attempted; however, analysis of the crude mixture by nmr and mass spectrometry suggested that **14** was absent and that **7b** had again been formed in *ca.* 60–70% yield.

Reaction of 4 with Methyl Iodide and Sodium Methoxide in Methanol.—The procedure employed was similar to that of Al-Khafaji[2a] and essentially equivalent to that used for the analogous reaction with ethyl iodide (*vide supra*). Addition of methyl iodide (40 ml, 91 g, 0.64 mol) to a boiling solution of **4** (1.71 g, 8.29 mmol) and sodium methoxide (2.00 g, 37.0 mmol) in methanol (100 ml) required 50 min; stirring and refluxing were continued for 40 min after the addition was complete. Concentration of the pale yellow solution afforded 0.83 g (47%) of spiroanthrone **7b**, mp 229.5–232.5°. Two recrystallizations of the product from methanol–benzene gave pure **7b** as slender, bright yellow needles: mp 237–239° (lit.[2a] mp 227–228°); ir (CS_2) 1667 cm^{-1} (anthrone C=O), no OH; nmr (CCl_4) δ 7.9–8.5 (m, 5; 6-, 8-, 11-, 1′-, and 8′-H), 6.7–7.6 (m, 10; 4-, 5-, 9-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-, and 7′-H), 4.14 (s, 3, CH_3), 3.33 (poorly resolved t, 2, J = 6 Hz, CH_2Ar), and 2.24 ppm (poorly resolved t, 2, J = 6 Hz, CH_2CH_2Ar); mass spectrum (70 eV) *m/e* 426.1607 (weak; calcd for $C_{31}H_{22}O_2$, 426.1620) and 410.1300 (strong; calcd for $C_{30}H_{18}O_2$, 410.1307).

Anal. Calcd for $C_{31}H_{22}O_2$: C, 87.30; H, 5.20. Found: C, 87.44; H, 5.26.

Recrystallization of 0.10 g of pure **7b** (mp 237–239°) from methanol–benzene, using the low-melting form of **7b** (*vide supra*) for seeding, gave 0.08 g of flat orange needles that melted sharply at the lower temperature.

Oxidation of 4 with Molecular Oxygen.—A suspension of **4** (0.50 g, 2.4 mmol) in dry benzene (3.0 ml) was degassed by the freeze–thaw method and then stirred rapidly (magnetic bar) in the dark at 24–25° under an atmosphere of pure oxygen. After 122.4 hr the total absorbed oxygen amounted to 24.7 ml (volume corrected to 0° and 760 mm, 1.10 mmol), and at this point the rate of oxygen uptake had decreased to a negligibly small value. The final reaction mixture had a strong formaldehyde odor and contained a white solid, which was recovered by filtration and washed several times with fresh benzene. This solid (fraction A) weighed 0.07 g and gave a doubtful positive test for peroxide(s) with potassium iodide in acetic acid. Evaporation of the combined filtrate and washings yielded 0.50 g of pale yellow powder (fraction B), whose peroxide test was definitely positive. Analysis by nmr showed that fractions A and B contained anthraquinone (**17**), spiro[anthracene-9(10H),2′-oxiran]-10-one (**18**), and **4**; these identifications were confirmed by nmr peak enhancements resulting from addition of the pure substances. Fraction B also contained a material that exhibited a sharp singlet at δ 2.14 ppm ($CDCl_3$). Double verification was obtained for the presence of **18** by adding the authentic epoxide[22] to solutions of B in two different solvents ($CDCl_3$, C_6D_6). Enhancement of a singlet assigned to the methylene protons of **18** (δ 3.38 ppm in $CDCl_3$, 2.67 ppm in C_6D_6) occurred in both cases, and enhancement of several aromatic peaks was also observed. The mass spectrum (70 eV) of fraction A showed strong parent peaks for **17** and **4** at *m/e* 208.0534 (calcd for $C_{14}H_8O_2$, 208.0524) and 206.0734 (calcd for $C_{15}H_{10}O$, 206.0732), respectively. The mass spectrum (70 eV) of fraction B also contained intense parent peaks for **17** (*m/e* 208.0534) and **4** (*m/e* 206.0748), as well as a weak parent peak for **18** (*m/e* 222.0665; calcd for $C_{15}H_{10}O_2$, 222.0681. The parent peak of pure **18** was shown to be weak at 70 eV). Quantitative calculations based on the nmr spectrum showed that the composition of fraction A was **17**, 77%; **18**, 4%; **4**, 19%. On the assumption that the material resonating at 2.14 ppm was peroxide **16**, the composition of fraction B was estimated by nmr as **16**, 19%; **17**, 23%; **18**, 37%; **4**, 21%. Thus the total yields of **16**, **17**, **18**, and recovered **4** were estimated to be 17, 34, 35, and 23%, respectively.

An attempt to reproduce the published preparation[11] of **16** gave none of the desired product.

Registry No.—**4**, 4159-04-0; **7a**, 24165-82-0; **7b**, 24215-76-7; **12**, 24165-83-1.

Acknowledgment.—The author is indebted to Mr. H. J. Tarski for excellent technical assistance, and to Dr. H. G. Schutze for strong administrative support.

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[22] G. L. Buchanan and D. B. Jhaveri, *J. Org. Chem.*, **26**, 4295 (1961); J. Rigaudy and L. Nédélec, *Bull. Soc. Chim. Fr.*, 400 (1960).

Reaction of a Quinone Methide with Tri-*n*-butylphosphine[1]

W. H. STARNES, JR., AND J. J. LAUFF[2]

Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas 77520

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Quinone methide **2** reacts with tri-*n*-butylphosphine in benzene or *n*-heptane solution to form an isolable inner salt, (3,5-di-*t*-butyl-4-oxybenzyl)tri-*n*-butylphosphonium betaine (**4**). Betaine **4** can also be prepared by dehydrochlorination of phosphonium chloride (**3**) with methanolic sodium methoxide. The betaine retains its structure in polar solvents (methanol, ethanol, dimethyl sulfoxide, or acetone), but, when warmed with relatively nonpolar solvents (benzene, toluene, *p*-dioxane, or cyclohexene), it decomposes to form bisphenol **9** and tri-*n*-butylphosphine as major products. Decomposition of **4** in the presence of benzaldehyde gives considerable amounts of stilbenol **8** and tri-*n*-butylphosphine oxide; decomposition in the presence of chloroprene gives, *inter alia*, spirotrienone **13**. These observations and the results of experiments with model compounds suggest that the decomposition of **4** probably produces ylide **5** and quinone methide **2**, *in situ*, and that bisphenol **9** then results from a sequence involving addition of **5** to **2**, followed by prototropic shifts and loss of tri-*n*-butylphosphine. The reactions of quinone methide **2** with triethyl phosphite and tri-*n*-butylphosphine are briefly compared.

Observations made during the course of previous work[3] suggested that quinone methides were involved as reactive intermediates during the inhibition of autoxidation by certain synergistic antioxidant systems containing hindered phenols and compounds of trivalent phosphorus. It appeared that separate investigations of quinone methide–phosphorus(III) nucleophile reactions might provide insight into the overall inhibition process, and this supposition prompted an examination of the reaction of triethyl phosphite with quinone methide **2**.[4] Since the results of that study were both interesting and unexpected,[4] we felt that information about the behavior of **2** toward other trivalent phosphorus nucleophiles would be desirable for purposes of comparison. The reaction of **2** with tri-*n*-butylphosphine was therefore investigated, and the present paper describes the results obtained. To our knowledge, no other reactions of quinone methides with phosphines have previously been described in the literature.

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[1] (a) Paper VII of a series on oxidation inhibitors. (b) Paper VI: W. H. Starnes, Jr., *J. Org. Chem.*, **35**, 1974 (1970). (c) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 25, 1970.

[2] Summer employee, 1968.

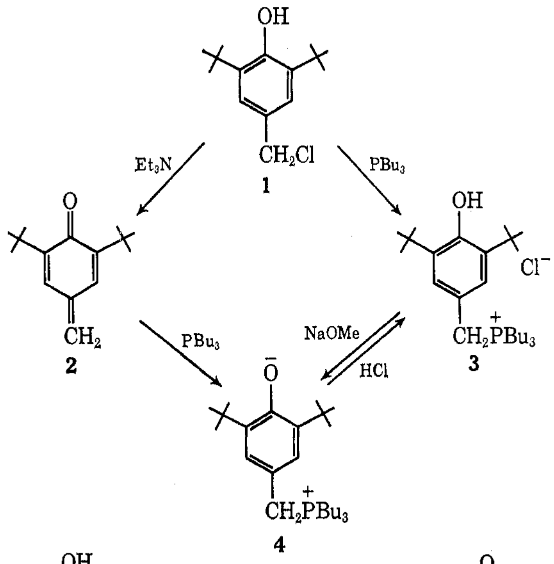
[3] W. H. Starnes, Jr., and N. P. Neureiter, *ibid.*, **32**, 333 (1967).

