AN INVESTIGATION OF NEW METHODS FOR THE SYNTHESIS OF BENZYNE

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Monica H. Narang

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ABSTRACT

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by Monica H. Narang

New synthetic routes to benzyne were examined in this investigation. An attempt was made to generate di-tert. butylbenzyne, in order to study the steric effect of the tert -butyl groups on the reactivity of benzyne. In the course of this investigation, three different types of compounds were examined as possible precursors of benzyne.

The first group of compounds prepared was the phosphazines, o-quinonetriphenylphosphazine(V) and 2,4-di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine(VIII). It was predicted that these phosphazines, on thermal decomposition, would form benzyne together with nitrogen and a tertiary phosphine oxide. However, it was found that benzyne was not a major product in the decomposition of these phosphazines.

Next, betaine XVIII and XXII were examined as possible precursors of benzyne. These betaines, on thermal decomposition were expected to yield benzyne and a tertiary phosphine oxide. Preparation of betaine XVIII was attempted but unsuccessful. However betaine XXII was prepared, but on thermal decomposition gave phenol and triphenylphosphine oxide.

Lastly, 1,4-di-tert. butyl-2-bromobenzene(XXV) was prepared and treated with a strong base, potassium tertiary butoxide, to generate benzyne. Tetracyclone was added to the reaction mixture in the hopes of trapping benzyne by a Diels-Alder addition. The tertiary butoxide ion was observed to attack tetracyclone, instead of XXV, to form an α,β-unsaturated ketone.

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By

Monica H. Narang

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INTRODUCTION

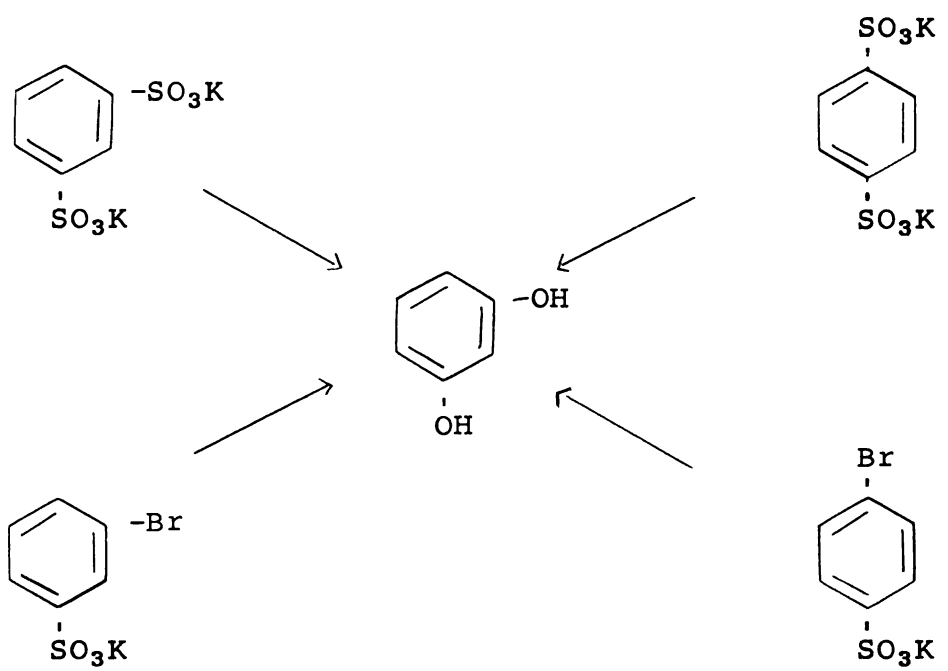
Benzyne, C_6H_4, is the parent of the family of arynes, not one of which has ever been isolated. Indeed, even physical detection of the short-lived C_6H_4 species was not reported till 1960. Notwithstanding, the chemistry of benzyne and its derivatives is a flourishing branch of organic chemistry, laden with interest for both the synthetic and mechanisms chemist.

The majority of reactions interpreted in terms of the benzyne intermediate involved the prsence of a halogen atom; however, such an atom is not essential to the mechanism. Any group which is sufficiently electronegative can give rise to benzyne. Thus, reactions of perchloroylaromatic compounds with strong neucleophiles[1] and the conversion of aryl sulfonates to phenates have been interpreted in terms of benzyne type intermediates.

The present investigation was undertaken to find new synthetic routes to benzyne. Some phosphazines, betaines and 1,4-di-tert. butyl-2-bromobenzene were examined as possible precursors of benzyne. An attempt was made to synthesize di-tert. butylbenzyne. It was proposed that the tertiary butyl groups would hinder reaction at the triple bond of benzyne, thus making di-tert. butylbenzyne more stable than unsubstituted benzyne.

HISTORY AND FORMULATION OF BENZYNE

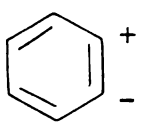
Benzyne chemistry is only 13 years old, though the observation of rearrangements in nucleophilic aromatic substitutions, which have been interpreted to give benzyne-type intermediates, can be traced back for 85 years. It was during the sixties of the last century that Kekule and Wurtz discovered the transformation of sodium benzenesulfonate to phenol with molten alkali.[2,3] By the seventies the preferred formation of resorcinol in alkaline fusion of benzene-1,4-disolfonate or 4-bromobenzenesulfonate also became known.[4,5]



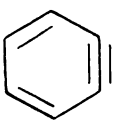
Aryne intermediates were proposed as early as 1902 by Stoermer and Kahtert.[6] They were the first to suggest that nucleophilic aromatic substitution proceded via a primary elimination to give an aryne intermediate. They accounted

for their unsuccessful attempts to isolate the aryne intermediate in terms of a pronounced Bayer strain in the intermediate. This explanation was not generalized, and therefore, sank into oblivion.

Bachmann and Clarke in 1927,[7] accounted for the triphenylene formed in the reaction of chlorobenzene with sodium, as a trimerization of "phenylene radicals" C_6H_4. Wittig in 1942 advanced the aryne hypothesis.[8,9] He postulated the formation of 0-lithiophenyl from fluorobenzene and phenyllithium via the "dipolar phenylene" intermediate (Ia). He considered this intermediate to be permanently polarized. Although Ib was also mentioned in this connection; Ia and Ib were not regarded as being identical.



Ia



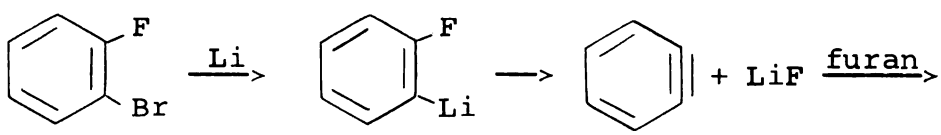
Ib

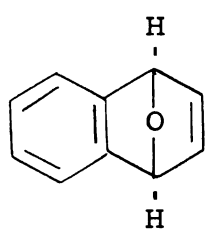
Morton et. al. also used the dipolar phenylene to interpret the reaction of chlorobenzene with amyl sodium.[10]

Another decade passed before John D. Roberts, in 1953,[11] published experiments which put the benzyne hypothesis on on the road to general acceptance. Roberts investigated the isotope distribution in aniline obtained from chlorobenzene-(1-^{14}C) with potassium amide in liquid ammonia. He postulated that the reaction proceeded through a benzyne

intermediate. The name benzyne was coined by Roberts. Husigen and Rist in Munich treated o- and m-fluoroanisole with phenyllithium and isolated, after carbonation practically identical mixtures of isomeric methoxybiphenylcarboxylic acids.[12]

The benzyne intermediate with its very reactive triple bond is a good dienophile. The formation of the benzyne intermediate in any reaction is demonstrated by trapping the benzyne with dienes like furan or anthracene. Wittig showed that o-bromofluorobenzene reacts with lithium metal in furan solution to form naphthalene-1,4-endoxide in 76% yield.[13]





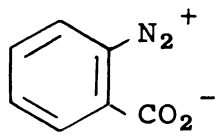
Similar reactions occur with other cyclic dienophiles; the reaction with anthracene is useful for preparation of the unique hydrocarbon triptycene which has the geometry of a three-blade water wheel all three benzene rings being equivalent.[14,15]

The fact that non-cyclic dienes do not give such adducts speaks for a one-step mechanism,[16] a true Diels-Alder reaction. Unlike most dienophiles, the short-lived benzyne intermediate cannot wait for open-chain dienes to assume the requisite cis-like conformation which is guaranteed in cyclic dienes. In the absence of a diene the benzyne intermediate dimerizes to form biphenylene.

