The Reaction between Triphenylphosphine and 2-Bromocyclohexanone

By P. A. Chopard and R. F. Hudson

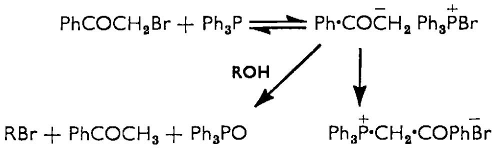
In non-hydroxylic solvents a mixture of α- and β-oxophosphonium salts and triphenylphosphine dibromide was formed in the reaction between triphenylphosphine and 2-bromocyclohexanone, probably by initial attack on bromine. The proton n.m.r. spectrum of the dissolved salts showed the presence of a vinylic proton attributed to the quasi-phosphonium salt. The reaction is very strongly catalysed by alcohols and water, under which conditions high yields of phosphine oxide are obtained together with cyclohexanone, 2-cyclohex-1-enylcyclohexanone, and small yields of cyclopentane carboxylic acid. The relative electrophilic reactivity of chlorine and bromine in positive halogen compounds is discussed.

α-HALOGENOKETONES are very reactive towards nucleophiles and several explanations of the high *S*N2 reactivity, as for example in the formation of quaternary ammonium and phosphonium salts

$$R'CO{\cdot}CH_2Cl + R_3P \longrightarrow R_3\overset{+}{P}CH_2COR'\overset{-}{Cl} \rightleftharpoons R_3P{=}CH{\cdot}COR' + HCl$$

have been advanced.[1]

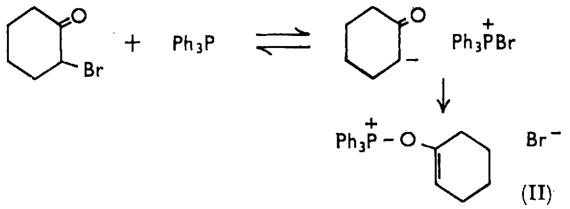
Borowitz and Virkhaus[2] have shown that phenacyl bromide gives the quaternary salt (I) by preliminary attack on bromine, followed by rearrangement of the ion-pair



(I)

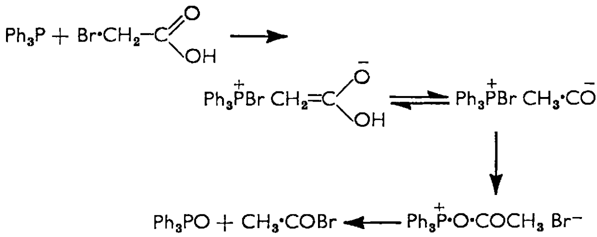
and a similar mechanism has been suggested for other reactions, *e.g.*, α-bromo-γ-butyrolacetone.[3] These reactions are interesting in that the alkylated product, *i.e.*, the product of the direct *S*N2 displacement on carbon, is formed by initial attack on positive halogen.

Different products are obtained from other α-bromo- and α-chloro-ketones and similar derivatives. Thus 2-bromocyclohexanone (and 2-bromocyclopentanone[3]) gives a highly hygroscopic salt[4] which is thought to be the quasi-phosphonium salt (II) formed by initial attack on bromine. The influence of the structure of the ketone on the nature of the product has recently been discussed.[3]



(II)

Similarly triphenylphosphine attacks the bromine atom of bromoacetic acid to give the phosphine oxide,[5] *viz.*,



In contrast to the α-bromoketone, 2-chlorocyclohexanone is very unreactive towards triphenylphosphine (although it reacts normally[6] with trialkyl phosphites showing that Ph_3P is unreactive towards the C=O group, whereas trialkyl phosphites are reactive towards it) showing that bromine is very electrophilic compared

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[1] P. D. Bartlett and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, 1958, **80**, 5808.

[2] I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, 1963, **85**, 2183.

[3] P. A. Chopard, R. F. Hudson, and G. Klopman, *J. Chem. Soc.*, 1965, 1379.

