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, $H_0 = pK + \log (C_B/C_{BH^+})$, 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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Received November 12, 1965

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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(1) This work was supported in part by grants from the National Science Foundation (GP-3511), the Research Corporation, and the General Faculty Research Committee of the City College of New York. The purchase of the Cary Model 14 spectrophotometer used in this work was made possible by a grant from the National Science Foundation (GP-3646) to the City College of the City University of New York.
(2) To whom inquiries should be addressed.
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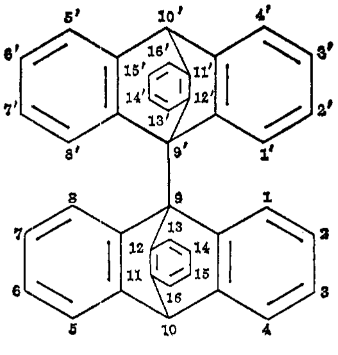

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further, to confirm the structure assignment made by Bartlett and Greene for their "compound x." The present synthesis of bitriptycyl involves the addition of benzyne to 9,9′-bianthryl. For this purpose, benzyne was generated from anthranilic acid,[6] 1,2-bromofluorobenzene,[7] and 1,2,3-benzothiadiazole 1,1-dioxide.[8] The yields of bitriptycyl ranged from approximately 5–20%. The synthesis involving benzyne generated from anthranilic acid was the most convenient and generally gave the highest yields and the purest product. The isolation of bitriptycyl was considerably simplified by the extreme insolubility of this hydrocarbon in acetone. Bitriptycyl melts at 577° with decomposition, and in the absence of oxygen appears to be thermally stable up to its melting point.

The proof of structure of bitryptycyl is based on the following facts. Carbon and hydrogen analysis is consistent with the formula $C_{40}H_{26}$. The mass spectrum shows a base peak at m/e 506 (molecular ion), a strong peak at m/e 253 (triptycyl ion plus a double charged molecular ion) and a metastable ion at approximately m/e 127. These data serve to establish the molecular weight and also indicate that cleavage of the molecular ion to the triptycyl ion is an important process. The ultraviolet spectrum, $\lambda_{\max}^{\text{dioxane}}$ 280 mμ (log ϵ 3.69), 272 (3.63), and 266 (sh) (3.38), compares favorably with the ultraviolet spectrum of triptycene, $\lambda_{\max}^{\text{dioxane}}$ 279 mμ (log ϵ 3.67), 271 (3.55), and 265 (sh) (3.32). The infrared spectrum is relatively simple and agrees with the published spectrum of Bartlett and Greene's "compound x."

Our interest in the bitriptycyl system arises from the possibility that suitably substituted derivatives, *e.g.*, a 2,2′-disubstituted bitriptycyl, may exhibit conformational stability. We are presently investigating this possibility.

Experimental Section

Infrared and ultraviolet spectra were determined on Perkin-Elmer Model 137 and Cary Model 14 spectrophotometers, respectively. Mass spectra were determined on an Associated Electrical Industries MS-9 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The melting point of bitriptycyl is uncorrected.[9]

Reaction of 9,9′-Bianthryl and Anthranilic Acid and *n*-Butyl Nitrite.—Solutions of anthranilic acid (4.12 g, 30 mmoles) and *n*-butyl nitrite (3.49 g, 34 mmoles), each in 27 ml of 2-butanone, were simultaneously added during a 3.5-hr period to a stirred refluxing solution of 9,9′-bianthryl[10] (0.50 g, 1.4 mmoles) in 25 ml of 2-butanone. The *n*-butyl nitrite solution was always in slight excess over the anthranilic acid solution. The reaction mixture was refluxed for an additional 1 hr and allowed to stand at room temperature for at least 12 hr in order to ensure complete precipitation of the product. The solid was filtered and repeatedly triturated with acetone. Two crystallizations from nitrobenzene gave a white solid: mp 577 ± 5° dec; ν^{Nujol} 1284 (w), 1151 (m), 1133 (w), 1036 (m), 915 (m), 808 (m), 771 (m), 753 (m), 745 (s), and 738 (s) cm^{-1}; $\lambda_{\max}^{\text{dioxane}}$ (10-cm cell) 280 mμ (log ϵ 3.69), 272 (3.63), and 266 (sh) (3.38); m/e 506 (base peak), m/e 253 (56% of base peak), and m/e approximately 127 (metastable ion). For comparison, triptycene has $\lambda_{\max}^{\text{dioxane}}$ 279 mμ (log ϵ 3.67), 271 (3.55), and 265 (sh) (3.32).

Anal. Calcd for $C_{40}H_{26}$: C, 94.83; H, 5.17. Found: C, 94.96; H, 5.15.

Acknowledgment.—The authors thank Dr. William Milne of the National Institutes of Health for the measurement and interpretation of the mass spectra.

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Magnetic Nonequivalence of a Thiophosphate Ester

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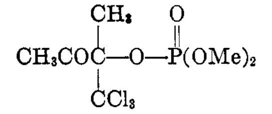
Received November 12, 1965

Magnetic nonequivalence due to molecular asymmetry has been reported for a variety of compounds.[1-3] Roberts, *et al.*,[4] studied nmr spectra of 1-phenylethyl benzyl ether and related compounds. In particular, the effect of the proximity of an asymmetric center on the extent of magnetic nonequivalence was investigated. Sidall and Prohaska[5] have observed nonequivalence of the alkoxyl groups on a variety of phosphorus esters. This effect was explained by a preferred conformation of these esters. Bentrude[6a] recently reported that



$$\mathrm{CH_3CO\overset{CH_3}{\underset{CCl_3}{C}}{-}O{-}\overset{O}{\overset{\|}{P}}(OMe)_2}$$

shows magnetically nonequivalent methoxyl groups ($\Delta = 4$ cps), ascribed to the asymmetric carbon in the molecule.

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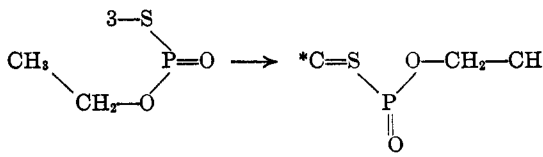

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