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A NOVEL PHOTO-REACTION OF SULFUR DIOXIDE WITH FLUOROOLEFINS

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Sulfur trioxide with fluoroolefins gives cyclic adducts, mainly β-sultones (1-3), but the addition of sulfur dioxide to the same fluoroolefins has never been observed. Sulfur dioxide has been claimed to react under free-radical initiation only with the highly reactive C_2F_4, to afford a polysulfone (4). We found no reaction between SO_2 and C_3F_6 when heated up to 140° under pressure with free-radical initiators.

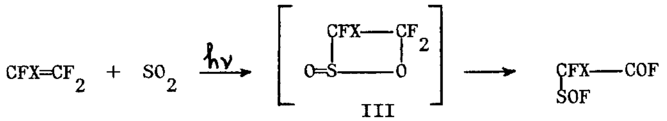
Sulfur dioxide reacts readily, however, with perfluoroolefins such as C_2F_4 and C_3F_6 in the condensed phase under UV irradiation, to give very good yields of 1:1 addition products, which are α-fluorosulfinyl-acylfluorides.

A solution of C_2F_4 (1.2 moles) and SO_2 (2.5 moles) in CF_2Cl_2 (1500 g.) kept at ca. -32° under -90° reflux and N_2 atmosphere, was irradiated for 30 hr. with a 70-watt Hanau immersed mercury-lamp (medium pressure). Fractionation then gave 79 g. of fluorosulfinyl-difluoroacetylfluoride (I) b.p. 49°, which accounted for ca. 80% of the reacted C_2F_4.

Similarly, irradiation at -30° of a mixture of SO_2 (12 moles) and C_3F_6 (12 moles) yielded, after 25 hr., 310 g. of 2-fluorosulfinyl-tetrafluoropropionylfluoride (II), b.p. 60°, accounting for more than 95% of the reacted C_3F_6.

The F^{19} NMR spectrum revealed that II was actually made up of two forms, according to the presence of two asymmetric centers, one of which being the sulfur atom of the sulfinylfluoride group.

The formation of α-fluorosulfinyl-acylfluorides might be envisioned to proceed through rearrangement of an intermediate cyclic adduct III:



III

(X = F, CF_3)

We have been unable, however, to demonstrate the formation of III; this would indicate a large degree of instability of such a cyclic intermediate, whose rearrangement could be likely induced by a trace amount of fluoride ions, in analogy to what has been established for the base-catalyzed rearrangement of β-sultones (3).

We have briefly examined some reactions of I and II: water caused hydrolysis and in both cases subsequent SO_2 elimination leading to difluoroacetic acid and 2,3,3,3-tetrafluoropropionic acid, b.p. 127° (5), respectively.

With methanol, the diesters $CFX(SO_2CH_3)COOCH_3$ (X = F, b.p. 40°/1 torr; X = CF_3, b.p. 45°/1 torr) were obtained. Reaction of I with aniline in diethylether gave the (N-phenylsulfinamide) difluoroacetanylide, m.p. 122°. Hydrolysis of II with 35% H_2O_2 at 90° yielded, in addition to $CF_3CFHCOOH$ (35%) and CF_3COOH (50%), 15% conversion to CF_3CFHSO_3H, b.p. 111-113°/16 torr.

For each of the new compounds satisfactory analytical data have been obtained and their IR and NMR spectra were consistent with the assigned structure. (Boiling and melting temperatures are uncorrected).

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