PART I
STUDIES OF THE SODIUM TUNGSTATE-HYDROGEN PEROXIDE OXIDATION OF 2-SUBSTITUTED-1,3,5,6,7-PENTACHLOROBICYCLO[3.2.0] HEPTA-2,6-DIEN-4-ONES

PART II
THE REACTION OF TETRACHLOROCYCLOPROPENE WITH POLYCHLOROETHYLENES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
CHARLES WILLIAM BAUER
1969

This is to certify that the

thesis entitled

PART I STUDIES OF THE SODIUM TUNGSTATE-HYDROGEN PEROXIDE OXIDATION OF 2-SUBSTITUTED-1,3,5,6,7-PENTACHLOROBICYCLO [3.2.0] HEPTA-2,6-DIEN-4-ONES

PART II THE REACTION OF TETRACHLOROCYCLOPROPENE WITH POLYCHLOROETHYLENES

presented by

Charles William Bauer

has been accepted towards fulfillment
of the requirements for

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Eugene Le Goff
Major professor

Date 11 December 1969

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ABSTRACT

PART I

STUDIES OF THE SODIUM TUNGSTATE-HYDROGEN PEROXIDE OXIDATION OF 2-SUBSTITUTED-1,3,5,6,7-PENTACHLOROBICYCLO[3.2.0]HEPTA-2,6-DIEN-4-ONES

PART II

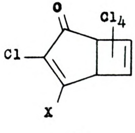
THE REACTION OF TETRACHLOROCYCLOPROPENE WITH POLYCHLOROETHYLENES

By

Charles William Bauer

This study was initiated as an effort to prepare new members of the oxocarbon series (1). This goal was not achieved, but several new and interesting compounds were prepared.

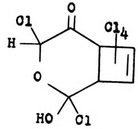
Sodium tungstate-hydrogen peroxide oxidation of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones 7a, 7b, and 7c resulted in the formation of the same two major products.



7

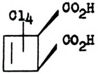
a. X = Cl
b. X = OH
c. X = OCH_3

One of the major products was identified as 1,2,4,6,7,8-hexachloro-2-hydroxy-3-oxabicyclo[4.2.0]oct-7-en-5-one 13. Assignment of this structure to compound 13 is rather unsatisfying because of the presence of the chlorohydroxy function. However, the available evidence suggests this to be the correct structural assignment.



13

The second major product has been identified as tetrachloro-3-cyclobutene-cis-1,2-dicarboxylic acid 14.



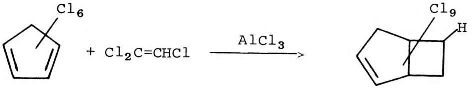
14

A third product resulting only from the reactions involving 7c was identified as the methyl half-ester of the diacid 14. The formation of this product only in the reactions of 7c has implications relating to the mechanisms of the reactions involved. Some suggestions concerning possible mechanisms are included as are suggestions for further study.

Charles William Bauer

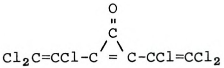
PART II

This study was initiated in an effort to determine if the reaction of tetrachlorocyclopropene with trichloroethylene in the presence of anhydrous aluminum chloride might be similar to the reaction of hexachlorocyclopentadiene with trichloroethylene (2,3).



47

The results are quite different however in that no bicyclic products analogous to 47 were isolated. The product is rather bis(trichlorovinyl)cyclopropenone 52.



$$Cl_2C{=}CCl{-}\overset{\overset{O}{\|}}{C}\!\!\!\!\!\!\!\!\underset{}{C{=}C}{-}CCl{=}CCl_2$$

52

The same reaction using 1,2-dichloroethylene yielded bis(1,2-dichlorovinyl)cyclopropenone 54.

Some mechanistic considerations are discussed.

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1. R. West and D. L. Powell, J. Amer. Chem. Soc., 85, 2577 (1963).
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3. A. Roedig and L. Hornig, Ann. Chem., 598, 208 (1956).

PART I

STUDIES OF THE SODIUM TUNGSTATE-HYDROGEN PEROXIDE OXIDATION OF 2-SUBSTITUTED-1,3,5,6,7-PENTACHLOROBICYCLO[3.2.0]HEPTA-2,6-DIEN-4-ONES

PART II

THE REACTION OF TETRACHLOROCYCLOPROPENE WITH POLYCHLOROETHYLENES

By

Charles William Bauer

A THESIS

Submitted to
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Department of Chemistry

1969

To Sue and My Parents

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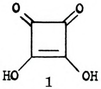
PART I

STUDIES OF THE SODIUM TUNGSTATE-HYDROGEN PEROXIDE OXIDATION OF 2-SUBSTITUTED-1,3,5,6,7-PENTACHLOROBICYCLO[3.2.0]HEPTA-2,6-DIEN-4-ONES

INTRODUCTION

An interest in the synthesis of aromatic oxocarbon compounds (1,2) led to the study reported herein.

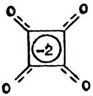
In a communication published in 1960, West pointed out that the anion of the then recently synthesized compound diketocyclobutenediol 1 (3), now commonly referred to as squaric acid, represented "... one member of a general series of symmetrical electron delocalized anions, $C_nO_n^{-2}$, salts of which may be considered as a new class of aromatic substances." (4).



1

In a subsequent paper (1), molecular orbital calculations for a large number of oxygenated anions were reported. Included among those systems studied, in addition to the monocyclic species ranging from three- to eight-membered rings, were several bicyclic systems.

To date, studies of only four of the aromatic oxocarbon anions have been reported. Included are the dianions of squaric acid 2, croconic acid 3, and rhodizonic acid 4 (1,2,5,6,7), and the tetraanion of tetrahydroxyquinone 5 (1,2,8).



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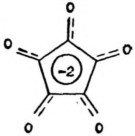

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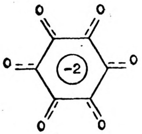

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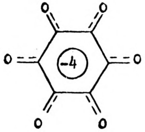
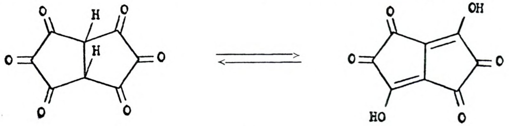


5

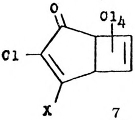
Since no report concerning the synthesis and study of any of the bicyclic members for which the calculations had been reported (1,2) had been published, and since some compounds which appeared to be suitable precursors were available from previous work, attempts were made to prepare some of the bicyclic oxocarbons. A major effort was expended toward the synthesis of the oxocarbon compound 6.



6

These attempts proved to be unsuccessful. However, as a result of the methods and approaches used in the attempted synthesis of 6, an interest in the oxidation and hydrolysis

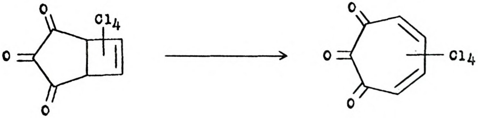
of polychloro organic compounds as an approach to polyoxygenated systems, including the oxocarbons, resulted. This interest and the ready availability of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-one system **7** (9), led to the study reported herein.



7

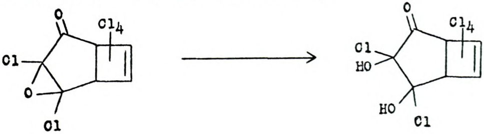
a. X = Cl
b. X = OH
c. X = OCH_3

The initial thought was to study the epoxidation of **7a** expecting the eventual product to be the bicyclic triketone **8** or the monocyclic triketone **9** which could result from ring opening of **8** which would be expected to be highly strained.



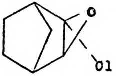
8 **9**

Should the epoxide of **7a**, *i.e.*, **10**, be formed, one might anticipate, on hydrolysis of **10**, the formation of the chlorohydroxy intermediate **11** which would be expected to lose hydrogen chloride to give triketone **8**.



10 **11**

The literature contains several reports of α-chloro epoxides and their reactions (10). Those systems reported in the literature contain only one α-chloro substituent, and with the exception of the 2-chlorobicyclo[2.2.1]hept-2-ene exo-oxide system 12, the α-chloro epoxides studied undergo molecular rearrangement with chloride migration. In addition to the products resulting from chloride migration, those resulting from Wagner-Meerwein rearrangements are formed in the rearrangement reactions of 12 (10f).



12

Thus, 10 would be of interest not only as a possible precursor to triketone 8 and the oxocarbons, but also because a study of this type compound, i.e., an α,α'-dichloroepoxide system, to our knowledge, has not been reported in the literature.

The sodium tungstate-hydrogen peroxide oxidizing system was chosen for two reasons. For the epoxidation of an α,β-unsaturated carbonyl system such as 7, a nucleophilic epoxidizing reagent is preferred (11). In the sodium tungstate-hydrogen peroxide system, the reactive species is thought to be the pertungstate anion (12) which would have the necessary nucleophilic character, and indeed the above system has been used as a nucleophilic epoxidizing reagent

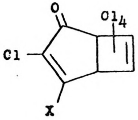
system (12). Also, this reagent combination had been used by us previously with rather good results. Reaction of the above combination with tetraethyl ethenetetracarboxylate, which is very hindered sterically and quite electron poor, gave a 60 per cent yield of the corresponding epoxide (13).

The results of the initial epoxidation reaction using 7a were much different than anticipated, and therefore, a study of the epoxidation reactions of systems 7b and 7c was conducted. Thus the research reported in Part I is that having to do with the study of the sodium tungstate-hydrogen peroxide oxidation of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones 7a, 7b, and 7c and the products of these reactions.

RESULTS AND DISCUSSION

A. Products

The sodium tungstate-hydrogen peroxide oxidation of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones 7a, 7b, and 7c afforded the same two major products in varying yields depending on which of the three starting compounds was used. The general range of yields of products from the various reactants is shown in Table 1.



$\xrightarrow[Na_2WO_4 \cdot H_2O]{30\% \ H_2O_2}$ 13 + 14

$C_7H_2O_3Cl_6$ $C_6H_2O_4Cl_4$

7

a. X = Cl
b. X = OH
c. X = OCH_3

The data in Table 1 suggest that the products formed may be at least in part arising from compound 7b since, 7b has been isolated from the reactions involving 7a and 7c. This possibility will be discussed later when possible mechanisms are considered.

Table 1. Product yields from the oxidation of 7a, 7b, and 7c.

Starting Compound	% Starting Material Recovered[a]	% 7b[a]	% Product 13 $C_7H_2O_3Cl_6$[a]	% Product 14 $C_6H_2O_4Cl_4$[a]	% Product 15 $C_7H_4O_4Cl_4$[a]
7a	40-45	0-15	15-20	15-20	0
7b	0	0	20-25	40-50	0
7c	10-15	0-20	35-45	20-30	2-20

[a] Per cent of product recovered after chromatography. Yields based on starting polychloro compound used.

The possibility that 7b was resulting from the hydrolysis of 7a and 7c in the reactions involving these compounds was studied by allowing them to react under conditions identical to those for the oxidation reactions except that no hydrogen peroxide was added to the reaction mixture. The results of these reactions are given in Table 2 along with the results for some other hydrolysis reactions involving compounds 7a, 7b, and 7c.

The results in Table 2, which show that 7b is a product of the hydrolysis of both 7a and 7c, along with the results shown in Table 1 would suggest that under the conditions used for the oxidation reactions the hydroxy compound 7b might be formed. The possible formation of 7b in the reactions of 7a and 7c will be discussed more fully later when possible mechanisms are considered.

Table 2. Product yields from the hydrolysis of **7a**, **7b**, and **7c**.

Starting Material	% Recovered Starting Material	% **7b**	% **16** Sodium Salt
7a [a]	32	47	0
7b [a]	16	16	55
7c [a]	0	18-22	48-60
7a [b]	38	38	0
7c [b]	0	92	0
7b [c]	0	0	90

[a] Reaction using sodium tungstate but no hydrogen peroxide.

[b] Reaction using neither sodium tungstate nor hydrogen peroxide, rather only ethanol and water.

[c] Reaction using sodium carbonate rather than sodium tungstate and no hydrogen peroxide.

On analysis of products **13** and **14**, it became evident that neither was epoxide **10** or triketone **8** or **9**. The analytical and mass spectral results agree in suggesting a formula of $C_7H_2O_3Cl_6$ for compound **13** (mp 129-130°). This result is surprising for several reasons. First, product **13** contains six atoms of chlorine while compounds **7b** and **7c** contain only five atoms of chlorine. Second, both chemical and spectral evidence show compound **13** to contain a carbon-hydrogen bond in addition to an hydroxyl function. The infrared spectrum of **13** shows a carbon-hydrogen absorption near 3000 cm^{-1} and an oxygen-hydrogen stretching absorption

at 3350 cm^{-1}. None of the three starting compounds contains a carbon-hydrogen bond.

The nmr spectrum of 13 shows a sharp singlet at δ 6.25 (1H) and a broad singlet at δ 5.20 (1H) which disappears after treatment of the sample with deuterium oxide. The nmr and infrared spectra suggest that a single hydroxyl function and a single hydrogen bonded to carbon are present in compound 13. This structural arrangement was further substantiated by the formation of a monoacetate 17 (mp 183-184°) on treatment of 13 with acetic anhydride. The analysis of compound 17 corresponds to a compound of formula $C_9H_4O_4Cl_6$. The infrared spectrum of 17 shows no hydroxyl absorption. The nmr spectrum of 17 contains two sharp singlets at δ 6.00 and δ 2.25 in a ratio of one to three. The spectrum shows no change on treatment with deuterium oxide.

The infrared spectrum of 13 provides significant information in addition to that noted above, *i.e.*, that carbon-hydrogen bonding is present and that an hydroxyl function is also present. In addition, a carbonyl absorption at approximately 1790 cm^{-1} and a carbon-carbon double bond absorption at approximately 1630 cm^{-1} are present. The absorptions which may be attributed to the carbonyl function and the double bond in the cyclobutene ring in compound 7a occur at 1750 and 1620 cm^{-1} respectively. This comparison suggests that the carbonyl function in 13 is no

longer part of an α,β-unsaturated system and that the cyclobutene ring has remained intact.

Chlorinated cyclobutene systems show characteristic infrared absorption in the region of 1600 to 1640 cm^{-1} (14), and specifically, the double bond absorption of hexachlorocyclobutene is reported to occur at 1635 cm^{-1} while hexachlorobutadiene shows absorptions at 1611 and 1570 cm^{-1} (15). This further suggests that the cyclobutene ring is present in compound 13.

The ultraviolet spectrum of 7a (9) shows a maximum absorption at approximately 260 mμ with a shoulder at approximately 280 mμ. Compound 13 shows only a broad region of absorption below 225 mμ which suggests the presence of an isolated carbonyl function rather than one which is in conjugation with a double bond.

Thus the ultraviolet and infrared spectral data would suggest that 13 contains a cyclobutene ring and an isolated carbonyl function which is no longer part of the α,β-unsaturated system as in the starting compounds 7a, 7b, and 7c. One may then begin assigning a structure to compound 13 considering the above information.

The remaining portion of the molecule must then be composed of $C_2H_2O_2Cl_2$. One of the oxygen atoms is part of the hydroxyl group. Since only one carbonyl absorption is evident in the infrared spectrum of 13 and one hydroxyl function is present, the remaining oxygen atom must be involved in an ether linkage. Based on the empirical formula of 13, *i.e.*, $C_7H_2O_3Cl_6$, and the rule of rings plus double bonds (16), compound 13 must contain four rings and/or double bonds. Considering the previous evidence that one carbonyl function and a cyclobutene ring are present, one is left with the choice of either one additional ring or one additional double bond being present in the molecule. The evidence would suggest that the remaining oxygen is involved as an ether rather than an hydroxyl or carbonyl function. Thus the two remaining carbon atoms would have to be joined by a double bond if there were to be an additional double bond rather than a ring structure in the molecule. This is unlikely since there is no conjugation evident in the system and since such an arrangement would necessitate that the hydroxy function be present as part of an enol system. It thus appears that a bicyclic system containing an ether likage is the more likely choice.

The mass spectrum of 13 (Table 7) is very complex and therefore difficult to analyze. That of its acetate 17 (Table 8) is much less complex and lends itself more readily to analysis.

The first major fragmentation loss in the mass spectrum of **17** is that of $C_3O_3Cl_3$. The peak at m/e = 43 corresponding to C_2H_3O is the most intense in the spectrum while that at m/e = 44 corresponding to CO_2 is also quite intense. One might then consider that the loss of $C_3H_3O_3$ actually occurs as the loss of C_2H_3O and CO_2.

Loss of $C_3H_3O_3$ (or $C_2H_3O\cdot$ and CO_2) yields an even electron ion $C_6HOCl_6^+$ which appears to lose CO and $CHCl_2^+$ giving a neutral fragment of high stability corresponding to C_4Cl_4 m/e = 188, 190, etc. This neutral fragment should contain three rings and/or double bonds and might be tetrachlorocyclobutadiene. Peaks in the spectrum corresponding to CO, m/e = 28 and $CHCl_2^+$, m/e = 83, 85, and 87 are present in significant intensities.

A significant feature in the mass spectra of both **13** and its acetate **17** is the presence of a rather intense peak at m/e = 44 which may be assigned to CO_2. The presence of carbon dioxide as a product in the fragmentation of **13** suggests that two of the oxygen atoms are bonded to a common carbon atom. This indicates that the ether oxygen is bonded to the carbon bearing either the hydroxyl or the carbonyl function.

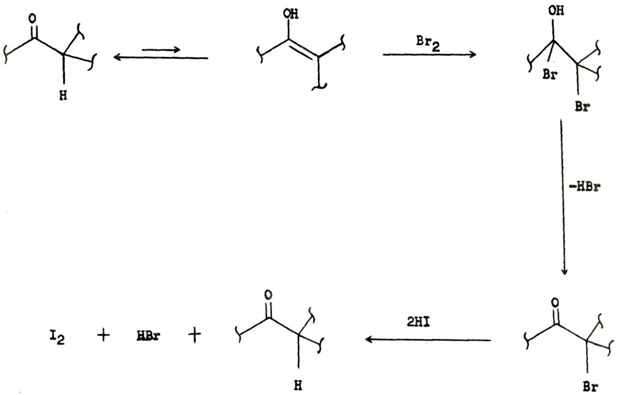
To this point, the only chemical evidence cited concerning the structure of compound **13** is the fact that a monoacetate is formed when **13** is allowed to react with acetic anhydride. Additional chemical evidence concerning the structure of **13** is available.

On heating **13** to its melting point of 130^{0}, a gas is evolved which is acidic to moist pH paper and gives a positive test for halogen (17). This suggests that the gas evolved is hydrogen chloride. Attempts to isolate some identifiable compound on pyrolysis of **13** were unsuccessful and only a yellow-orange oil was isolated.

In an effort to determine whether the hydroxyl function and the single hydrogen atom were bonded to the same carbon atom, *i.e.*, whether **13** contained a secondary hydroxyl function, attempts were made to oxidize **13**. Oxidations using reagent systems ranging from the relatively mild neutral Jones reagent (18) to acetic acid-chromium trioxide and to aqueous chromic acid resulted only in the recovery of starting material. These results suggest that either the secondary hydroxyl function is not present or that for some reason it is unreactive. The first possibility seems more likely since the oxidation of alcohols under the above conditions is not very subject to steric effects (18).

A test for the presence of an enol was conducted in an effort to determine whether the hydrogen atom in **13** is α to the carbonyl function. The reactions involved in this test are outlined below (19). The reaction upon which the test is based is the oxidation of iodide to iodine by an α-bromoketone.

Compound **13** gives a positive result using the test described above. Blank tests using **13** but no bromine and using none of compound **13** do not give positive results. Therefore,



Scheme 1. Reactions involved in the test for enol formation.

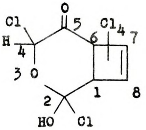
the results would suggest that an α-bromoketone is formed from an enol form of **13**. However, an effort to isolate a bromoketone from the direct bromination of **13** resulted only in the recovery of starting material. Thus, acceptance of the positive results of the above mentioned test as evidence for the presence of an enol of **13** and hence the hydrogen atom being α to the carbonyl function may be questioned.

One additional reaction of **13** appears to be quite pertinent to the question of its structure. Reaction of **13** with ethylene glycol in benzene using a catalytic amount

of *p*-toluenesulfonic acid afforded a crystalline substance **18** (mp 157.5-159.0°) which, based on mass spectral and chemical analysis, is a compound of formula $C_9H_5O_4Cl_5$. This compound displays a carbonyl absorption in the infrared at 1760 cm^{-1} and a carbon-carbon double bond absorption at approximately 1630 cm^{-1}. In the nmr spectrum of **18**, a single peak is present at δ 6.77 in addition to a broad region of absorption between δ 4.0 and δ 5.0. The peak at δ 6.77 is significant since its presence suggests that the proton giving rise to the low field absorption in **13** is still present in compound **18**. Points of major significance concerning this compound are the fact that no hydroxyl absorption is observed in the ir, a carbonyl function is still present even though a ketal has apparently been formed, the new product contains one chlorine atom fewer than the starting compound, and a proton absorbing at quite low field is still present.

Consideration of this information together with the previously noted information concerning **13** suggests that apparently the ketal of **13** is formed which loses hydrogen chloride resulting in the formation of a new carbonyl function. The fact that the low field absorption is still present in the nmr of **18** suggests that the single hydrogen atom in **13** is bonded to a carbon atom also bearing a chlorine atom rather than the hydroxyl function because the hydoxyl function is not present in **18**. Loss of hydrogen chloride apparently from the ketal of **13** in the above reaction and

from 13 when it is heated to 130°, indicates the presence of a chlorohydroxy function in 13. Consideration of the available information concerning 13, its reactions, and the reactions involved in its formation lead to the suggestion of the structure below for this compound.



13

1,2,4,6,7,8-Hexachloro-2-hydroxy-3-oxabicyclo[4.2.0]oct-7-en-5-one

A brief summary of the above results leading to the structure suggested for compound 13 is given in Scheme 2.

