A New Synthesis of Diarylmethylphosphonic Acids and Their Esters from Aromatic Ketones and Trialkyl Phosphites[1]

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Trialkyl phosphites react with some aromatic ketones to give diarylmethylphosphonic acids or their esters, small amounts of tetraarylethylenes, and tetraarylethanes. In addition to the expected products, fluorenone gives appreciable quantities of 9-diphenylenephenanthrone. The limitations and possible course of the new reactions are discussed.

Although the reaction of quinones[2] and of vicinal diketones[3-5] with trialkyl and triaryl phosphites has been studied extensively, simple ketones have been neglected. Acetone[6] and 4-methyl-4-dichloromethylcyclohexadien-1-one[7] are inert to triethyl phosphite but cyclohexanone reacts with diphenyl N-phenylphosphoramidite to give an α-phenoxyphosphonamidate[8]; benzophenone is claimed, without supporting experimental evidence or declaration of products formed, to react vigorously at room temperatures with triethyl phosphite.[6]

1,2-Dibenzoylethylene reacts with triethyl phosphite to give 2,5-diphenylfuran and triethyl phosphate.[9] More recently α,β-unsaturated ketones were reported[10] to react with triethyl phosphite in ethanol at room temperatures to give a 1,6-diketone or a γ-ketophosphonate, or their mixtures. The source of oxygen to produce triethyl phosphate in these and other reactones[5,9] is obscure but apparently does not arise by reductive deoxygenation of the carbonyl group.

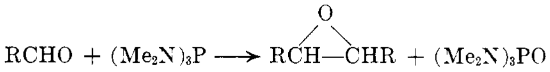
$$(XCOCH{=}CHY-)_2 \xrightarrow{(EtO)_3P} (XCOCH_2CHY-)_2 + XCOCH_2CHYP(O)(OEt)_2$$

This diversity of reactions among quinones, vicinal diketones, and α,β-unsaturated ketones serves only to emphasize the dearth of studies involving simple ketones. Additional investigations were warranted to ascertain whether diaryl ketones react with esters of trivalent phosphorus acids.

We considered that trialkyl phosphites would deoxygenate ketones to generate carbenes. Subsequent reactions would then lead to trialkoxyphosphoranes and tetrasubstituted oxiranes or ethylenes. Credence for such expectations was afforded by a paper[11] describing the isolation of 1,2-bis(2-furyl)ethylene and stilbene in small quantities along with appreciable amounts of triethyl phosphate from reaction products of triethyl phosphite with furfural and benzaldehyde, respectively. Furthermore, while our work was in progress, Ramirez and his co-workers[12] had suggested the possibility of a carbene intermediary in the reaction of phthalic anhydride with trialkyl phosphites but did not pursue this attractive idea further. After our paper had been submitted for publication, Mark reported[13] that hexamethylphosphorus triamide deoxygenates a variety of aldehydes to give oxiranes and hexamethylphosphoric triamide under mild conditions. Extension of this reaction to ketones has not yet been demonstrated.

$$(RO)_3P + R'_2CO \longrightarrow (RO)_3PO + R'_2C:$$

$$(RO)_3P + R'_2C: \longrightarrow (RO)_3P^+-\bar{C}R'_2$$



$$RCHO + (Me_2N)_3P \longrightarrow RCH\overset{O}{-}CHR + (Me_2N)_3PO$$

It was further considered alternatively, by analogy to reactions of phosphites with 1,2-diketones,[3-5] that simple ketones would undergo a pinacol condensation with the formation of a cyclic glycol phosphate. Recently, Ramirez and his co-worker provided some support for this possibility quite elegantly with reactions involving 1,2-diketone–phosphite adducts and aldehydes.[14]

Experimental[15]

The results described for triisopropyl phosphite are typical for other tertiary phosphite esters of alcohols bearing at least one β-hydrogen.

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[1] A. C. Poshkus and J. E. Herweh, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17-O.

[2] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **23**, 778 (1958); (b) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, *ibid.*, **81**, 587 (1959); (c) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959); (d) T. Reetz, U. S. Patent 2,935,518 (1960); (e) E. C. Ladd, U. S. Patents 2,553,417 (1951) and 2,609,376 (1952); (f) V. A. Kukhtin, N. S. Garif'yanov, and K. M. Orekhova, *Zh. Obshch. Khim.*, **31**, 1157 (1961); (g) K. M. Kirillova and V. A. Kukhtin, *ibid.*, **32**, 2338 (1962).

[3] G. H. Birum and J. L. Dever, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958, p. 101-P; U. S. Patents 2,961,455 (1960) and 3,014,949 (1961).

[4] (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960); (b) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963). References to earlier work are given in b.

