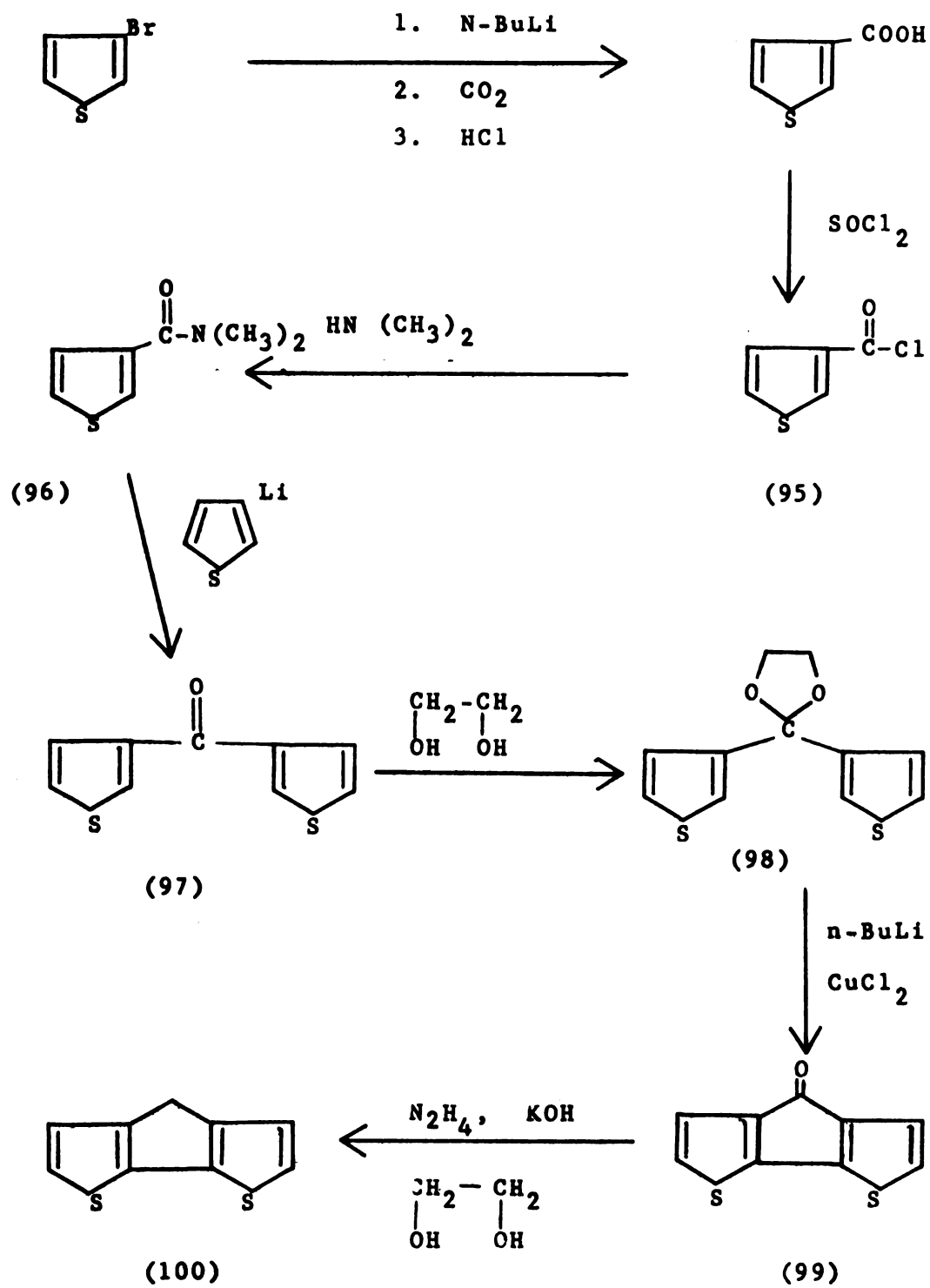
The Wynberg method (Ref. 83) of oxidative coupling was subsequently used to prepare cyclopenta (1,2-b:4,3-b') dithiophene from the dibromide in a 75% yield (Chart 18).

Using the method of Fuson and Porter (Ref. 96) the compound (91 p60) was then brominated in benzene solution with an equimolar amount of N-bromosuccinimide to give a 42% yield of the brominated cyclopenta thiophene (92 p60).

The Ingold and Jessop procedure (Ref. 97) was used to condense the bromocyclopenta thiophene with dimethyl sulfide, to obtain the sulfonium salt (93 p60). Treatment of this salt with a 10% sodium hydroxide solution precipitated the sulfur ylid (94 p60). Like the fluorenyl ylid (2 p60),

the thiophene ylid (94 p60)decomposed upon exposure to the atmosphere at room temperature to a dark black amorphous tar with the liberation of dimethyl sulfide.

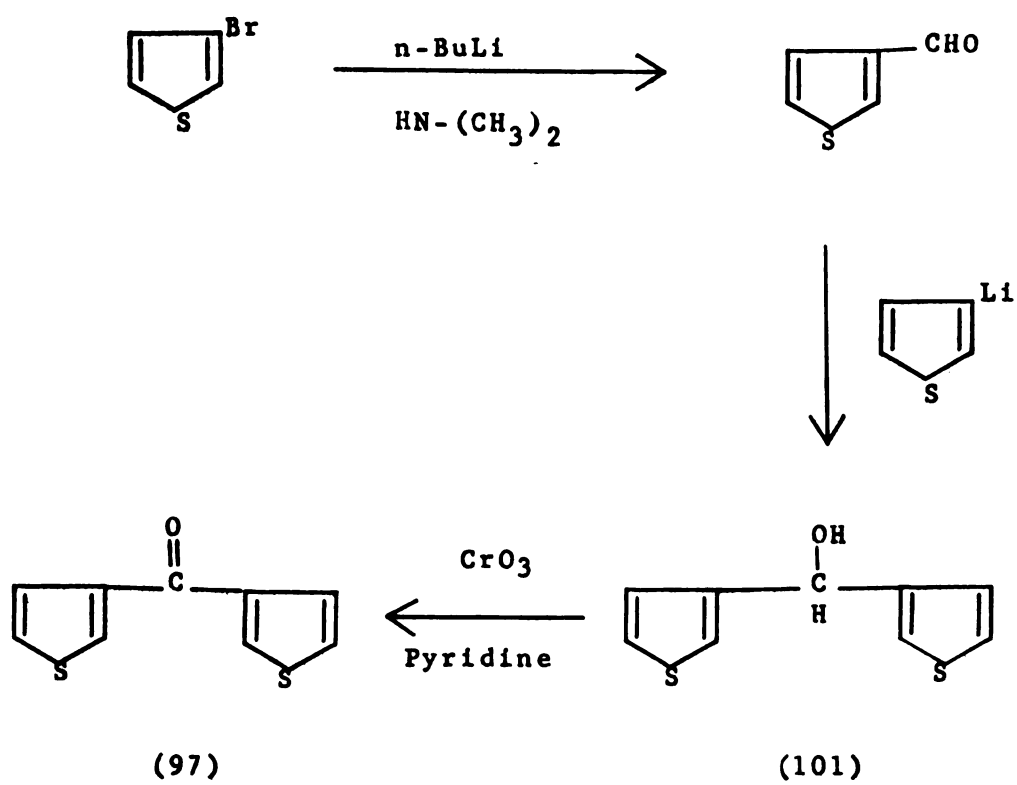
In connection with attempts to prepare other cyclopentadithiophenes, it was necessary to prepare 3-(3-thienoyl)thiophene (97 p63).. Previously, 3-(3-thienoyl)thiophene was obtained only in low yield on dry distillation of the calcium salt of 3-thiophene carboxylic acid (Ref. 98). Initial attempts to synthesize 3-(3-thienoyl)thiophene(97 p63) centered around the reaction of 3-cyanothiophene with 3-thienyllithium. This method would be analogous to the preparation of 3-benzothienone from benzonitrile and 3-thienyllithium in 75% yield (Ref. 99). However, when substituting 3-cyanothiophene in this procedure only a few per cent yield of the desired ketone was obtained and the majority of the cyanothiophene was recovered unchanged. It is well known that thiophene is very reactive in metalation with organolithium compounds (Ref. 100, 101). It is possible that the ability of sulfur to expand its valence shell to a decet could be responsible for the stabilization of the carbanion and also of the transition state leading toward its formation. Due to the strong electron-attracting effect of the cyano group the acidity of the 2-hydrogen was increased. Thus, its reactivity with organolithium

CHART 19

compounds surpasses that of the cyano group and led mainly to metalation even at -70° , as recently confirmed by Gronowitz (Ref. 91).

The method of Taft (Ref. 85) was then used to prepare 3-(3-thienoyl) thiophene (Chart 19 p63). An ethereal solution of 3-bromothiophene was treated with n-butyllithium and then dry ice to give 3-thiophene carboxylic acid in 86% yield. The acid was converted to the corresponding acid chloride (95 p63) with thionyl chloride. Treatment of this acid chloride with gaseous dimethyl amine led to an over-all yield of 51% of N,N-dimethyl -3-thiophenecarboxamide (96 p63) from 3-bromothiophene. The reaction of this compound with 3-thienyllithium in ether solution at -70° , followed by hydrolysis and distillation afforded a 73% yield of a white solid which was shown to be identical to 3-(3-thienoyl) thiophene (97p63) previously prepared by Gronowitz (Ref. 91).

The Gronowitz procedure (Ref. 91)(Chart 20 p65) was used to prepare 3-(3-thienoyl)thiophene (97 p65) on a half mole scale, as it was found to be the easier and faster method. The 3-thiophene carboxaldehyde, prepared from 3-bromothiophene, n-butyllithium and dimethylformamide, was treated with 3-thienyllithium to give di-(3-thienyl carbinol (101 p65) which was then oxidized in the crude state to the corresponding ketone (97 p65) in an over-all yeild of 74%.

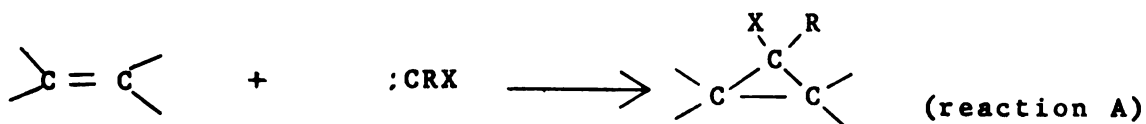
CHART 20

The acetal group has been shown to exert an -I effect due to the electron attracting effect of the two oxygens (Ref. 102) and the ketal group was also expected to exert a similar effect. The 3-(3-thienoyl) thiophene was converted to acyclic ketal by direct ketalization with ethylene glycol using p-toluenesulphonic acid as a catalysis and removing the water formed by azeotropic distillation with benzene. The yield of di-(3-thienyl) ketone ethylene ketal (98 p63) was 81%.

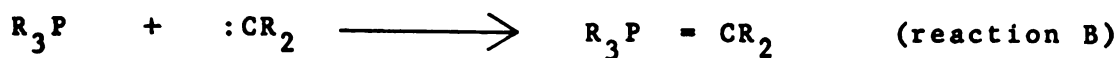
The ketal was then converted to the 2,2'-dilitho salt with n-butyllithium at -70° via a high dilution technique, followed by oxidative coupling with anhydrous copper (II) chloride.

Following acid hydrolysis of the oxidation reaction mixture, the crystalline ketone (99 p63) was obtained in 71% yield. The direct formation of the ketone was due to the rapid hydrolysis of the ketal during the isolation procedures. The experimental procedure of King and Nord (Ref. 88) was employed to reduce the ketone to the cyclopentadithiophene (100 p63) using 85% hydrazine hydrate and potassium hydroxide in ethylene glycol.