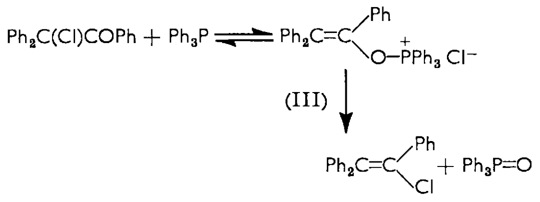
[4] I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, 1962, 471; S. Trippett, *J. Chem. Soc.*, 1962, 2337.

[5] D. B. Denney and L. C. Smith, *J. Org. Chem.*, 1962, **27**, 3407.

[6] P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, 1965, **21**, 1961.

with chlorine.[7] This conclusion is supported by the reactivity of 2,4,6-trimethylphenacyl bromide and unreactivity of the corresponding chloro-compound towards triphenylphosphine.[8]

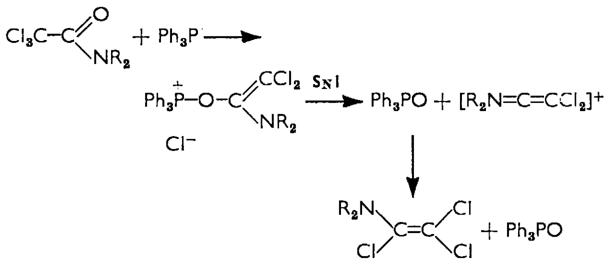
Several chloro-compounds which give particularly stable carbanions also form quasi-phosphonium salts. Thus Speziale and Partos [9] have isolated the hygroscopic salt (III) from the reaction between triphenylphosphine and αα'-diphenylphenacyl chloride:



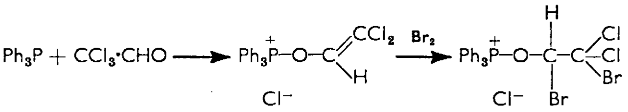
although the α-phenyl compound gives a phosphonium salt which easily decomposes to diphenylacetylene: [10]

$$PhCHCl{\cdot}COPh + Ph_3P \longrightarrow Ph_3PO + Ph{\cdot}C{\equiv}C{\cdot}Ph + HCl$$

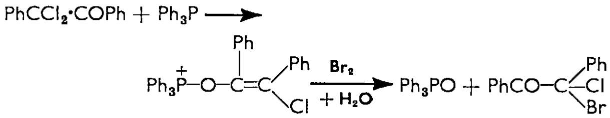
The salt (III) is quite stable, but at 150—200° it gives chlorotriphenylethylene. The reaction between triphenylphosphine and trichloroacetamides [11] leading to the chloro-olefin directly may proceed by a similar mechanism:



Chloral gives an adduct which is probably the quasi-salt as it is readily brominated,[12]



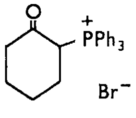
and the corresponding reactions of dichlorodeoxybenzoin lead to bromochlorodeoxybenzoin (IV) on hydrolysis:



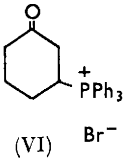
In the reaction between triphenylphosphine and phenacyl bromide, evidence for the initial attack on bromine can be obtained by reaction of the ion-pair with water or an alcohol.[2] When the product is a quasi-phosphonium salt, such a test cannot be applied, since the salt is very reactive, but we have assumed an initial attack on bromine in the two cases above owing to the extreme unreactivity of the corresponding chloro-compounds. Moreover, quasi-phosphonium salts derived from α-bromoketones have so far not been isolated and characterised, their presence having been inferred from the nature of the products of subsequent reaction.[4,12] We have now re-examined the reaction between triphenylphosphine and 2-bromocyclohexanone and found it to be more complex than hitherto supposed.*

Reaction in Non-hydroxylic Solvents.—The reaction in methylene chloride is very slow compared with that in ether.[3] The initial rapid formation of triphenylphosphine oxide (a few per cent.) may be due to traces of water. The subsequent reaction requires several hours for an appreciable change in the infrared spectrum.

