tilled under vacuum. The temperature of the oil bath was gradually raised to 160°. A forerun, 20 g, bp 39° (0.15 mm), was followed by the main fraction which afforded 132.7 g (96.3%) of X: bp 42–44° (0.15 mm); $n^{20}D$ 1.5324. The ir spectrum was superimposable with that of X, obtained above.

C. With Triphenylphosphine in Ether.—A solution of IX, 34.8 g (0.1 mol), in 50 ml of ether was added dropwise with stirring to a solution of triphenylphosphine, 52.4 g (0.2 mol), in 1000 ml of ether at 25–35°. After the addition was complete, no starting material could be detected in solution by means of glpc. Water, 500 ml, was added dropwise with stirring. Triphenylphosphine oxide precipitated out shortly afterward and was removed by suction-filtration. The ether layer was dried ($CaCl_2$) and evaporated to dryness. The crude product was purified by distillation to give 39.8 g (82.1%) of 1,1,2,4,4-pentachloro-1-buten-3-one (XII): bp 89° (9 mm); $n^{20}D$ 1.5440; d^{20}_4 1.6628 [lit.[24] bp 99–100° (13 mm); $n^{20}D$ 1.4442]; ir (film) 5.9 (C=O) and 6.5 μ (C=O); uv max 212 mμ (ε 7953) and 271 (3071); nmr δ 6.76.

Anal. Calcd for C_4HCl_5O: C, 19.8; H, 0.4; Cl, 73.2. Found: C, 20.0; H, 0.7; Cl, 73.2.

1-Phenyl-4,5-dichloro-3-dichloromethylpyrazole (XIV).—To a solution of 24.25 g (0.1 mol) of XII in 300 ml of ether was added dropwise a solution of 21.6 g (0.2 mol) of phenylhydrazine in 50 ml of ether. After 30 min 200 ml of water was added. The organic layer was dried (Na_2SO_4) and evaporated to dryness. The crude pyrazole was purified by distillation under vacuum to give 12.43 g (42%) of pure XIV, which solidified: bp 142° (0.4 mm); mp 55–55.5° [lit.[21] mp 57.5–58°; bp 155° (0.8 mm)]; uv max 247 mμ (ε 11,566); nmr δ 7.00 (aliphatic H) and 7.45 (aromatic H).

Anal. Calcd for $C_{10}H_6Cl_4N_2$: C, 40.5; H, 2.0; Cl, 47.9; N, 9.5. Found: C, 40.4; H, 2.2; Cl, 47.5; N, 9.7.

(24) A. Roedig and H. J. Becker, *Ber.*, **89**, 906 (1956).

Reaction of Octachlorobutanone (IX) and 1,1,2,4,4,4-Hexachloro-1-buten-3-one (X) with Trialkyl Phosphites.—The results are summarized in Table I. The general procedures are illustrated by the reactions of IX and X with trimethyl phosphite.

A.—To a stirred solution of IX, 34.8 g (0.1 mol), in 50 ml of ether was added dropwise trimethyl phosphite, 24.8 g (0.2 mol). The reaction was exothermic and the ether started to boil. The reaction mixture was heated to reflux for 10 min. Ether was removed under vacuum and the residual oil was distilled to give 13.0 g (90%) of dimethyl phosphorochloridate (IVa), bp 60–62° (8 mm), identical (glpc) with the product obtained by dechlorination of I with trimethyl phosphite (see above). The vinyl phosphate XVI (R = CH_3) distilled at 88–89° (0.01 mm): 26.6 g (76%); $n^{20}D$ 1.5173; d^{20}_4 1.5869. The ester is a colorless liquid and turns light yellow on storage for several weeks when exposed to sunlight: uv max 208 mμ (ε 20,088) and max 247 (7375); ir (film) 6.35 (C=C) and 7.7 μ (P→O).

B.—To a stirred solution of X, 10.65 g (0.0385 mol) in 20 ml of ether, was added trimethyl phosphite, 6.2 g (0.05 mol), dissolved in 20 ml of ether. The reaction was exothermic. Ether was removed and the residual oil was purified by distillation to give 12.9 g (95.5%) of XVI (R = CH_3): $n^{20}D$ 1.5163; d^{20}_4 1.5899; uv and ir spectrum were identical with the product obtained in A.

Registry No.—II, 13340-09-5; IVa, 813-77-4; V, 18791-16-7; VIIa, 18766-86-4; VIIb, 18791-17-8; X, 13340-11-9; XII, 13340-10-8; XIV, 18767-09-4; XVI (R = Me), 18767-10-7; XVI (R = C_2H_5), 18767-11-8; XVI [R = $CH(CH_3)_2$], 18767-12-9; XVI (R = $CH_2CH{=}CH_2$), 18767-13-0; XVI (R = n-C_4H_9), 18767-14-1; XVI (R = n-C_5H_{11}), 18767-15-2; XVI (R = n-C_6H_{13}), 18791-18-9.

The Reactions of Triphenylphosphine with α-Halobenzyl Phenyl Ketones and with α-Mesyloxybenzyl Phenyl Ketone[1]

IRVING J. BOROWITZ,[2] PAUL E. RUSEK, AND REIN VIRKHAUS

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, and the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033

Received October 21, 1968

The reactions of α-bromobenzyl phenyl ketone (**11**) and α-chlorobenzyl phenyl ketone (**14**) with triphenylphosphine are described. Both enol phosphonium and ketophosphonium halides are formed in ratios dependent upon reaction conditions. The enol phosphonium halides are solvolyzed to deoxybenzoin (**16**) and converted into diphenylacetylene (**17**). Debromination of **11** to **16** occurs with triphenylphosphine in the presence of methanol. α-Mesyloxybenzyl phenyl ketone (**19**) reacts with triphenylphosphine to give only the α-ketophosphonium mesylate *via* displacement of mesylate ion. Probable mechanisms for the observed reactions and the relationships of these reactions to the reactions of other α-halo ketones with phosphines are discussed.