[5] (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); (b) V. A. Kukhtin and K. M. Orekhova, *Zh. Obshch. Khim.*, **30**, 1208 (1960); (c) V. A. Kukhtin and K. M. Kirillova, *Dokl. Akad. Nauk SSSR*, **140**, 835 (1961); (d) V. A. Kukhtin, K. M. Kirillova, and R. R. Shagidullin, *Zh. Obshch. Khim.*, **32**, 649 (1962); (e) V. A. Kukhtin, *et al.*, *ibid.*, **32**, 2038 (1962); (f) V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, *ibid.*, **32**, 2333 (1962).

[6] V. A. Ginsburg and A. Yakubovich, *ibid.*, **30**, 3987 (1960).

[7] B. Miller, *J. Org. Chem.*, **28**, 345 (1963).

[8] V. S. Abramov and N. A. Il'ina, *Dokl. Akad. Nauk SSSR*, **125**, 1027 (1959).

[9] V. A. Kukhtin and K. M. Orekhova, *Zh. Obshch. Khim.*, **30**, 1526 (1960).

[10] (a) R. G. Harvey, E. R. DeSombre, and E. V. Jensen, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17-O; (b) R. G. Harvey and E. V. Jensen, *Tetrahedron Letters*, 1801 (1963).

[11] B. A. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1030 (1960).

[12] F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961).

[13] V. Mark, *ibid.*, **85**, 1884 (1963).

[14] F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963), and earlier references cited here.

[15] Unless otherwise specified solvents and reagents were purified by distillation or crystallization. All reactions were carried out in a nitrogen atmosphere. Neutralization equivalents were determined in 50% aqueous ethanol. Melting points and boiling points are uncorrected. Infrared and thermogravimetric analyses and the analysis for P and Cl were carried out by the analytical group at our center under the supervision of Dr. Robert Newton. Carbon and hydrogen analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Diisopropyl Diphenylmethylphosphonate. A.—Benzophenone (9.1 g., 0.050 mole) and triisopropyl phosphite (52.0 g., 0.25 mole) were refluxed (170°) for 72 hr.; 3.2 g. of propylene was evolved.[16] Distillation of the pale orange solution gave 37 g. of triisopropyl phosphite [b.p. 43–47° (3.0 mm.), $n^{20}\text{D}$ 1.4103], and 8.0 g. of triisopropyl phosphate [b.p. 68° (3.6 mm.), $n^{20}\text{D}$ 1.4073].[17] The still residue (13.5 g.), chromatographed over alumina, gave 0.6 g. of tetraphenylethylene, 4.0 g. of benzophenone, 6.8 g. of diisopropyl diphenylmethylphosphonate (m.p. 82–84°), and 0.6 g. of an unidentified oil. All solids were identified by their melting and mixture melting points with authentic compounds and by their infrared spectra. Diisopropyl diphenylmethylphosphonate was further characterized by its molecular weight determined cryoscopically in benzene (found, 339; calcd., 332), hydrolysis with concentrated hydrochloric acid to the known diphenylmethylphosphonic acid (80% yield), m.p. 237–239°,[18] and neutralization equivalent of the acid (found, 129; calcd., 124).

Authentic diisopropyl diphenylmethylphosphonate (m.p. 83–84°) was synthesized from diphenylchloromethane and triisopropyl phosphite in 32% yield by the Michaelis–Arbuzov reaction.

Anal. Calcd. for $C_{19}H_{25}O_3P$: C, 68.63; H, 7.59; P, 9.34. Found: C, 68.69; H, 7.26; P, 9.29.

B.—In another experiment with an excess of benzophenone (0.25 mole) and 0.050 mole of triisopropyl phosphite, 0.4 g. of propylene was evolved. Distillation gave 4.5 g. of triisopropyl phosphate, 2.7 g. of diisopropyl phosphite, and 40.3 g. of benzophenone. The pale yellow acidic residual oil (7.3 g.) was hydrolyzed with concentrated hydrochloric acid to give 2.3 g. of diphenylmethylphosphonic acid. The neutral product (3.0 g.) was chromatographed over alumina into tetraphenylethylene (0.5 g.), tetraphenylethane (0.3 g., m.p. 214–217°),[19] benzophenone (0.7 g.), and an unidentified mushy solid (0.7 g.). The remainder could not be eluted from the column.

