761. *The Dealkylation of Alkyl Aryl Ethers and Sulphides by Diaryl-phosphide and -arsenide Ions*

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The diphenylphosphide ion rapidly dealkylates certain alkyl aryl ethers with the formation of a phenol and the alkyldiphenylphosphine. The reaction with anisole compared with the reaction with phenetole and other simple alkyl phenyl ethers is so rapid that it is almost selective. Suitable cyclic ethers undergo a similar type of fission. Alkyl aryl sulphides give the arylthiol and the alkyldiphenylphosphine.

A shorter investigation of the diphenylarsenide ion indicates that it exerts a similar but rather slower reaction on the above ethers and sulphides.

THE dealkylation of certain ethers by the action of diarylphosphide ions was first recorded by Mann, Tong, and Wystrach,[1] who showed that the diphenylphosphide ion, Ph_2P^-, generated in tetrahydrofuran solution by the action of lithium aluminium hydride on diphenylphosphine, when boiled with anisole gave methyldiphenylphosphine, but with phenetole gave no detectable tertiary phosphine. This marked difference in the reactivities of the methoxyl and ethoxyl groups was also shown by the similar reduction of *m*-methoxyphenylphenylphosphinic acid (I), which gave the secondary phosphine (II) as the phosphide ion, which then underwent demethylation with transference of the methyl group to the phosphorus atom of the unchanged ion, thus giving a mixture of the secondary phosphine (II) and the tertiary phosphine (III); longer heating completed the demethylation giving *m*-hydroxyphenylmethylphenylphosphine (IV).[2,3] The *m*-ethoxyphenylphenylphosphinic acid, subjected to this reduction, gave solely the secondary phosphine [as compound (II)], the anion of which left the ethoxyl group unaffected.[1,4]

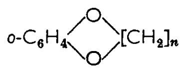
$m\text{-MeO}\cdot C_6H_4\cdot PPh(:O)OH$ (I)

$m\text{-MeO}\cdot C_6H_4\cdot PPhH$ (II)

$m\text{-MeO}\cdot C_6H_4\cdot PPhMe$ (III)

$m\text{-HO}\cdot C_6H_4\cdot PPhMe$ (IV)

$HO\cdot[CH_2]_n\cdot PPh_2$ (V)



(VI)

$o\text{-HO}\cdot C_6H_4\cdot O\cdot[CH_2]_n\cdot PPh_2$ (VII)

$Ph_2P\cdot[CH_2]_n\cdot PPh_2$ (VIII)

The general reaction of the phosphide ion on an alkyl aryl ether is of the type:

$$PhOMe + Ph_2P^- \longrightarrow PhO^- + Ph_2PMe$$

and the yields of the phenol and the phosphine from anisole have been recorded.[2,5] A modified reaction occurs with certain cyclic ethers. For example, the diphenylphosphide ion in tetrahydrofuran reacts with the solvent on long boiling to give 4-hydroxybutyldiphenylphosphine (V; $n = 4$);[5,6] the 3,5-dimethylphenylphenylphosphide ion similarly gives 4′-hydroxybutyl-3,5-dimethylphenylphenylphosphine.[7]

We have now investigated more widely the scope of this dealkylation of ethers by diarylphosphide ions.[8] The diphenylphosphide ion, generated in tetrahydrofuran solution under nitrogen by the action of a petroleum solution of butyl-lithium (1·1 equiv.), was boiled with each ether (1·1 equiv.) for a standard 4 hours, which was extended only when the reaction was particularly slow. After distillation of the solvent and the addition of water

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[1] F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1155.
[2] K. B. Mallion and F. G. Mann, *Chem. and Ind.*, 1963, 1558.
[3] K. B. Mallion and F. G. Mann, preceding Paper.
[4] R. C. Hinton, F. G. Mann, and D. Todd, *J.*, 1961, 5454.
[5] K. B. Mallion and F. G. Mann, *Chem. and Ind.*, 1963, 654.
[6] K. B. Mallion and F. G. Mann, *J.*, 1964, 6121.
[7] M. J. Gallagher, E. C. Kirby, and F. G. Mann, *J.*, 1963, 4846.
[8] F. G. Mann and M. J. Pragnell, *Chem. and Ind.*, 1964, 1386.

to the residue, the tertiary phosphine was extracted with ether, and the alkaline aqueous layer then acidified and the phenol extracted with ether. When, however, the reaction had proceeded to only a small extent, evaporation of the first ether extract gave a mixture of the unchanged aryl ether and diphenylphosphine, and the tertiary phosphine; when the two phosphines had closely similar boiling points, the phosphine fraction was oxidised to give diphenylphosphinic acid and the tertiary phosphine oxide, the former being then extracted with alkali.

