# **DECEMBER 1958** 2011

 $pH$   $\tilde{p}$  with acetic acid. Further purification could be obtained bv recrystallization from water.

*Procedure B: 6-hydroxypurines.* **A** mixture of the 5-acetamido-4amino-6-hydroxypyrimidine and formamide in the ratio of 1 **g.** of pyrimidine to 10 ml. of formamide was heated under reflux for 15-30 min. The reaction mixture was diluted with an equal volume of water and chilled to give the purine.

*Procedure* C': *6-hydroxy-8-methylpurines.* **-4** solution of the **~5-acetamido-4-amino-6-hydroxypyrimidine** in phosphorus oxychloride was stirred at 55' for 16 hr. and then concentrated at reduced pressure. The residue was decomposed with ice and water and the resulting mixture adjusted to **pH** 8 with aqueous ammonia. The products thus obtained were recrystallized from water for purification.

TABLE I		
Compound Prepared	Proce- $_{\rm dure}$	Yield. %
5-Acetamido-4-amino-6-hydroxy-2- methylpyrimidine <sup>4</sup>	А	65
5-Acetamido-2,4-diamino-6-hydroxy- pyrimidine <sup>1</sup>	А	93
5-Acetamido-4-amino-2,6-dihydroxy- pyrimidine <sup>2</sup>	A	83
$6-Hvdroxv-2-methv1$ purine <sup>5</sup>	В	86.5
Guanine	R	89.5
Xanthine	B	97
$2.8$ -Dimethyl-6-hydroxypurine <sup>6</sup>	С	73
2-Amino-6-hydroxy-8-methylpurine <sup>7</sup>	С	75
7-Hydroxy-5-methyl-v-triazolo[d]- pyrimidine	D	79

*Procedure D: ?-hydroxy-5-methyl-v-triazolo[d]pyrimidine.*<br>Acetamido-6-amino-4-hydroxy-2-methylpyrimidine (3.2) 5-Acetamido-6-amino-4-hydroxy-2-methylpyrimidine 9.) was heated under reflux for 10 min. with 50 ml. of concentrated hydrochloric acid. The reaction mixture was evaporated to dryness under reduced pressure and the residue dissolved in 50 ml. of warm water. This solution was cooled to 10' and treated with a total of **2.0 g.** of sodium nitrite in small portions. The reaction mixture was stirred for **1** hr. at 0" and the precipitate collected to give **2.1 g.**  (79%) of 7-hydroxy-5-methyl-v-triazolo[d]pyrimidine, m.p.  $265 - 267$ ° (dec.).

**41 41.** Fonnd: C, **35.40;** H, 4.17; N, 41.07. *Anal.* Calcd. for **CjHSN50.H20:** C, 35.50; H, 4.17; N,

Acknowledgment. We are indebted to Dr. John Harmon of the Grasselli Chemicals Department for the synthetic method used for the preparation of the 6-hydroxy-8-methylpurines.

CONTRIBUTIOX *So.* 471 EXPERIMENTAL STATION E. I. DU PONT DE NEMOURS AND CO. CENTRAL RESEARCH DEPARTMENT WILMINGTON, DEL.

(4) *Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>: C, 46.15; H, 5.52; N, 30.76. Found: C, 46.51; H, 5.75; N, 30.89.<br>(5) R. K. Robins, K. J. Dille, C. H. Willits, and B. F.

Christensen, *J. Ani. Chem. Soc.,* **75,** 263 (1953).

- (6) **F.** Craveri and *G.* Zoni, *Chirnicn (Milan),* **13, 173**  (1957).
	- *(7) W. Traube, Ann.*, 432, 266 (1923).

# **Ethers Derived from Fluoroolefins**

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As part of a program aimed at the synthesis of highly fluorinated epoxides, we have prepared some new ethers by base-catalyzed reaction of alcohols with perfluoro-olefins and dichloroperfluoro-olefins. Numerous examples of such reactions appear in the literature, $1^{-10}$  most of which are regarded by their authors as proceeding by nucleophilic addition of alcohol to the double bond, followed in some cases by spontaneous elimination of hydrogen halide, whereas in other cases the saturatedethers may be isolated. Park *et al.*<sup>9</sup> have summarized the factors governing elimination *vs.* nonelimination of hydrogen halide by the adduct when the starting olefin is a perhalol-alkene. In agreement with their generalizatiou, we have prepared saturated ethers (I and 11) by the addition of methanol and ethanol, respectively to perfluoro-l-heptene. They are liquids which may be distilled, although they release hydrogen fluoride slowly on standing.