Recent work has shown that the reactions of triphenylphosphine with α-bromoacetophenone (**1**) and with α-bromopropiophenone (**2**) give the corresponding α-ketotriphenylphosphonium bromides in aprotic solvents.[3,4] Our kinetic studies indicate that both **1** and **2** probably react with triphenylphosphine *via* displacement of bromide ion under aprotic conditions.[5,6]

We and others have previously postulated that the reactions of certain α-halo ketones such as 2-bromodimedone and the α-halobenzyl phenyl ketones (desyl halides) with triphenylphosphine can involve the formation of enol phosphonium salts.[7,8] Enol phosphonium salts including **7–10** have been isolated from the reaction of triphenylphosphine with chlorobenzhydryl phenyl ketone **3**,[9] the corresponding bromo ketone **4**,[10a] dibromobenzyl phenyl ketone **5**,[10b] dibromopropiophenone (**6**), and from other α-dihalo ketones[10a] (Scheme I).

It has been suggested that enol phosphonium salts may arise *via* displacement by triphenylphosphine on halogen of an α-halo ketone to give an enolate halotri-

(1) This investigation was supported by National Science Foundation Grants GP 1354 and 5978. This is part IX of the series, Organophosphorus Chemistry.

(2) To whom correspondence should be addressed at the Belfer Graduate School of Science, Yeshiva University.

(3) (a) I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963); (b) I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

(4) (a) F. Ramirez and S. Dershowitz, *ibid.*, **22**, 41 (1957); (b) A. V. Dombrovskii and M. I. Shevchuk, *Zh. Obshch. Khim.*, **33**, 1263 (1963).

(5) I. J. Borowitz and H. Parnes, *J. Org. Chem.*, **32**, 3560 (1967).

(6) H. Parnes, Yeshiva University, unpublished results.

(7) I. J. Borowitz and L. I. Grossman, *Tetrahedron Lett.*, 471 (1962).

(8) D. B. Denney and L. C. Smith, *J. Org. Chem.*, **27**, 3404 (1962).

(9) R. D. Partos and A. J. Speziale, *J. Amer. Chem. Soc.*, **87**, 5068 (1965).

(10) (a) K. C. Kirby, Jr., Yeshiva University, unpublished results; (b) P. E. Rusek, Yeshiva University, unpublished results.

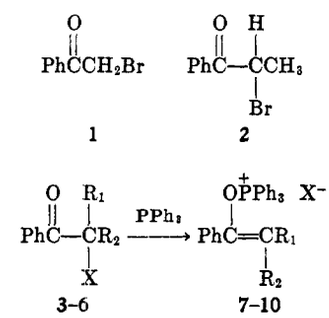
TABLE I

THE REACTIONS OF α-BROMOBENZYL PHENYL KETONE WITH TRIPHENYLPHOSPHINE

Reaction conditions	Time	Yields, %[a] α-Ketophosphonium bromide	Enol phosphonium bromide	Deoxybenzoin	Diphenylacetylene	Triphenylphosphine oxide
Benzene[b,c] (0.13 *M*)	24 hr	58		34[d]	4	44
Benzene–methanol[b]	23 hr	0		100[d]		100
Acetonitrile[b]	4 days	29		49	19	
Glyme[b] (1.3 *M*)	24 hr	79		15		
Glyme, room temp	2 weeks	13	73[f,g]			
Acetonitrile[e] (0.16 *M*)	7 days	21	70[f,g]	9		
Nitromethane[e]	7 days	15	70[f,g]	15		
Glyme–methanol[e]	24 hr			100[f]		100[f]
Nitromethane–methanol[e]	24 hr			100[f]		100[f]
Acetonitrile–methanol[e]	24 hr			100[f]		100[f]

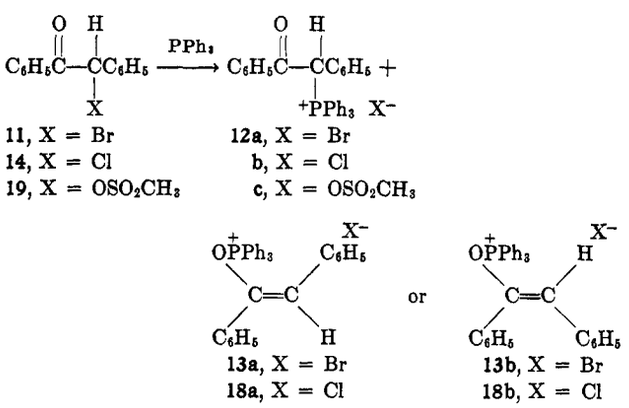
[a] 1.0–1.1 equiv of PPh_3 was used. Isolated yield unless otherwise indicated. [b] At reflux. [c] Same result from reaction in glyme (24 hr) or in toluene (24, 48 hr) at reflux. [d] By uv or vpc analysis. [e] At room temperature. [f] By nmr analysis. [g] Actually isolated.