Our results are summarised in Table 1; it should be noted that there is considerable evidence that the fission of ethers by nucleophilic reagents proceeds by an S_N2 mechanism.[9]

It will be seen that anisole gave phenol and methyldiphenylphosphine in the increased yields of 83 and 87%, respectively.[2,5] Phenetole gave phenol (10%) and ethyldiphenylphosphine (5%); the isolation of this phosphine contrasts with its apparent absence in earlier experiments [1] in which the diphenylphosphide ion was generated by the action of lithium aluminium hydride in diphenylphosphine. It is in harmony however with the more recent finding that a more rapid reaction is obtained when the *m*-methoxyphenylphenylphosphide ion is generated by the interaction of the phosphine (II) with butyllithium rather than with lithium aluminium hydride.[3]

Phenyl n-propyl and phenyl isopropyl ethers reacted even more slowly and at almost the same speed, a result which is not consistent with an S_N2 mechanism. The yields of phenol and the tertiary phosphines were so low, however (that of the phosphine had moreover to be determined by distillation and oxidation), that this apparent discrepancy may arise by experimental error.

Benzyl phenyl ether reacts approximately as fast as does anisole, in agreement with other investigations on their relative reaction rates under S_N2 conditions.[10] Allyl phenyl ether reacts as expected rather more slowly, and benzyl *p*-hydroxyphenyl ether much more slowly to produce hydroquinone and benzyldiphenylphosphine.

Catechol methylene ether (1,3-benzodioxole) (VI; $n = 1$), on being heated for 4 hours, gave catechol (13%) and the intermediate *o*-hydroxyphenoxymethyldiphenylphosphine (VII; $n = 1$) (33%); heated for 10 hours, it gave yields of 18 and 31·5%, respectively. These yields of catechol showed that some of the phosphine (VII; $n = 1$) must have reacted further to give catechol and bis(diphenylphosphino)methane (VIII; $n = 1$), but this residual diphosphine could not be purified.

These results indicate, however, that in the methylene ether the initial opening of the ring to give the compound (VII; $n = 1$) was much faster than the subsequent fission of this compound to catechol and the diphosphine. In the case of catechol ethylene ether (VI; $n = 2$), after being heated for 4 hours, the extent of the overall reaction, measured by the catechol formed (12%), was closely similar to that of the methylene ether, but the intermediate phosphine (VII; $n = 2$) (3%) has low stability for it was being rapidly transformed into the diphosphine (VIII; $n = 2$).

It has been calculated that the release of electrons from the oxygen atoms to the benzene nucleus occurs more readily in catechol ethylene ether (1,4-benzodioxan) (VI; $n = 2$) than in the methylene ether; [11] consequently nucleophilic attack of the ethylene ring system should occur more rapidly than in the methylene system. The contrary result in our work, where fission of the methylene system is faster than that of the ethylene system, may therefore be due to greater strain in the five-membered system; this receives support from our results with tetrahydro-furan and -pyran discussed below. The greater stability of the *o*-hydroxyphenoxymethyldiphenylphosphine (VII; $n = 1$), compared with that of the ethylene homologue (VII; $n = 2$), is probably based primarily on the steric factor. The nucleophilic attack of the large diphenylphosphide ion occurs on the side-chain carbon atom directly joined to the oxygen atom, and this carbon atom will clearly

[9] R. L. Burwell, *Chem. Rev.*, 1954, **54**, 615.

[10] A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25.

[11] A. G. Evans, G. C. Hampson, C. G. May, and H. Spedding, *J.*, 1949, 1524.

