

SUBSTITUTION AND REARRANGEMENT REACTIONS
RESULTING FROM THE REACTION OF GRIGNARD REAGENTS
WITH SOME ALICYCLIC POLYFLUORINATED OLEFINS
THE EFFECT OF RING SIZE ON PRODUCT DISTRIBUTION.

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(Received 5 October 1966)

Although the reaction of substituted fluoroolefins with nucleophiles, such as ethoxide, has received considerable attention in recent years (1), little is known concerning the subsequent attack by excess Grignard reagent on the initially formed substitution product in these systems.

It has been reported (2) that products arising from either substitution of the second halogen atom or rearrangement with accompanying displacement of an allylic halogen can occur when the olefin is treated with an excess of the nucleophile, the course of the reaction being determined by the nature of the vinylic halogen.

Several recent reports (3,4) of work carried out utilizing metal hydrides as nucleophiles indicate that products resulting from both substitution and rearrangement reactions are obtained from the same reaction. The rearranged product predominated in the cyclopentenyl- and cyclohexenyl- systems

while substitution products predominate with polyfluorinated cyclobutenes.

When the vinylic halogen was fluorine, only vinylic displacement was observed under the reaction conditions employed. Both substitution and rearrangement were observed when the vinylic halogen was chlorine; the ratio of rearranged to substituted products was also found to be dependent on the nature of the metal atom.

We would like to report apparently similar results obtained in this laboratory from the reaction of polyfluorocycloalkenes with Grignard reagents. As with metal hydride reductions, only vinylic substitution (I) occurred when the vinylic halogen was fluorine (5). When the vinylic halogen was chlorine, products resulting from both substitution of the vinylic halogen (I) and rearrangement (II) were isolated. The dependence on ring size of the I/II ratio is similar to that reported for metal hydride attack (4).

In order to evaluate the effect of the steric bulk of the attacking group on the ratio (I/II) of the products, reactions were run using both ethylmagnesium bromide and isopropylmagnesium bromide in tetrahydrofuran.

Satisfactory results were not obtained in the case of isopropylmagnesium bromide owing to the reluctance of the monoalkyl compounds to undergo further reaction and to other competing reactions (7). Likewise, an attempt to evaluate a possible solvent effect was inconclusive as only low

conversion to dialkyl compounds was effected when diethyl ether was employed as the solvent.

TABLE I

Product Distribution Resulting from Grignard Reagent Attack on Alicyclic Polyfluorinated Olefins

| $ \begin{array}{c} \text{C-X} \\ \diagup \quad \diagdown \\ (\text{CF}_2)_n \\ \diagdown \quad \diagup \\ \text{C-X} \end{array} \xrightarrow{\text{RMgBr}} \begin{array}{c} \text{C-R} \\ \diagup \quad \diagdown \\ (\text{CF}_2)_n \\ \diagdown \quad \diagup \\ \text{C-R} \end{array} + \begin{array}{c} (\text{CF}_2)_{n-1} \text{-CR}_2 \\ \quad \\ \text{CF} = \text{C-X} \end{array} $ | | | | | | | |
|---|----|-----|-------------------|-----------------|------|----------|-----|
| | | | | (I) | (II) | | |
| n | X | R | solvent | (I) | (II) | (I)/(II) | |
| 2 | F | -Et | Et ₂ O | 100 | | | (5) |
| 3 | F | -Et | THF | 100 | | | |
| 2 | Cl | -Et | Et ₂ O | a | | | |
| 2 | Cl | -Et | THF | 82 ^b | 18 | 4.6 | (6) |
| 3 | Cl | -Et | THF | 60 ^b | 40 | 1.5 | |

a) Less than 1% of the reaction products, under the reaction conditions employed, were the desired dialkyl compounds.

b) Small amounts of the 1-ethyl-2-chloro compounds were isolated in addition to the dialkyl compounds.

It is uncertain at this time whether or not these reactions constitute a failure of the carbanion stabilization hypothesis. Burton (4) has cited the large bulk of the attacking nucleophile and the central metal atom as possible

sources of these deviations. It is possible that these reagents represent a "limiting case" (8) where steric interactions have increased to a point where they override the electronic directive effects. It should also be noted that the solvating ability of the solvents employed in these reactions differ markedly from those employed in alkoxide attacks e.g. alcohols. Thus, formation of a discrete carbanion would be favored in the case of alkoxide attack in alcohol, relative to attack by a nucleophile in a solvent such as diethyl ether or diglyme. Further work is in progress in connection with these problems.

Acknowledgements: This work was supported in part by the U. S. Army Natick Laboratories, Natick, Mass. and by the Minnesota Mining and Manufacturing Co., St. Paul, Minn. and for which grateful acknowledgement is made.

References

- 1 R. D. Chambers and R. H. Mobbs in Advances in Fluorine Chemistry, IV, Butterworth, 1965, p. 50.
- 2 J. D. Park, J. R. Lacher and J. R. Dick, J. Org. Chem., 31, 1116, (1966).
- 3 W. J. Feast, D. R. A. Perry, and R. Stephens, Tetrahedron, 22, 433, (1966).
- 4 D. J. Burton and R. L. Johnson, Tet. Letters, 2681, (1966).
- 5 J. D. Park and R. Fontanelli, J. Org. Chem., 28, 258, (1963).
- 6 R. Sullivan, J. R. Lacher, and J. D. Park, J. Org. Chem., 29, 3664, (1964).
- 7 To be reported in a subsequent communication.
- 8 J. D. Park, G. Gropelli, and J. H. Adams, Tet. Letters, in press.