Duplicate chemical analyses and mass spectral data confirm that 13 has a formula $C_7H_2O_3Cl_6$. The spectral properties are consistent with the proposed structure. The uv spectrum suggests no conjugation is present in the molecule; the ir spectrum is consistent with the presence of the hydroxyl function, the carbonyl function, and the chlorocyclobutene ring, and the carbon-hydrogen function; the nmr spectrum is also consistent for a molecule containing a single proton absorbing at quite low field (δ 6.52) in

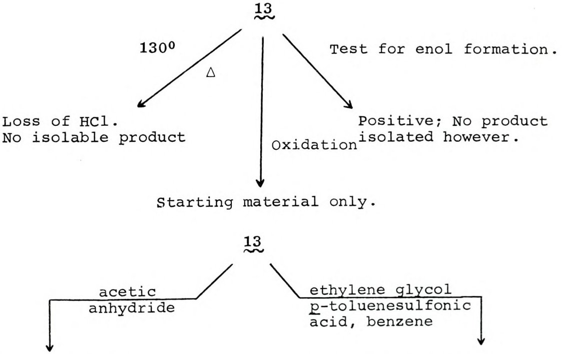
13 (mp 129-130°)

$C_7H_2O_3Cl_6$

uv (methanol) No absorption above 225 mμ.

ir (KBr) 3350 (O-H), 3000 (C-H), 1790 (C=O), and 1630 cm^{-1} (chlorocyclobutene C=C).

nmr (acetone-d_6) δ 6.52 (s); (acetonitrile) δ 6.25 (s, 1) and δ 5.20 (broad s, 1). Absorption at δ 5.16 not present after treatment of the sample with D_2O.



17 (mp 183-184°)

$C_9H_4O_4Cl_6$

ir (KBr) no O-H, 1810 (C=O), 1760 (C=O), and 1630 cm^{-1} (chlorocyclobutene C=C).

nmr ($CDCl_3$) δ 6.00 (s, 1) and δ 2.25 (s, 3).

18 (mp 157.5-159°)

$C_9H_5O_4Cl_5$

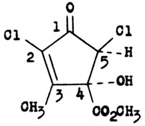
ir (KBr) no O-H, 1760 (C=O), and 1630 cm^{-1} (chlorocyclobutene C=C).

nmr ($CDCl_3$) δ 6.77 (s, 1) and δ 4.0 to δ 5.0 (bm, 4).

Scheme 2. Spectral and chemical properties of 1,2,4,6,7,8-hexachloro-2-hydroxy-3-oxabicyclo[4.2.0]oct-7-en-5-one 13 and compounds 17 and 18 derived from 13.

addition to the absorption due to the hydroxyl function which disappears after treatment with D_2O. That such a low field absorption might be predicted for a methine proton is discussed below.

The proton at C-5 in compound 19 is reported to absorb at δ 4.56 (20). Replacement of a methylene group with an ether oxygen causes the protons on adjacent methylene groups to be shifted downfield by approximately 2 ppm as shown in Table 3. Thus one might predict that the proton at C-4 in compound 13 would absorb in the region of δ 6.5. The results given in Scheme 6 for compounds 13, 17, and 18 are all quite consistent with this prediction.



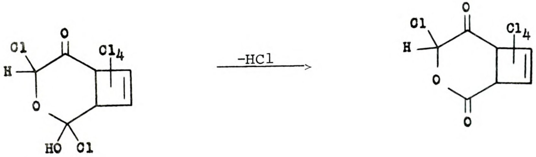
19

The loss of hydrogen chloride from 13 on heating is quite significant since a system containing the chlorohydroxy function would be expected to lose hydrogen chloride very readily. Indeed, the very fact that the structure proposed for 13 contains such a functionality is the major argument against that structure. However, the great majority of evidence tends to support the structure suggested.

Table 3. Chemical shifts of ethers and analogous hydrocarbons (21).

Compound	Chemical Shift of $-C\underline{H}_2-$ (δ)	Difference in Chemical Shifts
Pentane	1.27	2.09 ppm
Diethyl Ether	3.36	
Cyclopentane	1.51	2.12
Tetrahydrofuran	3.63	
Cyclohexane	1.45	2.11
Tetrahydropyran	3.56	

Loss of hydrogen chloride from 13 should yield the lactone shown below which was not isolated. It is believed that at the temperature to which 13 must be heated for loss



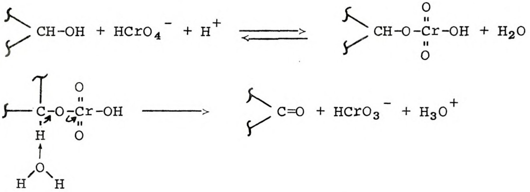
13

20

of hydrogen chloride to occur, *i.e.*, 130^0, the lactone is unstable. For this reason, no identifiable products could be isolated from the pyrolysis of 13.

The results of the oxidation reactions suggest that the hydrogen atom and the hydroxyl function are not bonded to the same carbon atom. A probable mechanism for the

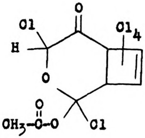
oxidation of alcohols by Cr^{VI} as outlined by House (22) and shown below requires the presence of a proton. A reaction proceeding by this mechanism would not be likely to occur with **13** since it would require loss of chlorine as an electron deficient species.



Scheme 3. Proposed mechanism of Cr^{VI} oxidation of secondary Alcohols.

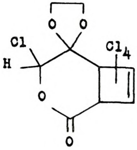
A compound having the structure proposed for **13** might be expected to give a positive test for enol formation since the α-hydrogen atom is present. However, there is some question why the α-bromo compound has not been isolated. Attempts to prepare the bromo compound have not been extensive.

The reaction of **13** with acetic anhydride to give acetate **17** further confirms the presence of a single hydroxyl function. The spectral properties of **17** are consistent with the structure proposed for it.



17

Of major significance is the ketalization reaction of 13 which yields compound 18. The significant points concerning this compound are that it contains five chlorine atoms rather than the six found in 13 and that no hydroxyl function is present. The structure proposed for 18 is that of the lactone shown below.



18

The fact that only five atoms of chlorine are present in 18 and that the low field hydrogen absorption (δ 6.77) is still present in the nmr strongly suggest that the two chlorine atoms in 13 which are not part of the cyclobutene ring are bonded to different carbon atoms. The loss of hydrogen chloride from 13 and the absence of the hydroxyl function and one atom of chlorine in 18 suggest that one of

the chlorine atoms and the hydroxyl function are bonded to the same carbon atom in 13, *i.e.*, that a chlorohydroxy function is present.

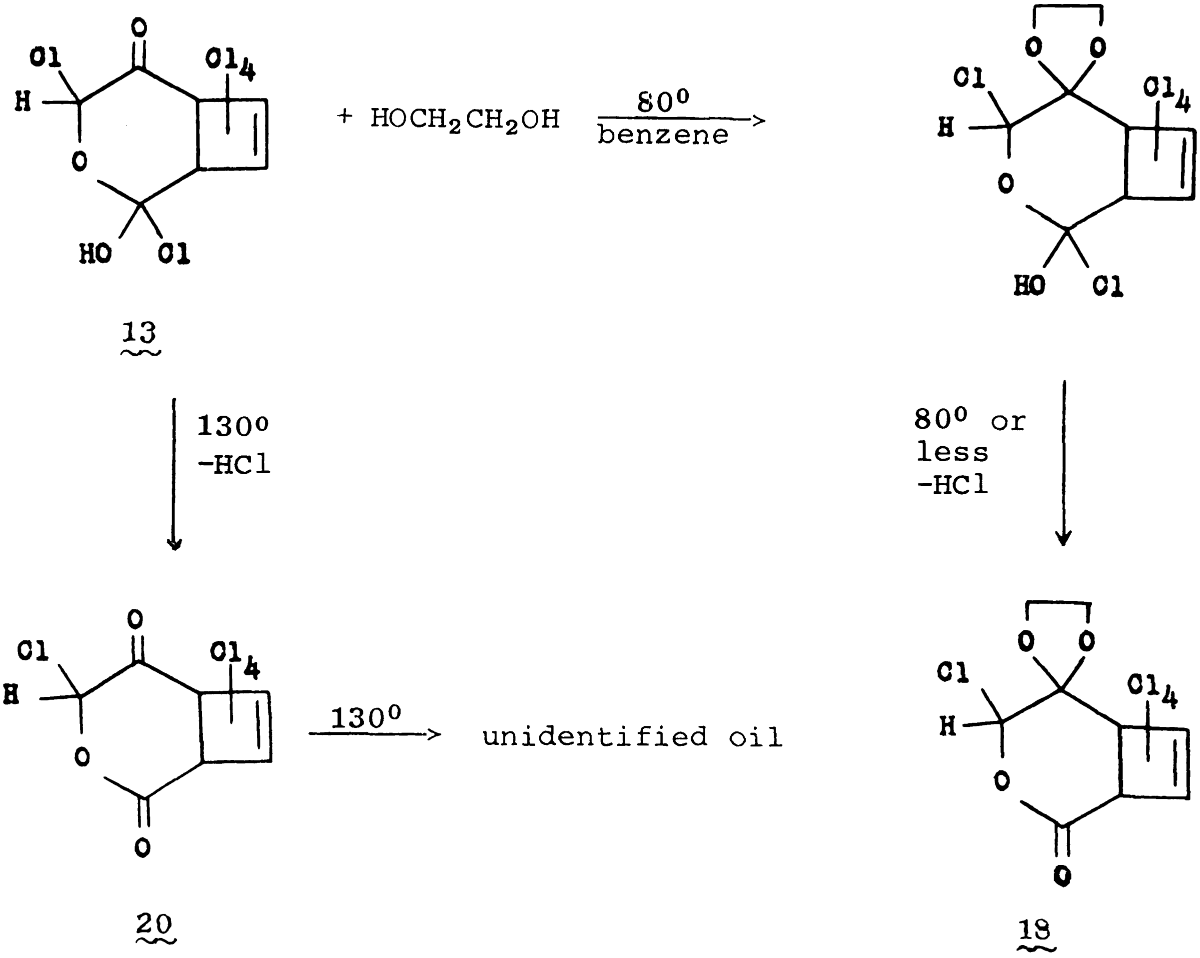
Apparently, the relief of strain which results from formation of the ketal of 13 is sufficient to allow for the loss of hydrogen chloride at lower temperature, *i.e.*, at or below the 80^0 temperature of refluxing benzene in the ketalization reaction. The formation of 18 results in a system containing only one sp^2 center in the six-membered ring. Thus, energetically one might predict that 18 should be no worse than 13. However, as noted previously, loss of hydrogen chloride from 13 would result in the formation of the keto lactone 20 which contains two sp^2 centers in the six-membered ring and is apparently not stable at 130^0. These considerations are briefly outlined below.

The spectral and chemical factors considered together suggest that compound 13 has the proposed structure. To propose a structure containing a chlorohydroxy function for a compound of such apparent stability is not particularly satisfying. However, after many doubts and reconsiderations, and for the lack of a better suggestion, this is the structure which we would propose as best fitting the available information.

The structural analysis of the remaining compounds proved to be somewhat less difficult.

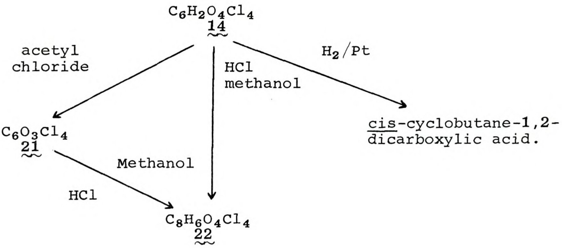
Compound 14 (mp $156.5\text{-}157.5^0$) analyzed for a compound of formula $C_6H_2O_4Cl_4$. The presence of a broad absorption

from 3000 to 2500 cm^{-1} in the infrared spectrum of 14 suggested that it contained a carboxylic acid function. A moderately strong absorption at ~1640 cm^{-1} suggested that the cyclobutene ring was still present in the molecule. As noted above, the double bond absorption in hexachlorocyclobutene is reported to occur at 1635 cm^{-1} (15).



Scheme 4. Possible mechanistic route from 13 to 18.

A number of chemical transformations involving acid 14 which give further information concerning its structure are outlined in Scheme 5 following.

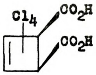


Scheme 5. Reactions of tetrachloro-3-cyclobutene-cis-1,2-dicarboxylic acid 14.

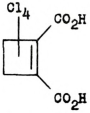
Acid 14 may be converted to its methyl ester 22 in very good yield by treating a methanol solution of the acid with dry hydrogen chloride. Evidence that the cyclobutene ring is retained in the ester is again found in the infrared spectrum. The carbon-carbon double bond absorption occurs at ~1635 cm^{-1} almost identical to that absorption in the acid. The nmr spectrum of 22 displays only a single sharp peak at δ 3.75.

Treatment of 14 with acetyl chloride affords an anhydride 21 (mp 137.0-138.5°) which may be converted to the methyl ester 22 as shown in Scheme 5. Compound 21 displays absorptions in the infrared typical for anhydrides, *i.e.*, two carbonyl absorptions at 1860 and 1795 cm^{-1} (25), and in addition an absorption at 1625 cm^{-1} which may be assigned to the double bond of the cyclobutene ring as noted previously.

The acid may be hydrogenated yielding *cis*-cyclobutane-1,2-dicarboxylic acid, identified by comparison of infrared spectrum with a standard spectrum (32). This, in addition to the above chemical and spectral evidence, strongly suggests that **14** is a tetrachlorocyclobutene dicarboxylic acid. The fact that the nmr spectrum of the dimethyl ester **22** shows only a single peak for the methyl groups limits the possible structures for diacid **14** to those two shown below.



14a

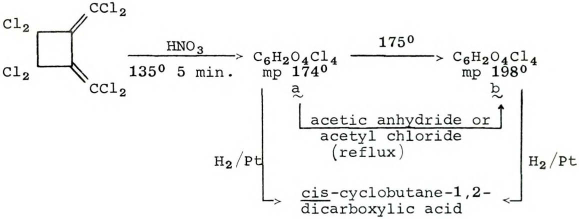


14b

Some additional facts indicate that the diacid should be assigned structure **14a** rather than **14b**. The ultraviolet spectrum of the diester **22** has a maximum absorption at 212 mμ (log ε = 3.98). This low wavelength absorption suggests that there is no conjugation between the double bond and the ester functions. One might compare the uv spectrum with that of the dimethyl ester of 1-cyclobutene-*cis*-1,2-dicarboxylic acid which shows a maximum absorption at 232 mμ (log ε = 3.94) (26). Also, the position of the double bond absorption in the infrared spectrum at 1635 cm^{-1} suggests that the cyclobutene ring is not conjugated with the ester functions.

Further, it seems doubtful that under the conditions of the reactions involved that the double bonds in the starting polychloro compounds 7a, 7b, and 7c would isomerize. A further, and perhaps weak, point is that formation and isolation of the anhydride analogous to 14b might be difficult and even unlikely.

A compound said to have structure 14a had been reported previously in the literature (27,28). Scheme 6 gives a brief outline of the report noted.



Scheme 6. Reaction sequence involving perchloro-1,2-dimethylene cyclobutane.

The authors suggest that the two compounds a and b are the <u>cis</u> and <u>trans</u> isomers of tetrachloro-3-cyclobutene-1,2-dicarboxylic acid. In addition to the differences in the melting points, the two compounds above have infrared spectra much different from that of compound 14 (28).

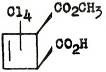
The results outlined in Scheme 6 are somewhat puzzling. For example it seems unlikely that heating with acetyl

chloride or acetic anhydride should cause a *cis*-*trans* isomerization in a fully chlorinated system such as **14a**. It would seem likely that such a procedure would at best result in the formation of an anhydride as was our experience with compound **14**. If an anhydride were formed as an intermediate in the reaction of compound **a**, it seems curious that such would result in a *cis*-*trans* isomerization. There might also be some question as to why the *cis*- and *trans*-dicarboxylic acids should both give *cis*-cyclobutane-1,2-dicarboxylic acid on hydrogenation.

We are unable to explain the results in Scheme 6, but we feel that product **14** is tetrachloro-3-cyclobutene-*cis*-1,2-dicarboxylic acid. Thus, **21** and **22** would be the analogous anhydride and dimethyl ester respectively. Considering our study, the results outlined in Scheme 6 would apparently require some alternative explanation.

Compound **15** (mp 93.5-95°) is unique in that it is a product only in the reactions involving **7c**. Purification of **15** was quite difficult, but an analytical sample was eventually prepared. Analysis of this sample showed it to be a compound of formula $C_7H_6O_5Cl_4$. The infrared spectrum of **15** is quite similar to those of diacid **14** and its dimethyl ester **22**. On treatment of a methanol solution of **15** with hydrogen chloride, the dimethyl ester **22** results. The analysis and spectral properties coupled with the fact that **15** is so readily converted to the dimethyl ester **22** suggest that **15** is the methyl half-ester of diacid **14** and that

apparently one molecule of bound water was present in the analytical sample. The empirical formula of the analytical sample might then be more correctly written as $C_7H_4O_4Cl_4 \cdot H_2O$. The nmr spectrum of a carefully dried sample of 15 displayed two singlet absorptions at δ 11.07 and δ 3.87 in a ratio of one to three. This is an agreement with the spectrum one might predict for compound 15.

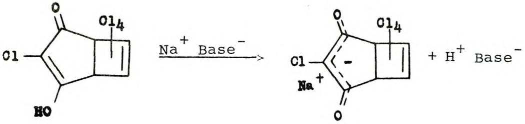


15

Compound 15 will be discussed more fully when mechanisms are considered. Also, at that time, a possible reason why a third major product is formed only in the reaction of 7c will be discussed.

One additional compound encountered during this study deserves some mention. As noted in Table 2, a compound 16 was isolated from several different reactions. This compound was recovered in yields ranging from zero to greater than 90 per cent depending on reaction conditions. We have been unable to obtain a satisfactory analysis for this compound, but based on the evidence at hand, we feel rather certain concerning its identity. The infrared spectrum of 16 displays no carbonyl absorption but rather a strong broadened region of absorption from 1585 to 1540 cm^{-1} which is

characteristic of organic salts (25). Extraction with nitric acid of a residue remaining after burning a sample of 16 and evaporation of the acid yields a residue which gives a positive test for sodium ion using magnesium uranyl acetate reagent. Acidification of a methanol solution of 16 yields a white crystalline material identified as 7b which suggests that compound 16 is the sodium salt of 7b.



7b 16

Additional evidence that 7b is acidic and may react with weak bases is shown by its reaction with sodium carbonate. In this instance, a nearly quantitative yield of the sodium salt of 7b, *i.e.*, 16, was isolated and then reconverted to 7b as described above.

This reaction pathway is apparently not significant under the usual reaction conditions when hydrogen peroxide is present since none of 16 is isolated from those reactions. Also, the reaction mixture becomes acidic apparently due to the presence of hydrogen chloride which might be formed when the diacid 14 is formed. Therefore, the acidic nature of the reaction mixture would preclude the formation of 16.

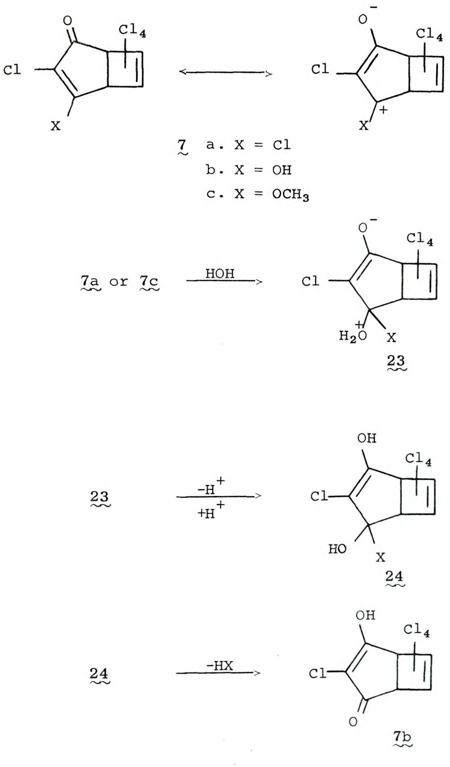
However, sodium tungstate is apparently a sufficiently strong base to react with **7b** to form **16** under neutral conditions.

B. Discussion of Possible Mechanisms

The fact that the same two major products **13** and **14** result from the reactions of all three starting compounds suggests that a common precursor may be involved. Evidence that this precursor might be **7b** has been noted previously. The data in Table 1 which show that **7b** is sometimes isolated from the reactions involving **7a** and **7c** and in Table 2 which suggest that **7b** may be formed from **7a** and **7c** under the reaction conditions used in this study would give some support to the suggested intermediacy of **7b**. The conversion of **7a** or **7c** to **7b** may be occurring by the pathway shown in Scheme 7 or some related mechanism.

Product **13** is apparently formed from **7b** since both contain the hydroxyl function. Also, it seems unlikely that hydrolysis of the chloro or methoxy function to hydroxyl would occur after the oxidation of **7a** or **7c**. This point will become more evident when the probable structure of the product of the oxidation reaction is discussed.

Evidence that the diacid product **14** may be formed from **13** is available in that the reaction of **13** under the usual reaction conditions affords a 30 per cent yield of **14** in addition to recovered starting material. Evidence suggesting that product **14** may be formed directly from **7a** and **7b**



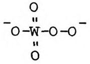
Scheme 7. Mechanistic proposal for the hydrolysis of 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones **7a** and **7c** to **7b**.

is available. The indirect evidence for this is the isolation of product **15** from the reaction of **7c**. This product which is the methyl half-ester of **14** could not be resulting from the esterification of **14** because the solvent used in the reaction is ethanol. Therefore, the methyl group must be coming from the starting methoxy compound, and **15** must be formed directly from **7c**. The connection between this fact and the suggestion that **14** may be formed directly from **7a** and **7b** will be discussed later.