TABLE 1

Products from the interaction of the Ph_2P^- ion and various ethers and sulphides in boiling tetrahydrofuran

Ethers	Time of boiling (hr.)	Phenolic product	Tertiary phosphine product	Intermediate tertiary phosphine product
Anisole	4	Phenol 83%	Ph_2PMe 87%	—
Phenetole	,,	,, 10%	Ph_2PEt 5%	— *
Phenyl n-propyl	,,	,, 3%	Ph_2PPr^n *ca.* 5%	— *
Phenyl isopropyl	,,	,, 3%	Ph_2PPr^i *ca.* 3%	— *
Benzyl phenyl	,,	,, 88%	Ph_2PBz 82%	—
Benzyl *p*-hydroxyphenyl	,,	*p*-$C_6H_4(OH)_2$ 47%	,, 43%	—
Allyl phenyl	,,	Phenol 78%	$Ph_2PC_3H_5$ 76%	—
Catechol methylene	,,	*o*-$C_6H_4(OH)_2$ 13%	†	(VII; $n = 1$) 33%
,,	10	,, 18%	†	,, 31·5%
Catechol ethylene	4	,, 12%	(VIII; $n = 2$) 7%	(VII; $n = 2$) 3% *
Tetrahydrofuran	7	(V; $n = 4$) 22% ‡		
Tetrahydropyran	13·5	(V; $n = 5$) *ca.* 4%		
Sulphides				
Methyl phenyl	4	PhSH 41%	Ph_2PhMe 39%	
Benzyl phenyl	,,	,, 79%	Ph_2PBz 79%	

* The phosphine (V; $n = 4$) was also isolated. † The diphosphine (VIII; $n = 1$) was not isolated. ‡ This result quoted from refs. 5 and 6, the experimental conditions being almost identical.

have much greater steric protection in the methylene phosphine (VII; $n = 1$) than in the ethylene homologue (VII; $n = 2$).

The action of the phosphide ion on tetrahydrofuran itself, giving, after being boiled for 7 hours, a 22% yield of 4-hydroxybutyldiphenylphosphine (V; $n = 4$),[5,6] is much more rapid than that on tetrahydropyran, which after 13·5 hours gave only a 4% yield of the 5-hydroxypentyl analogue (V; $n = 5$). In these two compounds, where the electronic factors must be closely similar, the lower stability of the five-membered-ring system is manifest.

The results obtained in a brief investigation of the dealkylation of alkyl aryl sulphides by the diphenylphosphide ion, to give the arylthiol and the alkyldiphenylphosphine, are given in Table. 1 The experiments, carried out under the previously described conditions, show that the fission of benzyl phenyl sulphide is rather slower than that of benzyl phenyl ether, but the fission of methyl phenyl sulphide is considerably slower than that of anisole.

In general, the fission of thioethers occurs more slowly than that of comparable ethers, with both acidic and basic reagents,[9,12] although sodium in liquid ammonia reacts at much the same speed with both classes of compounds. The comparatively slow fission of methyl phenyl sulphide in our work is unexpected.

We find that the diphenylarsenide ion effects nucleophilic fission of ethers and thioethers almost as well as the diphenylphosphide ion. The results, all obtained by boiling the reaction mixture for 4 hours, are given in Table 2.

TABLE 2

Products from the interaction of the Ph_2As^- ion and ethers and sulphides in boiling tetrahydrofuran

Compound	Phenolic product	Tertiary arsine
Anisole	Phenol (80%)	Ph_2AsMe (85%)
Phenetole	,, (12%)	Ph_2AsEt (6%) *
Benzyl phenyl ether	,, (81%)	Ph_2AsBz (74%)
Benzyl phenyl sulphide	Thiophenol (73%)	,, (71%)

* 4-Hydroxybutyldiphenylarsine was also obtained.

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[12] G. K. Hughes and E. O. P. Thompson, *J. Proc. Roy. Soc. New South Wales*, 1950, **83**, 269.

It is clear that the speed of dealkylation of an alkyl aryl ether (or sulphide) by the phosphide or arsenide ion will depend on the nature of the ion and on the reactivity of the C-1 atom of the alkyl group, the latter being probably the main factor involved.

Our results show that diaryl-phosphide or -arsenide ions may have wide scope for the dealkylation of appropriate ethers and thioethers. The method has three valuable qualities: (*a*) the diaryl-phosphines and -arsines are readily prepared; (*b*) the reaction is carried out in mild non-aqueous almost neutral conditions, in strong contrast with the classical methods which involved boiling in hot acidic solutions (hydriodic or hydrobromic acid, or a phosphoric–sulphuric acid mixture); (*c*) the products of the reaction, namely a phenol or thiophenol and a tertiary phosphine or arsine, can be readily separated by an aqueous alkali–ether extraction; (*d*) the reaction of (in particular) the phosphide ion with an ethoxyl group is so slow compared with the reaction with a methoxyl group that a compound containing both such groups could be completely demethylated before significant de-ethylation had occurred.