Bis(4-chlorophenyl)methylphosphonic Acid.—Triisopropyl phosphite (52.0 g.) and 4,4′-dichlorobenzophenone (12.5 g.) were refluxed for 72 hr. Propylene (27 g.) and isopropyl alcohol (0.7 g.), identified as its 2,4-dinitrobenzoate, were evolved. The hygroscopic acidic solid (35.7 g.) was extracted with cold water and the white water-insoluble mixture was extracted with aqueous sodium hydroxide. Acidification of the alkaline extracts gave 13.9 g. of bis(4-chlorophenyl)methylphosphonic acid. After recrystallization from ethanol the acid melted at 253–254°.

Anal. Calcd. for $C_{13}H_{11}Cl_2O_3P$: C, 49.21; H, 3.50; Cl, 22.37; P, 9.78; neut. equiv., 159. Found: C, 49.37; H, 3.84; Cl, 22.40; P, 9.98; neut. equiv., 170.

The alkali-insoluble residue (2.7 g.) was separated into a benzene-soluble fraction (1.5 g.) consisting of tetra(4-chlorophenyl)ethylene (m.p. 213–218°[20a]) as shown by ozonization to 4,4′-dichlorobenzophenone in 96% yield, and 4,4′-dichlorobenzophenone (0.3 g.). The benzene-insoluble portion (1.2 g.) was recrystallized from acetone–ethanol solution, m.p. 328–329° dec.

Anal. Calcd. for $C_{26}H_{18}Cl_4$ [1,1,2,2-tetra(4-chlorophenyl)-ethane][20b]: C, 66.10; H, 3.84; Cl, 30.04. Found: C, 66.41; H, 3.91; Cl, 29.47.

Failure to find a suitable solvent prevented the determination of molecular weight.

Another run with four times the quantity of reagents used before (180° for 72 hr.) gave only 26 g. of propylene. Distillation of diisopropyl phosphite and triisopropyl phosphate left an oily solid (86 g.) consisting mainly of diisopropyl bis(chlorophenyl)methylphosphonate. A portion of the product was recrystallized from hexane as white glistening plates (m.p. 107–108°) and corresponds to an 85% yield of the pure ester.

Anal. Calcd. for $C_{19}H_{23}Cl_2O_3P$: C, 56.82; H, 5.78; Cl, 17.72; P, 7.73; mol. wt., 401. Found: C, 56.42; H, 5.81; Cl, 18.04; P, 7.66; mol. wt. (cryoscopically in benzene), 387.

The remaining crude ester (81 g.) was hydrolyzed to the phosphonic acid (yield 47 g.).

4-Chlorodiphenylmethylphosphonic Acid.—This acid, m.p. 231–235° after recrystallization from water–ethanol, was prepared in a 70% yield from 4-chlorobenzophenone and triisopropyl phosphite.

Anal. Calcd. for $C_{13}H_{12}ClO_3P{\cdot}0.5H_2O$: Cl, 12.18; P, 10.63; active hydrogen, 1.02; neut. equiv., 146. Found: Cl, 12.23; P, 10.56; active hydrogen, 0.77[21]; neut. equiv., 133.

Thermogravimetric analysis in a nitrogen atmosphere at a heating rate of 6°/min. shows a 3.0% weight loss in the range 250–350° followed by an additional weight loss of 50% at 360–425°. Water and traces of ethanol were identified by gas phase chromatography in the vapors evolved at 310°.

1,2-Diphenyl-1,2-bis(4-chlorophenyl)ethylene, presumably a mixture of *cis* and *trans* isomers melting over a broad range of 148–180°, also was isolated in 12% yield. Ozonization converted this mixture exclusively into the original ketone.

Reaction of Triisopropyl Phosphite with Fluorenone.—Using the same conditions as before but with 0.050 mole of fluorenone and 0.25 mole of triisopropyl phosphite as reactants led to a recovery of 20.1 g. of triisopropyl phosphite and 8.6 g. of triisophosphate. The still residue (12.8 g.) extracted with petroleum ether (b.p. 30–60°) left 3.6 g. of a white crystalline solid, m.p. 262–264°, identified as 9-diphenylenephenanthrone[22] by its mixture melting point, molecular weight (found, 335), and infrared spectrum.

The petroleum ether solution was washed with 5% aqueous sodium hydroxide. Acidification of the basic extracts gave 0.5 g. of an unidentified orange oil; the aqueous solution contained no phosphate ions (test with ammonium phosphomolybdate). Evaporation of the washed petroleum ether solution left 8.8 g. of a viscous orange oil; chromatography over alumina gave an unidentified orange-red solid (1.6 g.) melting over a broad range and an orange slurry (4.8 g.). The latter was digested in hot concentrated hydrochloric acid and made basic with sodium hydroxide, and the basic solution was extracted with ether; 0.9 g. of an orange oil was found in the ether layer. Acidification of the aqueous basic solution gave 2.9 g. of a cream-colored powder, m.p. 220–250°. The product, 9-fluorenylphosphonic acid, was purified by dissolution in acetone and precipitation with benzene, m.p. 255–259°.

