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THE EFFECT OF RING SIZE AND NUCLEOPHILE SIZE IN SOME SUBSTITUTION AND REARRANGEMENT REACTIONS OF ALICYCLIC POLYFLUORINATED OLEFINS

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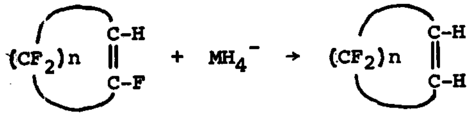
While the substitution reaction of polyfluorinated olefins with nucleophiles is probably the best known reaction in organic fluorine chemistry (1), further reaction of the substituted olefins with nucleophiles has been investigated to a limited extent. In general, alicyclic polyfluorinated olefins have been utilized for additional work. Two general types of behavior have been observed, (a) substitution of the second halogen atom by the nucleophile, or (b) rearrangement with displacement of an allylic halogen.

Using lithium aluminum hydride as the nucleophilic agent, Stephens and co-workers (2) have recently reported the substitution and rearrangement reactions of some polyfluorinated cyclopentenes and cyclohexenes. These authors obtained both substitution and rearrangement reactions with the predominant product being the rearrangement compound.

This recent report by Stephens has prompted us to report similar work which has been carried out in our laboratory using metal hydrides as nucleophiles. We have investigated cyclobutene and cyclopentene systems employing both lithium aluminum hydride in ether at 0°C. and sodium borohydride in diglyme at 0°C. as nucleophilic agents. The results of some of our work are summarized in Table I.

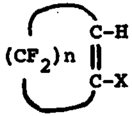
When the vinylic halogen was fluorine, only vinylic displacement was observed under the conditions of our reactions. However, when the vinylic halogen was



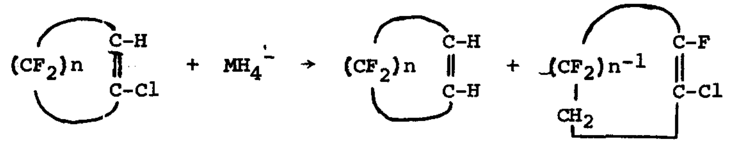
n = 2,3 M = B,Al

chlorine, both substitution and rearrangement were observed. The ratio of II/I was found to be dependent on the ring size of the olefin and the size of the nucleophile.

TABLE I

 mMoles	n	MX_4^- mMoles	M	X	I mMoles	II mMoles	$\frac{II}{I}$
25	3	12.5	Al	F	22	--	---
25	3	12.5	B	F	17	--	---
25	2	12.5	Al	F	23	--	---
25	2	12.5	B	F	16	--	---
50	3	25.0	Al	Cl	4	44	11
50	3	25.0	B	Cl	4	20	5[a]
25	2	12.5	Al	Cl	6	10	1.7[b]
25	2	25.0	B	Cl	15	3	0.2[c]

a. 21 mMoles of starting olefin recovered. b. 4 mMoles of unidentified product found.
c. 7 mMoles of starting olefin recovered.



n = 2,3 M = B,Al I II

Stephens and co-workers have rationalized the products obtained from their lithium aluminum hydride reductions on the basis of the most stable carbanion hypothesis recently proposed by Park and co-workers (3). This type of argument adequately explains the cyclopentene system but does not explain the reductions of the cyclobutene system. In fact, the substitution product (I) becomes the predominant product in the reduction of 1-hydro-2-chlorotetrafluorocyclobutene with sodium borohydride, contrary to what would have been expected on the basis of carbanion stabilization. The ratios of II/I also showed a striking variation depending upon whether borohydride or aluminum hydride was employed as the nucleophile. Although a solvent effect cannot be definitely ruled out, the larger amount of the rearrangement product (II) obtained in both ring systems with aluminum hydride suggests this is simply a steric effect with the larger nucleophile exhibiting greater discrimination for attack at the least hindered positions. The larger proportion of the substitution product (I) in the cyclobutene system may reflect a greater ease of vinylic displacement in this ring system in contrast to the five-membered system. However, since Park (4) has reported only rearrangement in this system with ethoxide as the nucleophile, the larger amounts of substitution in reactions with metal hydrides perhaps suggest that the metal atoms (B, Al) may be assisting the displacement of the vinylic halogen. Additional work is in progress with other systems to determine this possibility.

In summary, the carbanion stabilization hypothesis does not adequately explain the reactions of metal hydrides with alicyclic polyfluorinated olefins. This may be due to the nature of the nucleophile itself rather than to a limitation of this hypothesis. Consequently some caution should be observed in rationalizing the results of these metal hydride reactions on this basis.

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REFERENCES

1. For an excellent summary of these reactions, see Chapter 3 by R. D. Chamber and R. H. Mobbs in

Advances In Fluorine Chemistry, IV, Butterworth, 1965.

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

3. J. D. Park, J. R. Dick, and J. H. Adams, J. Org. Chem. 30, 400 (1965).

4. J. D. Park, L. H. Wilson, and J. R. Lacher, J. Org. Chem. 28, 1008 (1963).