Boron trichloride and tribromide may also be used for the demethylation of ethers under mild conditions.[13]

EXPERIMENTAL

All operations involving phosphines or arsines were performed throughout under nitrogen. In view of the small scale of the dealkylation experiments, great accuracy is not claimed for the recorded yields, which were calculated on the phosphine or arsine employed.

Butyl-lithium was prepared in light petroleum (b. p. 40—60°) (referred to throughout as " petroleum ") by the standard method.[14] Diphenylphosphine was prepared by the action of lithium on triphenylphosphine in tetrahydrofuran.[15]

Diphenylarsine.—Sodium (6·1 g., 2 atom-equivs.) was dissolved in liquid ammonia (*ca.* 300 ml.) in a flask fitted with stirrer, nitrogen inlet, and reflux water condenser, and cooled to *ca.* $-65°$ in carbon dioxide–acetone. Triphenylarsine (40 g.) was added portion-wise, the blue-black colour of the solution changing to deep red. The stirring was further continued for 2 hr., and the ammonia then allowed to boil off. Cold, freshly boiled water (100 ml.) and ether (300 ml.) were added to the residue, the mixture becoming colourless. The ethereal layer was collected, and the aqueous layer extracted with ether (2 × 100 ml.). The united dried extracts, on evaporation, left a residue which on distillation gave diphenylarsine, b. p. 87—90°/0·25 mm. (23·5 g., 79%).

The following directions for the interaction of the phosphide ion and anisole are also general for most other ethers; only specific modifications for certain ethers are given later.

Anisole.—An ice-cooled solution of diphenylphosphine (9·1 g.) in dry tetrahydrofuran (110 ml.) was treated with a 1·2M-petroleum solution (45 ml.) of butyl-lithium (1·1 mol.); anisole (5·8 g., 1·1 mol.) was added and the deep red solution boiled under reflux for 4 hr. The solvent was distilled off as completely as possible, and the ice-cooled residue treated with ether (150 ml.) and freshly boiled water (50 ml.). The ethereal layer was separated and the aqueous residue further extracted (2 × 50 ml.); the united dried extracts on removal of the solvent gave a pale yellow oil (11·2 g.) the i.r. spectrum of which showed no P–H peak. Distillation at 0·2 mm. removed unchanged anisole uncondensed, and gave methyldiphenylphosphine (8·5 g., 87%), b. p. 90—108°, on redistillation, b. p. 87—90°/0·2 mm. The i.r. spectrum of the first distillate was identical with that of the authentic phosphine. The phosphine readily gave the ethiodide, m. p. and mixed m. p. 185—186°, from water.

The aqueous layer was acidified to pH 1 with dilute hydrochloric acid and similarly extracted with ether (5 × 50 ml.). The united fractions, on careful evaporation, gave a residue of phenol (3·81 g., 83%). A sample, treated with toluene-*p*-sulphonyl chloride in pyridine, gave phenyl toluene-*p*-sulphonate, m. p. and mixed m. p. 95·5—96°, from ethanol (Found: C, 62·7; H, 4·9. Calc. for $C_{13}H_{12}O_3S$: C, 62·85; H, 4·85%). All subsequent specimens of phenol were identified in this way.

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[13] T. G. Bonner, E. J. Bourne, and S. McNally, *J.*, 1960, 2929; D. L. Manson and O. C. Musgrave, *J.*, 1963, 1011; J. F. W. McOmie and M. L. Watts, *Chem. and Ind.*, 1963, 1658.

[14] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.

[15] J. Chatt and F. A. Hart, *J.*, 1960, 1378.

Phenetole.—The phosphine (9·2 g.), the butyl-lithium solution (47 ml., 1·1 mol.), and phenetole (6·7 g., 1·1 mol.) were treated precisely as above. The ether extract from the acidified residue gave phenol (0·48 g., 10%). The first ether extract, on evaporation, left an oil (12·1 g.) which on distillation at 0·3—0·35 mm. gave the fractions: (*a*) b. p. *ca.* 30°, phenetole (4·8 g., 65% recovery); (*b*) b. p. 97—135° (5·95 g.), mainly diphenylphosphine; (*c*) b. p. 135—155° (0·5 g.); (*d*) b. p. 155—174° (1·9 g.), mainly the phosphine (V; $n = 4$) with some secondary phosphine. The recovery of the phenetole was low, clearly because of incomplete condensation. A solution of fraction (*b*) in acetone (50 ml.) was treated dropwise with a slight excess of hydrogen peroxide (" 100 vol.") and then evaporated on a water-bath. The cold solid residue was shaken with benzene (50 ml.) and 10% aqueous sodium hydroxide (40 ml.). The benzene layer, when separated, again shaken with the hydroxide (20 ml.), dried, and evaporated, gave an oil which, when dissolved in ether and seeded, deposited ethyldiphenylphosphine oxide (0·54 g., 5%), m. p. 120·5—121° (lit.,[16] 120·5—121°). Evaporation of the benzene mother-liquor left an oil which did not give a second crop. Acidification of the alkaline extract deposited diphenylphosphinic acid (4·7 g.), m. p. 189—191°.