The available evidence thus suggests that **14** is formed from **13** as well as from **7a** and **7b** directly and that **7b** is involved as an intermediate in the reactions of **7a** and **7c**.

The questions which must be discussed then are 1) by what mechanism may the formation of **13** be occurring, 2) how may diacid **14** be formed from **7a**, **7b**, and **13**, and 3) by what mechanism might the methyl half-ester **15** be formed, and what connection does the mechanism of its formation have with the answer to question 2? Possible answers to these questions will be discussed below.

One might profit by first considering how the expected oxidation reaction may proceed. As noted previously, the sodium tungstate-hydrogen peroxide reagent system was chosen because of its proven utility in the oxidation of α,β-unsaturated carbonyl systems (12,13). The available evidence (12,29) indicates that the reactive species is some form of pertungstate ion which for simplicity will be written as below.



$$^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{W}}-O-O^{-}$$

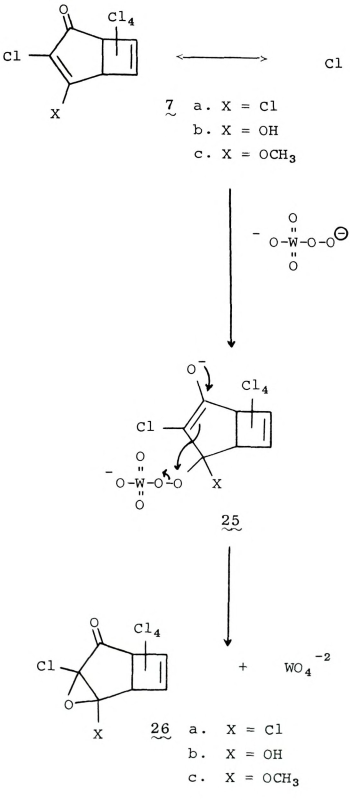
This is apparently the nucleophilic species which reacts with α,β-unsaturated carbonyl systems such as those involved in this study.

Therefore, the initial oxidation of the compounds used in this study, *i.e.*, the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones **7a**, **7b**, and **7c**, may be occurring in the manner shown in Scheme 8.

Considering the starting materials and the reagent system involved, it seems quite probable that **26** is the primary intermediate resulting from the oxidation reaction.

The identity of **x** is of importance. As noted previously, it seems likely that in the reaction leading to the formation of **13**, **7b** is involved; therefore **26b** would be the likely intermediate. Also, it seems quite unlikely that hydrolysis of **26a** or **26c** to yield **26b** would occur since the epoxide might be expected to be more subject to hydrolysis than the chloro or the methoxy function. There is evidence, however, that **26a** and **26c** may be involved in the reaction.

Assuming that **26b** is the precursor to product **13**, one might then consider what further reactions such a molecule might undergo. Since **26b** is an unusual molecule rich in functionalities, predictions concerning its further reactivity may be difficult, but one may start by considering possible reaction pathways leading from the epoxide function.

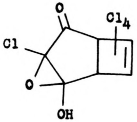


7 a. $X = Cl$
b. $X = OH$
c. $X = OCH_3$

25

26 a. $X = Cl$
b. $X = OH$
c. $X = OCH_3$

Scheme 8. Mechanistic proposal for the formation of 26.

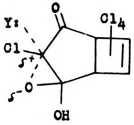


26b

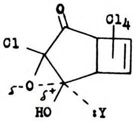
The usual reactions of epoxides in solution are of two general types (30,31). The first and most thoroughly studied involves attack of a nucleophile on one of the carbon atoms of the epoxide ring resulting in cleavage of the carbon-oxygen bond of which the carbon atom undergoing attack is a member. The final product is an alcohol. This type of reaction may occur under basic, neutral, or acidic conditions.

The reaction mixture studied contains water, ethanol, and pertungstate ion and is also acidic. There should be ample opportunity for nucleophilic attack on 26b. There would seem to be no steric factor which would direct nucleophilic attack to either the chloro or the hydroxy bearing carbon atom. Therefore, one might suppose that electronic factors would be more important. Accepting the proposed mechanisms for nucleophilic cleavage of epoxides under acidic conditions which suggest that the carbon atom being attacked has at some stage in the reaction positive character (30), the preferred point of attack would be the carbon bearing the chlorine atom. The two intermediates to consider

are 27a and 27b with 27a being less favorable since the positive character would be on the carbon adjacent to the carbonyl function.



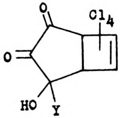
27a



27b

Y = HOH,
EtOH,
WO_5^{-2}

Such attack, whatever the nucleophile might be, would yield a system which would be expected to lose chloride readily to give the α-diketone 28.



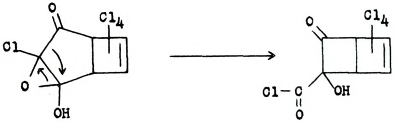
Y = -OH, -OEt, $-O-O-WO_3^-$

28

The significant point in this discussion is that although a species such as 28 is probably involved in the reaction, it seems unlikely that 13 is resulting from a reaction pathway including 28. Thus, the first major type of reaction of epoxides in solution, i.e., nucleophilic attack with resultant cleavage of one of the carbon-oxygen bonds, does not appear to provide an answer to the question of how 13 might be formed.

The second major type of reaction of epoxides in solution is that of rearrangement in which one of the substituent groups migrates resulting in formation of an aldehyde or ketone. Such rearrangements may also involve ring contraction or expansion and are usually catalyzed by Lewis acids although heat is sometimes sufficient to cause such rearrangement (30,31). Assuming, however, that such a reaction might occur under the conditions used, one might consider the possible products.

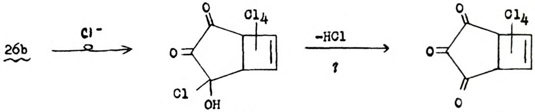
Migration of the hydroxyl group is quite unlikely since it is a poor leaving group. Also, such migration would require positive character in the transition state at the carbon α to the carbonyl function which is unfavorable as noted above. Since migration of acyl groups is quite favorable (30), one might consider the product resulting from such a rearrangement.



26b 29

There is no evidence that 29 or a product resulting from further reaction of 29 is formed in the reaction. Rearrangement with migration of the hydroxyalkyl group which would also yield a bicyclo[2.2.0]hexanone is also unlikely for the same reasons.

The final possibility then is migration of the chloride atom. As noted in the introduction, few studies of chloro epoxides have been conducted, and the majority of these have been studies of the pyrolysis of monochloro epoxides (10). Results of thermal reactions (10e, 10f, 10g) and solution reactions (10b, 10c, 10d) indicate, however, that chloride has a strong tendency to migrate. Such migration in 26b might be expected to give product 30 or possibly 8.



30 8

Again, no product like 13 would be expected from this reaction.

Thus, a consideration of the normal reactions of epoxides in solution is not very helpful in determining a possible mechanism for the formation of 13. It does, however, seem quite probable that some of the systems which would result from the expected reactions of 26b such as 28 and 30 are involved in the formation of the other products, namely 14 and 15. This possibility will be discussed more fully later.

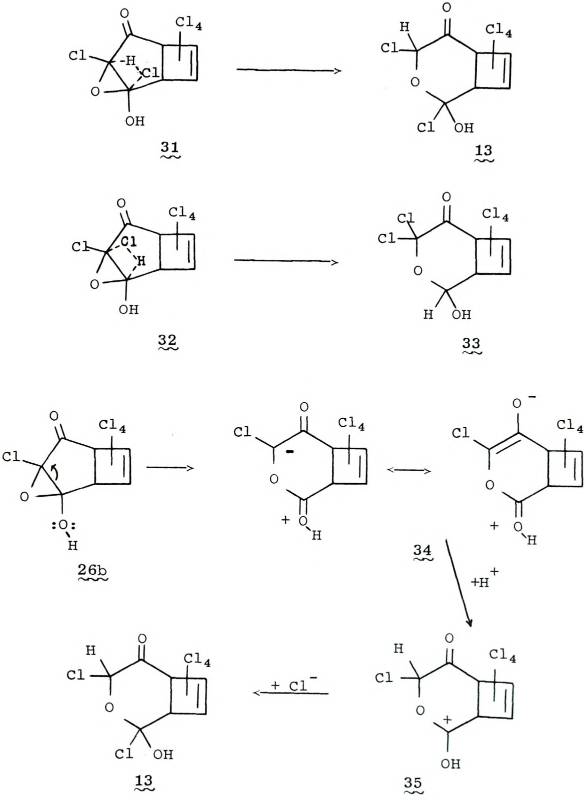
One must now consider some alternative pathway leading to 13. Assuming for the time that 26b is indeed the precursor to 13, one is left with a single reaction pathway.

This involves cleavage of the carbon-carbon bond of epoxide **26b**. Although such an apparent cleavage of the carbon-carbon bond is known in some thermal (32) and photochemical reactions (33) of epoxides, only one such reaction has been reported in the solution chemistry of epoxides (34).

What appears to be happening is the addition of hydrogen chloride across the carbon-carbon bond in **26b**. Such direct cleavage of the carbon-carbon bond is reported in the reaction of tetracyanoethylene oxide with pyridine (34). This is *in effect* what appears to be happening. In fact, **13** may be resulting from some totally different pathway which has not been considered. A significant amount of thought has not led to any other more satisfactory mechanism for the formation of **13**. Nevertheless, those mechanisms shown in Scheme 9 are not very satisfying.

A four-center addition concerted or otherwise is not meant to be implied by structure **31**. Rather, this structure is meant to show what is in effect occurring. Addition of hydrogen chloride in the reverse manner would lead to product **33** which is much more satisfying structurally in that it contains no chlorohydroxy function. This does not appear to be the final product.

The reaction involving **34** is somewhat more satisfying in that **34** seems a reasonable intermediate. Also, a reaction somewhat similar to that leading to the formation of **34** is reported in the literature (35). Treatment of the dihydroxytetraphenylcyclopentenone **36** with acid yields the



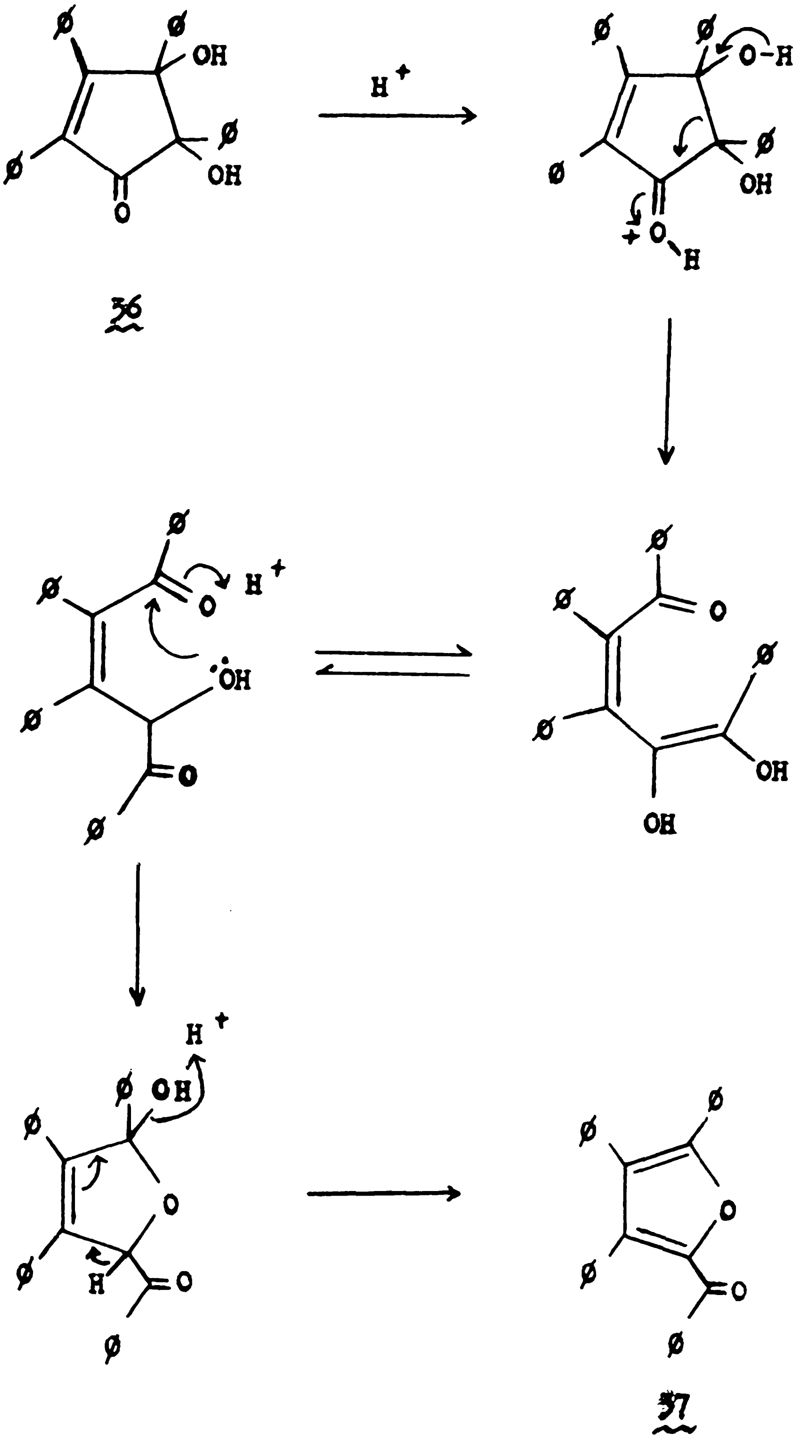
Scheme 9. Mechanistic proposal for the formation of 13.

benzoyltriphenylfuran 37. The proposed mechanism is that shown below. The first step is the one of significance since in this step the carbon-carbon bond is broken.

The addition of chloride to species 35 in the manner shown is not very satisfying for two reasons. First, this addition leads to the chlorohydroxy function. One might suspect that loss of a proton from 35 would be more favorable than addition of chlorine. Second, if chloride addition is occurring by some mechanism which involves chloride as a nucleophile, one might expect the addition of chloride ion to the reaction mixture to have some effect on the yield of 13. However, addition of sodium chloride to the reaction mixture seemed to have little effect on the yield of 13.

Thus, the mechanism by which 13 is formed is very much open to speculation. It is clear, however, that 13 contains six atoms of chlorine while 7a and 7c contain only five. Thus, addition of one atom of chlorine, by whatever the mechanism, is required.

Compound 13 has proven to be a very difficult compound in two respects. The structural analysis has been difficult, and although the available evidence tends to support the proposed structure, such a structural assignment is rather unsatisfying because of the presence of the chlorohydroxy function. It is felt, however, that 13 may be stable toward the loss of hydrogen chloride from this functionality because of the nature of the molecule. That is, loss of hydrogen



Scheme 10. Mechanistic scheme for the conversion of 2,3-dihydroxytetraphenylcyclopentenone 36 to 2-benzoyltriphenylfuran 37.

chloride would require the formation of a system of high strain and would therefore be a high energy process. This is evidenced by the fact that 13 must be heated to 130° before loss of hydrogen chloride occurs. That loss of hydrogen chloride may occur at lower temperature in the appropriate system is suggested by the fact that the product of ketalization of 13, *i.e.*, 18 has no hydroxy function and contains only five atoms of chlorine.

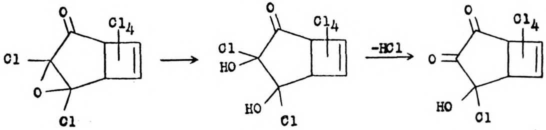
The second major difficulty related to 13 is that of suggesting a plausible mechanism for its formation. Here again, one has difficulty, if not failure, in suggesting an adequate and at the same time satisfactory mechanism. Suggestions concerning the mechanism are very speculative, and the possibility certainly exists that some totally reasonable and sufficient mechanism for the formation of 13 which we have not thought of may be available. We feel, however, that the systems involved in this study are rather different, and that one might therefore expect their chemistry to be unique in some respects.

The second major question to be discussed concerns the formation of the diacid 14. There appear to be several possible mechanisms leading to 14 which are worthy of consideration.

The first to be considered will be those from the epoxide 26b. As noted previously, considering the usual reactions of epoxides in solution, one might predict the formation of an α-diketone such as 28 from the reaction of

26b. Such diketones are known to undergo Baeyer-Villiger oxidation with peroxide as well as with peracids to give diacids in aqueous media (36). One might then expect 14 to be formed by a mechanistic pathway like that shown in Scheme 11. It then seems quite likely that 14 could result from the further reaction of 26b.

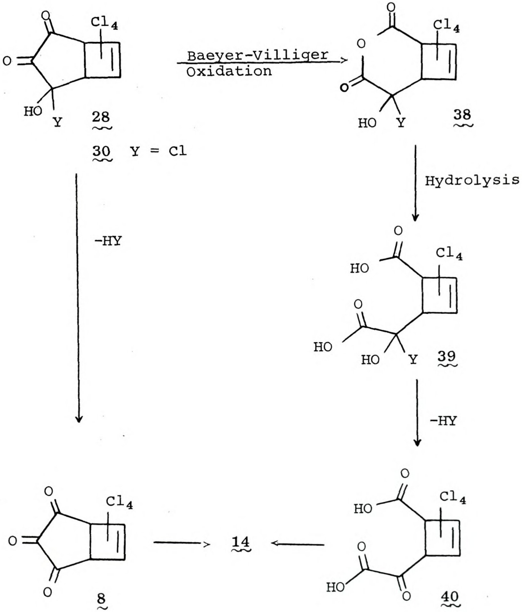
There is also indirect evidence to suggest that 14 may be formed directly from 7a rather than by a pathway involving the conversion of 7a to 7b. The epoxide of 7a, *i.e.*, 26a, if formed might be expected to react further to give 30 which could yield 14 as shown in Scheme 11.



26a 11 30

It is therefore possible that 14 is being formed from 7a directly and from 7b derived from 7a.

The indirect evidence which suggests that 7a may be reacting directly to yield 14 is found in the reaction of 7c. As was noted previously, only in the reaction of 7c is a third product observed. This product was identified as the methyl half-ester of 14, and the fact that it is the methyl rather than the ethyl ester indicates that it is formed directly from 7c. A possible mechanism for the formation



Y = -Cl, -OH, -OEt, -O-O-WO$_3^-$

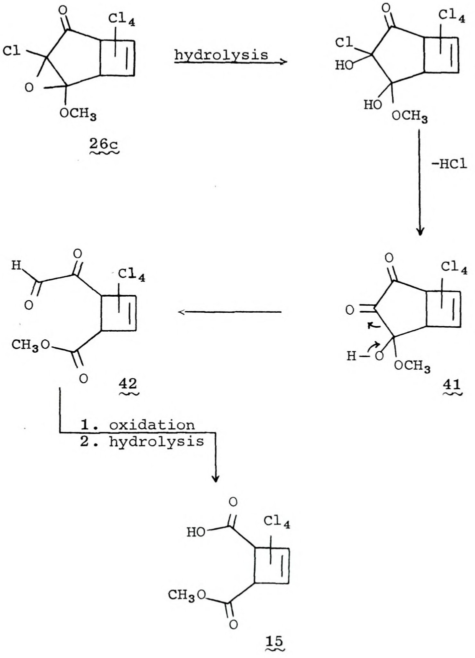
Scheme 11. Mechanistic proposal for the formation of diacid 14 from diketone 28.

of this product is shown in Scheme 12. Oxidation of **42** to the keto acid and its oxidation to **15** are quite reasonable reactions under the conditions (36).

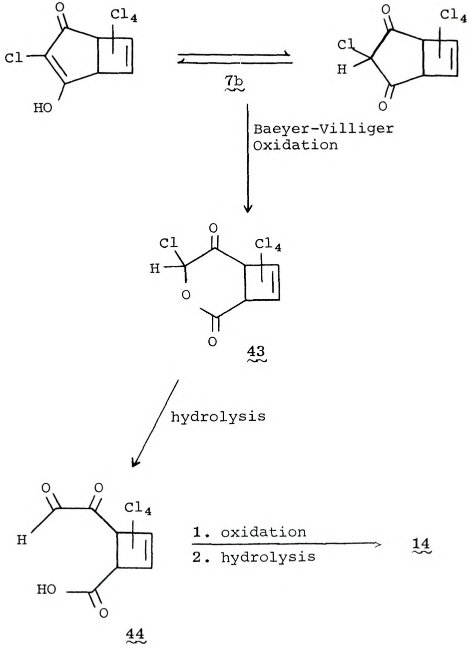
Two additional points concerning Scheme 12 should be noted. First, compound **41** could react to give **14** in the manner shown in Scheme 11. This reaction may be competing with that leading to the formation of **15**, and perhaps for this reason, the yield of **15** is low. Second, the reaction of **7a** or **7b** in the manner shown in Scheme 12 would yield **14**. Because of this, one is not able to say whether **7a** and **7c** are reacting in this manner.

Another possible reaction pathway leading to **14** is that shown in Scheme 13, which involves direct formation from **7b** rather than the intermediate epoxide **26b**. This sequence involves Baeyer-Villiger oxidation of the β-diketo form of **7b**. Such compounds, *i.e.*, β-diketones, *sometimes* react abnormally under Baeyer-Villiger oxidation conditions (36); there might then be some question about this sequence. It is a possibility nonetheless.

