246. *The Phosphobetaines: Preparation and Properties.*

By S. Trippett and D. M. Walker.

β-Ketoalkyltriphenylphosphonium salts have been prepared by the action of esters, including formates, and of acid chlorides on Wittig reagents. The phosphobetaines $Ph_3P{:}CHR$ ($R = CN$, $CO{\cdot}NH_2$, CHO) react with aldehydes, but not with ketones, to give the corresponding αβ-unsaturated compounds.

The groups R, in the phosphorane $R_3P{:}CXY$ taking part in the Wittig olefin synthesis, may be phenyl or methyl. In the phosphobetaines $Ph_3P{:}CH{\cdot}COR$, replacement of phenyl by methyl does not give useful reactivity towards ketones.

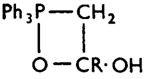
Michaelis and Köhler [1] showed that when the phosphonium salts $Ph_3P{\cdot}CH_2{\cdot}COR^+ X^-$ (R = Me or Ph), prepared by the action of triphenylphosphine on the corresponding α-halogeno-ketones, were treated with aqueous alkali, stable halogen-free compounds were obtained. They were termed phosphobetaines and assigned the structure (II). Wittig and Schöllkopf [2] obtained the phosphonium salt (I; R = Ph) by reaction of methylenetriphenylphosphorane with ethyl benzoate, and, on the basis of infrared evidence (lack of hydroxyl absorption at 3 μ and of carbonyl absorption below 6·5 μ) gave to the betaine the hydrogen-bonded structure (III). Ramirez and Dershowitz,[3] however, showed the true molecular formulæ of these betaines to be less by a molecule of water than those required by structures (II) and (III), and formulated them as true phosphoranes (IV; R = Me or Ph), stabilised by resonance. In agreement with this, the betaines with benzaldehyde gave triphenylphosphine oxide and benzylidene-acetone or -acetophenone.

$Ph_3P{\cdot}CH_2{\cdot}COR'\ X^-$

(I)

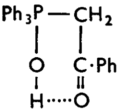
$Ph_3P{:}CH{\cdot}COR$

(IV)



$$\begin{array}{l}\mathrm{Ph_3P{-}CH_2}\\ \quad\ |\qquad |\\ \quad\ \mathrm{O{-}CR{\cdot}OH}\end{array}$$

(II)



$$\begin{array}{l}\mathrm{Ph_3P{-}CH_2}\\ \quad\ |\qquad |\\ \quad\ \mathrm{O}\quad\ \mathrm{C{\cdot}Ph}\\ \quad\ |\qquad \|\\ \quad\ \mathrm{H\cdots\cdots O}\end{array}$$

(III)

$Ph_3P{:}CR{\cdot}CO_2Et$

(V)

$Ph_3{:}CH{\cdot}CHO$

(VI)

They did not react with ketones. The betaines (V; R = H or Alk), prepared by the action of alkali on the phosphonium salts, have also been used [4] in Wittig reactions with aldehydes, particularly in the carotenoid field. We have previously described [5] the preparation of $Ph_3P{:}CH{\cdot}CO{\cdot}NH_2$ and of $Ph_3P{:}CH{\cdot}CN$; these have now been shown to react with aldehydes to give αβ-unsaturated amides and nitriles, but neither these, nor the ethoxycarbonyl betaine (V; R = H), reacted with ketones.[*]

We have now prepared the aldehyde betaine (VI) by addition of methylenetriphenylphosphorane to an excess of ethyl formate, having failed in attempts to quaternise triphenylphosphine with chloroacetaldehyde or with bromoacetal. After our preliminary communication,[6] Dr. Martin Grayson of the American Cyanamid Co. kindly informed us that success in the quaternisation with chloroacetaldehyde depends upon having anhydrous conditions, and that a solution of the chloroacetaldehyde–water azeotrope in chloroform can be made anhydrous by distillation of the chloroform–water azeotrope. This method makes the phosphorane (VI) readily available by the action of aqueous alkali or ethanolic

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[*] *Added in Proof.*—See, however, Sugasawa and Matsno *Chem. and Pharm. Bull.* (*Japan*), 1960, **8**, 819, for the reaction between ethoxycarbonylmethyltriphenylphosphonium bromide and cyclohexanones in methanol at room temperature in the presence of sodium methoxide

[1] Michaelis and Köhler, *Ber.*, 1899, **32**, 1566.