Benzyne chemistry has developed very rapidly since its general acceptance in 1953. To date, a number of reactions which give rise to benzyne intermediates have been reported. Muller demonstrated the formation of benzyne from o-dihalobenzene on treatment with two moles of tetraphenyl-disodioethane. $(Ph_2NaC)_2$.[17]

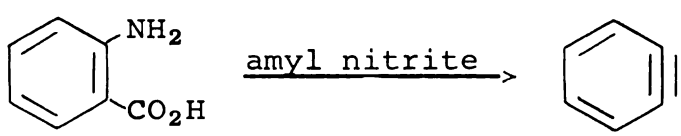
In the early sixties of this century Scott reported that perchloroylaromatic compounds on treatment with strong nucleophiles gave benzyne type intermediates.[1] While Wittig and Ebel reported that bis-[o-iodophenyl]-mercury forms 64% biphenylene on pyrolysis at 600^0.[18]

However, the long sought goal of preparing benzyne in the absence of metal cations, halide ions or strong bases was first achieved by M. Stiles.[19] He isolated benzene-diazonium-2-carboxylate(II), the zwitterionic diazonium salt from anthranilic acid.

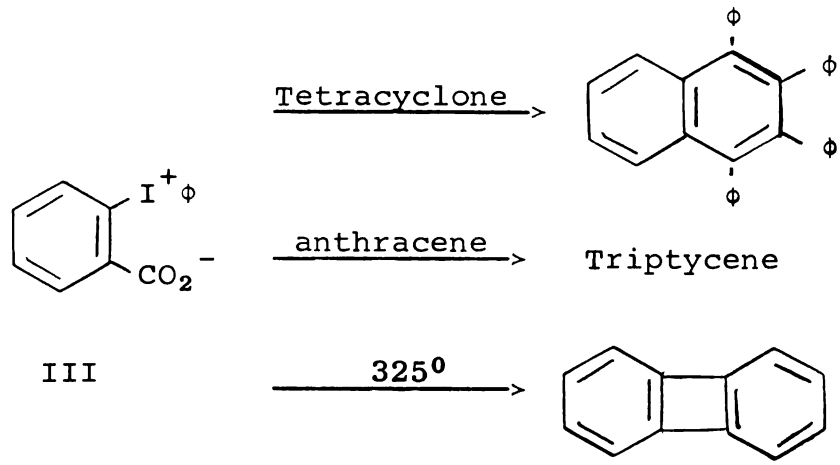


II

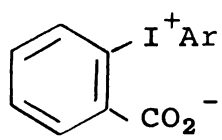
This salt, on mild pyrolysis at 35^0 to 60^0 gave benzyne which was trapped with furan antracene, carboxylic acids and tert. butyl alcohol. This reaction was further perfected by L. Friedman,[20] when he formed benzyne via aprotic diazotization of anthranilic acid, with amyl nitrite.



E. LeGoff has prepared benzyne by the decomposition of diphenyliodonium-2-carboxylate(III) in diglyme.[21] The benzyne intermediate formed was trapped with tetraphenyl-cyclopentadienone and anthracene to yield 1,2,3,4-tetra-phenyl naphthalene and triptycene respectively. Biphenylene was obtained from compound III by flash photolysis at 325^0.



Two years later, Beringer studied the effects of substituents on the rearrangement of 2' aryliodoniobenzoates (IV) and their cleavage to benzyne.[22] As expected, the introduction of the electron withdrawing nitro group facilitated the formation of ester via intramolecular nucleophilic substitution. The formation of benzyne was affected indirectly, as ester formation provided a competitive mode of reaction of the betaines.

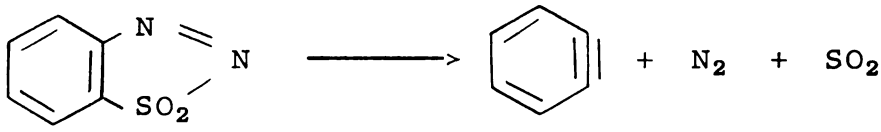


IV

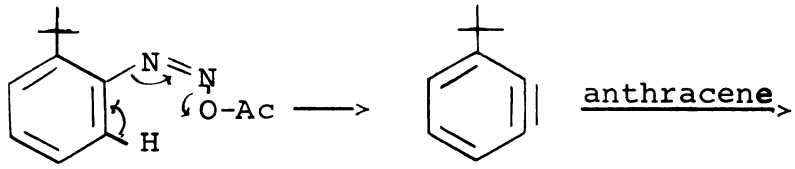
Ar = phenyl, mesityl, p-cyclohexylphenyl, 2,4-dimethoxyphenyl, m-nitrophenyl, and 2-methyl-5-nitrophenyl.

Within the short span of four years, from 1962 to 1965, a number of reactions which formed benzyne intermediates were reported.[23,24,25,26,27,28,29,30,31,32,33] Some interesting reactions reported were: the decomposition of

1,2,3-benzothiadiazole-1,1-dioxide at 60^0 or at 10^0 in solution to give benzyne, nitrogen and sulphur dioxide;[23]



Cadogon's decomposition of p-tert. butyl-N-nitroso-acetanilide in benzene to form tert. butylbenzyne, which was trapped by anthracene to form tert. butyl triptycene;[31]



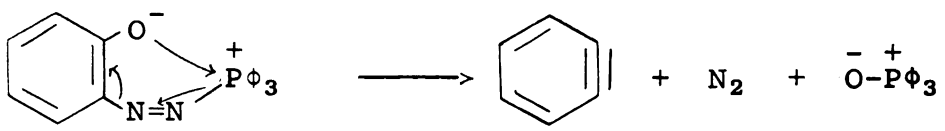
tert. butyl-triptycene.

Fields' pyrolysis of phthalic anhydride at 640^0 to form benzyne.[32] Fields also reported that phthalic anhydride on electron impact loses carbon monoxide and carbon dioxide to give benzyne.

This year three papers, reporting new methods for the preparation of benzyne, were published. Levy has demonstrated the formation of benzyne by the diazotization of o-aminephenylboronic acid.[34] Meyerson and Fields have reported that o-sulphobenzoic anhydride,[35] like phthalic anhydride, on pyrolysis at 690^0 yields, benzyne, sulphur dioxide and carbon dioxide. The latest paper is that of Franck and Yanagi.[36] They have been successful in making di-tert. butylbenzene by the diazotization of 2,5-di-tert. butylaniline.

