

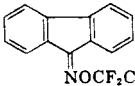
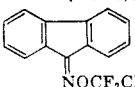
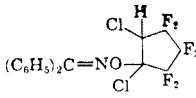
Communications TO THE EDITOR

Fluorinated *O*-Alkyl Oximes. Solid Derivatives of Fluorinated Olefins

Sir:

We wish to report the reaction between oximes and fluorinated olefins giving addition compounds, *O*-alkyl oximes, which are either solids or liquids depending on the oxime used in the reaction. The reaction is brought about in pyridine, or pyridine and benzene, in the presence of sodium hydroxide or potassium hydroxide and at 5° to 25° depending on the olefin. Most fluorinated ethylenes and other similarly substituted olefins undergo this reaction. Yields are usually high, ranging from 60 to 95%, most often closer to the latter value. The solids are easily recrystallized from ethanol. High molecular weight oximes such as benzophenone oxime and fluorenone oxime always gave solid products in the reactions studied so far; lower molecular weight oximes such as acetone oxime give liquid products.

Examples of these oximino ethers are the following: (satisfactory analytical data have been obtained on all of the compounds reported).

Compounds	M.P. °
$(C_6H_5)_2C=NOCF_2CFCIH$	33.5
	56.0
$(CH_3)_2C=NOCF_2CFCIH$	b.p. 75.5/50
$(C_6H_5)_2C=NOCF_2CCl_2H$	63
$(CH_3)_2C=NOCF_2CCl_2H$	b.p. 66/18
$(C_6H_5)_2C=NOCF_2CFHCF_2$	39.5
	52
$(C_6H_5)_2C=NOCF_2CBF_2H$	72.5-73
$(C_6H_5)_2C=NOCF_2Cl_2H$	118
$(C_6H_5)_2C=NOCF_2CH_2Cl$	66.5
$(C_6H_5)_2C=NOCF_2CH_2Br$	71
	73

Under the same conditions 1,1-difluoroethylene, 1,2-dichloro-1,2-difluoroethylene, bromoethylene, and tetrachloroethylene did not react.

An attempt to obtain hydrolytic scission at the double bond of these ethers by means of dilute hydrochloric acid resulted in an attack at a carbon-bearing fluorine, giving off hydrogen fluoride with a subsequent attack on the glass apparatus.

This hydrolysis is believed to be analogous to the hydrolysis of fluorinated ethers having the structure $-CH_2-O-CF_2-$ which hydrolyze to esters $-CH_2-O-C-$ when treated with strong acid.



More work in this respect is in progress and will be reported in detail in the near future.¹

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Stereochemistry of the Claisen Rearrangement¹

Sir:

Aside from the interesting interpretive arguments of Hart² based on the experimental findings of Alexander and Klüber,³ the stereochemistry of the Claisen rearrangement has not received any attention. Since the retention of configuration suggested by Hart is not in accord with the results of work on the closely related S_Ni' reaction,⁴ we should like to report that we cannot confirm the suggestions made by Hart.

Assuming that the point of bond severance and the point of attachment of the migratory allyl group must lie on the same side of the benzene ring it may be seen that inversion of configuration requires the formation of a *trans* double bond between the α and β carbon atoms of Fig. 1. This correspondence between the stereochemistry at the double bond and the asymmetric atoms holds for the 32 possible transition states (all combinations of initial *cis* or *trans* and final *cis* or *trans* double bonds, boat or chair conformation and R. or S configuration) providing only that the initial assumption is valid. The relation between double bond geometry and configurational changes for all cases is given in

(1) This research was supported in part by the National Science Foundation as grant NSF-G7432. Paper number four on the Claisen Rearrangement.

(2) H. Hart, *J. Am. Chem. Soc.*, **76**, 4033 (1954).

(3) E. R. Alexander and R. W. Klüber, *J. Am. Chem. Soc.*, **73**, 4304 (1951).

(4) H. L. Goering and R. W. Greiner, *J. Am. Chem. Soc.*, **79**, 3464 (1957); H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958). F. Caserio, G. E. Dennis, R. H. deWolfe, and W. G. Young, *J. Am. Chem. Soc.*, **77**, 4182 (1955).