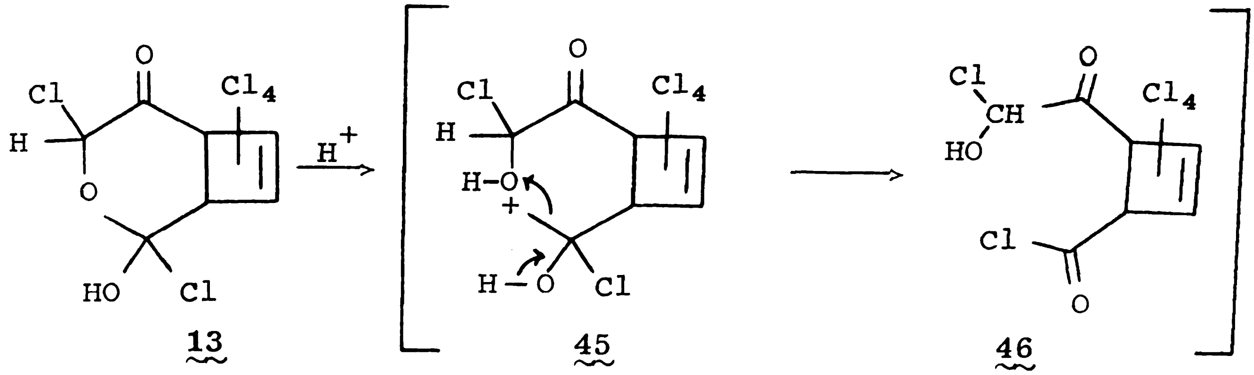
One additional consideration is the formation of **14** from **13** which has been shown to occur under the reaction conditions as noted previously. The mechanism suggested below seems possible. However, the attempted hydrolysis of **13** using 2*N* hydrochloric acid afforded only starting material. Thus, one might question the hydrolysis of **13** to **44**.



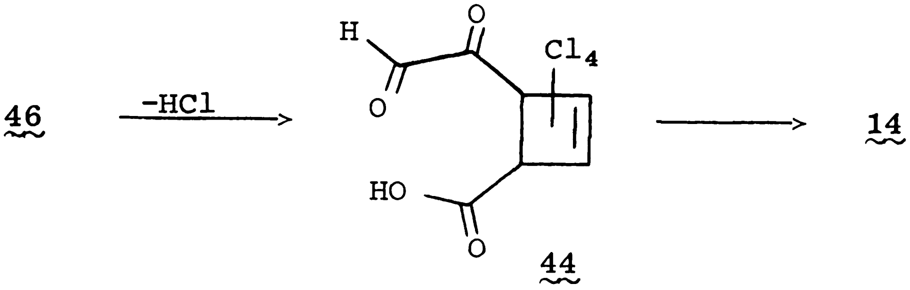
Scheme 12. Mechanistic proposal for the formation of the methyl half-ester 15 of diacid 14.



Scheme **13**. Mechanistic proposal for the formation of diacid 14 from 7b.



13 45 46



44

Obviously there are many possible routes to 14, and those presented here are only suggestions. The reactants and reaction conditions used are such that mechanistic suggestions are at best speculative and at worst futile considering the information at hand. It is therefore obvious that a great amount of research concerned with the study of the mechanisms of these reactions might be conducted.

C. Conclusions

One might conclude from the previous discussion that more questions have been posed than have been answered. This is indeed true, and perhaps not too surprising when one considers the reactants and reactions studied. Some rather unusual and little studied systems were subjected to

unusual reaction conditions; one might therefore expect some unusual results.

Several major problems are involved in a study dealing with highly chlorinated organic compounds. Unlike the chemistry of polyfluoro organic compounds which has been and is being studied quite extensively, the chemistry of polychloro organic compounds has been studied much less extensively. However, the chemistry of polychloro compounds, like that of polyfluoro compounds, is unique in that the reactions of such compounds are different from the reactions of "normal" organic compounds.

Another major difficulty unique to the study of polychloro organic compounds is that of structural analysis. That such is the case is obvious from this study as well as from the fact that numerous examples of errors in structural assignments may be found in the literature (9,23,24). No extremely valuable tool such as nuclear magnetic resonance is available for the structural analysis of polychloro organic compounds. A technique which does show great promise is that of nuclear quadropole resonance which is only now beginning to be used in the study of polychloro organic compounds (24,37,38). This has not yet become a routine analytical tool such as nmr. Therefore, structural analysis of polychloro organic compounds at this time depends largely upon classical organic reactions which may take unusual and unexpected directions when applied to the unique systems involved. The obvious answer to the question

of the structure of 13 would be an X-ray analysis. There is some question whether such a study is warranted, however.

Definitive conclusions concerning this study are difficult to make. An unusual structure has been proposed for compound 13 which is apparently formed in a unique manner. Further, we have assigned a structure to compound 14 which had previously been assigned to compound having properties very much different from those of 14 (27,28)

As noted previously, there is a possibility that the structure we have assigned to 13 is in error. However, we feel that the available evidence supports the proposed structure and feel obliged to suggest it if for no other reason than that we cannot suggest a more satisfying structure which fits the available data.

The discussion of mechanistic possibilities is totally speculative. As such, it is quite open to criticism, further speculation and discussion, and hopefully, further study. Therefore, at this stage, any conclusions about mechanisms would be unwarranted.

D. Suggestions for Further Study

One obvious suggestion is that of a nuclear quadropole resonance study of a series of polychloro organic compounds of known structure such as 7 and related compounds so that one might begin to build a fund of empirical data such as that available for the analysis of nmr and ir spectra. The usefulness of such data in the analysis of unknown structures is obvious.

Further study concerning the mechanisms of the reactions involved in this study would be quite useful. The possibilities in this direction are many.

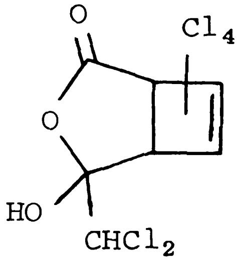
A third suggestion for further study would be to extend the reaction to related systems and to use different oxidation methods.

Thus, it is obvious that this study has been quite preliminary and has suggested many new problems while solving few.

Addendum:

An alternative structure for compound **13**, suggested by Professor William Reusch, is that of the γ-lactone shown below.

Studies to distinguish between this structure and that proposed for compound **13** in the text of this report are to be carried out.



EXPERIMENTAL

A. General Procedures

Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. The nmr spectra were obtained using a Varian A-60 instrument with chemical shifts reported as δ values measured from an internal standard of tetramethylsilane. The uv spectra were recorded on a Unicam Model SP-800 spectrophotometer using 1 cm quartz cells. Mass spectra were determined using a Hitachi Perkin-Elmer Model RMU-6 low resolution instrument.

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan or Galbraith Laboratories, Inc., Knoxville, Tennessee.

B. Sodium Tungstate-Hydrogen Peroxide Oxidation of 2-Substituted-1,3,5,6,7-Pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-ones 7a, 7b, and 7c

The same general procedure was used in the reaction of all three compounds. A description of the procedure used in a typical reaction is given below.

To a suspension of 10 mmol of the polychloro compound 7a, 7b, or 7c (9) and 1.65 g (5 mmol) of sodium tungstate dihydrate in 25 ml of absolute ethanol was added 20 ml of 30% hydrogen peroxide over a 15 min period. The suspension was then stirred at room temperature for 45 min and at reflux for 2.5 hr. The solvent was then removed under vacuum and the residue chromatographed directly or extracted thoroughly with ether. In the latter case, the extracts were washed once with saturated sodium chloride solution, dried over magnesium sulfate, and the solvent removed. The oil which remained was then chromatographed. In either case, chromatography was on a column of 70 g of silicic acid.

Elution with chloroform yielded only starting material when 7a or 7c were the reactants. Using the more polar carbon tetrachloride-ethyl acetate (10:3) solvent system, 7b, 13, and 15 (15 only from the reaction of 7c) were isolated. Using the still more polar carbon tetrachloride-methanol (10:4) solvent system, the diacid 14 was isolated. Yields of the various products are given in Table 1.

Recrystallization of product 13 from carbon tetrachloride provided an analytical sample of colorless crystals: mp 129-130°; uv (methanol) absorption below 225 mμ; ir (KBr) Figure 4; nmr (acetone-d_6) δ 6.52 (s); nmr (acetonitrile) δ 6.25 (s, 1) and δ 5.20 (broad s, 1); absorption at δ 5.20 disappears after deuterium exchange; mass spectrum Table 7.

Anal. Calcd for $C_7H_2Cl_6O_3$: C, 24.24; H, 0.58; Cl, 61.34.
Found: C, 24.10; H, 0.63; Cl, 61.35.
C, 24.02; H, 0.56; Cl, 61.50.

Recrystallization of product **14** from benzene afforded an analytical sample as white crystalline flakes: mp 156.5-157.5°; uv (H_2O) absorption below 225 mμ; ir (KBr) Figure 7.

Anal. Calcd for $C_6H_2Cl_4O_4$: C, 25.75; H, 0.72; Cl, 50.67.
Found: C, 25.57; H, 0.72; Cl, 50.55.

Recrystallization of product 15 two times from carbon tetrachloride-methylene chloride and careful drying afforded an analytical sample of fine white powder: mp 93.5-95.0°; ir (KBr) Figure 11; nmr ($CDCl_3$) δ 11.07 (s, 1) and - 3.87 (s, 3).

Anal. Calcd for $C_7H_4O_4Cl_4 \cdot H_2O$: C, 29.95; H, 1.94; Cl, 45.46.
Found: C, 27.01; H, 1.87; Cl, 45.50.

C. Preparation of the Acetate **17** of Compound **13**

A reaction mixture consisting of 175 mg (0.5 mmol) of **13**, 2 ml of acetic anhydride, and a few drops of acetyl chloride was stirred at 80° for 6 hr. The clear yellow solution was then allowed to stand overnight at room temperature. Chromatography of the yellow-brown oil, which remained after removal of the solvent under vacuum, on a column of 5 g of silicic acid using chloroform as the eluent afforded an analytical sample of **17** as small white crystals: mp 183-184°; ir (KBr) Figure 5) nmr ($CDCl_3$) δ 6.00 (s, 1) and δ 2.25 (s, 3); mass spectrum, Table 8.

Anal. Calcd for $C_9H_4O_4Cl_6$: C, 27.80; H, 1.04; Cl, 54.70.
Found: C, 27.88; H, 1.04; Cl, 54.80.

D. The Ketalization Reaction of Compound 13

A reaction mixture composed of 347 mg (1 mmol) of 13, 93 mg (1.5 mmol) of ethylene glycol, and a few crystals of p-toluenesulfonic acid in 20 ml of benzene was refluxed for 24 hr using a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction. The benzene solvent was distilled off under vacuum leaving an oily residue which was chromatographed on a column of 10 g of silicic acid. Elution with chloroform yielded 165 mg (46%) of an oil which crystallized on standing for a few days. Recrystallization from carbon tetrachloride-hexane afforded an analytical sample of 18 as white crystals: mp 158-159°; ir (KBr), Figure 6; nmr ($CDCl_3$) δ 6.77 (s, 1) and δ 4.0 to δ 5.0 (bm, 4); mass spectrum, Table 9.

Anal. Calcd for $C_9H_5O_4Cl_5$: C, 30.50; H, 1.42; Cl, 50.02.
Found: C, 30.65; H, 1.53; Cl, 50.07.

E. Sodium Tungstate-Hydrogen Peroxide Oxidation of Compound 13

To a suspension of 694 mg (2 mmol) of product 13 and 330 mg (1 mmol) of sodium tungstate dihydrate in 4 ml of absolute ethanol was added 4 ml of 30% hydrogen peroxide over a period of 15 min. The suspension was stirred at room temperature for 1 hr and at reflux for 2.5 hr. The solvent was removed under vacuum and the residue chromatographed on a column of 14 g of silicic acid using in the order listed, chloroform, carbon tetrachloride-ethyl acetate (10:3), and carbon tetrachloride-methanol (10:4) as eluents. Two products were recovered and identified as the starting compound (45%) and tetrachloro-3-cyclobutene-1,2-dicarboxylic acid, **14**, (30%) by comparison of melting points and spectra with authentic samples.

The diacid product was also converted to its dimethyl ester as described elsewhere. This product was in all respects identical to the diester prepared previously.

F. Attempted Oxidations of Compound 13

1. Oxidation Using Jones Reagent (18).

To a solution of 347 mg (1 mmol) of **13** in 6 ml of acetone cooled in an ice bath was added 0.5 ml of chromic acid solution prepared by dissolving 2.0 g (0.02 mol) of chromium trioxide in 5 ml of water, adding 3.0 g (0.03 mol) of concentrated sulfuric acid, and diluting to 10 ml. This solution was allowed to warm to room temperature over a 1 hr period and then stirred at room temperature for 3.5 hr. After addition of 2 ml of isopropyl alcohol and 210 mg of sodium bicarbonate, the mixture was filtered. The filter cake was washed thoroughly with acetone. Removal of the acetone from the combined filtrates yielded a green oil which on chromatography on a column of 12 g of silicic acid afforded 84% of the starting compound **13**.

Repetition of the reaction as above yielded only the starting compound.

2. Oxidation with Chromium Trioxide in Acetic Acid (10f).

A solution of 347 mg (1 mmol) of **13** in 3 ml of glacial acetic acid was added to a solution of 98 mg (0.98 mmol) of chromium trioxide in 5 ml of glacial acetic acid. The reaction mixture was stirred 8 hr at room temperature. Evaporation of the acetic acid was accomplished by passing a stream of air over the reaction mixture. The residue was taken up in 20 ml of water which was then extracted thoroughly with ether. Removal of the ether after drying yielded only a crystalline material identified as **13**.

3. Oxidation with Chromic Acid.

A solution of 150 mg (0.5 mmol) of potassium dichromate in 2 ml of water and 1 ml of concentrated sulfuric acid was added to a suspension of 174 mg (0.5 mmol) of **13** in 1 ml of water. After stirring at room temperature for 2.5 hr, the reaction mixture was extracted thoroughly with ether. Removal of the solvent after drying over magnesium sulfate, yielded an oil which crystallized on standing. This material was identified as **13**.

G. The Attempted Hydrolysis of **13**

A solution of 278 mg (0.8 mmol) of **13** in 3 ml of tetrahydrofuran and 3 ml of 2*N* hydrochloric acid was stirred at

room temperature for 2 hr and at reflux for 6 hr. One hour after the start of reflux an additional 1 ml of THF was added. On cooling, the solution separated into two phases. The lower aqueous phase was separated from the upper organic phase and extracted with ether. The extracts were combined with saturated sodium chloride solution, dried over magnesium sulfate, and the solvent removed. Recrystallization of the residue afforded only starting material.

H. The Thermolysis of **13**

A sample of 175 mg (0.5 mmol) of **13** in an evacuated sealed tube was heated to 120-130° for 0.5 hr. The yellow-red oil which resulted was chromatographed on a column of 6 g of silicic acid. Elution with chloroform gave 123 mg of red-orange oil. Distillation of this oil gave a golden yellow oil. This material was not identified. A very puzzling fact is that the infrared spectrum of the distilled sample contained several absorption bands in the region 3000 to 2900 cm^{-1} which is caracteristic of carbon-hydrogen absorptions (25). This absorption was not present in the ir of the sample before distillation.

I. The Determination of Hydrogen Chloride as a Product of the Thermolysis of **13**

A piece of moist pH paper gives an indication of acidity when placed over a capillary tube containing **13** which is heated to 130°.

A test for halide ion which involves the use of a test paper containing silver ferrocyanide (17) which is moistened with a ferric sulfate solution was used to determine whether halide is evolved when 13 is melted. A positive test is indicated by a blue color ascribed to the formation of Prussian blue according to the formula shown below.

$$Ag_4[Fe(CN)_6] + X^- \xrightarrow{Fe_2(SO_4)_3} 4AgX + Fe[Fe(CN)_6]^-$$

A procedure like the above using the appropriate test paper gave a positive result. One may thus conclude that hydrogen chloride is evolved when 13 is heated to 130°.

J. Test for Enol Formation in 13

The reactions involved in this test have been discussed in the text of this report (19).

A few drops of bromine water was added to an ethanol solution of 13. After a few minutes, a saturated solution of sulfosalicylic acid was added to the above solution until the yellow-orange color disappeared. A few drops of 5% potassium iodide solution and starch solution were then added. After a few minutes, the solution took on a purple color which became more intense on standing.

A control experiment like the above except that 13 was not added to the ethanol did not become colored on standing overnight.

Similarly, a control in which no bromine was added to the ethanol solution of 13 did not become colored.

These results suggest that an α-bromoketone is formed from **13** on treatment with bromine. However, as noted in the text, such a compound has not yet been isolated.

K. Hydrogenation of Tetrachloro-3-cyclobutene-*cis*-1,2-dicarboxylic Acid **14**

The hydrogenation of 570 mg (2 mmol) of the diacid **14** in 75 ml of water using 50 mg of platinum oxide catalyst was carried out at room temperature and atmospheric pressure. The reaction was stopped after the system had taken up 260 ml (12 mmol) of hydrogen. Removal of the water under vacuum afforded a crystalline material the infrared spectrum of which was identical to that of *cis*-cyclobutane-1,2-dicarboxylic acid. The material melted over a wide range. Attempted recrystallizations were not successful. Chromatography using carbon tetrachloride-methanol (10:4) eluent afforded a white crystalline material with properties identical to those of *cis*-cyclobutane-1,2-dicarboxylic acid (27,39); ir (KBr) Figure 10.

L. Esterification of Tetrachloro-3-cyclobutene-*cis*-1,2-dicarboxylic Acid **14**

Hydrogen chloride gas was bubbled into a cooled solution of 280 mg (1 mmol) of diacid **14** in 10 ml of anhydrous methanol. The flask was stoppered with a drying tube containing calcium chloride and the solution stirred at room temperature for 18 hr. On removal of the solvent, a white

crystalline material was present. This material chromatographed on a column of 5 g of silicic acid using chloroform eluent gave 234 mg (76%) of white crystalline diester 22 mp 66-68°. Recrystallization from 95% ethanol-water afforded an analytical sample as fine white needles: mp 68.5-69.2°; ir (KBr) Figure 9; uv max (heptane) 212 mμ (ϵ = 9500); nmr ($CDCl_3$) δ 3.75 (s).

Anal. Calcd for $C_8H_6O_4Cl_4$: C, 31.20; H, 1.96; Cl, 46.05.
Found: C, 31.25; H, 1.95; Cl, 46.15.

In subsequent preparations of the ester, it was found that chromatography is not necessary. The crude product recovered after removal of the methanol may be recrystallized directly.

M. Preparation of the Anhydride 21 of Tetrachloro-3-cyclobutene-*cis*-1,2-dicarboxylic Acid 14

A solution of 280 mg (1 mmol) of diacid 14 and 4 ml of acetyl chloride was refluxed for 2 hr. The flask was then stoppered and stored in a refrigerator for 2 days. On removal of the solvent under vacuum, a crystalline solid was left. Purification by sublimation two times afforded 135 mg (51%) of analytical sample: mp 137-138.5°; ir (KBr) Figure 5.

Anal. Calcd for $C_6O_3Cl_4$: C, 27.52; H, 0.00; Cl, 54.15.
Found: C, 27.36; H, 0.15; Cl, 54.07

N. Esterification of Anhydride 21

A solution of 32 mg of the anhydride in 3 ml of anhydrous methanol saturated with hydrogen chloride gas was stirred at room temperature for 4 hr. Removal of the solvent and chromatography of the residue gave 5 mg of white crystals identified as the dimethyl ester of tetrachloro-3-cyclobutene-1,2-dicarboxylic acid by comparison of its infrared spectrum and melting points with those of an authentic sample prepared from the diacid 14.

O. Esterification of the Methyl Half-Ester 15 of Tetrachloro-3-cyclobutene-*cis*-1,2-dicarboxylic Acid 14

A solution of 420 mg of the methyl half-ester of tetrachloro-3-cyclobutene-1,2-dicarboxylic acid 15, which was used without purification other than chromatography, in 15 ml of methanol saturated with hydrogen chloride was stirred at room temperature for 24 hr. The solvent was removed, the residue extracted with ether, the extracts dried over magnesium sulfate, and the ether removed. Chromatography of the residue on a column of 12 g of silicic acid using chloroform eluent afforded 240 mg of crystalline material mp 66-68°. Recrystallization from 95% ethanol-water yielded fine white crystals identified as the dimethyl ester of tetrachloro-3-cyclobutene-1,2-dicarboxylic acid 22 by comparison of melting point and infrared spectrum.

P. Hydrolysis Reactions of 7a, 7b, and 7c with Sodium Tungstate Present

The same general procedure was used for all three systems.

To a suspension of 5 mmol of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-one 7a, 7b, or 7c and 0.83 g (2.5 mmol) of sodium tungstate dihydrate in 10 ml of absolute ethanol, 7 ml of water was added over a period of 5 min. The white suspension was stirred at room temperature for 15 min and at reflux for 2.5 hr. The solvent was then removed under vacuum and the residue chromatographed on a column of 40 g of silicic acid. The solvents used in elution were chloroform, carbon tetrachloride-ethylacetate (10:3), and carbon tetrachloride-methanol (10:4) in that order. The results are shown in tabular form below.

Table 4. Product yields from the hydrolysis of 7a, 7b, and 7c.

Starting Material	% Starting Material Recovered	% 2-Hydroxy-(7b) Recovered	% Sodium Salt 16
7a (2-Chloro-)	32	47	0
7b (2-Hydroxy-)	16	16	55
7c (2-Methoxy-)	0	22	60

Q. Hydrolysis Reactions of 7a and 7c Using Only Ethanol and Water

The same procedure was used in the reaction of 7a and 7c. To a suspension of 5 mmol of the 2-substituted-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-one 7a or 7c in 10 ml of absolute ethanol, 7 ml of water was added over a 5 min period. The suspension was then stirred at room temperature for 35 min and at reflux for 2.5 hr. The solvent was then removed under vacuum and the residue chromatographed on a column of 40 g of silicic acid using progressively more polar eluents starting with chloroform, then carbon tetrachloride-methyl acetate (10:3) and finally carbon tetrachloride-methanol (10:4). The results are given in the table below.

Table 5. Product yields from the hydrolysis of 7a and 7c with ethanol and water.