[2] Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.

[3] Ramirez and Dershowitz, *J. Org. Chem.*, 1957, **22**, 41.

[4] Isler, Gutmann, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1957, **40**, 1242.

[5] Trippett and Walker, *J.*, 1959, 3874.

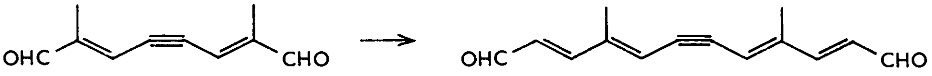
[6] Trippett and Walker, *Chem. and Ind.*, 1960, 202.

triethylamine on the phosphonium chloride. Our original difficulties may have been due to the lack of reactivity of chloroacetaldehyde hydrate, $Cl\cdot CH_2\cdot CH(OH)_2$, or to the fact that the phosphonium chloride $Ph_3P\cdot CH_2\cdot CHO^+Cl^-$ decomposes to triphenylphosphine oxide when heated in the presence of water.

Formylmethylenetriphenylphosphorane is stable to hydroxylic solvents at room temperature. When refluxed in benzene with an aldehyde, it gave triphenylphosphine oxide and the corresponding αβ-unsaturated aldehyde:

$$R\cdot CHO + Ph_3P{:}CH\cdot CHO \longrightarrow R\cdot CH{:}CH\cdot CHO + Ph_3PO$$

Thus benzaldehyde gave cinnamaldehyde (60%), n-heptaldehyde gave non-2-enal (81%), and the dialdehyde (VII) gave the dialdehyde (VIII). However, the phosphorane (VI) did not react with ketones.


(VII) (VIII)

1-Formylethylidenetriphenylphosphorane was similarly prepared by the action of ethyl formate on ethylidenetriphenylphosphorane. With aldehydes, it gave the unsaturated aldehydes $R\cdot CH{:}CMe\cdot CHO$.

Reaction of Wittig reagents with esters other than formates is in general slow and gives poor yields of β-keto-alkylphosphonium salts. With acid chlorides, a more rapid reaction gives the β-keto-alkylphosphonium chlorides in 30—50% yield. Benzylidenetriphenylphosphorane with esters gave only unchanged starting materials; with acid chlorides, the phosphonium chlorides $Ph_3P\cdot CHPh\cdot COR^+Cl^-$ were obtained.

The β-keto-alkylphosphonium salts were unchanged on treatment with sodium borohydride or diborane, and on attempted Meerwein–Ponndorf reduction or hydrogenation with a platinum catalyst. With zinc and acetic acid, they, and the phosphobetaines, gave triphenylphosphine and a ketone (~95%). The reaction of Wittig reagents with acid chlorides, followed by reduction with zinc and acetic acid, constitutes a formal ketone synthesis.

$$Ph_3P\cdot CH_2\cdot COR^+\,X^- \xrightarrow[AcOH]{Zn} Ph_3P + CH_3\cdot COR$$

Of the stable phosphoranes $Ph_3P{:}CH\cdot COR$ so far prepared, none reacts with ketones. This is a failure in the first step of the Wittig reaction, nucleophilic attack on carbon, not in the subsequent elimination of phosphine oxide. It seemed possible that successive replacement of the phenyl groups by methyl might increase the nucleophilic character of the phosphoranes to the point where this reaction became possible. Wittig and Reiber[7] reported that methylenetrimethylphosphorane, $Me_3P{:}CH_2$, gave with benzophenone the betaine $Ph_2C(\cdot O^-)\cdot CH_2\cdot PMe_3^+$, but that this would not eliminate trimethylphosphine oxide, and it was suggested[2] that this was because hyperconjugation of methyl reduced the oxygen-affinity of the phosphorus atom. Johnson and LaCount,[8] however, showed later that fluorenylidenetrimethylphosphorane with *p*-nitrobenzaldehyde gave 4-nitrobenzylidenefluorene, and, more recently, the same workers[9] have described similar successful Wittig reactions using fluorenylidenetributylphosphorane. These are very favourable cases for olefin formation, and it seemed desirable to investigate the general Wittig reaction with mixed methyl-phenyl-phosphoranes.