Phenyl n-Propyl Ether.—The phosphine (5·05 g.), butyl-lithium (1·1 mol.), and the ether (4·06 g., 1·1 mol.) were treated as the anisole, and two ether extracts obtained. The extract from the acidified aqueous layer on evaporation gave phenol (0·08 g., 3%).

The first ethereal extract, on distillation, gave a fraction (*a*), b. p. 70—78°/14 mm. (2·7 g., 67%), recovered phenyl ether; continued distillation, at 0·25 mm. gave (*b*), b. p. 87—130° (2·7 g.), mainly diphenylphosphine; (*c*), b. p. 130—145° (0·4 g.); (*d*), b. p. 145—165° (1·06 g.), mainly the phosphine (V; $n = 4$). Fraction (*b*) was oxidised with hydrogen peroxide–acetone (as before) and the benzene extract gave a sticky solid, m. p. 80—85°. To ensure complete oxidation, the solid was heated at 100° in alkaline permanganate solution for 1 hr., cooled, and filtered. The filtrate and the manganese dioxide were extracted with benzene, and the united extracts gave diphenyl-n-propylphosphine oxide (0·35 g.), m. p. 99—100° (lit.,[17] 100—101°) after several recrystallisations from ethyl acetate–petroleum.

Phenyl Isopropyl Ether.—This ether (7·8 g.), the phosphine (9·7 g., 1 mol.), and butyl-lithium (1·1 mol.) were treated precisely as in the above experiment, giving phenol (0·13 g., 3%). The phosphine extract gave similar fractions, (*a*) 6·67 g. (86% recovery of ether), (*b*) 6·9 g., phosphine and secondary phosphine, (*c*) mainly the phosphine (V; $n = 4$). Fraction (*b*) on oxidation gave diphenylisopropylphosphine oxide (0·35 g., *ca.* 3%), m. p. 133—136° (lit.,[16] 145—146°) from benzene; there was insufficient material for complete purification.

Benzyl Phenyl Ether.—Interaction of the phosphine (8·0 g.), butyl-lithium (1·1 mol.), and this ether (8·7 g., 1·1 mol.) yielded phenol (3·45 g., 88%), and benzyldiphenylphosphine (10·8 g., 82%), which solidified undistilled when lower-boiling fractions had been removed. It was identified as the methiodide, m. p. 239—240° (lit.,[18] 229—230°,[17] 243—245°) from ethanol (Found: C, 57·15; H, 4·8. Calc. for $C_{20}H_{20}IP$: C, 57·4; H, 4·8%) and the oxide, m. p. 192·5—194° (lit.,[19] 192—193°) (Found: C, 78·3; H, 6·1; P, 10·8. Calc. for $C_{19}H_{17}OP$: C, 78·0; H, 5·9; P, 10·6%).

Benzyl p-*Hydroxyphenyl Ether.*—The phosphine (5·4 g.) was treated in this case with butyl-lithium (2·2 mol.) and the ether (6·4 g., 1·1 mol.) The ethereal extract of the "phenolic" material solidified when the solvent was removed. The residue (4·85 g.) was twice extracted with hot benzene; the undissolved residue gave *p*-hydroquinone (1·5 g., 47%), m. p. and mixed m. p. 171—173°, and a ditoluene-*p*-sulphonate, m. p. 162—163·5° (lit.,[20] 159°) from ethanol. The benzene extract gave the unchanged ether (2·67 g.). Fractional distillation of the ethereal extract of the phosphine material gave diphenylphosphine (1·88 g., 35% recovery) and benzyldiphenylphosphine (3·45 g., 43%) which readily crystallised and gave the methiodide, m. p. and mixed m. p. 238·5—240°, from ethanol.

