

iodine (0.1 mole per mole of hexafluoro-2-butyne) gave a 70.5% yield of nearly pure II as a pale yellow solid, m.p. 209–211° (with previous softening).

The infrared spectrum (carbon tetrachloride) has strong absorption at 8.1–8.3, 8.51, and 9.51 μ , with much weaker bands at 7.12, 7.43, 7.61, and 7.73 μ . Additional bands for II at 8.63 μ , 8.75 μ , 12.41 μ s, 13.35 μ s and 13.79 μ s are detected by use of a potassium bromide wafer. The trimer crystals are monoclinic. X-ray diffraction data were determined from a single crystal grown from acetone. There are four formula weights per unit cell with a space group of $C_{2h}^2P2_1/c$, $a_0 = 9.42$, $b_0 = 16.54$, $c_0 = 8.98$. The β angle is 99.5°. Assuming a molecular weight of 486.24, the x-ray density is 2.33.⁷ The density at 25° ("Ultracene") is 2.2603, corresponding to a molecular weight of 470.

The trimer (50% in acetone) has an F^{19} resonance at –945 c.p.s. at 40 mc./sec., relative to trifluoroacetic acid = 0.⁸

b. *Thermal*. An 80-cc. stainless steel bomb containing 25 g. (0.155 mole) of I was heated for 7 hr. at 275° and 7 hr. at 285°. A pressure drop from 905 p.s.i. at 275° to 390 p.s.i. at 285° occurred during this time. After cooling and venting the bomb, there was obtained 15.1 g. of fluffy solid. Sublimation of 14 g. of this material at 100°, 1 mm. for 2 hr. yielded 4.47 g. of wet crystals. Pentane extraction of this material left 3.53 g. of II, m.p. 210–212° (sealed capillary).

Hydrolysis of II. Approximately one half of 11.0 g. (0.023 mole) of II was dissolved in 1 l. of hot absolute ethanol. Then one third of a solution of 3.4 g. (0.052 mole) of potassium hydroxide in 35 ml. of ethanol and 2 ml. of water was added during 20 min. The rest of the trimer was dissolved in the mixture, and the remainder of the base was added slowly. After standing overnight at room temperature, the volume was reduced to 150 ml., and the hot solution was decanted from precipitated potassium fluoride. Upon cooling the solution in an ice-salt bath, there was obtained 4.22 g. of colorless leaflets, m.p. 72–76°. Recrystallization from pentane gave 3.0 g. (27%) of ethyl pentakis(trifluoromethyl)benzoate (IV), m.p. 89–90°.

Anal. Calcd. for $C_{14}H_5F_{15}O_2$: C, 34.30; H, 1.03; F, 58.14. Found: C, 34.51; H, 1.40; F, 58.24.

Carbonyl absorption in the infrared was at 5.67 μ (potassium bromide disk) and the proton NMR spectrum indicated the presence of an ethyl group. The fluorine NMR spectrum had complex absorption in the CF_3 region which is consistent with the unsymmetrical, highly crowded structure IV.

Attempts to isolate other hydrolysis products from this reaction were unsuccessful.

CONTRIBUTION No. 575 FROM THE
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS & COMPANY, INC.
WILMINGTON 98, DEL.

(7) E. A. Braude and F. C. Nachod, *Determination of Organic Structures by Physical Methods*, Academic Press Inc., N. Y., 1955, p. 468.

(8) The convention employed here is that resonances occurring at high field relative to the reference are assigned positive values.

Hexa(trifluoromethyl)benzene¹

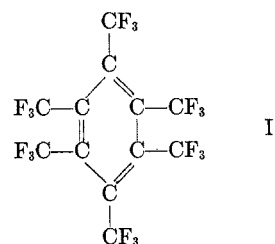
H. C. BROWN, H. L. GEWANTER, D. M. WHITE, AND
W. G. WOODS²

Received October 16, 1959

The thermal reaction of perfluorobutyne-2 under autogenous pressure has been reported previously³

as producing a white, crystalline compound believed to be the polycyclic tetramer. Further examination of this compound by Ekstrom⁴ led to the incorrect assignment of the structure as octa(perfluoromethyl)cyclooctatetraene.