DISCUSSION

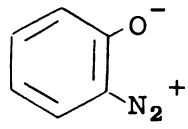
In the course of this investigation, different phosphorus compounds were prepared and tested as possible benzyne precursors. The first part of this investigation involved the preapration and study of o-quinonetriphenylphosphazine (V). It was proposed that this compound could be thermally decomposed to give benzyne by the elimination of nitrogen and triphenylphosphine oxide. Both nitrogen and triphenylphosphine oxide are good leaving groups.



V

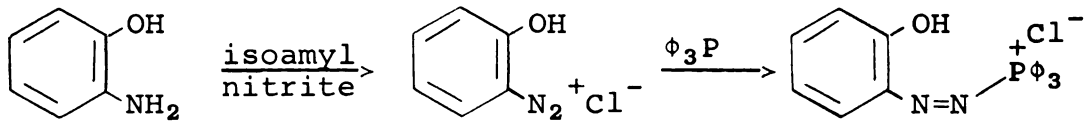
This proposal was also justified on the grounds that both nitrogen and triphenylphosphine oxide have large heats of formation. Thus the above reaction would yield a new synthetic route to benzyne, if this method was successful. The next step would be the preparation of 2,5-di-tert. butylphosphazine, which should decompose to 2,5-di-tert. butylbenzyne. This benzyne derivative should not be very reactive, because of the two tert. butyl groups substituted on either side of the triple bond. The steric effect of the tert.-butyl groups may stabilize the benzyne intermediate long enough, so that the nature of the triple bond may be investigated.

However, the first step in the preparation of the phosphazine required the preparation of o-benzoquinone diazide (VI). Diazide VI is extremely unstable and decomposes even at room temperature. All attempts to prepare VI from o-amino phenol were unsuccessful.



VI

The procedure was modified and the reaction was repeated. The diazonium salt from o-amino phenol was generated in solution and triphenylphosphine was added to it. (2-Hydroxyphenylhydrazino)triphenyl phosphonium chloride (VII), m.p. 164-165^0 was isolated from the reaction mixture

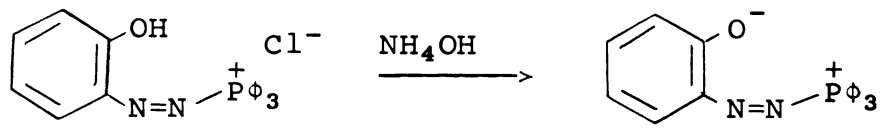


VII

A mixed melting point of o-amino phenol and VII showed that VII is not o-amino phenol. This was further confirmed by the I.R. spectrum of VII. Two bands at 3300 and 3400 cm^{-1} corresponding to the amino group in the I.R. of o-amino phenol were not observed in the spectrum of VII. Although, a new band at 705 cm^{-1} which may be due to the phosphorous, nitrogen bond was observed.

The preparation of the o-quinonephosphazine (V) was attempted by neutralizing VII with different bases. With

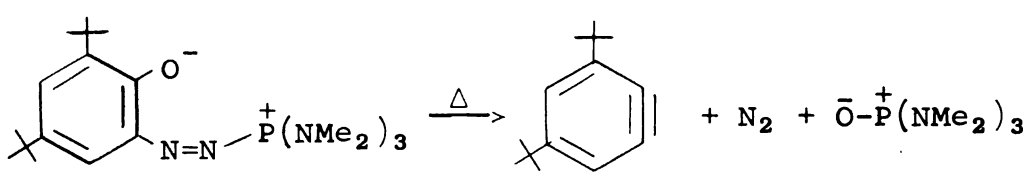
ammonium hydroxide a pink precipitate m.p. **160-161°**, probably V, was obtained. This precipitate on standing turned orange m.p. **148-155°**.



VII V

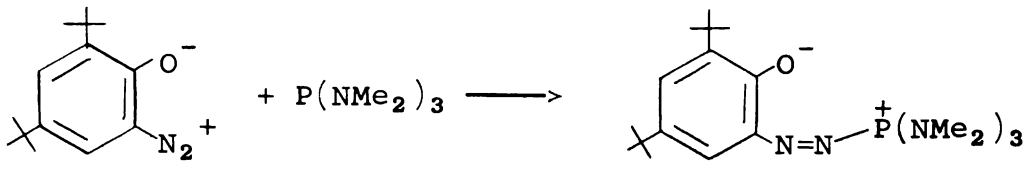
The I.R. spectrum of V does not show a band at **3100** cm^{-1} for the -OH group, which is observed in the spectrum of VII. Change in the m.p. of V, on standing, indicated that this compound may be undergoing decomposition. To study the products of decomposition, V was thermally decomposed by addition to molten anthracene. Anthracene melts at **213°**. This temperature is high enough to decompose V. If benzyne should form during the decomposition process, it would give triptycene, by a Diels-Alder addition with anthracene. The reaction mixture was worked up as reported in Organic Synthesis for the preparation of triptycene.[14] However, no triptycene was detected. This strongly suggested that benzyne is not a major product of decomposition of V.

2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine (VIII) was next tested as a possible benzyne precursor.



VIII XI

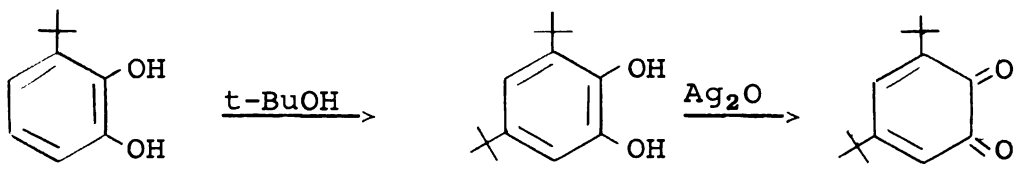
Compound VIII was prepared instead of the 2,5-di-tert. butyl phosphazine, because the 2,4-ditert. butyl-o-benzoquinone diazide (IX) which was used to prepare VIII has been reported in the literature.[37]



IX X VIII

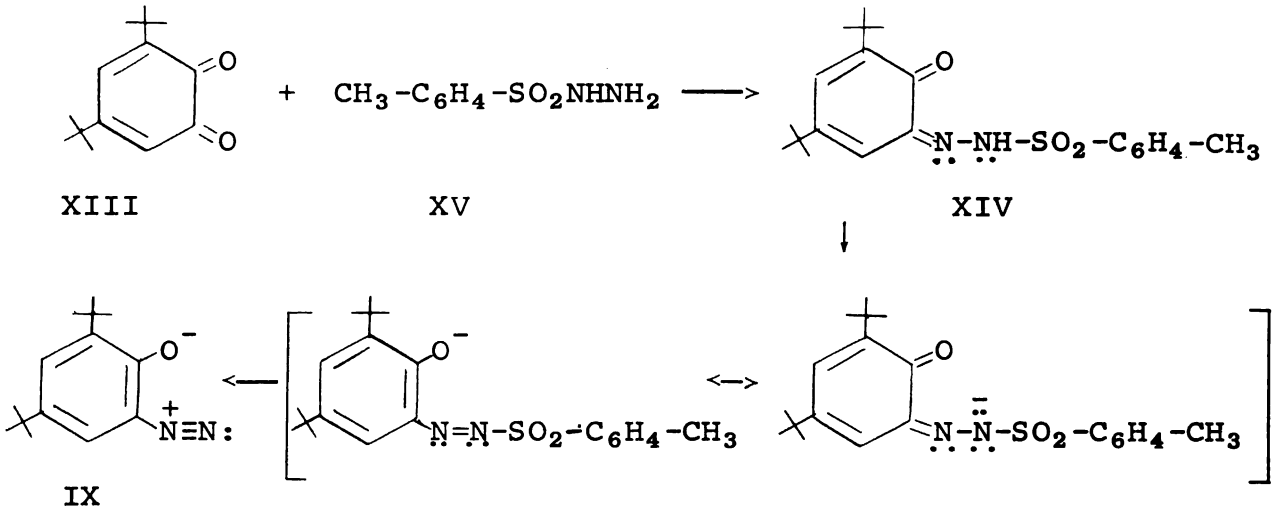
Further, tris(dimethylamino)phosphine (X) was used in lieu of triphenylphosphine,[38] as it is more basic and thus forms a more stable phosphazine. Also, because of the more basic nature of X, the phosphorous atom should have a greater affinity for the ortho-substituted oxygen. This would encourage the formation of tris(dimethylamino)phosphine oxide (XI). Besides, XI is water soluble and thus can be easily separated from the reaction products.

