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PERFLUORO[CYCLOBUTANESPIRO-2'-(EPOXYETHANE)]

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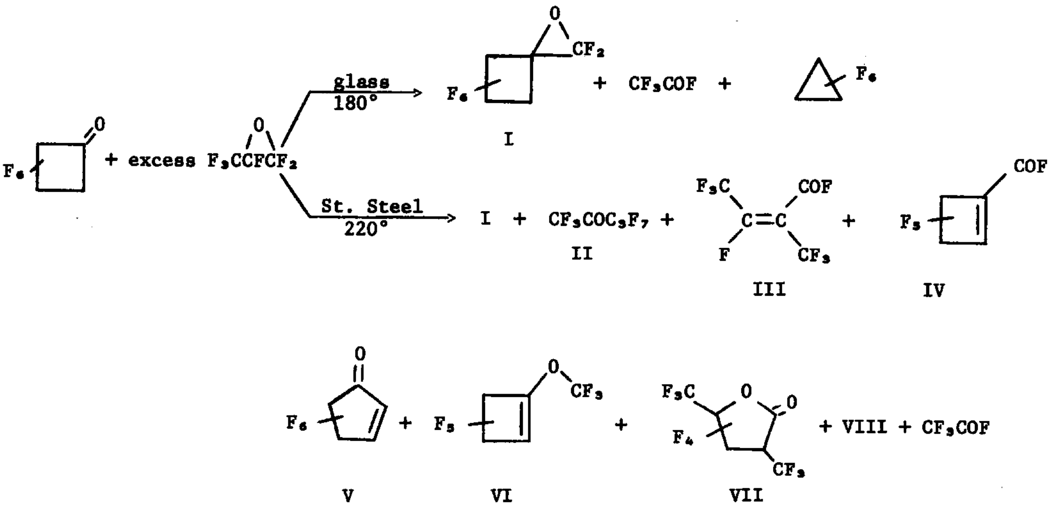
Perfluorinated epoxides have aroused considerable interest[1] as versatile organic intermediates. This communication reports the preparation of the title compound I (the first perfluorospiroepoxide), the formation of an unusual series of products in attempts to prepare I by variation of reaction conditions, and several reactions of I.

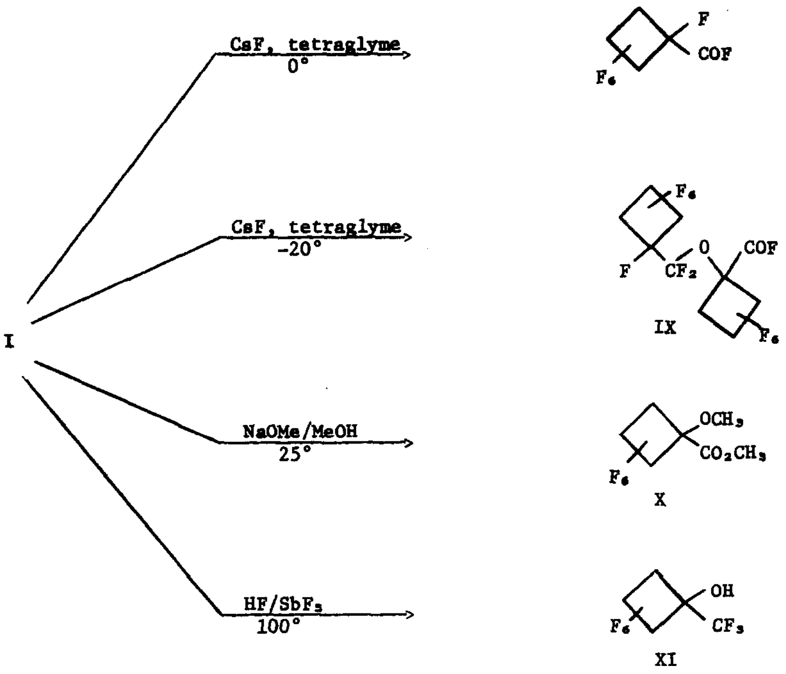
When hexafluorocyclobutanone[2] and excess hexafluoropropylene epoxide[3] are heated together at 180° in a sealed glass ampoule, I, b.p. 18-21°, is formed in yields exceeding 90%. The infrared spectrum of I shows a COC band at 6.55μ while its mass spectrum exhibits m/e 228 (m^+). Its ^{19}F NMR[4] (neat) showed absorptions at 31.2 (CF_2) 49.4 (2 F of 2 CF_2, 1/2 AB, J = 243 Hz), 54.9 (2 F of 2 CF_2, 1/2 AB), 58.4 (CF_2). Interestingly, if the same reactants are heated in stainless steel vessels at temperatures exceeding 220°, I and a series of products II[5] - VIII are formed from the ensuing reaction.



