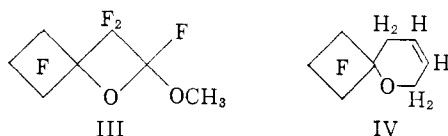
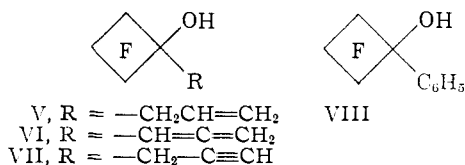


for 12 hours at 300° in a sealed tube. However, ketones with fluorine atoms attached to both α -carbon atoms have been shown to have unusual chemical properties,² and the added effect of ring strain in I enhances its reactivity. In many reactions the carbonyl group takes part in formation of four- and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

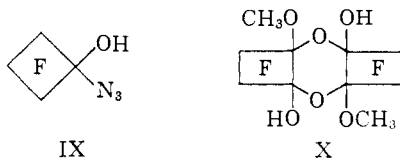


Perfluorocyclobutanone (I) reacts at room temperature with a variety of unsaturated compounds to give cyclobutanols. For example, propylene gave the allylcyclobutanol V, b.p. 114°, 88% yield; *anal.* Calcd. for $C_7H_6OF_6$: C, 38.2; H, 2.8; F, 51.8. Found: C, 38.4; H, 2.8; F, 51.4. Similarly methylacetylene 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 azidocarbonyl (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° (*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, $C_3F_7\text{COCOC}_3F_7$,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
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 WILMINGTON, DELAWARE

RECEIVED APRIL 3, 1961

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).