SCHEME I



3, 7, X = Cl; $R_1 = R_2$ = Ph
4, 8, X = Br; $R_1 = R_2$ = Ph
5, 9, X = R_1 = Br; R_2 = Ph
6, 10, X = R_1 = Br; $R_2 = CH_3$

SCHEME II



phenylphosphonium ion pair. Such an ion pair could then recombine to give the observed enol phosphonium salt.[7,11] The actual mechanism of enol phosphonium salt formation has remained unsettled. It is being investigated by us with the aid of the related reactions of appropriate α-halo ketones with optically active methylpropylphenylphosphine.[12]

We now report our results on the reactions of triphenylphosphine with the α-halobenzyl phenyl ketones and with α-mesyloxybenzyl phenyl ketone. Ketophosphonium and enol phosphonium salts as well as derived products are formed in these reactions.

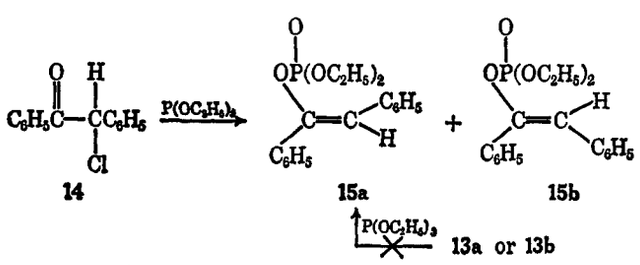
Results and Discussion

The Reactions of α-Bromobenzyl Phenyl Ketone.—α-Bromobenzyl phenyl ketone (desyl bromide) **11** reacts with triphenylphosphine in various solvents at room temperature (0.13–0.16 *M*) to give small yields (5–21%) of the α-ketophosphonium bromide **12** (Table I). High yields (58–85%) of **12** are obtained at higher temperature (80–111°) or with higher concentrations of the reagents. The best procedure for obtaining a high yield of **12** (79–85%) involves reaction of **11** with triphenylphosphine (1.3 *M* each) in dimethoxyethane (glyme) at reflux temperature (Scheme II).

The room-temperature reactions of **11** with triphenylphosphine, as followed by nmr spectroscopy, give the enol phosphonium bromide **13** as the main product (70–95%). The enol phosphonium bromide exhibits a vinyl proton doublet at τ 3.38 with J_{PH} = 1.8 Hz. The presence of one vinyl proton doublet probably indicates that only one isomer of **13** is present. It is anticipated that if both geometric isomers of **13** were present two vinyl proton doublets with different J_{PH} values would be observed. Two doublets are observed for several enol phosphates derived from the reactions of α-halo ketones with triethyl phosphite.[13] Thus α-chlorobenzyl phenyl ketone **14** reacts with triethyl phosphite to give a 1:2 ratio of **15b**:**15a** with vinyl doublets at τ 3.31 (J = 2.5 Hz) and 3.65 (J = 1.0 Hz).[14] Our evidence indicates that the smaller J_{HP} value most probably belongs to the *trans* isomer **15a**.

An attempt to convert **13** to **15a** and/or **15b** directly by treatment with triethyl phosphite was unsuccessful

SCHEME III



(11) A. J. Speziale and L. J. Taylor, *J. Org. Chem.*, **31**, 2450 (1966).

(12) (a) O. Korpiun and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 4784 (1967); (b) D. B. Denney and N. G. Adin, *Tetrahedron Lett.*, 2569 (1966); (c) L. Horner and H. Winkler, *ibid.*, 455 (1965).

(13) I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

(14) S. Firstenberg, Yeshiva University, unpublished results.

TABLE II
THE REACTIONS OF α-CHLOROBENZYL PHENYL KETONE (14) WITH TRIPHENYLPHOSPHINE

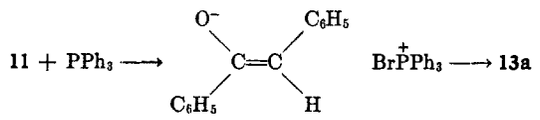
Reaction conditions	Time	Yields, %[a] α-Ketophosphonium bromide	Enol phosphonium bromide	Diphenylacetylene	Deoxybenzoin	Triphenylphosphine oxide
Benzene, reflux	20 hr	12[b,c]		17	31	82
Acetonitrile, reflux	10 days	31.5		14	41	*e*
Glyme, reflux	24 hr	12			78	*e*
Methanol[d]	38 days	41			*e*	*e*
Glyme[d]	14 days		100,[f] 85[g]			
Acetonitrile[d]	7 days	50[f]	50[f]			*e*
Nitromethane[d]	7 days	53–61			29	*e*
Glyme–methanol[d]	14 days				86	*e*
Acetonitrile–methanol[d]	14 days	48			32	*e*
Nitromethane–methanol[d]	14 days	56			33	*e*

[a] 1.0–1.1 equiv of PPh_3 was used. Isolated yield unless otherwise indicated. [b] Same yield from reaction in toluene (24 hr) at reflux. [c] Unreacted **14** was recovered (25%). [d] At room temperature. [e] Present by tlc. [f] Yield by nmr. [g] Actually isolated.

(Scheme III). The displacement of triphenylphosphine from an enol phosphonium salt with the more nucleophilic diethylphenylphosphine has been noted.[15] We have successfully used tributylphosphine in such a displacement (see Experimental Section). Even though displacement by triethyl phosphite should irreversibly lead to an enol phosphate, the poorer nucleophilicity of the phosphite when compared with that of triphenylphosphine[16] renders such displacement unlikely.