It soon became apparent that the Wittig olefin synthesis is not dependent on the nature of the groups R in the participating phosphorane $R_3P{:}CXY$. The series of phosphoranes $Me_{3-n}Ph_nP{:}CHPh$ ($n = 0$—3) all gave benzylidenefluorene on reaction with fluorenone, and the phosphoranes with $n = 0$ or 1 reacted with cyclohexanone to give

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[7] Wittig and Reiber, *Annalen*, 1949, **562**, 177.

[8] Johnson and LaCount, *Chem. and Ind.*, 1959, 52.

[9] Johnson and LaCount, *Tetrahedron*, 1960, **9**, 130.

benzylidenecyclohexane. Repetition of the unsuccessful reaction reported by Wittig and Reiber between methylenetrimethylphosphorane and benzophenone gave 1,1-diphenylethylene (40%). However, the elimination of trimethylphosphine oxide, required to afford an unconjugated double bond, is relatively difficult. Methylenetrimethylphosphorane and cyclohexanone in boiling tetrahydrofuran gave no detectable methylenecyclohexane: in 2,2′-dimethoxydiethyl ether at 100°, 15% of the desired olefin was formed.

Among the stable phosphoranes $Me_{3-n}Ph_nP{:}CH{\cdot}COR$, the gradual replacement of the phenyl by methyl reduced the stability to water, and the only complete series isolated was that derived from phenacyl bromide, *i.e.*, where $R = Ph$ and $n = 0$—3. Even here, the early members ($n = 0, 1$) were prepared at 0°, and were hydrolysed rapidly at room temperature in contact with water. High yields of benzylideneacetophenone were obtained on reaction with benzaldehyde, but none of the series reacted with ketones. These phosphoranes (with $R =$ Me, OEt, or H; and $n = 0$—2) could not, in general, be prepared by the action of alkali at 0° on solutions of the quaternary salts in chloroform, the phosphine oxide being formed in each case. Attention was therefore turned to the generation of the phosphoranes *in situ*, by the action of a suitable base on the phosphonium salts in solution with the carbonyl compound.

(Ethoxycarbonylmethyl)dimethylphenylphosphonium bromide, with pyridine and benzaldehyde in boiling nitromethane, gave, after hydrolysis, cinnamic acid (22%), but the same conditions were not successful with the corresponding trimethylphosphonium salt. Sodium ethoxide and piperidine were also ineffective in promoting the latter condensation, but, in the presence of triethylamine, (ethoxycarbonylmethyl)trimethylphosphonium bromide and benzaldehyde gave, after hydrolysis, a 48% yield of cinnamic acid. Under the same conditions, (ethoxycarbonylmethyl)trimethylphosphonium bromide did react with cyclohexanone, but the yield of cyclohexylideneacetic acid was only 3%. We therefore concluded that the increased nucleophilic character of the phosphobetaines on replacement of the phenyl by methyl had not given a useful reactivity towards ketones.

EXPERIMENTAL

Unless otherwise stated, light petroleum refers to the fraction of b. p. 60—80°. All experiments were carried out under oxygen-free nitrogen.

Reaction of Benzaldehyde with Cyanomethylenetriphenylphosphorane.—A solution of benzaldehyde (1·65 g.) and the phosphorane (4·7 g.) in benzene (50 ml.) was refluxed for 12 hr., light petroleum (150 ml.) added, and the solution set aside at room temperature to crystallise. Filtration then gave triphenylphosphine oxide (4·2 g.). Evaporation of the mother-liquors and distillation of the residue gave cinnamonitrile (1·3 g.), b. p. 137—138°/19 mm., $\lambda_{max.}$ 4·45,10·34 μ.

Reaction of Benzaldehyde with Carbamoylmethylenetriphenylphosphorane.—A solution of benzaldehyde (0·33 g.) and the phosphorane (1 g.) in benzene (25 ml.) was refluxed for 20 hr. and the solvent evaporated. Extraction of the residue with hot light petroleum gave, on cooling, triphenylphosphine oxide, m. p. 155°. Evaporation of the mother-liquors and sublimation of the residue gave cinnamamide (0·1 g.), m. p. 146—147° (Found: N, 9·2. Calc. for C_9H_9NO: N, 9·5%).

n-Heptaldehyde under the same conditions gave the amide of non-2-enoic acid (14%), m. p. (from light petroleum) 130—131° (Found: C, 69·9; H, 10·9; N, 9·4. Calc. for $C_9H_{17}NO$: C, 69·7; H, 10·9; N, 9·0%).