Allyl Phenyl Ether.—The ether (5·55 g.) gave phenol (2·74 g., 78%), identified as before, and allyldiphenylphosphine (6·42 g., 76%), b. p. 144—145°/0·9 mm. (Found: C, 79·4; H, 6·6. Calc. for $C_{15}H_{15}P$: C, 79·6; H, 6·7%), giving a *methiodide*, m. p. 142·5—143·5°, from ethanol (Found: C, 52·3; H, 5·2. $C_{16}H_{18}IP$ requires C, 52·2; H, 4·9%) and a *methopicrate*, m. p.

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[16] A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395.
[17] S. Trippett, *J.*, 1961, 2813.
[18] P. Beck, H. Hoffmann, and L. Horner, *Chem. Ber.*, 1959, **92**, 2088.
[19] A. Michaelis and W. La Coste, *Ber.*, 1885, **18**, 2116.
[20] W. Borsche and R. Frank, *Annalen*, 1926, **450**, 84.

99—101°, from ethanol (Found: C, 56·6; H, 4·2; N, 8·7. $C_{22}H_{20}N_3O_7P$ requires C, 56·3; H, 4·3; N, 9·0%).

Catechol Methylene Ether (VI; *n* = 1).—This was prepared by Ghosh's method.[21] When the ether (2·35 g.) was added to an ice-cold mixture of diphenylphosphine (6·5 g., 1·8 mol.) in tetrahydrofuran (110 ml.) and butyl-lithium (2·0 mol., 1·1M in petroleum solution), the red colour changed rapidly to black. The solution was boiled for 10 hr. and then worked up as for anisole. The "phenolic" ether extract on evaporation left catechol (0·68 g., 18%), m. p. 103·5—104°, mixed m. p. 104—105°, from light petroleum (b. p. 60—80°); the i.r. spectrum was identical with that of an authentic specimen.

Evaporation of the "phosphine" ethereal extract, ultimately at 15 mm., gave a viscous reddish-black oil (8·7 g.), which when distilled at 0·2 mm. gave the fractions: (*a*) b. p. 90—140° (2·08 g.); (*b*) b. p. 140—176° (0·85 g.); (*c*) b. p. 176—200° (3·38 g., 31·5%). The residue solidified on cooling. Fraction (*a*) was diphenylphosphine. Fraction (*c*), which showed a phenolic OH peak at 3600 cm.$^{-1}$, when redistilled gave the o-*hydroxyphenoxymethyldiphenylphosphine* (VII; *n* = 1), b. p. 167—168°/0·25 mm. (Found: C, 73·8; H, 5·6; P, 10·5%; *M* (cryoscopy in benzene), 319. $C_{19}H_{17}O_2P$ requires C, 74·0; H, 5·6; P, 10·1%; *M*, 308). This phosphine, when boiled with methanolic methyl iodide for 8 hr., gave a viscous red oil, which in turn gave a perchlorate as a gum, and an oily picrate which could not be solidified.

The black residue from the main fractionation could not be obtained crystalline although it almost certainly contained the diphosphine (VIII; *n* = 1). It was therefore extracted with chloroform, the solvent removed, and the residue boiled with methanolic methyl iodide for 3 hr. Removal of the solvent gave an intractable brown glass.

Repetition of the above experiment with 4 hours' heating gave catechol (13%) and the phosphine (VII; *n* = 1) (33%).

Catechol Ethylene Ether (VI; *n* = 2).—When this ether[21] (4·1 g.) was added as before to a mixture of the phosphine (11·8 g., 2·1 mol.) in tetrahydrofuran (150 ml.) and butyl-lithium (2·3 moles) solution, the red mixture did not darken. After the usual working up, the residue was shaken with ether (150 ml.) and air-free water (100 ml.), giving two clear layers with a small quantity of a white solid at the interface. The ether layer and the solid were separated, and the aqueous layer, after further extraction with ether, was acidified to pH 1 as before and separately extracted with ether.

The latter ether extract, on evaporation, gave catechol (0·84 g., 12%) which after trituration with petroleum had m. p. 100—104°, mixed m. p. 104—105°; its i.r. spectrum was identical with that of an authentic sample.