Numerous examples of the reaction of halocarbenes with olefins to yield halogen substituted cyclopropanes, have been reported since the initial communication on this subject by Doering and Hoffmann (Ref.119) (Reaction A p68). Further, the electrophilic nature of the carbenes in such reactions has been clearly demonstrated (Ref. 120, 121,122). Accepting the description of halocarbenes in terms of carbon in the singlet state in which an electron pair fills one orbital, leaving one orbital unoccupied, one might expect to find reactions of halocarbene with other nucleophiles in addition to those of olefins. The recent observation that tertiary phosphines are nucleophilic (Ref. 123,124) suggested that the interaction of these two reagents should produce phosphine-methylenes, such a reaction has recently been reported (Reaction B, p68) (Ref.125,126,127,128). A logical extension of this work was the substitution of nucleophilic sulfides (Ref. 129) for tertiary phosphines. Thus, the reaction between divalent sulfur compounds and carbenes was investigated as a possible synthetic route to the formation of a new class of sulfur ylids, the dihalo derivatives (Reaction C p68). The Wittig type reaction of such an ylid could provide a novel synthesis of 1,1-dihaloepoxides (Reaction D p68).

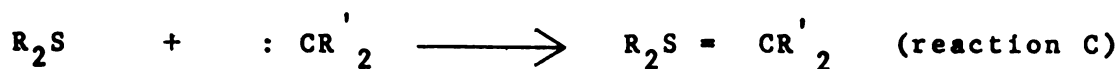
CHART 21

where R=H, alkyl, phenyl, halogen



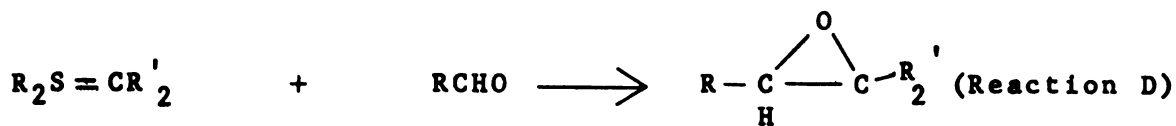
where R=alkyl, phenyl

R'=H, alkyl, or halogen



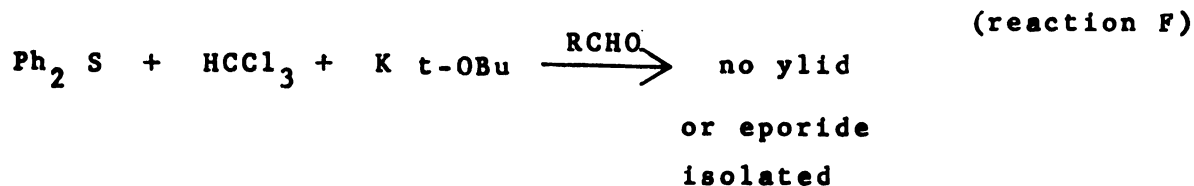
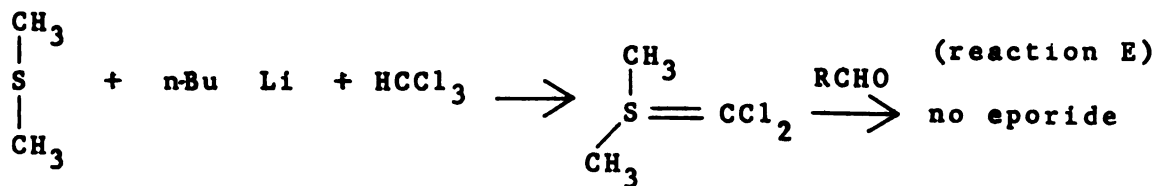
where R=alkyl, phenyl

R'=alkyl, halogen



R = alkyl, phenyl,

R' = halogen



Treatment of a solution of n-butyllithium and dimethyl sulfide with chloroform at $0-5^{\circ}$ produced a golden yellow solid. Preliminary attempts to isolate the material in a pure state only resulted in the formation of large amounts of dimethyl sulfide and an unidentifiable product.

Butyllithium was added to a mixture of dimethyl sulfide and chloroform at 0° , followed in 5 minutes by benzaldehyde to give a yellow slurry. The mixture was stirred at room temperature for an hour. Product isolation gave various fractions from which only benzaldehyde and dimethyl sulfide were identified by infrared analysis. (Reaction E p68)

The above experiment was repeated using n-butyl-lithium, dimethyl sulfide, chloroform and benzophenone. After filtering the reaction mixture the residue was washed first with ethyl ether and then with water. Removal of the residual solvent left brown oil which contained only benzophenone and dimethyl sulfide as determined by infrared analysis. The filtrate obtained above was concentrated in vacuo to a red oil which also contained dimethyl sulfide and benzophenone.

Repeating the above experiment using n-butyl-lithium, dimethyl sulfide, chloroform and p-nitro-

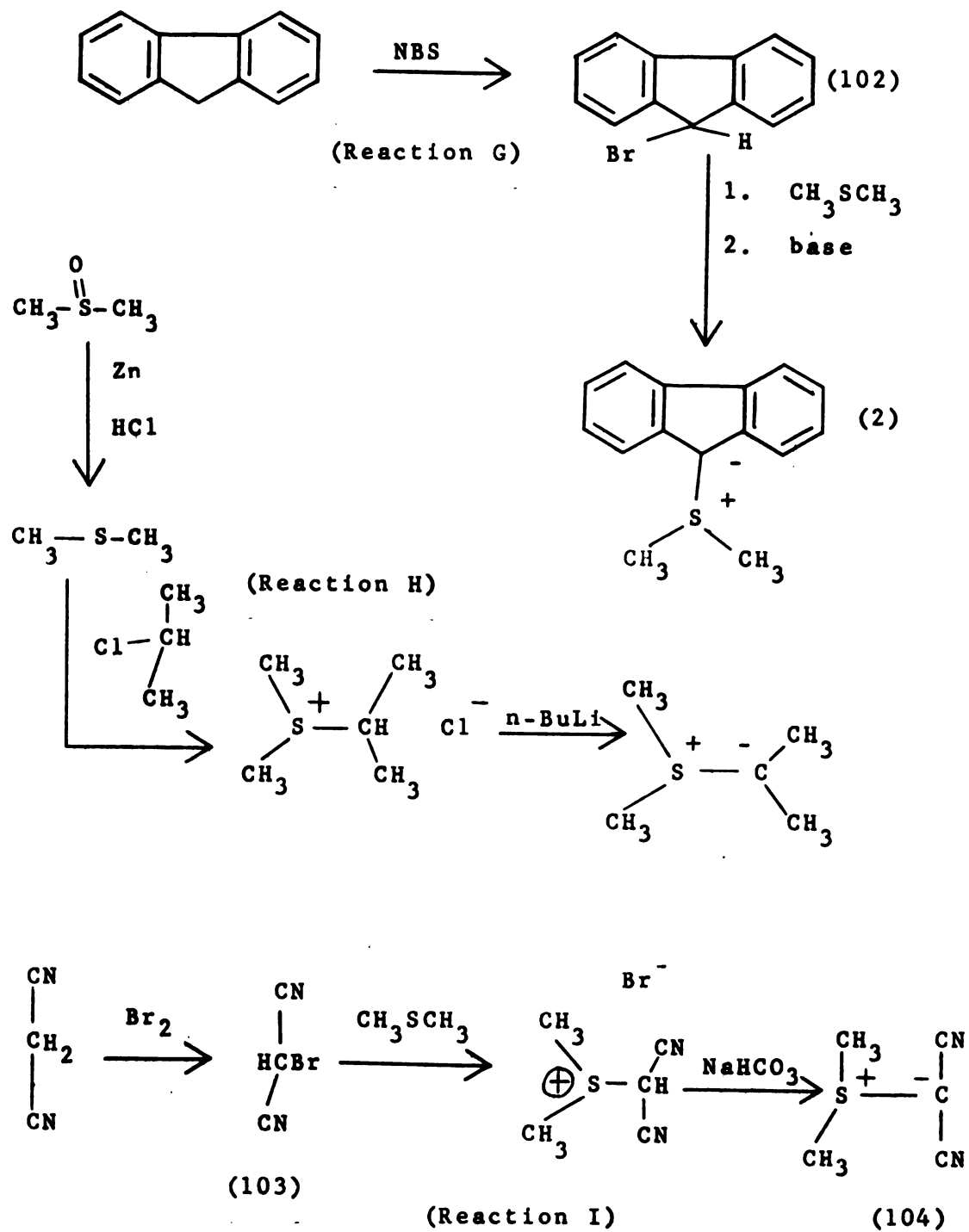
benzaldehyde gave only starting materials on applying product isolation procedures to the reaction mixture.

Potassium t-butoxide was added to diphenyl sulfide in a chloroform-pentane solution at 0°. After stirring for 30 minutes, benzophenone was added and the mixture was stirred for an additional 13 hours. Filtration of the mixture and fractionation of the filtrate yielded again only starting materials. (Reaction F, p68)

Using n-butyllithium, chloroform, diphenyl sulfide and benzaldehyde, only starting materials could be isolated from the reaction mixture using the product isolation procedures described above. With the more reactive carbonyl compound, p-nitrobenzaldehyde, similar results were obtained; infrared analysis indicated only starting materials.

The only isolated sulfur ylids prepared to date were reported by Ingold and Jessop (Ref. 97) who prepared them by treating the corresponding sulfonium salt with a base. Extension of this route was investigated as a possible method for the preparation of new sulfur ylids. The work of Ingold and Jessop (Ref. 97) and Johnson (Ref. 130) was repeated by combining dimethyl sulfide and 9-bromofluorene (102 p71) in nitromethane and allowing the mixture to stand until

CHART 22



the sulfonium salt precipitated. Dimethyl sulfide was prepared by the zinc-hydrochloric acid reduction of dimethylsulfoxide. 9-Bromofluorene was obtained in a 47% yield by the bromination of fluorene with N-bromo-succinimide. The sulfonium salt formed was treated with 10% sodium hydroxide to precipitate the ylid, dimethyl-sulfonium fluorenylide (2 p71) in an 82% yield (Reaction G,p71).

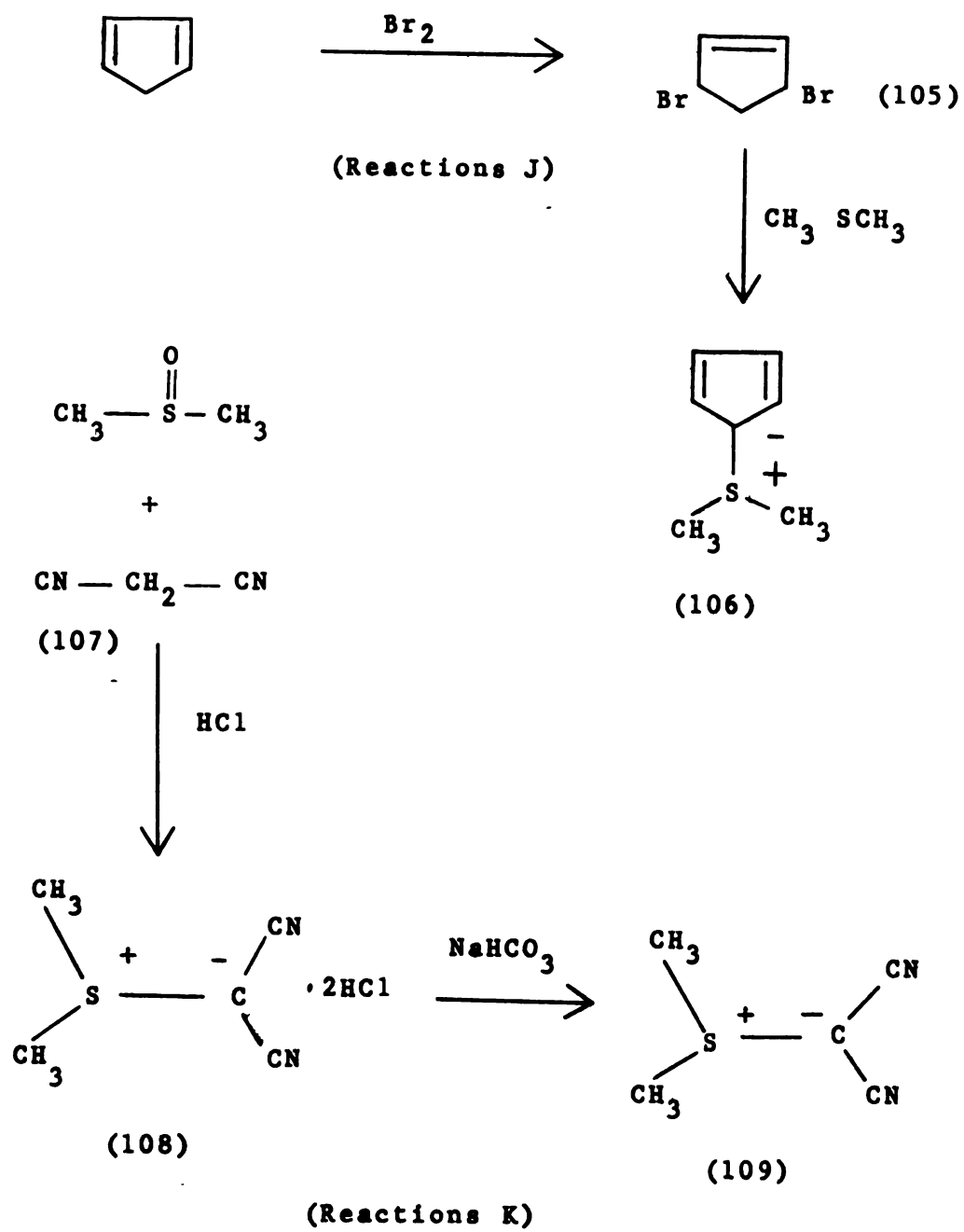
Using this experimental procedure dimethyl sulfide was combined with isopropyl chloride in nitromethane at room temperature. The resulting dimethylisopropyl-sulfonium chloride was treated with strong base in an attempt to remove the tertiary hydrogen and form the ylid. Efforts to isolate the ylid were unsuccessful, as were attempts to trap the ylid with benzophenone or para nitrobenzaldehyde (Reaction H p71).

