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Mercury-sensitized Photolysis of Fluoroolefins. I. 1,1-Dichloro-2,2-difluoroethylene

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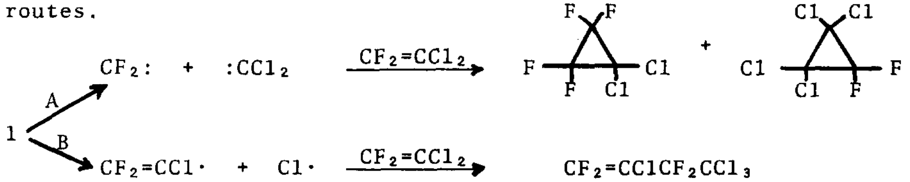
This communication illustrates the results of our first investigation into the photolysis reactions of fluoroolefins. Previous to this work results published concerning the ultraviolet irradiation of fluoroolefins have been fairly limited and the results obtained diversified. Irradiation of tetrafluoroethylene[2-4] yielded hexafluorocyclopropane, the reaction being considered to proceed <u>via</u> the intermediate formation of difluorocarbene. Similarly, the flash photolysis of chlorotrifluoroethylene[5] yielded difluorocarbene and chlorofluorocarbene. Park, et al.,[6,7] irradiated several iodofluoroethylenes and obtained in the case of iodotrifluoroethylene the dimer, 4,4-diiodohexafluoro-1-butene, $CF_2{=}CFCF_2CFI_2$.

We had expected that irradiation of 1,1-dichloro-2,2-difluoroethylene **I** would have produced chlorofluorocyclopropanes arising from cleavage of the unsaturated linkage representative of tetrafluoroethylene (Path A) or the linear dimer $CF_2{=}CClCF_2CCl_3$ formed from the splitting of the carbon-chlorine bond similar to iodotrifluoroethylene (Path B) or products arising from both these routes.



However, the vapor phase photolysis of **I** gave in 95% conversion and in yields up to 90% a mixture of 1,1,4,4-tetrafluorohexachlorobutane **II**, 1,1,3,3,6,6-hexafluorohexachloro-1-hexene **III** and 1,1,3,3,6,6,8,8-octafluorohexachloro-1,7-octadiene **IV** in the approximate ratio 1:2:1, respectively. A small amount, 10%, of higher boiling material was also obtained. We propose the following mechanism to account for the products obtained.

$Hg + h\nu\ (2537\text{Å}) \longrightarrow Hg^*$ 1

$Hg^* + CF_2{=}CCl_2 \longrightarrow Hg + CF_2{=}CCl_2^*$ 2

$CF_2{=}CCl_2^* \longrightarrow CF_2{=}CCl\cdot + Cl\cdot$ 3

$Cl\cdot + CF_2{=}CCl_2 \longrightarrow CF_2ClCCl_2\cdot$ 4

$CF_2{=}CCl\cdot + CF_2{=}CCl_2 \longrightarrow CF_2{=}CClCF_2CCl_2\cdot$ 5

$2\ CF_2ClCCl_2\cdot \longrightarrow CF_2ClCCl_2CCl_2CF_2Cl$ II 6

$CF_2ClCCl_2\cdot + CF_2{=}CClCF_2CCl_2\cdot \longrightarrow CF_2{=}CClCF_2CCl_2CCl_2CF_2Cl$ III 7

$2\ CF_2{=}CClCF_2CCl_2\cdot \longrightarrow CF_2{=}CClCF_2CCl_2CCl_2CF_2CCl{=}CF_2$ IV 8

It is suggested that the initial step is the formation of the chlorine and difluorochlorovinyl free radicals, and, although the existence of a fluorovinyl free radical has little precedence in the literature, Park[6,7] has also proposed that the first step in the ultraviolet irradiation of iodofluoroethylenes was the formation of a fluorovinyl free radical.