2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine (VIII) was prepared in four steps. The first step involved the preparation of 2,4-di-tert. butyl catechol (XII) by the alkylation of 2-tert. butyl catechol,[39] which was readily available. The second step involved the preparation of 2,4-di-tert. butyl o-benzoquinone (XIII) by the oxidation of XII with silver oxide.[40]



XII XIII

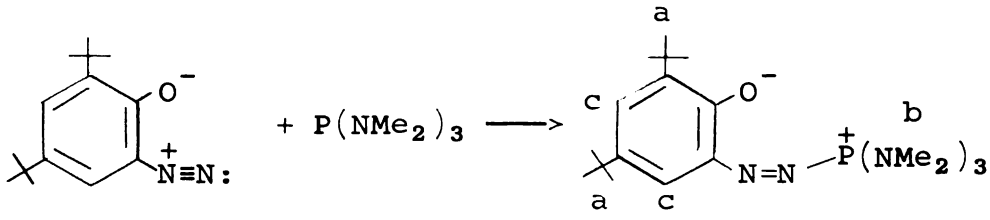
The tosyl hydrazone (XIV) was prepared by treating the quinone (XIII) with 4-toluenesulfonylhydrazine (XV).[37] Hydrazone XIV was chromatographed over a column of basic alumina to give quantitative yields of 2,4-di-tert. butyl-o-benzoquinone diazide (IX). This was a new one-step procedure discovered to make pure quinone diazide (IX), from the hydrazone.



XIII XV XIV

IX

Lastly, IX was coupled with tris(dimethylamino)phosphine (X) to give 2,4-di-tert. butyl-o-quinone-tris(dimethylamino)-phosphazine (VIII), m.p. 151-155°.[41]



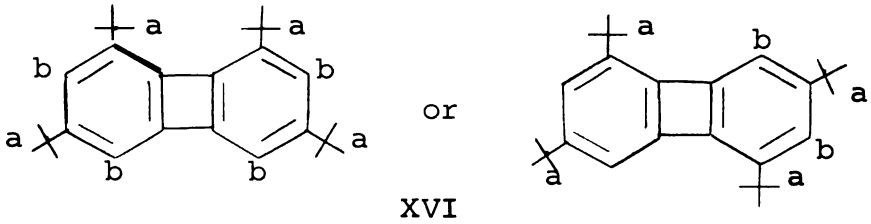
IX X VIII

Phosphazine VIII is a new compound and its structure was confirmed by the nmr spectrum. The two tert.-butyl groups (a) show sharp singlets at τ 8.76 and τ 8.67. The methyl groups (b) show a doublet at τ 7.25 (J = 9 cps.) and the two

aromatic protons (c) show an AB quartet at τ 2.27 (J = 3 cps).

In order to study whether di-tert. butylbenzyne was produced on decomposition of VIII, the preparation of di-tert. butyl triptycene was attempted using VIII. No triptycene could be recovered from the reaction products. The products of decomposition were then studied. Compound VIII was decomposed in refluxing xylene. The decomposition product, tris(dimethylamino)phosphine oxide (XI), was removed by washing the xylene solution with water. The I.R. spectrum of XI matched the spectrum of a pure sample, thus exhibiting its formation.

The residue from the xylene solution was chromatographed and the major product (unknown A) collected, using v.p.c. Unknown A was suspected to be tetra-tert. butyl biphenylene (XVI). The nmr supports this supposition.



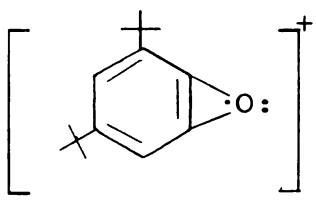
XVI

The absorption of the tert. butyl groups (a) is seen as a doublet at τ 8.60 (J = 7.5 cps) and the aromatic protons (b) absorb at τ 2.83.

The u.v. spectrum of biphenylene is recorded in the literature and shows two main regions of absorption, one of high intensity between 235-260 mμ and the other at lower intensity in the region of 330-370 mμ.[42] The intensity of

the absorption at 250 mμ is 10 times greater than at 350 mμ. The u.v. spectrum of unknown A was taken. Two regions of absorption were observed, one at 250 mμ and the other at 359 mμ. A comparison of the two spectra indicated that unknown A absorped in the same regions as biphenylene and that the ratio between the intensity of absorptions in the two regions was very similar, (unknown A $\varepsilon\lambda_{250}/\varepsilon\lambda_{359}$ 9.53:1; biphenylene $\varepsilon\lambda_{250}/\varepsilon\lambda_{359}$ 10:1). This further suggested that unknown B was a biphenylene derivative XVI.

A mass spectrum of VIII was taken. A very small peak at mass 188 corresponding to di-tert. butylbenzyne was observed. However, a large peak at mass 204 was observed. This peak corresponds to a fragment $C_{14}H_{20}O$ and may possess a structure such as XVII. If this peak corresponds to

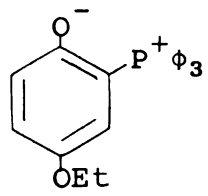


XVII

fragment XVII, then it strongly suggests that the carbon oxygen bond is difficult to break and is stronger than the carbon, nitrogen bond. If the carbon, oxygen bond is not broken when bombarded by an electron beam of an energy of 70 volts, it is very unlikely that this bond could be broken thermally when a smaller amount of energy is available. Therefore, unknown A is not likely to be tetra-tert. butyl biphenylene XVI.

However, no definite conclusion can be made on the basis of the mass spectrum, due to certain limitations of our mass spectrometer. For example, the long tube between the bulb containing the sample and the ionization chamber presents ample opportunity for rearrangement to take place, during the transfer of the sample to the ionization chamber. If benzyne was produced during the transfer, it would dimerize or react with another species. Thus, no peak for the benzyne species would be recorded in the mass spectrum.