The use of bromomalononitrile (103 p71) to form sulfonium salts was investigated in an effort to provide added resonance stabilization to the ylid by delocalization of the electrons in the carbon 2-p orbital by the nitrile group. Bromomalononitrile was combined with dimethyl-sulfide in chloroform to yield a crystalline solid which was recovered by filtration and transferred to a solution of sodium bicarbonate. Extraction of the alkaline solution with chloroform and removal of the solvent

gave a mass of dark brown crystals which were recrystallized from isopropyl alcohol. White crystals of dimethylsulfonium dicyanomethylide (104 p71) were obtained in 14% yield (Reaction J p71).

In preparation of bromomalononitrile (103 p71) via the direct bromination of malononitrile the purity of the product was greatly improved by recrystallization from ethyl ether at -70°C . However, the material was obtained in low yield.

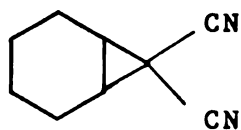
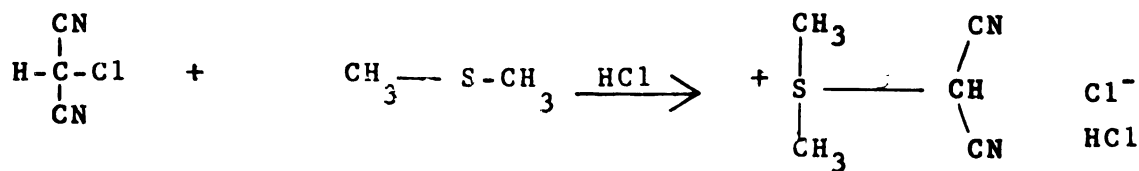
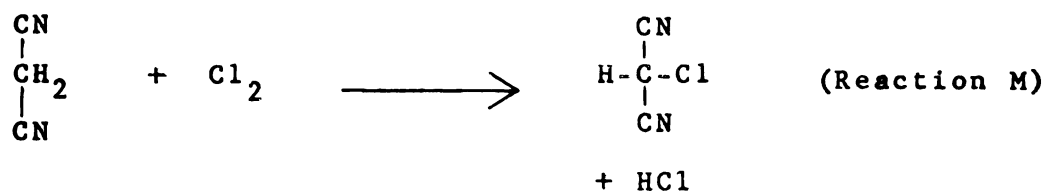
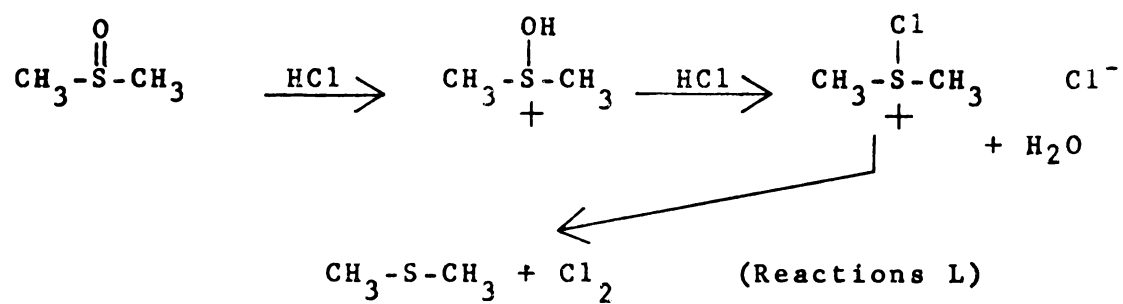
In an attempt to prepare additional sulfur ylids, the method of Ramirez and Levy (Ref. 131) was used with the aim of preparing dimethylsulfonium cyclopentadienylide (106 p74), (Reaction J p74). Cyclopentadiene was brominated according to the method of Young, Hall and Winstein (Ref. 132) to give a 34% yield of cis-3,5-dibromocyclopentene (105 p74). This bromide was added to dimethylsulfide to form the corresponding sulfonium salt which should then dehydrohalogenate to give the ylid (106 p74), dimethylsulfonium cyclopentadienylide. When cis-3,5-dibromocyclopentene (105 p74) was added to a chloroform solution of dimethylsulfide, a white precipitate formed after several minutes. Treatment of the sulfonium salt with sodium hydroxide solution led to the isolation of 5-dimethylsulfonium cyclopentadienylide in 54% yield.

CHART 23

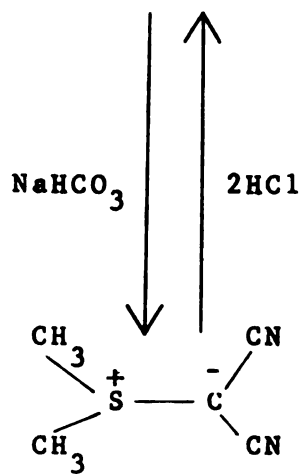
The interaction of dimethylsulfoxide and malononitrile (107 p74) with a dehydrating agent was investigated as a route to sulfur ylids. The use of ordinary dehydrating agents presented a problem due to their explosive reactivity with dimethylsulfoxide (Ref. 133). The use of anhydrous hydrogen chloride permitted the dehydration of dimethylsulfoxide and malononitrile. When hydrogen chloride was bubbled into a solution of dimethylsulfoxide and malononitrile at 0° a precipitate formed. This was identified as the dihydrochloride of dimethylsulfonium dicyanomethylide (108 p74) formed in a 60% yield. Treatment of this salt with sodium bicarbonate solution and extraction with chloroform led to the isolation of dimethylsulfonium dicyanomethylide (109 p74) in a 51% yield.

The above reaction was repeated using diethyl and di-n-propyl sulfoxide. A yellow solid precipitated upon addition of hydrogen chloride. However, treatment of the solid with base did not permit the isolation of the corresponding ylid.

A proposed mechanism for the reaction of dimethyl sulfoxide, malononitrile and hydrogen chloride to dimethylsulfonium dicyanomethylide is given in Chart 24 p76. It is similar to the mechanism suggested by Hunsberger and Tien (Ref. 134) for the reaction of dimethyl

CHART 24

(110)



(Reactions N)
(109)

sulfoxide and ethyl alpha bromoacetate. Initially, hydrogen chloride is oxidized to chlorine and dimethyl sulfoxide is reduced to dimethyl sulfide (Reaction L, p76). Reaction M, p76 is the chlorination of malononitrile by the liberated chlorine to give chloromalononitrile. The chloromalononitrile then reacts with the dimethyl sulfide formed in the initial reaction to give dimethyldicyanomethylsulfonium chloride (Reaction N, p76). The sulfonium salt is subsequently treated with base to give the ylid (B) (109) dimethylsulfonium dicyanomethylide.

In an attempt to establish the mechanism of this reaction, malononitrile was added to dimethylsulfoxide hydrochloride. However, only starting materials were recovered. Elimination of the solvent resulted in the formation of a dark brown intractable mass from which no pure material could be isolated.

Pyrolysis of the ylid gave a red brown liquid which was determined by infrared analysis to be a mixture of dimethylsulfide and tetracyanoethylene. Dimethylsulfide was identified by its characteristic odor and by comparison of the infrared spectra of the gas collected in a cold trap during pyrolysis. Thus, a homolytic cleavage of the C=S appears to have taken place. Little experimental evidence supports the existence of dicyanocarbene (Ref. 139, 140, 141).

It is expected that dicyanocarbene should be a relative stable diradical due to the two electronegative cyano groups attached to the divalent carbon, and that it would be somewhat less reactive toward condensation with double bonds than dihalo or dialkyl carbenes. Ultraviolet irradiation of dimethylsulfonium dicyanomethylide gave dimethylsulfide and tetracyanoethylene as determined by infrared analysis. However, treatment of cyclohexene with the ylid under reflux conditions or in the presence of ultraviolet irradiation did not permit the isolation of the expected 7,7-dicyanonorcarane (110 p76)

Treatment of the ylid with maleic anhydride gave a white crystalline solid, having a melting point of 39-41°C. Attempts to identify this material failed and it was concluded that a polymeric material had formed.

Attempts to carry out a Diels-Alder reaction with the ylid and several dienes, including butadiene, acrylonitrile or methyl methacrylate were unsuccessful.

EXPERIMENTAL

2-Thiophenecarboxylic Acid

To a stirred mixture of 84.0 g. (1.0 mole) of thiophene and 200 ml. of anhydrous ether contained in a two liter flask fitted with a stirrer, thermometer, and Allihn condenser, was added dropwise 640 ml. of 1.6 N n-butyllithium ether solution while maintaining the reaction temperature at -10° . The solution was refluxed for 30 minutes and then cautiously added to a rapidly stirred slurry of dry ice suspended in anhydrous ether. A vigorous reaction ensued, after which the mixture was allowed to warm to room temperature. The slurry was poured into a beaker containing 50 ml. of concentrated hydrochloric acid, 200 g. ice and 300 ml. water. The ether layer was separated, the aqueous phase extracted several times with ether, and the combined ether phase was washed with 20% sodium hydroxide. The alkaline extract was boiled with activated charcoal and filtered. The filtrate was acidified with hydrochloric acid and the white solid was recovered by filtration on a Buchner funnel, washed with 50 ml. of cold water, and dried to give 121 g. (0.94 mole, 94%) of the crude acid. The crude acid was recrystallized from water giving 106 g. (0.83 mole, 83%) of a white crystalline material, melting point $129-130^{\circ}$. Literature value, melting point 130° (Ref. 104).

2,3-Dibromo-5-thiophenecarboxylic Acid

A 100 g. quantity of 2-thiophenecarboxylic acid (0.78 mole) was added slowly to 750 g. (4.7 moles) of bromine contained in a 1000 ml. three-necked flask fitted with a stirrer and a reflux condenser. External cooling of the reaction flask was required to prevent evaporation of bromine during the vigorous evolution of the hydrogen bromide. Addition of the acid required three hours. The reaction mixture was stirred overnight and then heated on a steam bath to remove excess bromine. Cautiously, the solid mass was poured into a saturated ammonium carbonate solution to destroy all trace of excess bromine. Concentrated hydrochloric acid was added to precipitate the crude acid. The solid product was recovered by filtration and recrystallized from ethanol in the presence of activated charcoal to obtain a light brown crystalline material (209 g. 0.73 mole, 92%), melting point 226-227°. Literature value, melting point 225-227° (Ref. 105).