Formylmethyltriphenylphosphorane.—(*a*) To a stirred suspension of methyltriphenylphosphonium bromide (10·7 g.) in ether (100 ml.), ethereal 1·16N-butyl-lithium (25 ml.) was added, and the solution was stirred for 0·5 hr. and slowly added to a stirred solution of ethyl formate (2·7 g.) in ether (50 ml.). After 0·5 hr., the solution was extracted with dilute hydrochloric acid (2 × 100 ml.), and the combined extracts were made alkaline with dilute sodium hydroxide and extracted with benzene (3 × 200 ml.). Evaporation of the extracts gave *formylmethylenetriphenylphosphorane* (6·1 g.), m. p. (from acetone) 186—187° (decomp.) (Found: C, 78·9; H, 5·8. $C_{20}H_{17}OP$ requires C, 78·9; H, 5·6%).

(*b*) *Chloroacetaldehyde–water azeotrope (b. p. 85·5°; 96·5 g.) was added to chloroform

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* Personal communication from Dr. M. Grayson.

(1·5 l.), and the chloroform–water azeotrope (b. p. 56°; 800 ml.) was removed through a column until the solution was anhydrous. Triphenylphosphine (131 g.) was added to the resulting clear solution, which, after refluxing for 5 hr., was set aside at room temperature overnight. Removal of solvent under reduced pressure then gave crude *formylmethyltriphenylphosphonium chloride* (166·5 g.), m. p. (from chloroform–ethyl acetate) 212—213° (decomp.) (Found: C, 70·2; H, 5·7; P, 8·85. $C_{20}H_{18}ClOP$ requires C, 70·5; H, 5·3; P, 9·1%). Treatment of the phosphonium salt in ethanol with triethylamine, or in water with dilute sodium hydroxide, gave the above phosphorane, m. p. 187—188° (decomp.).

Reaction of Formylmethylenetriphenylphosphorane with Aldehydes.—(a) *Benzaldehyde.* A solution of benzaldehyde (0·86 g.) and the phosphorane (2·6 g.) in benzene (50 ml.) was refluxed for 24 hr., solvent removed under reduced pressure, and the residue extracted with a little cold ether. The residue crystallised from light petroleum to give triphenylphosphine oxide (1·6 g.), m. p. 154—155°. Evaporation of the extract gave an oil (1·06 g.; $\lambda_{max.}$ 286 mμ) which gave a 2,4-dinitrophenylhydrazone (2·1 g.), m. p. and mixed m. p. with cinnamaldehyde 2,4-dinitrophenylhydrazone, 253°.

Under the same conditions, n-heptaldehyde gave an oil ($\lambda_{max.}$ 224 mμ) which gave *non-2-en-1-al 2,4-dinitrophenylhydrazone*, m. p. (from methanol) 117—118° (Found: C, 56·2; H, 6·25; N, 17·1. $C_{15}H_{20}N_4O_4$ requires C, 56·2; H, 6·25; N, 17·5%).

(b) *2,7-Dimethylocta-2,6-dien-4-yne-1,8-dial.* A solution of the dialdehyde (0·55 g.) and formylmethylenetriphenylphosphorane (2·06 g.) in benzene (100 ml.) was refluxed for 16 hr. and solvent then removed under reduced pressure. Counter-current distribution (50 transfers) of the residue in the system benzene–light petroleum–methanol–water (1 : 1 : 1 : 0·5) gave from the leading tubes 4,9-dimethyldodeca-2,4,8,10-tetraen-6-yne-1,12-dial [10] (0·1 g.), m. p. (from acetone–water) 163—164°, $\lambda_{max.}$ 371, 390 mμ (ε 69,450, 67,890 in ethanol).