Starting Material	% Starting Material Recovered	% 2-Hydroxy- (7b)
7a (2-Chloro-)	38	38
7c (2-Methoxy-)	0	92

R. Reaction of 2-Hydroxy-1,3,5,6,7-pentachlorobicyclo[3.2.0]hepta-2,6-dien-4-one **76** with Sodium Carbonate

A suspension consisting of 1.47 g (5 mmol) of **7b** and 0.27 g (2.5 mmol) of sodium carbonate in 10 ml of absolute ethanol to which 7 ml of water had been added over a period of 5 min, was stirred at room temperature for 15 min and at reflux for 2.5 hr. The solvent was then removed under vacuum and the residue recrystallized from ethanol-benzene. A nearly quantitative yield of product **16** as fine white needles resulted: dec. $\sim 300^0$; ir (KBr) Figure 12.

1. Acidification of Product **16**

Hydrogen chloride gas was bubbled through a methanol solution of the above product for approximately 3 minutes. Almost immediately, large quantities of white solid formed. The reaction mixture was filtered and the solvent removed from the filtrate. A white crystalline product shown to be the starting hydroxy compound **7b** was isolated in 82% yield based on **7b** used in the initial reaction.

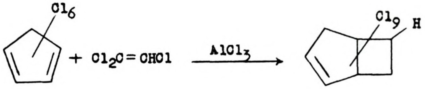
PART II

THE REACTION OF TETRACHLOROCYCLOPROPENE WITH POLYCHLOROETHYLENES

INTRODUCTION

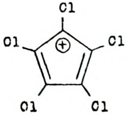
The bicyclic systems studied in Part I of this thesis are derived from 6-H-Nonachlorobicyclo[3.2.0]hept-2-ene 47 which is the product of the novel reaction of hexachlorocyclopentadiene with trichloroethylene in the presence of anhydrous aluminum chloride at 80 to 110° (39,9).

a)



47

No mechanistic details concerning this reaction have been published. Speculation might suggest that possibly the pentachlorocyclopentadienyl cation 48 is involved in the reaction (9a). Evidence for the possible existence of this species is presented in the literature as noted below (40,41).

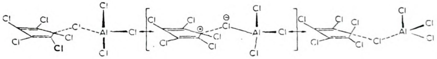


48

In the mass spectrum of hexachlorocyclopentadiene, the most abundant ion may be assigned the formula $C_5Cl_5^+$ (41) which according to the rule of rings plus double bonds (16) would correspond to a system containing three rings and/or double bonds. The authors suggest that this ion is indeed the pentachlorocyclopentadienyl cation 48 which fits the classification noted above in that it has the required three rings and/or double bonds.

Spectral evidence that the pentachlorocyclopentadienyl cation 48 exists as a triplet in the ground state has been published by Breslow and coworkers (42).

Schafer and Fritz (43) suggest structure 49 shown below rather than a symmetrical pentachlorocyclopentadienyl cation structure for a red resinous material isolated from the reaction of hexachlorocyclopentadiene with aluminum chloride.



49

There appears to be some justification for considering the intermediacy of a species with some cationic character. The red-purple color reported by Breslow (42) and by Schafer and Fritz (43) and observed in the reaction of hexachloropentadiene with trichloroethylene suggests the possibility of an intermediate possessing some cationic character.

A mechanism involving 48 or some related species such as 49 in an electrophilic reaction with trichloroethylene and subsequent cyclization to give product 47 might be suggested in view of the above information.

The thought that perhaps the analogous reaction using tetrachlorocyclopropene rather than hexachlorocyclopentadiene under the same reaction conditions might afford some information concerning the mechanism of the reaction led to the study reported herein.

Tetrachlorocyclopropene 50 reacts exothermically with anhydrous aluminum chloride to form trichlorocyclopropenium tetrachloroaluminate 51 (44).

50 51

Considering this favorable reaction to form the aromatic trichlorocyclopropenium ion 51, one might suspect that 51 would be the reactive species involved in an electrophilic reaction with trichloroethylene.

If the product formed in this reaction should prove to be the bicyclic analogue of 47, one might then have some slight additional support for the involvement of the pentachlorocyclopentadienyl cation 48 in reaction a. Great care would need to be exercised in comparing results from

the two reactions, for the two cationic species **48** and **51** are very different. The pentachlorocyclopentadienyl cation **48** is at best predicted to be an unstable system while the trichlorocyclopropenium ion **51** has been shown to be a stable species which exhibits properties characteristic of an aromatic system (44).

For the above reasons and with the realization that even if a product analogous to **47** should result from the reaction of tetrachlorocyclopropene **50** with trichloroethylene in the presence of aluminum chloride great care in drawing conclusions would be necessary, the reaction of tetrachlorocyclopropene with trichloroethylene was studied.

Since the results of this study were rather interesting, the study was extended to include the reaction of tetrachlorocyclopropene with 1,2-dichloroethylene (*cis* and *trans*) and with tetrachloroethylene.

After the work was in progress, a study concerning the reaction of tetrachlorocyclopropene with 1,1-dibromo-, 1,1-dichloro-, and 1,1-dimethylethylene was reported (45).

RESULTS AND DISCUSSION

A. The Reaction of Tetrachlorocyclopropene with Trichloroethylene

Chromatography of an oily material isolated from the reaction of tetrachlorocyclopropene with trichloroethylene in the presence of anhydrous aluminum chloride afforded, in addition to an intractable yellow-orange oil, a crystalline product **52** (mp 151-152°).

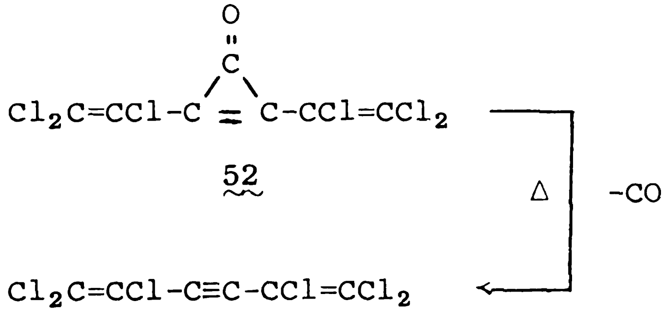
The appearance of the infrared spectrum of **52** with absorption bands at 1905 (m), 1865 (s), and 1825 (s) cm^{-1} immediately suggested the possibility that compound **52** might be a cyclopropenone since cyclopropenones characteristically show absorption in this region (46). The mass spectrum and elemental analysis of **52** showed it to be a compound of formula C_7OCl_6. From the mass spectrum, it appears that a facile cleavage of carbon monoxide occurs as might be expected for a cyclopropenone (46a,47). On melting, **52** was observed to evolve gas. The red liquid which resulted solidified on cooling to room temperature.

When a sample of compound **52** was heated in an evacuated sealed tube to 150° for 15 minutes, a new orange crystalline compound **53** (mp 52.0-52.5°) was isolated. Analysis showed this compound to have an empirical formula of C_6Cl_6. The

mass spectra of 52 and 53 are very similar in the region corresponding to C_6Cl_6, *i.e.*, m/e = 282, and below. This suggests that 53 is formed by the loss of carbon monoxide from 52.

The infrared spectrum of 53 contains very few bands. Of major significance, however, is a weak band at 2190 cm^{-1} which may be attributed to a disubstituted acetylenic bond (25). There is no infrared absorption near 756 cm^{-1} which is the region of ≡C-Cl absorption (48).

The above evidence suggests that 52 is a bis(trichlorovinyl)cyclopropenone and that 53 is bis(trichlorovinyl)-acetylene formed by the loss of carbon monoxide from 52 a reaction which is general for cyclopropenones (46a, 46c, 47).



$$Cl_2C{=}CCl{-}\overset{\overset{O}{\|}}{C}{-}C{=}C{-}CCl{=}CCl_2 \quad \textbf{52} \xrightarrow[-CO]{\Delta} Cl_2C{=}CCl{-}C{\equiv}C{-}CCl{=}CCl_2 \quad \textbf{53}$$

52

53

The ultraviolet spectra of 52 and 53 will be discussed later.

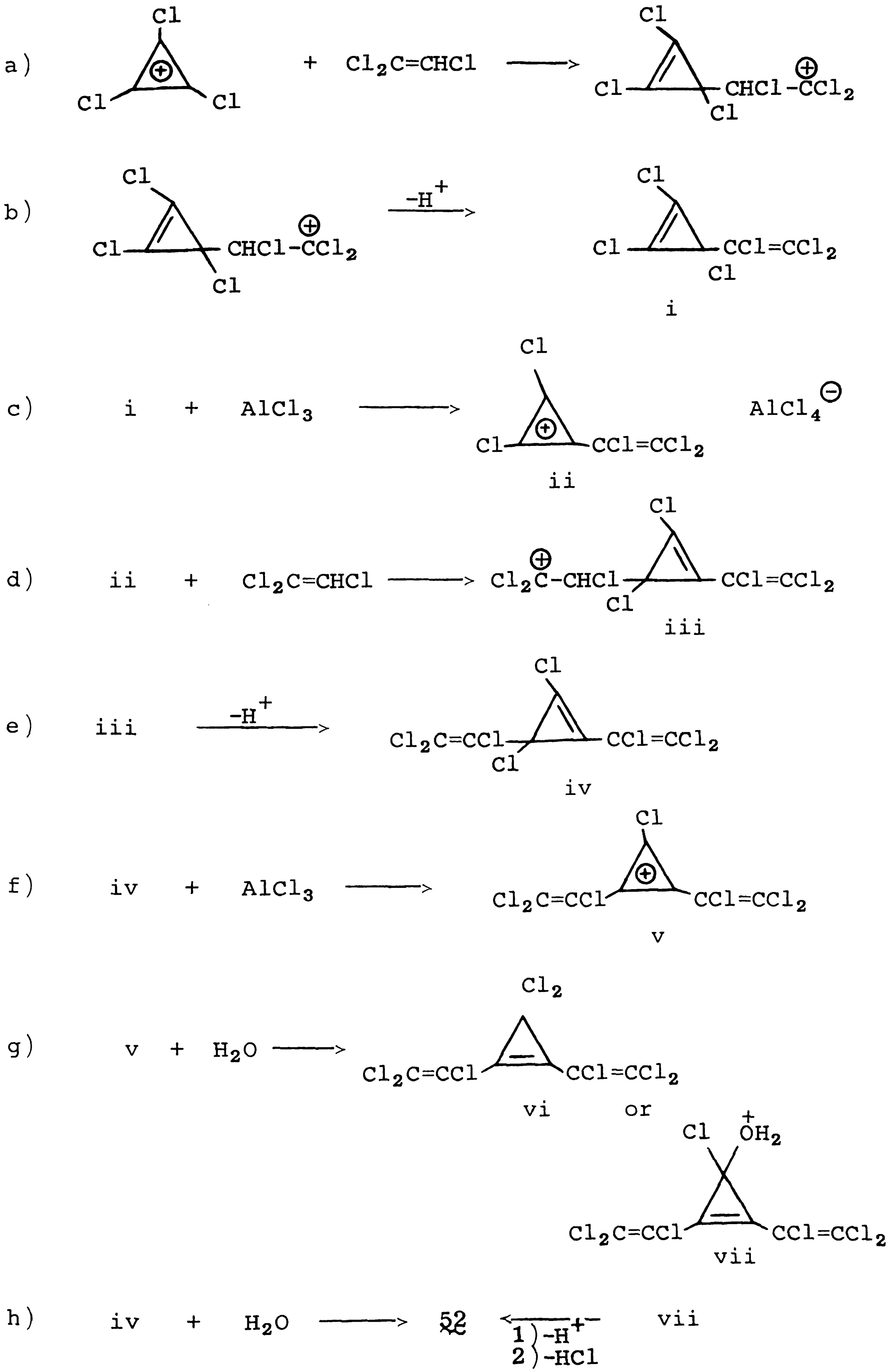
Suggesting a possible mechanism for the formation of cyclopropenone 52 from the reaction of tetrachlorocyclopropene with trichloroethylene is not too difficult when one considers some other examples of reactions of

tetrachlorocyclopropene, and the fact that the product of the reaction is a cyclopropenone is not too surprising.

Several examples of electrophilic substitution reactions of trichlorocyclopropenium tetrachloroaluminate 51 with benzene and substituted benzenes to give aryltrichlorocyclopropenes and diarylcyclopropenones have been reported (49,50). Thus, one might consider the possibility of a similar electrophilic substitution reaction with trichloroethylene. However, trichloroethylene might be expected to be a rather poor system to enter into an electrophilic substitution reaction as the electron rich partner because of the presence of three electronegative chlorine atoms. Also, since 51 is an aromatic species, its reactivity as an electrophile might be greatly decreased.

The results suggest that a favorable combination of factors is present in the above reaction and that the trichlorocyclopropenium ion does apparently undergo an electrophilic substitution reaction with trichloroethylene. Perhaps 51 is after all a more reactive electrophile than might be anticipated because it is in fact a cation in addition to being an aromatic species. At any rate, the following mechanism may be suggested. (Scheme 14)

There is a question whether the product of step g is vi or vii. Precedence for the formation of 1,1-dichloro compounds from chlorocyclopropenium (44) and chlorotropylium salts (51) on hydrolysis may be found in the literature. Also, in a few instances, compounds such as vi have been

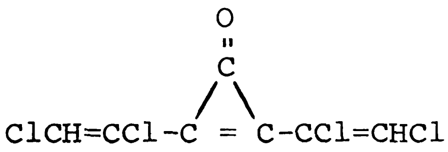


Scheme 14. Mechanistic proposal for the formation of bis-(trichlorovinyl)cyclopropenone **52**.

isolated (44,45). Thus, one might be inclined to favor the pathway involving hydrolysis of vi.

B. The Reaction of Tetrachlorocyclopropene with 1,2-Dichloroethylenes

The reaction of a mixture of cis- and trans-1,2-dichloroethylene with tetrachlorocyclopropene in the presence of anhydrous aluminum chloride gave similar but much less satisfactory results than the reaction with trichloroethylene. A maximum of 16 per cent yield of crystalline bis(1,2-dichlorovinyl)cyclopropenone 54 was isolated. The analytical and spectral data support the cyclopropenone structure for 54. No evidence on which to base the stereochemistry of 54 is available.



54

When trans-1,2-dichloroethylene, bp $49\text{-}52^0$, was used in the reaction, a five per cent yield of 54 and a seven per cent yield of α,β-dichloroacrylic acid resulted. Using cis-1,2-dichloroethylene, bp $58\text{-}60^0$, yields of 17 per cent of the cyclopropenone 54 and 11 per cent of the acrylic acid were isolated. The differences in yield may or may not be significant since the reaction conditions were somewhat different for the various reactions. What is significant is that at best a yield of less than 20 per cent of

cyclopropenone 54 was isolated. An effort to maximize yields was not put forth, but several reactions under various conditions gave yields which did not vary greatly.

There is some evidence to suggest that possibly the lower boiling points of the 1,2-dichloroethylenes, and hence the lower refluxing temperatures of the reaction mixtures as compared to that of trichloroethylene, may be significant.

Table 6. Yields of cyclopropenones from the various dichloroethylenes.

Polychloroethylene	bp	Reflux Time (hrs)	% Yield of Cyclopropenone[c]
1. trans-1,2-Dichloroethylene[d]	49-52°[a]	8.0	5
2. cis-1,2-dichloroethylene[d]	58-60°[a]	5.0	17
3. Mixture of 1 and 2[d]		13.5	12
4. Mixture of 1 and 2[e]		10.0	16
5. 1,1,2-Trichloroethylene[e]	87°[b]	5.0	47

[a] Boiling points of isomers as observed on distillation of commercial mixture of cis- and trans-1,2-dichloroethylene.

[b] Boiling point recorded on label.

[c] Data taken from reactions giving highest yields.

[d] Data for 1,2, and 3 from reactions using a ratio of tetrachlorocyclopropene to aluminum chloride of 10 to 7.5.

[e] Data for 4 and 5 from reactions using a ratio of tetrachlorocyclopropene to aluminum chloride of 4 to 1 and 10 to 3 respectively.

Considering the data in Table 6, one might suggest that reaction temperature is of significance although the data

in Table 6 are by no means conclusive on this point.

A very significant factor is the amount of aluminum chloride used. For example, in the reaction of trichloroethylene with tetrachlorocyclopropene, when the ratio of tetrachlorocyclopropene to aluminum chloride is ten to three, the yield of cyclopropene is approximately 50 per cent. If however, the ratio is ten to seven and one-half, the yield of cyclopropenone is less than five per cent. In both instances, a significant amount of red-orange intractable oil is present. This is thought to be a polymeric material. There is evidence presented in the literature which shows that high polymers are formed in the reactions of polychloro compounds catalyzed by aluminum chloride when significantly more than catalytic amounts of aluminum chloride are used (52,53).

A study of the effect of excess aluminum chloride on the reactions using the 1,2-dichloroethylenes was much less conclusive as the data in Table 6 show. In the reactions in which a ratio of tetrachlorocyclopropene to aluminum chloride of ten to seven and one-half was used, a large amount of intractable oil resulted, and the maximum yield of **54** was 12 per cent. In a reaction using a ratio of tetrachlorocyclopropene to aluminum chloride of four to one, the yield of **54** was 16 per cent. These results are for reactions in which the dichloroethylene used was a mixture of the *cis* and *trans* isomers. It may be noted from the data in Table 6 that the greatest yield of **54** results when the *cis* isomer of 1,2-dichloroethylene is used. Perhaps a reaction using the *cis* isomer and a smaller amount of aluminum chloride relative to the amount of tetrachlorocyclopropene used might afford a significantly greater yield of **54**.

Attempts to prepare bis(1,2-dichlorovinyl)acetylene **55** from **54** were not successful due to the small quantities of **54** available. There seems to be no reason why **55** could not be prepared in a manner analogous to the preparation of **53** from **52**. On melting compound **54**, a gas is evolved and a red liquid is formed which crystallizes on cooling. This suggests that **55** probably is formed from **54** on melting.

It thus appears that the reactions of tetrachlorocyclopropene with *cis*- and *trans*-1,2-dichloroethylene and 1,1,2-trichloroethylene are quite analogous. A mechanism similar to that proposed for the reaction of trichloroethylene may be written for the reactions of 1,2-dichloroethylene. In all cases, it is necessary, if the proposed mechanism is to hold, that the polychloroethylene system contain at least one hydrogen atom which may be lost as a proton. Considering this factor, it became of interest to see what course the reaction might take if no hydrogen atom were present in the polychloroethylene system. For this reason, the reaction of tetrachlorocyclopropene with tetrachloroethylene in the presence of anhydrous aluminum chloride was included in this study.

C. The Reaction of Tetrachlorocyclopropene with Tetrachloroethylene

The only product isolated from the reaction of tetrachlorocyclopropene with tetrachloroethylene in the presence of anhydrous aluminum chloride was α,β-dichloroacrylic acid. This product was also isolated from the reactions in which trichloroethylene and the 1,2-dichloroethylenes were used. It is believed that the acrylic acid results from the hydrolysis of tetrachlorocyclopropene **50** or trichlorocyclopropenium tetrachloroaluminate **51**.

The work-up procedure for all the reactions studied includes either pouring the reaction mixture on ice and extracting with ether or methylene chloride and then washing thoroughly with water or extracting the reaction mixture directly then washing the extracts with water. Using either procedure, there is ample opportunity for hydrolysis of any unreacted tetrachlorocyclopropene **50** or trichlorocyclopropenium tetrachloroaluminate **51**. The product of the aqueous hydrolysis of **50** has been reported to be α,β-dichloroacrylic acid (46a,54), and on pouring **51** into water, the product is reported to be **50** (44). Thus it seems likely that the acid may be coming from either one or both **50** and **51**.

A question remains as to why no product from the addition of **51** to tetrachloroethylene is isolated. It would appear that electronic factors are more important than steric factors since the double bond in tetrachloroethylene

should not be greatly hindered. Also, since 51 is an aromatic species, it might be unreactive toward the apparently quite electron poor tetrachloroethylene. This seems unlikely, however, in view of the reactivity of 51 as an electrophile in the previous reactions studied. One might then conclude that the reason no apparent reaction between 51 and tetrachloroethylene is observed is due rather to the unreactivity of tetrachloroethylene as an electron source.

D. The Reaction of Tetrachlorocyclopropene with 1,1-Dibromo-, 1,1-Dichloro-, and 1,1-Dimethylethylene (45)

The results of this study as described in the Abstracts of the Division of Organic Chemistry from the 156th National Meeting of The American Chemical Society, September 1968, are analogous to those from our study. Divinyl cyclopropenones are reported to be isolated in yields of 20 to 60 per cent. The ultraviolet spectra are reported to be characteristic of triene systems with maxima near 300 mμ.

The ultraviolet spectra of bis(trichlorovinyl)cyclopropenone 52, bis(trichlorovinyl)acetylene 53, and bis(1,2-dichlorovinyl)cyclopropenone 54 show evidence for extended conjugation with maxima above 300 mμ and extinction coefficients of approximately 20,000.

The report of Tobey, Whittemore, and Lourandos (45) does not make reference to any of the acetylenes which might result from loss of carbon monoxide from the cyclopropenones such as bis(trichlorovinyl)acetylene 53 prepared from bis-(trichlorovinyl)cyclopropenone 52 by us.

E. Conclusions

The results of this study provide no information concerning the mechanism of the reaction between hexachlorocyclopentadiene and trichloroethylene. Some unusual divinyl cyclopropenones did, however, result. Also, the scope of the participation of the trichlorocyclopropenium ion **51** in electrophilic substitution reactions was extended.

As noted previously, electrophilic substitution reactions between **51** and aryl systems are well known (49,50). This work and that of Tobey, Whittemore, and Lourandos (45) show that the trichlorocyclopropenium ion is capable of reacting as an electrophile with systems which might be considered to be rather poor systems to be involved in electrophilic substitution reactions as the electron rich member. This may not in fact be too surprising since **51** is after all a cationic species. It seems, however, that the limit to the electrophilic reactivity of **51** with electron poor ethylenes is reached in the reaction with tetrachloroethylene since no addition or substitution product is observed.