While there is yet no firm evidence for the stereochemical assignment for **13** we favor the *trans* geometry of **13a** on the basis of the observed J_{PH} value of 1.8 Hz and mechanistic reasoning as follows. If enol phosphonium salts are formed *via* the recombination of enolate halotriphenylphosphonium ion pairs then *trans* geometry is expected for **13** since the enolate of deoxybenzoin should be more stable in the *trans* configuration and should react in this configuration (Scheme IV).

SCHEME IV

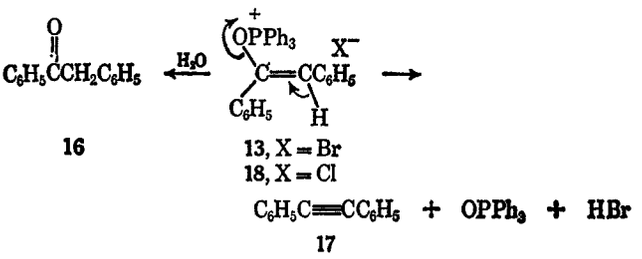


A similar argument can be made for the conversion of **14** into **18a.**

While the room temperature reactions of **11** with triphenylphosphine give only **12** and **13** the higher temperature reactions give **12** and several products derived from **13,** *i.e.*, deoxybenzoin (**16**) and diphenylacetylene (**17**). A number of enol phosphonium salts have been postulated to be or actually are solvolyzed by water to give the corresponding ketone.[9,10,17] We believe that the presence of **16** in our reactions is due to the hydrolysis of **13** by residual moisture in the reaction system or by hydrolysis during work-up.

The formation of **17** is of special interest in that it indicates a synthetic use for enol phosphonium salts. We[7] and others[17,18] have postulated that the previously observed[18,19] formation of **17** from **14** is *via* the enol phosphonium chloride **18.** We demonstrate as will follow that **17** does form from **18,** although to a small extent. Our evidence is sufficient to state that the formation of **17** from **11** is *via* **13** (Scheme V).

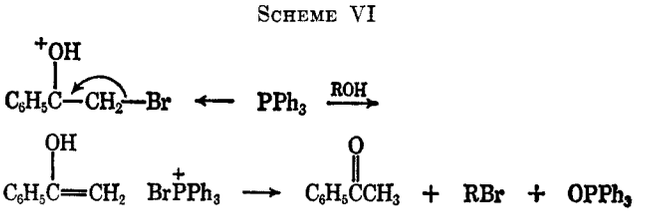
SCHEME V



The debromination of **11** to **16** with triphenylphosphine in the presence of methanol is quantitative in nonpolar or polar solvents (Table I). The debromination of α-bromo ketones by triphenylphosphine and a protic species has been found to be a general reaction[3,7,17,20a] failing only in the case of α-bromocamphor which presents an especially hindered situation.[15,20b]

Our most recent work[6] indicates that the debromination reaction is acid catalyzed in several cases including **2** and **11** and that it most probably involves a change of mechanism from the SN2 type of pathway which is involved in α-ketophosphonium salt formation from **1** or **2**[5,6] (Scheme VI).

SCHEME VI



It now appears that the debromination reaction probably involves attack by phosphine on the bromine of a protonated α-bromo ketone.[21]

The Reactions of α-Chlorobenzyl Phenyl Ketone (14).—The reactions of **14** with triphenylphosphine are summarized in Table II. Enol phosphonium chloride

(15) H. Hoffmann, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964).
(16) G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18**, 38 (1964).
(17) H. Hoffmann and H. J. Diehr, *Tetrahedron Lett.*, 583 (1962).
(18) S. Trippett, *J. Chem. Soc.*, 2337 (1962).
(19) S. Trippett and D. M. Walker, *ibid.*, 2976 (1960).
(20) I. J. Borowitz, K. C. Kirby, Jr., P. E. Rusek, and R. Virkhaus, *J. Org. Chem.*, **33**, 3686 (1968); (b) G. Gonis, Lehigh University, unpublished results.
(21) Our kinetic studies on the debromination reaction are in progress and will be reported elsewhere.

18 is the only product in glyme at room temperature. Reaction in polar solvents, acetonitrile or nitromethane, at room temperature gives 50–61% yields of the ketophosphonium chloride **12b**. The trend toward higher yields of ketophosphonium salt in reactions in polar solvents or those done at higher temperatures in nonpolar solvents noted for **11** is also evident for **14**. Thus reaction of **14** with triphenylphosphine in glyme, benzene, or toluene at reflux gives 12% **12b** as compared with none in glyme at room temperature.

Reaction of **14** with triphenylphosphine in the presence of protic species generally leads to about the same yields of **12b** as do the corresponding reactions in the absence of a protic species. It appears that the lack of dehalogenation in this case is related to the reactions of α-chloracetophenone,[3a] α-chloroacetone,[3a] or α-chloropropiophenone[10b] wherein the yields of α-ketophosphonium chloride are not significantly decreased by the initial presence of a protic species; *i.e.*, displacement of chloride ion occurs even in the presence of protic species.

The yields of desoxybenzoin observed in all of the reactions probably arises from the secondary hydrolysis of the enol phosphonium chloride which forms to some extent under all of the conditions studied. Evidence for the presence of the enol phosphonium chloride in room temperature reactions is based on proton nmr measurements and direct isolation of **18** (see the Experimental Section).

