

ture of *cis* and *trans* isomers, IV and V. The high melting yellow isomer (m.p. 162.5°; λ max 219 μ , ϵ 11,560; shoulder at 250 μ , ϵ 3,000; shoulder 310 μ , ϵ 480. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.58. Found: C, 78.31; H, 6.57) is tentatively assigned the *cis*-configuration on the basis of its ready thermal conversion to the lower melting, colorless isomer (m.p. 132.5–133°; λ max 223 μ , ϵ 7,300, λ max 249 μ , ϵ 3,350, shoulder 310 μ , ϵ 480. *Anal.* Found: C, 78.66; H, 6.82). Support for this assignment is found in the presence of a band at 968 cm^{-1} in the infrared spectrum (potassium bromide pellet) of the *trans* isomer (out-of-plane C–H deformation) which was absent in the *cis*-isomer. Attempts to isomerize the lower to the higher melting isomer (*trans* to *cis*) failed.

Molecular models indicate that the *trans* isomer is less strained than the *cis*. Clemmensen reduction of V gave [8]paracyclophane (VI), a camphoraceous smelling liquid. *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.28; H, 10.70. Found: C, 89.36; H, 10.35.

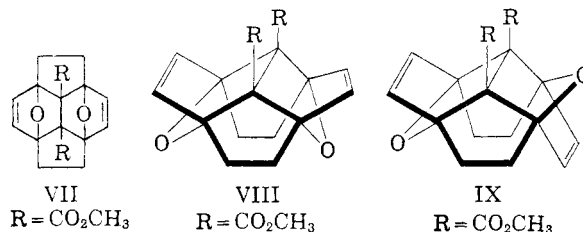
The ultraviolet absorption spectrum of VI (λ max 224 μ , ϵ 6,840, λ max 265.5 μ , ϵ 403, λ max 274 μ , ϵ 407, shoulder 315 μ , ϵ 28) indicates that the benzene ring is seriously bent from its normal planar configuration. Comparison of the spectrum of VI and of [2.2]paracyclophane suggests that some but not all of the spectral abnormalities of the latter compound are associated with the deformations of the benzene rings.^{4,5}

Molecular models of V and of derived compounds that retain the *trans* double bond suggest that the substance is a racemate because of steric stabilization of conformation. The stereochemistry of the system is currently being investigated.

Although compounds I, II or III do not react with ordinary dienophiles, reaction of II (not I or III) with dicarbomethoxyacetylene occurred readily at 100° to give VII,⁶ m.p. 162.5–163° (decomposition). *Anal.* Calcd. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.50. Found: C, 65.39; H, 5.38. On pyroly-

sis VII gave back starting materials, a fact that indicates absence of a deep-seated rearrangement in formation of VII. Reduction of VII with hydrogen and platinum gave the thermally stable tetrahydro derivative, m.p. 229–230°. *Anal.* Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.64. Found: C, 64.84; H, 6.62.

The interesting question of whether VII possesses detailed structure VIII or IX is under investigation.



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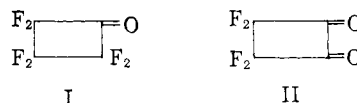
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RECEIVED MARCH 27, 1961

PERFLUOROCYCLOBUTANONES

Sir:

We wish to report the synthesis of two extraordinary perfluoroketones starting with tetrafluoroethylene (TFE). Perfluorocyclobutanone (I) is light yellow in the liquid state, absorbs at 5.4 μ in the infrared (the lowest recorded for any ketone) and is quantitatively converted to perfluorocyclopropane and carbon monoxide by light. Perfluorocyclobutane-1,2-dione (II) is deep blue in the gaseous, liquid and solid states.



Both compounds are exceptionally reactive and undergo a variety of addition reactions involving the carbonyl groups.