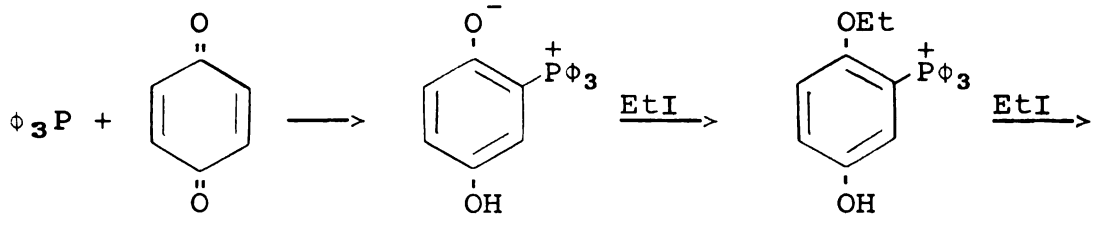
It was then decided to test betaine XVIII as a possible benzyne precursor. This compound has not been reported in the literature. (2,5-Diethoxyphenyl)triphenylphosphonium



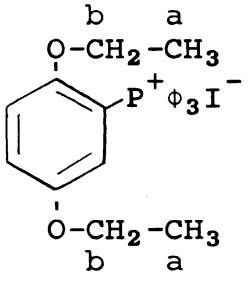
XVIII

iodide (XIX) was required for the preparation of the betaine. Compound XIX can be synthesized in three steps.[43] The first step involves the preparation of adduct (betaine) XX of triphenylphosphine and p-benzoquinone. Betaine XX was alkylated to give (2-ethoxy, 5-hydroxy-phenyl)triphenyl-phosphonium iodide (XXI). Compound XXI was further alkylated to yield (2,5-diethoxyphenyl)phosphonium iodide XIX. This reaction yielded a tarry product. Suitable solvents were found to extract XIX from the tarry reaction mixture. But the

yields were poor.



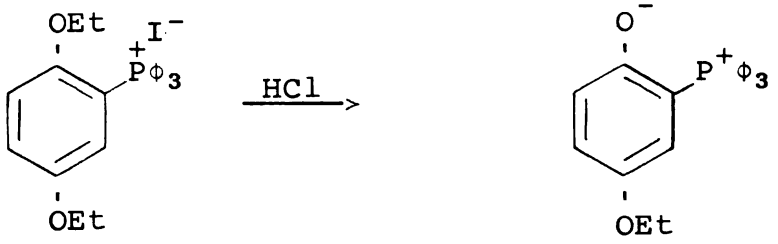
XX XXI



XIX

An nmr spectrum of compound XIX was taken in chloroform. The spectrum indicated that the two methyl groups (a) absorb in different regions. One methyl group shows a triplet at τ 9.32 (J = 7.5 cps) and the other, a triplet at τ 8.62 (J = 7.5 cps). The methylene protons (b) show a quartet at τ 5.92 (J = 7 cps)

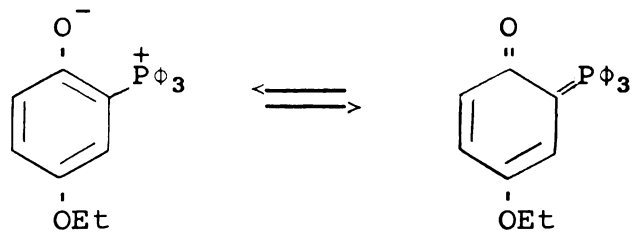
Since ethers can be cleaved by strong acids, the preparation of betaine XVIII was attempted by treating XIX dissolved in methanol with concentrated hydrochloric acid.



XIX XVIII (attempted)

It was expected that the ethyl group, of the ethoxy substituent, ortho to the phosphonium group would split off in

preference to the one in the meta position. This was expected because the phenolate ion generated in the ortho position could be stabilized by resonance.



XVIII

Red crystals (unknown B) were collected from the methanol solution, m.p. **145-146°**. The nmr of unknown B showed two triplets of τ 9.42 (J = 7.25 cps) and τ 8.72 (J = 7.25 cps), and a quartet at τ 6.02 (J = 7 cps). This nmr spectrum was very similar to that of **XIX** but the melting points of the two compounds differed by **84-85°** and, while unknown B was bright red, **XIX** was white in color. Hence, unknown B could not be **XIX**. This is further indicated by the carbon, hydrogen analysis.

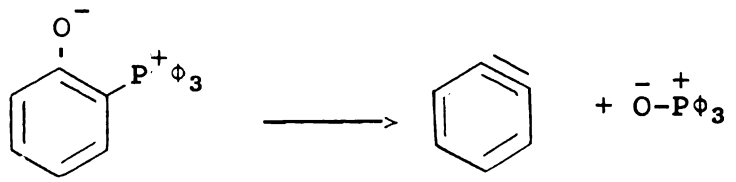
	%C	%H	
Compound XIX	54	4.52	calcd.
Betaine XVIII	78.5	5.78	calcd.
Unknown A	41.61	3.45	determined

That unknown B is not **XIX** is clearly evident. Inspection of the analytical results further indicated that unknown B could not be the betaine XVIII.

At this stage it may be pointed out that the nmr spectrum of unknown B indicated that it had the same aliphatic groups

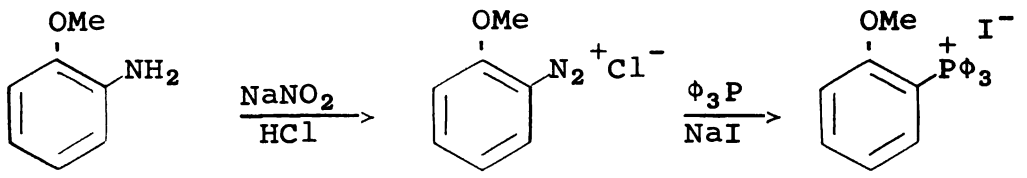
as XIX. Hence it was suggested that unknown B probably differed from XIX in the nature and number of phenyl groups on the phosphorous atom.

The Wittig reaction shows that betaines decompose to give an olefin and a tertiary phosphine oxide. Hence, to test this reaction for an aromatic betaine, XXII was prepared. It was proposed that triphenylphosphine oxide could be cleaved from XXII to yield benzyne. Moreover, in this case, no nitrogen molecule intervenes between the phosphorous atom and the aromatic ring as in the phosphazines. This should make the reaction much simpler.



XXII

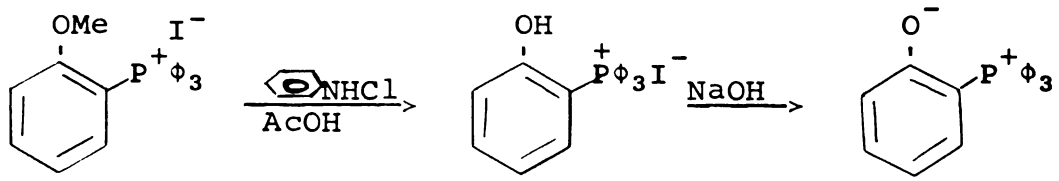
To prepare betaine XXII, (o-methoxyphenyl)triphenylphosphonium iodide (XXIII) was required. Triphenylphosphine was added to the diazonium salt of o-anisidine, to yield XXIII.



XXIII

(o-Hydroxyphenyl)triphenylphosphonium iodide (XXIV)) was formed by splitting the methyl group of XXIII with pyridine

hydrochloride and acetic acid. XXIV was neutralized with NaOH to give betaine XXII.[44]



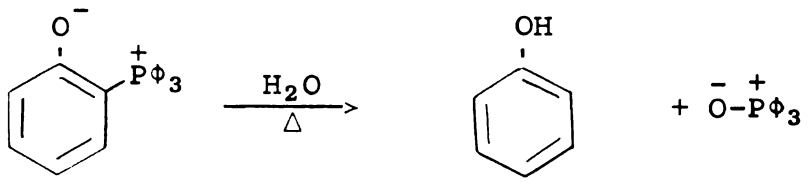
XXIII XXIV XXII

The above compounds are not reported in the literature, although the para isomers are known.[44] The most important evidence demonstrating the structure of XXII, XXIII and XXIV was the band at 3060 cm^{-1} for the -OH group in the I.R. spectrum of XXIV which was not observed in the spectrum of XXII and XXIII. The analysis of XXII and XXIII were consistent with the structures proposed. The u.v. spectra of the three compounds are recorded in the experimental section.

