A Method of reducing Phenols to Aromatic Hydrocarbons.

By G. W. KENNER and N. R. WILLIAMS.

[Reprint Order No. 5839.]

Simple phenols are easily converted by means of diethyl phosphorochloridate or tetraethyl pyrophosphate into aryl diethyl phosphates. The aromatic hydrocarbons corresponding to the phenols are the principal products of reaction between these esters and solutions of sodium or lithium in liquid ammonia. The reaction is much less successful with dihydric phenols.

IT was shown by Sowa and his co-workers (*J. Amer. Chem. Soc.*, 1937, **59**, 603, 1488; 1938, **60**, 94) that diaryl ethers react with a solution of sodium in liquid ammonia according to the equation $ArOAr' + 2Na + NH_3 = ArH + Na{\cdot}NH_2 + NaOAr'$. An analogous reaction might take place with an aryl ester of any oxy-acid, provided that the acyl residue is not easily attacked by the sodium solution. We have been led to investigate this possibility by the notion that a generally successful reaction, coupled with an esterification step, would provide another method of reducing phenols to aromatic hydrocarbons. The aryl toluene-*p*-sulphonates were the obvious choice, but they are very sparingly soluble in liquid ammonia. We found that the methanesulphonyl derivatives of *p*-phenylphenol and α-naphthol are likewise insoluble, but that *m*-acetamidophenyl and *p*-methoxyphenyl methanesulphonate are both moderately soluble in liquid ammonia and are reduced by sodium in about 40% yield to acetanilide and anisole, respectively. In contrast with the sulphonic esters, all the aryl diethyl phosphates which we have examined are freely soluble in liquid ammonia. In many cases their reduction takes the expected course; it has already been recorded that sodium phosphate is produced from diphenyl hydrogen phosphate by reaction with sodium in liquid ammonia (Baddiley and Thain, *J.*, 1953, 1610).

The aryl esters of diethyl phosphoric acid were prepared from both the acid chloride and the acid anhydride. The most convenient method was to add the calculated quantity of triethylamine to a carbon tetrachloride solution of the phenol and diethyl phosphite, made directly from ethanol and phosphorus trichloride (McCombie, Saunders, and Stacey, *J.*, 1945, **380**). Diethyl phosphorochloridate was produced by base-catalysed reaction between the phosphite and carbon tetrachloride (Atherton, Openshaw, and Todd, *J.*, 1945, 660; Atherton and Todd, *J.*, 1947, 674; Steinberg, *J. Org. Chem.*, 1950, **15**, 637) and the over-all reaction was :

$$\mathrm{ArOH + HO{\cdot}P(OEt)_2 + CCl_4 + NEt_3 = ArO{\cdot}P(O)(OEt)_2 + CHCl_3 + NHEt_3Cl}$$

Alternatively, an aqueous solution of the sodium phenoxide was treated with the water-soluble anhydride, tetraethyl pyrophosphate, which is commercially available. A slight disadvantage of this procedure was that the precipitated ester extracted some of the anhydride from the aqueous phase. All the esters of monohydric phenols prepared so far have been viscous oils showing no tendency to crystallise.

All the aryl diethyl phosphates listed in Table 1 were reduced easily when either lithium or sodium was added to their solutions in liquid ammonia. The amount of metal required according to the following equation was consumed before the blue colour appeared :

$$\mathrm{ArO{\cdot}P(O)(OEt)_2 + 2M + NH_3 = ArH + M{\cdot}NH_2 + MO{\cdot}P(O)(OEt)_2}$$

At the end of the reaction it was convenient to add alcohol before isolating the products. The presence of alcohol during the reduction, or the use of excess of metal, gave poor results, presumably owing to reduction of the aromatic nucleus (Birch, *Quart. Rev.*, 1950, **4**, 69). The yields of hydrocarbon (Table 2) varied around 75% and therefore the above equation does not account for the whole of the reaction. The minor products were the phenol and a bicarbonate-soluble oil, possibly the aryl ethyl hydrogen phosphate. These substances could have arisen from attack by the metal on the phosphoryl groups. This may have been the major course of reaction in the cases of *o*- and *p*-chlorophenyl diethyl phosphates, or ammonolysis may have competed with the sluggish reduction; considerable quantities of the chlorophenols were produced by reaction with either sodium or lithium. The latter did not dissolve smoothly in the usual way. Gilman, Zoellner, and Selby (*J. Amer. Chem. Soc.*, 1933, **55**, 1252) have recorded failure to metalate *p*-dibromobenzene and *p*-bromochlorobenzene with lithium, although good yields were obtained with other aryl bromides. The diethyl phosphate of methyl salicylate gave about 20% of methyl benzoate despite the obvious side-reactions of the methoxycarbonyl group.