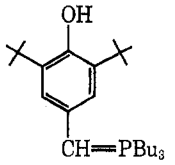
[4] W. H. Starnes, Jr., J. A. Myers, and J. J. Lauff, *ibid.*, **34**, 3404 (1969).

Results and Discussion

Quinone methide **2**, an unisolable species,[5] was generated *in situ* by allowing chloromethylphenol **1** to react with triethylamine in hydrocarbon solvents[5c,6] (Scheme I). Dropwise addition of tri-n-butylphosphine (1 mol equiv) to a dilute solution of **2** (0.027 M) in n-heptane caused a vigorous reaction leading to immediate precipitation of a solid product. The solid was shown by various analyses to be a 1:1 adduct (yield, 87%) of the phosphine and the quinone methide; it was also formed in benzene under similar conditions.

SCHEME I





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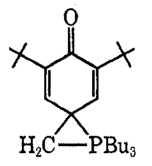

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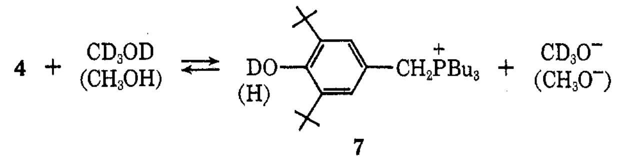
Mechanistic preconceptions suggested that the adduct could be prepared independently *via* the alternative route shown in Scheme I. This expectation was readily confirmed. Alkylation of tri-n-butylphosphine with chloromethylphenol **1** gave phosphonium chloride **3** in 97% yield. Addition of excess sodium methoxide to a methanol solution of **3**, followed by addition of water, afforded a white precipitate (yield, 84%) that was identical with the adduct obtained directly from **2**. The adduct was converted to its alternative precursor, **3** (yield, 90%) by treatment with dry HCl in methanol. These observations were considered to provide definitive evidence for attack by tri-n-butylphosphine on the methylene group of **2**.

At this point three possible structures for the adduct (**4**, **5**, and **6**) seemed worthy of consideration. Though fairly stable *in vacuo*, the substance underwent slow oxidative decomposition on exposure to air, an observation tending to exclude structure **6**. The material's lack of color argued against the ylide formulation[7] **5**, and its solubility properties (soluble in polar organic solvents, slightly soluble in water, insoluble in solvents of low polarity) were clearly more compatible with the betaine structure (**4**) than with either of the alternatives.[7] The high-resolution mass spectrum of the compound showed strong peaks corresponding to the parent m/e values for **2** and tri-n-butylphosphine, a result verifying neither structure but perhaps comprising a modicum of evidence against **5**. Stronger evidence in favor of **4** was forthcoming from the ir spectrum (Nujol) which showed no bands attributable to OH or C═O absorption. Furthermore, nmr measurements provided excellent evidence for equilibration of **4** with its conjugate acid (**7**) in methanol-d_4, and the existence of this equilibrium was strongly supported by uv studies on solutions of the adduct in methanol and methanolic sodium methoxide. The nmr results also showed that, in methanol-d_4, the benzyl protons of **4** were quickly replaced by deuterium. This observation suggested the possible presence of low equilibrium concentrations of ylide **5** and/or its conjugate anion; however, no independent evidence was obtained for the formation of these species in methanol solution. Low-temperature ir measurements showed that the adduct did not cyclize to the spirodienone structure **6** in ethanol at −93°,[8] and further studies by nmr showed that the betaine structure was also retained in methanol-d_4 at −90° and in dimethyl sulfoxide-d_6 or acetone-d_6 at room temperature. All available information thus indicates that the adduct has the betaine structure, **4**, in the solid state and in solvents of relatively high polarity.



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Inner salt tautomers of phosphonium ylides have frequently been postulated as reactive intermediates, but only a few substances of this type have actually been isolated heretofore. Of particular interest in this regard are the 1:1 adducts formed from 3-benzylidene-2,4-pentanedione and trialkyl- or dialkylphenylphosphines.[9] The enhanced stability of these isolable betaines relative to that of other possible isomers (ylides or cyclized structures containing pentavalent phosphorus) evidently results from the cooperative interaction of several favorable factors; *viz.*, relatively low anion basicity due to resonance stabilization, relatively low acidity of benzyl hydrogen caused by the presence of electron-donating substituents on phosphorus, steric hindrance to bimolecular prototropy, and the necessity of placing a relatively electropositive carbon substituent in an apical position of phosphorus(V) (an energetically

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(5) (a) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, No. 25, 9 (1960); (b) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963); (c) N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963); (d) B. R. Loy, *ibid.*, **31**, 2386 (1966).

(6) W. H. Starnes, Jr., *ibid.*, **31**, 3164 (1966).

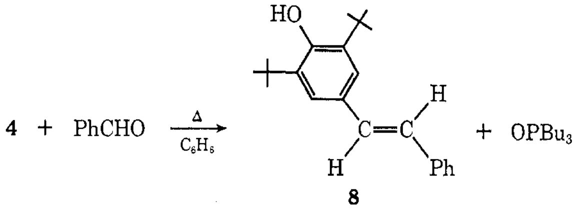
(7) *Cf.* A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 63.

(8) No carbonyl absorption could be detected under these conditions. Carbonyl absorption is observed in the 1610–1655-cm^{-1} region for analogous spirodienones containing carbon in place of phosphorus: G. A. Nikiforov, B. D. Sviridov, and V. V. Ershov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 542 (1968).

(9) F. Ramirez, J. F. Pilot, and C. P. Smith, *Tetrahedron*, **24**, 3735 (1968).

unfavorable arrangement[9,10]) in order for cyclization to occur. The stability of **4** relative to that of **5** and **6** can be rationalized on similar grounds; moreover, one notes that in this case the cyclized structure **6** should also be disfavored by the absence of aromatic resonance and by the presence of steric strain associated with the three-membered ring.

Since betaine **4** was obviously more polar than either of its possible isomers, it appeared that isomerization of the betaine might occur if the substance could be brought into solution in solvents of low polarity. In order to investigate this possibility, betaine **4** was heated under reflux with a solution of benzaldehyde (1.0 mol equiv) in benzene. The betaine quickly dissolved, and after 1.5 hr of heating the mixture afforded *trans*-3,5-di-*t*-butyl-4-stilbenol (**8**, 55%) and tri-*n*-butylphosphine oxide (crude yield, 83%) on work-up. These are the products to be expected from a typical Wittig reaction; thus their presence can be taken as evidence for rearrangement of **4** to ylide **5** under the reaction conditions. In a related experiment, a benzene solution of quinone methide **2** (1.0 mol equiv) was slowly added to a stirred solution of tri-*n*-butylphosphine (1.0 mol equiv) and benzaldehyde (1.1 mol equiv) in benzene at 50°. Under these conditions formation of **4**, isomerization of **4** to **5**, and entrapment of **5** with benzaldehyde were all evidently accomplished concurrently, since stilbenol **8** and tri-*n*-butylphosphine oxide were again found to be major reaction products (isolated yields were 58 and 73%, respectively).



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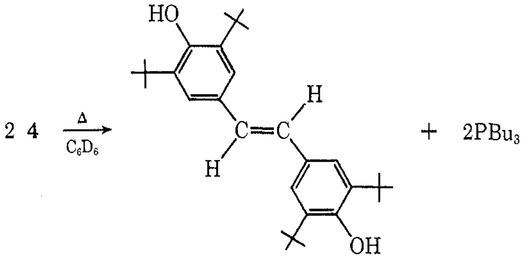
Betaine **4** was allowed to react with *n*-heptaldehyde in benzene under a variety of conditions. Tri-*n*-butylphosphine oxide was formed in every case, and the presence of the other Wittig product, 2,6-di-*t*-butyl-4-(1-octen-1-yl)phenol, was strongly suggested by mass spectrometric analysis. However, the pure alkenyl phenol (a mixture of *cis* and *trans* isomers?) could not be isolated. Attempts were also made to carry out Wittig reactions with betaine **4** and a variety of ketones (diethyl ketone, acetophenone, benzophenone), but these experiments gave little (if any) of the desired olefinic products. The transient intermediate responsible for olefin formation was thus shown to be a highly selective species whose reactivity toward carbonyl compounds resembled the reactivity previously reported for phosphonium ylides containing resonance-stabilized carbanion moieties.[11] This observation was consistent with our formulation of the intermediate as **5**, although the intermediate's total inertness toward ketones was still somewhat surprising. Realizing that a rapid side reaction could be partly responsible for this apparent lack of affinity, we next attempted to identify the other products formed from **4** under conditions conducive to its isomerization.