To synthesize I, methyl trifluorovinyl ether, available from sodium methoxide and TFE,¹ was treated with TFE at 175° to give a 65% yield of methoxyheptafluorocyclobutane, b.p. 56° (*Anal.* Calcd. for $C_5H_3F_7O$: F, 62.7. Found: F, 62.6). Hydrolysis of this ether in 95% sulfuric acid at 175° in a sealed vessel gave a solution of perfluorocyclobutanone hydrate. On heating this solution at atmospheric pressure, I distilled at 1° in 75% yield (*Anal.* Calcd. for C_4F_6O : F, 64.0; mol. wt., 178. Found: F, 63.4; mol. wt. by vapor density, 176) then its hydrate, b.p. 128°, m.p. 52°, 14% yield (*Anal.* Calcd. for $C_4H_2O_2F_6$: C, 24.5; H, 1.0; neut. eq., 196. Found: C, 24.0; H, 1.3; neut. eq., 195). When phosphorus pentoxide was added to the above sulfuric acid solution of the hydrate, the distillation gave only I in over 90% yield.

Perfluorocyclobutanone (I) is very stable thermally, being recovered unchanged after heating

(1) S. Dixon, U. S. Patent 2,917,548 (1959).

(3) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.*, **24** [6] 18 p. (1947).

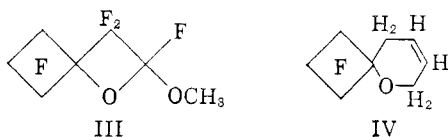
(4) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(5) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter and E. Heilbronner, *J. Am. Chem. Soc.*, **81**, 5977 (1959).

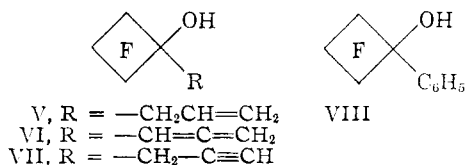
(6) O. Diels and S. Olson [*J. prakt. Chem.*, **156**, 285 (1940)] observed that one mole of dicarbomethoxyacetylene reacted readily with two moles of furan to give a compound similar to VII, but lacking the two extra methylene bridges.

for 12 hours at 300° in a sealed tube. However, ketones with fluorine atoms attached to both α -carbon atoms have been shown to have unusual chemical properties,² and the added effect of ring strain in I enhances its reactivity. In many reactions the carbonyl group takes part in formation of four- and six-membered rings, and a large number of unusual additions to the carbonyl group have been observed.

Reaction of I with methyl trifluorovinyl ether at room temperature gave 2,3,3,5,5,6,6,7,7-nonafluoro-2-methoxy-1-oxaspiro[3.3]heptane (III, b.p. 98°, 91% yield; *anal.* Calcd. for $C_7H_3O_2F_9$: C, 29.0; H, 1.0; F, 59.0. Found: C, 29.2; H, 1.3; F, 58.7). Compound I behaves as a potent dienophile as illustrated by its reaction with butadiene below 0° to give quantitatively the adduct IV, b.p. 84° at 110 mm. (*anal.* Calcd. for $C_8H_6F_6O$: C, 41.1; H, 2.6; F, 49.1. Found: C, 41.5; H, 2.8; F, 49.0).

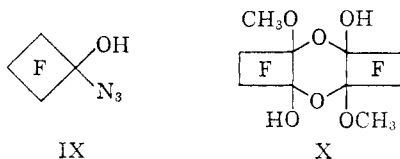


Perfluorocyclobutanone (I) reacts at room temperature with a variety of unsaturated compounds to give cyclobutanols. For example, propylene gave the allylcyclobutanol V, b.p. 114°, 88% yield; *anal.* Calcd. for $C_7H_6OF_6$: C, 38.2; H, 2.8; F, 51.8. Found: C, 38.4; H, 2.8; F, 51.4. Similarly methylacetylene gave the allene VI (b.p. 121°, 53% yield) and allene gave the acetylene VII (b.p. 116°, 47% yield). *Anal.* Calcd. for $C_7H_4OF_6$: C, 38.6; H, 1.9; F, 52.3. Found for VI: C, 39.1; H, 2.1; F, 51.8. Found for VII: C, 38.7; H, 2.1; F, 52.1.



Aromatic compounds add readily to I. For example, benzene reacts below 25° in the presence of aluminum chloride catalyst to give the phenylcyclobutanol VIII, b.p. 134° at 130 mm., 96% yield; *anal.* Calcd. for $C_{10}H_6F_6O$: C, 46.9; H, 2.4; F, 44.5. Found: C, 47.0; H, 2.8; F, 44.5.