Diphenylacetylene is a minor product in the reactions of **14** with triphenylphosphine. We have not obtained the high yield (90%) of **17** from **14** as noted by Trippett and Walker.[19]

The recovery of starting material in the benzene reaction indicates that **14** reacts more slowly with triphenylphosphine than does **11**. This reactivity difference of bromo ketone > chloro ketone has been noted for numerous sets of α-bromo and α-chloro ketones in reaction with triphenylphosphine.[6,22]

We note that the presence of electron-withdrawing groups on the carbon bearing the halogen of an α-halo ketone enhances enol phosphonium salt formation. Thus, while chloroacetophenone and chloropropiophenone react with triphenylphosphine to give ketophosphonium chlorides, **14** gives both enol and ketophosphonium chlorides and α-chlorobenzhydryl phenyl ketone (**3**) gives only enol phosphonium chloride.[9] A similar distribution of products exists for the corresponding α-bromo ketones.[3,10b]

We believe that the above results are best explained by mechanistic pathways involving SN2 type of displacement of halide ion for the ketophosphonium halides, and attack on halogen followed by recombination of the resultant ion pair for the enol phosphonium halides.[23] The latter pathway will be elaborated upon in the next section of our Discussion. Attack on halogen is electronically enhanced by electron-withdrawing phenyl groups while displacement of halide ion is sterically retarded by them.

The major difference between the α-bromo ketone and the α-chloro ketone series is that the initial presence of protic species causes all of the α-bromo ketones to be debrominated completely while the chloro ketones still give α-ketophosphonium chloride formation. We presume that attack on bromine by triphenylphosphine is a more facile process than attack on chlorine since the latter is less polarizable, *i.e.*, not so "soft" as is bromine.[24]

The Reactions of α-Mesyloxybenzyl Phenyl Ketone (19).—Reaction of benzoin with methanesulfonyl chloride and triethylamine gives **19** in 69% yield. Reaction of **19** with triphenylphosphine in glyme at reflux gives the α-ketophosphonium mesylate **12c** in 81% yield. No other products are noted in this reaction which is the method of choice for the preparation of **12**. The yield of **12c** is not significantly decreased (80%) when **19** is treated with triphenylphosphine in a 4:1 mixture of glyme–methanol. Thus these reactions, as those of other α-keto mesylates with triphenylphosphine, involve simple displacement of mesylate ion. The α-keto mesylate reactions thus serve as simplified models for the more complex reactions of the comparable α-halo ketones with triphenylphosphine.

The lack of enol phosphonium salt formation from **19**, when compared with the behavior of **11** and **14**, again suggests that attack on halogen is involved in enol phosphonium salt formation. This is especially so since **19** reacts more slowly with triphenylphosphine than does **11** or **14**; *i.e.*, the possibility that the clean formation of **12c** from **19** merely involves a faster SN2-type reaction than is found for **11** or **14** is eliminated. It appears that other pathways are available to **11** or **14** that are not available to **19**. The most likely of these pathways is attack on halogen (Scheme IV).

Attack on oxygen by "soft" phosphorus, while found in certain cases where there is really no competitive alternative,[25] is an unlikely process for monohalo ketones. This is due to the lack of polarization for the oxygen atom which is "hard" as compared with the polarizable or "soft" bromine or chlorine atom.[24] Enol phosphonium salts may conceivably be formed by attack of triphenylphosphine at carbonyl oxygen[18,26] or by addition to carbonyl carbon and rearrangement of the phosphorus moiety to oxygen (as suggested by us for the formation of certain enol phosphates[13]). It is difficult to see why these pathways should be completely absent for the mesylate **19** in comparison with the α-halo ketones **11** or **14**.

Reactions of the Enol Phosphonium Salts.—The addition of water to a mixture of **12** and **13** causes the disappearance of the vinyl proton doublet at τ 3.38 and the appearance of the methylene singlet of deoxybenzoin (**16**) at τ 5.7 as followed by nmr spectrometry, *i.e.*, the enol phosphonium salt **13** is readily hydrolyzed by water to **16**.

No reaction occurs if **13** is heated at reflux in glyme for 24 hr or kept at room temperature for 1 week. A similar recovery of **13** occurs if it is treated with triphenylphosphine in glyme at reflux or room tempera-

(22) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, Inc., New York, N. Y., 1965, pp 146–151.

(23) Our results with optically active methyl-*n*-propylphenylphosphine agree with these conclusions and will be published elsewhere.

(24) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

(25) For examples of organophosphorus reactions which are likely to involve addition to carbonyl oxygen, see (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) I. J. Borowitz and M. Anschel, *Tetrahedron Lett.*, 1517, 5032 (1967).

(26) F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, *J. Org. Chem.*, **33**, 25 (1968).

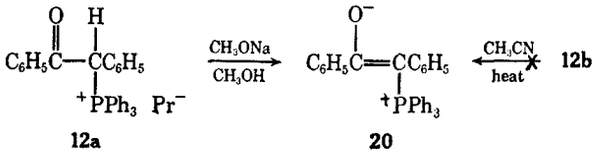
ture for 3 days. There is no formation of diphenylacetylene nor any conversion of **13** into the ketophosphonium salt **12**. Diphenylacetylene (**17**) is formed in 17% yield from the treatment of **13** with acetonitrile at reflux for 64 hr and in 28% yield from similar treatment of **18**.

These results indicate that the enol phosphonium salts **13** and **18** can be decomposed to diphenylacetylene as we had originally suggested. The origin of **17** in some of the reactions of **11** and **14** with triphenylphosphine is thus explained.

The Role of Ketoylide 20.—Conversion of **12a** into α-phenylphenacyltriphenylphosphorane (**20**) is accomplished in 88% yield upon treatment with sodium methoxide in methanol at room temperature (Scheme VII). Treatment of **20** with acetonitrile at reflux gives no reaction. It has been previously noted by Trippett and Walker[19] that **20** decomposes to give **17** under pyrolytic conditions at 300°. Our control experiment indicates that **20** is not involved in the formation of **17** under normal reaction conditions in solution. Furthermore **20** is reasonably stable to hydrolysis[27] and it cannot reasonably be the precursor of desoxybenzoin in the reactions outlined in Tables I and II.