α-Formylethylidenetriphenylphosphorane.—To a stirred suspension of ethyltriphenylphosphonium iodide (4·1 g.), in ether (100 ml.), ethereal 1·16N-butyl-lithium (9 ml.) was added, and the resulting solution added slowly to a stirred solution of ethyl formate (1 g.) in ether (50 ml.). The suspension was then extracted with dilute hydrochloric acid, and the extract made alkaline with dilute sodium hydroxide and extracted with benzene. Removal of the benzene under reduced pressure, and crystallisation of the residue from benzene–light petroleum, gave *α-formylethylidenetriphenylphosphorane* (1·2 g.), m. p. 220—222° (Found: C, 79·4; H, 6·3. $C_{21}H_{19}OP$ requires C, 79·25; H, 6·0%).

A solution of the phosphorane in chloroform was shaken with dilute hydrochloric acid. Evaporation of the chloroform, and crystallisation of the residue from ethanol–ether, gave *α-formylethyltriphenylphosphonium chloride*, m. p. 231—233° (Found: C, 70·7; H, 5·35. $C_{21}H_{20}ClOP$ requires C, 71·1; H, 5·65%).

Reaction of α-Formylethylidenetriphenylphosphorane with Benzaldehyde.—A solution of benzaldehyde (0·33 g.) and the phosphorane (1 g.) was refluxed for 24 hr., solvent removed under reduced pressure, and the residue extracted with a little cold light petroleum (b. p. 40—60°). Crystallisation of the residue from benzene–light petroleum gave triphenylphosphine oxide (0·8 g.), m. p. 154—155°. Evaporation of the extract gave an oil ($\lambda_{max.}$ 283 mμ) from which *α-methylcinnamaldehyde 2,4-dinitrophenylhydrazone* (0·6 g.), m. p. (from ethyl acetate) 207—208°, was obtained (Found: C, 59·1; H, 4·35. $C_{16}H_{14}N_4O_4$ requires C, 58·9; H, 4·3%).

Under the same conditions, heptaldehyde gave an oil ($\lambda_{max.}$ 227 mμ) which gave *2-methylnon-2-en-1-al 2,4-dinitrophenylhydrazone* (72%), m. p. (from ethanol) 115—116° (Found: C, 57·65; H, 6·75; N, 17·0. $C_{16}H_{22}N_4O_4$ requires C, 57·5; H, 6·6; N, 16·8%).

Reaction of Methylenetriphenylphosphorane with Ethyl Acetate.—To a stirred suspension of methyltriphenylphosphonium bromide (1·8 g.) in ether (60 ml.), ethereal 1·3N-butyl-lithium (4·5 ml.) was added, and the solution was stirred for 0·5 hr. and then added slowly to a stirred solution of ethyl acetate (0·45 g.) in ether (20 ml.). Solvent was removed and the residue extracted with chloroform. The extract was washed with dilute hydrochloric acid, dried, and evaporated. Crystallisation of the residue from ethanol–ether gave acetonyltriphenylphosphonium chloride (16%), m. p. and mixed m. p. 236—237°.

Reaction of Benzylidenetriphenylphosphorane with Acetyl Chloride.—To a stirred suspension of benzyltriphenylphosphonium bromide (2·17 g.) in ether (75 ml.), ethereal 1·3N-butyl-lithium (4 ml.) was added. After 0·5 hr., the resulting solution was added slowly to a stirred solution

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[10] Isler, Gutmann, Lindlar, Montavon, Rüegg, Ryser, and Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.

of acetyl chloride (0·4 g.) in ether (25 ml.), and the solvent then removed. The residue was extracted with chloroform and the extract washed with dilute hydrochloric acid and with water, dried, and evaporated. Crystallisation of the residue from aqueous ethanol gave *α-phenylacetonyltriphenylphosphonium chloride* (47%), m. p. 172—173° (Found: C, 72·2; H, 5·75. $C_{27}H_{24}ClOP,H_2O$ requires C, 72·2; H, 5·8%). Addition of dilute sodium hydroxide to the quaternary salt gave *α-phenylacetonylidenetriphenylphosphorane*, m. p. (from aqueous ethanol) 167—168° (Found: C, 81·6; H, 5·7. $C_{27}H_{23}OP$ requires C, 82·0; H, 5·8%).