Mass spectrometric analysis of crude product mixtures obtained from "Wittig reactions" of **4** showed that a by-product with molecular formula $C_{30}H_{44}O_2$ had been formed in every case. Since a by-product having this composition could only result from a bimolecular process involving two molecules of **4**, separate studies of the decomposition of **4** were clearly in order. Samples of the betaine were therefore warmed in benzene-d_6 until complete dissolution occurred, and the solutions were then analyzed immediately by nmr and vpc. The analyses showed that bisphenol **9** ($C_{30}H_{44}O_2$) and tri-*n*-butylphosphine had been formed in yields amounting to *ca.* 80% and 95–100%, respectively. Minor by-products were also detected (but not identified), and analogous decompositions of the betaine in *p*-dioxane, toluene-d_8, or cyclohexene were found to give similar results. The reaction in cyclohexene gave no detectable by-products derived from the solvent, an observation militating against an already unlikely route to **9** involving dimerization of a carbene. Decompositions of betaine samples containing two benzyl deuteriums (*vide supra*) gave bisphenol-**9**-d_4 labeled at the hydroxyls and the vinyl positions.



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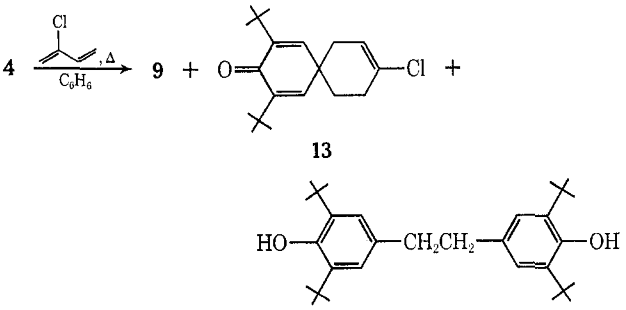
A plausible mechanism for the decomposition of **4** is shown in Scheme II. This mechanism is consistent with several items of information. In an attempt to secure direct evidence for reversion of **4** to its precursors (eq 1, Scheme II), the betaine was decomposed in benzene containing a large excess of chloroprene. This reaction gave spirotrienone **13** and bisphenol **14**, together with bisphenol **9** and unidentified products. The formation of **13** constitutes good evidence for the intermediacy of quinone methide **2**, since the Diels–Alder reaction of chloroprene and **2** is known to be facile,[12] and no other reasonable routes to **13** are apparent. Quinone methide **2** could also have been the precursor of bisphenol **14**,[13] *via* a process involving the corresponding bisphenoxy radical.[5b–d]



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[10] F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968), and references cited therein.

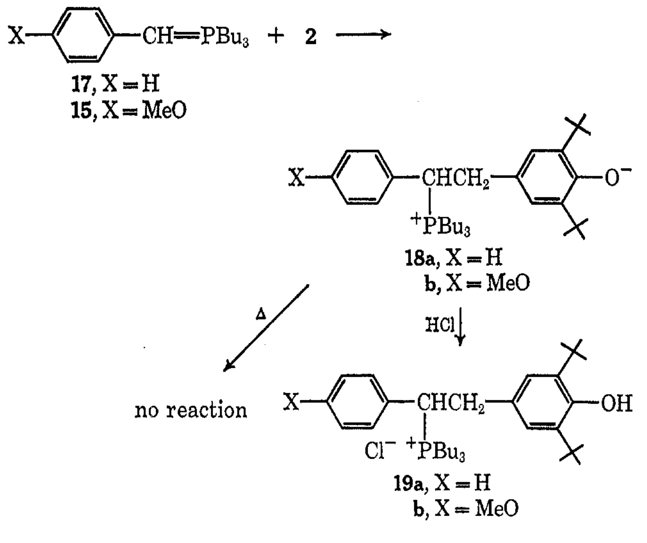
[11] For references to related cases and a comprehensive mechanistic rationale, see ref 7, pp 152–171.

[12] J. D. McClure, *J. Org. Chem.*, **27**, 2365 (1962).

[13] Vpc analyses suggested that small amounts of **14** were also produced in betaine decompositions performed without chloroprene. However, in these experiments **14** was neither isolated nor characterized.

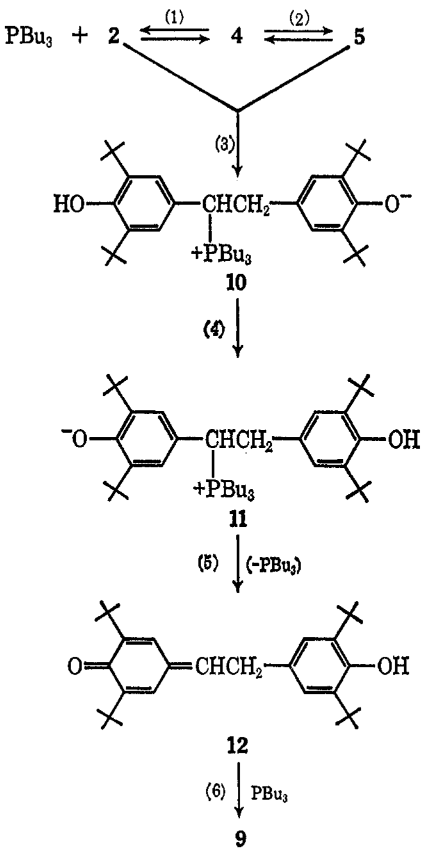
Since the spontaneous free-radical dimerization of 2 does *not* give bisphenol **9**,[5b,c] the coupling process leading to **9** is clearly best considered to involve nucleophilic displacement or addition. Ylide **5**, a highly nucleophilic species, is probably formed from **4** (eq 2) under the reaction conditions (*vide supra*). Betaine **10** could be formed by reaction of **5** with **2** (eq 3, Scheme II), or by reaction of **5** with **4** in a process involving S$_N$2 displacement of tri-n-butylphosphine. However, an equimolar mixture of ylide **15** and phosphonium chloride **16** failed to react after 16.4 hr in benzene at 50°—a result that made the S$_N$2 route to **10** seem highly unlikely. In contrast, eq 3 of Scheme II was expected to occur with ease,[14] and this supposition was supported by the behavior of quinone methide **2** toward ylide **17**, an analog of ylide **5**. In benzene at room temperature the reaction with **17** was rapid and essentially quantitative; it afforded an adduct that was isolated as the hydrochloride (**19a**) after treatment with HCl. A reaction of **2** with ylide **15** gave a similar result; however, in this case the product hydrohalide (**19b**) was not purified.

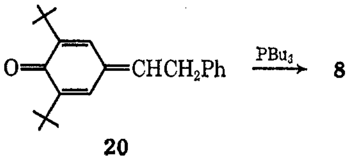
$$\underset{\mathbf{15}}{p\text{-MeOC}_6\text{H}_4\text{CH}{=}\text{PBu}_3} + \underset{\mathbf{16}}{p\text{-MeOC}_6\text{H}_4\text{CH}_2\overset{+}{\text{P}}\text{Bu}_3\ \text{Cl}^-} \xrightarrow[\text{C}_6\text{H}_6]{\Delta} \text{no reaction}$$



Although direct conversion of **10** to **9** seemed possible *a priori*, experiments with betaines **18a** and **18b** showed that this type of β elimination was not a favored process. Benzene solutions of **18a** and **18b** still afforded practically quantitative yields of the corresponding hydrochlorides (**19a** and **19b**) even after extended periods of refluxing (up to 92.5 hr), and an identical result was obtained in a similar experiment where equimolar amounts of **18a** and **19a** were employed.[15] Since the preparations of **18a** and **18b** had involved dehydrohalogenation of phosphonium chlorides with n-butyllithium, it also seemed advisable to show that complexation with lithium chloride[16] could not have been responsible for the high stabilities of the two betaines in question. Phosphonium chloride **3** was therefore allowed to react with n-butyllithium (1.0 mol equiv) in benzene at room temperature, and the resulting mixture (which presumably contained **4** and lithium chloride) was heated under reflux for 1.0 hr. As expected, a considerable amount of bisphenol **9** was formed. The inherent stability of **10** thus appears to be much less than that of **18a** or **18b**, a result making an indirect conversion of **10** to **9** (Scheme II, eq 4–6) seem an attractive possibility. Loss of tri-n-butylphosphine from betaine **11** (eq 5, Scheme II) appears quite reasonable by analogy with eq 1 of Scheme II, and the phosphine-catalyzed isomerization of quinone methide **12** (eq 6, Scheme II) is consistent with previous observations relating to this quinone methide's base-catalyzed isomerization.[4] In an indirect test for the feasibility of eq 6 of Scheme II, quinone methide **20** was

SCHEME II





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subjected to the action of tri-n-butylphosphine in benzene. This experiment gave the anticipated result: quantitative formation of stilbenol **8** in an extremely rapid reaction. Scheme II thus appears to conform with all relevant facts, although information about certain mechanistic details is lacking.[17]

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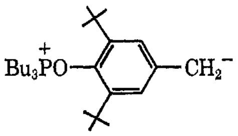
[14] *Cf.* H. J. Bestmann and H. J. Lang, *Tetrahedron Lett.*, 2101 (1969).