The first isolable azidocarbino (IX) was obtained by the reaction of hydrazoic acid with I at -15° in methylene chloride. The product distilled at 34° at 20 mm., m.p. 4-5.5° (77% yield). *Anal.* Calcd. for $C_4HF_6N_3O$: F, 51.6. Found: F, 51.6. Small samples exploded when held in a flame.



(2) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

Perfluorocyclobutane-1,2-dione (II), b.p. 35°, was synthesized in 30-50% yields by sulfuric acid hydrolysis of 1,2-dimethoxyperfluorocyclobutane, prepared in 83% yield by thermal dimerization of methyl trifluorovinyl ether at 150°³ (*Anal.* Calcd. for $C_4F_4O_2$: F, 48.7; mol. wt., 156. Found: F, 48.7; mol. wt., 157.5 by vapor density).

The blue color undoubtedly is related to the required *cis* relationship of the two carbonyl groups in the four-membered ring along with the strong inductive effect of the fluorine atoms. The linear perfluoro-1,2-diketone, $C_3F_7COCOC_3F_7$,⁴ is yellow. Leonard and Mader⁵ have shown that in alicyclic 1,2-diketones having no α -hydrogens the long wave length absorption varies regularly as the angle between the planes of the carbonyl groups is decreased by decreasing ring size. Shoppee⁶ has reported that 4,4,5,5-tetramethyl-1,2,3-cyclopentanetrione is blue. Perfluorocyclobutane-1,2-dione gives no e.p.r. signal, so the color cannot be ascribed to free radical character.

The blue diketone II polymerizes easily but can be kept unchanged over phosphorus pentoxide. Reaction with methanol gave mainly the bis-methylhemiketal,⁷ m.p. 39-42° (*anal.* Calcd. for $C_6H_8F_4O_4$: F, 34.7. Found: F, 34.7); however, a small amount of the dioxane X or isomer thereof, m.p. 182-183°, was also formed. (*Anal.* Calcd. for $C_{10}H_8F_8O_6$: C, 31.9; H, 2.1; F, 40.4; mol. wt., 376. Found: C, 32.1; H, 2.6; F, 39.9; mol. wt., 365 (ebullioscopic in acetone).)

The diketone II also underwent many of the unusual reactions of the monoketone I, for example with dienes, propylene, methyl trifluorovinyl ether and aromatic compounds. Reaction occurred at one and both of the carbonyl groups in addition to formation of some dioxane-hemiketal structures analogous to X.

Details on the preparation and reactions of these perfluorocyclobutanones will be reported in future publications.

(3) D. I. McCane, U. S. Patent 2,982,786 (1961).

(4) J. J. Drysdale and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 5111 (1960).

(5) N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

(6) C. W. Shoppee, *J. Chem. Soc.*, 269 (1936).

(7) Prepared by Dr. R. M. Scribner of these laboratories.

CONTRIBUTION NO. 691

CENTRAL RESEARCH DEPARTMENT

EXPERIMENTAL STATION

E. I. DU PONT DE NEMOURS AND CO.

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A HIGHER HYDRIDE OF YTTERBIUM

Sir:

The rare-earth metals, with two exceptions, are known to react with hydrogen at moderate temperatures and atmospheric pressure to form hydrides approaching RH_3 .¹ The lighter rare-earth trihydrides have a face-centered cubic structure while those of samarium and beyond are hexagonal

(1) A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, **146**, 149 (1925); R. Viillard, *Compt. rend.*, **221**, 144 (1945); R. N. R. Mulford and C. E. Holley, Jr., *J. Chem. Phys.*, **59**, 1222 (1955); W. L. Korst, Ph.D. Thesis, University of Southern California, 1956; V. I. Mikheeva and M. E. Kost, *Doklady Akad. Nauk S.S.S.R.*, **115**, 100 (1957); R. Streck and K. Dialer, *Z. anorg. allgem. Chem.*, **306**, 141 (1960).