EXPERIMENTAL

A. The Reaction of Tetrachlorocyclopropene with Trichloroethylene

1. The Reaction Using a 10 to 3 Ratio of Tetrachlorocyclopropene and Aluminum Chloride.

To a stirred suspension of 0.4 g (3 mmol) of anhydrous aluminum chloride in 10.0 g of trichloroethylene was added 1.8 g (10 mmol) of tetrachlorocyclopropene. After stirring at room temperature for one hour and at reflux for five hours under a blanket of nitrogen, the reaction mixture, which contained a red oil, was allowed to cool to room temperature. On cooling, a tan solid formed. The reaction mixture was extracted with methylene chloride and the extracts washed thoroughly with water and with saturated sodium chloride solution. The extracts were then filtered through magnesium sulfate and concentrated. The yellow oil which resulted was chromatographed on a column of 40 g of silicic acid using chloroform as the eluent. The chromatography yielded, in addition to 1.44 g of yellow-orange oil, 1.40 g (47%) of white crystalline bis(trichlorovinyl)cyclopropenone **52**. Recrystallization from chloroform-pentane afforded an analytical sample as colorless plates: mp 151-152°; ir (KBr) Figure 13; uv (heptane) Figure 16; mass spectrum (70 eV)

m/e (relative intensity) $M^{+\cdot}$, 316 (1.0), 314 (2.0), 312 (2.5), 310 (1.5); $(M-28)^{+\cdot}$, 290 (9.2), 288 (33.7), 286 (78.7), 284 (97.5), 282 (50.2); $(M-63)^{+}$, 255 (4.0), 253 (21.2), 251 (63.7), 249 (100.0), 247 (63.0).

Anal. Calcd for C_7OCl_6:	C, 26.88; H, 0.00; Cl, 68.00.
Found:	C, 26.84; H, trace; Cl, 67.92.

2. The Reaction Using a 10.0 to 7.5 Ratio of Tetrachlorocyclopropene and Aluminum Chloride

A mixture of 1.0 g (7.5 mmol) of anhydrous aluminum chloride, 1.8 g (10 mmol) of tetrachlorocyclopropene and 10.0 g of trichloroethylene was stirred at room temperature for one hour and refluxed for six hours. The system was allowed to react under a blanket of nitrogen. A tan solid formed as the reaction mixture cooled. Work-up as above yielded, after chromatography, 2.82 g of yellow-orange oil and 0.05 g (1.5%) of the cyclopropenone **52**. In addition, on using a more polar eluent of carbon tetrachloride and ethyl acetate in a ratio of ten to three, 0.03 g (2%) of α,β-dichloroacrylic acid was isolated.

B. The Thermolysis of Bis(trichlorovinyl)cyclopropenone 52

In an evacuated sealed tube, 300 mg (1 mmol) of bis(trichlorovinyl)cyclopropenone **52** was heated to 155-160° for 15 minutes. Chromatography of the red-orange solid, which formed when the tube was allowed to cool, on a column of 10 g of silicic acid using chloroform as the eluent gave 257 mg (94%) of bis(trichlorovinyl)acetylene **53** as red-orange

crystals. Recrystallization from pentane at -15° gave an analytical sample of 53 as fine orange-pink needles: mp 52.0-52.5°; ir (KBr) Figure 14; uv (heptane) Figure 17; mass spectrum (70 eV) m/e (relative intensity) $M^{+\cdot}$, 290 (3.8), 288 (13.3), 286 (30.0), 284 (38.1), 282 (19.5); $(M-35)^+$, 255 (3.3), 253 (14.3), 251 (41.4), 249 (68.5), 247 (41.8); 142 (100.0).

Anal. Calcd for C_6Cl_6: C, 25.31; H, 0.00; Cl, 74.69.
Found: C, 25.31; H, 0 ; Cl, 74.66.

C. The Reactions of Tetrachlorocyclopropene with 1,2-Dichloroethylenes

1. The Reaction Using a Mixture of cis- and trans-1,2-Dichloroethylene and a 10.0 to 7.5 Ratio of Tetrachlorocyclopropene and Aluminum Chloride.

A suspension of 1.0 g (7.5 mmol) of anhydrous aluminum chloride in 1.8 g (10 mmol) of tetrachlorocyclopropene and 10 ml of 1,2-dichloroethylene (a mixture of cis and trans isomers) was stirred at room temperature under nitrogen for three hours and at reflux for 13.5 hours. The excess solvent was evaporated by passing a stream of air over the reaction mixture. The light brown solid which resulted was extracted with methylene chloride and chloroform. The extracts were combined, washed thoroughly with water and with a saturated sodium chloride solution, filtered through magnesium sulfate, and concentrated. The yellow-brown oil which resulted was chromatographed on a column of 40 g of silicic acid. Elution

with chloroform gave 2.03 g of yellow-brown oil. Further elution with the more polar carbon tetrachloride-ethyl acetate (10:3) solvent system afforded 0.30 g (12%) of rust colored solid. Recrystallization two times from carbon tetrachloride-pentane provided an analytical sample of bis-(1,2-dichlorovinyl)cyclopropenone **54** as fine very light tan needles: mp 126.5-127.5°; ir (KBr) Figure 15; uv (heptane) Figure 18; mass spectrum (70 eV) *m/e* (relative intensity), Molecular ion not present in spectrum. $(M-28)^{+\cdot}$, 220 (10.4), 218 (36.8), 216 (77.8), 214 (63.2); $(M-63)^{+}$, 185 (4.9), 183 (31.2), 181 (100.0), 179 (100.0).

Anal. Calcd for $C_7H_2OCl_4$: C, 34.47; H, 0.83; Cl, 58.14.
Found: C, 34.45; H, 0.85; Cl, 58.23.

2. The Reaction Using a Mixture of *cis*- and *trans*-1,2-Dichloroethylene and a 4 to 1 Ratio of Tetrachlorocyclopropene and Aluminum Chloride.

A reaction mixture consisting of 1.1 g (6.2 mmol) of tetrachlorocyclopropene and 0.2 g (1.5 mmol) of anhydrous aluminum chloride in 6.0 g of a mixture of *cis*- and *trans*-1,2-dichloroethylene was stirred at room temperature under nitrogen for one hour and at reflux for ten hours. The clear brown reaction mixture was allowed to cool and poured into a separatory funnel to which 30 ml of methylene chloride was then added. After shaking thoroughly, 15 ml of water was added to the separatory funnel, the system thoroughly mixed, and the two phases separated. The aqueous solution was extracted once more with methylene chloride and two times

with ether. The extracts were combined and washed with a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated. Chromatography of the oil which remained, as in reaction 1 above, afforded 0.25 g (16%) of cyclopropenone 54.

3. The Reaction Using *trans*-1,2-Dichloroethylene.

A suspension of 1.8 g (10 mmol) of tetrachlorocyclopropene and 1.0 g (7.5 mmol) of anhydrous aluminum chloride in 8 ml of *trans*-1,2-dichloroethylene (bp 49-52°), which was distilled from a commercial mixture of *cis*- and *trans*-1,2-dichloroethylene, was stirred under nitrogen for two and one-half hours at room temperature and at reflux for eight hours. The reaction mixture was then stirred at room temperature for 12 hours. The reaction mixture was poured onto ice, the aqueous system extracted with methylene chloride, chloroform, and ether, the extracts washed two times with saturated sodium chloride solution, dried over magnesium sulfate, and concentrated. The golden yellow oil which resulted was chromatographed on a column of 40 g of silicic acid. Elution with chloroform gave 1.81 g of yellow-red oil. Elution with a carbon tetrachloride-ethyl acetate solution (10:3) gave 0.13 g (5%) of a rust colored solid shown to be bis(1,2-dichlorovinyl)cyclopropenone 54. Further elution with the same solvent mixture afforded 0.10 g (7%) of α,β-dichloroacrylic acid identified by comparing its infrared spectrum and melting point with those given in the literature

(see the experimental section for the reaction of tetrachlorocyclopropene with tetrachloroethylene).

4. The Reaction Using *cis*-1,2-Dichloroethylene.

To a stirred suspension of 1.0 g (7.5 mmol) of anhydrous aluminum chloride in 8 ml of *cis*-1,2-dichloroethylene (bp 58-60°), which had been distilled from a commercial mixture of *cis*- and *trans*-1,2-dichloroethylene, was added 1.8 g (10 mmol) of tetrachlorocyclopropene. The reaction mixture was stirred at room temperature under nitrogen for four hours, at reflux for five hours, and again at room temperature for 12 hours. The clear red-brown solution was then poured onto ice. The aqueous system was then extracted two times each with ether and chloroform and the extracts washed with saturated sodium chloride solution. The extracts were dried over magnesium sulfate, concentrated, and the yellow-brown oil which resulted chromatographed on a column of 40 g of silicic acid. Elution with chloroform afforded 1.94 g of yellow-red oil and on further elution with chloroform 0.32 g (13%) of bis(1,2-dichlorovinyl)cyclopropenone **54**. Elution with the carbon tetrachloride-ethyl acetate (10:3) solvent system gave an additional 0.09 g (4%) of **54** and 0.16 g (11%) of α,β-dichloroacrylic acid.

D. The Reaction of Tetrachlorocyclopropene with Tetrachloroethylene

A reaction mixture consisting of 1.8 g (10 mmol) of tetrachlorocyclopropene, 1.0 g (7.5 mmol) of anhydrous aluminum chloride, and 10.0 g of tetrachloroethylene was stirred at room temperature under nitrogen for two hours and at approximately 80^0 for three hours. The reaction mixture was poured on ice. The aqueous system was extracted three time with ether, the extracts washed one time with saturated sodium chloride solution, dried over magnesium sulfate, and concentrated by distilling off the ether at atmospheric pressure and the excess tetrachloroethylene and unreacted tetrachlorocyclopropene under vacuum. The oil which remained was chromatographed on a column of 40 g of silicic acid. Elution with chloroform gave only a small amount of oil. Elution with carbon tetrachloride-ethyl acetate (10:3) afforded 0.32 g (22%) of crystalline α,β-dichloroacrylic acid. Two recrystallizations from pentane provided and analytical sample: mp 85-86^0, lit. 86^0 (55). The infrared spectrum of the analytical sample was identical to that of an authentic sample of the acid as shown in the "Sadtler Index of Standard Infrared Spectra" (56).

Anal. Calcd for $C_3H_2O_2Cl_2$: C, 25.56; H, 1.43.
Found: C, 25.51; H, 1.48.

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APPENDIX

Table 7. Mass spectrum of compound 13

m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity
350	0.3	269	2.8	207	2.1	145	1.9	77	2.5
348	0.4	268	1.9	205	4.3	143	4.9	76	2.5
346	0.5	267	5.0	203	7.5	141	5.0		
344	0.3	266	2.5	201	7.2			63	1.5
		265	5.0			133	2.5	61	2.5
332	0.4	264	1.8	199	4.6	131	2.9		
330	0.8	263	2.9	197	5.1			56	1.9
328	0.9	261	1.8			120	4.1		
326	0.5			193	3.7	118	5.4	49	2.9
		239	3.8	192	6.6			48	2.9
314	0.9	237	6.5	191	6.3	111	2.4	47	3.1
312	2.3	235	8.4	190	14.5				
310	3.2	234	3.4	189	3.7	109	2.1	45	1.6
308	2.1	233	6.9	188	10.6	107	3.2	44	14.0
		232	5.9					43	6.3
297	0.6	231	5.0	183	2.4	103	3.2		
295	1.3	230	5.0	181	2.8			38	41.2
293	1.9					98	1.6	37	4.1
291	1.3	229	7.6	171	4.0	96	3.7	36	100.0
		227	13.2	169	7.1			35	10.0
278	1.6	225	12.8	167	5.4	89	2.2		
276	3.5					87	5.0	28	12.0
274	2.8	223	1.8	157	1.8				
		221	4.6	155	4.0	85	4.3	18	13.2
		219	9.0	153	4.0	83	7.1	17	3.8
		217	6.8						

Table 8. Mass spectrum of compound 17.

m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity
394	0.3	268	0.3	207	0.3	122	0.7	65	0.4
392	1.0	267	0.4	205	0.9	120	3.5	63	0.8
390	2.1	266	0.4	203	2.0	118	5.4		
388	2.6	265	0.5	201	1.4			61	0.7
386	1.5	264	0.3			113	0.6	60	0.9
		263	0.4	194	2.1	111	1.6		
332	0.3			192	8.5			50	0.4
331	0.3	261	0.2	190	17.9	110	0.3	49	0.6
330	0.5	259	0.3	188	13.6	109	0.5	48	1.1
329	0.4	257	0.2			108	0.8	47	1.0
328	0.7			185	0.4	107	0.8		
327	0.2	242	0.3	183	1.0	106	0.6	45	1.3
326	0.4	241	0.3	181	1.1			44	8.9
		240	0.7			98	0.4	43	100.0
307	0.4	239	0.9	157	1.4	96	1.2	42	2.1
305	1.2	238	1.1	155	4.1	94	0.9	41	0.5
303	2.8	237	1.3	153	4.5				
301	3.1	236	0.7			89	0.5	38	1.7
299	1.7	235	0.9	145	0.4	87	1.5	36	4.7
				143	0.9	85	3.5		
295	0.4	220	0.3	141	0.9	83	5.9	29	0.4
293	0.6	218	0.4					28	7.1
291	0.4	216	0.4	133	0.6	78	0.4		
				131	0.9	76	1.1	18	4.4
								17	0.9
						73	0.5		
						71	1.1	15	6.6
								14	0.7

Table 9. Mass spectrum of compound 18.

m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity	m/e	Rel. Intensity
358	2.4	251	11.7	187	7.5	123	4.8	73	6.3
356	7.5	249	47.6	185	12.9	121	10.5	71	11.1
354	11.1	247	100.0			119	15.6		
352	6.9	245	88.6	173	6.9			65	4.5
		243	50.6	171	18.9	113	6.0	63	9.6
323	3.9	241	50.6	169	18.6	111	9.9	61	6.6
321	13.5								
319	27.0	233	6.0	159	5.7	110	3.0	45	1.2
317	21.1	231	11.4	158	4.2	109	6.9	44	7.5
		229	9.3	157	9.3	108	13.2	43	13.5
295	5.1			156	11.4	107	9.6	42	3.0
293	17.1	221	10.8	155	8.1	106	19.5		
291	32.3	219	21.8	154	12.0			38	5.4
289	27.3	217	15.9	153	9.0	96	9.6	37	2.1
								36	13.8
286	21.8	205	10.8	151	4.2	89	3.6	35	5.4
284	65.3	203	22.4	149	12.6	87	11.7		
282	91.6	201	21.8	147	13.8	86	5.4	29	9.0
280	55.5	199	8.4			85	14.7	28	11.4
				145	10.2	84	14.7	27	7.5
270	3.6	193	10.5	143	26.6	83	17.7	26	3.3
268	9.9	191	20.2	141	26.3				
266	15.0	189	15.9			78	3.9	18	4.5
264	10.2			136	6.3	77	5.4	17	1.5
				135	6.3	76	6.9		
				134	8.4			15	4.5
				133	14.4				
				131	14.4				

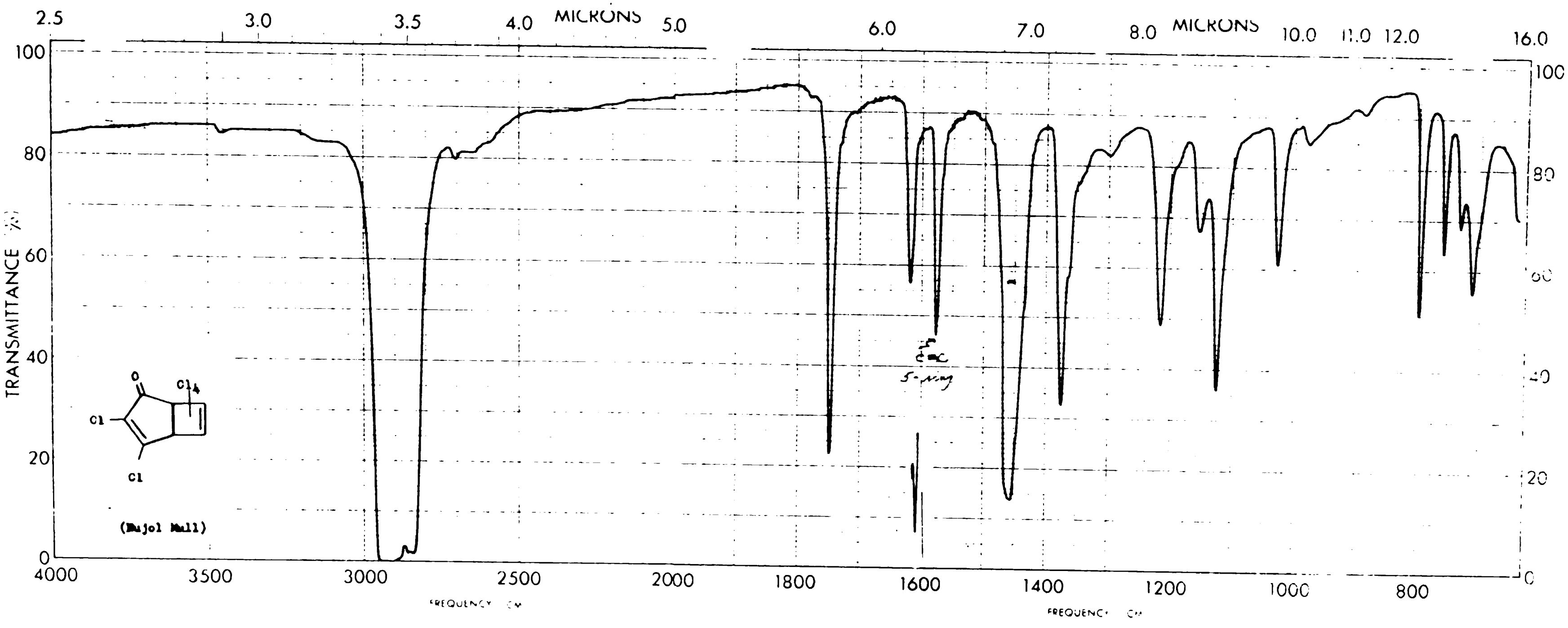

Figure 1. Infrared spectrum of 1,2,3,5,6,7-hexachlorobicyclo[3.2.0]hepta-2,6-dien-4-one 7a

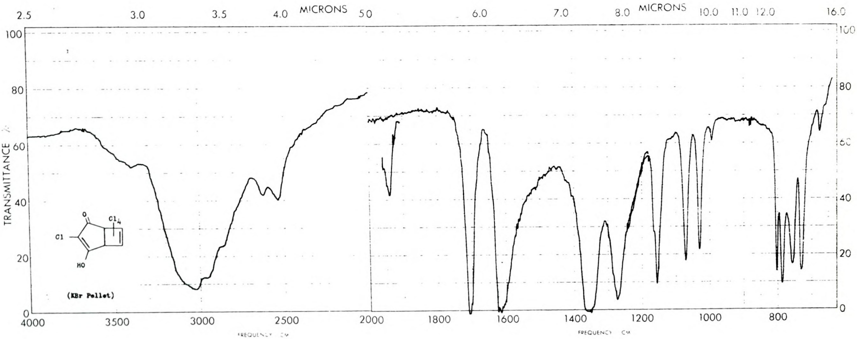

Figure 2. Infrared spectrum of 2-hydroxy-1,3,5,6,7-pentachlorobicyclo[3.2.0]-hepta-2,6-dien-4-one 7b.

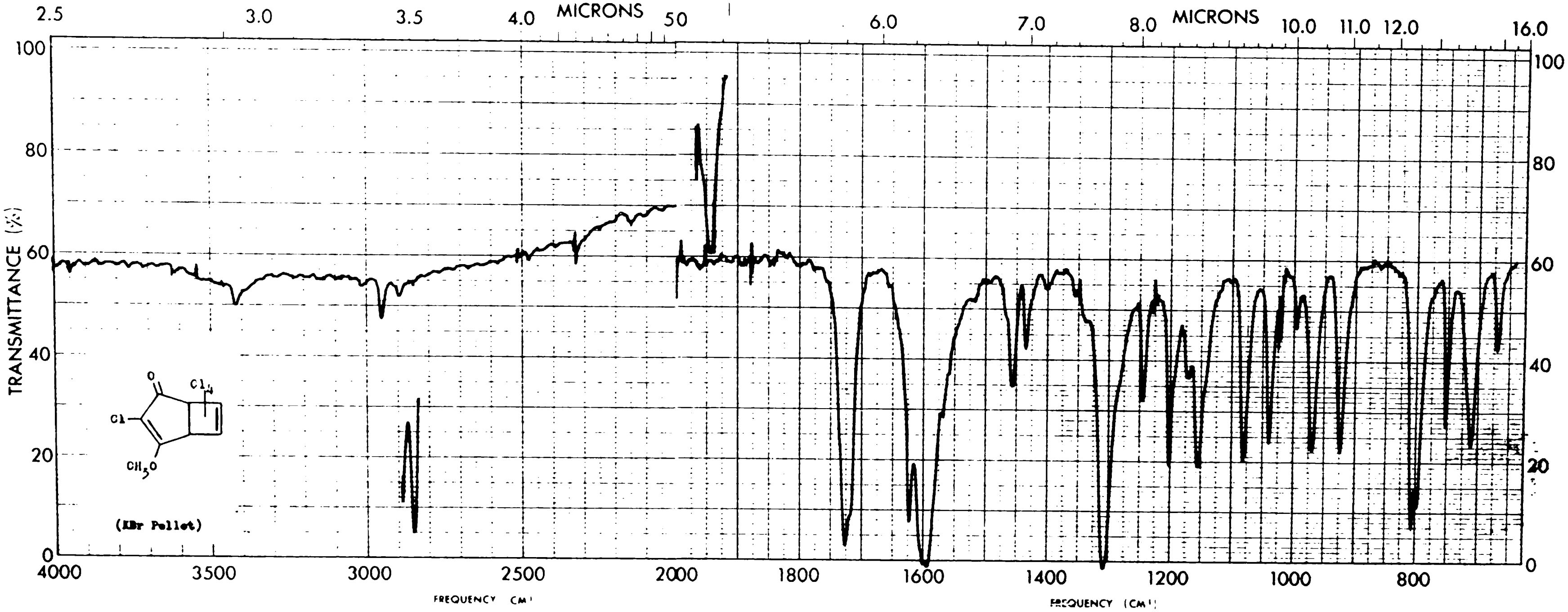

Figure 3. Infrared spectrum of 2-methoxy-1,3,5,6,7-pentachlorobicyclo[3.2.0]-hepta-2,6-dien-4-one 7c.