2-3-Dibromothiophene

This dihalothiophene was prepared according to the procedure of Steinkopf (Ref. 106). 2,3-Dibromo-5-thiophenecarboxylic acid (230 g. 0.8 mole), mercuric acetate (572 g. 1.1 mole) and 2000 ml. of acetic acid were mixed and heated at reflux with stirring for six hours in a

5 liter three-necked flask fitted with a reflux condenser. The mixture was cooled and filtered to recover the mercuric acetate derivative. This was suspended in a liter of 20% aqueous sodium chloride, contained in a 5 liter flask fitted with a reflux condenser and heated for two hours at the suspension's reflux temperature. The reaction solution was then treated with 200 ml. of concentrated hydrochloric acid and exhaustively steam distilled using a Barret tube to collect the product. The oily layer was dried in contact with anhydrous magnesium sulfate. Distillation of the crude material gave 148 g. (0.6 moles, 85%) of 2,3-dibromothiophene boiling point 110° at 31 mm. Literature value, boiling point $93-95^{\circ}$ at 15 mm. (Ref. 85).

3-Bromothiophene

A 252 g. (3.1 moles) quantity of thiophene was placed in a two liter three-necked flask fitted with a reflux condenser, an addition funnel, and a mechanical stirrer. Bromine, 1464 g. (470 ml., 9.2 moles) was added dropwise to the well stirred solution while holding the reaction temperature at 0° . After adding the bromine, the mixture was stirred at room temperature for 48 hours to remove the hydrogen bromide. A solution containing 480 g. (8.6 moles) of potassium hydroxide dissolved in 100 ml.

of methanol was added, and the mixture was heated at its reflux temperature for six hours, followed by steam distillation to obtain 890 g. of 2,3,5-tribromothiophene. A 648 g. quantity of the yellow oil was transferred to a three liter flask fitted with a reflux condenser and a mechanical stirrer. To the oil were added 320 ml of glacial acetic acid, 1200 ml. of water, and 185 g. (2.83 g. atoms) of zinc dust. Addition of the zinc dust initiated an exothermic reaction which held the reaction mixture at its reflux temperature for 30 minutes. It was maintained at this temperature for an additional 18 hours and then steamed distilled until all organic material had been removed. The organic layer was dried over anhydrous magnesium sulfate and distilled under reduced pressure into two major fractions. The lower boiling fraction was identified as 3-bromothiophene, boiling point 68-69 at 34 mm. Hg, (135 g., 0.83 mole, 41%), $n_D^{20} = 1.5898$. Literature value for 3-bromothiophene, boiling point 58° at 20 mm. Hg. (Ref. 107). The higher boiling fraction was determined to be a mixture of 2,3-dibromothiophene and 2,4-dibromothiophene by infrared and n.m.r. spectra.

2,3-Dibromothiophene

Following the experimental procedure of S. Gronowitz (Ref. 84), 630 g. (3.94 moles) of bromine in 250 ml. of carbon tetrachloride were added dropwise during eight hours at room temperature to 620 g. (3.8 moles) of 3-bromothiophene in 250 ml. of carbon tetrachloride. After stirring overnight, the solvent was removed in vacuo, 100 g. (2.5 moles) of sodium hydroxide were added and the alkaline mixture was heated on a steam bath for four hours, filtered, and distilled. A total of 888 g. (3.67 moles) (96%) of 2,3-dibromothiophene, boiling point 110° at 31 mm. Hg were obtained. Literature value (Ref. 108), boiling point $94-96^{\circ}$ at 15 mm. Hg.

Anhydrous Copper (II) Chloride

A 1 l. flask was charged with 300 g. of finely ground $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 700 ml. of freshly distilled thionyl chloride. The evolution of sulfur dioxide and hydrogen chloride began at once and was accompanied by an appreciable decrease in reaction temperature. After the gas evolution ceased, the flask was equipped with a reflux condenser, and the slurry was refluxed for 2 hours. The condenser was then removed and the excess thionyl

chloride was removed in vacuo. The flask containing the product was transferred immediately to a vacuum desiccator containing potassium hydroxide and stored for two days to remove the remaining thionyl chloride.

3,3'-Dibromo-2,2'-bithienyl

This compound was prepared according to the procedure of Gronowitz (Ref. 86). To a stirred mixture of 138 g. (0.57 moles) of 2,3-dibromothiophene 100 ml. of anhydrous ether was added dropwise 394 ml. of 1.6 N n-butyllithium ether solution while keeping the reaction temperature at -70° . After five minutes 100 g. (0.74 mole) of anhydrous CuCl_2 was cautiously added. After being set aside at -70° for 2 hours the mixture was allowed to warm to room temperature overnight. It then was treated under external cooling with 4 N hydrochloric acid. The ether phase was extracted several times with 4 N hydrochloric acid to remove cuprous chloride and then extracted with water. It was subsequently dried and the ether and butyl bromide were removed in vacuo. The residue was recrystallized from ligroin using norit. The yield of pure product was 47 g. (0.14 moles) (51%) of 3,3'-dibromo-2,2'-bithienyl, which crystallized into almost perfect

cubic crystals, melting point 103-104°. Literature value (Ref. 86) melting point 102-104°.

3,3'-Dicarboxy-2,2'-bithienyl

The 3,3'-dilitho-2,2'-bithienyl was prepared as previously described from 40.0 g. (0.124 mole) of 3,3'-dibromo-2,2'-dithienyl and 156 ml. of 1.6 N n-butyl-lithium ether solution. The yield 22.0 g. was (70%) of crude acid. The product was washed twice with ether and then recrystallized from glacial acetic acid, yielding 14 g. (0.055 moles) (44%) of 3,3'-dicarboxy-2,2'-bithienyl, melting point 289-291°. Literature value, melting point 289-291° (Ref. 86).

Attempted cyclization of 3,3'-dicarboxy-2,2'-bithienyl

In a 50 ml. distilling flask, fitted with a thermometer, was placed an intimate mixture of 14 g. (0.055 mole) of powdered 3,3'-dicarboxy-2,2'-bithienyl and 2 g. (0.011 mole) of finely ground crystallized barium hydroxide. The mixture was gradually distilled by heating in an oil bath to 350° during about one hour, and maintained at that temperature until only a small amount of dry residue remained in the flask. The distillate

was dissolved in 25 ml. of ether and the ether solution was washed twice with 5 ml. portions of water, and dried. The ether was removed and the residue was taken up in ethanol. The resulting solution was treated with Norite and filtered. Attempted isolation of the expected ketone gave no positive results.

Tetrabromothiophene

To 252 g. (3.0 moles) of thiophene in a three liter beaker, and immersed in an ice bath, was added dropwise 656 ml. (12.0 moles) of bromine, during 9 hours. The final 200 ml. of bromine were added without external cooling at room temperature. The mixture was then air dried to remove the unreacted bromine. The yield of the crude bromide was 1165 g. (96%). A small sample of the crude material was dissolved in hot chloroform, treated with Norite, cooled and filtered to obtain an analytical sample of the pure tetrabromothiophene, melting point, 114-116°. Literature value, melting point, 114° (Ref. 109).

3-Bromothiophene and 3,4-dibromothiophene

Into a three liter three-necked flask fitted with a reflux condenser, stirrer and a condenser-Barret tube for steam distillation was introduced, in the order given, 450 ml. of water then, with vigorous stirring, 300 g. of zinc powder and 300 ml. of acetic acid. The stirred mixture was heated to boiling, and 425 g. (1.06 moles) of crude tetrabromothiophene were added continuously through the reflux condenser. The yellow oil distillate was collected at frequent intervals and returned to the reaction vessel. After four hours the oily material was collected and the operation was discontinued. The organic layer was washed with water, sodium carbonate solution and again with water, dried over anhydrous magnesium sulfate and fractionated. After 124 g. (0.76 mole, 72%) of 3-bromothiophene, boiling point 157-159°, $n_D^{20} = 1.5900$, had distilled, there was obtained 61 g. (0.254 mole, 24%) of 3,4-dibromothiophene, boiling point 115° at 20 mm. Hg, $n_D^{20} = 1.6394$. Literature values: 3-bromothiophene, boiling point 159-161°, $n_D^{20} = 1.5919$; (Ref. 110); 3,4-dibromothiophene, boiling point 94-95° at 12 mm. Hg, $n_D^{20} = 1.6380$ (Ref. 110).

2-Thenoyl Chloride

During 30 minutes, 260 g. (2.2 moles) of thionyl chloride were added to 56 g. (0.44 mole) of 2-thiophenecarboxylic acid contained in a 500 ml. flask fitted with a reflux condenser. The reaction was set aside at room temperature for 18 hours and then heated under reflux for 2 hours. The excess thionyl chloride was removed by distillation, and the residue was distilled in vacuo to obtain 57 g. (0.39 mole, 89%) of a colorless liquid boiling at 124° at 64 mm. Hg. Literature value, boiling point 72° at 5 mm. Hg (Ref. 111).

N,N-Dimethyl-2-thiophenecarboxamide

A 57 g. (0.39 mole) quantity of 2-thenoyl chloride was added to 300 ml. of anhydrous ether in a 500 ml. flask fitted with a stirrer, reflux condenser, thermometer, and gas inlet tube. The mixture was cooled to -30° and gaseous dimethyl amine was bubbled into acid chloride-ether solution at a moderate rate. External cooling was necessary to maintain the reaction temperature below 0° . Following addition of the dimethyl amine the solution was washed first with water

and then with a dilute hydrochloric acid solution. The ether layer was separated, dried and the ether removed. The residue was distilled to obtain 40.7 g. (0.26 mole, 68%) of a colorless oil which boiled at 135° at 3 mm.

Hg. The oil solidified on cooling, melting point 43-44°. Literature value: Taft reports a boiling point of 105-106° at 0.6 mm. Hg but no elemental analysis (Ref. 85).

Calc'd. for C_7H_9SNO : C, 54.16; H, 5.84; S, 20.66; N, 9.02

Found: C, 53.97; H, 5.80; S, 21.02; N, 9.12

N,N-Dimethyl-2-thienyl Ketone

An n-butyllithium ether solution (175 ml. of 1.6 N, 0.28 mole), and 100 ml. of anhydrous ether were placed in a 500 ml. three-necked flask fitted with a mechanical stirrer, a reflux condenser, an addition funnel, a -70 to +50° thermometer, and a Drierite tube. Into the n-butyllithium solution, cooled to -70°, was added a 40 g. (0.244 mole) quantity of 2-bromothiophene in 100 ml. of anhydrous ether. After several minutes, 38 g. (0.242 mole) of N,N-dimethyl-2-thiophenecarboxamide dissolved in 25 ml. of ether was added dropwise at -70° during a 30 minute period. A yellow-white solid formed immediately. The white slurry was allowed to warm to

room temperature and then poured into a saturated ammonium chloride solution. The ether layer was separated; the aqueous layer was extracted with 200 ml. of ether, and the combined extracts were dried over anhydrous magnesium sulfate. The ether was removed on a steam bath. The residue was distilled in vacuo to give a light yellow colored oil which immediately crystallized on cooling, boiling point 171-175° at 6-7 mm Hg. The solid was recrystallized from petroleum ether to give white needles, 27 g. (0.14 mole, 58%), melting point 87-88°. Literature value, boiling point, 189-190° at 10 mm. Hg, melting point 88-89° (Ref. 112).

Di-2-thienylmethane

The experimental procedure of King and Nord (Ref. 89) was employed in the preparation of this compound. A solution containing 5 g. (0.0258 mole) of di-2-thienyl ketone, 6.0 ml. (0.11 mole) of 85% hydrazine hydrate and 25 ml. of ethylene glycol was stirred in a 100 ml. flask fitted with a Vigreux column and distilling head. The reaction solution was heated at 160° to remove excess hydrazine and water. The residue was cooled to 40°, the Vigreux column was replaced by an Allihn condenser, 5.5 g. of potassium

hydroxide were added, and the basic reaction mixture was heated until the evolution of nitrogen initiated (about 100°). The mixture was refluxed for two hours and then extracted with several portions of ether. The ether phase was washed first with 1:1 hydrochloric acid, then with water and dried over anhydrous magnesium sulfate. The ether was removed and the residue was recrystallized from petroleum ether to yield a small quantity of needles, melting point, 43-44°. It is suggested that alcohol be used as a recrystallizing solvent as the compound was appreciably soluble in petroleum ether. The yield crude di-2-thienylmethane was 4.0 g., (86%). Literature value, melting point, 45-47°, 125-126° at 9 mm. Hg (Ref. 113).