As a further control, ketophosphonium chloride **12b** was shown to be stable to acetonitrile at reflux. No conversion to any other species was found. Thus the enol and keto phosphonium salts do not interconvert and seem to be forming *via* separate pathways.

SCHEME VII



Experimental Section[28]

All of the solvents used were distilled from phosphorus pentoxide, calcium hydride, or lithium aluminum hydride. Reactions were conducted under an atmosphere of dry nitrogen. Organic solutions were dried over magnesium sulfate.

α-Bromobenzyl phenyl ketone was prepared by the bromination of deoxybenzoin in ether in 84% yield, mp 54.5–56° (from EtOH), lit.[29] mp 54–56°.

α-Chlorobenzyl phenyl ketone was obtained from Aldrich Chemical Co., mp 66.5–68° (from hexane), or prepared as in the literature:[30] mp 66.0–67.0°, lit.[30] mp 66–67°.

α-Mesyloxybenzyl Phenyl Ketone.—Methanesulfonyl chloride (2.15 g, 0.0189 mol) in dry benzene (40 ml) was added dropwise over 1 hr to a well-stirred mixture of benzoin (4.0 g, 0.0189 mol) and triethylamine (3.82 g, 0.0378 mole) in benzene (20 ml). After 1 hr of stirring and removal of triethylamine hydrochloride by filtration, the resultant solution was washed with water, dried, evaporated *in vacuo*, and recrystallized from EtOAc and from cyclohexane to give **19** as a white solid (3.80 g, 0.0131 mol, 69%), mp 120–121°. The ir spectrum (CH_2Cl_2) exhibited peaks at 5.89 (C=O), 7.40, and 8.50 μ (OSO_2CH_3); nmr ($CDCl_3$), singlets at τ 6.95 (OSO_2CH_3) and 3.15 (COCH) and a multiplet at 2.0–2.9 (10 aromatic H).

Anal. Calcd for $C_{15}H_{14}O_4S$: C, 62.06; H, 4.85; S, 11.04. Found: C, 62.18; H, 5.00; S, 10.91.

The Reaction of α-Bromobenzyl Phenyl Ketone with Triphenylphosphine. A. In Nonpolar Solvents at Reflux.—α-Bromobenzyl phenyl ketone (2.00 g, 0.00727 mol) and triphenylphosphine (2.02 g, 0.00769 mol) were heated at reflux in benzene (55 ml) for 24 hr. Insoluble white material (2.70 g) was extracted with hot benzene to leave α-phenylphenacyltriphenylphosphonium bromide (**12a**) (2.26 g, 0.0042 mol, 58%), mp 239.5–241° dec, as an insoluble residue. The ir spectrum (KBr) exhibited peaks at 6.08 (s), 6.97 (s), 7.81 (m), 8.30 (m), 9.18 (s) and 10.06 μ (m); nmr ($CDCl_3$), multiplets at τ 1.5–3.0 (aromatic H) and a doublet centered at 1.04 (methine H, $J_{^{31}PH}$ = 12.5 Hz). The analytical sample had mp 243–244° dec (from aqueous EtOH).

Anal. Calcd for $C_{32}H_{26}OPBr$: C, 71.51; H, 4.88. Found: C, 71.72; H, 5.08.

The benzene extract gave crude triphenylphosphine oxide (0.88 g, 0.00317 mol, 44%), mp 149–155°, identified by tlc and its ir ($CHCl_3$) spectrum on a cyclohexane-insoluble fraction. The cyclohexane-soluble fraction gave diphenylacetylene (0.05 g, 0.00028 mol, 4%), identified *via* its uv absorption maximum at 292 mμ and desoxybenzoin (*ca.* 0.50 g, 0.0025 mol, 34%), identified *via* tlc, ir, and mixture melting point (as below).

Similar reactions in glyme (24 hr) or in toluene (24 or 48 hr) gave **12a** in 58% yield. Reaction of more concentrated solutions of α-bromobenzyl phenyl ketone and triphenylphosphine (1.3 *M* each in dry glyme at reflux for 6 hr) gave **12a** in 79–85% yield with desoxybenzoin and triphenylphosphine oxide as the other products.

B. In Acetonitrile at Reflux.—A mixture of α-bromobenzyl phenyl ketone (2.99 g, 0.0109 mol) and triphenylphosphine (3.09 g, 0.0118 mol) in acetonitrile (70 ml) was kept at reflux for 4 days. Removal of the solvent *in vacuo* gave an oil which was slurried in glyme to give **12a** (1.70 g, 0.00315 mol, 29%), mp 239.5–241.0° (ir, nmr spectra as above). The residual mixture was dried *in vacuo*, dissolved in benzene (3 ml), and chromatographed on a column of silica gel (100 g). Elution with benzene (progress monitored *via* tlc) gave diphenylacetylene (0.362 g, 0.00207 mol, 19%), mp 58–59.5°, mmp 57.5–59.5°. Further elution with benzene gave deoxybenzoin (1.05 g, 0.0054 mol, 49%), mp 54–56° (from methanol), mmp 53–56°.