Anal. Calcd. for $C_{13}H_{11}O_3P$: P, 12.60; neut. equiv., 123. Found: P, 12.20; neut. equiv., 129.

Diisopropyl Diphenylmethyl Phosphate.—This compound was prepared from equimolar amounts of diisopropyl phosphorochloridate and sodium diphenylmethylate in 68% yield, b.p. 135–136° (0.05 mm.), $n^{20}\text{D}$ 1.5139.

Anal. Calcd. for $C_{19}H_{25}O_4P$: C, 65.62; H, 7.18; P, 8.91; mol. wt., 348. Found: C, 66.01; H, 6.85; P, 8.87; mol. wt. (cryoscopically in benzene), 356.

Results

From these and related studies it is concluded that phosphate esters of alcohols bearing at least one hydrogen β to the hydroxyl group react with aromatic ketones to give high yields of diarylmethylphosphonic acid, its ester, or their mixtures; the relative amount of acid increases with longer reaction time and higher temperature. Ketones less basic than benzophenone, *e.g.*, 4,4′-dimethoxybenzophenone, do not react or do so sluggishly; but the more basic ones,[23] *e.g.*, 4,4′-dichlorobenzophenone, react readily to give high yields and excellent conversions to the phosphonic acid or its ester. The reactions are slow,[24] normally requiring 1–3 days at 170° when triisopropyl phosphite is a reactant.

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[16] Identified by conversion to 1,2-dibromopropane, b.p. 140° (755 mm.), $n^{20}\text{D}$ 1.5187. Reported b.p. 140°, $n^{20}\text{D}$ 1.5203 ("Handbook of Chemistry and Physics," 40th Ed., C. D. Hodgman, Ed., Chemical Rubber Publishing Co., 1958).

[17] A. Vogel and D. Cowan [*J. Chem. Soc.*, 16 (1943)] reported b.p. 83.5° (5 mm.), $n^{20}\text{D}$ 1.4057.

[18] W. Jensen and C. Noller [*J. Am. Chem. Soc.*, **71**, 2384 (1949)] reported m.p. 234–237°.

[19] D. Sayles and M. S. Kharasch, *J. Org. Chem.*, **26**, 4210 (1961).

[20] (a) J. Norris, R. Thomas, and B. Brown [*Ber.*, **43**, 2947 (1910)] reported m.p. 216–217°. (b) O. Grummitt, A. Arters, and J. Stearns [*J. Am. Chem. Soc.*, **73**, 1856 (1951)] reported that the compound decomposes at 300–325°.

[21] Active hydrogen (Geller Laboratories, Charleston 2, W. Va.) was determined after drying *in vacuo* 2 hr. at 110°. The anhydrous acid contains 0.71% active hydrogen.

[22] M. Gomberg and W. E. Bachman, *J. Am. Chem. Soc.*, **49**, 252 (1927).

[23] R. Stewart, M. Granger, R. Moodie, and L. Muenster, *Can. J. Chem.*, **41**, 1065 (1963).

[24] Contrary to unsubstantiated claims by Ginsburg and Yukubovich, triethyl phosphite does not react with benzophenone at room temperatures. The Russian authors did not isolate, characterize, or identify their reaction products.

Attempts to improve yields or decrease reaction times by addition of sodium ethoxide, aluminum chloride, mercuric acetate, cuprous chloride, dialkyl phosphites, or water were ineffective.

Benzophenone is inert toward trimethyl and triphenyl phosphite or triphenylphosphine. The reactants were recovered almost quantitatively after heating them for several days at about 160°.

Detailed studies on the reaction of triisopropyl phosphite with benzophenone show that the major primary reaction can be expressed stoichiometrically as shown.

$$\mathrm{2(Me_2CHO)_3P + Ph_2CO \longrightarrow Ph_2CHP(O)(OCHMe_2)_2 + (Me_2CHO)_3PO + C_3H_7}$$

Thus 1 mole of phosphate is found for every molecule of ketone reacting. When the reaction mixture is neutral, the amount of propylene obtained corresponds to that given in the equation; otherwise, larger quantities of propylene are evolved. Since both triisopropyl phosphite and phosphate are thermally stable under neutral conditions at temperatures used, the enhanced quantities of propylene must arise by thermolytic decomposition of the dialkyl alkylphosphonates.[25] When a solution of diisopropyl diphenylmethylphosphonate and benzophenone was heated, 2 moles of propylene were evolved for each mole of the phosphonate; diphenylmethylphosphonic acid was produced in 95% yield. An excess of phosphite in these reactions retards or prevents such thermolyses since the esters of the phosphonic acid can be recovered in good yields if the reaction times are not prolonged.

