a lesser extent. Also, the preferred conformations of this molecule place the carbonyl group in a somewhat favorable position for complex formation.[34,36] Since these steric effects would be minimal in smaller rings, one would predict that cycloheptanone and cyclohexanone, respectively, should follow cyclooctanone in the BF_3 basicity series.

Thus, as a result primarily of steric factors, cyclopentanone emerges as a strong complexing agent for BF_3, in spite of its low proton basicity as compared to other members of this series. Previous studies in these laboratories[20-24] have implied that, if pK_{BH^+} values for two bases differ by one or more units, essentially all the BF_3 will be complexed by the stronger ligand. Since cyclopentanone can compete with all the larger cycloalkanones in BF_3 solution, steric factors reduce the effective basicity of the latter by at least a factor of 10.

In addition to the relative basicity, which is a fundamental molecular property, the fraction of BF_3 complexed by each base in a mixture depends on the concentration of the components. For instance, when cyclopentanone and cyclohexanone are mixed in equal concentrations, cyclopentanone complexes approximately two-thirds of the BF_3. However, these bases complex equal fractions when the cyclohexanone concentration is twice that of cyclopentanone (see Table II). In other words, the relationship, $f \propto b \cdot c$, where f is the BF_3 fraction complexed, b is the relative basicity of the molecule toward BF_3, and c is the base concentration, seems to hold for these systems. Thus, at equal concentrations, $f_1/f_2 = b_1/b_2$ provides a measure of the relative basic strength of these compounds. Assuming that basicity is not concentration dependent, the fraction of BF_3 complexed at various base concentrations can be estimated from $f_1/f_2 =$ constant (c_1/c_2). This relationship holds within 10–20% when tested in these mixtures and it provides a justification for the normalization procedure used in the development of the Table II data.

Registry No.—Adduct of BF_3 and 4,4-dimethylcyclohexanone, 39209-78-4.

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On the Dehydroxylation of Phenols by Cleavage of Their Diethyl Phosphate Esters with Alkali Metals in Liquid Ammonia[1]

Roberto A. Rossi[2] and Joseph F. Bunnett*

University of California, Santa Cruz, California 95064

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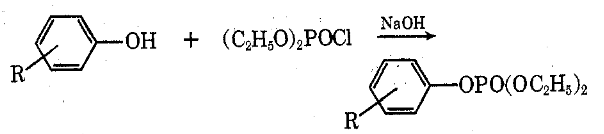
In a method due to Kenner and Williams, the phenolic hydroxyl group is replaced by hydrogen in a two-step process: the phenol is converted to an aryl diethyl phosphate ester, which is then cleaved with an alkali metal in ammonia. Reinvestigation of the method with use of glpc shows it to be convenient and to give high yields of dehydroxylation products. Complications are encountered in the dehydroxylation of 1-naphthol, but allyl, acetyl, and (in part) nitro substituents survive the procedure unscathed.

A communication by Musliner and Gates,[3] announcing a new method for the dehydroxylation of phenols, started with the sentence: "Up to the present time, no general method has been available for the removal of phenolic hydroxyl groups." The communication goes on to describe the method they developed, which involves conversion of phenols to heterocyclic ethers (especially 1-phenyl-5-tetrazolyl ethers) which are then cleaved by hydrogenolysis over 5% palladium on carbon. However, it fails to mention an attractive method of considerable generality which had been described 11 years earlier. We have reinvestigated the older method, and have formed a high opinion of it.

The method to which we refer, due to Kenner and Williams,[4] involves conversion of the phenol to the corresponding aryl diethyl phosphate ester, and then cleavage of the latter with an alkali metal in liquid ammonia. The modification of it which we employed is sketched in eq 1 and 2. Kenner and Williams reported high yields of dehydroxylation products from several alkoxy-, alkyl-, or acetamido-substituted phenols.



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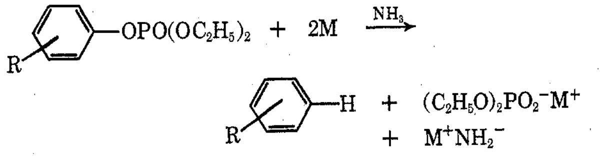

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The method was also studied and employed by Pelletier and Locke[5] for the small-scale dehydroxylation of several phenols, most of which were derived from polycyclic aromatic systems. The yields that they ob-

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[1] Research supported in part by the National Science Foundation.

