Tetrahedron Letters No.38, pp. 3247-3248, 1969. Pergamon Press. Printed in Great Britain.

THE ADDITION OF CHLOROXYTRIFLUOROMETHANE AND CHLOROXYSULFUR PENTAFLUORIDE TO PERHALOOLEFINS

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(Received in USA 16 June 1969; received in UK for publication 14 July 1969)

Only recently have chloroxy* fluorocarbon compounds and chloroxysulfur pentafluoride been synthesized(1,2). We wish to report their facile addition to haloolefins to produce ethers, a reaction of significant synthetic utility.

In a typical procedure chloroxytrifluoromethane (4.5 mmol) was condensed with tetrafluoroethylene (5.2 mmol) at -196° and allowed to warm, a vigorous reaction occurred below room temperature. Fractionation of the products in a vacuum line gave 2-chloro-1,1,2,2-tetrafluoroethyl trifluoromethyl ether (2.2 mmol) in 50% yield.

$$CF_3OCl + CF_2{=}CF_2 \longrightarrow CF_3OCF_2CF_2Cl$$

No attempt has been made to optimize the reaction conditions. The ether was identified by its molecular weight (gas density) found: 222, calc. 220.5; boiling point of 10° (lit(3) 10.6°) and spectral data. The F^{19} n.m.r. spectrum (in ppm from $CFCl_3$) showed the CF_3 group as a triplet of triplets at 55.3, the CF_2 as a quartet of triplets at 88.7 and the CF_2Cl group as a triplet of quartets at 73.5 ($J_{2,3}$=9.23, $J_{1,2}$=1.90, $J_{1,3}$=0.58 Hz, the J subscripts refer to C atoms numbered from the ethyl moiety). The infrared spectrum (gas) displayed very strong bands in the CF region (1350 to 1100 cm^{-1}) and the following absorptions were observed (in cm^{-1}): 1350 s, 1280 vs, 1250 vs, 1190 vs, 1160 vs, 1120 s, 995 s, 895 s, 860 s, 826 s, 696 m, 665 m, 610 m.

Chloroxytrifluoromethane added similarly to chlorotrifluoroethylene to produce two isomers, 2,2-dichloro-1,1,2-trifluoroethane trifluoromethyl ether (I) and 1,2-dichloro-1,2,2-

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*The name chloroxy, rather than hypochlorite, is preferred by us in analogy to the fluoroxy compounds.

trifluoroethane trifluoromethyl ether (II). The isomers were not separated, the molecular weight of the mixture (gas density) was 238, calc. 237. The F^{19} n.m.r. of II has been reported previously$^{(4)}$ and could be subtracted from the joint spectrum, the ratio of the integrated intensities indicated a ratio of I to II in the range of 2.5 to 3; the n.m.r. spectrum of I was unambiguous: the CF_3 group was a triplet of doublets at 55.8, the CF_2 was a quartet of doublets at 87.2 and $CFCl_2$ was a triplet of quartets at 76.2; the splitting constants were $J_{2,3}$= 9.5, $J_{1,2}$=7.0 and $J_{1,3}$=0.7 Hz, the 0.7 Hz splitting was not resolved on the triplet of quartets but was easily measured on the triplet of doublets. The infrared spectrum of the mixture was also consistent with the proposed structures.

$$CF_3OCl + CF_2{=}CFCl \longrightarrow \underset{I}{CF_3OCF_2CFCl_2} + \underset{II}{CF_3OCFClCF_2Cl}$$

$$SF_5OCl + CF_2{=}CF_2 \longrightarrow SF_5OCF_2CF_2Cl$$

Similarly, SF_5OCl was added to C_2F_4 forming in 50% yield 2-chloro-1,1,2,2-tetrafluoroethyl sulfur pentafluoride ether, b.p. 41°, molecular weight: found: 279.2, calc. 278.5. The infrared spectrum (gas) was very similar to that reported for other SF_5 ethers$^{(5)}$, with absorptions in the CF region at 1200 and 1135 and in the SF_5 region at 820 and 605 cm^{-1}, other distinguishing absorptions were at 1320 m, 990 vs, 930-945 vs doublet, and 900 s. Evidence was found for the formation of dimers in the reaction of CF_3OCl with chlorotrifluoroethylene, and non volatile oils were formed in the reaction of CF_3OCl with 1,2-dichlorodifluoroethylene.

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