

Contribution No. 379 from the
Central Research Laboratories
Minnesota Mining and Manufacturing Company

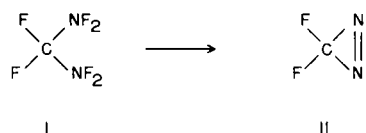
Synthesis of Difluorodiazirine (I)

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Sir:

The dicyclopentadienyliron and dicumenechromium induced reductive-defluorination of fluorocarbon difluoroamines and secondary fluoroamines to the corresponding fluoroimines or azomethines has been the subject of a previous publication (2). The present paper describes the reductive-defluorination reaction of bis(difluoroamino)difluoromethane [the preparation of bis(difluoroamino)difluoromethane is described in reference (3)] in which difluorodiazirine is the major product. Previous papers from these laboratories have described the use of difluorodiazirine as a difluorocarbene precursor (4).

It has been observed that bis(difluoroamino)difluoromethane (I) undergoes a facile oxidation-reduction reaction with dicyclopentadienyliron and dicumenechromium. In this reaction, elimination of fluoride ions, and cyclization leads to the formation of difluorodiazirine in high yield. When either dicyclopentadienyliron or dicumenechromium in halocarbon solvent (xylene hexafluoride, methylene chloride, chloroform, etc.) is used as the reducing system, the reaction leading to II is essentially free of by-products.

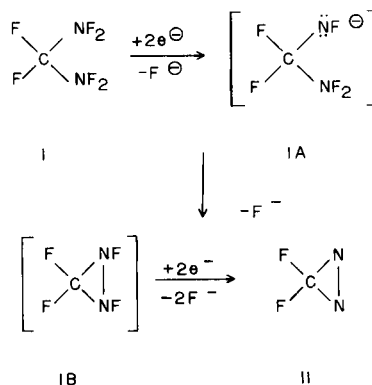


In a typical experiment employing dicyclopentadienyliron as the reducing agent, 4.84 g. (26.0 millimoles) of sublimed dicyclopentadienyliron was weighed into a 20-ml. glass ampoule, followed by the addition of 6 ml. of xylene hexafluoride solvent. The sample was degassed at -196° and 1.62 g. (10.4 millimoles) of bis(difluoroamino)difluoromethane (3) was condensed into the ampoule by appropriate vacuum transfer techniques. The sealed ampoule was periodically shaken for four days while at room temperature. Preliminary separation of the products from the solvent was accomplished by fractional distillation-condensation techniques using -23° , -78° and -196° receivers. A vapor phase chromatographic analysis of the -196° receiver indicated the following product composition: difluorodiazirine (CF_2N_2) (78%), unreacted bis(difluoroamino)difluoromethane ($\text{CF}_2(\text{NF}_2)_2$) (20%) and unknowns (2%). Separation by vapor phase chromatography on a unit employing a 1/2" o.d. tube, six meters long and packed with 33% FC-45 (Minnesota Mining and Manu-

facturing Company) on Celite afforded 0.51 g. (65%) of pure difluorodiazirine having the properties reported previously (4a).

Anal. Calcd. for CF_2N_2 : C, 15.4; F, 48.7; N, 35.9; mol. wt., 78. Found: C, 15.5; F, 48.5; N, 35.8; mol. wt., 77.

The formation of difluorodiazirine from bis(difluoroamino)difluoromethane can be rationalized as involving a primary step similar to that previously postulated in the reductive-defluorination reaction (2); the two-electron reduction of the nitrogen-fluorine bond leading to the nitrogen-anion (IA). Cyclization by direct displacement of fluoride leads presumably to the transient existence of the perfluorodiaziridine (IB) which undergoes further reductive-defluorination.



Acknowledgment.

The author is indebted to Mr. D. P. Babb for valuable technical assistance, Dr. J. J. McBrady and Mr. R. A. Meiklejohn for infrared and nuclear magnetic resonance interpretation and Mr. P. B. Olson and Mr. B. W. Nippoldt for analytical determinations.

This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688, and was monitored by the Bureau of Naval Weapons.

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Received May 5, 1966

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