Cyanogen Bromide

The procedure of Hartman and Dreger was used to prepare this compound (Ref. 114). A 1 l. round bottomed flask, surrounded by an ice bath and provided with a stirrer, a separator funnel, and an outlet tube, was set up in the hood. To the flask was added 50 g. (16 ml., 0.31 mole) of bromine and 5.0 ml. of water. To the stirred bromine solution was added gradually a solution of 17.0 g. of sodium cyanide (0.35 mole) in

125 ml. of warm water. The temperature of the reaction mixture was kept below 30° . On completion of the reaction the cyanogen bromide was distilled from the reaction mixture steam bath, using a 50 ml. flask. The distillate was warmed with about 10 g. of anhydrous calcium chloride, filtered, and again distilled. The product collected boiled at $61-62^{\circ}$. The yield of the white crystalline solid was 22 g. (72%). Literature values of this extremely toxic material were boiling point $60-62^{\circ}$, melting point $49-51^{\circ}$ (Ref. 114).

Attempted Preparation of 3,3'-dibromo-2,2'-dithienyl ketone from cyanogen bromide and 3-bromo-2-thienyllithium

Into 60 g. (0.248 mole) of 2,3-dibromothiophene in 200 ml. of ether, cooled to -70° , was added dropwise 73 ml. of 1.6 N n-butyllithium as previously described. The 3-bromo-2-thienyllithium solution was added dropwise at -70° to 22 g. (0.21 mole) of cyanogen bromide in 100 ml. of anhydrous ethyl ether in a 500 ml. flask. A red brown solution formed immediately. The solution was allowed to warm to room temperature overnight and was then refluxed for an hour on a water bath. The reaction mixture was hydrolyzed with cold, dilute hydrochloric acid. The solution was extracted with several portions of ether, and the combined extracts

were dried over anhydrous magnesium sulfate. The ether was removed over a steam bath leaving a dark amorphous material from which no substituted thienyl ketone could be isolated.

3-Bromo-2-thiophenecarboxylic Acid

This compound was prepared according to the procedure of Gronowitz (Ref. 115). Into 61 g. (0.25 mole) of 2,3-dibromo-thiophene in 200 ml. of anhydrous ether cooled to -70° and vigorously stirred, was poured 165 ml. of 1.6 N-butyllithium ether solution. After a 10 minute reaction period the solution was poured onto dry ice and product isolation was carried out as previously described. Recrystallization of the crude sulfur heterocyclic acid from a water-ethanol solution gave a pure, white product in the form of needles, melting point 195° , yield 40 g. (0.193 mole) 78%. Literature value, $193-195^{\circ}$ (Ref. 107).

3-Bromo-2-thenoyl chloride

After a mixture of 3-bromo-2-thiophenecarboxylic acid (40 g., 0.19 moles) and thionyl chloride (40 g., 0.33 moles) had been heated under reflux for an hour, the excess thionyl chloride was removed by distillation under reduced pressure. The crude residual acid chloride was purified by distillation in vacuo using a distilling column to obtain 45 g. (0.16 moles, 84%), m.p. 48-50°, of pure product.

Calc'd. for $C_5H_2SBrOCl$: C, 26.62; H, 0.89; S, 14.22;

Br, 35.43; O, 7.09; Cl, 15.72.

Found: C, 27.17; H, 0.92; S, 13.96;

3-Bromo-N,N-dimethyl-2-thiophenecarboxamide

A 45 g. quantity (0.16 moles) of 3-bromo-2-thenoyl chloride was mixed with 200 ml. of anhydrous ether in a 500 ml. three-necked flask fitted with a stirrer, a reflux condenser, a thermometer, and a gas inlet tube. The mixture was cooled to -30° and gaseous dimethyl amine was admitted below the surface of the mixture at a moderate rate. The reaction temperature was held below -30° and after the addition of the dimethyl amine, the solution was washed with water and then with a dilute hydrochloric acid solution. The ether layer was dried and the ether removed. The residue was

distilled at 139-142° at 0.9 mm. Hg to give 21 g. (0.09 moles, 57%), $n_D^{20} = 1.5922$.

Calc'd for C_7H_8BrSNO : C, 35.9; H, 3.43; S, 13.7; N, 5.98;
Br, 34.1

Found: C, 35.91; H, 3.50; S, 13.57; N, 5.74; Br, 34.18

Attempted preparation of 3,3'-dibromo-2,2'-dithienyl Ketone

A 23.4 g. (0.1 moles) quantity of 3-bromo-N,N-dimethyl-2-thiophenecarboxamide dissolved in 100 ml. of anhydrous ether was added to a solution of 3-bromo-2-thienyllithium. The latter solution was prepared by adding 24.2 g. (0.1 moles) 75 ml. of 1.6 N n-butyllithium dropwise at -70° to 2,3-dibromothiophene in 100 ml. of ether. Distillation of the product following hydrolysis of the reaction solution gave a dark brown oil from which no pure material could be isolated.

4-Bromo-3-thiophenecarboxylic Acid

To a solution of 61 g. (0.25 moles) of 3,4-dibromothiophene in 100 ml. of anhydrous ether precooled to a temperature of -70°, was added rapidly 165 ml. of 1.6 N n-butyllithium. The reaction solution was stirred for two minutes and then treated immediately with an excess of solid carbon dioxide in ether. Product isolation was carried out as previously described. On acidification of the solution a white precipitate formed.

This was collected by filtration and after recrystallization from water-ethanol solution, yielded the pure product in the form of small fine needles, m.p. 158-159°, 42 g. (82%). Literature value, 157-159° (Ref. 116)

4-Bromo-3-thenoyl Chloride

During 30 minutes, 42 g. (0.20 moles) of 4-bromo-3-thiophenecarboxylic acid was treated with 163 g. (1.87 moles) of thionyl chloride in a 500 ml. round bottom flask fitted with a reflux condenser. The reaction solution was held at its reflux temperature for an hour by heating it on a steam bath. The excess thionyl chloride was removed by distillation using a 10 cm. Vigreux column to obtain 51 g. (0.226 moles, 90%) of the crude material.

4-Bromo-N,N-dimethyl-3-thiophenecarboxamide

A 60 g. (0.276 moles) quantity of 4-bromo-3-thenoyl chloride was treated with 135 g. (3.0 moles) of dimethyl amine in an experimental procedure already described. Distillation of the crude product at 155-160° 3 mm. Hg gave 44.1 g. (69%) of the pure product, m.p. 86-87°. Calc'd for C_7H_8BrSNO : C, 35.9; H, 3.43; S, 13.7; N, 5.98; Br, 34.1
Found: C, 36.11; H, 3.58; S, 13.58; N, 6.11; Br, 34.12

Attempted preparation of 3,3'-dibromo-4,4'-dithienyl ketone

A 23.4 g. (0.1 moles) quantity of 4-bromo-N,N-dimethyl-3-thiophene-carboxamide in 100 ml. of tetrahydrofuran was allowed to interact with 0.1 mole of 3-bromo-4-thienyllithium in the manner described previously. Product isolation from the reaction mixture gave a dark brown oily material from which no ketone could be obtained after repeated fractionation.

3-Bromo-2-thiophenecarboxaldehyde

The mixture of 3-bromothiophene (82 g., 0.5 moles), dimethylformamide (46.0 g., 0.64 moles) and phosphorus oxychloride (96.0 g., 0.62 moles) was heated under reflux for 4.5 hours. After being set aside overnight, the reaction mixture was poured into ice water, neutralized with sodium acetate, and extracted with ether. The ethereal extract was washed with water, then with an aqueous solution of sodium bicarbonate, and dried over magnesium sulfate. Removal of the ether and vacuum distillation of the residue gave 37 g. (0.19 moles, 39%) of pure product, b.p. 108° at 2 mm. Hg. Literature value, b.p. 91-92° at 3 mm. Hg. (Ref. 92).

3-Bromo-2-thiophenecarboxaldehyde

A 340 ml. volume of 1.6 N n-butyllithium ether solution was added dropwise to 121 g. (0.5 moles) of 2,3-dibromothiophene in 200 ml. of anhydrous ether at -70° . After 10 minutes, the solution of organic metal complex, was slowly added to a stirred solution of 47.0 g. (0.65 moles) of N,N-dimethylformamide in 250 ml. of ether. The reaction mixture was stirred for 30 minutes and then hydrolysed with a saturated ammonium chloride solution. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were dried and distilled, yielding 77 g. (81%) of 3-bromo-2-thiophenecarboxaldehyde at $114-116^{\circ}$ at 11 mm. Hg, m.p. $24-25^{\circ}$. Literature value, $113-115$ at 10 mm. Hg, m.p. $24-25^{\circ}$ (Ref. 93).

Bis-(di-3-bromo-2-thienylmethyl) ether

The experimental method of Gronowitz (Ref. 91) was used to prepare this compound. To a solution of 3-bromo-2-thienyllithium prepared at -70° from 160 ml. of 1.6 N n-butyllithium ether solution (0.256 moles) and 60 g. (0.25 moles) of 2,3-dibromothiophene in 150 ml. of anhydrous ether was added dropwise 42.0 g. (0.22 moles) of 3-bromo-2-thiophenecarboxaldehyde in 100 ml. of anhydrous ethyl ether. A half hour after adding the

alkyl lithium compound the cooling bath was removed and an hour later the solution was hydrolyzed with dilute hydrochloric acid. The ether phase was washed with water, dried and the ether was removed over a steam bath. After setting the solution aside overnight, the solid residue was recovered by filtration and recrystallized from pet ether (60-90°), to obtain 66 g. of a mixture of di-(3-bromo-2-thienyl) carbinol and bis-(di-3-bromo-2-thienylmethyl) ether. A single crystallization from ligroin gave 43.0 g. of almost pure bis-(di-3-bromo-2-thienylmethyl) ether, crystallizing in larger cubic prisms, m.p. 166-167°. Two additional recrystallizations of this material from benzene gave an analytically pure ether, m.p. 168°.

Calc'd. for $C_{18}H_{10}S_4Br_4O$: C, 31.4; H, 1.16; S, 18.6;
Br, 46.5

Found: C, 31.97; H, 1.32; S, 18.97; Br, 45.97

Di-(3-bromo-2-thienyl) carbinol

The above procedure was modified using the same quantities of starting materials, 160 ml. of 1.6 N n-butyllithium ether solution, 60.0 g. (0.25 moles) of 2,3-dibromothiophene and 42.0 g. (0.22 moles) of 3-bromo-2-thiophenecarboxaldehyde. The cooling bath was removed an hour after adding the n-butyl lithium and when the temperature of the solution had reached room temperature

it was hydrolyzed with a saturated ammonium chloride solution. The ether phase was separated, washed with water, dried and the ether was removed at room temperature in a rotary evaporator. The solid residue was recrystallized from ligroin (60-90°) giving 57.0 g. (69%) of di-(3-bromo-2-thienyl) carbinol, m.p. 91-92°, as in the form of fine white needles which decomposed in about five minutes after removal of the solvent to a black amorphous tar.