To investigate if benzyne is a product of decomposition of betaine XXII, the preparation of triptycene was attempted using XXII. It was found that benzyne is not a major product of decomposition of XXII, as no triptycene was detected. To further investigate the formation of benzyne from betaine XXII, its mass spectrum was taken. However, no peak at mass 76, corresponding to benzyne, was observed. This may once again be due to the limitations of the mass spectrometer.

To study the products of decomposition of betaine XXII, it was heated in a sealed, evacuated tube. Phenol and triphenylphosphine were the two main products recovered. It was suspected that moisture present in betaine XXII caused

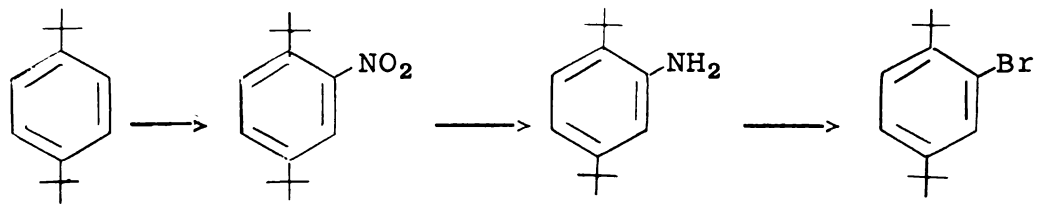
its hydrolysis to form phenol.



Thus a study of phosphazines and betaines indicated that benzyne is not a major product of decomposition of these compounds.

Since bromobenzene forms benzyne on treatment with a strong base like potassium tertiary butoxide,[45] an attempt was made to form 1,4-di-tert. butylbenzyne, by treating 1,4-di-tert. butyl-2-bromobenzene (XXV) with potassium tertiary butoxide.

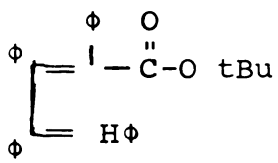
Compound XXV was obtained by the following sequence of reactions. p-Di-tert. butylbenzene (XXVI) was nitrated to give 1,4-di-tert.butyl-2-nitrobenzene (XXVII) which on reduction with iron and hydrochloric acid formed 1,4-di-tert. butyl-2-aminobenzene (XXVIII).[46] The amino compound was diazotized and brominated to give XXV.[47]



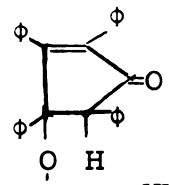
XXVI XXVII XXVIII XXV

Compound XXV was then treated with potassium tertiary butoxide and tetracyclone (XXIX). Tetracyclone, a diene, was used in the hopes of trapping benzyne as a Diels-Alder

adduct. A white compound was recovered from the solution. The carbon and hydrogen analysis indicated the formula of this compound to be $C_{33}H_{30}O_2$. Structures XXX and XXXI were proposed for this compound.

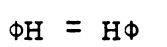


XXX

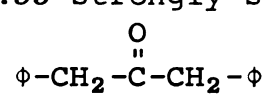


XXXI

The nmr supports structure XXXI. A singlet at τ 8.95 for the tert. butyl protons and a multiplet at τ2.81 for the aromatic protons was observed in the nmr spectrum. The integration ratio between the two peaks is 1:2.3. The theoretical ratio should be 1:2.22. Thus the experimental ratio agrees with the theoretical ratio. However, it was the small peak observed at τ 5.55 which helped to distinguish between structure XXX and XXXI. The vinylic proton in structure XXX can be compared to the vinylic protons in stilbene (XXXII). These protons are observed in the nmr spectrum at τ 3.0.[48] However, the benzylic proton of structure XXXI, lies adjacent to a carbonyl; such protons are observed between τ 6.5 and τ 5.0. For example, the benzylic protons in dibenzylketone (XXXIII) are observed at τ 6.30.[48] Thus, the peak at τ5.55 strongly suggests



XXXII

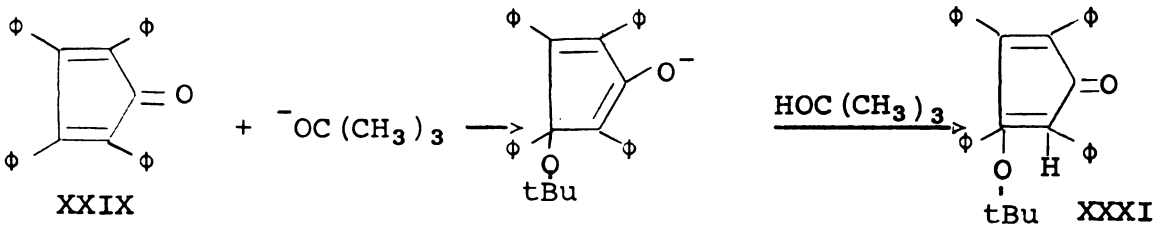


XXXIII

that the structure of compound $C_{33}H_{30}O_2$ is XXXI.

The I.R. of this compound was also studied. Absorptions for the aromatic C-H stretch and C-C stretch were observed at 2594 cm^{-1} and 1600 cm^{-1} respectively. The carbonyl absorption was observed at 1695 cm^{-1}. The I.R. data could not be used to differentiate between structure XXX and XXXI as α-β unsaturated esters and α-β unsaturated ketones absorb in the same region of the I.R. spectrum.

The formation of XXXI can be explained by a Michael reaction of tertiary butoxide ion with tetracyclone (XXIX).



The Diels-Alder adduct of tetracyclone and benzyne was not detected. Therefore benzyne may not be a major product of the reaction.

EXPERIMENTAL

A. General Procedures and Apparatus.

All infrared spectra were obtained on a Perkin-Elmer 237B Grating Infrared Spectrophotometer. Ultraviolet spectra were determined in 1 cm quartz cells using a Beckman DB Spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60 high resolution spectrometer, using tetra-methylsilane as a reference. Mass spectra were obtained by a Consolidated Electrodynamics Corporation Mass Spectrometer Type 21-103C. Vapor phase chromatography was done on an Aerograph model A-90-P3 Gas Chromatograph.

Melting points were determined on a Uni-melt capillary melting point apparatus and are uncorrected.

Microanalysis determinations were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and by Micro-Tech Laboratories, Inc., Skokie, Illinois.

B. Preparation of (2-hydroxyphenylhydrazino)triphenylphosphonium chloride VII.

A solution of freshly sublimed o-amino phenol (4 g., 0.036 mole) in absolute alcohol (100 ml.) was saturated with hydrogen chloride gas. Iso-amyl nitrite (4 ml.) was added to the solution at 0^0. The solution was then stirred for 15 minutes. Triphenylphosphine (9.61 g., 0.036 mole) was added dropwise with stirring. The white precipitate formed was filtered off, yield 12.55 g., m.p. 168^0.