Reactions in the absence of solvent at higher temperatures led to mixtures of salts (V—VII) in varying proportions (see Table 1).



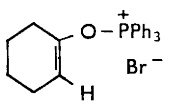
(V)



(VI)

Ph_3PBr_2

(VII)



(VIII)

The isolation of triphenylphosphine dibromide (VII) in yields of up to 15% by crystallisation from chloroform solutions of the reaction products, shows directly that attack on positive bromine occurs. The β-salt (VI) is probably formed by an E_2 elimination of 2-bromocyclohexanone produced by the enolate ion, followed by a Michael addition of triphenylphosphine to the αβ-unsaturated ketone, as in Scheme 1.

TABLE 1

	Yield (%)	
Conditions	β-Salt	α-Salt
100°; 15 min.	11	—
80°; 1 hr.	17	—
70°; 3 hr.	21	—
80°; 2½ hr.	25	*ca.* 10
25°; 30 days	25	18

The α-salt (V) may be formed by reaction of the enolate ion with the bromophosphonium ion according to the mechanism previously described.

The observations summarised in Table 1, however, show that the α-salt (V) was isolated only after a considerable reaction time, whereas the β-salt (VI) was isolated in reasonable yield after short times.

This suggests that the α-salt may be produced by decomposition of an intermediate, possibly the quasi-salt (VIII). In no case could this salt be isolated, which

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* Professor I. J. Borowitz, of Lehigh University, Pennsylvania has examined this system independently and has isolated the α- and β-salts (private communication).

[7] R. F. Hudson, *Chem. Soc. Special Publ. No. 19*, 1965, 93.

[8] R. F. Hudson and G. Salvadori, *Helv. Chim. Acta*, 1966, **49**, 96.

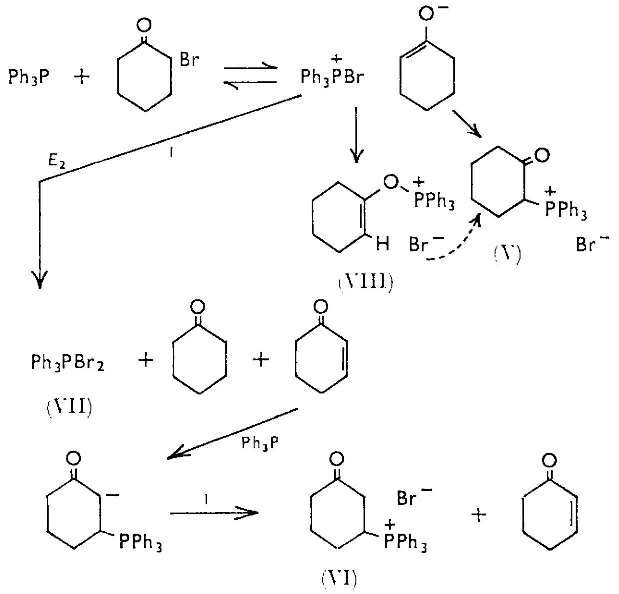
[9] A. J. Speziale and R. D. Partos, *J. Amer. Chem. Soc.*, 1963, **85**, 3312.

[10] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 1960, 2976; 1959, 3874.

[11] A. J. Speziale and R. C. Freeman, *J. Amer. Chem. Soc.*, 1960, **82**, 903.

[12] H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 1962, **13**, 583.