 $CF_3(CF_2)_4CHFCF_2OR$   $CF_3(CF_2)_4CHFCO_2C_2H_5$  $I, R = CH<sub>3</sub>$ <br> $II, R = C<sub>2</sub>H<sub>6</sub>$  $\overrightarrow{III}$ ,  $\overrightarrow{R} = \overrightarrow{CC}$ l<sub>3</sub> 11'

The methyl ether **(1)** underwent smooth chlorination; even with a large excess of chlorine, only three of the four hydrogen atoms were substituted. In view of the well known inertness of a C--H bond adjacent to fluorocarbon groups, the trichlorinated product is almost certainly the trichlorornethyl ether (111). It is exceptionally stable, distilling unchanged at  $202-204$ ° and resisting attack by sulfuric acid, by di-t-butyl peroxide and by strong ultraviolet rays. The ethyl ether (11) was converted by  $90\%$  sulfuric acid<sup>9</sup> to the ester IV in low yield.

Park, Lacher, *et al.<sup>4,7</sup>* and Barr, Rapp, *et al.<sup>5</sup>* have found that the perhalocyclobutenes V and VI yield

- (1) W. E. Hanford and G. W. Rigby, U. S. Patent **2,409,274.**
- (2) **W. T.** Miller, Jr., E. W. Pager, and **I'.** H. Grisn-old, *J.* **Am.** *Chem. SOC.,* **70,** 431 (1848).
- (3) J. D. Park, D. K. Vail, D. R. Lea, and J. R. Lacher, *J. Am. Chem. Soc.*, 70, 1550 (1948).
- **(4)** J. **D.** Park, AI. L. Sharrah, and J. **R.** I,acher, *J.* Am.
- *Chem.* **SOC., 71,** 2337 (1949). (5) **J.** T. Barr, **I<.** E. Rapp, R. 1,. Pruett, **C.** T. Bahner, J. D. Gibson, and R. **Ii.** Lafferty, *J.* Ani. *('hem. SOC.,* **72, 4480** (1950).
- (6) **J. D.** Park, **AI.** L. Sharrah, W. H. Breeii, and J. R. Lacher, *J. Am. Chenz. SOC.,* **73,** 1329 (1951).
- *(7)* J. D. Park, C. M. Snow, and **J.** R. I.aclier, *J.* Am. *('hem. SOC.,* **73, 2342** (1951).
- (8) **P.** Tarrant and H. C. Bron-11, *J. Am. ('hem.* Soc., **73,**  1781 (1951).
- (9) J. D. Park, W. M. Sweeney, S. L. Hopwood, Jr., and J. R. Lacher, *J. Am. Chem. Soc.,* **78,** 1685 (1956).
- (10) R. J. Koshar, T. C. Simmons, and F. W. Hoffmann, *.I* **.4m.** *Chem. Soc.,* **79, 1741 (1957).**



The 1,2-dichlorotetrafluorocyclobutene *(VI)* gave ethers of structure VII, but with excess alcohol and alkali triethers were formed with the probable structure X.' We have found that the analogous 1,2-dichlorohexafluoro cyclopentene (VIII) behaves in similar fashion with ethanol and alkali to yield the ethyl ether IX. This may be converted with additional ethanol and alkali to the triether, probably XI. In his doctoral thesis,<sup>11</sup> Latif reported similar results with VI11 and methanol, but claimed structure XI1 for the triether. Their extreme inertness makes structure-proof of the triethers difficult. Park *et al.*<sup>7</sup> postulate that their triethers were formed by direct displacement of the "allylic" fluorine atoms of the monoether VI1 to yield X. Since there is little precedent for "allylic" displacement of fluoride in such highly fluorinated structures, we propose the more plausible mechanism:

$$
\frac{\text{VII}}{\text{IX}}\frac{\text{HOR}_{\bullet}(\overline{C_{F_2}})_{n}}{\text{XIII}}\cdot\frac{\text{CHCl}_{\bullet}(\overline{C_{F_2}})_{n}}{\text{KIII}}\cdot\frac{\text{CHCl}_{\bullet}(\overline{C_{F_2}})_{n}}{\text{CHOR}_{\bullet}}\cdot\frac{\text{CHCl}_{\bullet}(\overline{C_{F_2}})_{n-1}}{\text{CHOR}_{\bullet}}\cdot\frac{\text{CHO}}{\text{CHOR}_{\bullet}}\cdot\frac{\text{HOR}_{\bullet
$$

Both our monoether  $(IX)$  and triether  $(XI)$  resisted all efforts to cleave the ether linkages with sulfuric acid, hydriodic acid, or aluminum chloride. They were also inert to chlorine, to bromine and to hydrogen with Adams catalyst at two atmospheres.

