

Tetrafluorofuran

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NONE of the fully fluorinated 5-membered aromatic heterocycles has been prepared up till now; we now report the first synthesis of tetrafluorofuran. The method is outlined in the Scheme. The fluorination of tetrahydrofuran was carried out in the usual manner¹ over stirred cobalt trifluoride at 100–120°; very little ring-breakdown appeared to occur and fractional distillation gave a mixture of C₄H₂F₆O isomers, b.p. 37–61°, in about 15% overall yield. Treatment of these mixed isomers with fused potassium hydroxide²—the reaction with aqueous alkali was

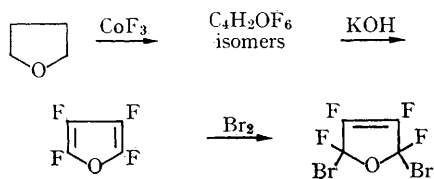
very slow—gave about 25% conversion into tetrafluorofuran. This compound has b.p. 17°; ν_{\max} at 1750 and 1480 cm.⁻¹ (*cf.* furan at 1579 and 1486 cm.⁻¹); and λ_{\max} (hexane) at 232 m μ (ϵ , 700) together with strong end-absorption; its ¹⁹F n.m.r. spectrum was a typical A₂X₂ [δ_A , 137; δ_B , 196 (p.p.m. upfield from CFCI₃ as internal reference); J_{AA} , 20.5; J_{XX} , -5.0; J_{AX} , 15.5; J_{AX}' , -13.5 (all c./sec.)]; it showed major mass peaks at 140 (C₄F₄O⁺) 93 (C₃F₃⁺).

Rather surprisingly, tetrafluorofuran is spontaneously converted in the gas or liquid phase, and

even in the presence of hydroquinone, into a white, presumably polymeric, solid, m.p. $>250^\circ$. This reaction occurs quite rapidly, the pure liquid tetrafluorofuran becoming solid in a few hours at room temperature. The solid is slightly soluble ($>1\%$ w/w at 15°) in hexafluorobenzene and insoluble in common organic solvents. Self-additions as rapid as this are rare among unsaturated fluoro-compounds.

Tetrafluorofuran does not behave like a simple fluoro-olefin³ in that it does not noticeably react with sodium methoxide in methanol at room temperature over one hour. At 60° a reaction occurred but this could have been subsequent to polymerisation and we have not been able to isolate any single products. The furan does, however, react rapidly with one mole of bromine at room temperature to give what appears to be a 3:2 mixture of the two 2,5-dibromo-adducts; the ^{19}F n.m.r. spectrum of the product showed two A_2X_2 patterns and no peaks which could be ascribed to 2,3-adducts. The rate of this bromine

addition was qualitatively reminiscent of those shown by hydrocarbon olefins and in contrast to those of fluoro-olefins or fluoro-aromatics,⁴ both of which add halogens sluggishly.



If this behaviour is typical therefore, tetrafluorofuran is unlike a fluoro-olefin or a polyfluoroaromatic and its low nucleophilic and high electrophilic reactivity seem to suggest that it still has furan-like characteristics in spite of the four fluorines.

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³ A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp. New York, 1958, p. 156.

⁴ J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature*, 1956, **178**, 199; Ref. 3, p. 33.