in an atmosphere of nitrogen. The wine-colored reaction mixture was cooled to room temperature and, after being washed twice with 200-ml. portions of ether, was added drop-wise to a stirred, ice-cold solution of 75 g. of sodiun hydroxide in 200 ml. of water. The mixture was extracted with five 150-ml. portions of ether and the combined ethereal extract was dried over potassium carbonate, after being washed with water. Removal of the solvent *in vacuo* and distillation of the residue through a semimicro column afforded 3.8 g. (72%) of dihydroisoindole as a colorless oil, b.p. 115° at 30 mm., n_D^{24} 1.5698, d_4^{20} 1.081, which solidified in the refrigerator, m.p. 16.0–16.5°. The *picrate*, obtained as silky, yellow needles from ethanol, had m.p. 195–196° (reported[5] 196–197°).

The *2-trifluoroacetyl derivative* of I was prepared by treating an ethereal solution of dihydroisoindole with a slight excess of methyl trifluoroacetate and allowing the mixture to stand overnight at room temperature. Evaporation of the solvent *in vacuo* followed by recrystallization of the residue from 50% methanol yielded long, felted needles, m.p. 80.5–81.0° (with sublimation).

Anal. Calcd. for $C_{10}H_8F_3NO$; C, 55.82; H, 3.75; F, 26.49; N, 6.51. Found: C, 55.9; H, 3.7; F, 26.0; N, 6.6.

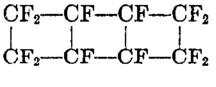
DEPARTMENT OF CHEMISTRY
BOSTON COLLEGE
CHESTNUT HILL 67, MASS.

Thermal Reactions of Perfluorobutyne-2 and Perfluoropropene[1]

HENRY C. BROWN

Received April 2, 1957

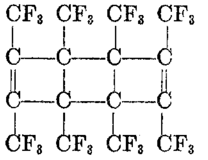
The tendency toward formation of the cyclobutane ring and the thermal stability of this structural conformation has been noted in several instances in studies of reactions of fluorocarbons with C—C multiple bonds. For example, tetrafluoroethylene readily forms perfluorocyclobutane when heated under pressure.[2] Formation of a cyclobutane ring also occurs in the dimerization of trifluorochloroethylene to give 1,2 dichlorohexafluorocyclobutane.[3] Miller,[4] by heating the unsaturated dimer of perfluorobutadiene, produced a saturated dimer believed to have the fused tricyclic structure (I).


I

We have found that perfluorobutyne-2 and perfluoropropene undergo a cyclization reaction that appears to be similar to that of the previously studied fluorocarbon olefins.

Perfluorobutyne-2, $CF_3C{\equiv}CCF_3$, forms a white, crystalline tetramer when heated under autogenous pressure. The solubility properties of this product are interesting and somewhat unusual for fluorocarbons. It is slightly soluble in ethylene dichloride, carbon tetrachloride, ethyl alcohol, and benzene at room temperature. The solubility in each of these solvents increases markedly with increasing temperature. This compound is very soluble in acetone and in ethyl ether at room temperature. It does not show unsaturation by reaction with potassium permanganate in acetone but its infrared spectrum shows a weak absorption band at 5.72μ, which is in the region expected for C—C unsaturation in fluorocarbons.

A fused polycyclic structure (II) is proposed for this tetramer of perfluorobutyne-2 on the basis of data obtained to date. Its crystallinity and other physical properties seem to favor this symmetrical type of structure. C—C double bonds in the position shown would not be expected to react readily with potassium permanganate under the mild conditions employed. The infrared absorption spectrum[5] shows the following peaks (microns): 5.72, weak; 6.75, weak; 7.15, moderate; 7.30, moderate; 7.47, moderate; 7.73, strong; 8.10–8.40, (unresolved) very strong; 8.52, very strong; 9.53, very strong; and 14.85, moderate.


II

The saturated cyclic dimer of perfluoropropene has not been described previously although Haszeldine[6] has reported formation of a trimer, tetramer, and pentamer from ultraviolet irradiation of perfluoropropene. We have found that perfluoropropene can be thermally dimerized by heating under autogenous pressure. The infrared spectrum of the saturated product, perfluorodimethylcyclobutane, shows the following peaks (microns): 7.22, moderate; 7.40, strong; 7.55, strong; 7.68, very strong; 7.95, very strong; 8.20, very strong; 9.38, weak; 9.58, weak; 11.00, strong; 11.35, strong; 13.45, weak, 13.63, moderate; and 13.82; moderate. This perfluoropropene dimer shows no unsaturation by infrared analysis, permanganate oxidation, or halogen addition. No higher boiling fractions that might indicate the presence of a linear dimer or higher polymers were found in the reaction product. Data is not yet available to show whether this compound as produced is a head-head dimer (III)

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[1] This work was supported 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.

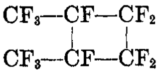
[2] A. F. Benning, F. B. Downing, and R. C. McHarness, U. S. Patent **2,384,821** (September 18, 1945).

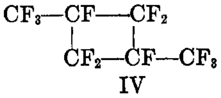
[3] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[4] W. T. Miller, *Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds;* McGraw-Hill Book Co., N. Y. (1951), p. 604.

[5] Infrared spectrum taken in carbon tetrachloride with a Perkin-Elmer Model 21 double beam spectrophotometer.

[6] R. N. Haszeldine, *J. Am. Chem. Soc.*, **75**, 3559 (1953).


III


IV

or head-tail dimer (IV). In general, unsymmetrical fluoroolefins tend to form head-head dimers and therefore (III) would be the expected form.