[15] Under the conditions of these experiments, betaines **18a** and **18b** might have been converted (at least in part) to the corresponding ylide isomers. However, this rearrangement would not invalidate the use of **18a** and **18b** as models for testing the direct conversion of **10** to **9**, since isomerization to an ylide is a potential reaction path for **10** also.

[16] *Cf.*, *inter alia*, ref 7, p 135 and 136 and literature cited therein; also R. F. Hudson, "Structure and Mechanism in Organo-phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, p 225.

[17] For example, reversal of eq 2 of Scheme II has not been demonstrated experimentally.

We now wish to consider the possibility of an alternative mechanism for decomposition of **4** involving betaine **21** as the nucleophilic intermediate. Betaine **21** could result from addition of tri-*n*-butylphosphine to **2** in a reaction competitive with the reverse process of eq 1 of Scheme II. Addition of **21** to a second molecule of **2** would give a dimeric betaine (**22**) which might decompose to quinone methide **12** and tri-*n*-butylphosphine. Phosphine-catalyzed isomerization of **12** to **9** would then complete the reaction sequence. A mechanism involving betaine **21** can also account for the formation of Wittig products from aldehydes and **4**. Reaction of **21** with an aldehyde would give betaine **23**, a species which might rearrange into betaine **24**. Tri-*n*-butylphosphine oxide and an alkenylphenol could then result from fragmentation of **24**, *via* a process formally depicted as an internal β elimination.



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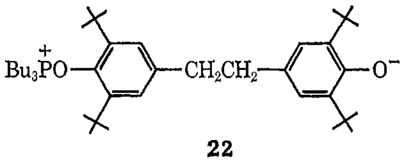

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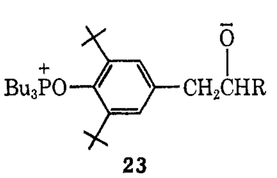

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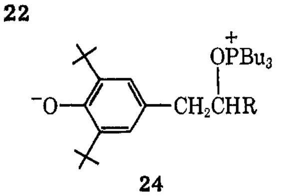

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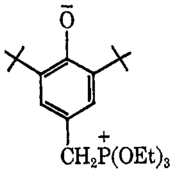
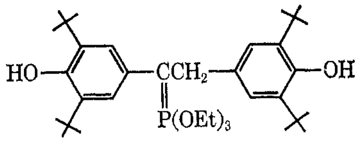
Although schemes involving **21** have not been excluded experimentally, these mechanisms seem improbable for a number of reasons. To the extent that reaction rates are influenced by the resonance stabilizations of products, formation of stilbenols by fragmentation of betaines **18a** and **18b** appears much more likely than formation of quinone methide **12** by fragmentation of betaine **22**. Betaines **18a** and **18b** were actually found to be quite *stable* toward fragmentation; thus on this basis the possibility that **22** would give **12** appears remote indeed. Furthermore, the nucleophilic intermediate's high selectivity toward carbonyl compounds appears more compatible with structure **5** than with structure **21**, since **21** should be a very reactive species having low discriminative ability. Finally, we note that there is no extant evidence for addition of a trivalent phosphorus nucleophile to the carbonyl group of a *p*-quinone methide,[1b,4] the reaction of triethyl phosphite with quinone methide **2** having been conclusively shown not to involve a process of this type.[4]

The reactions of quinone methide **2** with triethyl phosphite[4] and tri-*n*-butylphosphine can now be compared in detail. At room temperature in relatively nonpolar media these reactions give entirely different types of isolable products. Nevertheless, mechanistic studies[4] have shown that the initial intermediate in the phosphite reaction is betaine **25**, a species analogous to **4**. Since triethyl phosphite is a relatively weak nucleophile (weaker than the phosphine),[18] formation of **25** is relatively slow.[4,19] On the other hand, rearrangement of **25** into the corresponding ylide should be relatively fast (faster than the rearrangement of **4** to **5**), owing to the presence of three relatively electronegative groups on phosphorus.[20] Thus, as a consequence of these kinetic features, betaine **25** is destined to remain a reactive intermediate,[4] while betaine **4** is an isolable species. However, at slightly elevated temperatures, betaine **4** gives bisphenol **9** *via* a mechanism (Scheme II) which is probably closely analogous to the mechanism of formation of **9** from **2** in the reaction with triethyl phosphite.[4] The phosphite reaction also affords significant amounts of a trimer of **2**, *via* a mechanism involving ylide **26** as a key intermediate,[4] whereas little (if any) trimer is formed in the decomposition of betaine **4**. These divergent results suggest that betaines **10** and **11** are converted into their ylide isomer (the analog of **26**) at relatively slow rates, a circumstance which could be occasioned by the presence of electron-donating alkyl groups on phosphorus.[20] Finally, we note that relatively high concentrations of quinone methide **12** could be reached in the reaction of **2** with triethyl phosphite[4] but not in the analogous reaction (decomposition of **4**) involving tri-*n*-butylphosphine. This dissimilarity probably reflects differences in the rate of conversion of **12** to **9** and may thus be related to the different basicities (or nucleophilicities toward hydrogen) of the trivalent phosphorus reagents.[21]



25



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Summarizing the foregoing remarks, we conclude that the overall reactions of quinone methide **2** with triethyl phosphite and tri-*n*-butylphosphine are probably quite similar mechanistically, and that the observed differences between these reactions with regard to product type are rationalizable in terms of differences in the rates of corresponding mechanistic steps. The rate differences appear to be consistent with the relative nucleophilicities and basicities of the phosphite and the phosphine, and with the expected effects of substituent electronegativity on rates of ylide formation.

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[18] (a) This order of reactivity has been established for displacements on saturated carbon, and it is commonly assumed to hold for other types of reactions involving nucleophilic attack by trivalent phosphorus reagents. (b) See A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., Amsterdam, 1967, pp 15–17, 37, and 38, and references cited therein. (c) Tri-*n*-butylphosphine is said to be more reactive than trimethyl phosphite toward an olefinic carbon atom of *trans*-dibenzoylethylene: F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966).

[19] Consideration should also be given to the possibility that **4** and **25** are formed reversibly. If this is indeed the case, the equilibrium constant for formation of **25** should be much less than that for formation of **4**, owing to the different nucleophilicities of the trivalent phosphorus reagents.

[20] For a brief discussion of the effects of phosphorus substituents on ease of ylide formation, see ref 7, p 13.

[21] Toward protons, tri-*n*-butylphosphine is reported to be a stronger base than triethyl phosphite: C. A. Streuli, quoted by L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, **81**, 4200 (1959). A rough estimate of the basicity of tri-*n*-butyl phosphite provides further support for the conclusion that trialkyl phosphites are weaker bases than trialkylphosphines (ref 18b, p 15).

Experimental Section[22]

Materials.—Tri-*n*-butylphosphine contained no impurities detectable by vpc or nmr analysis and was used as received; we are indebted to Carlisle Chemical Works, Inc., for a generous gift of this material. Benzene (B & A ACS reagent grade), *n*-heptane (reagent grade, Humble Oil and Refining Co.), and *p*-dioxane (Matheson Coleman and Bell Spectroquality grade) were dried over sodium ribbon and stored under nitrogen. Cyclohexene (Phillips "Pure" grade) was percolated over alumina just prior to use. Benzaldehyde, *n*-heptaldehyde, and chloroprene were redistilled under nitrogen and used immediately after purification. *n*-Butyllithium was obtained from Foote Mineral Co. as a solution in hexane and was used as received. Gaseous HCl was dried by passage through H_2SO_4. All other chemicals used were highly purified articles of commerce. Purities were verified by spectral measurements, vpc analyses, and the determination of appropriate physical constants.

Instrumental Analysis.—Ultraviolet, 100-MHz nmr, and high resolution mass spectra were recorded with Cary Model 14, Varian Model HA-100, and AEI MS-9 spectrometers, respectively. The nmr measurements were made at ambient temperature (except where noted otherwise) on dilute solutions containing TMS as the internal standard. Nmr peak multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), dt (doublet of triplets), m (multiplet). Exact mass measurements are referred to C = 12 amu. Conventional ir spectra were obtained with a Perkin-Elmer instrument, Model 21; low-temperature ir measurements were made with a Beckman IR-12 spectrometer equipped with a VLT-2 variable low temperature unit. Programmed temperature vpc analyses were done with an F & M instrument (Model 500) equipped with a 6 ft × 0.25 in. (o.d.) stainless steel column containing SE-30 (5%) on 40–60 mesh Chromosorb W, acid washed, DMCS treated. The carrier gas was helium; column temperature was increased from 100 to 350° at the rate of 8°/min. Vpc peak areas were measured with a planimeter.