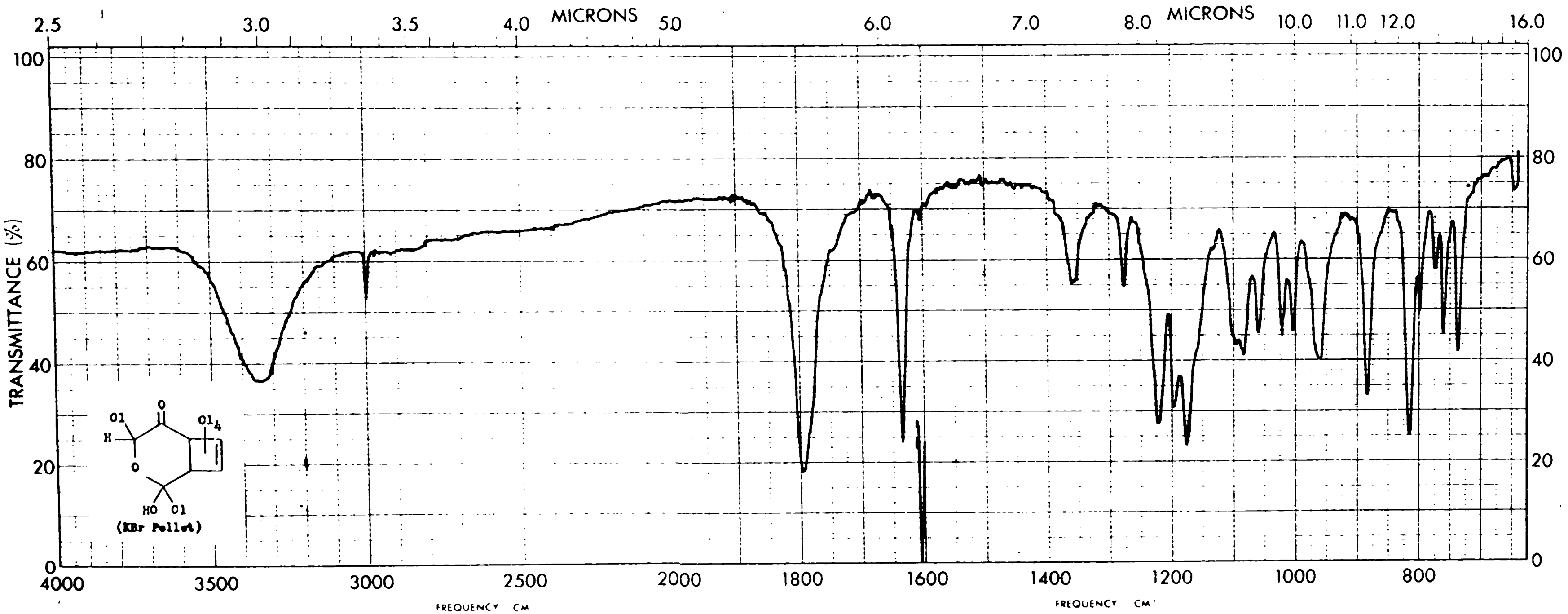

Figure 4. Infrared spectrum of 1,2,4,6,7,8-hexachloro-2-hydroxy-3-oxabicyclo-[4.2.0]oct-7-en-5-one 13.

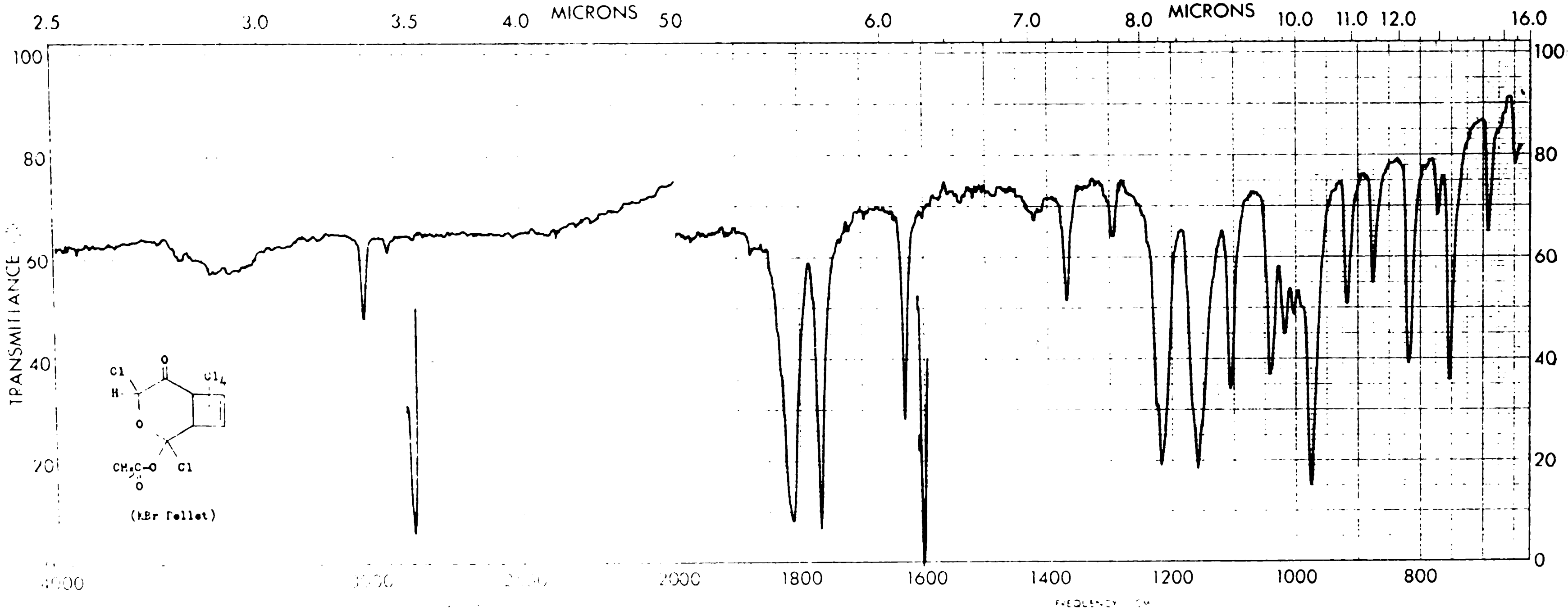

Figure 5. Infrared spectrum of the acetate 17 of compound 13.

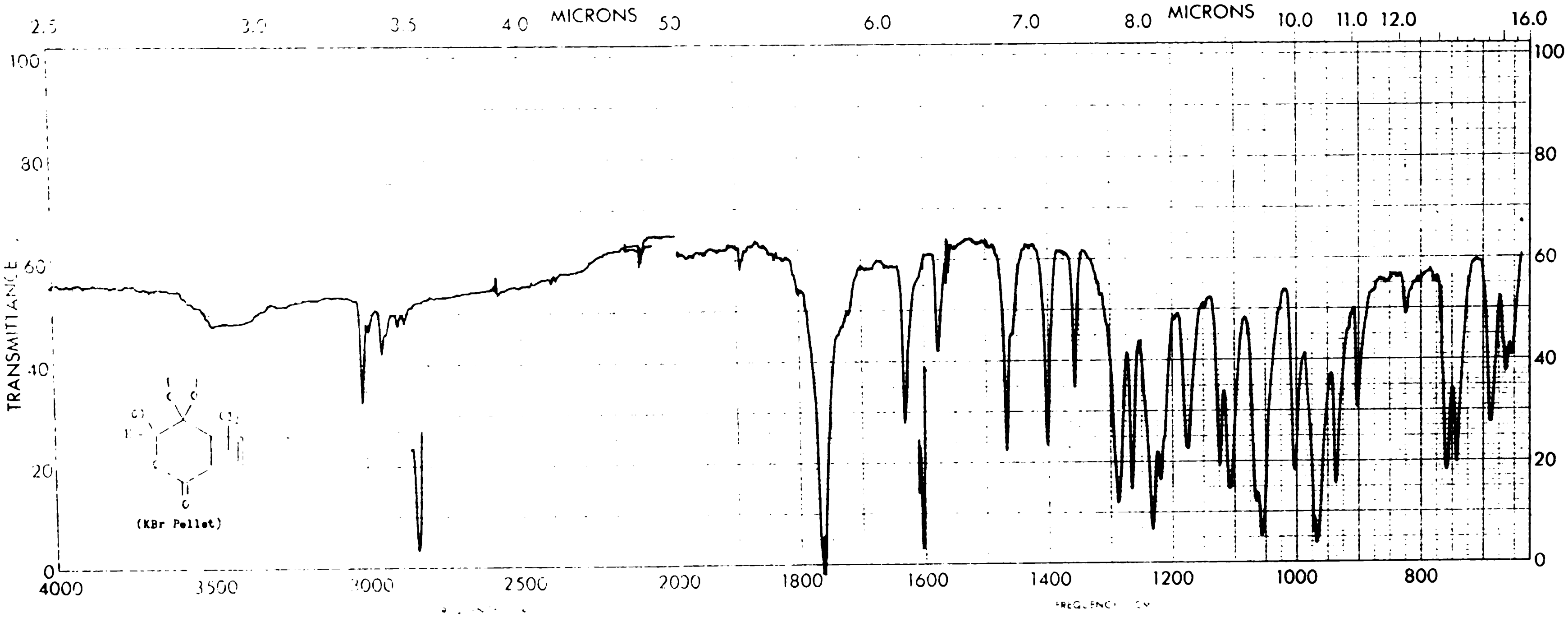

Figure 6. Infrared spectrum of ketal 18.

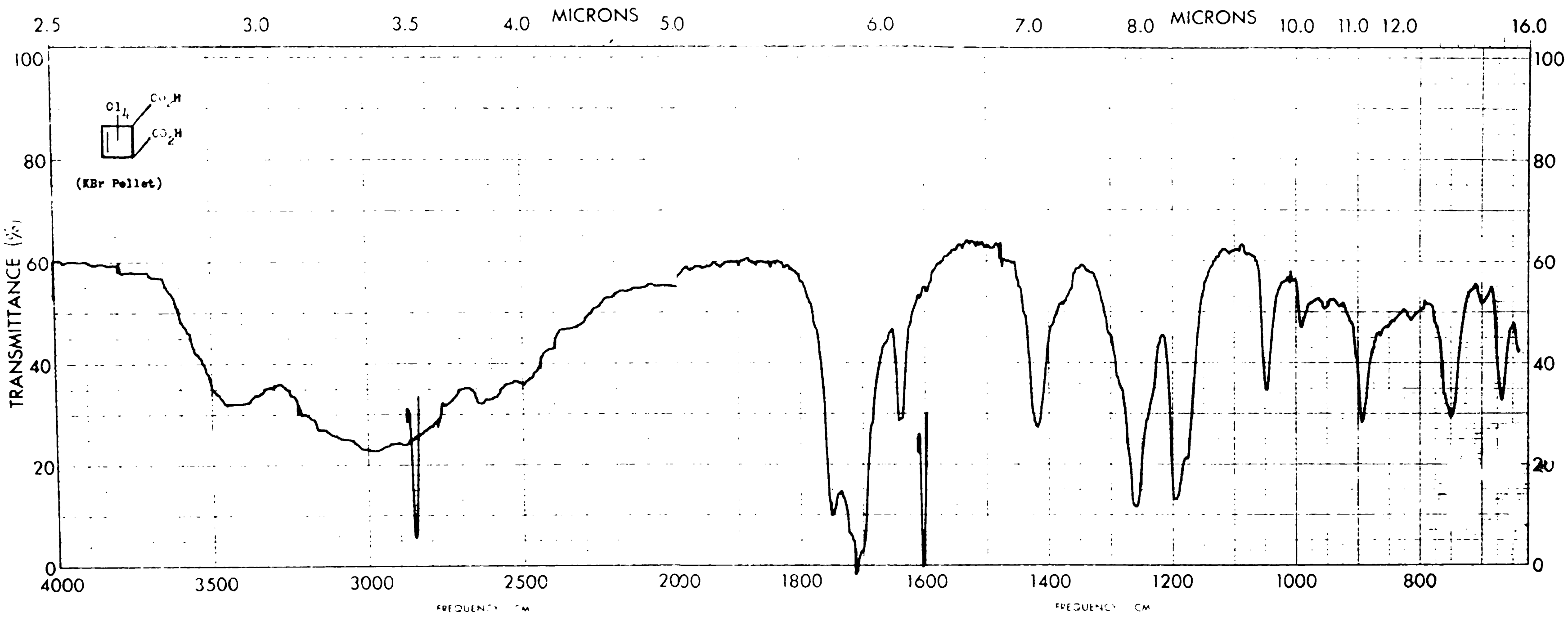

Figure 7. Infrared spectrum of diacid 14.

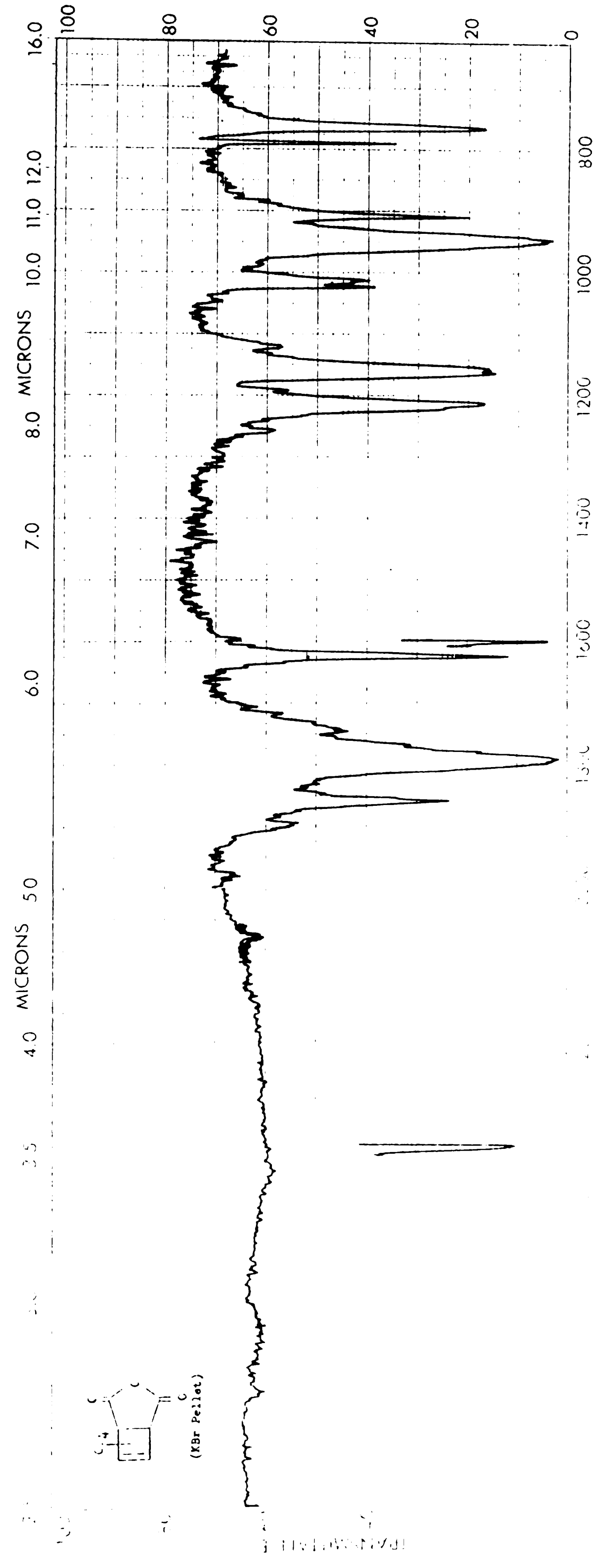

Figure 8. Infrared spectrum of the anhydride 21 of diacid 14.

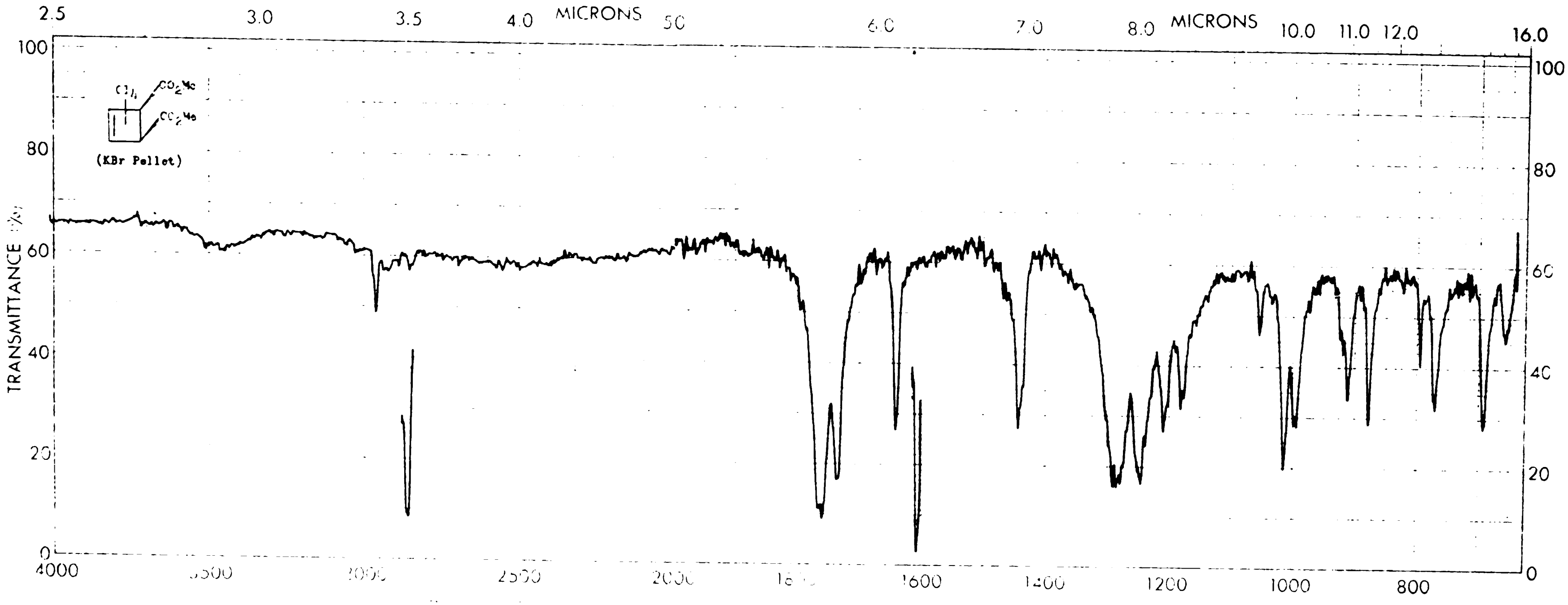

Figure 9. Infrared spectrum of the dimethyl ester 22 of diacid 14.

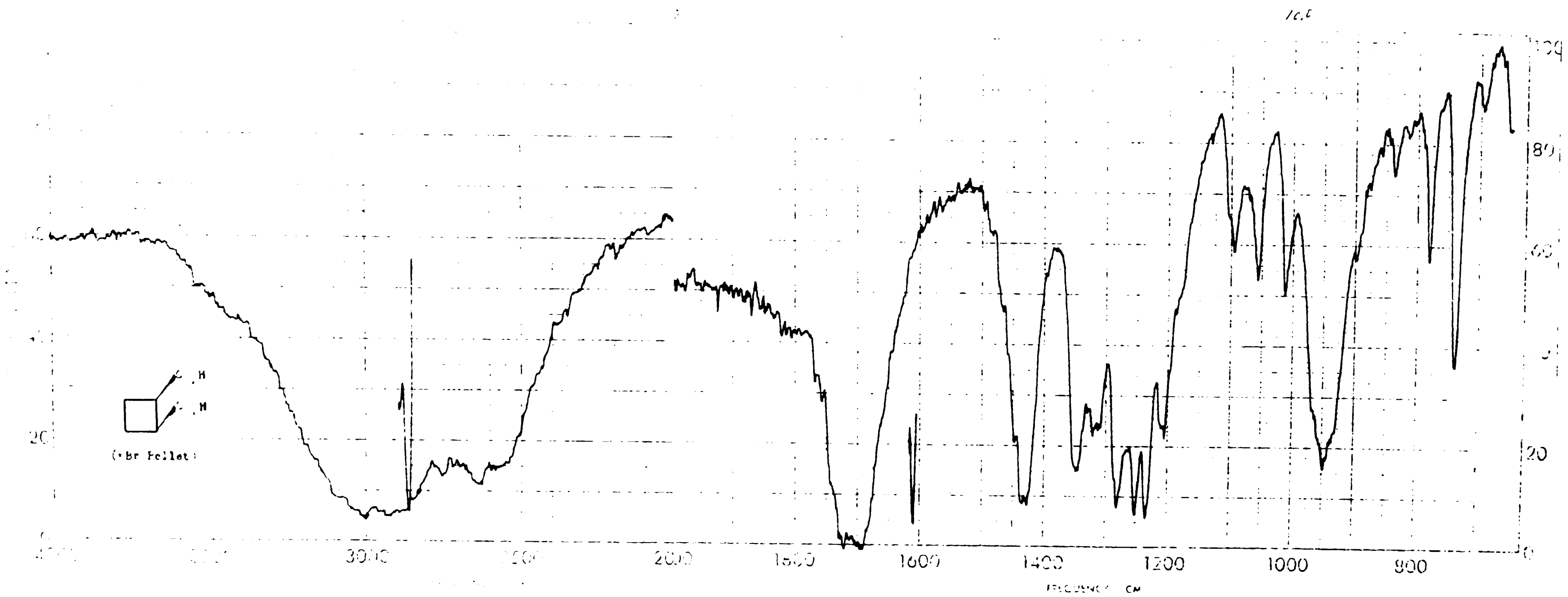

Figure 10. Infrared spectrum of <u>cis</u>-cyclobutane-1,2-dicarboxylic acid.