The earlier united ether extracts gave an oil (15·3 g.), which, on distillation at 0·35 mm., gave the fractions: (*a*) b. p. 60—85° (2·7 g.); (*b*) b. p. 85—125° (6·8 g.); (*c*) b. p. 125—180° (3·1 g.), and a residue (1·67 g.) which solidified on cooling. Fraction (*a*) was the recovered ether (VI; *n* = 2); (*b*) was diphenylphosphine; (*c*) was the phosphine (V; *n* = 4) containing some diphenylphosphine. The residue was ethylene-1,2-bis(diphenylphosphine) (VIII; *n* = 2) (7%), m. p. 143—145° (lit.,[22] 143—144°) from ethanol (Found: C, 77·8; H, 6·1. Calc. for $C_{26}H_{24}P_2$: C, 77·9; H, 6·5%); it gave a dimethiodide, m. p. 305—307° (lit.,[15] 306—307°), from methanol.

The insoluble white material (0·54 g., 3%) was almost certainly the lithium salt of 2-(*o*-hydroxyphenoxyl)ethyldiphenylphosphine (VII; *n* = 2). After thorough trituration with water it still contained lithium and was apparently unaffected. The phosphine was liberated by N-sulphuric acid and extracted with ether. Evaporation of ether gave an oil, almost certainly the phosphine (VII; *n* = 2); its i.r. spectrum showed an OH band, and the bands of a monosubstituted benzene. A solution in methanolic methyl iodide, when boiled for 3 hr. and evaporated, gave a glass, which in turn gave a methopicrate, m. p. 108—110°, from aqueous methanol. The absence of an OH band in the spectrum and the analysis indicated that the phenolic group had also been methylated, and that this compound was 2-(o-*methoxyphenoxy*)-*ethyldiphenylphosphine methopicrate* [Found: C, 57·8; H, 4·7; N, 7·5. $C_{28}H_{26}N_3O_9P$ (A) requires C, 58·0; H, 4·5; N, 7·25%. $C_{27}H_{24}N_3O_9P$ (B) requires C, 57·3; H, 4·3; N, 7·4%]. [The values (A) and (B) are those of the methoxy- and hydroxy-compounds, respectively.]

Tetrahydrofuran.—The results with this compound (Table 1), obtained similarly to those with tetrahydropyran, have been recorded.[5,6]

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[21] B. N. Ghosh, *J.*, 1915, **107**, 1597.

[22] W. Hewertson and H. R. Watson, *J.*, 1962, 1490.

Tetrahydropyran.—The chilled diphenylphosphine (18·4 g., 1 mol.) in dry tetrahydropyran (175 ml.) was treated with butyl-lithium (1·2 mol., 1·2M in petroleum solution). The deep red solution was boiled under reflux for 13½ hr., and unchanged pyran was distilled off as completely as possible. The residue was treated with water and then thoroughly extracted with ether. Evaporation of the extract gave an oil (20·7 g.), which on distillation at 0·3 mm. gave the fractions: (*a*) b. p. 80—130° (16·6 g.); (*b*) b. p. 130—160° (0·3 g.); (*c*) b. p. 160—188° (1·2 g.). Fraction (*a*) was recovered diphenylphosphine (90%). Fraction (*c*), a rather viscous oil, had an i.r. spectrum identical with that of the phosphine (V; $n = 4$) apart from a band at 1750 cm.$^{-1}$: there is little doubt that this fraction was 5-hydroxypentyldiphenylphosphine (V; $n = 5$) (*ca.* 4%), but insufficient material precluded a decisive identification. Crystalline derivatives could not be obtained.

Methyl Phenyl Sulphide.—Diphenylphosphine (10·46 g., 0·91 mol.) in ice-cold tetrahydrofuran (150 ml.) was treated in turn with butyl-lithium (1·1 mol.) and the sulphide (7·7 g., 1·1 mol.), and the deep red solution was boiled for 4 hr. After the usual working up, evaporation of the second ether extract gave thiophenol, which, in ethanol solution, was identified and estimated by the addition of ethanolic mercuric chloride, the insoluble mercurichloride, PhSHgCl, being precipitated. This compound (8·04 g., corresponding to 41% thiophenol), when washed with ethanol and dried, had m. p. and mixed m. p. 192° (decomp.) (lit.,[23] 191·5°).

The first ether extract, on distillation, gave the recovered sulphide (3·4 g., 44%), b. p. 76—83°/15 mm., and then the fractions: (*a*) b. p.96—125°/0·3 mm. (9·4 g.); (*b*) b. p. 125—165°/0·3 mm. (1·3 g.). Fraction (*b*) was mainly the phosphine (V; $n = 4$). Fraction (*a*), after hydrogen peroxide oxidation as before, gave methyldiphenylphosphine oxide (4·7 g., corresponding to 39% tertiary phosphine), m. p. 111—112° (lit.,[19] 111—112°) from ether.

