Journal of Fluorine Chemistry, 17 (1981) 447–451

Received: August 20, 1980

SELECTIVE REDUCTION OF 1-CHLORO-2-IODOPERFLUOROCYCLOALKENES WITH SODIUM TRIMETHOXYBOROHYDRIDE

SARASWATHI NATARAJAN and ROBERT L. SOULEN

Chemistry Department, Southwestern University, Georgetown, Texas 78626 (U.S.A.)

SUMMARY

In contrast to other chemical reducing agents, it has been found that sodium trimethoxyborohydride will selectively reduce 1-chloro-2-iodoperfluorocycloalkenes to give good yields of 1-hydro-2-chloroperfluorocycloalkenes. The selective displacement of iodine by hydrogen is discussed in terms of HSAB principles.

INTRODUCTION

Several striking anomalies have been reported in the literature when metal hydrides are used as reducing agents with perfluoroolefins or haloperfluoroolefins [1]. The stronger reducing agents, such as lithium aluminum hydride frequently cause olefin rearrangement via an Sn-2' loss of allylic fluorine in addition to the expected vinylic halogen displacement by hydrogen [2,3]. In a careful study of the use of lithium aluminum hydride and sodium borohydride with various substituted perfluorocyclobutenes and perfluorocyclopentenes Burton and co-workers concluded that the Park carbanion stabilization mechanism [4] could not satisfactorily explain the selectivity of halogen displacement from the vinylic positions [5,6,7].

In the review paper by Burton [1] an unpublished report is given on the reduction of 1-chloro-2-bromo and 1-chloro-2-iodoperfluorocyclobutenes and perfluorocyclopentenes with lithium aluminum hydride and sodium borohydride. The results of this study disclosed that one could expect a mixture of products in which chlorine and bromine or iodine was displaced from the vinylic position. An exception to this observation was the reduction of

1-chloro-2-iodoperfluorocycloalkene with lithium aluminum hydride which gave the corresponding 1-hydro-2-chloroperfluorocycloalkene as the sole product. This result contradicts an earlier conclusion that product distributions and variations were due to the larger nucleophilic ($AlH_4^- > BH_4^-$) attacking selectively at the least hindered vinylic position [8]. It is apparent that in the case of reducing agents containing more than one M-H bond that the mechanism of vinylic halogen displacement is not straightforward and may indeed change during the course of the reaction as MH_4^- is converted to MX_3H^-. The possibility of initial coordination of the vinylic halogen with the reducing agent or the attack of hydride on halogen, rather than on the vinyl carbon cannot be overlooked.

RESULTS AND DISCUSSION

In this paper we wish to report on a brief study of the reaction of sodium trimethoxyborohydride with a series of 1-chloro-2-iodoperfluorocycloalkenes under roughly comparable conditions. It is our position that under Hard Soft Acid Base principles (HSAB theory) the hydride ion (soft base) should attack preferentially at the Soft carbon center to displace iodine rather than chlorine. In contrast to previous studies which have employed reducing agents of the type MH_4^- we have selected a reducing agent which has only one M-H bond. In this way, the Hard-Soft character of the reducing agent is constant throughout the chemical reaction.

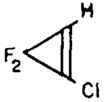
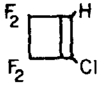
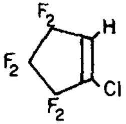
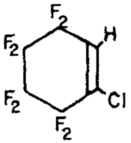
Except for the cyclopropene case, all reactions were carried out by adding a suspension of the reducing agent in THF to the chloroiodoalkene at 0°C then stirring for three hours at room temperature. Due to the low boiling point of the reduced cyclopropene this reaction was maintained at 0°C for the same time period and throughout the work-up procedure.

In all cases, only one reduced product was found in the crude reaction mixtures by gas chromatographic analysis. Some of the physical properties of 1-hydro-2-chloroperfluorocycloalkenes are given in the following table. For the most part, this information has not been available in previous reports. The data which we found compares closely with reported literature values [5, 9].

Our n.m.r. data for 1-hydro-2-chloro-3,3-difluorocyclopropene compares favorably with the spectral values reported for 3,3-difluorocyclopropene. Craig has found for the latter compound a fluorine resonance triplet at -105 ppm ($CFCl_3$ standard) and a proton resonance triplet at 7.6 ppm (TMS standard) [10].