(3,5-Di-*t*-butyl-4-oxybenzyl)tri-*n*-butylphosphonium Betaine (4) from 4-Methylene-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (2) and Tri-*n*-butylphosphine.—A solution of quinone methide **2** (2.0 mmol) in *n*-heptane (75 ml) was prepared by dehydrochlorination of chloromethylphenol **1** (0.51 g, 2.0 mmol) with triethylamine (0.21 g, 2.1 mmol) according to a previously described procedure.[6] The solution was degassed by stirring and bubbling with nitrogen; then 0.41 g (2.0 mmol) of tri-*n*-butylphosphine was added dropwise during 2 min while stirring and nitrogen bubbling were continued. A precipitate of **4** appeared immediately. Stirring with introduction of nitrogen was continued for 5 min more. The betaine was then recovered by suction filtration, washed thoroughly on the filter with several portions of petroleum ether (bp 30–60°) and ether, and dried overnight at room temperature under vacuum (*ca.* 5 mm). The pale lavender solid thus obtained weighed 0.73 g (87%) and melted at 92–94° (pale blue-green melt); spectral comparisons showed it to be identical with a sample of betaine **4** prepared by the alternative route described below. Reactions of quinone methide **2** with tri-*n*-butylphosphine in benzene gave similar results.

(3,5-Di-*t*-butyl-4-hydroxybenzyl)tri-*n*-butylphosphonium Chloride (3).—Tri-*n*-butylphosphine (40.60 g, 0.201 mol) was added dropwise during 0.5 hr to a stirred solution of chloromethylphenol **1** (50.96 g, 0.200 mol) in benzene (500 ml). After an additional 0.7 hr of stirring, the mixture was allowed to stand undisturbed for 5.3 hr and then filtered with suction. The recovered solid was washed twice with benzene and then twice with ether; after drying *in vacuo* at 60° it weighed 89.2 g (97%), melted at 183–184°, and contained no impurities that could be detected by nmr analysis. Recrystallization of a small sample from toluene gave **3** as tiny white flakes: mp 186–187°; ir (Nujol) 3600 cm^{-1} (weak, sharp, hindered phenol OH); nmr (CD_3OD) δ 7.11 (d, 2, J = 3 Hz, aromatic H), 3.68 (d, 2, J = 14 Hz, CH_2Ar), 1.97–2.37 (m, 6, 3 CH_2Pr), 1.26–1.72 (m with strong s at 1.45 ppm, 30, 3 $CH_2CH_2CH_3$ and 2 *t*-Bu), and 0.97 ppm (highly distorted t, 9, $J \cong 7$ Hz, 3 CH_2CH_3); for uv spectrum, see Table I.

Anal. Calcd for $C_{27}H_{50}ClOP$: C, 70.94; H, 11.03; Cl, 7.76; P, 6.78. Found: C, 70.91; H, 11.17; Cl, 7.94; P, 6.63.

Betaine 4 from Phosphonium Chloride (3).—A solution of **3** (1.15 g, 2.52 mmol) in methanol (5 ml) was degassed by stirring and bubbling with nitrogen. Sodium methoxide (0.41 g, 7.6 mmol) was then added, and after an additional 5 min of stirring and bubbling, the mixture was poured into water (50 ml), stirred until precipitation appeared to be complete (*ca.* 5 min), and filtered using suction. The solid was quickly washed in succession with water (three portions) and dry ether (four portions), then dried under vacuum (*ca.* 5 mm) to give 0.89 g (84%) of **4** as white microcrystals: mp 92–94° (pale blue-green melt; very slow rates of heating gave melting points that were lower by 3–4°); soluble in methanol, ethanol, dimethyl sulfoxide, or acetone; sparingly soluble in water; insoluble at room temperature in petroleum ether (bp 30–60°), ether, benzene, toluene, *p*-dioxane, or carbon tetrachloride; ir (Nujol) no OH or C=O; ir (EtOH) no C=O at temperatures ranging from 25 to −93°; nmr (CD_3OD) δ 6.85 (d, 2, J = 3 Hz, shifts upfield upon addition of NaOMe, aromatic H), 3.45 (d, 2, J = 13 Hz, disappears after 2–2.5 hr of standing due to D exchange with solvent, CH_2Ar), 1.87–2.26 (m, 6, 3 CH_2Pr), 1.26–1.74 (m with strong s at 1.41 ppm, 30, 3 $CH_2CH_2CH_3$ and 2 *t*-Bu), and 0.97 ppm (highly distorted t, 9, $J \cong 7$ Hz, 3 CH_2CH_3); nmr (CD_3OD, −90°) equivalent to spectrum in CD_3OD at room temperature, except for line broadening and loss of fine structure due to viscosity effects; nmr [$(CD_3)_2SO$ or $(CD_3)_2CO$] similar to spectrum in CD_3OD; mass spectrum (64 eV) m/e 218.1670 (strong; calcd for $C_{15}H_{22}O$, 218.1671) and 202.1837 (strong; calcd for $C_{12}H_{27}P$, 202.1850).

Anal.[23] Calcd for $C_{27}H_{49}OP$: C, 77.09; H, 11.74. Found: C, 76.87; H, 11.79.

The uv spectra of betaine **4** and two related compounds are presented in Table I. On the basis of these data and published uv data for 2,6-di-*t*-butylphenols containing *para* substituents which do not undergo strong resonance interaction with the ring,[24] the maxima at 269 and 300 mμ may be assigned to the phenolate moiety of **4**, while the maxima at 234 and 276–282 mμ can be ascribed to the cation **7** resulting from protonation of the betaine by methanol. In pure methanol the log ε values obtained for **4** are strongly dependent on betaine concentration (*cf.* the two tabulated values of log ε for the 300-mμ band), owing to concentration effects on the position of the equilibrium be-

TABLE I

ULTRAVIOLET SPECTRA[a]

	MeOH		0.5 *M* NaOMe, MeOH	
Compd	λ_{max},[b] mμ	Log ε	λ_{max},[b] mμ	Log ε
4[c]	234	3.95[d]	234[e,f]	3.62
	276	3.28[g]	269	4.13
	282[e]	3.23[g]	300[e]	3.71
	300[e]	2.31[g]	365[h]	2.54[h]
	300[e]	2.87[i]		
	365[j]	2.18[j,k]		
3	234	3.94	234[e,f]	3.69
	276	3.19	269	4.16
	282[e]	3.17	300[e]	3.73
			365[l]	1.67[l]
16	231	4.18	231	4.19
	278	3.18	278	3.18
	284	3.12	284	3.12

[a] From 220 to 500 mμ unless noted otherwise. [b] ±1 mμ, wavelength scale not calibrated. [c] Region scanned, 220–400 mμ. [d] [**4**] = 5.16 × 10^{-5} *M*. [e] Shoulder. [f] Presence uncertain; may have been an instrumental artifact. [g] [**4**] = 5.16 × 10^{-4} *M*. [h] Bisphenol **9**, 5.0 mol %. [i] [**4**] = 2.58 × 10^{-3} *M*. [j] Bisphenol **9**, 5.0 mol % (calculated from spectrum in 0.5 *M* methanolic NaOMe). [k] [**4**] = 5.16 × 10^{-3} *M*. [l] Bisphenol **9**, 0.7 mol %.

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[22] Boiling points and melting points are uncorrected. The melting points were determined with a Fisher-Johns apparatus. Unless noted otherwise, elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Drierite was used as the drying agent for organic solutions. Distillations were done with a spinning-band column (24 in. × 8 mm); evaporations were carried out on rotary evaporators at room temperature under 5–10 mm of pressure. A major part of the instrumental analytical work was performed by the Analytical Division of this laboratory.

[23] Macrocombustion analysis was by Mr. E. Bowers, Humble Oil and Refining Co., Baytown, Texas.

[24] L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, **85**, 3397 (1963); C. H. Rochester, *J. Chem. Soc.*, 676 (1965).

tween **4** and **7**. Rapid equilibration would cause time averaging of the chemical shifts and thus accounts for the relatively simple nmr spectrum observed for **4** in CD_3OD. Addition of methoxide ion increases the **4**:**7** ratio, thereby enhancing the average shielding experienced by the aromatic protons and causing their resonance position to shift upfield (*vide supra*). In 0.5 *M* methanolic NaOMe different samples of **4** gave values of log ε (365 mμ) ranging from 2.54 to 2.86. This observation, together with the much lower value of log ε (365 mμ) obtained for betaine samples generated *in situ* from **3**, suggested that the 365-mμ band was produced by an impurity. Stilbenediol[25] **9** was obviously a possible contaminant, and indeed, the uv spectrum of this phenol in 0.5 *M* methanolic NaOMe was found to contain a strong band at 365 mμ. This band is evidently produced by an anionic species, since it does not appear in the spectrum of **9** in pure methanol. Its presence in the spectrum of **4** in pure methanol thus indicates proton transfer from **9** to the betaine's phenoxide moiety. A $\pi \rightarrow d$ or $\pi \rightarrow \pi^*$ transition involving the C=P chromophore[26] of ylide **5** was also considered as a possible explanation for the presence of the 365-mμ band; however, this rationale appears unacceptable in view of the absence of the band from the spectrum of phosphonium chloride **16** under basic conditions. In 0.5 *M* methanolic NaOMe the 365-mμ band of pure **9** has log ε 3.84, this value was used to compute the mole per cent of **9** present in samples of **3** and **4**.