When a similar procedure was used, benzylidenetriphenylphosphorane and benzoyl chloride gave α-benzoylbenzylidenetriphenylphosphorane,[5] m. p. 191—192°; methylenetriphenylphosphorane with acetyl chloride gave acetonyltriphenylphosphonium chloride (38%), m. p. 235—236°, and with benzoyl chloride gave phenacyltriphenylphosphonium chloride (27%), m. p. 260—261°.

Reduction of Acetonyltriphenylphosphonium Chloride with Zinc and Acetic Acid.—The phosphonium chloride (1·73 g.) was dissolved in chloroform (25 ml.), zinc dust (12 g.) added, and the solution refluxed for 2 hr. during which acetic acid (50 ml.) was added in small portions. Steam-distillation of the residue into a solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid gave acetone 2,4-dinitrophenylhydrazone (97%), m. p. and mixed m. p. 128—129°. Ether-extraction of the residue from steam-distillation gave triphenylphosphine (67%), m. p. 79·5°.

In a similar way, phenacyltriphenylphosphonium bromide gave acetophenone 2,4-dinitrophenylhydrazone (95%), m. p. and mixed m. p. 236°, and triphenylphosphine (56%).

Phosphonium Salts derived from Methyldiphenylphosphine.—Methyldiphenylphosphine (b. p. 120—122°/0·2 mm.) was prepared by the reduction of methyldiphenylphosphine oxide with lithium aluminium hydride according to the general instructions of Horner *et al.*[11] The phosphonium salts were prepared by mixing benzene solutions of equimolecular amounts of phosphine and halide at 0°.

Benzylmethyldiphenylphosphonium bromide had m. p. (from chloroform–benzene) 245—246° (Found: C, 64·5; H, 5·35. $C_{20}H_{20}BrP$ requires C, 64·5; H, 5·4%).

Methylphenacyldiphenylphosphonium bromide had m. p. (from benzene–light petroleum) 70—72°, but was very hygroscopic and could not be satisfactorily analysed. A chloroform solution at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave (*benzoylmethylene*)*methyldiphenylphosphorane*, m. p. (from acetone–light petroleum) 123—124° (Found: C, 76·75; H, 6·0. $C_{21}H_{19}OP,\frac{1}{2}H_2O$ requires C, 76·9; H, 6·1%).

Acetonylmethyldiphenylphosphonium chloride had m. p. (from chloroform–ethyl acetate) 170—171° (Found: C, 65·35; H, 6·35. $C_{16}H_{18}ClOP$ requires C, 65·7; H, 6·15%). A chloroform solution at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave *acetonylidenemethyldiphenylphosphorane*, m. p. (from benzene–light petroleum) 113—115° (Found: C, 74·55; H, 6·65. $C_{16}H_{17}OP$ requires C, 75·0; H, 6·65%).

(*Ethoxycarbonylmethyl*)*methyldiphenylphosphonium bromide* had m. p. (from acetone) 119—120° (Found: C, 55·65; H, 5·5. $C_{17}H_{20}BrO_2P$ requires C, 55·6; H, 5·45%). Addition of alkali to an aqueous solution of the phosphonium salt at 0° gave a transient precipitate. Chloroform-extraction of the resulting solution gave methyldiphenylphosphine oxide, m. p. and mixed m. p. 113—114°.

Phosphonium Salts Derived from Dimethylphenylphosphine.—*Benzyldimethylphenylphosphonium bromide* had m. p. 158° (Found: C, 58·5; H, 6·0. $C_{15}H_{18}BrP$ requires C, 58·25; H, 6·0%).

Acetonyldimethylphenylphosphonium chloride had m. p. (from acetone) 107—108° (Found: C, 57·1; H, 6·9. $C_{11}H_{16}ClOP$ requires C, 57·2; H, 6·95%). Addition of alkali to an aqueous solution of the quaternary salt at 0° gave dimethylphenylphosphine oxide, m. p. 117—118°.

(*Ethoxycarbonylmethyl*)*dimethylphenylphosphonium bromide* had m. p. (from acetone–benzene) 124—125° (Found: C, 46·8; H, 5·8. $C_{12}H_{18}BrO_2P$ requires C, 47·2; H, 5·9%).