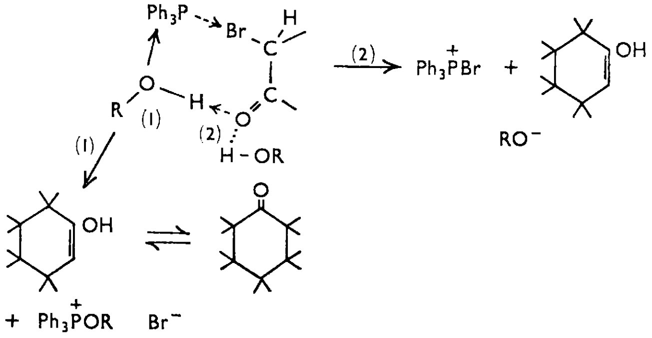
is not surprising in view of the complex mixture of phosphonium salts formed. Some evidence for the salt (VIII) was obtained, however, from the proton n.m.r. spectrum of the mixture of salts precipitated by the addition of an excess of ether to the initial reaction mixture followed by solution in deuteriochloroform. A vinylic proton (τ = 4·66 p.p.m.) in a ratio of 1/30 relative to the aromatic protons was detected, in addition to complex absorptions between τ = 6 and 9 p.p.m. due to the cyclohexane derivatives. If the vinylic proton is indeed due to (VIII), this is present in the mixture of salts to the extent of *ca.* 50%.



Scheme I

1. 2-Bromocyclohexanone

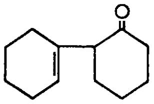
Reaction in the Presence of Water or Alcohols.—The reaction is extremely rapid in the presence of 1—2 equiv. of water or alcohols, being essentially complete within 1 min. in all cases examined, leading to completely different products from those described in the previous section. The powerful catalysis which has been observed[8,13] (and the products) is best explained by assuming hydrogen bonding at the carbonyl group, possibly with synchronous attack on the incipient phosphonium ion by the alcohol molecule (Scheme 2).

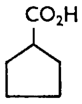


Scheme 2

The products obtained are summarised in Table 2.

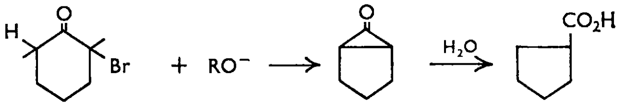
In addition to phosphine oxide, identified as a mixture of Ph_3PO,HBr and Ph_3PO,H_2O in up to 86% yield and cyclohexanone obtained in a maximum yield of 50%, two other carbonyl products, identified as the olefinic ketone (IX) and the carboxylic acid (X) respectively were isolated.


(IX)



(X)

The latter, formed only in small yield (3—5%) probably arises from the Favorski rearrangement of the bromo-ketone promoted by the alkoxide ion, derived from step (2) in Scheme 2:



The water (part of which is bound to phosphine oxide) presumably comes from the condensation responsible for the formation of (IX), which is usually a major product. The enol form, produced by the catalytic mechanism (2) reacts with cyclohexanone, probably through a hydrogen-bonded adduct (Scheme 3).

This is, in fact, an acid-catalysed aldol condensation,

TABLE 2

Products of the reaction between triphenylphosphine and 2-bromocyclohexanone in the presence of an alcohol or water

	$(Ph_3PO)_2,HBr,H_2O$		Yield (%)				
ROH (equiv.)	P	Br^-	RBr	Total ketones	Cyclo-hexanone	(IX)	(X)
MeOH (1)	80	40	—	~70	52	—	—[a]
EtOH (1)	70	35	—	~60	18	35	5
Pr^iOH (1)	83	41	—[b]	~60	30	30	
Bu^nOH (1)	72	36	30	57	—	—	—[a]
Bu^nOH (1)	74	37	12	~60	28	30	3
Bu^nOH (2)	86	43	35	59	14	—	—[a]
Bu^nOH (5)	58	29	12	43	6	—	—[a]
H_2O (5)	83	41	—	30	30	—	—

[a] Not separated. [b] Detected.