A redetermination of the molecular weight of the product, both by ebullioscopic method in benzene and by isothermal distillation in benzene, gave a value of 472, which is reasonably close to the value of 486 expected for the trimer of perfluorobutyne. Further consideration has therefore been given to the structure and additional data obtained which shows conclusively that this compound is actually the previously unreported hexa(trifluoromethyl)benzene (I).



The fluorine nuclear magnetic resonance in dilute tetrahydrofuran of two samples of the trimer was determined at 40 megacycles/sec. and about 10,000 gauss and only one, single unsplit peak was found. This peak is found displaced 433 c.p.s. to lower magnetic fields than the fluorine resonance of benzotrifluoride and some 2,320 c.p.s. to higher fields from the fluorine peak of tribromofluoromethane, the latter being used as an internal standard. It was shown conclusively that this one peak contained all the fluorine atoms in the fluorocarbon, as no detectable resonance could be found at $\pm 5,000$ c.p.s. from the observed peak. Furthermore, known solutions of the perfluorobutyne trimer and benzotrifluoride were prepared in which the ratios of the number of fluorine atoms due to the trimer to those due to benzotrifluoride were 0.988 : 1.010. The spectra were run and the integrated areas of the two peaks determined with a planimeter which gave values of 0.99 ± 0.09 and 1.11 ± 0.12 for the ratios. Coupled with the observation that only one peak can be detected, this result shows clearly that the trimer contains only one type of fluorine atom.

The ultraviolet absorption spectrum (max 285 $m\mu$, $\log \epsilon = 2.20$) of the perfluorobutyne trimer tends to confirm the presence of an aromatic ring. The ultraviolet extinction coefficient of this com-

(1) This work was supported in part by the Office of Naval Research under Contract N-onr 580(03); NR 356-333 with the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Present address: U. S. Borax Research Corporation, Anaheim, California.

(3) H. C. Brown, *J. Org. Chem.*, **22**, 1256 (1957).

(4) B. Ekstrom, *Ber.*, **92**, 749 (1959).

pound, when compared with the extinction coefficients for trifluoromethyl benzene and *bis*(trifluoromethyl)benzene, is in the expected range. The ultraviolet curve showed a smoothing out effect with an electron donating solvent such as ether when compared with the spectrum determined in chloroform. The inductive effect of the eighteen fluorine atoms would be expected to make the ring very electron deficient and could account for this phenomenon.

The solubility characteristics of the trimer are appropriate to an electron deficient structure, as it has a low solubility in benzene but is soluble in electron rich solvents. A solubility in tetrahydrofuran greater than that in ethyl ether is consistent with the greater basicity of the former.

The melting point of the perfluorobutylene trimer is in the range expected for hexa (trifluoromethyl)benzene. A plot of the melting points of the methylbenzenes *vs.* the melting points of the known trifluoromethylbenzenes is linear.

All the evidence shown above is based on the physical properties of the trimer and substantiates the proposed aromatic ring structure. We would like to report, in addition, that unequivocal chemical confirmation of the ring structure was obtained by vapor phase chlorination of the trimer under ultraviolet irradiation to produce chlorotrifluoromethane and hexachlorobenzene.

Preparation of hexa(trifluoromethyl)benzene has been modified to include a relatively cold reservoir in the pyrolysis tube for condensation of the product as formed. Yields of 68% of the resublimed or recrystallized product have been obtained.

Further work on reactions of hexa(trifluoromethyl)benzene promoted by free radical attack and also by the attack of nucleophilic reagents is in progress.