Benzyl Phenyl Sulphide.—This sulphide (11·4 g.), similarly treated with the phosphine (9·6 g., 0·91 mol.) and butyl-lithium (1 mole) and worked up, gave the mercurichloride (14·06 g., corresponding to 78·5% thiophenol), and benzyldiphenylphosphine, isolated as the methiodide (17·0 g., corresponding to 79% of tertiary phosphine), m. p. and mixed m. p. 242—243°, from ethanol.

Diphenylarsine.—Experiments with this arsine were carried out under the same conditions as those with the phosphine, with 4 hours' heating throughout. Anisole (7·15 g.), the arsine (13·8 g., 1 mol.) in the tetrahydrofuran (180 ml.), and the 1·18M-solution (56 ml.) of butyl-lithium (1·1 mol.) gave a red solution. After the reaction, working up gave phenol (4·53 g., 80%), identified as before, and methyldiphenylarsine (12·5 g., 85%), b. p. 112—115°/0·35 mm., identified as the methiodide, m. p. 215—216° (lit.,[24] 190°,[25] 211—213°) from ethanol (Found: C, 43·4; H, 4·4. Calc. for $C_{14}H_{16}AsI$: C, 43·5; H, 4·2%), and as bis(methyldiphenylarsine)-dibromopalladium, m. p. 168° (lit.,[26] 178°) from acetone (Found: C, 41·3; H, 3·6. Calc. for $C_{26}H_{26}As_2Br_2Pd$: C, 41·4; H, 3·5%).

Phenetole (6·85 g.), similarly treated, gave phenol (0·58 g., 12%); the first ether extract gave recovered phenetole (4·7 g.) and, at 0·4 mm., fractions: (*a*) b. p. 105—140° (6·8 g.); (*b*) b. p. 140—174° (0·3 g.); (*c*) b. p. 175—190° (4·6 g.). Fraction (*c*), the i.r. spectrum of which showed a strong OH band, on redistillation gave 4-*hydroxybutyldiphenylarsine*, b. p. 172—174°/0·4 mm. (Found: C, 63·6; H, 6·6. $C_{16}H_{19}AsO$ requires C, 63·6; H, 6·3%); it gave a *methiodide*, m. p. 147—148° from ethanol (Found: C, 45·8; H, 5·3. $C_{17}H_{22}AsIO$ requires C, 45·9; H, 5·0%). Fraction (*a*) on oxidation gave an oily residue (0·8 g.), undoubtedly ethyldiphenylarsine oxide, which was converted into the hydroxypicrate and, after four recrystallisations from ethanol, had m. p. 101—102° (lit.,[27] 116°) and was still impure, probably having undergone some hydrolysis (Found: C, 49·6; H, 4·0; N, 8·5. Calc. for $C_{20}H_{18}AsN_3O_8$: C, 47·7; H, 3·6; N, 8·35%).

Benzyl phenyl ether (8·0 g.) gave phenol (3·06 g., 81%), and benzyldiphenylarsine (9·26 g., 74%), m. p. 63—65°, b. p. 176—178°/0·3 mm. (Found: C, 71·2; H, 5·1. Calc. for $C_{19}H_{17}As$: C, 71·2; H, 5·4%). It was further identified as the methiodide, m. p. 186—188° (lit.,[28] 193°)

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(Found: C, 52·0; H, 4·4. Calc. for $C_{20}H_{20}AsI$: C, 51·95; H, 4·4%), and as the *bisarsine-dibromopalladium*, orange crystals, m. p. 200° (decomp.) from aqueous dimethylformamide (Found: C, 50·6; H, 3·8. $C_{38}H_{34}As_2Br_2Pd$ requires C, 50·3; H, 3·8%).

Benzyl phenyl sulphide (10·5 g.) similarly gave thiophenol mercurichloride (3·86 g., corresponding to 73% yield of thiophenol), m. p. and mixed m. p. 192°, and benzyldiphenylarsine, identified as the pure methiodide (15·64 g., corresponding to a 71% yield of the arsine), m. p. and mixed m. p. 186—187°. Unchanged sulphide (3·35 g., 32%), m. p. 40—42°, with an authentic sample 41—43°, was recovered.

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