$$\mathrm{Ph_2CHP(O)(OCHMe_2)_2 \longrightarrow Ph_2CHP(O)(OCHMe_2)OH + C_3H_7}$$

$$\mathrm{Ph_2CHP(O)(OCHMe_2)OH \longrightarrow Ph_2CHPO_3H_2 + C_3H_7}$$

In order to test the hypothesis that carbenes and, consequently, trialkoxyphosphoranes are intermediates, reactions of triisopropyl phosphite with diphenylcarbene were attempted; but the generation of the carbene from diphenyldiazomethane in presence of the phosphite was frustrated by other reactions preceding carbene formation[26] and this approach was abandoned.

Other approaches were based on the hypothesis that ylides will dissociate into a carbene and a phosphine. Either through dissociation and combination or by direct exchange, reaction with the phosphite was expected. When the reaction was carried out with triisopropyl phosphite and diphenylmethylenetriphenylphosphorane, propylene, acetone, isopropyl alcohol, tetraphenylethylene, and *sym*-tetraphenylethane were identified among the reaction products. Some evidence was obtained for 2-methyl-1,1-diphenylpropylphosphonic acid but diphenylmethylphosphonic acid was not found. The complex reaction of phosphites with ylides failed to provide significant clues.

$$\mathrm{Ph_3\overset{+}{P}\overset{-}{C}Ph_2 \rightleftarrows Ph_3P + Ph_2C:}$$

$$\mathrm{Ph_3\overset{+}{P}\overset{-}{C}Ph_2 + (Me_2CHO)_3P \rightleftarrows Ph_3P + (Me_2CHO)_3\overset{+}{P}\overset{-}{C}Ph_2}$$

Reactions of triisopropyl phosphate with diisopropyl diphenylmethylphosphonate and of triisopropyl phosphite with diisopropyl diphenylmethyl phosphate also were examined for possible elucidation of the ketone–phosphite reaction. In each case about 80% of the propyl groups was eliminated as propylene; some 2-methyl-1,1-diphenylpropane[27] and phosphorus-containing acids, tentatively identified as 2-methyl-1,1-diphenylpropylphosphonic acid on the basis of its neutralization equivalent, were obtained. The latter acid also appears to be present in the small amount of unidentified residue from triisopropyl phosphite–benzophenone reaction products. It is significant that in neither case was diphenylmethylphosphonic acid isolated from the acidic fractions. These phosphorus-bearing acidic fractions were resistant to cleavage by hot concentrated hydrochloric acid, but fusion with sodium hydroxide gave sodium phosphate and unidentified high-boiling saturated hydrocarbons bearing phenyl groups. These results indicate a Michaelis–Arbuzov type of reaction between triisopropyl phosphite and diisopropyl diphenylmethyl phosphate. Subsequent reactions must occur between the phosphate and phosphonate–possibly alkylation of the diphenylmethyl moiety–to account for the remaining 20% of isopropyl groups and the failure to find any diphenylmethylphosphonic acid. It will be recalled that diisopropyl diphenylmethylphosphonate is converted almost quantitatively into the acid when heated with benzophenone.

$$\mathrm{(Me_2CHO)_3P + (Ph_2CHO)P(O)(OCHMe_2)_2 \longrightarrow Ph_2CHP(O)(OCHMe_2)_2 + (Me_2CHO)_3PO}$$

It is appropriate to compare our results with benzophenone to those of others with phthalic anhydride,[12] benzaldehyde,[11] and nitrobenzaldehydes.[28] With the exception of the nitrobenzaldehydes the reactions are slow and deoxygenation is a major reaction.

Biphthalyl is the main product from the reaction of triisopropyl phosphite with phthalic anhydride[12,29]; if certain hydrogen donors are present, high yields of diisopropyl phthalide-3-phosphonate can be achieved. Benzophenone, however, gives diisopropyl diphenylmethylphosphonate as a major product, tetraphenylethylene in small amounts only (roughly one-tenth the molar quantity of the phosphonate), and lesser amounts of tetraphenylethane regardless of the conditions. Neither water nor diisopropyl phosphite affect the yield of diisopropyl diphenylmethylphosphonate or other reaction products. Trimethyl and triphenyl phosphite are ineffective reagents for both phthalic anhydride and benzophenone. Furthermore, trimethyl phosphite was not isomerized to the methyl phosphonate as was the case with phthalic anhydride.[12]

Judged by the quantity of triethyl phosphite converted to the triethyl phosphate, benzaldehyde and 2-

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(25) A. E. Canavan, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 331 (1962).