C. Attempted Preparation of Triptycene Using o-Quinone-triphenylphosphazine V.

VII was treated with ammonium hydroxide. V was observed to form and was filtered off from the solution. (2.5 g., 0.0059 mole) of V was added slowly to molten anthracene (1 g., 0.0059 mole) in a pyrex test tube. The mixture was extracted with hot diglyme (40 ml.). Maleic anhydride (1 g., 0.010 mole) was added to the diglyme extract, and it was refluxed for half an hour. The reaction mixture was then set aside, at room temperature, for 2 hours. Maleic anhydride, anthracene adduct was removed by filtration. The filtrate was refluxed with sodium hydroxide (15 ml., 1N) for 2 hours. When cool, the solution was poured into water (500 ml.). The brown residue, filtered from the water solution, was dissolved in carbon tetrachloride (40 ml.) and chromatographed on a column of acid-washed alumina (50 g.) using carbon tetrachloride (100 ml.) for elution. The carbon tetrachloride solution on evaporation gave a small amount of brown residue which was not triptycene.

D. Preparation of 2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine VIII.

2,4-Di-tert. butyl-pyrocatechol XII. To 2-tert. butyl pyrocatechol (20 g.) dissolved in acetic acid (40 ml.), were added tert. butyl alcohol (40 ml.) and concentrated sulphuric acid (8 ml.). The solution was stirred for 3 hours and then allowed to stand at room temperature for 30 hours. The reaction mixture was then stirred into

cold water (1 l.) and the crystals formed were filtered off. Recrystallization from petroleum ether (b.p. 30-60°) gave a yield of 13.4 g. of product, m.p. 98-100°. The melting point reported in the literature is 98-100°. (39)

2,4-Di-tert. butyl-o-benzoquinone XIII. To 2,4-di-tert. butyl pyrocatechol (15 g.) in ether (225 ml.), after treatment with sodium sulphate (15 g.) and cooling to 0°, was added silver oxide (18 g.). The mixture was stirred for 3 hours, at 0°, and filtered. The residue was extracted with ether. The filtrate and ether extract were taken together in a large evaporating dish from which the ether was evaporated using an air blast. Quantitative yields of red needle-like crystals of 2,4-di-tert. butyl-o-benzoquinone were obtained, m.p. 111-113°. The melting point recored in the literature is 113-114°. (40)

2,4-Di-tert. butyl-o-quinone diazide IX. p-Tosylhydrazide (11.4 g.) was suspended in methanol (60 ml.) and concentrated hydrochloric acid (6 ml.) and the solution was cooled to -8° to -12°. 2,4-Di-tert. butyl-o-benzoquinone was dissolved in methanol (150 ml.) and added dropwise with stirring. Yellow orange crystals of the tosylhydrazone quickly formed; yield 14.2 g., m p. 89° with decomposition. The melting point reported in the literature is the same. (37)

The tosylhydrazone (15 g.) was dissolved in methylene chloride (15 ml.) and chromatographed on a column of basic

alumina (375 g.). Quantitative yields of 2,4-di-tert. butyl-o-benzoquinone diazide were obtained, m.p. 73°. The melting point reported in the literature is 76°. (37)

Tris(dimethylamino)phosphine X. Phosphorous trichloride (43.5 ml., 68.5 g.) in anhydrous ether (200 ml.) was added dropwise to di-methyl amine (149 g.) in anhydrous ether (750 ml.) at -20°. The mixture was stirred for 2 hours at room temperature. The precipitate formed was filtered off and washed with ether. The combined ether solutions were fractionated and gave hexa-methyl phosphorous triamide (50 ml.); $b.p._{12}$ 49°. The boiling point recorded in the literature is $b.p._{12}$ 49°. (38)

2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine VIII. Tris(dimethylamino)phosphine (X) (2 ml.) was added to 2,4-di-tert. butyl-o-quinone diazide (IX) (2.32 g., 0.1 mole) dissolved in a minimum amount of benzene. After a few minutes the solution was observed to take on a deep red color. On addition of pet. ether (b.p. 30-60°) and cooling, crystals were observed to separate our ot the solution. The crystals were filtered off, yield 3.4 g., m.p. 151-155°.

E. Attempted Preparation of Triptycene Using 2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)phosphazine VIII.

The procedure followed was the same as has been outlined earlier. However, no triptycene was obtained from the reaction.

F. Decomposition of 2,4-Di-tert. butyl-o-quinone-tris-(dimethylamino)phosphazine VIII.

2,4-Di-tert. butyl-o-quinone-tris(dimethylamino)-phosphazine (6 g.) was added to boiling xylene (40 ml.) in a round bottom flask. The xylene solution was washed with water. The water extract on evaporation gave an oily residue. The xylene solution gave a red colored residue on evaporation. This residue was dissolved in carbon tetrachloride and chromatographed on a column of basic alumina. The residue from the first fraction obtained from the alumina column was redissolved in cyclohexane and chromatographed on a smaller column of basic alumina and eluted with cyclohexane. Two fractions were collected. Fraction A (1.0 g.) and fraction B (0.4 g.). Fraction A was dissolved in a small quantity of chloroform and put through the the gas chromatograph using column S.E.-30 at 230^0. The sample (unknown A) corresponding to the two major peaks was collected. Twenty trial were run using 50 micro liters of chloroform solution at a time, to collect enough quantity of the sample for identification. The major peak was observed at a retention time of 5 minutes. At this point there were two peaks that overlapped. Lowering of the column temperature did not bring about an effective separation. U.v. spectrum of unknown B λ_{max}^{hexane} 250 (ε 7870), 359 (ε 1139). (Based on molecular wt. of 376).

The chromatogram for fraction B showed the same major peaks, as fraction A, except that they were much smaller,

No significant quantity of the samples could be obtained from fraction B.

G. Attempted Preparation of Betaine XVIII.

Adduct (Betaine) from Triphenylphosphine and p-Benzoquinone XX. Solutions of p-benzoquinone (2.5 g., 0.023 mole) and triphenylphosphine (6.08 g,, 0.023 mole) in anhydrous benzene were mixed in a dry nitrogen atmosphere (inert bag). There was no immediate change; gradually, after several minutes, a deep red color developed in the solution and a precipitate began to appear. After 20 hours at room temperature (inert bag) the precipitate was collected (7.8 g.); it consisted of fine, yellow-greenish crystals, m.p. 262-266°. The value for the melting point reported in the literature is 262-266°. (43)

(2-Ethoxy, 5-hydroxyphenyl)triphenylphosphonium Iodide XXI. A solution of betaine (5.0 g.) in methanol was refluxed with excess of ethyl iodide (3.5 ml.), for 10 hours. Removal of solvent left a residue which was dissolved in chloroform and re-precipitated with ether; yield 6.6 g., m.p. 232-235°. The value for the melting point reported in the literature is 224-231° (43)

(2,5-Diethoxyphenyl)triphenylphosphonium Iodide XIX. (2-Ethoxy,5-hydroxyphenyl)triphenylphosphonium iodide (3.5 g.) was added to a solution of sodium (0.15 g.) in methanol (35 ml.). Excess ethyl iodide (3.5 ml.) was added and the

solution was refluxed for 12 hours. The residue remaining after evaporation was taken up in chloroform and the chloroform solution was washed with 5% aqueous sodium hydroxide and with water. Evaporation of the dried chloroform solution left an oily residue. The residue was treated with ethyl acetate containing a few drops of methanol. The ethyl acetate solution dissolved the oil and left behind a light green residue; m.p. 212-215°. The value for the melting point reported in the literature is 212-215°. (43) On crystallization from methanol the product collected was white in color, m.p. 230°.