[2] Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

[3] W. J. Musliner and J. W. Gates, Jr., *J. Amer. Chem. Soc.*, **88**, 4271 (1966).

[4] G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).

[5] S. W. Pelletier and D. M. Locke, *J. Org. Chem.*, **23**, 131 (1958).

tained were modest (17–50%). They pointed out that the yields reported by Kenner and Williams were of crude products. In the case of the dehydroxylation of β-naphthol, Kenner and Williams reported naphthalene yields of 88 and 95%, but Pelletier and Locke carefully examined the crude product and found that only about half of it was actually naphthalene. Critics have perhaps drawn the inference that the method is one of mediocre worth.

Some closely related reactions, the cleavage of alcohol and enol diethyl phosphate or tetramethylphosphorodiimidate esters in fashion analogous to eq 2, have been reported by Ireland and coworkers.[6,7]

The investigations of Kenner and Williams and of Pelletier and Locke were conducted without benefit of gas–liquid partition chromatography. Making use of this technique, we have been able to reexamine with ease the question of product purity. We have also extended the method to phenols with substituents not involved in previous studies. We conclude that the method is an excellent one. However, it has some limitations, which we shall discuss.

Preparation of Phosphate Esters.—Kenner and Williams[4] converted phenols to the corresponding aryl diethyl phosphates in high yields by reaction with diethyl phosphite and triethylamine in CCl_4 solution; diethyl phosphorochloridate, $(C_2H_5O)_2POCl$, is apparently formed *in situ* and then reacts with the aryloxide ion much as in eq 1. We performed the esterification according to eq 1, after Bliznyuk, *et al.*[8] This straightforward method also gives high yields, as summarized in Table I.

The Step of Reductive Cleavage.—The general procedure is to dissolve the aryl diethyl phosphate in liquid ammonia with diethyl ether as cosolvent, cool the solution to −78°, and add small chunks of lithium, sodium, or potassium metal with stirring until a faint blue color persists. For phosphate esters with substituents, such as alkyl and alkoxy groups, that are resistant to solvated electrons and amide ions, the ester (in ether solution) may alternatively be added to excess alkali metal in ammonia. The mixture is then acidified by addition of solid NH_4Cl and products are isolated by standard techniques. A number of reductive cleavages are summarized in Table II. In most cases yield determination was by glpc, but in a few it was by isolation and weighing.

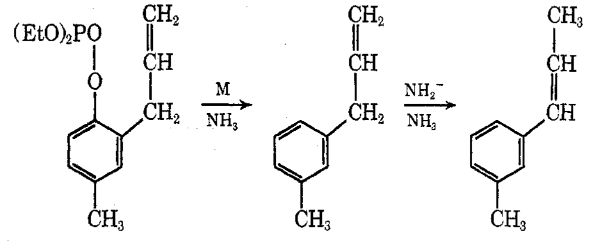
The aryl diethyl phosphate (aryl DEP) esters derived from phenol, 2,6-dimethylphenol, and 2-methoxy-4-methylphenol were reduced respectively to benzene (77%), *m*-xylene (92%), and *m*-methoxytoluene (77%). By the alternative procedure in which the ester is added to excess potassium metal in ammonia, 2,6-dimethylphenyl DEP gave *m*-xylene in 88% yield.

However, when 2-biphenylyl DEP was treated with potassium metal according to the usual procedure, not only biphenyl (85%) but also a dihydrobiphenyl (13%) were obtained. Biphenyl itself is reduced by alkali metals in liquid ammonia,[9a] and it readily accepts an electron to form a radical anion which is relatively stable in the absence of good proton donors.[10] Acting on the hypothesis that some biphenyl radical anion was formed under reduction conditions and that it was converted to a dihydrobiphenyl during acidification with NH_4Cl, we tried adding sodium benzoate to the reaction mixture before NH_4Cl. Sodium benzoate has a high affinity for electrons, and it has been used in other studies as an "electron mop."[11,12] When sodium benzoate was added, there was an immediate color change, from green to orange-yellow, and then to colorless on addition of NH_4Cl, and the product obtained was biphenyl (96%) free of dihydrobiphenyl.