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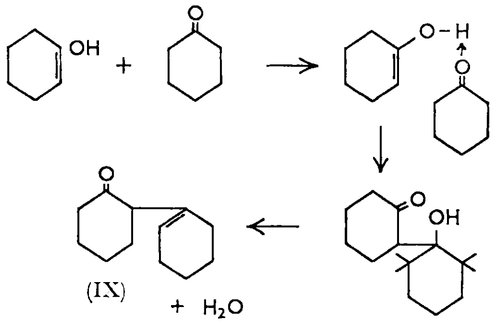
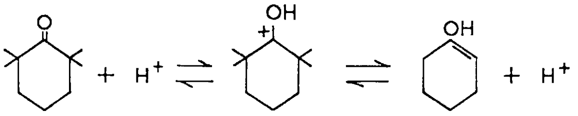
[13] H. Hoffmann and H. J. Diehr, *Angew. Chem., Internat. Edn.*, 1964, **3**, 737.

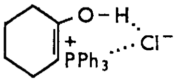
and cyclohexanone gives[14] compound (IX) rapidly in the presence of acid. Whereas the base-catalysed condensation is easy to visualise and proceeds in the same way as a Claisen condensation, the acid-catalysed process is more difficult to interpret, but probably involves the equilibria of Scheme 4 followed by interaction of the enol with the carbonium ion. (This probably involves π–π^* interaction of the kind which is found in the reaction between vinyl ethers and tetracyanoethylene[15] and in similar processes.[16]) It is noteworthy that the enol–keto equilibrium is considerably more favourable for cyclohexanone than for the corresponding non-cyclic ketones (pK_a difference is *ca.* 3—4). This is also shown by the existence of the α-phosphonium salt in two forms, one of which is thought to be the hydrogen-bonded structure (XI).



Scheme 3



Scheme 4



(XI)

Electrophilic Power of Chlorine and Bromine.—Although the above results do not establish the formation of the quasi-phosphonium salt (VIII), as postulated in previous Papers, there is no doubt that triphenylphosphine rapidly attacks the positive bromine atom to give a variety of products derived from the intermediate ion-pair. On the other hand, 2-chlorocyclohexanone is completely inert, even in boiling alcohol, which supports previous observations.[3] This very large difference in electrophilic reactivity is rather surprising in view of the similar properties of chlorine and bromine, *e.g.*, radii, polarisability, and compressibility.

Nucleophilic reactivity towards electronically saturated centres is determined mainly by the polarisability and repulsive coefficients of the interacting atoms,[17] which are related to the energies of the excited *atomic* levels. These are, however, found to be very similar for chlorine and bromine (*e.g.*, the 4*s* level of Cl is 2·86 ev below the continuum, the 5*s* level of Br is 2·74 ev below the continuum,[18] the transitions $3p \longrightarrow 3d$ and $4p \longrightarrow 4d$ are not observed).

We may consider the energy of the lowest unoccupied *molecular* orbital of the electrophil to be a more appropriate measure of reactivity. Some information on this can be derived from measurements of charge-transfer spectra of tertiary amines and halogen compounds.[19] In contrast to tertiary phosphines, tertiary amines do not react with CCl_4 and $BrCCl_3$ except under photoexcitation,[16] although fairly strong charge-transfer bands are observed at 25,000 and 26,500 cm.$^{-1}$, respectively.[19] Nucleophilic reaction can be imagined to occur by the transfer of an electron from the nucleophil to the unoccupied molecular orbital responsible for this transition, followed by bond formation as follows:

$$R_3P + ClCCl_3 \rightleftharpoons R_3\overset{\bullet}{P}{}^{+}[Cl{\cdot}CCl_3]^{-} \longrightarrow R_3\overset{+}{P}Cl + \overset{-}{C}Cl_3$$

If the transition state is similar to the charge-transfer complex, the energy difference of the absorption bands of 0·3 ev suggests a difference of *ca.* 10^5 between the electrophilic reactivity of bromine and chlorine. This may overestimate the difference to some extent as exchange is neglected, but this treatment does suggest that bromine is considerably more electrophilic than chlorine, as observed experimentally.