Phenacyldimethylphenylphosphonium bromide had m. p. (from chloroform–benzene) 177—178° (Found: C, 56·7; H, 5·1. $C_{16}H_{18}BrOP$ requires C, 57·0; H, 5·35%). A solution of this quaternary salt in chloroform at 0°, shaken with dilute sodium hydroxide, dried, and evaporated, gave (*benzoylmethylene*)*dimethylphenylphosphorane*, m. p. (from benzene–light petroleum) 126—127° (Found: C, 74·85; H, 6·8. $C_{16}H_{17}OP$ requires C, 75·05; H, 6·5%).

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[11] Horner, Hoffmann, and Beck, *Chem. Ber.*, 1958, **91**, 1583.

(Formylmethyl)dimethylphenylphosphonium chloride did not crystallise.

Phosphonium Salts Derived from Trimethylphosphine.—To a stirred solution of methylmagnesium iodide, prepared from magnesium (16 g.) and methyl iodide (40 ml.) in ether (200 ml.) and cooled in ice–salt, a solution of phosphorus trichloride (14·7 g.) in ether (50 ml.) was added during 3 hr. The resulting solution was stirred for 0·5 hr. at room temperature and then distilled from an oil-bath into a solution of the reacting halide in ether, cooled in ice. The temperature of the oil-bath was slowly raised to 200°, and held there for 1 hr.

Trimethylphenacylphosphonium bromide had m. p. (from ethanol–ether) 205—206° (Found: C, 46·35; H, 5·65. $C_{11}H_{16}BrOP,\frac{1}{2}H_2O$ requires C, 46·5; H, 5·7%). Addition of aqueous alkali at 0° to a solution of the quaternary salt in ethanol gave *(benzoylmethylene)trimethylphosphorane,* 130—131° (Found: C, 67·8; H, 7·75. $C_{11}H_{15}OP$ requires C, 68·0; H, 7·75%).

(Ethoxycarbonylmethyl)trimethylphosphonium bromide, m. p. (from acetone) 160—162°, was very hygroscopic and always had an odour of trimethylphosphine (Found: C, 33·7; H, 6·35. $C_7H_{16}BrO_2P,\frac{1}{2}H_2O$ requires C, 33·3; H, 6·75%).

Acetonyltrimethylphosphonium chloride did not crystallise.

Reaction of Benzylidenephosphoranes with Fluorenone.—To a stirred solution of benzylidenemethyldiphenylphosphorane, prepared from the phosphonium bromide (3·7 g.) and ethereal 1·4N-butyl-lithium (8 ml.) in ether (100 ml.), a solution of fluorenone (1·8 g.) in ether (25 ml.) was slowly added. The resulting suspension was refluxed for 1·5 hr. and filtered. Evaporation of the filtrate, and crystallisation of the residue from ethanol, gave benzylidenefluorene (60%), m. p. and mixed m. p. 75—76°.

In a similar way, benzylidenedimethylphenylphosphorane gave 53%, and benzylidenetrimethylphosphorane gave 42% of benzylidenefluorene.

Reaction of Benzylidenephosphoranes with Cyclohexanone.—To a stirred solution of benzylidenedimethylphenylphosphorane, prepared from the quaternary bromide (7·8 g.) and ethereal 1·3N-butyl-lithium (19·5 ml.) in tetrahydrofuran (120 ml.), a solution of cyclohexanone (2·5 g.) in tetrahydrofuran (25 ml.) was slowly added. The solution was refluxed overnight, solvent removed under reduced pressure, and the residue extracted with a little cold ether. Distillation of the extract gave benzylidenecyclohexane (72%), b. p. 128—130°/14 mm.

Benzylidenetrimethylphosphorane similarly gave an 80% yield of benzylidenecyclohexane.

Reaction of Benzoylmethylenephosphoranes with Benzaldehyde.—A solution of (benzoylmethylene)trimethylphosphorane (2·3 g.) and benzaldehyde (1·26 g.) in benzene (50 ml.) was refluxed for 18 hr., solvent evaporated, and the residue extracted with cold light petroleum. Evaporation of the extract, and crystallisation of the residue from aqueous ethanol, gave benzylideneacetophenone (92%), m. p. 55—56°. The residue from the extraction crystallised from light petroleum to give trimethylphosphine oxide (95%), m. p. 138—140°.