The success of these experiments with monohydric phenols encouraged the hope that it would be possible to use the reaction as a stage in the reduction of quinones to aromatic hydrocarbons. However, benzene could not be detected as a product of the reaction between the bis(diethyl phosphoryl) derivative of quinol and 4 equivs. of lithium. Nor did reaction with 2 equivs. of lithium appear to give diethyl phenyl phosphate, which can itself be reduced in good yield to benzene. On the other hand, the derivatives of resorcinol and catechol gave modest yields of benzene (30% and 15% respectively) on reduction with either lithium or sodium. Similarly in the naphthalene series, no naphthalene could be obtained from the esters of 1 : 4- and 1 : 5-dihydroxynaphthalene, but about 20% was produced from the 1 : 6-, 2 : 6-, and 2 : 7-isomers. In all these cases the product was mainly a mixture of alkali-soluble oil and neutral oil of high boiling point. Thus the method seems to have little practical value for dihydric phenols, but the nature of the reaction with the quinol derivative deserves further investigation.

Another way of reducing phenols to aromatic hydrocarbons (Kenner and Murray, *J.*, 1949, S 178) consists in hydrogenating the toluene-*p*-sulphonates in presence of Raney nickel. When the two methods are equally effective the new one is more convenient. Hydrogenolysis of the phosphate esters of *m*-acetamidophenol and 3 : 5-xylenol was unsuccessfully attempted with a sample of Raney nickel which catalysed the toluene-*p*-sulphonate reduction. Some 10% of reduction was detected when platinised nickel (Levering, Morritz, and Lieber, *J. Amer. Chem. Soc.*, 1950, **72**, 1190) was used, but this was not consistently reproducible. Hydrogenation with Adams platinum catalyst has often been used for the removal of phenyl groups from phosphates (Brigl and Müller, *Ber.*, 1939, **72**, 2121) and it produced *N-cyclo*hexylacetamide from *m*-acetamidophenyl diethyl phosphate. Interruption of the reaction when only one mol. of hydrogen had been absorbed yielded, not acetanilide, but a mixture of the hexahydro-compound and unchanged ester. We therefore believe that saturation of the aromatic ring is essential for the platinum-catalysed cleavage of the carbon–oxygen link and is not merely a subsequent process as originally postulated by Brigl and Müller (*loc. cit.*). This is reasonably explained by the assumption that it is the intermediate allyl-type phosphates which suffer hydrogenolysis.

EXPERIMENTAL

Preparation of Aryl Diethyl Phosphates.—(a) *From diethyl phosphite.* Triethylamine (14·3 c.c., 0·104 mole) was added slowly with vigorous shaking to an ice-cooled solution of the phenol (0·1 mole) in carbon tetrachloride (30 c.c.) and diethyl phosphite (13·4 c.c., 0·104 mole; McCombie, Saunders, and Stacey, *J.*, **1945**, 380). Towards the end of the addition triethylamine hydrochloride began to separate as white needles and eventually a solid mass was formed. This was kept overnight at room temperature and then diluted with water. The organic layer was washed once with dilute hydrochloric acid, four times with dilute sodium hydroxide solution, and once with water before being dried (K_2CO_3) and evaporated under reduced pressure. The residual yellow-brown syrup, obtained in the yield recorded in Table 1, was pure enough for use in reductions, but was distilled in a tube at 120°/10^{-2} mm. before analysis.

(b) *From tetraethyl pyrophosphate.* Tetraethyl pyrophosphate (25·4 c.c., 0·104 mole; supplied by Albright and Wilson Ltd.) was added in one portion to a solution of the phenol (0·1 mole) in N-sodium hydroxide (104 c.c.). The mixture was vigorously shaken and became opaque in 15—30 sec. The brown oil which separated was extracted into ethyl acetate (50 c.c.) and washed with N-sodium hydroxide (4 × 50 c.c.) and then water. Evaporation of the dried (K_2CO_3) ethyl acetate left the tabulated yield of red-brown oil.

TABLE 1. *Aryl diethyl phosphates*, ArO·P(O)(OEt)$_2$.