(26) A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, **27**, 2700 (1962).

(27) B.p. 103–105° (0.45 mm.), $n^{22}\mathrm{D}$ 1.5698. *Anal.* Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63; mol. wt., 210. Found: C, 91.92; H, 8.08; mol. wt. (cryoscopically in benzene), 198. P. Sabatier and M. Murat, [*Ann. chim.* (France), [9]**4**, 253 (1915)] gave b.p. 285–286°, $n^{16}\mathrm{D}$ 1.560.

(28) V. A. Kukhtin and K. M. Kirillova, *Zh. Obshch. Khim.*, **31**, 2226 (1961). An incorrect assignment of structure is given in *Chem. Abstr.*, **56**, 3507*e* (1962).

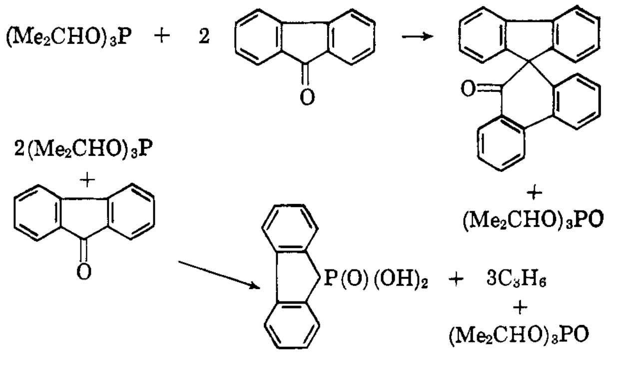
(29) We have confirmed this work but the biphthalyl proved to be a mixture of two species of acicular crystals: one, citron yellow, showed yellow fluorescence in ultraviolet light; the other, bright orange, fluoresced brilliantly orange. The orange crystals sublimed, simultaneously transforming into the yellow form, when heated to about 240°. The infrared spectra of the two forms are essentially similar. The two forms are *cis–trans* isomers; the less stable orange compound is probably the *cis* isomer and constitutes about 20% of the total mixture of biphthalyl.

furfuraldehyde are extensively deoxygenated.[11] The only products isolated that can be attributed to deoxygenation were small amounts of stilbene and 1,2-bis(2-furyl)ethylene in quantities comparable to tetraphenylethylene obtained from benzophenone. Appreciable yields of α-alkoxybenzylphosphonate were claimed based on analysis of impure samples and analogy to work of other investigators. Such compounds are commonly obtained from reactions of aldehydes with phosphites.[6,8,30] Analogous compounds were not found in our reactions with benzophenone or other diaryl ketones.

In contrast to the other carbonylic compounds, nitrobenzaldehydes react easily with trialkyl phosphites[28]; there is no evidence of phosphates as primary reaction products and, consequently, for deoxygenation either at the carbonyl or at the nitro group.[31]

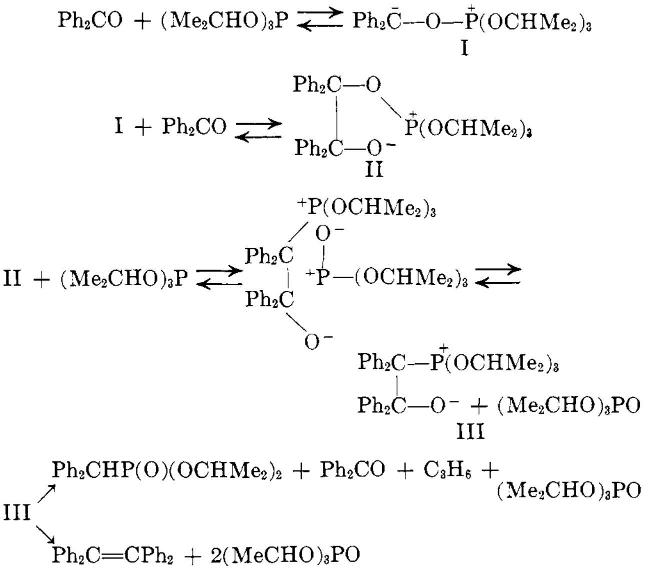
The results of Kukhtin and Kirillova,[28] who obtained trialkyl phosphates only after treating the reaction mixture or the aldehyde–phosphite adduct with ethanol or water, bears comparison with those of Mark[13] who found hexamethyl phosphoric triamide as a primary reaction product when hexamethylphosphorus triamide reacts with aldehydes.