C. In Various Solvents Containing Methanol.—A mixture of α-bromobenzyl phenyl ketone (3.00 g, 0.0159 mol), triphenylphosphine (2.85 g, 0.00159 mol), and methanol (1.50 g, 0.0477 mol) in acetonitrile (20 ml) was stirred at room temperature for 24 hr. After removal of the solvent *in vacuo*, the nmr spectrum of the residue indicated triphenylphosphine oxide and deoxybenzoin (100% yield); nmr ($CDCl_3$), a multiplet at τ 1.7–3.0 (25 aromatic H) and a singlet at 5.80 (2 methylene H). The same results were obtained from reactions in methanol–benzene at reflux and methanol–glyme or methanol–nitromethane at room temperature. Work-up of the benzene–methanol reaction by chromatography on acid-washed alumina gave (1) deoxybenzoin (99–100%) *via* elution with benzene and (2) triphenylphosphine oxide, mp 149–157° (100%), *via* elution with 95% ethanol.

D. In Aprotic Solvents at Room Temperature.—α-Bromobenzyl phenyl ketone (6.0 g, 0.0218 mol) and triphenylphosphine (6.06 g, 0.0231 mol) were stirred in glyme (15 ml) at room temperature until the lack of a precipitate with mercuric chloride indicated the absence of triphenylphosphine[3b] (2 weeks). The resultant solid was filtered under nitrogen and dried *in vacuo* to give a mixture of the ketophosphonium bromide **12a** and the enol phosphonium bromide **13** (10.2 g, 0.0187 mol, 86%). The mixture consisted of 15% **12a** and 85% **13** corresponding to a 13% yield of **12a** and a 73% yield of **13**: ir (CH_2Cl_2), 3.0–3.5, 6.00 (C=O), 7.0, 9.0, and 9.6–10.4 μ; nmr ($CDCl_3$), a doublet centered at τ 0.75 (methine H of **12a**, $J_{^{31}PH}$ = 12.5 Hz), a multiplet at 1.5–3.0 (25 aromatic H), and a doublet centered at 3.38 (vinyl proton of **13**, $J_{^{31}PH}$ = 1.8 Hz).

Similar results were obtained in acetonitrile and in nitromethane at room temperature (Table I).

The Reaction of α-Chlorobenzyl Phenyl Ketone with Triphenylphosphine. A. In Aprotic Solvents at Reflux.—α-Chlorobenzyl phenyl ketone (**14**) (11.30 g, 0.0491 mol) and triphenylphosphine (13.10 g, 0.050 mol) were heated at reflux in dry glyme (15 ml) for 24 hr to give α-phenylphenacyltriphenylphosphonium chloride (**12b**) (2.9 g, 0.0059 mol, 12%): mp

(27) H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962).

(28) The instrumental and other techniques used have been recorded previously.[3b]

(29) H. Limpricht and H. Schwanert, *Ann.*, **155**, 59 (1870).

(30) A. M. Ward, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 159.

237–240°; ir (CH_2Cl_2), 6.0 (C=O), 6.95, and 9.06 μ; nmr ($CDCl_3$), a multiplet at τ 1.4–3.1 (25 aromatic H) and a doublet centered at 0.35 (methine H, $J_{^{31}PH}$ = 12.5 Hz). Thin layer chromatography showed triphenylphosphine oxide and deoxybenzoin (isolated in 78% yield) to be the only other species formed. The same yield of **12b** was obtained from reactions in benzene or in toluene (Table II). Similar reaction of **14** (1.32 g, 0.0057 mol) in acetonitrile (40 ml) at reflux for 10 days, followed by a work-up as for the reaction of **11** (above), gave **12b** (0.90 g, 0.0018 mol, 31.5%), mp 237–240°, diphenylacetylene (0.143 g, 0.00081 mol, 14%), mp 57–59° [from petroleum ether (bp 30–60°)], deoxybenzoin (0.462 g, 0.0023 mol, 41%), and triphenylphosphine oxide.

B. In Aprotic Solvents at Room Temperature.—Reaction of **14** (11.3 g, 0.0491 mol) and triphenylphosphine (13.0 g, 0.050 mol) in glyme (15 ml) for 14 days at room temperature (reaction complete by lack of precipitate with mercuric chloride) gave the enol phosphonium chloride **18** as a white solid which could be filtered under nitrogen from the mixture (20.9 g, 0.0425 mol, 85% isolated yield, 100% yield by nmr): ir (CH_2Cl_2), 3.2–3.5, 7.0, 9.0, 9.9, and 10.1 μ; nmr ($CDCl_3$), a multiplet at τ 1.7–3.0 (25 aromatic H) and a doublet centered at 3.45 (1 vinyl H, $J_{^{31}PH}$ = 2.0 Hz).

Similar reaction of **14** and triphenylphosphine (0.050 mol each) in acetonitrile (15 ml) (Table II) gave, after removal of the solvent *in vacuo*, a 1:1 mixture of enol and ketophosphonium salts as an oil: nmr ($CDCl_3$), a multiplet at τ 1.7–3.0 (25 aromatic H) and doublets centered at 3.45 (vinyl H of **18**, $J_{^{31}PH}$ = 2.0 Hz) and 0.35 (methylene H of **12b**, $J_{^{31}PH}$ = 12.5 Hz). Similar reaction in nitromethane gave **14** (53–61%) and deoxybenzoin (29%), mp 54–56°. No diphenylacetylene was found in these reactions (tlc).

