

Notes

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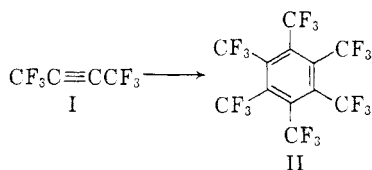
The Trimerization of Hexafluoro-2-butyne

J. F. HARRIS, JR., R. J. HARDER, AND G. N. SAUSEN

Received October 12, 1959

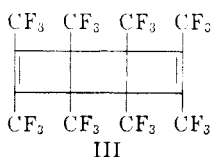
The trimerization of alkyl and aryl substituted acetylenes to give substituted benzenes is well known,¹ but there appear to be no reports of trimerization of a fluoroalkyl acetylene.²

We have found that the novel hexakis(trifluoromethyl)benzene (II) can be obtained in yields of 70 to 75% by heating hexafluoro-2-butyne (I) with trifluoromethyl iodide or iodine at 260° under pressure. Smaller yields have also been obtained by heating the butyne alone at 275°.



Hexakis(trifluoromethyl)benzene (II) is a colorless, crystalline, readily sublimable compound melting at 210–212° (sealed capillary). The fluorine nuclear magnetic resonance spectrum in acetone consists of a single, unsplit resonance line, indicating that the fluorine atoms are all equivalent. The results of cryoscopic molecular weight measurements in benzene were about 4 to 7% higher than the value calculated for the trimer, while the molecular weight determined by the x-ray method was 3% low. However, mass spectrometric analysis showed the parent ion of mass 486 and a series of ions logically derived from it.

The infrared spectrum of the trimer is characterized by many of the bands reported by Brown³ for a compound, m.p. 208–209°, which was obtained by heating I at 320°, and to which the tetrameric structure III was assigned on the basis of an ebullioscopic molecular weight determination.⁴ The



(1) (a) A. W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948); (b) D. C. McKinley, *Ind. Eng. Chem.*, **44**, 995 (1952).

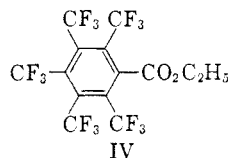
(2) Monofluoroacetylene has been reported to trimerize spontaneously; W. J. Middleton and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 803 (1959).

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

ultraviolet spectrum of the trimer is also strikingly similar (λ_{\max} 287 m μ , $\log \epsilon$ 2.22) to that reported by Ekström⁵ for Brown's compound (λ_{\max} 287 m μ , $\log \epsilon$ 2.24). The similarities in reaction conditions, melting point, and, NMR infrared and ultraviolet spectra lead us to suggest that Brown's compound is actually the trimer (II).

Because of the bulkiness of trifluoromethyl groups, it was not possible to construct a model (Stuart-Briegleb) of the trimer without distorting the benzene ring from its normal planar configuration. It was, in fact, not possible to place more than three trifluoromethyl groups in adjacent positions without ring distortion. The resulting model had the trifluoromethyl groups locked in a highly crowded conformation. The unusual behavior of the trimer toward basic hydrolysis (see below) might be attributed to its highly crowded structure.

The trimer was found to be resistant to hydrolysis by sulfuric acid or by a chlorosulfonic acid-sulfuric acid mixture, in contrast to the ready hydrolysis reported for *m*- and *p*-bis(trifluoromethyl)benzene under these conditions.⁶ However, hydrolysis by bases occurs readily; treatment of the trimer with two moles of potassium hydroxide in ethanol led to the formation of ethyl pentakis(trifluoromethyl)benzoate (IV) in 27% yield.



EXPERIMENTAL

Hexakis(trifluoromethyl)benzene (II). *a. Catalytic.* A mixture of 11.1 g. (0.068 mole) of hexafluoro-2-butyne, 1.8 g. (0.009 mole) of trifluoromethyl iodide, and 0.3 ml. of perfluorodimethylcyclohexane was sealed in a platinum tube under a nitrogen atmosphere, and the tube pressured externally with nitrogen. The tube was heated at 260° under 1000 atm. pressure for 15 hr. The reaction mixture was cooled below 0°, filtered, and the solid residue was air-dried. There was thus obtained 7.89 g. (71.1%) of hexakis(trifluoromethyl)benzene (II), melting at 209–210° (sealed capillary). The melting point was unchanged by recrystallization from acetone, benzene, or methanol.

Anal. Calcd. for $C_{12}F_{18}$: C, 29.65; F, 70.35; mol. wt., 486. Found: C, 29.78; F, 70.45; mol. wt., 505, 522 (cryoscopic in benzene).

Replacement of the trifluoromethyl iodide catalyst with

(4) Ebullioscopic molecular weight determinations (benzene) on the trimer carried out in our laboratory resulted in very high values (825, 850). This may be due to the volatility of the compound, resulting in the loss of material during the determination.

(5) B. Ekström, *Chem. Ber.*, **92**, 749 (1959).

(6) P. G. Scheurer and G. M. le Fabe, *J. Am. Chem. Soc.*, **72**, 3308 (1950).

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 8.63m, 8.75m, 12.41s, 13.35s and 13.79s μ 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

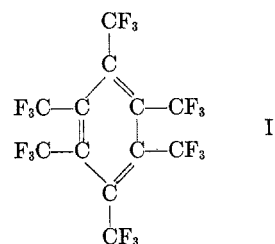
H. C. BROWN, H. L. GEWANTER, D. M. WHITE, AND
W. G. WOODS²

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 μ , $\log \epsilon = 2.20$) 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).