Similarly, (benzoylmethylene)methyldiphenylphosphorane gave benzylideneacetophenone (73%) and methyldiphenylphosphine oxide (95%), m. p. and mixed m. p. 113—114°; (benzoylmethylene)dimethylphenylphosphorane gave benzylideneacetophenone (50%) and dimethylphenylphosphine oxide (50%), m. p. and mixed m. p. 117—118°.

Reaction of Methylenetrimethylphosphorane with Benzophenone.—To a stirred suspension of tetramethylphosphonium iodide (4·4 g.) in ether (150 ml.), ethereal 1·3N-butyl-lithium (17 ml.) was added and the suspension stirred at room temperature for 30 hr. A solution of benzophenone (3·7 g.) in ether (50 ml.) was then slowly added, the ether removed by distillation and replaced by tetrahydrofuran, and the suspension refluxed for 3 days. Evaporation of the tetrahydrofuran, and extraction of the residue with ether, gave an oil which, on distillation, gave a fraction, b. p. 141—143°/12 mm. Traces of benzophenone were removed from this by treatment with Girard reagent " T." The residue of 1,1-diphenylethylene (40%) had an infrared spectrum identical with that of authentic material.

Reaction of Methylenetrimethylphosphorane with Cyclohexanone.—To a stirred suspension of tetramethylphosphonium iodide (7·3 g.) in 2,2′-dimethoxydiethyl ether (120 ml.), ethereal 1·3N-butyl-lithium (26 ml.) was added. After 15 min. the solution became clear. A solution of cyclohexanone (3·3 g.) in 2,2′-dimethoxydiethyl ether (15 ml.) was then added, and the resulting suspension heated at 100° for 20 hr. and distilled through an efficient column under a reflux-ratio head. A fraction of b. p. 95—115° was collected which, on redistillation, gave methylenecyclohexane (0·5 g.), b. p. 104—108°, identified by infrared spectrum and by gas–liquid chromatography.

Reaction of (Ethoxycarbonylmethyl)dimethylphenylphosphonium Bromide with Benzaldehyde *and Pyridine.*—A solution of the phosphonium bromide (1·4 g.), benzaldehyde (0·5 g.), and pyridine (1 ml.) in nitromethane (25 ml.) was refluxed for 18 hr., solvent then removed under reduced pressure, and the residue extracted with benzene. The extract was washed several times with water, then evaporated, and the residue was extracted with cold light petroleum to give, on evaporation of the extract, an oil, $\lambda_{max.}$ 275 mμ. Alkaline hydrolysis of this gave cinnamic acid (0·15 g.), m. p. and mixed m. p. 132—133°.

Reaction of (Ethoxycarbonylmethyl)trimethylphosphonium Bromide with Benzaldehyde and Triethylamine.—A suspension of the phosphonium bromide (5 g.) and triethylamine (2·5 g.) in 2,2′-dimethoxydiethyl ether (100 ml.) was stirred at room temperature overnight, benzaldehyde (1·2 g.) added, and the solution heated at 90° for 20 hr. Solvent was then removed under reduced pressure, the residue extracted with cold ether, and the extract distilled. A fraction of b. p. 135—145°/13 mm. was collected. Alkaline hydrolysis of this gave cinnamic acid (0·8 g.), m. p. and mixed m. p. 132—133°.

Reaction of (Ethoxycarbonylmethyl)trimethylphosphonium Bromide with Cyclohexanone and Triethylamine.—A solution of the quaternary bromide (10·3 g.) and triethylamine (5·1 g.) in nitromethane (100 ml.) was stirred at room temperature for 3 hr., cyclohexanone (4·15 g.) added, and the solution refluxed for 24 hr. Solvent was then removed under reduced pressure and the residue extracted with cold ether. The extract was washed with dilute hydrochloric acid and with water, dried, evaporated, and distilled to give cyclohexanone (0·53 g.), b. p. 47°/15 mm., and a fraction (1·3 g.), b. p. 100—115°/15 mm. Alkaline hydrolysis of this fraction gave two crystalline acidic products: a substance (0·15 g.), m. p. (from aqueous ethanol) 122—123°, $\lambda_{max.}$ 226 mμ (ε 11,000 in ethanol), 3·2, 5·68 μ (Found: C, 68·25; H, 8·05%), and cyclohexylideneacetic acid (0·15 g.), m. p. and mixed m. p. 88—89°.

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