In air betaine **4** slowly decomposes to an amorphous purple mass. Storage under vacuum reduces the rate of this decomposition.

Phosphonium Chloride (3) from Betaine 4.—A solution of **4** (0.50 g, 1.2 mmol) in methanol (10 ml) was saturated with gaseous HCl and then dried. The drying agent was removed by vacuum filtration and washed with several portions of methanol to dissolve the adhering gummy precipitate. Evaporation of the combined filtrate and washings, followed by trituration of the residue with ether, afforded 0.49 g (90%) of white crystals, mp 182–183.5°, which were identified as **3** by a mixture melting point determination and ir spectral comparisons.

Reactions of Betaine 4 with Aldehydes. A. Benzaldehyde.—A freshly prepared sample of **4** (6.32 g, 15.0 mmol) was added to a solution of benzaldehyde (1.59 g, 15.0 mmol) in benzene (60 ml), and the mixture was refluxed under nitrogen with stirring for 1.5 hr. Removal of solvent under vacuum, followed by vacuum fractionation of the residue, gave three fractions: (1) bp 75–126° (mostly 126°) at 0.75–0.95 mm, 2.70 g; (2) bp 176–178° (temperature possibly inaccurate owing to low distillation rate) at 1.0 mm, 2.54 g; and (3) bp *ca.* 215° at 0.75 mm, 0.75 g. Fraction 1 was shown to be mostly tri-*n*-butylphosphine oxide (crude yield, 83%) by the usual variety of spectral comparisons with authentic material. Similar comparisons indicated that fraction 2 was stilbenol **8** (yield, 55%) in essentially pure form. Crystallization of fraction 2 from methanol–water, followed by low-temperature recrystallization from a very small amount of ether, gave a sample of **8** melting at 92.5–93° (lit. mp 90–91°,[4] 91–93°[27]). Spectral data indicated that fraction 3 was a complex mixture.

B. *n*-Heptaldehyde.—Three reactions were carried out in dry benzene under nitrogen, using the following conditions (millimoles of aldehyde per millimole of **4**, milliliters benzene per millimole of **4**; temperature, °C; reaction time, hr): 1.0, 6, 25–30, 116.5; 1.0, 4, reflux, 46.2; 10.0, 10, 49–53, 6.1. The mass spectra of the crude product mixtures all showed a strong peak at *m/e* 316 (exact *m/e* from one run, 316.2763; calcd for $C_{22}H_{36}O$, 316.2766); this was shown to be a parent ion by comparative intensity measurements at low and high voltages (10 and 70 eV). The presence of this peak, together with peaks at *m/e* 301 (strong at 70 eV, presumably $C_{21}H_{33}O$) and 245 (medium at 70 eV, presumably $C_{17}H_{25}O$), suggested that the anticipated Wittig product, 2,6-di-*t*-butyl-4-(1-octen-1-yl)phenol, had been formed to some extent. Yet attempts to recover the pure phenol by fractional distillation under vaccum were not successful. Qualitative vpc, ir, and mass spectral analyses showed that the other Wittig product, tri-*n*-butylphosphine oxide, had been formed in all of these experiments. A minor amount of a second liquid phase (apparently water) was formed in the reactions run at elevated temperatures. The reaction run at 25–30° yielded a small amount of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde, which was isolated and identified by an nmr spectral comparison *vs.* authentic material.

***trans*-3,5-Di-*t*-butyl-4-stilbenol (8) from Quinone Methide 2, Tri-*n*-butylphosphine, and Benzaldehyde.**—A solution of tri-*n*-butylphosphine (16.21 g, 80.1 mmol) and benzaldehyde (9.29 g, 87.5 mmol) in benzene (80 ml) was warmed to 50° and kept at 50 ± 1° while a freshly prepared solution of **2** [80.1 mmol, obtained in the usual way from 20.40 g (80.1 mmol) of **1** and 8.44 g (83.4 mmol) of triethylamine] in benzene (500 ml) was added dropwise with stirring under nitrogen during 1.0 hr. Stirring under nitrogen at 50 ± 1° was continued for an additional 6.5 hr, and the mixture was then allowed to stand at room temperature under nitrogen overnight. Following successive extractions with 5% hydrochloric acid (three 200-ml portions) and 2 *N* sodium carbonate (three 200-ml portions), the organic moiety was dried, concentrated under vacuum, and distilled to recover two major fractions: (1) bp 120–124° at 0.13–0.27 mm, 12.83 g; and (2) bp 171–178° at 0.25–0.33 mm, 15.32 g. Ir and nmr spectral comparisons showed that fraction 1 was tri-*n*-butylphosphine oxide (73%). Crystallization of fraction 2 from aqueous methanol afforded 14.32 g (58%) of stilbenol **8** in two crops: mp 93–94° (12.52 g) and 91–93° (1.80 g). Both crops gave an nmr spectrum that was identical with the spectrum of an authentic specimen.[4]

Decompositions of Betaine 4 in Aprotic Solvents.—Mixtures of the betaine and C_6D_6 were prepared in nmr sample tubes and thoroughly degassed by bubbling with nitrogen. The tubes were then stoppered tightly and warmed gently until homogeneous solutions were obtained. Immediate examination of these solutions by nmr showed that all of the betaine had decomposed, and that bisphenol **9** and tri-*n*-butylphosphine were the major decomposition products. These identifications were confirmed by peak enhancements resulting from the addition of authentic specimens. Minor peaks arising from one or more unidentified by-products appeared in the olefinic–aromatic regions of the spectra, and qualitative comparisons showed that by-product yields were lowest when freshly prepared samples of **4** were employed. Several reaction mixtures were analyzed quantitatively by programmed temperature vpc, using pure compounds for calibration and *n*-eicosane for internal standardization. In this way the yields of bisphenol **9** and tri-*n*-butylphosphine were found to be *ca.* 80 and 95–100%, respectively.

Decompositions of betaine **4** were also carried out in anhydrous *p*-dioxane, $C_6D_5CD_3$, or cyclohexene, using a procedure identical to that described above. For runs in cyclohexene, the solvent was evaporated under nitrogen and replaced by C_6D_6 prior to product analysis. Nmr measurements showed that bisphenol **9** and tri-*n*-butylphosphine were the major products of all of these reactions, and that by-products derived from the solvent were not formed in experiments where cyclohexene was employed. The cyclohexene results were confirmed by programmed temperature vpc and mass spectral analyses.

A solution of **4** in CD_3OD was allowed to stand at room temperature until the nmr spectrum showed that the benzylic protons had been completely replaced by deuterium. Most of the solvent was then evaporated under nitrogen, and the residue was taken to complete dryness under vacuum. After addition of C_6D_6, the deuterated betaine was decomposed in the usual way. The nmr spectrum of the decomposition products showed no peaks for the olefinic or hydroxyl protons of **9** but was otherwise identical with the spectra obtained previously.

2,4-Di-*t*-butyl-9-chlorospiro[5.5]undeca-1,4,8-trien-3-one (13).—This compound was obtained by reaction of chloroprene with quinone methide **2**. The procedure followed was similar to that described by McClure,[12] except that the quinone methide solution was prepared separately by our usual method[6] and then added to the diene. Recrystallization of the crude product from methanol and then from ethanol gave **13** as white needles: mp 110–111° (lit.[12] mp 111–112°); uv max (isooctane) 241 mμ (log ε 4.05) and 367 (1.32) [lit. uv max (isooctane)[12] 242 mμ (log ε 3.96), uv max (solvent not specified)[28] 241 mμ (log ε 3.93) and 363 (1.28)]; nmr (CCl_4) δ 6.49 (s, 2, 1- and 5-CH), 5.74–5.91 (m, 1, 8-CH), 2.29–2.56 (m, 2, 10-CH_2), 2.05–2.21 (m, 2, 7-CH_2), 1.71 (t, 2, *J* = 6.4 Hz, 11-CH_2), and 1.22 ppm (s, 18, 2 *t*-Bu). The nmr spectrum seems inconsistent with a possible alternative structure, *viz.*, the 8-chloro isomer of **13**. The 8-chloro formulation would appear to require coupling of the 1.71

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[25] C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

[26] *Cf.* ref 7, pp 63, 64, and 74, and references cited therein; S. O. Grim and J. H. Ambrus, *ibid.*, **33**, 2993 (1968).

[27] H.-D. Becker, *ibid.*, **34**, 1211 (1969).

[28] W. R. Hatchard, *J. Amer. Chem. Soc.*, **80**, 3640 (1958).