The reaction of triisopropyl phosphite with fluorenone proceeds along three different paths to give 9-diphenylenephenanthrone (44% yield based on fluorenone), 9-fluorenylphosphonic acid (24% yield), and what appears to be a mixture of fluorenylide and isopropylidenefluorene. The low mole ratio of triisopropyl phosphate produced to fluorenone consumed (0.8) is due to the formation of the cyclic pinacolone. Pinacolones were not found in reactions with other ketones. These results indicate quite strongly a pinacolyl intermediate.



Discussion

As a consequence of this investigation it is unlikely that carbenes are intermediates[1] in the sequence of reactions involving diaryl ketones and trialkyl phosphites. This conclusion follows from these observations: (1) the relative amount of tetraphenylethylene formed is unchanged whatever the mole ratio of reactants used; (2) tetraphenylethylene oxide is not formed even when the reactions are carried out in an excess of benzophenone[32]; (3) isopropylbenzhydryl ether is not found when isopropyl alcohol is added to the reaction mixture; (4) neither trimethyl or triphenyl phosphite nor triphenylphosphine are effective deoxygenating agents for diaryl ketones; and (5) diethyl or diisopropyl phosphite either had no effect or decreased the amount of diphenylmethylphosphonic acid produced when added to the reaction mixture. If a carbene were formed, then reactions carried out in an excess of a diaryl ketone would give predominantly a tetraaryloxirane and some tetraarylethylene. On the other hand, reactions carried out in excess trialkyl phosphite would give a methylene trialkoxyphosphorane by combination of the carbene with the phosphite. Such a phosphorane can be expected to give a phosphonate by hydrogen transfer from the alkoxy group bearing a hydrogen on the β-carbon; the corresponding methyl homolog cannot do so. The latter was expected to give tetraarylethylene and dimethyl 1,1-diarylethylphosphonate. These reasonable expectations are not supported by experimental data and our original carbene hypothesis must be rejected.[33] The following proposal is submitted to accommodate our observations.



A first step is the formation of an intramolecular phosphonium salt I.[34] Such an intermediate was proposed earlier[28,35] to interpret some reactions between simple

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(30) G. Kamai and V. A. Kukhtin, *Zh. Obshch. Khim.*, **27**, 2372 (1956).

(31) J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 361 (1962).

(32) A small amount of product, identified as tetraphenylethylene oxide by its melting point and mixture melting point with the authentic compound, was isolated in one of our earlier experiments. Subsequent search showed no evidence for this oxirane. Furthermore, we found that only 15% of tetraphenylethylene oxide is converted to tetraphenylethylene by triisopropyl phosphite at 175° in 72 hr. At least 75% of each reactant was recovered. Thus any oxirane formed would have been detected.

(33) Ramirez and his students also found no evidence for a speculated carbene intermediate in their phthalic anhydride-trialkyl phosphite reaction[12] when authentic "trapping" reagents for carbenes, *e.g.*, olefins or secondary amines, were used. In absence of experimental validation concerning reactions of authentic carbenes with dialkyl phosphites, the formation of phthalide-3-phosphonic acid is not cogent evidence for a speculated carbene intermediate, however attractive such a working hypothesis may be. It must be emphasized that under similar conditions tetrachlorophthalic anhydride failed to give the phthalidephosphonic acid. Furthermore, phthalide-3-phosphonic acid was reported to be formed with dialkyl phosphites even in absence of trialkyl phosphites.

(34) Oxygen as a preferred site of attachment by trivalent phosphorus compounds has been suggested by many chemists and their contributions are reviewed adequately. See ref. 12; F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956); L. Horner and H. Hoffmann, *Angew. Chem.*, **63**, 473 (1956); J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962); A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).

(35) V. A. Ginsburg and A. Yakubovich, *Zh. Obshch. Khim.*, **30**, 3979 (1960). In a recent communication F. Ramirez, A. V. Patwardhan, and S. R. Heller, [*J. Am. Chem. Soc.*, **86**, 514 (1964)] proposed a tetraalkoxyphosphorane structure for a 2:1 propionaldehyde–triethyl phosphite adduct.

aldehydes and trialkyl phosphates. Similarly, Ramirez, Ramanthan, and Desai[14] speculated an analogous intermediate of an α,β-diketone during the synthesis of conjectured cyclic phosphoranes from relatively stable 1:1 α,β-diketone–phosphite adducts and α,β-diketones, α-keto esters, and aldehydes. Extension of the reaction to simple ketones has not been reported. Moderately stable adducts of quinones[2] and 1,2-diketones[3-5] with phosphorus covalently bonded to the oxygen are known.