TABLE 1

Properties of 1-Hydro-2-chloroperfluorocycloalkenes *

Product		Yield [a]	^{1}H,ppm	^{19}F,ppm [f]	ν = C-H, cm^{-1}	ν C=C, cm^{-1}
	b	2.57	6.2 t J=2 Hz	-102.8 d J=2 Hz	3150	1770
	c	0.67	6.75 m	-112.8 m -117.2 m	3100	1595
	d	0.56	6.57 m	-108.8 m -115.8 m -130.9 m	3090	1635
	e	0.26	6.45 m	-108.1 m -113.6 m -134.1 m -135.3 m	3060	1660

a This is a ratio of the product peak area/starting peak area as determined by gas-chromatography of the crude reaction mixture.
b New compound.
c Lit. values: ^{1}H, 6.77 ppm, ν C=C, 1596 cm^{-1} [5,9]
d Lit. values: ^{1}H, 6.50 ppm, ν C=C, 1640 cm^{-1} [5,9]
e Lit. values: ν C=C, 1660 cm [9].
f Fluorine n.m.r. values were determined using $CFCl_3$ as an internal standard.

* Proton n.m.r. spectra were obtained on a Perkin Elmer R-12A using TMS as an internal standard.

Fluorine n.m.r. spectra were obtained on a Varian 56/60 using $CFCl_3$ as an internal standard.

Infrared spectra were obtained on a Beckman IR-8 using sealed NACl cells.

The yield values given below for the reduced compounds are a rough estimate of the reactivity order of the haloperfluorocycloalkenes. When one considers that the cyclopropene reaction was carried out approximately 30 degrees lower than the other cycloalkenes, the extreme reactivity of the 3-membered ring case can be appreciated.

EXPERIMENTAL

General procedure: A suspension of sodium trimethoxyborohydride in THF (1 g/20 ml) was slowly added to a stirred solution of the 1-chloro-2-iodoperfluorocycloalkene in THF (1 g/1 ml) at 0°C. After all the reducing agent was added (ca. 1/2 hour) the solution was stirred at room temperature for 3 hours. [The cyclopropene reaction was maintained at 0°C for 3 hours before work-up]. The reaction mixture was then poured into ice water and the organic layer washed twice with ice water saturated with salt then dried over anhydrous calcium chloride. The crude products were analyzed by gas chromatograph using a 25' column packed with SF-1265 on chromosorb P, 80-100 mesh. Pure samples of the reduced products were prepared using the same column.

ACKNOWLEDGEMENTS

We wish to thank the Robert A. Welch Foundation for their support of this research. The assistance of Dr. Ben Shoulders in the F-19 and H-1 spectra is gratefully acknowledged.

The authors acknowledge Professor D.J. Burton for his helpful discussions on the mechanism of vinylic halogen displacement by hydrogen.

REFERENCES

1 F.J. Mettile and D.J. Burton, Fluorine Chem. Revs., P. Tarrant (editor), Vol. 1, Marcel Dekker Inc., New York, 1967, pp. 315-358.

2 D.E.M. Evans, W.J. Feast, R. Stephens and J.C. Tatlow, J.Chem. Soc. (1963) 4828.

3 W.J. Feast, D.R.A. Perry and R. Stephens, Tetrahedron, 22 (1966) 433.

4 J.D. Park, R.J. McMurtry and J.H. Adams, Fluorine Chem. Revs., 2 (1969) 55.

5 D.J. Burton and R.L. Johnson, J. Amer. Chem. Soc., 86 (1964) 5361.

6 R.L. Johnson and D.J. Burton, Tetrahedron Letters, (1965) 4079.

7 D.J. Burton and F.J. Mettille, Inorg. Nucl. Chem. Letters, 4 (1968) 9.

8 D.J. Burton and R.L. Johnson, Tetrahedron Letters, (1966) 2681.

9 J.D. Park, C.D. Bertino and B.T. Nakata, J. Org. Chem., 34 (1969) 1490.

10 N.C. Craig, R.A. MacPhaill and D.A. Spiegel, J. Phys. Chem., 82 (1978) 1056.