δ triplet with the δ 2.05–2.21 multiplet, whereas inspection of the latter band immediately shows that it is not broad enough to incorporate a triplet with J = 6.4 Hz (the width reported for the multiplet is that of the total absorption envelope, rather than the separation of the two outermost maxima). McClure's hypothesis[12] concerning the structure of **13** is thus considered to be correct.

Decomposition of Betaine 4 in the Presence of Chloroprene.—A solution of chloroprene (8.85 g, 100 mmol) in dry benzene (10 ml) was degassed by bubbling with nitrogen. Betaine **4** (0.42 g, 1.0 mmol) was then added, and the mixture was stirred under nitrogen at 50 ± 1° for 1.0 hr. After cooling to room temperature, the mixture was extracted with 5% hydrochloric acid (two 50-ml portions), washed with 5% sodium bicarbonate solution (two 50-ml portions), dried, and evaporated under vacuum. An nmr spectrum showed that the composition of the residue (0.21 g) was complex; however, the presence of an appreciable amount of trienone **13** was clearly revealed by the appearance of peaks previously assigned (*vide supra*) to the 1- and 5-CH, 8-CH, 7-CH_2, 11-CH_2, and *t*-butyl groups of this compound (the 10-CH_2 multiplet was obscured by resonances from other products). These peaks had the correct multiplicities and relative intensities, and their origin was confirmed by intensity enhancements resulting from the addition of authentic **13**. A rough analysis of the residue by programmed temperature vpc indicated the presence of bisphenol **9** (evidently the major constituent), trienone **13**, bisphenol **14**, and unidentified compounds. Compounds **9**, **13**, and **14** were identified by retention times and, in the case of **14**, by comparing the ir and nmr spectra of a trapped fraction with the spectra of an authentic specimen.[29]

***p*-Methoxybenzyltri-*n*-butylphosphonium Chloride (16).**—Tri-*n*-butylphosphine (10.12 g, 50.0 mmol) was added under nitrogen during 5 min to a stirred solution of *p*-methoxybenzyl chloride[30] (7.83 g, 50.0 mmol) in dry benzene (25 ml). The nitrogen-blanketed mixture was then stirred at reflux temperature for 3.1 hr, kept at room temperature for an additional 6.7 hr, and evaporated under vacuum to give a solid residue which was suspended in ether, filtered with suction, and washed thoroughly on the filter with several fresh portions of ether. Drying of the solid under vacuum at 60° gave 17.11 g (95%) of pure **16** as white microcrystals: mp 105–106.5°; nmr ($CDCl_3$) δ 6.8–7.5 (AA'BB' portion of AA'BB'X m where X is phosphorus, 4, by computer calculation,[31] $J_{AA'}$ = 2.5, $J_{BB'}$ = 2.5, J_{AB} = $J_{A'B'}$ = 8.9, $J_{AB'}$ = $J_{A'B}$ = 0.1, J_{AX} = $J_{A'X}$ = 2.0, J_{BX} = $J_{B'X}$ = 0.0 Hz; aromatic H), 4.22 (d, 2, J = 15 Hz, CH_2Ar), 3.79 (s, 3, CH_3O), 2.2–2.6 (m, 6, 3 CH_2Pr), 1.2–1.7 (m, 12, 3 $CH_2CH_2CH_3$), and 0.92 ppm (highly distorted t, 9, $J \cong$ 6 Hz, 3 CH_2CH_3); for uv spectrum, see Table I.

Anal. Calcd for $C_{20}H_{36}ClOP$: C, 66.93; H, 10.11; Cl, 9.88; P, 8.63. Found: C, 66.96; H, 10.09; Cl, 10.07; P, 8.67.

Attempted Reaction of *p*-Methoxybenzylidenetri-*n*-butylphosphorane (15) with Phosphonium Chloride (16).—A solution of **16** (1.80 g, 5.01 mmol) in dry benzene (15 ml) was thoroughly degassed by the freeze–thaw method and blanketed with nitrogen. *n*-Butyllithium in hexane (1.55 ml of 15.20% solution, 2.50 mmol) was then added through a rubber septum by means of a hypodermic syringe, and the mixture was stirred under nitrogen at 50 ± 1° for 16.4 hr. After saturation with dry HCl, the mixture was filtered to remove a small amount of infusible white solid (very hygroscopic, presumably LiCl), which was quickly washed with several fresh portions of benzene. Evaporation of the combined filtrate and washings yielded a colorless, semicrystalline residue (1.98 g, presumably contained some LiCl) whose only organic constituent was **16**, judging from the material's nmr spectrum.

Tri-*n*-butyl(α-phenyl-3,5-di-*t*-butyl-4-hydroxyphenethyl)phosphonium Chloride (19a).—*n*-Butyllithium (12.25 ml of a 15.20% solution in hexane, 19.8 mmol) was added under nitrogen to a well-stirred suspension of powdered benzyltri-*n*-butylphosphonium chloride[32] (6.60 g, 20.1 mmol) in dry benzene (75 ml). Stirring under nitrogen was continued for 2.0 hr; then a freshly prepared solution of quinone methide **2** [20.0 mmol, from 5.10 g (20.0 mmol) of phenol **1** and 2.11 g (20.9 mmol) of triethylamine] in dry *n*-heptane (90 ml) was added to the stirred mixture during 4 min. Following an additional 5 hr of stirring under nitrogen, the well-agitated mixture (now containing a reddish tar) was acidified by dropwise addition of 2.5 *M* hydrochloric acid (50 ml). During the acidification period (10 min) a white precipitate of **19a** appeared. After treatment of the mixture with 5 ml of concentrated hydrochloric acid and 10 more min of stirring, the precipitate was recovered by suction filtration and washed thoroughly with petroleum ether (bp 30–60°). The crude, air-dried product weighed 10.2 g (94%) and melted at 182–186°; upon recrystallization from benzene (with filtering to remove a small amount of insoluble material) it afforded 7.78 g (72%) of white crystals melting at 189–190.5°. A further recrystallization from benzene gave tiny, snow-white needles of pure **19a**: mp 189.5–191.5°; ir (CS_2) 3630 cm^{-1} (sharp and weak, hindered phenol OH); nmr ($CDCl_3$) δ 7.2–7.6 (m, 5, C_6H_5), 6.86 (s, 2, *meta* H of tetrasubstituted ring), 5.08 (s, 1, OH), 4.61 (overlapping dt appearing as a five-peak m, 1, J_{HP} = 15, J_{HH} = 8 Hz, $ArCH_2CHP$), 3.33 (distorted t, 2, $J_{HP} \cong J_{HH} \cong$ 8 Hz, $ArCH_2CHP$), 2.2–2.7 (m, 6, 3 CH_2Pr), 1.2–1.6 (m with strong s at 1.34 ppm, 30, 3 $CH_2CH_2CH_3$ and 2 *t*-Bu), and 0.91 ppm (highly distorted t, 9, $J \cong$ 6 Hz, 3 CH_2CH_3).

Anal. Calcd for $C_{34}H_{56}ClOP$: C, 74.62; H, 10.32; Cl, 6.48; P, 5.66. Found: C, 74.49; H, 10.36; Cl, 6.57; P, 5.62.

In a similar experiment, the quinone methide solution was added during 20 min, and the mixture was acidified 15 min after the addition was complete. The crude product (**19a**) was recovered in quantitative yield; it melted at 179–181° and contained only traces of impurities detectable by nmr analysis.

Attempted Decompositions of Betaines 18a and 18b.—A solution of betaine **18a** was obtained in the manner described above by rapid addition of a solution of quinone methide **2** [from 2.55 g (10.0 mmol) of phenol **1** and 1.06 g (10.5 mmol) of triethylamine] in dry benzene (60 ml) to a solution of ylide **17** [from 6.21 ml (10.0 mmol) of 15.20% *n*-butyllithium in hexane and 3.30 g (10.0 mmol) of benzyltri-*n*-butylphosphonium chloride] in dry benzene (40 ml). The mixture was refluxed vigorously with stirring under nitrogen for 5.0 hr, then cooled to room temperature, and saturated with gaseous HCl. After filtering with suction to remove a white solid (infusible and hygroscopic, evidently LiCl, 0.45 g, 106%), the solution was reduced by boiling to a volume of *ca.* 30–40 ml, cooled to room temperature, and diluted with petroleum ether (*ca.* 75 ml, bp 30–60°). The precipitate was recovered by vacuum filtration and washed repeatedly with petroleum ether; it weighed 4.86 g and was shown by nmr analysis to be essentially pure **19a** (yield, 89%) containing no detectable amount of stilbenol **8**. Evaporation of the combined filtrate and washings yielded 0.44 g of pale brown, very viscous oil containing **19a** (50–75 mol %) and unidentified compounds, but very little (if any) of **8** (analysis by nmr).

n-Butyllithium (0.62 ml of a 15.20% solution in hexane, 1.0 mmol) was added to a nitrogen-flushed suspension of phosphonium chloride **19a** (1.09 g, 1.99 mmol) in dry benzene (20 ml). The mixture was refluxed under nitrogen with stirring for 17.8 hr, cooled to room temperature, acidified with gaseous HCl, and then filtered with suction to remove LiCl. The LiCl was washed repeatedly with benzene, and the combined filtrate and washings were evaporated under vacuum. Nmr analysis showed that the solid residue was essentially pure **19a** (1.10 g, 101%); no trace of **8** could be detected.