C. In Methanol or Methanol-Containing Solvents.—Reaction of **14** and triphenylphosphine (0.017 mol each) in methanol (20 ml) for 5.5 weeks at room temperature gave, after removal of the solvent *in vacuo*, an oil which was slurried in glyme to give **12b** (3.44 g, 0.007 mol, 41%), mp 238.5–240.5°. The residue contained triphenylphosphine oxide and deoxybenzoin (by tlc on silica gel using 5% EtOAc–C_6H_6 for development). Similar reaction and work-up as for **11** for reactions done in methanol-containing solvents gave yields indicated in Table II.

The Reactions of α-Mesyloxybenzyl Phenyl Ketone with Triphenylphosphine.—Reaction of **19** and triphenylphosphine (0.00655 mol each) in glyme (15 ml) at reflux for 24 hr gave **12c** as a white powder (3.05 g, 0.0053 mol, 81%): mp 247–248.5°; ir (CH_2Cl_2), 5.98 (C=O) and 8.3–8.5 μ ($^-OSO_2CH_3$); H^1 nmr ($CDCl_3$), a multiplet at τ 1.6–3.1 (25 aromatic H and 1 methine H) and a singlet at 7.25 (3 H of OSO_2CH_3); ^{31}P nmr ($CDCl_3$), −25.6 ppm (H_3PO_4 = 0).[31] A similar reaction in 4:1 (v/v) glyme–methanol gave **12c** in 80% yield.

The Conversion of the Enol Phosphonium Halides 13 and 18 into Diphenylacetylene.—A 1:1 mixture of the ketophosphonium chloride **12b** and the enol phosphonium chloride **18** (a total of 0.022 mol) was heated at reflux for 64 hr in acetonitrile (500 ml) to give recovered **12b** (4.87 g, 0.0099 mol, 45.5%), mp 239–241°, mmp 238–241.5°. The residual oil was chromatographed over silica gel (200 g). Elution with benzene gave diphenylacetylene (0.54 g, 0.0030 mol, 28% based on **18**), mp 57–57.5°, mmp 57.5–60°. The reaction mixture also contained deoxybenzoin and triphenylphosphine oxide (tlc).

Similar treatment of the enol phosphonium bromide **13** gave diphenylacetylene (17%), deoxybenzoin, and triphenylphosphine oxide.

Reaction of **13** in glyme at reflux with or without the presence of triphenylphosphine (1 equiv) for 3–7 days led to recovered **13** in 82 and 95% yields, respectively.

The Hydrolysis of the Enol Phosphonium Bromide 13.—Water (4 drops) was added to a solution of **13** (0.602 g, 0.0011 mol) in $CDCl_3$ (1 ml) in a nmr tube. After 5 min of shaking, **13** was completely hydrolyzed since the nmr spectrum showed the absence of the vinyl proton of **13** at τ 3.3 and the presence of the methylene protons of desoxybenzoin at 5.8.

Attempted Reaction of 13 with Triethyl Phosphite.—The enol phosphonium bromide **13** (2.0 g, 0.0037 mol) and triethyl phosphite (0.616 g, 0.0037 mol) were heated at reflux for 3 days in dry benzene (10 ml, distilled from $LiAlH_4$) to give a black mass which contained triethyl phosphate, triphenylphosphine oxide, and deoxybenzoin (tlc).

The Reaction of 13 with Tributylphosphine.—Tributylphosphine (0.189 g, 0.000934 mol) was added to **13** (0.501 g, 0.000934 mol) in $CDCl_3$ (1 ml). Triphenylphosphine was formed immediately (by tlc and formation of the adduct with mercuric chloride).

The Formation of α-Phenylphenacyltriphenylphosphorane (20).—Sodium methoxide (0.21 g, 0.0039 mol) in methanol (10 ml) was added to a stirred solution of **12a** (2.00 g, 0.0037 mol) in methanol (25 ml) and stirring was continued for 30 min.[4b] The resultant solution was poured into water (200 ml) to give a white precipitate which was washed with water and recrystallized twice from EtOAc to give **20** (1.5 g, 0.0033 mole, 88%): mp 195–197° (lit.[28] mp 192–194°); uv, λ_{max}^{MeOH} 320 (ϵ 7200), 275, 267.5, 262 mμ; ir ($CHCl_3$), 6.68 (vs), 6.75 (vs), 6.95 (s), 7.23, 8.85, 9.04 (s), 9.33, 9.73, 10.0, and 10.33 μ; tlc (25% MeOH–C_6H_6), R_f 0.74 *vs.* 0.59 for triphenylphosphine oxide.

A solution of **20** (0.253 g, 0.00055 mol), mp 190–195°, in acetonitrile (10 ml) was heated at reflux for 24 hr to leave only **20** (0.25 g, 100%), mp 187–194°.

The Stability of α-Phenylphenacyltriphenylphosphonium Chloride in Acetonitrile at Reflux.—A solution of **12b** (0.30 g, 0.00061 mol) in acetonitrile (10 ml) was heated at reflux for 24 hr to give recovered **12b** (0.31 g, 100%), mp 233–238°, ir ($CHCl_3$) identical with that of genuine **12b**.

Registry No.—Triphenylphosphine, 603-35-0; **11**, 1484-50-0; **12a**, 1530-47-8; **12b**, 19254-98-9; **12c**, 19254-99-0; **14**, 447-31-4; **19**, 19255-01-7.

Acknowledgment.—We are indebted to Professor Claibourne E. Griffin, University of Pittsburgh, for the early nmr spectra and to Professor Grace Borowitz, Upsala College, for stimulating discussions and aid in obtaining ^{31}P nmr spectra.

(31) The ^{31}P nmr spectrum was kindly determined by Jeolco, Inc., at 24.29 and at 40 MHz on JNM C-60HL and C-100 spectrometers.