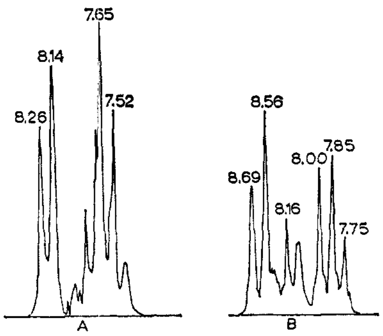

Figure 1.—Nmr spectrum of (A) nitrobenzene in 96% H_2SO_4 and (B) protonated nitrobenzene in 34% SO_3–66% H_2SO_4. The band positions are in parts per million downfield from tetramethylsilane with $(CH_3)_4N^+Cl^-$ as an internal standard.

In the course of proton magnetic resonance (pmr) studies in oleum, it was convenient to check these results. For this purpose, the pmr spectra of nitrobenzene, nitromethane, nitroethane, and 2-nitropropane were measured as a function of acid concentration. Let us say at the outset that the pmr data did not yield values of $[B^+]/[BH]$ of sufficient precision to test or establish any acidity functions. However, they did provide a reliable check on the acidity required for half-protonation.

The pmr spectra of nitrobenzene and protonated nitrobenzene are shown in Figure 1. Although complex, one was smoothly graded into the other and it was no problem to estimate that nitrobenzene was half-protonated in 99–100% H_2SO_4. This is in exact agreement with the earlier ultraviolet[1] and conductrimetric[2] studies.

Nitromethane exhibited a single pmr band of normal width. It moved from a position 4.45 ppm downfield from tetramethylsilane (tetramethylammonium ion used as a secondary standard throughout) in 0–18% SO_3 (in H_2SO_4) to 4.59 in 23% SO_3 to 4.73 in 27–31% SO_3. The position was 4.33 in CCl_4. The data indicates that nitromethane is half-protonated in 23% SO_3 and this is not in good agreement with the conductimetric work.

Nitroethane gave similar results. In CCl_4, the pmr spectrum consists of a triplet at 1.56 and a quartet at 4.42 ppm (both with $J = 7$ cps). In 0–20% SO_3, these are at 1.56 and 4.61. In 23% SO_3, they are at 1.64 and 4.86. In 27–32% SO_3, they are at 1.68 and 5.03. Again, half-protonation occurs at 23% SO_3. With both nitromethane and nitroethane, the solutions were 5% by weight and the values of % SO_3 are corrected for acidity used up in protonating CH_3NO_2. The method of making this small correction has been described.[5]

2-Nitropropane partially decomposed during the act of mixing. The isopropyl doublet was at 1.54 in CCl_4, 1.57 in 70% H_2SO_4 to 15% oleum, and 1.67 in 25–34% oleum. However, in 15–34% oleum the spectrum though stable, contained extraneous bands accounting for over 60% of the total area.

A final problem deals with the definition of protonation. Several Russian workers speak of ketones as half-protonated in 10% H_2SO_4, whereas American workers accept the value of 80% H_2SO_4. More germane to this note, the Russian workers refer to nitromethane as being "protonized" throughout 35–85% H_2SO_4.[6] The discrepancy arises because the Russian workers are concentrating on conductimetric techniques and treat nitromethane as protonated when it becomes loosely hydrogen bonded to H_3O^+ and thus migrates as a cation. In our work and this note, nitromethane is regarded as protonated when it accepts H^+ and becomes covalently bonded to such an attached proton.

Acknowledgment.—A grant from the National Science Foundation aided in the purchase of the Varian A-60 nmr instrument.

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The Basicity of Alcohols and Ethers

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Arnett and Anderson[1] established the base strengths of aliphatic alcohols in aqueous mineral acids and Arnett and Wu[2] established the base strengths of ethers. Their method was to observe the changes in distribution coefficient of the alcohol or ether between an inert organic solvent and various concentrations of aqueous sulfuric acid. The concentration of alcohol or ether in the nonaqueous phase was determined by gas chromatography. A representative selection of their estimates of base strengths appear in Table I.

In the present work, solubility studies were made in order to evaluate the basicities. Solubilities were used many years ago by Hammett[3] and the method is virtually identical in theory with the distribution method.[3,4] The novel feature was to include a phenyl group into the structure, but at a sufficient distance from the basic site to make its extinction coefficient independent of protonation. The observed extinction in the aqueous phase at 260–270 mμ was thus a measure of the sum of the concentration of B and BH^+.

In all cases, the solubility decreased from 0 to 20% H_2SO_4 due to salting out. From 20 to 35% H_2SO_4 a shallow minimum existed. From 35 to 60% H_2SO_4, the solubility increased. The data were treated on the assumption that the solubility of free alcohol or ether does not vary from 20 to 60% H_2SO_4 and that the increase in solubility observed is due solely to an increasing proportion of protonation. The uncertainties and errors in this method have been discussed.[2,4]

It was not felt that the data were of sufficient precision to test any acidity function equation so that we are content to simply list in Table I the best estimate of the per cent H_2SO_4 at which C_B equalled C_{BH^+}. Also listed are estimates of the same value for comparable compounds from previous literature work.