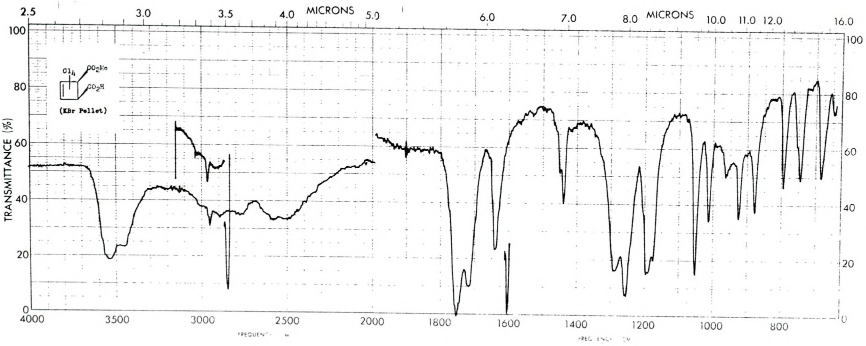

Figure 11. Infrared spectrum of the methyl half-ester of diacid 14.

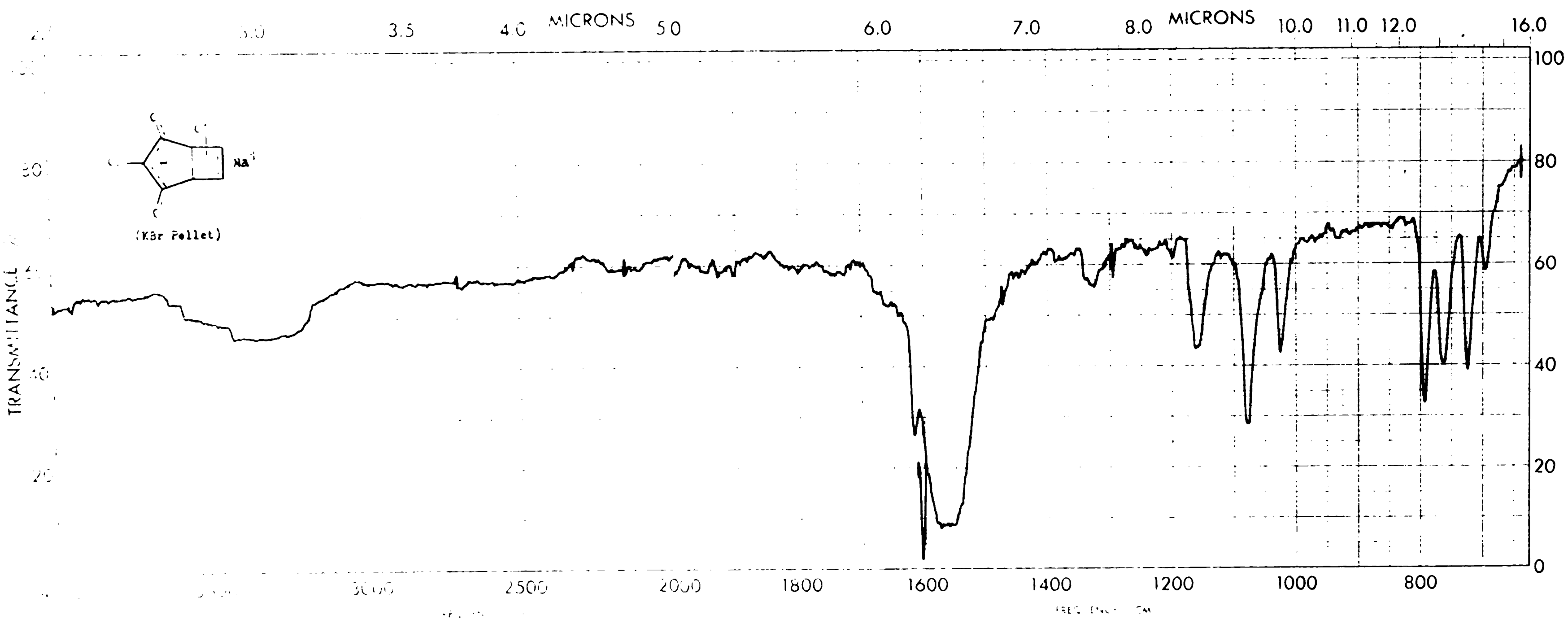

Figure 12. Infrared spectrum of the sodium salt 16 of compound 7b.

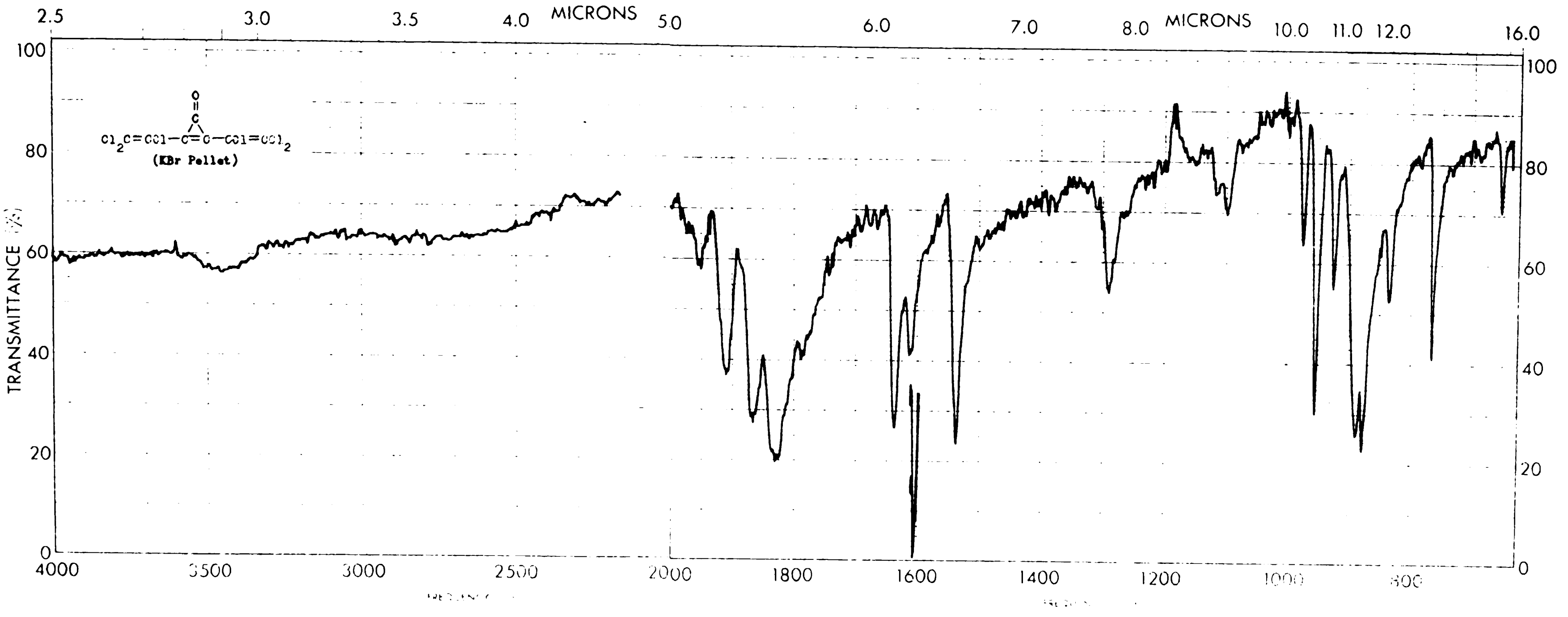

Figure 13. Infrared spectrum of bis(trichlorovinyl)cyclopropenone 52.

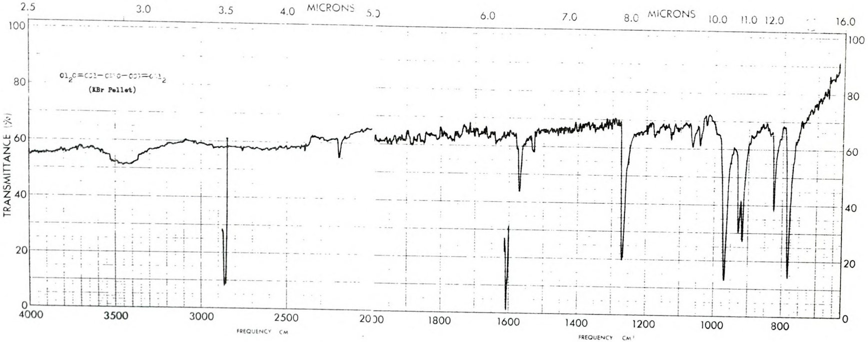

Figure 14. Infrared spectrum of bis(trichlorovinyl)acetylene 53.

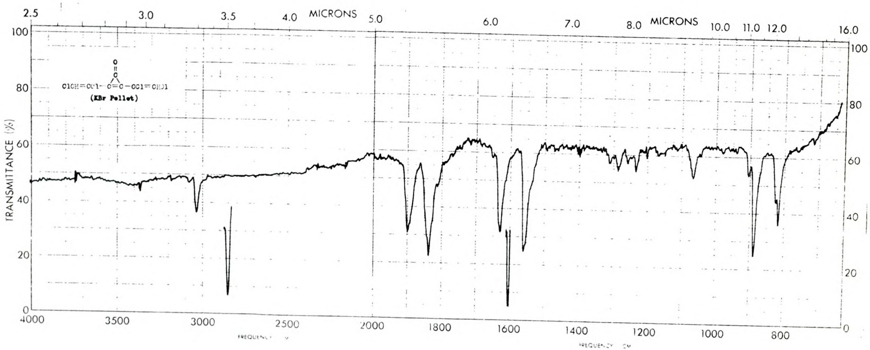

Figure 15. Infrared spectrum of bis(1,2-dichlorovinyl)cyclopropenone 54.

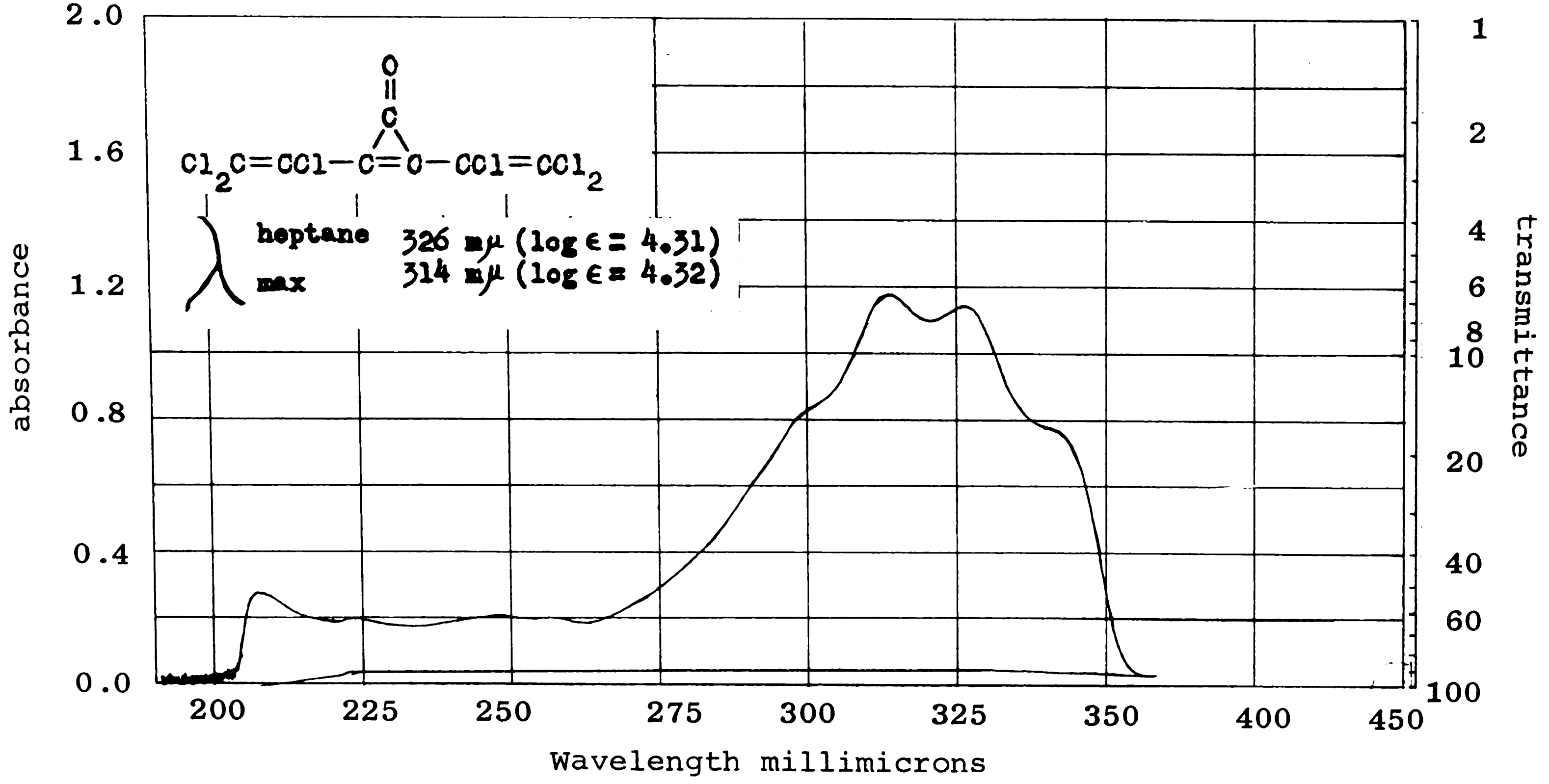

Figure 16. Ultraviolet spectrum of bis(trichlorovinyl)cyclopropenone 52.

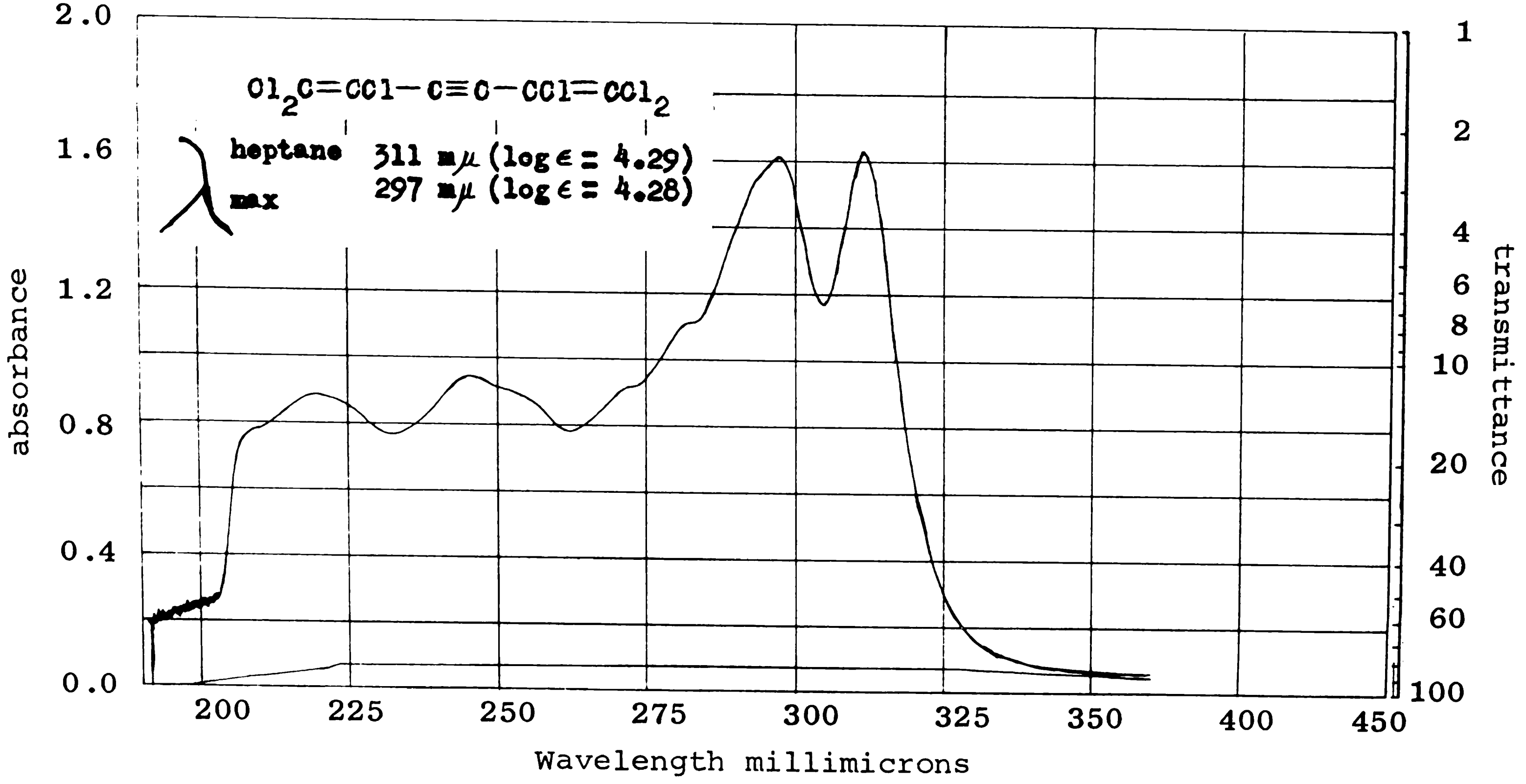

Figure 17. Ultraviolet spectrum of bis(trichlorovinyl)acetylene 53.

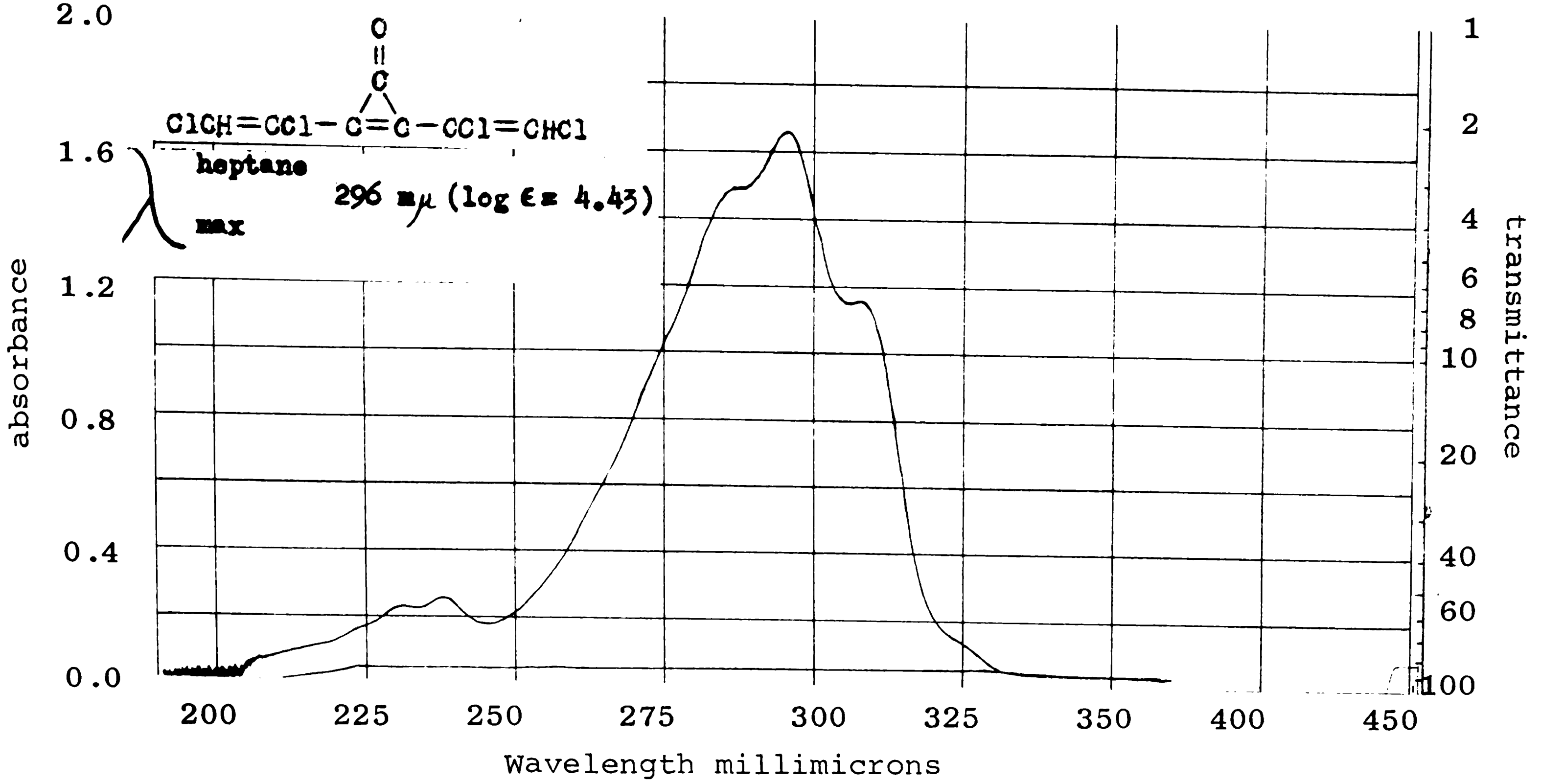

Figure 18. Ultraviolet spectrum of bis(1,2-dichlorovinyl)-cyclopropenone 54.