From this experience, and with attention to the work of Pelletier and Locke[5] as well as the known affinity of naphthalene for electrons,[10] it was anticipated that similar problems would be encountered in the reductive cleavage of 1-naphthyl DEP. Therefore sodium benzoate was added before NH_4Cl in all runs. Extensive reduction to 1,4-dihydronaphthalene nevertheless occurred. In three runs, the highest yield of naphthalene obtained was 25%; it was always accompanied by 1,4-dihydronaphthalene, in yields as high as 41%, but the sum of yields of these two products never exceeded 43% in any run. The further products were not identified.

Reduction of *m*-acetylphenyl DEP with sodium metal afforded acetophenone in 71% yield. It is noteworthy that the carbonyl group survived in such an electron-rich environment. Nonenolizable ketones readily accept electrons to form ketyls, but enolizable ketones tend to form enolate ions instead.[13] It is probable that the enolate ion of *m*-acetylphenyl DEP was rapidly formed and that the carbonyl group remained protected in that way until acidification with NH_4Cl at the end of the process.[14]

Dehydroxylation of 2-allyl-4-methylphenol was a challenge because conceivably the double bond of the allyl group might shift into conjugation with the ring under the rather basic conditions of the dephosphation step.[15] If so, the double bond might also be reduced.[9b] Both complications were experienced when 2-allyl-4-methylphenyl DEP (**1**) was reductively cleaved by excess potassium metal without sodium benzoate aftertreatment; besides 28% of the product of straight-



(3)

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[6] R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969).

[7] R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Amer. Chem. Soc.*, **94**, 5098 (1972).

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[10] L. M. Dorfman, *Accounts Chem. Res.*, **3**, 224 (1970).

[11] A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

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[13] G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

[14] An alternative possibility, suggested by a referee, is that amide ion may add to the carbonyl group, forming the anion of a carbinolamine and thereby protecting the carbonyl group from reduction; *cf.* P. J. Hamrick, Jr., and C. R. Hauser, *J. Amer. Chem. Soc.*, **81**, 2096 (1959).

[15] *Cf.* E. A. Rabinovich, I. V. Astaf'ev, and A. I. Shatenshtein, *Zh. Obshch. Khim.*, **32**, 748 (1962), and references cited therein.

TABLE I

ARYL DIETHYL PHOSPHATES[a] FROM PHENOLS

Phenol	Phenol Registry no.	Yield,[b] %	Ester Registry no.	n^{23}D	Bp, °C (Torr)
Unsubstituted	108-95-2	87	2510-86-3	1.4761[c]	135–136 (3)[d]
2,6-Dimethyl	576-26-1	72[e]	39604-15-4	1.4852	119–120 (0.2)
2-Phenyl	90-43-7	84	39835-01-3	1.5408	153–155 (0.15)
2-Allyl-4-methyl	6628-06-4	80	39835-02-4	1.4907	142–144 (1.5)
2-Methoxy-4-methyl	93-51-6	98	39538-67-5	1.4903	144.5 (0.8)
3-Acetyl	121-71-1	65[e]	17027-73-5	1.4937[f]	143–145 (0.08)[f]
4-Nitro	100-02-7	72[e,g]	311-45-5	1.5071	164–167 (0.75)
1-Naphthol	90-15-3	90[e]	33650-14-5	1.5444	152–154 (0.03)

[a] Satisfactory analyses for C and H, by Micro-Tech Laboratories, Skokie, Ill., were obtained for all new compounds. [b] Preparation according to eq 1. [c] Lit. n^{17}D 1.475;[4] n^{20}D 1.4829.[8] [d] Lit.[8] bp 135–136° (3 Torr). [e] Diethyl ether used as solvent in esterification. [f] n^{20}D 1.4926; bp 139–140° (0.12 Torr): M. I. Gunar, T. N. Shumyatskaya, E. B. Mikhalyutina, K. D. Shvetsova-Shilovskaya, and N. N. Mel'nikov, *Zh. Obshch. Khim.*, **38**, 2254 (1968). [g] 40% conversion and 45% recovery of unreacted 4-nitrophenol.