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TABLE I

VALUES OF PER CENT SULFURIC ACID AT WHICH THE ALCOHOL OR ETHER IS HALF-PROTONATED

Alcohols	% H_2SO_4	pK^a	Method and ref
Primary			
Methanol	41	−2.5	Raman spectra[b]
1-Butanol	39.5	−2.3	Distribution[c]
8-Phenyloctanol	41	−2.5	Solubility
Secondary			
2-Propanol	(50)		Interpretation of kinetics[d]
2-Butanol	36.5	−2.2	Distribution[c]
11-Phenyl-2-undecanol	39	−2.3	Solubility
Tertiary			
2-Methyl-2-propanol (*t*-butyl)	41.5	−2.6	Distribution[c]
	55 ± 5		Interpretation of kinetics[e]
2-Methyl-2-butanol	38.5	−2.3	Distribution[c]
2-Methyl-11-phenyl-2-undecanol	41	−2.5	Solubility
Ethers			
Dimethyl	54	−3.83	Distribution[b]
Diethyl	52	−3.59	Distribution[f]
Methyl butyl	52	−3.50	Distribution[f]
Methyl 4-phenylbutyl	49	−3.2	Solubility

[a] Calculated from the equation, $H_0 = \mathrm{p}K + \log (C_B/C_{BH^+})$, using the values of H_0 tabulated by M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). [b] N. Deno and M. J. Wisotsky, *J. Am. Chem. Soc.*, **85**, 1735 (1963). [d] P. D. Bartlett and J. O. McCollum, *ibid.*, **78**, 1441 (1956). [e] N. Deno, T. Edwards, and C. Perizzolo, *ibid.*, **79**, 2108 (1957). [f] See ref 2.

4-Phenyl-1-butanol and its corresponding secondary and tertiary alcohols were studied. The results were erratic and although we suspect cyclization to tetralin derivatives, this was not verified.

Experimental Section

Solubility Determinations.—A mixture of 150 ml of the aqueous acid and 0.2 g of the alcohol or ether were swirled until an aliquot of the solution gave a constant extinction at λ_{max} (260–270 mμ).

Preparation of Compounds.—The route to 8-phenyloctanol was as follows. Suberic acid was converted to the anhydride by refluxing with acetic anhydride. Excess acetic acid and anhydride were removed by distillation and the suberic anhydride condensed with benzene using aluminum chloride. This is the method of Hill,[5] who reported a yield of 7-benzoylheptanoic acid of 78%. We obtained 65%. This acid was reduced to crude 8-phenyloctanoic acid in 80% yield by reduction with amalgamated zinc and hydrochloric acid using the Clemmenson conditions.[6] Reduction of the crude acid with $LiAlH_4$ in ether gave a 56% yield of 8-phenyl-1-octanol, bp 146–147° (2.5 mm).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.5; H, 10.8. Found: C, 81.5; H, 10.9.

10-Phenyldecanoic acid, bp 224–225° (14 mm), was prepared in a manner identical with the preparation of 8-phenyloctanoic acid, but using decanedioic acid in place of octanedioic (suberic) acid. The acid chloride, bp 180–184° (12 mm), was prepared by refluxing the acid with thionyl chloride and a trace of pyridine. The acid chloride was treated with dimethylcadmium by the method of Cason[7] to produce 11-phenyl-2-undecanone, bp 137–139° (3 mm), in 40% yield. A $LiAlH_4$ reduction in ether converted the ketone quantitatively to 11-phenyl-2-undecanol, bp 133–134° (13 mm).

Anal. Calcd for $C_{17}H_{28}O$: C, 82.2; H, 11.4. Found: C, 82.0; H, 11.6.

Treatment of 11-phenyl-2-undecanone with excess CH_3MgI quantitatively produced 2-methyl-11-phenyl-2-undecanol, bp 130–131° (7 mm).

Anal. Calcd for $C_{18}H_{30}O$: C, 82.4; H, 11.5. Found: C, 82.0; H, 11.6.

Methyl 4-phenylbutyl ether was prepared by the reaction of 4-phenyl-1-butanol with potassium metal in ether followed by addition of excess iodomethane. The boiling point of the ether, 108–109° (11 mm), was in accord with the literature.[8]

Acknowledgment.—Support from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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Bitriptycyl[1]

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While numerous experiments conducted over the past fifteen years could have been expected to yield bitriptycyl (I), this hydrocarbon has yet to be unequivocally described. Thus, coupling fails to take place when 9-bromotriptycene is heated with copper, zinc, or silver.[3,4] Similarly, bitriptycyl has not been reported among the products resulting from the reaction of 9-triptycyllithium with cobalt chloride, copper chloride, or nickel chloride, or the silver-catalyzed thermal decomposition of 9,9′-ditriptycylmercury, or the copper- or silver-catalyzed thermal decomposition of 9,9′-ditriptycyldiselenide.[4] Bartlett and Greene,[5] in the course of studying the thermal decomposition of ditriptoyl peroxide, isolated a small amount of a high-melting solid, "compound x," which they suggested might be bitriptycyl.

We now wish to report a synthesis of bitriptycyl, to describe the properties of this hydrocarbon, and

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(2) To whom inquiries should be addressed.
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