$$CF_2{=}CFI \xrightarrow{h\nu} CF_2{=}CF\cdot + I.$$

$$CF_2{=}CClI \xrightarrow{h\nu} CF_2{=}CCl\cdot + I\cdot$$

In steps 4 and 5 of the proposed mechanism the attack by the generated free radicals is at the CF_2 group of I, this being consistent with the results obtained by Park[7] who indicated that the attacking fluorovinyl radical attaches itself to the variously substituted vinyl carbon atoms in the following order:

$$CH_2 > CFH,\quad CHCl > CF_2 > CFI,\quad CCl_2$$

Furthermore, it is the expected route since $CF_2ClCCl_2\cdot$ is more stable than $CCl_3CF_2\cdot$ because of the increased stablizing effect of chlorine over fluorine. II was independently synthesized from 1,1-difluoro-2-iodotrichloroethane by coupling with zinc in acetic anhydride[8] or by ultraviolet irradiation.[9]

$$CF_2{=}CCl_2 + ICl \xrightarrow{CH_2Cl_2} CF_2ClCCl_2I \xrightarrow[\text{or } h\nu]{\substack{Zn/(CH_3CO)_2O\\ CH_2Cl_2}} \text{II}$$

The F^{19} nmr spectra[10] were consistent with those expected from the proposed structures. II exhibited a singlet at -23.17 ppm arising from the pair of equivalent difluoromethyl groups. The geminal fluorine atoms in III produced a triplet of doublets and a quartet centered at -8.09 and

-6.76 ppm, respectively, arising from coupling with the difluoromethylene group. The difluoromethylene group exhibited a broad triplet of quartets centered at +15.70 ppm. The terminal difluorochloromethyl group comprised of triplet of triplets centered at -23.23 ppm. The spectrum of IV was poorly resolved but peaks arising from the geminal fluorine atoms were centered at -8.09 and -6.84 ppm. The difluoronethylene group exhibited a complex pattern centered at +15.47 ppm.

Further photolysis reactions of fluoroolefins are planned. Exploratory reactions with other fluoroolefins including CF_2=CFBr and CFCl=CFCl indicate that this type of free radical process in not limited to CF_2=CCl_2.

The experimental work was carried out as follows.[11] A 1.5 liter quartz tube fitted with a 50 ml flask was placed inside a 8 module Rayonet Photochemical Chamber Reactor. The tube was evacuated and then filled to atmospheric pressure with CF_2=CCl_2.[12] As the reaction proceeded the non-volatile compounds condensed out and were collected in the flask and more olefin was then added. When sufficient material was collected, the product was distilled under reduced pressure and gave, after repurification (a) $CF_2ClCCl_2CCl_2CF_2Cl$, b.p. 66-67°/5 mm. Hg (lit. b.p. 143°/110 mm Hg), identified by its infrared spectrum by comparison with that of a authentic spectrum.[9] (b) CF_2=$CClCF_2CCl_2CCl_2CF_2Cl$, b.p. 67°/1 mm Hg. (Analysis[13] Calcd for: C, 18.00; F, 28.6; Cl, 53.4; m.w. 399. Found: C, 18.35; F, 28.28; Cl, 53.55; m.w. 400.) (c) CF_2=$CClCF_2CCl_2$-CCl_2CF_2CCl=CF_2, m.p. 68.5° (Analysis Calcd for: C, 20.82; F, 33.0; Cl, 46.2; m.w. 461. Found: C, 21.08; F, 32.92; Cl, 46.15; m.w. 450).

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10. The F^{19} nmr spectra were obtained using a Varian DP-60 Spectrometer operating at 56.4 MC. The chemical shifts were determined by placing an audio-frequency sidebond of the external reference CF_3COOH at the peak position being measured. Positive values of chemical shifts to high field are negative values of chemical shifts to low field. We express our thanks to W.S. Brey, Jr. and C. Watkins for running the spectra.

11. All boiling points are uncorrected:

12. Obtained form Peninsular ChemResearch, Inc., and used without further purification.

13. Carried out by Galbriath Laboratories, Inc., Knoxville, Tennessee.