TABLE II

REACTIONS OF ARYL DIETHYL PHOSPHATES WITH ALKALI METALS IN LIQUID AMMONIA–DIETHYL ETHER SOLUTION AT −78°[a]

Aryl moiety	Aryl DEP, mmol	K metal,[a] mmol	NH_3, ml	Ether, ml	Products	Yield, %[b]	Product identification[c]
Phenyl	50	125	70	20	Benzene	77	Glpc,* ir,* ms[l]
2,6-Dimethylphenyl	5	150	150	25	*m*-Xylene	92	Glpc,* ir,* ms
	32[d]	136	300		*m*-Xylene	88[d]	
2-Methoxy-4-methylphenyl	68	115	250	50	*m*-Methoxytoluene	77[e]	Ms, nmr, bp
2-Biphenylyl	20	44	350	50	Biphenyl	85[f]	Glpc,* ir,* ms, nmr,* mp
					Dihydrobiphenyl	13[f]	Ms, nmr
2-Biphenylyl	15	*g, h*	200	20	Biphenyl	96	
1-Naphthyl	36	*g, h*	400	50	Naphthalene	28 (22)[e]	Glpc,* nmr, mp
					1,4-Dihydronaphthalene	3	Ms, nmr, bp
1-Naphthyl	18	40[h]	330	33	Naphthalene	25	
					1,4-Dihydronaphthalene	15	
1-Naphthyl	18	130[h]	350	38	Naphthalene	2	
					1,4-Dihydronaphthalene	(30[e])	
3-Acetylphenyl	16	43[h,i]	400	50	Acetophenone	71 (52)[e]	Glpc,* ir,* ms, nmr, bp
4-Nitro	8	17[j]	200		Nitrobenzene	13	Glpc*
2-Allyl-4-methylphenyl	49	135	200	40	*m*-Propyltoluene	32[k]	Ir, ms, nmr
					m-Allyltoluene	28[k]	Ir, ms, nmr, bp, *n*D
					1-(*m*-Tolyl)propene	15[k]	Ir, ms, nmr
2-Allyl-4-methylphenyl	13	*g, h*	250	30	*m*-Allyltoluene	65	
					1-(*m*-Tolyl)propene	20	
2-Allyl-4-methylphenyl	26	*g, h, j*	200	50	*m*-Allyltoluene	81 (77[e])	

[a] The metal is K unless otherwise noted. [b] Yield by glpc unless otherwise noted. [c] An asterisk denotes identity to authentic sample; boiling point, melting point, and *n*D, where cited, were in agreement with literature values. [d] Alternative procedure used; see text. [e] Yield by isolation and weighing. [f] Isolated total yield of hydrocarbons, 92%. [g] Not determined. [h] Sodium benzoate added before NH_4Cl. [i] Sodium metal. [j] Lithium metal. [k] Isolated total yield of hydrocarbons, 76%. [l] Mass spectrum.

forward dephosphation, *m*-allyltoluene (**2**), there was obtained 15% of its isomer, 1-(*m*-tolyl)propene (**3**), and 32% of the further reduction product, *m*-propyltoluene.

The situation was much improved when the reaction mixture was treated with sodium benzoate before acidification with NH_4Cl; only *m*-allyltoluene (65%) and 1-(*m*-tolyl)propene (20%) were formed. In order to suppress the complication of double-bond migration, it was necessary to use lithium instead of potassium metal; now *m*-allyltoluene was obtained, free of isomers or further reduction products, in 81% yield. $LiNH_2$ is only slightly soluble in liquid ammonia and, although doubtless formed, was thereby kept out of contact with the *m*-allyltoluene product. The latter was consequently protected from amide ion catalyzed double-bond migration. Thus, dehydroxylation of the rather sensitive 2-allyl-4-methylphenol can be achieved cleanly and in good yield if lithium metal is used in the dephosphation step.

An even greater challenge was dehydroxylation of *p*-nitrophenol. Nitrobenzene has an enormous affinity for electrons, but *p*-nitrophenyl DEP seemed likely to accept electrons even more readily. It therefore was conceivable that dehydroxylation might be achieved by the Kenner–Williams method if the alkali metal were always in deficiency.

Another conceivable complication was reaction of the amide ion by-product with nitrobenzene to form benzenediazotate ion and other products.[16] Lithium metal was therefore employed in the attempt to reduce *p*-nitrophenyl DEP to nitrobenzene, because of the low solubility of $LiNH_2$.