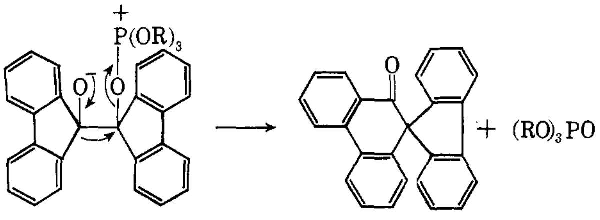
The speculated phosphonium salt I bears a *formal* resemblance, with charge inversion, to the aluminum alkoxide complex of carbonylic compounds proposed by several chemists, and for which evidence has been submitted,[36] as an intermediary in the Meerwein–Ponndorf–Oppenauer reaction.[37] Hydrogen transfer from the isopropyl to the anionic diphenylmethyl group with subsequent rearrangement of the diphenylmethyl phosphite to the phosphonate does not occur because acetone is not found in the reaction mixture. Diphenylmethanol, isolated in yields up to 35% when reactions are carried out in isopropyl alcohol, is probably due to hydrogen abstraction from isopropyl alcohol and alcoholysis of the tris(isopropoxy)diphenylmethoxy phosphonium cation.

$$\mathrm{Ph_2\overset{-}{C}{-}O\overset{+}{P}(OCHMe_2)_3 + Me_2CHOH \longrightarrow Ph_2CHO\overset{+}{P}(OCHMe_2)_3 + Me_2CHO^-}$$

$$\mathrm{Ph_2CH{-}O{-}\overset{+}{P}(OCHMe_2)_3 + Me_2CHOH \longrightarrow (Me_2CHO)_4P^+ + Ph_2CHOH}$$

It is attractive to consider that the ionic complex I could lead to explusion of propylene and formation of diisopropyl diphenylmethyl phosphate by an intramolecular hydrogen transfer from the isopropyl group to the carbanion moiety. A subsequent Michaelis–Arbuzov reaction, for which indirect evidence has been adduced, could account for the diphenylmethylphosphonate. This hypothesis, however, is untenable since the phosphate was not found when the reactions were carried out in an excess of benzophenone and it fails to explain the formation of tetraphenylethylene.

An intramolecular phosphonium alkoxide (II) probably forms the second step in the reaction. This intermediate is similar to the one postulated in the second stage of the reaction between simple aldehydes and trialkyl phosphites[28,35] and closely analogous to the α,β-diketone–phosphite adducts.[4,5,14] Transformation of fluorenone to 9-diphenylenephenanthrone is simply interpreted and lends credence to such a view.



In the penultimate step complex II must react with another phosphite molecule to give a new intermediate bearing a carbon–phosphorus bond with ejection of a phosphate. Such a phosphonium salt (III) can be expected to give six-membered ionic complexes with phosphates and provide some stabilization of III. The constant proportions of diphenylmethylphosphonic acid and tetraphenylethylene over a broad ratio of reactants suggests a common precursor. One likely possibility is III proposed earlier in a mechanism for the Wittig reaction[38] and suggested as a transient species during deoxygenation of oxiranes by phosphites.[39] Irreversible decomposition can take one of two courses: one leading to the phosphonate *via* a six-membered ring transition state with transfer of a methylic hydrogen to the carbon-bearing phosphorus, and the other to the tetraarylethylene through a four-centered cyclic mechanism as in the final step of the Wittig reaction.[39]

A diarylmethylenetrialkoxyphosphorane, either from III by dissociation[40] or from I by reaction with the phosphite ester, was rejected as a possible intermediate with considerable reluctance because of the constant proportions of diarylmethylphosphonic acid to tetraarylethylene formed at all ratios of reactants examined. If diarylmethylenetrialkoxyphosphorane were formed, high yield of diarylmethylphosphonic acid would be expected in presence of a large excess trialkyl phosphite; with a large excess of ketone present, tetraarylethylene would be the major product. The experimental results are inconsistent with this reasonable expectation.

The interpretation suggested here is consistent with most of our experimental observations. It fails, however, to provide a satisfactory explanation for the relative inertness of trimethyl or triphenyl phosphite and triphenylphosphine toward diarylketones and the formation of tetraarylethanes. Further work is obviously necessary to clarify the anomaly and to provide a more definitive answer on mechanism.

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(36) E. D. Williams, K. A. Krieger, and A. R. Day, *J. Am. Chem. Soc.* **75**, 2404 (1953).

(37) (a) A. L. Wilds, *Org. Reactions*, **2**, 178 (1944); (b) T. Bersin, "Newer Methods in Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 125.

(38) For example see reviews by U. Schollkopf [*Angew. Chem.*, **71**, 260 (1959)] and S. Trippett [*Quart. Rev.* (London), **17**, 406 (1963)].

(39) G. Wittig and W. Haag, *Ber.*, **88**, 1659 (1956).

(40) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963).