EXPERIMENTAL

Reagents.—Commercial triphenylphosphine was crystallised from ethanol (95% v/v), dried under vacuum, and stored over P_2O_5. Bromocyclohexanone, prepared by bromination of cyclohexanone in aqueous acetic acid,[20] was repeatedly distilled through a Vigreux column (40—42°/0·01 mm.) and then stored at 5° over molecular sieves (BDH, grade 4A). Occasionally it crystallised, m. p. 8—10°.

Chloroform (analytical grade) was passed through a column filled with neutral alumina (activity 1) before use; no attempt was made to store it after purification because of formation of phosgene.

Methylene chloride (analytical grade) was distilled from P_2O_5 and stored over silica gel. Dimethoxyethane (monoglyme) was distilled from lithium aluminium hydride and stored over molecular sieves. Ether was treated similarly and stored over sodium wire.

Reactions of Triphenylphosphine and Bromocyclohexanone in Aprotic Media.—(a) *Methylene chloride solvent.* Equivalent quantities of molar solutions of the reagents in methylene chloride were mixed under anhydrous conditions and the reaction was followed by infrared spectroscopy (Perkin-Elmer model 521 spectrophotometer). An early rapid change (a few minutes at room temperature corresponding

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[14] W. Hückel, O. Neunhofer, A. Gercke, and E. Frank, *Annalen*, 1929, **477**, 119.

[15] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210.

[16] E. M. Kosower, *Prog. Phys. Org. Chem.*, 1965, **3**, 81.

[17] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16; R. F. Hudson, *Chimia*, 1962, **16**, 173.

[18] Charlotte Moore, " Atomic Energy Levels," N.B.S. Circular No. 467, 1949.

[19] D. P. Stevenson and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149.

[20] R. Belcher, W. Hoyle, and T. S. West, *J. Chem. Soc.*, 1958, 2743.

to a few per cent. of reaction) was observed, as shown by an increase of the peak at 1180 cm.$^{-1}$ (P=O), after which practically no change was noticed. However, with longer reaction times (up to 4 days) new peaks appeared; *e.g.*, at 1625 cm.$^{-1}$ (olefinic absorption) and at 1120 cm.$^{-1}$ (P–O–C, or an absorption characteristic of phenyl-substituted phosphonium salts). During this period the P=O absorption remained unaltered.

(b) *No solvent.* Triphenylphosphine (0·01 to 0·2 mole) and bromocyclohexanone (1 equiv.) were heated under nitrogen, with magnetic stirring, until a clear solution resulted. Heating was then continued at 60—100° for variable periods after which the yellow mass was cooled and dissolved in methylene chloride. An infrared examination of this solution showed essentially the same pattern as above (a), with the intensities of the new peaks and the P=O band more pronounced. (When bromocyclohexanone was heated alone or when this reaction was performed using 2 equivs. of the bromoketone, a black resin resulted.)

The methylene chloride solution was then treated with successive portions of monoglyme, which resulted in the crystallisation of phosphonium salts. These were separated, purified by crystallisation from methylene chloride–monoglyme solutions, and identified as (A) 3-oxocyclohexylphosphonium bromide, m. p. 212—215° (called the β-salt) and (*B*) 2-oxocyclohexylphosphonium bromide, m. p. 240—242° (the α-salt). The yields of these salts varied with the reaction conditions (Table 1).

The filtrates were partially evaporated and diluted with ether which precipitated variable amounts of triphenylphosphine oxide (up to 47%); then the ether solution, after separation of most of the phosphine oxide, was evaporated under reduced pressure. The residue was passed through a 40 cm. column containing activated neutral alumina and eluted with ether until residual triphenylphosphine oxide began to appear. The ether was removed, the first fractions and the residue analysed by vapour-phase chromatography in a Perkin-Elmer model 116 apparatus, with helium carrier, polyethylene glycol (*M* 1500) filler, and temperatures of 110—220°. Cyclohexanone in yields of up to 38% was then obtained and identified by its retention time.