Calc'd. for $C_9H_6S_2Br_2O$: C, 30.52; H, 1.71; S, 18.11;

Br, 45.14

Found: C, 31.03; H, 1.85; S, 18.33; Br, 44.51

Di-(3-bromo-2-thienyl) ketone

This ketone was best prepared directly from 3-bromo-2-thiophenecarboxaldehyde and 3-bromo-2-thienyllithium without isolation of the intermediate carbinol. To 19.1 g. (0.1 moles) of 3-bromo-2-thiophenecarboxaldehyde cooled to -70° in 100 ml. of ether was added 3-bromo-2-thienyllithium prepared from 24.2 g. (0.1 moles) of 2,3-dibromothiophene in 100 ml. of anhydrous ether and 70 ml. of 1.6 N n-butyllithium ether solution (0.112 moles). After the reaction had been set aside for one hour at -70°, the cooling bath was removed. Four hours later the ether solution was added to a chromium trioxide-pyridine complex,

prepared by adding 32 g. (0.32 moles) of chromic anhydride in small portions with swirling to 350 ml. of reagent grade pyridine at 15-20°. The first phase of the reaction consisted of a slow anhydride without dissolving of the complex formation. After a few minutes, the red anhydride was transformed exothermally into a yellow solid which dissolved quite rapidly; the reaction temperature was kept below 30° during the addition of the anhydride. After about one-third of the chromic anhydride had been added and mostly dissolved, the yellow complex began to precipitate. At the end of the addition of the anhydride a slurry of the complex in pyridine remained. The reverse addition of pyridine to the chromic anhydride was reported to inflame. The carbinol pyridine-chromic anhydride complex was set aside overnight at room temperature. The solution was then poured into water (3 liters) and the aqueous solution was extracted several times with 200 ml. portions of benzene. The combined extracts were washed with water until all traces of chromium trioxide was removed then dried over anhydrous magnesium sulfate. Removal of the solvent gave yellow crystals, 21.0 g. (0.06 mole, 60%) of di-3-bromo-2-thienyl) ketone, m.p. 96-97°, after recrystallization from ligroin (60-90°). The product distilled at 175-185° at 1.5 mm. Hg. to give a slightly decomposed crystalline

material.

Calc'd for $C_9H_4S_2Br_2O$: C, 30.70; H, 1.14; S, 18.21;
Br, 45.40

Found: C, 30.94; H, 1.38; S, 17.90; Br, 45.22

Di-(3-bromo-2-thienyl) hydrazone

A 5.0 g. (0.0142 moles) quantity of di-(3-bromo-2-thienyl) ketone, 200 ml. of absolute ethanol, 1.0 g. (0.015 moles) of hydrazine hydrate and 10.0 g. (0.065 moles) of barium oxide were added to a 500 ml. flask fitted with a reflux condenser and a Drierite drying tube. The mixture was heated under reflux for five hours. On cooling the mixture in ice, yellow crystals formed which were recovered by filtration and recrystallized from ligroin (60-90°). Yield 4.0 g. (77%) of di-(3-bromo-2-thienyl) hydrazone, m.p. 191-193°.

Calc'd for $C_{18}H_6N_2S_2Br_2$: C, 29.5; H, 1.65; N, 7.67; S, 17.5
Br, 43.6

Found: C, 29.39; H, 1.61; N, 7.69; S, 17.67; Br, 43.45

3-3'-Dibromo-2,2'-dithienylmethane

The experimental method of Cram, Sahyum and Knox (Ref. 95) was used to prepare this compound. To a rapidly stirred mixture of 20 g. (0.178 moles) of sublimed potassium tert-butoxide (M.S.A. Research Corporation, Callery, Pa.) and 50 ml. of anhydrous dimethyl sulfoxide (Ref.117) was added, in small portions, 20 g. (0.055 moles) of the hydrazone, di-(3-bromo-2-thienyl) hydrazone during 4 hours. The solution became red-brown and nitrogen was evolved vigorously. The reaction mixture was shaken with a mixture of methylene chloride and water, and the organic layer was separated, washed with water, dried and the solvent was removed by evaporation to give a solid mass. Fractional distillation of this material at 185-188° at 2.5 mm Hg. gave 3.6 g (0.0107 mole, 20%). Literature values, 150-160° at 0.45 mm Hg, m.p. 37-38° (Ref.83).

3-Bromo-2-thienyl Chloride

This compound was prepared according to Wynberg's procedure (Ref.83). A rapid stream of hydrogen chloride was passed into a stirred mixture of 114.0 g. (0.70 moles) of 3-bromothiophene and 30 ml. of concentrated hydrochloric acid during 30 minutes while the reaction temperature was maintained at 0°. Following this, 79 ml. of 36% aqueous

formaldehyde was added dropwise to the stirred acidic halothiophene solution at 50° for an hour. The vigorously stirred mixture was cooled in an ice bath and saturated with hydrogen chloride gas. Gas admission was discontinued and the mixture was heated on a water bath for an hour at 80-90°. After cooling, the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed first with 10% sodium bicarbonate solution and then with water. After drying over magnesium sulfate, the ether was removed and the residue was fractionated to obtain 126 g. (85%, 0.59 moles) of 3-bromo-2-thienyl chloride, b.p. 134-135° at 32 mm. Hg, $h_d^{20} = 1.6036$. Literature value, b.p. 106.5-107.5° at 12 mm. Hg, $n_D^{20} = 1.6059$ (Ref.83).

3,3'-Dibromo-2,2'-dithienylmethane

A three-necked flask fitted with a mechanical stirrer, reflux condenser and a dropping funnel were charged with a solution of 150 g. (0.31 moles) of 3-bromothiophene and 5.0 g. (0.019 moles) of SnCl_4 in 500 ml. of carbon disulfide. The mixture was maintained at 20° and 64.0 g. (0.3 moles) of 3-bromo-2-thienyl chloride in 200 ml. of carbon disulfide was added dropwise during eight hours. The solution was stirred for another eight hours and then poured into a hydrochloric acid-ice mixture.

The layers were separated and the aqueous portion extracted with carbon disulfide. After washing with a 10% sodium bicarbonate solution and water, the solution was dried over anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator. Fractionation of the residue at 203-205° at 4 mm. Hg yielded 62 g. (0.184 mole, 62%). Literature values, 150-160° at 0.45 mm. Hg, m.p. 37-38° (Ref. 83).

Cyclopenta (1,2-b:4,3-b') dithiophene

The Wynberg procedure was used to prepare this compound. (Ref. 83). A solution of 3,3'-dilithio-2,2'-dithienylmethane was prepared at -70° as previously described from 45 g. (0.13 mole) of 3,3'-dibromo-2,2'-dithienylmethane in 500 ml. of anhydrous ether and 164 ml. of 1.6 N n-butyllithium (0.261 moles) in a 1000 ml. round bottomed flask. The yellow colored solution was poured into a pre-cooled dropping funnel (-20°), which was attached to a second 1000 ml. three-necked flask containing 40 g. (0.3 moles) of anhydrous CuCl_2 , predried at 130° for 30 minutes in 200 ml. of anhydrous ether. While stirring the ice-cooled suspension vigorously the dilithio compound was added dropwise during 8 hours. After stirring the solution at 0° overnight, the reaction mixture was acidified with 100 ml. of 2 N hydrochloric

acid and it was filtered to remove the grayish precipitate of cuprous chloride.

The ether layer was separated and the aqueous phase was extracted with ether. The combined ethereal extracts were washed several times with 4 N hydrochloric acid, then with a sodium bicarbonate solution, and finally with water. After drying over magnesium sulfate and removal of the solvent, the residue crystallized on cooling. Steam distillation of the residue gave 17.8 g. (75%) of crude cyclopenta (1,2-b:4,3-b') dithiophene. A single recrystallization of this material from ethanol yielded 15.5 g. (63%, 0.084 moles) of pure product, m.p. 67-68°. Literature values, m.p. 66-67°, the NMR spectra showed two doublets at τ 3.05 and τ 2.88, and a singlet at τ CH₂ 6.36 (Ref. 83).

7-Bromocyclopenta (1,2-b:4,3-b') dithiophene

A solution of 10 g. (0.056 moles) of cyclopenta (1,2-b:4,3-b') dithiophene in 50 ml. of dry thiophene-free benzene was heated for an hour at its reflux temperature with 10 g. (0.056 moles) of N-bromosuccinimide. The precipitated succinimide was removed by filtration, and the solvent was removed from the filtrate by distillation. The residue taken up in 50 ml. of hot, high boiling petroleum ether. On cooling, long needle-

like crystals of product crystallized from the solution.

The yield of pure product was 6.0 g. (0.0234 moles)

41%; m.p. 59-60°.

Calc'd for $C_9H_5S_2Br$: C, 42.00; H, 1.96; S, 24.9;

Br, 31.1

Found: C, 41.52; H, 1.99; S, 24.98; Br, 31.53

7-Dimethylsulfonium Cyclopenta (1,2-b:4,3-b')

dithiophenylide

Dimethyl-7-cyclopenta (1,2-b:4,3-b') dithienyl-sulfonium bromide was prepared according to the procedure of Ingold (Ref. 97). Dimethylsulfide, 12 g. (0.19 moles); 7-bromocyclopenta (1,2-b:4,3-b') dithiophene, 5 g. (0.0195 moles); and 25 ml. of nitromethane were placed in a 100 ml. flask and set aside for 24 hours. The solid product, dimethyl-7-cyclopenta (1,2-b:4,3-b') dithienylsulfonium bromide, was collected by filtration. The yield was 4.1 g. (0.0128 moles, 66%), m.p. 118°C.

To 4.1 g. (0.0128 moles) of this bromide in 100 ml. of water was added 10% sodium hydroxide solution until precipitation was complete. The yellow solid was recovered by filtration and washed first with water, then with 95% ethanol, absolute ethanol, and finally with ether. The solid was dried over anhydrous magnesium perchlorate to yield 2.4 g. (80%, 0.01 moles)

of the pure ylid, m.p. 57-60°C.

Calc'd for $C_{11}H_{10}S_3$: C, 55.5; H, 4.21; S, 40.3

Found: C, 54.69; H, 4.72; S, 41.05

4-Bromo-3-thiophenecarboxaldehyde

This compound was prepared in a manner similar to that used to obtain 3-bromo-2-thiophenecarboxaldehyde from 61 g. (0.25 mole) of 3,4-dibromothiophene in 100 ml. of ether, 172 ml. (0.275 moles) of 1.6 N-n-butyllithium and 28 g. (0.39 moles) of N,N-dimethyl-formamide in 150 ml. of anhydrous ether as a reaction media. The dibromothiophene was added rapidly to the n-butyllithium solution at -70°. Product isolation similar to that described earlier gave 30 g. (0.157 moles, 63%) of pure 4-bromo-3-thiophenecarboxaldehyde, b.p. 137-138° at 28 mm. Hg, $n_D^{20} = 1.6333$. Literature values b.p. 108-111.5° at 11 mm. Hg, $n_D^{20} = 1.6340$ (Ref. 93).

Di-(4-bromo-3-thienyl)ketone

A 24 g. quantity of 3,4-dibromothiophene, 19 g. (0.1 moles) of 4-bromo-3-thiophenecarboxaldehyde, and 67 ml. of 1.6 N of n-butyllithium (0.1072 moles) ether solution were combined in the manner previously described to form di-(4-bromo-3-thienyl) carbinol. Oxidation of the carbinol with 32 g. (0.32 moles) of CrO_3 in 350 ml. of

pyridine gave 19 g. (0.054 moles) of pure di-(4-bromo-3-thienyl) ketone, m.p. 108° , after the crude ketone has been recrystallized from ligroin ($60-90^{\circ}$).

Calc'd for $C_9H_4S_2Br_2O$: C, 30.70; H, 1.14; S, 18.21;
Br, 45.40

Found: C, 31.42; H, 1.08; S, 18.53; Br, 45.27

3-Cyanothiophene

This compound was prepared according to the procedure of Nishimura (Ref. 92). A mixture of 3-bromothiophene, 57 g. (0.35 moles), cuprous cyanide, 40 g. (0.44 moles) and quinoline, 240 ml. was heated at its reflux temperature for 4 hours. Vacuum distillation of the reaction mixture gave 120 ml. of distillate. The distillate was acidified with dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with water and dried over magnesium sulfate. After removal of the ether, vacuum distillation of the residual liquid gave 32 g. of a product boiling at $98-99^{\circ}$ at 29 mm Hg. The yield of the product was 0.29 mole, 83%. Literature value, $100-102^{\circ}$ at 30 mm. Hg. (Ref. 92).

Reaction of 3-thienyllithium on 3-cyanothiophene

To a solution of 3-thienyllithium prepared from 16.3g. (0.1 moles) of 3-bromothiophene and 67 ml. of 1.6 N n-butyllithium (0.107 moles) ether solution was added 11 g. (0.1 moles) of 3-cyanothiophene in 100 ml. of anhydrous ether at -70° . After 30 minutes, the solution was hydrolyzed with a saturated ammonium chloride solution. Attempted product isolation in the usual manner yielded none of the expected 3-(3-thenoyl)thiophene. Thiophene and 3-cyanothiophene were the only compounds isolated.