		Yield from				Found (%)		Reqd. (%)	
No.	Ar	(a)	(b)	n_D^{17}	Formula	C	H	C	H
1	Ph	95	—	1·475	$C_{10}H_{15}O_4P$	51·9	6·8	52·2	6·5
2	*p*-Me·C_6H_4	94	—	1·473	$C_{11}H_{17}O_4P$	54·0	7·0	54·1	7·0
3	*m*-Me·C_6H_4	96	—	1·472	$C_{11}H_{17}O_4P$	53·9	6·9	54·1	7·0
4	*o*-Me·C_6H_4	83	—	1·476	$C_{11}H_{17}O_4P$	54·2	7·1	54·1	7·0
5	*p*-MeO·C_6H_4	98	—	1·487	$C_{11}H_{17}O_5P$	51·0	6·5	50·7	6·6
6	*m*-MeO·C_6H_4	78	—	1·484	$C_{11}H_{17}O_5P$	51·0	6·9	50·7	6·6
7	*o*-MeO·C_6H_4	85	—	1·486	$C_{11}H_{17}O_5P$	50·6	7·1	50·7	6·6
8	*p*-NHAc·C_6H_4	89	—	1·510	$C_{12}H_{18}O_5NP$	50·0	6·5	50·1	6·3
9	*m*-NHAc·C_6H_4	—	91	1·509	$C_{12}H_{18}O_5NP$	49·9	6·4	50·1	6·3
10	*p*-C_6H_5·C_6H_4	87	—	1·548	$C_{16}H_{19}O_4P$	63·0	6·4	62·7	6·3
11	3 : 5-$C_6H_3Me_2$	—	84	1·480	$C_{12}H_{19}O_4P$	56·0	7·6	55·8	7·4
12	α-$C_{10}H_7$	—	91	1·547	$C_{14}H_{17}O_4P$	60·3	6·1	60·0	6·1
13	β-$C_{10}H_7$	97	73	1·544	$C_{14}H_{17}O_4P$	60·3	6·2	60·0	6·1

Reduction of Aryl Diethyl Phosphates.—The ester (about 15 g.) was dissolved in liquid ammonia (about 150 c.c., direct from a cylinder) in a 500-c.c. conical flask; no precautions were taken to exclude moisture. The metal (exactly 2 atomic proportions) was added in small pieces during about 5 min. (as fast as frothing would allow) to the solution, which was shaken by hand. In cases in which the solution was not too dark the blue colour then became persistent. Alcohol (2 mols.) was added and the ammonia allowed to evaporate while the flask was left for several hours. The product was taken up in ether (50 c.c.), washed with sodium hydrogen carbonate solution and sodium hydroxide solution, and recovered by evaporation. The tabulated yields refer to this material, which was found by subsequent distillation or recrystallisation to be of good quality. A series of experiments with esters 9 and 11 showed that the yield was unaffected by the following variations : dissolution of the ester in ether (25 c.c.) before addition of the ammonia, addition of a solution of the metal in ammonia, addition of a solution of the ester in ammonia to a solution of the metal in ammonia, omission of the final addition of ethanol. A less pure sample of acetanilide was obtained from ester No. 9 when ammonium chloride was added instead of ethanol.

TABLE 2. *Reduction of aryl diethyl phosphates.*

Ester no.	1	2	3	4	5	6	7	8	9	10	11	12	13
Yield on using Li	82[a]	75[b]	54[b]	63[b]	85	—	88	60	93	75	63	71	88
Yield on using Na	—	—	—	—	88	85	90	76	89	80	58	57	95

[a] Estimated from the intensity of ultra-violet absorption curve, identical in shape with that of pure benzene, after allowance for a loss of 45% during evaporation of the ammonia. [b] Toluene estimated in the same way as the benzene, with allowance for a loss of 25%.

Preparation of Aryl Methanesulphonates.—Methanesulphonyl chloride (1·1 mols.) was added to a solution of the phenol in a slight excess of N-sodium hydroxide. The mixture was immediately shaken vigorously in order to prevent coagulation of the chloride with the ester, which soon crystallised. The ester was collected and recrystallised from water or aqueous alcohol. m-*Acetamidophenyl methanesulphonate* (yield 78%), m. p. 107·5—108° (Found: C, 46·9; H, 4·7. $C_9H_{11}O_4NS$ requires C, 47·1; H, 4·8%), and p-*methoxyphenyl methanesulphonate* (yield 40%), m. p. 79·5—80° (Found: C, 47·2; H, 5·1. $C_8H_{10}O_4S$ requires C, 47·5; H, 5·0%), were reduced, as described above for the phosphates, by sodium in liquid ammonia to acetanilide (40%) and anisole (38%) respectively.

The authors thank Sir Alexander Todd, F.R.S., for his encouragement, and the Department of Scientific and Industrial Research for a Maintenance Allowance (N. R. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 2nd,* 1954.]