In the event, *p*-nitrophenyl DEP was treated with 2 equiv of lithium metal, added in small bits for the purpose of minimizing local zones with excess electrons. The resulting product mixture was unattractive, but 13% of nitrobenzene was obtained, as determined by glpc. We do not think of this reductive cleavage as

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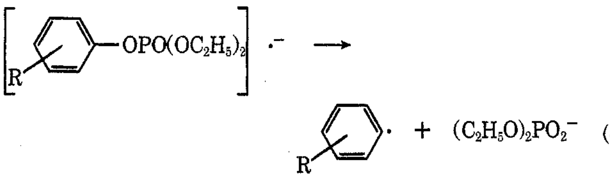
[16] F. W. Bergstrom and J. S. Buehler, *J. Amer. Chem. Soc.*, **64**, 19 (1942).

having preparative value, but rather as a demonstration that substituents exceedingly susceptible to reduction can at least partially survive.

Comparison with Other Dehydroxylation Methods.—Besides the method of Musliner and Gates,[3] mentioned in the introductory paragraph, the chief alternatives to the present method are procedures which involve conversion of the phenol to a diaryl ether, which is then cleaved by an alkali metal in liquid ammonia. The alkali metal cleavage of diaryl ethers was discovered by Sowa and coworkers,[17] and has been adapted for the purpose of dehydroxylating phenols by Sawa, Tsuji, and Maeda[18] and by Pirkle and Zabriskie.[19] The method of the latter workers, which is the more generally applicable, involves converting the phenol to its 2,4-dinitrophenyl ether, catalytic reduction to the 2,4-diaminophenyl ether, and finally cleavage with sodium metal in ammonia.

Both the method of Musliner and Gates[3] and that of Pirkle and Zabriskie[19] involve catalytic reduction steps which obliterate certain types of functionality, such as carbonyl groups, halogen and nitro substituents, and olefinic double bonds. The present method also involves strongly reducing conditions which can be expected to molest substituents sensitive to reduction, as well as partially to reduce polynuclear aromatic systems,[5] but it is to be noted that a carbonyl group, an olefinic double bond, and in part even a nitro group survived in cases we examined. On the whole, we consider the method outlined in eq 1 and 2 to be the most attractive, both for simplicity of operation and for the avoidance of complications, of those which are known.

Reaction Mechanism.—Solutions of alkali metals in liquid ammonia contain alkali metal cations and solvated electron anions, as well as aggregates of uncertain structure.[20] The immediate product of the acquisition of a solvated electron by an aromatic substrate is a radical anion.[21a] The radical anion may rupture according to eq 4, forming an aryl radical and a diethyl phosphate anion,[21b] or conceivably it might acquire a second electron to form a dianion, which then undergoes somewhat analogous fission to an aryl anion and the same phosphate anion.[22] Reaction according to eq 4 is indicated by the fact that, when an aryl diethyl phosphate in liquid ammonia is treated with an alkali metal in the presence of a strong nucleophile such as the acetone enolate ion[23] or the amide ion,[24] a product representing combination of aromatic moiety with nucleophile is obtained.



(4)

We have obtained evidence in other studies[25] that an aryl radical is unable to abstract a hydrogen atom from ammonia fast enough to compete with other processes, but that hydrogen atom abstraction from isopropoxide ion occurs quite readily. We therefore judge that the aryl radical immediately formed in eq 4 either abstracts a hydrogen atom from the diethyl ether which was present in our reaction mixtures, or that it acquires an electron to form an aryl anion which then takes a proton from the ammonia solvent.[26] We suspect that both modes of hydrogen acquisition are utilized, but we are unable at this time to specify how much reaction occurs by each mode.

Toxicity of Aryl Diethyl Phosphates.—*p*-Nitrophenyl DEP is highly toxic, and should be handled with the greatest care. Aryl DEP with less strongly electron-attracting substituents are less toxic,[27] but prudence dictates that they be handled with precautions against inhalation, ingestion, or contact with the skin. We experienced no manifestations of toxicity in our work with these compounds.

Experimental Section

General.—Boiling points are not corrected. Nmr spectra were recorded on Varian A56/60A and JEOLCO 60 MHz nuclear magnetic resonance spectrophotometers with CCl_4 as solvent and all spectra are reported in parts per million relative to TMS (δ). All ir spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer, using CCl_4 as solvent. Mass spectral measurements were obtained with a Hitachi Perkin-Elmer Model RMU-6E mass spectrophotometer. Glpc analyses were performed on a Varian Aerograph Model 200 with flame ionization detector. For determining yields, the molar responses of authentic samples were calibrated against those of suitable standards and peak areas were calculated using a Disc integrator. For preparative glpc, a Varian Aerograph Model A90-P3 was used with thermal conductivity detector using helium as carrier gas.