3-Thiophenecarboxylic Acid

This compound was prepared as described above from 82 g. (0.5 moles) of 3-bromothiophene, 320 ml. of 1.6 N n-butyllithium ether solution and solid carbon dioxide. Product isolation yielded 55 g. (0.43 moles, 86%) of pure material, m.p. $136-138^{\circ}$, after a simple recrystallization from water. Literature value, m.p. $137-138^{\circ}$ (Ref.118).

3-Thenoyl Chloride

This acid chloride was prepared from 3-thiophenecarboxylic acid, 55 g. (0.43 moles), employing thionyl chloride, 89 g. (0.75 moles) as previously described. The yield of product was 58 g. (0.39 moles, 93%), m.p. $47-48^{\circ}$, b.p. $95-97^{\circ}$ at 20 mm. Hg. Literature value,

b.p. 203-204° at 748 mm. Hg, 110-111° at 36 mm. Hg,
m.p. 51-52° (Ref. 118).

N,N-Dimethyl-3-thiophenecarboxamide

The tertiary amide was prepared in the already described manner from 58 g. (0.39 moles) of 3-thienoyl chloride and dimethyl amine. The yield of product was 38 g. (0.245 moles, 64%), m.p. 48-50°.

Calc'd for C₇H₉SN₂O: C, 54.16; H, 5.84; S, 20.66; N, 9.02

Found: C, 54.41; H, 5.98; S, 21.01; N, 8.88

Di-(3-thienyl)ketone

This material was prepared according to the experimental procedure of Taft (Ref. 85). A 155 g. (0.9 moles) quantity of N,N-dimethyl-3-thiophenecarboxamide was added to 640 ml. of 1.6 N n-butyllithium (1.02 moles) ether solution and 163 g. of 3-bromo-thiophene previously converted to 3-thienyllithium. The product isolated in the manner described above. Distillation of the crude product gave 127 g. (0.65 moles, 73%) of an oily material, b.p. 150-153° at 11-12 mm. Hg, m.p. 78-79°. The oil solidified on cooling and was recrystallized from an ethanol-water mixture to yield pure product in the form of fine white needles. Literature values, m.p. 78-80° (Ref. 91).

Di-(3-thienyl)ketone ethylene ketal

A mixture of di-(3-thienyl)ketone, 28 g. (0.14 moles), ethylene glycol, 15 g. (0.23 moles), 100 ml. of benzene and a few crystals of p-toluenesulphonic acid was heated at its reflux temperature in a 250 ml. flask equipped with a water separator, until no more water separated - 24 hours. The benzene layer was washed with sodium bicarbonate solution and water, dried and the benzene was removed in a rotary evaporator. The residue was taken up in hot ethanol and upon cooling fine crystals of the pure product formed. The yield of material was 27 g. (0.113 moles, 81%), m.p. 111-112°. Calc'd for $C_{11}H_{10}S_2O_2$: C, 55.5; H, 4.24; S, 26.9 Found: C, 55.59; H, 4.28; S, 26.65

Cyclopenta [2,1-b:3,4-b'] dithiophene-4-one

A high dilution procedure was used to prepare this compound. A solution of di-(2-lithio-3-thienyl)ketone ethylene ketal was prepared at -70° as previously described from 27 g. (0.113 moles) of di-(3-thienyl)ketone ethylene ketal in 500 ml of ether and 142 ml. of 1.6 N n-butyl-lithium (0.226 moles) in a 1000 ml. flask. The yellow solution was transferred to a dry ice-acetone cooled dropping funnel, which was attached to a 100 ml. creased, three-necked flask fitted with a high speed stirrer. Under anhydrous conditions, 40 g. (0.3 moles) of

anhydrous CuCl_2 and 200 ml. of ether were added to the flask. With rapid stirring the lithio solution was added dropwise during 8 hours. The solution was allowed to warm to room temperature overnight. The reaction mixture was then acidified with 2 N hydrochloric acid and it was filtered to remove the precipitate of cupous chloride.

The ether layer was separated and the aqueous phase was extracted with ether. The combined ethereal extracts were washed several times with 4 N hydrochloric acid, then with a sodium bicarbonate solution, and finally with water. After drying over magnesium sulfate and removal of the solvent, the residue crystallized on cooling. Steam distillation of the residue gave 17 g. of crude cyclopenta [2,1-b:3,4-b'] dithiophene-4-one. Recrystallization of the crude material from ethanol yielded 15.5 g. (0.08 moles, 71%) of pure product, m.p. 45-47°.

Calc'd for $\text{C}_9\text{H}_4\text{S}_2\text{O}$ C, 56.2; H, 2.1; S, 33.3; O, 8.3

Found C, 56.17; H, 2.16; S, 33.23

Cyclopenta [2,1-b:3,4-b'] dithiophene

The experimental procedure of King and Nord (Ref.89) was employed in the preparation of this compound. A solution containing 15.5g. (0.08 moles) of cyclopenta [2,1-b:3,4-b'] dithiophene-4-one, 12.0 ml. (0.22 moles) of

85% hydrazine hydrate and 25 ml. of ethylene glycol was stirred in a 250 ml. flask fitted with a Vigreux column and distilling head. The reaction solution was heated to 150° to remove excess hydrazine and water. The residue was cooled to room temperature. The Vigreux column was replaced by an Allihn condenser, 10.0 g. of potassium hydroxide were added, and the basic mixture was heated until the evolution of nitrogen initiated, about 100°. The mixture was refluxed for two hours and then extracted with several portions of ether. The ether phase was washed with 1:1 hydrochloric acid, then with water and dried over magnesium sulfate. The ether was removed and the residue was recrystallized from ethanol to yield 3.0 g. (0.017 moles, 21%), m.p. 73°. Literature value, m.p. 73-74.5° (Ref. 83)

The Reaction of Sulfonium Salts with Base and Aldehydes

Butyllithium ether solution (63 ml. of 1.6 N, 0.1 moles) was added to dimethylisopropylsulfonium chloride (14.0 g., 0.1 moles) in 200 ml. of heptane at 0° during a half hour. Benzophenone (18 g., 0.1 moles) was then added to the brown colored reaction mixture and the latter was warmed to 40-50° for an hour. After stirring the mixture until the solution had reached ambient

temperature, the mixture was filtered and the residue was washed with three 100 ml. portions of heptane. Removal of the solvent from the filtrate and the heptane washings in vacuo gave a dark brown oil which contained only starting material as indicated by infrared analysis.

The above experiment was repeated using 63 ml. of 1.6 N n-butyllithium ether solution and 15 g. (0.1 moles) of p-nitrobenzaldehyde. After filtration of the reaction mixture the residue was dried and dissolved in chloroform. The chloroform solution was extracted with water. The chloroform solution was dried and the solvent was removed in a rotary evaporator to yield a brown oil which contained only starting materials.

Bromomalononitrile

A modification of the method of Ramberg and Wideqvist (Ref. 137). was employed in the preparation of this material. During a 15 minute period, bromide (10.2 ml., 0.2 moles) was added dropwise to a solution of malononitrile (6.6 g., 0.1 moles) in 50 ml. of water contained in a 250 ml. round-bottomed flask. The reaction mixture was stirred during the addition of the halogen and then for an additional 10 minutes. Additional malononitrile (6.6 g., 0.1 moles) was added and the mixture was stirred for another 2 hours. After being set aside in a

refrigerator for 12 hours the solid was recovered by filtration to give, after washing with a little cold water and drying, 20.7 g. (72.3%, 0.143 moles) of dark colored crystalline material, m.p. 64-65°. This was recrystallized from ethyl ether to obtain a colorless crystalline solid. Literature value, m.p. 64.5-65.1° (Ref. 138).

Dimethylmalonylsulfonium bromide

Bromomalononitrile, 10 g. (0.069 moles) and dimethylsulfide, 6.0 g. (0.105 moles) were added to 50 ml. of chloroform in a 100 ml. round-bottomed flask. The flask was stoppered and set aside for three days. The solid material was collected by filtration and weighed 7 g. (0.034 moles), a 49% yield of crude material.

The Reaction of dimethylmalonylsulfonium bromide with base

The sulfonium salt, 7 g. (0.034 moles) was transferred to 50 ml. of chloroform and then treated with a 5% solution of sodium bicarbonate with rapid stirring at room temperature. The aqueous solution was filtered and extracted with chloroform. Removal of the solvent gave a crystalline mass that was recrystallized from isopropyl alcohol to give 1.0 g. (0.0083 moles) of dimethylsulfonium dicyanomethylide, m.p. 98°C; the overall yield was 12%.

Cis-3,5-Dibromocyclopentadiene

Cyclopentadiene, b.p. 40° , was obtained by distilling 85% commercial dicyclopentadiene through a short Vigreux column. The distillate was collected in a receiver cooled by immersion in a dry ice-acetone bath. A solution of 73.5 g. (1.11 moles) of cyclopentadiene in 56 ml. of chloroform was brominated during 10 minutes with a solution of 170 g. of bromine (1.06 moles) in 110 ml. of chloroform at -35° . A 10 ml. volume of pyridine was added, and the solution was warmed to 0° . Then 5 ml. of acetic acid were added to the solution followed by 5 g. of sodium chloride and 50 ml. of water. The organic layer was separated, dried over magnesium sulfate, and the majority of the chloroform was removed with a water aspirator vacuum. The remainder of the chloroform was removed via a vacuum pump while keeping the temperature of the reaction mixture at 0° . The red colored residue crystallized on being set aside overnight in a dry ice-acetone bath. The solid was quickly transferred to a previously chilled Buchner funnel, a rubber dam was applied and the aspirator vacuum was applied. After the major share of the oily material had passed through the filters, but before discoloration of the remaining solid commenced, the slightly oily white solid was removed from the filter and recrystallized from petroleum (60-90°)

ether to obtain 72.6 g. of pure material. The filtrate was diluted with 175 ml. of petroleum ether (30-60°) and heated to its boiling temperature. The clear supernatant liquid was decanted from the black oily layer and placed in contact with dry ice to insure crystallization of product. By this procedure there was obtained 34.9 g. of solid material which was recovered by rapid filtration. Recrystallization of the combined solids from petroleum ether (60-90°) gave 85.0 g. (0.325 mole, 29%) of cis-3,5-dibromocyclopentene, m.p. 45°. Literature value, m.p. 45° (Ref. 132).

5-Dimethylsulfonium Cyclopentadienylide

To a 6.6 g. (0.0295 mole) quantity of 3,5-dibromocyclopentene in 100 ml. of chloroform was added 6.0 g. (0.1 mole) of dimethylsulfide in 50 ml. of chloroform. The mixture was set aside overnight (24 hours) to interact and yield dimethyl-5-cyclopentadienylsulfonium bromide. A white solid precipitated from the reaction solution, which decomposed upon exposure to the atmosphere, to a red-brown mass. The sulfonium salt was converted to the ylid by treating the white solid with 1N sodium hydroxide. The aqueous solution was extracted with chloroform and the extract dried over magnesium sulfate. Removal of the solvent gave a crystalline mass that was recrystallized

from isopropyl alcohol to obtain 2 g. (0.0158 mole, 54%) of 5-dimethylsulfonium cyclopentadienylide, m.p. 135-136°. Calc'd for $C_7H_{10}S$: C, 66.66; H, 7.93; S, 25.39 Found: C, 66.94; H, 8.07; S, 25.19.

Dimethylsulfonium dicyanomethylide

A mixture of 95 g. (1.5 moles) of dimethylsulfoxide, 66.0 g. (1.0 mole) of malononitrile and 150 ml. of chloroform were stirred and precooled to 0° in a 500 ml. flask. Anhydrous hydrogen chloride gas was bubbled into the solution at a rate sufficient to keep the reaction temperature below 0°. After a short period of reaction a solid began to precipitate, and when precipitation was complete the addition of hydrogen chloride was stopped. The solid material, 160 g. (0.8 moles, 80%) of dimethylsulfonium dicyanomethylide dihydrochloride, m.p. 132-134° was recovered by filtration.