### EXPERIMENTAL

*l-Uethozy-2-hydroper\$uoroheptune* (I). **A** solution of sodium methoxide was prepared from  $96$  g. (3 moles) of methanol and 0.23 g. (0.01 gram atom) of sodium. To this was added dropwise, with stirring and cooling to 5°, 10.0 g. (0.0286 mole) of perfluoro-1-heptene, prepared by pyrolysis of sodium perfluoro-octanoate.<sup>12</sup> The reaction mixture was allowed to come to room temperature under continuous stirring. It was then poured into 200 ml. of cold water. The dense fluoro-organic layer was separated, washed with water, dried over CaCl, and distilled, yielding 3.40 g.  $(31\%)$  of clear colorless product at 129-131°. o-orgs<br>CaC<br>less p<br>——————————

(11) L. **A.** Latif, Ph.D. Thesis, Ohio State University (1952).

**(12)** J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H Smith, Jr. *.I. Am. Chenz. Soc.,* **75,** 4525 (1953).

Anal. Calcd. for C<sub>8</sub>H<sub>4</sub>OF<sub>14</sub>: F, 69.61. Found: F, 70.42.  $n_{\rm D}^{20} = 1.2992, d_{20}^{20} = 1.635$ . M.R. = 43.59. A.R. (F) = 1.30.

*1-Ethoxy-2-hydroperfluoroheptane* (II). By the same procedure as above, addition of ethanol to perfluoro-I-heptene gave a  $46\%$  yield of the ethyl ether (II), b.p. 144-146<sup>o</sup>.

Anal. Calcd. for C<sub>9</sub>H<sub>6</sub>OF<sub>14</sub>: F, 67.15. Found: F, 67.05.

*1-Trichloromethoxy-2-hydroperJluoroheptane* (111). Chlorine gas was bubbled slowly through 2.83 g. (0.0074 mole) of 1-methoxy-2-hydroperfluoroheptane (I) for 8 hr., with continuous illumination from a 300-watt tungsten lamp. The pale yellow reaction mixture was taken up in ether and the solution washed with aqueous NaHSO<sub>3</sub> and dried over Na2S04. Distillation yielded 3.40 g. (70%) of colorless oil at 202-204'.

*Anal.* Caled. for C<sub>8</sub>HOCl<sub>3</sub>F<sub>14</sub>: Cl, 21.91. Found: Cl, 21.66. The product was recovered unchanged after successive treatments with (a)  $98\%$  H<sub>2</sub>SO<sub>4</sub> at  $100^{\circ}$  for 2 hr., (b) ultraviolet irradiation for 7 hr., and (c) di-t-butyl peroxide at  $100^{\circ}$  for 2 hr.

*Ethyl 2-hydroperfluoroheptanoate* (IV). Four grams (0.01 mole) of 1-ethoxy-2-hydroperfluoroheptane was added to 25 g. of  $90\%$  sulfuric acid, and the mixture was heated at  $100^{\circ}$ for 6 hr. It was then poured into ice water and extracted with ether. The dried ether extract was concentrated and the residue was distilled at reduced pressure, yielding 0.71 g. (19%) of colorless liquid at  $66-67^{\circ}$  (3 mm.).

Anal. Calcd. for C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>F<sub>12</sub>: F, 60.94. Found: F, 61.31. *l*-Chloro-2-ethoxyhexafluorocyclopentene (IX). To a solution of 9.66 g. (0.17 mole) of potassium hydroxide in 150 ml. of absolute ethanol, 60 g. (0.245 mole) of 1,2-dichlorohexawas stirred and cooled in ice. The mixture was then allowed to come to room temperature, with continued stirring for an additional hour. It was filtered to separate the precipitated potassium chloride, and the filtrate was poured into 700 ml. of ice water. The dense organic layer was separated, dried over CaCl<sub>2</sub> and distilled, yielding 21.9 g. (0.089 mole) of unreacted 1,2-dichlorohexafluorocyclopentene at 90-91° and 29.2 g. (0.115 mole) of product  $(IX)$  at 143-144°.

*Anal.* Calcd. for  $C_7\hat{H}_5OCIF_6$ : CI, 13.92. Found: Cl, 13.97.  $n_{\rm D}^{20} = 1.3774.$ 

*ChlorotriethoxytetraJuorocy.,lopentene (structure XI postulated).* **A** mixture of 10 g. (0.039 mole) of 1-chloro-2-ethoxyhexafluorocyclopentene (IX), 10 g. (0.17 mole) of potassium hydroxide and 50 ml. of absolute ethanol was refluxed with stirring for 4 hr. The mixture was then filtered and the filtrate poured into 400 ml. of ice water. The dense organic layer was separated, dried over CaCl<sub>2</sub> and distilled, yielding 5.81 g. (49%) of product at  $224-225^{\circ}$ .

Anal. Calcd. for  $C_{11}H_{10}O_3ClF_4$ : Cl, 11.56. Found: Cl, 11.71.  $n_{\rm D}^{20} = 1.4193$ .

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# **Halogen Exchange Reaction of 1 ,l,l -Tribromo-3,3,3- trifluoropropanorie with Silver Fluoride**

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To our knowledge, halogen exchange using metal fhiorides has not been reported as a method of pre-