EXPERIMENTAL

Tetramer of perfluorobutyne-2. Perfluorobutyne-2 (30 g.) was placed in a previously evacuated 300-ml. stainless steel reaction vessel and heated at 320° for 31 hr. After cooling to room temperature, the reaction vessel was opened to the vacuum system and 23.8 g. of unreacted perfluorobutyne-2 recovered by transfer to a liquid-air cooled trap. The total solid material was removed by washing the reaction vessel with acetone. Subsequent removal of the acetone left a solid that was sublimed three times at atmospheric pressure, then recrystallized twice from benzene to produce 2.3 g. of white crystals, m.p. (sealed tube) 208–209°.

Anal.[7] Calcd. for $C_{16}F_{24}$: mol. wt. 648; C, 29.7; F, 70.3. Found: mol. wt. (ebullioscopic in benzene) 650; C, 29.9; F, 69.7.

Dimer of perfluoropropene. Perfluoropropene (150 g.) was condensed in a previously evacuated 300-ml. stainless steel reaction vessel and heated at 400° for 18 hr. Pressure in the vessel rose to a maximum of 2140 psi. and gradually decreased to 1100 psi. at the termination of the heating period. The vessel was cooled to room temperature, 73 g. of unreacted perfluoropropene recovered by transfer in the vacuum system, and the remaining higher boiling liquid fractionated in a column packed with nickel helices to give 72 g. of perfluorodimethylcyclobutane, b.p. 44.7–45.1°, d^{25} 1.667, n_D^{25} 1.2618.

Anal. Calcd. for C_6F_{12}: mol. wt., 300. Found: mol. wt. (Dumas), 300.

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

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[7] Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

2-Pyrones. XXVII.
4-Methyl-6-alkyl-2-pyrones

RICHARD H. WILEY AND J. G. ESTERLE

Received April 1, 1957

It has been demonstrated previously[1] that the acylation and subsequent decarboxylation of β-methylglutaconic anhydride (I) offers a unique procedure for the preparation of 4-methyl-6-alkyl-2-pyrones (III). The utility of this procedure is, however, limited by the fact that conditions required for successful isolation of the intermediate 5-acyl-β-methylglutaconic anhydride (II) where the acyl group has more than four carbons have never been devised. Because of the interest in certain of the structures available by this synthesis as intermediates in the biosynthesis of cholesterol[2] we have reinvestigated the possibility of preparing 4-methyl-6-alkyl-2-pyrones with 6-alkyl groups of four or more carbons by this route.

The results of these studies have established that the intermediate acyl-β-methylglutaconic anhydrides need not be isolated and purified. The crude acylated anhydrides can be decarboxylated and rearranged to the 4-methyl-6-alkyl-2-pyrones in overall yields of 12–45% from the anhydride. Using this technique we have prepared and characterized the seven 4-methyl-6-alkyl-2-pyrones described in Table I. These illustrate preparations with 5 to 10 carbon acyl halides and establish a correspondingly broader utility for the reaction. Infrared absorption data, summarized in Table IV, establish the presence of characteristic absorption maxima in the 1730–1736 cm.$^{-1}$; 1634–1647 cm.$^{-1}$; 1560–1567 cm.$^{-1}$; 1140–1220 cm.$^{-1}$; and 840 cm.$^{-1}$ regions. The first of these is a carbonyl stretching frequency characteristic of the 2-pyrone carbonyl. The 1640 cm.$^{-1}$ and 1560 cm.$^{-1}$ maxima are carbon-carbon double bond stretching frequencies and again serve to characterize the 2-pyrone structure. In the 2′-methylpropenyl derivative, in which there is a double bond conjugated with the ring unsaturation, the 1560 cm.$^{-1}$ maximum is shifted to 1536 cm.$^{-1}$ Three maxima occur in the 1140–1220 cm.$^{-1}$ region where absorption characteristic of the C—O stretching frequency in esters is observed. It has been noted previously[3] that unsaturated esters have two absorption maxima in this region. In the 2-pyrones there are three bands which occur at about 1200 cm.$^{-1}$, 1140 cm.$^{-1}$, and 1120 cm.$^{-1}$ in this region. One of these is presumably the adsorption maximum associated with the C—O stretching frequency. The maxima in 840 cm.$^{-1}$ region are the most prominent in the spectra. This is assigned to the C—H out of plane deformation of one of the ring C—H groups. It occurs in approximately the same place as the maximum observed for the C—H deformation in 1,3,5-substituted benzenes (835 cm.$^{-1}$)[4]. The ring hydrogens are situated between two substituents in each case. The 3-bromo derivatives, listed in Table II, were observed to have infrared absorption characteristics, summarized in Table IV, similar to those of the unsubstituted pyrones. The carbonyl stretching frequency is shifted to slightly longer wave lengths (1712–1730 cm.$^{-1}$). The intensities of the maxima associated with the carbon-carbon double bond stretching frequencies are reversed. The 1640 cm.$^{-1}$ maxima is the more intense of the two in the bromo compounds. In the bromo compounds the 1560 cm.$^{-1}$ maxima is shifted to 1529–1536 cm.$^{-1}$ There is generally only

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[1] Richard H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **74**, 3893 (1952).

[2] Richard H. Wiley and J. G. Esterle, *J. Org. Chem.*, **21**, 1335 (1956).

[3] L. J. Bellamy, *Infra-Red Spectra of Complex Molecules*, John Wiley and Sons, N. Y., 1954, p. 163.

[4] L. J. Bellamy, *op. cit.*, p. 68.