The dihydrochloride was treated with a 5% solution of sodium bicarbonate and the aqueous solution was then extracted with chloroform. The chloroform was removed leaving a crystalline mass, which was recrystallized from isopropyl alcohol to obtain 67 g. (0.53 moles, 42%) of dimethylsulfonium dicyanomethylide, m.p. 98-99°C. Calc'd for $C_5H_6SN_2$: C, 47.59; H, 4.79; N, 22.20; S, 25.41 Found: C, 47.54; H, 4.70; N, 22.40; S, 25.66.

Attempted Preparation of diethyl and dipropyl sulfonium dicyanomethylide

A 53 g. (0.5 moles) quantity of diethylsulfoxide, 22 g. (0.33 moles) of malononitrile and 50 ml. of chloroform were combined, stirred and precooled to 0° in a 500 ml. flask. Anhydrous hydrogen chloride was bubbled into the solution at a moderate rate to keep the reaction temperature below 0°C. After a short period of reaction time a solid precipitated from solution. The addition of hydrogen chloride was discontinued when the reaction ceased to be exothermic. The precipitate, a light yellow solid, weighing 38 g. was recovered by filtration. Attempts to form the ylid from this material failed.

A similar reaction with isopropyl sulfoxide gave a yellow precipitate from which no identifiable material could be isolated upon treatment with base.

Pyrolysis of Dimethylsulfonium dicyanomethylide

A two gram sample of dimethylsulfonium dicyanomethylide was heated in a test tube over a Meker burner to obtain a red-brown oil and the evolution of a gaseous product. The latter was collected in a liquid nitrogen trap and identified as dimethylsulfide by infrared analysis. The red-brown oil was extracted with benzene. An infrared spectra of the extract was found to be nearly identical to

an infrared spectra of a benzene solution of tetracyanoethylene. Thus, the ylid decomposed thermally by cleavage of the ylid bond.

Ultraviolet Decomposition of Dimethylsulfonium Dicyanomethylide

A 5 g. sample of dimethylsulfonium dicyanomethylide in 50 ml. of benzene was irradiated with a 275 watt G.E. sun lamp. The color of the solution changed from clear to a red-brown in color. Infrared analysis of the red-brown solution indicated dimethylsulfide, tetracyanoethylene and benzene were present.

The Reaction of dimethylsulfonium dicyanomethylide with cyclohexene

A 4 g. (0.032 mole) quantity of dimethylsulfonium dicyanomethylide was added to 50 ml. of cyclohexene and the mixture was heated at its reflux temperature for 18 hours during which the solution slowly turned yellow. The crystalline solid was recovered by filtration. Recrystallization of this from isopropyl alcohol gave only starting material, dimethyl sulfonium dicyanomethylide.

The Reaction of dimethylsulfonium dicyanomethylide with maleic anhydride

A solution of dimethylsulfonium dicyanomethylide (8 g., 0.063 moles), and maleic anhydride (7 g., 0.071 moles) in 75 ml. of benzene was heated at its reflux temperature overnight. The solvent was removed in a rotary evaporator to yield a solid mass which was recrystallized from pet ether, m.p. 39-41°C.

Analysis: C, 70.85; H, 5.03; S, 16.04; N, < 0.3

The Reaction of dimethylsulfide and dichlorocarbene with benzaldehyde

A hexane solution of n-butyllithium ether solution (0.1 mole, 63 ml. of 1.6N) was added dropwise to a rapidly stirred solution of 7 g. (0.11 moles) of dimethylsulfide, 16 g. (0.13 moles) of chloroform and 50 ml. of anhydrous ether at 0°. The reaction solution turned yellow in color and a solid precipitated. An ether solution of 11 g. (0.1 moles) of benzaldehyde was slowly added to the mixture and it was stirred for an hour. The mixture was filtered and the residue was washed with three 50 ml. portions of ether. Removal of the solvent gave a dark yellow colored liquid which identified as mainly benzaldehyde by infrared analysis.

The Reaction of dimethylsulfide and dichlorocarbene with benzaldehyde

Chloroform (12.0 g., 0.1 moles) in 200 ml. of heptane was added during a half hour to a well stirred, ice-cold mixture of dimethylsulfide (16 g., 0.25 moles) and potassium t-butoxide in 250 ml. of heptane. The resulting yellow colored suspension was concentrated to about 100 ml. in a rotary evaporator at 15-20°.

Benzophenone (18.2 g., 0.1 moles) in 100 ml. of heptane was added to the mixture and it was heated at 40-50° for a half hour. The mixture was finally heated to 70° on a steam bath and then set aside for 2 days at room temperature. The mixture was filtered and the residue was washed twice with 100 ml. portions of heptane, then with 100 ml. of water followed by drying. No identifiable material could be isolated from this material. Removal of the solvent from the combined filtrate and washings in vacuo yield a yellow colored oil. Recrystallization of this from ethanol-water gave 14.7 g. (80% recovery) of benzophenone.

The Reaction of dimethylsulfide and dichlorocarbene with
p-nitrobenzaldehyde

A hexane solution of n-butyllithium ether solution (0.1 moles, 63 ml., 1.6N) was added dropwise to a rapidly stirred solution of 68.0 g. (0.11 moles) of dimethylsulfide, 15.6 g. (0.13 moles) of chloroform and 50 ml. of anhydrous ethyl ether. The reaction solution turned yellow in color and a precipitate formed. Following the addition of the n-butyllithium ether solution, 15 g. (0.1 moles) of p-nitrobenzaldehyde in 50 ml. of anhydrous ether was slowly added and the solution was stirred for an hour. The mixture was filtered and the residue was washed with heptane (3-100 ml.). Removal of the solvent from the filtrate gave a crystalline mass which was identified by infrared analysis as p-nitrobenzaldehyde.

The Reaction of diphenylsulfide and dichlorocarbene with
benzaldehyde

To a solution of diphenylsulfide (19 g., 0.1 moles) and chloroform (12 g., 0.1 moles) in 200 ml. of heptane at 0° was added 63 ml. of 1.6N n-butyllithium ether solution (0.1 moles) with rapid stirring. After adding the organo metal solution, 11 g. of benzaldehyde (0.1 moles) in 50 ml. of heptane was added slowly while stirring the

solution rapidly, after which the solution was stirred for another hour at room temperature. The mixture was then filtered and the solvent was removed in a rotary evaporator to obtain a dark yellow solution that was found to contain benzaldehyde and diphenylsulfide by infrared analysis.

The Reaction of diphenylsulfide and dichlorocarbene with benzophenone

Butyllithium ether solution (63 ml. of 1.6 N, 0.1 moles) was added to a mixture of diphenylsulfide (18.6 g., 0.1 moles) and chloroform (12.0 g., 0.1 moles) in 200 ml. of heptane at 0-5° during 15 minutes. Benzophenone (18.0 g., 0.1 moles) in 50 ml. of heptane was added to the above solution and it was then warmed to 40-50°. After stirring the mixture until the temperature had dropped to room temperature, the mixture was filtered and the residue was washed with three 100 ml. portions of heptane. Removal of the solvent from the combined filtrate and washings gave a residue which contained none of the expected 1,1-dichloro-2,2-diphenylethylene oxide.

The above experiment was repeated using 63 ml. of 1.6 N n-butyllithium ether solution and a reaction period of 3.5 hours. After filtration of the reaction mixture

the residue was dried and dissolved in chloroform and the chloroform solution was extracted with 100 ml. of water. After drying the chloroform layer and removing the solvent in vacuo the residual brown oil contained only benzophenone and diphenylsulfide as determined by infrared analysis. The filtrate was concentrated in vacuo to a red oil and this was shown to contain only benzophenone and diphenylsulfide by infrared analysis.

The Reaction of diphenylsulfide and dichlorocarbene with benzophenone

Potassium t-butoxide (0.1 mole) was mixed with diphenylsulfide (18.6 g., 0.1 moles) in 250 ml. of petane in a round bottom three necked flask, chilled and stirred vigorously. To this mixture chloroform (12.0 g., 0.1 moles) in 200 ml. of petane was slowly added at 0°. After stirring for a half-hour, benzophenone (18.2 g., 0.1 moles) was added and the reaction mixture was stirred at room temperature for 13 hours. Filtration of the mixture gave a white solid, identified as potassium chloride. Concentration and distillation of the filtrate yielded only benzophenone and diphenylsulfide, identified by infrared analysis.

The Reaction of diphenylsulfide and dichlorocarbene
with p-nitro benzaldehyde

A solution of n-butyllithium ether solution (0.1 mole, 63 ml. of 1.6N) was added dropwise to a rapidly stirred solution containing 19 g. (0.1 moles) of diphenylsulfide, and 16 g. (0.13 moles) of chloroform in 50 ml. of heptane. The solution turned yellow in color and a precipitate formed. A solution of 15 g. of p-nitrobenzaldehyde (0.1 moles) in 50 ml. of heptane was slowly added to the solution and it was stirred for 3 hours. The mixture was filtered and the residue was washed with three 100 ml. portions of heptane. Removal of the solvent from the filtrate and washings yielded a yellow oil which contained diphenylsulfide and p-nitrobenzaldehyde determined by infrared analysis.

Dimethylsulfide

Dimethylsulfoxide, 78 g. (1.0 moles) and 75 g. of zinc powder were placed in a 500 ml. flask equipped with a dropping funnel and distilling head. Hydrochloric acid, 173 ml. of concentrated acid (2.0 moles), was added at such a rate sufficient to product a steady flow of dimethylsulfide. The dimethylsulfide was collected in a flask cooled by immersion in a dry ice-isopropyl alcohol bath. The yield of product was 47 g. (75%), b.p. 37°. Literature value, b.p. 37° (Ref. 135).

9-Bromofluorene

This compound was prepared according to the procedure of Fuson and Porter (Ref. 96). A solution of 99.6 g. of commercial fluorene (m.p. 108-111°) in 500 ml. of dry thiophene free benzene was heated for four hours at its reflux temperature with an equimolar amount (106.8 g.) of N-bromosuccinimide. The precipitate of succinimide which formed during the reaction was removed by filtration. The solvent was removed in a rotary evaporator, and the residue was recrystallized using 500 ml. of hot petroleum ether (60-90°), to obtain pure 9-bromofluorene. The yield of pure materials was 69 g. (47%), m.p. 103-104°. Literature value, m.p. 103-104° (Ref. 96).

9-Dimethylsulfonium Fluorenylide

The method of Ingold (Ref. 97) was used to prepare this ylid. Dimethylsulfide, (12 g. (0.19 moles), 9-bromofluorene, 10 g. (0.041 moles) and 25 ml. of nitromethane were placed in a 100 ml. flask and set aside overnight to interact and form dimethyl-9-fluorenyl-sulfonium bromide. Following a 24 hour reaction period the solid product was collected by filtration, in a yield of 9.1 g. (72%), m.p. 131-132°. Literature value 131-132° (Ref. 97, 130).

To 8.8 g. of this salt in 200 ml. of water was added 10% sodium hydroxide solution until precipitation was complete. The yellow color solid was recovered by filtration and washed first with water, with 95% ethyl alcohol, then with absolute ethanol and finally with ether. The solid was dried over anhydrous magnesium perchlorate to obtain 7.2 g. (82%) of the ylid, m.p. 120-122°. Literature value, m.p. 120-122° (Ref. 97, 130).

Dimethylisopropylsulfonium chloride

A solution of 62 g. of dimethylsulfide (1.0 moles), 79 g. (1.0 moles) of isopropyl chloride and 250 ml. of nitromethane was set aside for a week at room temperature in which time all the sulfonium salt had precipitated. Care was taken in transferring the salt to keep it in a dry atmosphere as it was quite hygroscopic.

The Reaction of sulfonium salts with potassium t-butoxide

The above sulfonium salt prepared by the procedure of Ramirez and McKelvie (Ref. 136) was added in a dry box filled with nitrogen to a vigorously stirred solution of potassium t-butoxide in 200 ml. of heptane at 0°. Benzophenone (10 g., 0.05 moles)

was then added to the mixture and it was stirred until its temperature reached room temperature. The mixture was then heated to 70-80° for three hours, cooled, and filtered. The brown colored residue contained both the starting materials as shown by infrared analysis. The filtrate was concentrated to an oil in vacuo and extracted with hexane, 50 ml. The hexane was removed by evaporation and the residual oil crystallized. Recrystallization of this solid from ethanol-water gave only crystals of benzophenone.

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