Reagents.—Diethyl phosphorochloridate (Aldrich Chemical Co.) and all phenols were commercially available and were used as received, except 2-methoxy-4-methylphenol and 2-allyl-4-methylphenol. Alkali metals were cut in small pieces and washed with dried pentane immediately before addition to reaction mixtures. Liquid ammonia was dried with potassium metal and distilled under nitrogen into the reaction flask. 2-Methyl-4-methylphenol was prepared from vanillin:[28] bp 101–102° (12 Torr) [lit.[28] bp 78–79° (4 Torr), 104–105° (13 Torr)]; nmr δ 2.05 (s, 3 H), 3.41 (s, 3 H), 6.18 (s, 1 H), and 6.3–6.8 (m, 3 H). *p*-Tolyl allyl ether was prepared from *p*-cresol:[29] bp 93–94° (13 Torr) [lit.[29] bp 91° (12 Torr)]; nmr δ 2.17 (s, 3 H), 4.28 (m, 2 H), 5.10 (m, 1 H), 5.20 (m, 1 H), 5.83 (m, 1 H), 6.60 (m, 2 H), and 6.83 (m, 2 H). Claisen rearrangement of this ether afforded 2-allyl-4-methylphenol:[29] bp 109–110° (9 Torr) [lit.[29] bp 112° (12 Torr)]; nmr δ 2.13 (s, 3 H), 3.25 (m, 2 H), 4.83 (m) and 5.05 (m, 2 H), 4.47 (s, 1 H), 5.83 (m, 1 H), and 6.4–6.8 (m, 3 H).

Esterification of Phenols.—Phenols were dissolved in toluene at 0–5°. Simultaneously were added from two separatory funnels diethyl phosphorochloridate and 20% aqueous NaOH, slowly and with good stirring, the temperature being kept at 5–10°. Addition time was about 2 hr, and the mixture was stirred for another 2 hr as it warmed to room temperature. When the phenol was not completely soluble in toluene, as with 1-naphthol, *m*-acetylphenol, and 2,6-dimethylphenol, ether was used as cosolvent. Esters were washed with 10% NaOH solution and with water; after drying, they were distilled under vacuum (see Table I).

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(17) P. A. Sartoretto and F. J. Sowa, *J. Amer. Chem. Soc.*, **59**, 603 (1937); F. C. Weber and F. J. Sowa, *ibid.*, **60**, 94 (1938).

(18) Y. K. Sawa, N. Tsuji, and S. Maeda, *Tetrahedron*, **15**, 144, 154 (1961).

(19) W. H. Pirkle and J. L. Zabriskie, *J. Org. Chem.*, **29**, 3124 (1964).

(20) M. Szwarc, *Progr. Phys. Org. Chem.*, **6**, 379 (1968); J. L. Dye, *Accounts Chem. Res.*, **1**, 306 (1968).

(21) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley, New York, N. Y., 1970, (a) p 149; (b) p 126.

(22) *Cf.* D. H. Eargle, Jr., *J. Org. Chem.*, **28**, 1703 (1963).

(23) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).

(24) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37**, 3570 (1972).

(25) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

(26) *Cf.* J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971); C. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

(27) R. L. Metcalf and R. B. March, *J. Econ. Entomol.*, **42**, 721 (1949); *Chem. Abstr.*, **44**, 3663 (1950).

(28) R. Schwarz and H. Hering, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 203.

(29) L. Claisen and O. Eisleb, *Justus Liebigs Ann. Chem.*, **401**, 21 (1913).

In an alternative preparation of phenyl DEP, phenol and a small excess of diethyl phosphorochloridate were dissolved in toluene at 3–5°, a 20% aqueous NaOH solution was slowly added with stirring, and then stirring was continued for 2 hr at room temperature. Product isolation as above afforded phenyl DEP in 81% yield.