Betaine XVIII - Attempted-. (2.5-Diethoxyphenyl)triphenylphosphonium iodide (0.5 g.) was dissolved in methanol (4 ml.) and the solution was treated with concentrated hydrochloric acid (1 ml.). Red crystals (unknown B) were observed to form in the solution. The crystals were filtered off at 48 hour intervals, m.p. 145-146°.

Analysis:	Calcd.	78.5% C	5.78% H
	Found.	41.61% C	3.45% H.

The above compound could not be identified.

H. Preparation of Betaine XXII.

(o-Methoxyphenyl)triphenylphosphonium Iodide XXIII. Sodium nitrite (3.45 g., 0.05 mole) in water (30 ml.) was added to o-anisidine (6.15 g., 0.05 mole) in concentrated hydrochloric acid (10 ml. ~ 0.1 mole). The diazonium salt formed was buffered by adding sodium acetate (8.1 g., 0.15 mole).

Thus adding 3 mole equivalents per mole equivalent of excess acid. Triphenylphosphine (13.114 g, 0.05 mole) in ethyl acetate (200 ml.) was added dropwise with stirring to the diazonium salt. The solution was observed to turn red. The aqueous layer was extracted with ether and the organic layer with water. The combined aqueous solutions were treated with sodium iodide. XXIII precipitated out of the solution. The compound was redissolved in methanol and re-precipitated with ether, m.p. 258-60°; infrared absorption spectrum of XXIII in chloroform, bands at: 2925 (s), 1600 (s), 1435 (s), 255 (m), 1110 (s). The u.v. absorption spectrum of XXIII at: $\lambda_{max}^{95\%\ EtOH}$ 292 (ε 4690), 276 (ε 4840), 269 (ε 4410).

Analysis: Calcd. for $C_{25}H_{22}OPI$: 60.5% C; 4.44% H

Found 61.07% C; 4.72% H.

Betaine XXII. (o-Methoxyphenyl)triphenylphosphonium iodide (4.16 g., 0.0084 mole), pyridine hydrochloride (12.5 g.) and acetic acid (5 ml.) were heated for 6 hours with stirring at 190-200°. The solution was poured into water and on treatment with sodium iodide gave (o-hydroxyphenyl)triphenylphosphonium iodide (XXIV), yield 5.3 g., m.p. 264° (aqueous methanol); infrared absorption spectrum of XXIV in chloroform at: 3060 (s), 1590 (s), 1440 (s), 1110 (s). The u.v. absorption spectrum of XXIV: $\lambda_{max}^{95\%\ EtOH}$ 296 (ε 5390), 276 (ε 5330), 269 (ε 5050).

Compound XXIV was dissolved in hot water and reprecipitated with sodium hydroxide to give betaine XXII, yield

2.46 g., m.p. 279-280° (aqueous methanol). Infrared absorption spectrum of XXII in chloroform at: 2925 (w), 1580 (s), 1430 (m), 1105 (m). The u.v. absorption spectrum of XXII: $\lambda_{max}^{95\ EtOH}$ 241 (ε 5310).

Analysis Calcd. for $C_{24}H_{19}OP$: 81.5% C 5.37% H

Found 80.34% C 5.40% H.

I. Attempted Preparation of Triptycene Using Betaine XXII.

The procedure followed was the same as outlined before. However, no triptycene could be prepared using betaine XXII.

J. Decomposition of Betaine XXII.

(a) Betaine XXII (1 g.) was heated at 300° in a test tube. The test tube was hooked to an aspirator. The yellow product obtained was chromatographed over a column of 25 g. of silicic acid. The column was eluted with chloroform (200 ml.), ethyl acetate (100 ml.) and 50% methanol in ethyl acetate (100 ml.). Phenol (0.3624 g.) was obtained from the chloroform solution. Triphenylphosphine (0.0770 g.) was also obtained from the chloroform solution. Some starting material was obtained from the other solutions.

(b) Betaine XXII (1 g.) was heated in a six inch pyrex test tube. The tube was evacuated (press 2 mm.). The products were chromatographed as before. Obtained were 0.2837 g. phenol, 0.2976 g. of triphenylphosphine oxide and 0.1986 g. of starting material. Therefore a total of 0.7799 g. of material was recovered.

K. Preparation of 1,4-Di-tert. butyl-2-bromobenzene.

1,4-Di-tert. butyl-2-nitrobenzene XXVII. Ninety percent HNO_3 (13.9 ml., 0.25 mole) was added to a solution of acetic acid (48 g., 0.8 mole) at 0^0. p-Di-tert. butyl benzene (1.9 g., 0.1 mole) was added to this mixture at -10^0. The resulting solution was quenched with ice and the precipitate formed was filtered off. Quantitative yields of the nitro compound were obtained, m.p. 85-85.8^0. The melting point reported in the literature is 87-88^0. (46)

1,4-Di-tert. butyl-2-aminobenzene XXVIII. Compound XXVII (7.05 g.) and iron filings (6 g., 40 mesh) were added to 50% ethanol (12 ml.) and hydrochloric acid (0.6 g.). The resulting solution was refluxed for 24 hours. The amine was extracted from the mixture by absolute alchol and recrystallized from alcohol, m.p. 103-104^0. The melting point reported in the literature is 103-104^0. (46)

1,4-Di-tert. butyl-2-bromobenzene XXV. A mixture of XXVIII (25 g.), cuprous bromide (36 g.), potassium bromide (30 g.) and 48% of hydrobromic acid (250 ml.) was cooled to -40^0. Solid sodium nitrite (8.5 g.) was added to the mixture over 60 minutes. After slow warming to room temperature, the reaction mixture was washed with petroleum ether (b.p. 40-60^0). The petroleum ether extract was chromatographed over a column of alumina. On elution of the column an orange colored solution was collected which was rechromatographed

over another alumina column. The yellow oil collected was distilled three times to obtain XXV (12.6 g.) as a light yellow colored liquid, b.p. 112-118°/1.5-1.75 mm. The boiling point reported in the literature is 154-156°/13 mm. (47) The bromo compound (0.2 ml.) was put through the gas chromatograph using column S.E.-30 at 200° to obtain 106 m.g. of pure colorless XXV. The nmr spectrum shows the two tert. butyl groups at τ 8.72 and τ 8.52. The aromatic protons exhibit a typical ABC spectrum A τ2.90, B τ 2.80 and C τ 2.52 (J_{AB} = 6.9 cps., J_{BC} = 1.5 cps., J_{AC} = 0.4 cps.)

L. Attempted Preparation of Benzyne from 1,4-Di-tert. butyl-2-bromobenzene XXV.

Compound XXV (2 g., 0.00744 mole) and tetracyclone (2.775 g., 0.00744 mole) were dissolved in benzene. Potassium tertiary butoxide (1.214 g., 0.00744 mole; contains 38% tert. butyl alcohol) was added and the resulting solution was refluxed for 24 hours. Excess benzene was distilled off and the concentrated solution was chromatographed over a column of alumina using cyclohexane and benzene (1:1). Tetracyclone was obtained in the first fraction. The column was then eluted with benzene-cyclohexane which on evaporation gave 0.340 g. of white crystals, XXXI, m.p. 164-165°. Crystallization from benzene-ethanol gave 0.159 g. of crystals, m.p. 169-170°. Infrared absorption spectrum of XXXI in carbon tetrachloride at: 2594 (s), 1695 (s), 1600 (m).

Analysis Calcd. for $C_{33}H_{30}O_2$:		86.5% C	6.55% H
	Found	87.63% C	6.76% H.

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