The β-salt was characterised by comparison with an authentic sample prepared from cyclohexenone and triphenylphosphine in the presence of acid.[6] The α-salt was identified by comparison with a sample prepared by the addition of acid to the corresponding betaine.[6] The infrared spectrum of the bromide in Nujol (CO stretching at 1695 cm.$^{-1}$) was not the same as the chloride previously reported (CO at 1600 cm.$^{-1}$). However, in solution (CHCl$_3$), both the chloride and the bromide showed two distinct absorption bands (at 1615 and 1700 cm.$^{-1}$). This suggests that the contribution of the enol form to the structure of these salts depends on ionic association, a factor which must be predominant in the crystalline state. The intensity of the 1700 cm.$^{-1}$ band is greater than that of the 1615 cm.$^{-1}$ band in the case of the bromide and less in the case of the chloride.

Triphenylphosphine oxide was crystallised from ethyl acetate–cyclohexane and identified by comparison with an authentic sample, m. p. 154—155°.

In other experiments, the crude reaction mixture (15—30 minutes' heating at 60—80°) was dissolved in chloroform. Variable amounts (up to *ca.* 15%) of large colourless hygroscopic crystals separated. Occasionally, the addition of small amounts of monoglyme accelerated the separation. The solid was collected and dried *in vacuo* (P$_2$O$_5$), m. p. 260—270°. This material was identified with triphenylphosphine dibromide obtained from the addition of bromine to triphenylphosphine in chloroform or acetonitrile by its infrared spectrum.

The calculated amount of bromine was not obtained from samples nor the controls. This is attributed to the high reactivity of the compound with moisture. Triphenylphosphine dibromide rapidly decomposes in air to a mixed salt containing Ph$_3$PO, HBr, and Ph$_3$PO,H$_2$O (m. p. 140—141°, from acetone). The following structure Ph$_3$P(OH)$_2$ - - - Ph$_3$P(OH)Br has been suggested by Steinkopf and Buchheim[21] for this compound. We find that in addition to the 30 phenyl protons its p.m.r. spectrum shows only one peak representing 3 protons at −1·23 p.p.m. (τ scale) which is in agreement with the presence of hydroxy-groups attached to phosphorus. Furthermore the ^{31}P resonance frequency in methanol is −32·8 p.p.m. relative to H$_3$PO$_4$ as compared to −26·5 p.p.m. reported for pure triphenylphosphine oxide.[22] Similar results (respectively, −1·18 and −32·8 p.p.m.) were obtained for the corresponding chloride, m. p. 110—112° (from monoglyme) obtained by hydrolysis of a triphenylphosphine–PCl$_5$ adduct. These results confirm the existence of strongly hydrogen-bonded PO groups.

In another case, the mixture formed by heating the reactants for 10—15 min. at 80° was dissolved in methylene chloride and diluted with approximately 10 vol. of ether. The heavy precipitate (*ca.* 30% by weight of the reactants) was washed with ether and dried under vacuum. Examination of the p.m.r. spectrum of this precipitate in deuteriochloroform showed the presence of a vinylic proton at τ = 4·66 p.p.m. in a ratio 1/30 relative to the aromatic protons. In addition, the n.m.r. spectrum showed complex absorptions between τ = 6 and 9 p.p.m. probably due to cyclohexanone derivatives. The infrared absorption at 1625 cm.$^{-1}$ was also clearly visible.

Reactions of Triphenylphosphine and Bromocyclohexanone in the Presence of an Alcohol.—(a) *Methylene chloride solution.* n-Butanol (1—2 equiv.) was added to a solution of triphenylphosphine (0·5M) and bromocyclohexanone (0·5M) in methylene chloride. The reaction was followed by observing the changes in the P=O peak at 1180 cm.$^{-1}$. This peak was approximately 90% developed after 1 min., and no further change was observed after the initial 10 min. at room temperature; no absorption was present between 1600 and 1650 cm.$^{-1}$.