A solution of phosphonium chloride **16** (3.59 g, 10.0 mmol) in dry benzene (40 ml) was degassed by bubbling with nitrogen and then treated with *n*-butyllithium in hexane (6.21 ml of 15.20% solution, 10.0 mmol). The mixture was stirred under nitrogen for 2.1 hr, combined with a freshly prepared solution of quinone methide **2** [from 2.55 g (10.0 mmol) of phenol **1** and 1.06 g (10.5 mmol) of triethylamine] in dry benzene (60 ml), and refluxed vigorously with stirring under nitrogen for 92.5 hr. Acidification with anhydrous HCl, followed by suction filtration, washing of the recovered LiCl with dry benzene, and evaporation under vacuum of the combined filtrate and washings afforded a semisolid residue which was shown to be mostly the phosphonium chloride **19b** (6.21 g, crude yield 108%) by nmr analysis ($CDCl_3$): δ 7.27–7.49 (AA' portion of AA'BB'X m having X = phosphorus, 2, aromatic H *meta* to CH_3O), 6.80–7.02 (BB' portion of the AA'BB'X m overlapping with s at 6.86 ppm, 4, aromatic H *ortho* to CH_3O, aromatic H *meta* to OH), 5.38 (broad s, 1, OH), 4.45 (overlapping dt appearing as a five-peak m, 1, J_{HP} = 15, J_{HH} = 8 Hz, $ArCH_2CHP$), 3.80 (s, 3, CH_3O), 3.29 (distorted t, 2, $J_{HP} \cong J_{HH} \cong$ 8 Hz,

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(29) C. R. Bohn and T. W. Campbell, *J. Org. Chem.*, **22**, 458 (1957).

(30) J. Lee, A. Ziering, L. Berger, and S. D. Heineman, *Jubilee Vol. Dedicated Emil Christoph Barell*, 264 (1946); *Chem. Abstr.*, **41**, 6246 (1947).

(31) We are indebted to Dr. J. J. R. Reed for performing this computation.

(32) G. Witschard and C. E. Griffin, *J. Chem. Eng. Data*, **9**, 255 (1964).

$ArCH_2CHP$), 2.2–2.6 (m, 6, 3 CH_2Pr), 1.2–1.7 (m with intense s at 1.34 ppm, 30, 3 $CH_2CH_2CH_3$ and 2 *t*-Bu), and 0.91 ppm (highly distorted t, 9, $J \cong 6$ Hz, 3 CH_2CH_3).

Reaction of Phosphonium Chloride (3) with *n*-Butyllithium.—*n*-Butyllithium solution (15.20% in hexane, 1.24 ml, 2.00 mmol) was added to a mixture of **3** (0.914 g, 2.00 mmol) and dry benzene (20 ml) that had previously been degassed by the freeze–thaw method and blanketed with nitrogen. After 2.0 hr of stirring at room temperature, the mixture was stirred for 1.0 hr under vigorous reflux, cooled (all operations described thus far were performed under nitrogen), saturated with anhydrous HCl, and filtered with suction. The precipitate (an infusible, hygroscopic white powder: presumably LiCl) was washed with several small portions of benzene, and the combined filtrate and washings were evaporated under vacuum. Nmr analysis showed that bisphenol **9** (yield, 55–65%) and phosphonium chloride **3** (recovery, 30–40%) were major constituents of the semisolid residue (0.95 g). These identifications were confirmed by peak enhancements produced by the addition of authentic specimens, and the presence of **9** was also indicated by vpc and mass spectral analysis.

***trans*-3,5-Di-*t*-butyl-4-stilbenol (8) from 4-Benzylmethylene-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (20).**—A solution of quinone methide **20** (0.31 g, 1.0 mmol) in dry benzene (5 ml) was degassed by bubbling with nitrogen. Tri-*n*-butylphosphine (0.20 g, 1.0 mmol) was then added with stirring, and the solution was allowed to stand at room temperature for 3.3 hr. Evaporation under vaccum left an oily residue that solidified when scratched. Drying of the solid on a porous plate gave snow-white microcrystals, mp 89.5–90°, which were shown to be essentially pure **8** by a mixture melting point determination and nmr analysis.

A solution of quinone methide **20** (0.073 *M*) and tri-*n*-butylphosphine (0.160 *M*) in C_6D_6 was examined by nmr 2–3 min after preparation. The spectrum showed that **20** had undergone quantitative conversion to **8** during the brief reaction period.

Registry No.—Tributylphosphine, 998-40-3; **2,** 2607-52-5; **3,** 24164-84-9; **4,** 24164-85-0; **8,** 21449-69-4; **13,** 24164-86-1; **16,** 24164-87-2; **19a,** 24164-88-3; **19b,** 24164-89-4.

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Diels–Alder Adducts of Acetoxy-1,3-dienes and *p*-Benzoquinone

JOSEPH WOLINSKY AND ROBERT B. LOGIN[1]

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

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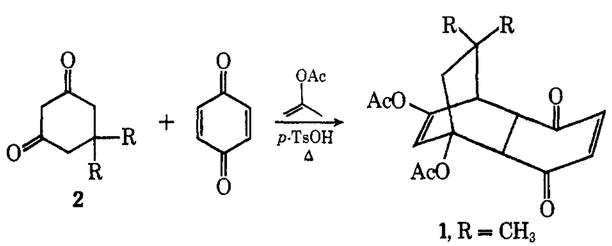
Cyclic acetoxy-1,3-dienes, generated *in situ* from 1,3-cyclohexanediones or isophorone, undergo Diels–Alder reaction with *p*-benzoquinone to afford 5,8-ethano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives. The hydrolysis, aromatization, and Grob fragmentation of these derivatives are discussed.

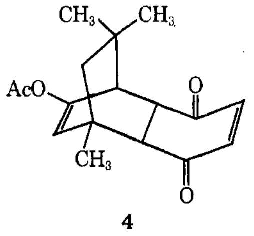
The first paper[2] in this series described the *in situ* generation of acetoxy-1,3-dienes by the reaction of isopropenyl acetate with a variety of cyclic enones and diones, and their reaction with maleic anhydride. We now report the reaction of these acetoxy-1,3-dienes with *p*-benzoquinone and describe the hydrolysis products obtained from the resulting adducts.

When dimedone (**2**, R = CH_3) or 1,3-cyclohexanedione is heated with an equivalent amount of *p*-benzoquinone in isopropenyl acetate containing a catalytic amount of *p*-toluenesulfonic acid, crystalline adducts **1** and **3** are obtained in about 55% yield.

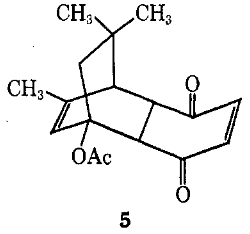


1, R = CH_3
3, R = H

Isophorone, which gives two different enol acetates, similarly afforded a mixture of adducts **4** and **5** in a 42:58 ratio.

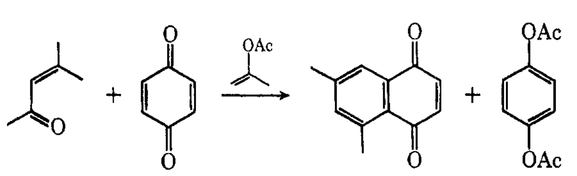


4



5

Attempts to condense *p*-benzoquinone with other conjugated carbonyl compounds such as crotonaldehyde, tiglaldehyde, and 2-cyclopentylidene–cyclopentanone[3] gave tars and no recognizable products other than hydroquinone diacetate. Mesityl oxide also gave a complicated mixture from which 4,7-dimethyl-1,4-naphthoquinone (14%) and hydroquinone diacetate (43%) were isolated. The naphthoquinone probably arises by elimination of acetic acid and dehydrogenation of the 1:1 adduct produced from 4-acetoxy-2-methyl-1,3-pentadiene.



The isolation of adducts **1**, **3**, **4**, and **5** is surprising in view of the powerful enol acetylating conditions employed in this Diels–Alder condensation. The failure to induce aromatization may in part be attributed to the inherent strain of the bicyclo[2.2.2]octadiene system which would be produced since treatment of **1** and **3** with aqueous acid resulted in hydrolysis of both acetate groups and aromatization to give ketoquinols **6a**

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[1] David Ross Fellow, 1968–1969.

[2] C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

[3] This conjugated ketone reacts readily with maleic anhydride under the conditions of this Diels–Alder reaction to give a 1:2 adduct, which will be described in a forthcoming publication.