The minor component, VIII, has not been fully characterized.

The reaction in stainless steel yields varying amounts of I (10-80% wt) and all but 15% of the remainder are compounds II-VIII and CF_3COF. Control experiments demonstrate that IV is a decomposition product of I. The spectral properties of III-VII are as follows: III [ir (gas) 5.4μ (CO), 5.8μ (C=C), m/e 228 (m^+), ^{19}F NMR (CCl_4) -126 (COF), -15.8 (CF_3, $J_{CF_3-CF_3}$ = 1.6 Hz), -11.8 (CF_3), -4.7 (CF)]; IV [ir (gas) 5.4μ (CO), 5.8μ (C=C), m/e 190 (m^+), ^{19}F NMR (CCl_4) -119 (COF), 6.1 (CF), 38.4 (CF_2), 41.4 (CF_2)]; V [ir (gas) 5.6μ (CO), 5.8μ (C=C), m/e 190 (m^+), ^{19}F NMR (CCl_4) 43.9 (CF_2), 48.6 (CF_2), 50.1 (CF), 65.1 (CF)]; VI [ir (gas) 5.4μ (C=CO), m/e 228 (m^+), ^{19}F NMR (CCl_4) -3.9 (CF_3), 52.2 (2 CF_2), 54.6 (CF)]; VII [ir (gas) 5.4μ (CO), m/e 275 (m^+ -19), ^{19}F NMR (CCl_4) -8.7 (CF_3), -3.2 (CF_3), 46.9 (CF), 52.0 (CF, 1/2 AB, J = 230 Hz), 52.1 (CF), 56.7 (CF, 1/2 AB)].

In glass, I is stable to heat (300°, 4 hr), light (Ultraviolet Products, Inc., 2.5 watt immersion lamp), radiation (^{60}Co source), and the action of Lewis acids (BF_3, 200°). I is recovered unchanged when heated at 200° in glass ampoules with stoichiometric amounts of potential dipolarophiles[6] (tetracyclone, CF_3NO, C_2F_4, propylene). I facilely rearranges to hexafluorocyclobutanoyl fluoride[7] by action of CsF in tetraglyme at 0°; in this reaction lower temperatures (-20°) favor dimerization to IX [ir (film) 5.3μ (CO), m/e 437 (m^+ -19) ^{19}F NMR (neat) -118.7 (COF), -3.5 (CF_2O), 45.2 (2 F of 2 CF_2, 1/2 AB, J = 230 Hz), 47.4 (2 F of 2 CF_2, 1/2 AB), 51.1 (4 CF_2), 112.1 (CF)]. It is notable that by comparing the reactivity of I with its open chain analog, perfluoroisobutylene oxide,[8] the incorporation of the strained 4-membered ring neither increases the degree nor the rate of oligomerization to any appreciable extent. Similarly, NaOMe/MeOH spontaneously converts I to its methoxy methyl ester X [b.p. 141-146, ir (film) 5.6μ (CO), m/e 252 (m^+), ^{19}F NMR (CCl_4) 44.8 (2 F of 2 CF_2, 1/2 AB, J = 223 Hz), 51.6 (2 F of 2 CF_2, 1/2 AB), 52.7 (CF_2), ^1H NMR (CCl_4) 4.15 ppm (OCH_3), 4.4 ppm (CO_2CH_3)]. Lastly, I is converted to the new perfluorotertiary alcohol XI, in 81% isolated yield by treatment with HF/SbF_5 at 100° for 18 hr. The properties of XI follow: [b.p. 64-65°, ir (film) 3.1μ (OH), ^{19}F NMR (neat) 54.7 (2 CF_2), 55.0 (F of CF_2, 1/2 AB, J = 231 Hz), 58.1 (F of CF_2, 1/2 AB), ^1H NMR (neat) 4 ppm (OH)].



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