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DIFLUOROCARBENE FROM DIFLUOROCHLOROACETONITRILE

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The Diels-Alder reaction of perfluoroalkylnitriles with butadiene in the gas phase at one atmosphere pressure leads to the production of 2-perfluoroalkylpyridines.(1) When perfluoroacetonitrile is the dieneophile, the conversion to the substituted pyridine is 100%; with difluorochloroacetonitrile, the conversion to 2-difluorochloromethylpyridine(2) is only 4%. Due to a much lower C-Cl bond energy in CF_2ClCN relative to the C-F or C-C bond strengths in CF_3CN, the reaction mechanism may differ with difluorochloroacetonitrile as dienophile.

The present communication reports the results of a series of experiments with CF_2ClCN and cyclohexene in the gas phase using the same temperature range (370° - 420°C) as in preceding Diels-Alder cyclization studies.(1,2) The possible occurrence of difluorocarbene (as a reactive intermediate) could be substantiated by the formation of difluoronorcarane and tetrafluoroethylene.

Experimental

Difluorochloroacetonitrile (b.p. -17°C, Columbia Organic Chemical Co.) and cyclohexene (b.p. 81°C, Eastman Organic Chemicals) were vacuum degassed at liquid nitrogen temperatures (-195°C) three times prior to use. The purity of all samples was checked by chromatographic analysis.

A series of experiments to explore the thermal stability of CF_2ClCN by itself established that C_2F_4 and CNCl are formed in the temperature range of the Diels-Alder studies (i.e., 400°C). The reaction of CF_2ClCN and cyclohexene was explored using the continuous flow assembly of this laboratory described elsewhere.(1)

Reactant mole ratios and contact times were varied in these experiments. Additional studies were undertaken in our 20 liter static reactor, also with varying reactant mole ratios and reaction times, and in the same temperature range, 370 - 420°C.

Separation of the liquid products from these experiments was possible with an Aerograph A-700 preparative chromatograph. Benzonitrile, 1 and 3-cyanocyclohexenes, α-chloro, α, α-difluorotoluene, o-chloro-α, α-difluorotoluene, and benzene were separated and confirmed. The ratios of these varied in the reaction product mixture, for each change of temperature and/or reaction time. For the recovery of the difluoronorcarane a Multiple Internal Reflectance infrared spectroscopy cell was used for collection. Difluoronorcarane was thus isolated in small amounts (1-4%) from each product mixture. Hydrogen chloride, difluoroacetonitrile, chlorodifluoromethane, tetrafluoroethylene, and cyanogen chloride were the salient compounds separated and confirmed from the gaseous fraction of the reaction product mixtures.

Identification of the liquid compounds was through Infrared, Ultraviolet, and NMR Spectroscopy, and also the boiling points and indexes of refraction for the liquid compounds. The results of microelemental analyses for the liquid compounds were within the accepted limits of error.

The infrared spectrum of the difluoronorcarane was found to be in exact accord with the results of Birchall, Cross, and Hazeldine.(3) The salient absorption bands were: 2915, 1488, 1449, 1333, 1274, 1205, 1120, 1099, 1026, 995, 952, 921, 883, 847, 800, 766, and 676 cm^{-1}. A notable feature was the absence of the absorption bands characteristic of the olefinic group. The boiling point was found to be 123°C (cf. lit., 121 - 123°C.(3)) Microelemental analyses were not gained owing to an insufficient amount of this compound.

The gaseous products were identified by chromatographic elution times and infrared spectroscopy.

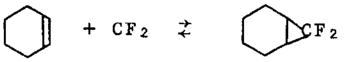
Discussion

In the thermal decomposition of difluorochloromethane, Gozzo and Patrick(4) noted that the major features of the reaction are the formation of C_2F_4, HCl and CF_2HCF_2Cl; a reversible dissociation into CF_2 and HCl was advanced as the major mode in the decomposition of CF_2HCl. While our studies were designed for product characterization so that the data do not lend themselves to a kinetic analyses, the formation of CNCl and C_2F_4 in the thermal decomposition of difluorochloroacetonitrile suggest an analogous reaction scheme:

$$CF_2ClCN \rightleftarrows CF_2 + CNCl \qquad (1)$$

$$2CF_2 \rightarrow CF_2 = CF_2 \qquad (2)$$

By contrast, CF_3CN shows exceptional thermal stability under comparable conditions(1,2); after 36 hrs. at 500°C, more than 98% is recovered unchanged. The low yields of the Diels-Alder product in the experiments at 400°C with CF_2ClCN as dienophile(1) may thus be attributed to the very significant thermal instability of this compound. The separation and isolation of difluoronorcarane in our experiments with cyclohexene and CF_2ClCN as reactants is additional support for the above scheme as the primary mode of decomposition. A CF_2 insertion reaction:



(3)

would account for the formation of difluoronorcarane from cyclohexene. The formation of difluoronorcarane using cyclohexene as the CF_2 ''getter'' has previously been reported by Birchall, Cross, and Hazeldine.(3)

Further qualitative support for the above initiation step in the decomposition of CF_2ClCN is seen in the identification of benzonitrile, and the isomeric cyanocyclohexenes in the reaction product mixture; the addition of CNCl to cyclohexene, with an HCl elimination, would account, in large part, for the formation of these cyclic nitriles. Chlorodifluoromethane and difluoroacetonitrile are understood as CF_2 insertions in HCl and HCN, respectively, as in the work of Gozzo and Patrick.(5) Similarly the formation of α-chloro-α,α-difluorotoluene and o-chloro-α,α-difluorotoluene are understood as due to further reactions of the difluoronorcarane with HCl, in which aromatization is favored at these moderately high temperatures. The relatively low yields of difluoronorcarane are undoubtedly due to the secondary processes competing for CF_2, and the further reactions leading to halogenated toluenes.

The novel observation in this work is the compartively mild conditions (400°C), under which CF_2ClCN decomposes thermally; this may qualify it as a compound for more detailed attention relative to difluorocarbene chemistry. Usually the reaction conditions for gas phase processes involving difluorocarbene chemistry are rather more severe(4-7) than those reported in this study.

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