(b) *Ether solution.* A solution of bromocyclohexanone (0·05 mole) in ether (15 ml.) was added during 5—10 min. to a solution of triphenylphosphine (0·05 mole) and an alcohol or water (1—5 equivs.) in ether (25 ml.). The ether started to boil and hydrated phosphine oxide hydrobromide was precipitated. After 2—3 hr., the solid was separated and identified by its m. p. and infrared spectrum. The volatile materials were removed under reduced pressure from the liquid fraction. The residue was then purified on alumina as described above and the eluate analysed by v.p.c. Among the products identified by their retention times and infrared spectra were the alkyl bromides and cyclohexanone, 2-cyclohex-1-enylcyclohexanone, and cyclopentanecarboxylic acid. 2-Cyclohex-1-enylcyclohexanone

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[21] W. Steinkopf and K. Buchheim, *Berichte*, 1921, **54**, 1024.

[22] F. Ramirez, D. Rhum, and C. P. Smith, *Tetrahedron*, 1965, **21**, 1941.

was identified by analysis (Found: C, 80·34; H, 10·02%. Calc. for $C_{12}H_{18}O$: C, 80·9; H, 10·01%) mass spectrum (sample obtained by preparative v.p.c.), and infrared comparison with an authentic sample.[14] Cyclopentanecarboxylic acid was identified by analysis (Found: C, 63·04; H, 8·68%. Calc. for $C_6H_{10}O_2$: C, 63·13; H, 8·83%), mass spectrum, and p.m.r. spectrum (1 proton singlet at $\tau = 0{\cdot}9$ p.p.m., 1 proton multiplet at $\tau = 7{\cdot}25$ p.p.m. and 8 protons as a complex band at $\tau = 8{\cdot}25$ p.p.m.). Table 2 shows the yields of the products in relation to the type and quantity of alcohol used. When water was used in place of alcohol, only cyclohexanone in 30% yield (infrared) was obtained. The fate of the remaining 70% of cyclohexanone is unknown.

TABLE 3

Products of the reaction between triphenylphosphine and 2-bromocyclohexanone (no solvent), with subsequent treatment with alcohol

		Products (%)					
Conditions	Alcohol	$(Ph_3PO)_2,HBr,H_2O$	Ph_3PO	RBr	Ketones		P^+ salts
40°, 6 hr.	Pr^iOH (1·1 eq.)	34	—	25	—	Detected	—
80°, 1 hr.	Pr^iOH (1 eq.)	Not measured	—	Detected	~10	—	~20
80°, 2½ hr.	MeOH (12·5)	Not measured	25	—	—	15	25

(c) In another series of experiments, triphenylphosphine and 2-bromocyclohexanone were heated without a solvent in conditions similar to those described above and an alcohol was added to the cold mixture. The products were extracted as described above. The results are shown in Table 3.

In addition, when an excess of methanol was used, a 10% yield of methyltriphenylphosphonium bromide was identified by comparison with an authentic sample (m. p. and infrared spectrum). Evidence for a competitive methylation of Ph_3P was obtained as follows: to a solution of triphenylphosphine (26·2 g., 0·1 mole) in methanol (50 ml.), bromine (8 g., 0·05 mole) was added dropwise with stirring. After several hours, the methanol was removed under reduced pressure and the residue crystallised from methylene chloride–tetrahydrofuran. A compound, m. p. 230—231° (12·1 g., 34%) identical to triphenylmethylphosphonium bromide (infrared) separated. With other alcohols no similar alkylation was observed.

Reaction of 2-Chlorocyclohexanone with Triphenylphosphine in Ethanol.—Triphenylphosphine (20 g., 0·076 mole) and 2-chlorocyclohexanone (10 g., 0·076 mole) were dissolved in ethanol (50 ml.). The solution was boiled overnight and the solvent partially removed under reduced pressure. This caused the crystallisation of triphenylphosphine (14·5 g., 72·5%), m. p. 78—80°.

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