EXPERIMENTAL

Hexa(trifluoromethyl)benzene. Hexafluorobutylene-2 (20 g., 0.123 mol.) was condensed into a previously evacuated heavy wall Pyrex tube 55 cm. \times 2.4 cm. designed to project from a vertical tube furnace approximately 6 in. The tube was then sealed and heated at 375° for 60 hr. The autogenous pressure in the 250 ml. tube was calculated to be about 25 atm. As the reaction proceeded, the solid product condensed in the exposed, relatively cool portion of the tube. The tube was cooled, opened, and the condensed solid removed and resublimed. Recrystallization from carbon tetrachloride gave 13.7 g. (68.5%) of pure hexa(trifluoromethyl)benzene, m.p. 209° (sealed tube).

Chlorination of hexa(trifluoromethyl)benzene. Hexa(trifluoromethyl)benzene (4.86 g., 0.01 mol.) was placed in a 500 cc. Vycor flask. Dry chlorine gas, 4.4 g. (0.062 mol.), was condensed into the flask, and the flask was sealed and heated to 260° under ultraviolet radiation supplied by a Hanovia utility lamp for 44 hr. The vessel was cooled and opened into a vacuum system to remove the volatile material which was subsequently bubbled through a 10% solution of sodium hydroxide to remove any unreacted chlorine. The remaining gas was identified by molecular weight determination (Dumas-104) and infrared spectra as chlorotrifluoromethane. The solid product was recrystallized from

benzene to give pure hexachlorobenzene, m.p. 229–230° mixed melting point with authentic samples 229–231°. The infrared spectra of this solid material also corresponded to that of an authentic sample of hexachlorobenzene.

DEPARTMENTS OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF FLORIDA
GAINESVILLE, FLA.

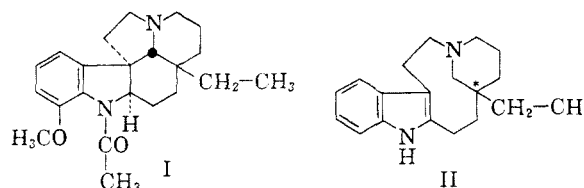
GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, N. Y.

Quebrachamine. II

HERMANN KNY AND BERNHARD WITKOP

Received October 1, 1959

The establishment by x-ray analysis of the structure I for aspidospermine^{1–3} makes II an attractive



formulation for quebrachamine.⁴ This note reports two further experiments designed to clarify the nature of the substituent, H or R, at the α -indole position, and identifies the "*N*(α)-acetyldihydroindole base" previously reported,⁴ as I.

The positive Ehrlich and Hopkins-Cole reactions of quebrachamine suggested an α -unsubstituted indole ring. Such α -unsubstituted indoles may be characterized or diagnosed by their α, α' -disulfides. Quebrachamine trichloroacetate reacted in benzene with disulfur dichloride to yield a crystalline disulfide, whose ultraviolet absorption peak showed the expected shift to longer wave lengths.⁵ Reductive hydrolysis, however, gave back quebrachamine. It must be concluded that quebrachamine disulfide is an abnormal disulfide in which two molecules of quebrachamine are linked together by an S-S bridge attached to an unknown position of the indole part. Tetrahydrocarbazole did not yield a disulfide.

Another reaction characteristic of α -unsubstituted indoles is their oxidation to (di)oxindole derivatives with *N*-bromosuccinimide.⁶ Quebrachamine under such conditions gave a tribromo com-

(1) S. C. Nyburg and J. F. D. Mills, *Tetrahedron Letters*, **11**, 1 (1959).

(2) G. F. Smith and J. T. Wrobel, *J. Chem. Soc.*, in press.

(3) H. Conroy, P. R. Brook, and Y. Amiel, *Tetrahedron Letters*, **11**, 4 (1959).

(4) Cf. B. Witkop, *J. Am. Chem. Soc.*, **79**, 3193 (1957).

(5) Cf. K. Freter, J. Axelrod, and B. Witkop, *J. Am. Chem. Soc.*, **79**, 319 (1957).

(6) A. Patchornik, W. B. Lawson, and B. Witkop, *J. Am. Chem. Soc.*, **80**, 4747 (1958).