Properties of Aryl Diethyl Phosphate Esters.—All the esters present a double triplet at δ 1.06–1.36, with $J_{HH} = 6.7–7.2$ and $J_{HP} = 0.8–0.9$ Hz, and a double quartet at δ 3.81–4.25 with $J_{HH} = 6.9–7.2$ and $J_{HP} = 8.2–8.6$ Hz, as well as the expected absorption due to the aryl groups. The infrared spectra of phenyl diethyl phosphate and its *p*-nitro derivative closely resembled those reported by Bellamy and Beecher;[30] the others showed characteristic absorption (as films) at 1267–1273 (P=O), 1183–1213 (POC, aromatic), 1156–1167 (POC, ethyl), 1095–1101 (?), 1028 (POC, aliphatic), and 955–964 cm^{-1} (?), assignments being after Bellamy.[31]

Reduction Reactions.—Dried liquid ammonia was condensed in a three-neck round-bottom flask (1 l.) under nitrogen at −78°; the flask was provided with a cold-finger condenser containing solid CO_2 in 2-propanol. Esters were dissolved in ether and added to the ammonia from a dropping funnel, with stirring. Alkali metal was added in small bits until a blue color persisted for at least 2 min. After 15 min, the reaction was quenched by adding solid NH_4Cl or sodium benzoate followed by NH_4Cl. The ammonia was then distilled off. When the product had substantial volatility and might codistil with the ammonia, ether (*ca.* 150 ml) was added immediately after the NH_4Cl and the ammonia was removed through a cold-finger condenser which was kept at −20° to −30° by adding small pieces of solid CO_2 to the 2-propanol. Products were isolated by standard techniques. Product structures were established and/or confirmed by physical property measurements as detailed in Table II.

In a typical experiment 18.6 g of 2-methoxy-4-methyl DEP dissolved in 50 ml of ether was added to 250 ml of dried liquid ammonia at −78°. Potassium metal (4.5 g) was added in pieces and the reaction solution was blue at the end. After 15 min of reaction it was quenched by adding NH_4Cl in excess and the solution became colorless. The liquid ammonia was distilled off, and the residue was treated with 150 ml of water and extracted with 100 ml of ether (twice). Ether extracts were washed with a saturated solution of NaCl in water and dried over anhydrous Na_2SO_4. The ether was removed and the residue was distilled under vacuum: bp 64–65.5° (12 Torr); yield 6.38 g (77%) of pure *m*-methoxytoluene; nmr δ 2.19 (s, 3 H), 3.53 (s, 3 H), 6.36 (m, 3 H), 6.36 (m, 3 H), and 6.75 (m, 1 H).

Cleavage of 2-Allyl-4-methyl DEP. Procedure A.—To 200 ml of liquid ammonia was added 13.9 g of ester dissolved in 40 ml of ether, and 5.2 g of K metal was added until a blue color persisted. The reaction was quenched with NH_4Cl and products were isolated much as described above, bp 67–85° (13 Torr), yield 4.90 g (76%). By glpc (20% Carbowax 20M on Chromosorb P, 130° isothermal, N_2 as a carrier gas, 3.2 mm × 1.22 m), three substances were found: *m*-propyltoluene (retention time 2.3 min, 32% yield), *m*-allyltoluene (retention time 2.9 min, 29% yield), and 1-(*m*-tolyl)propene (retention time 5.6 min, 15% yield). These compounds were separated by preparative glpc (10% Carbowax 20M on Chromosorb P, 6.4 mm × 1.22 m, 140°, He as carrier gas, 25 ml/min), and were identified by their nmr and mass spectra, as well as comparison of n_D values for *m*-propyltoluene[32] and 1-(*m*-tolyl)propene[33] with the literature. Also, for *m*-allyltoluene, ir 1640, 915, and 993 cm^{-1} (allylphenyl derivatives have absorption at 1640–1653, 905–925, and 985–1000 cm^{-1})[34] and $n^{23}{}_D$ 1.5084; and for 1-(*m*-tolyl)propene, ir intense absorption in 965 cm^{-1} (probably the trans isomer).[33]

Procedure B.—To 200 ml of dried liquid ammonia at −78° was added 7.4 g of the ester dissolved in 50 ml of ether, and Li metal was added in small pieces until blue color persisted. Solid sodium benzoate was added to discharge the blue color and solid NH_4Cl was added as a proton source. The liquid ammonia was evaporated and the residue was worked up as usual, giving an 81% yield of *m*-allyltoluene, pure by glpc. By distillation was obtained 2.65 g (77%) of pure *m*-allyltoluene, bp 64–66° (12 Torr) [lit.[35] bp 60° (11 Torr)].

Registry No.—Potassium 7440-09-7; sodium, 7440-23-5; lithium, 7439-93-2; ammonia, 7664-41-7.

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