

THE REACTION OF ETHOXIDE WITH
1, 2, 3, 3-TETRAHALOCYCLOBUTENES:
ELECTRONIC CONTROL OF NUCLEOPHILIC ATTACK

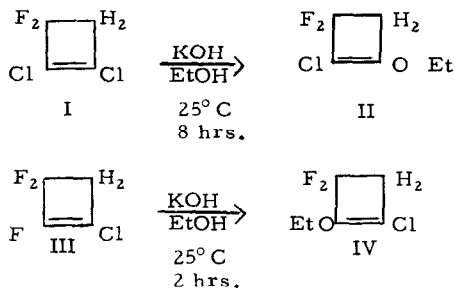
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Recent interest^{2,3,4} over the question of whether the attack of nucleophiles on polyfluorinated olefins is sterically or electronically controlled has prompted us to report on two pertinent reactions.



Both reactions, carried out according to the method of Park, *et al.*⁵ and followed by GLC, were specific and quantitative. After the workup of II, a trace of another compound was detected having a different GLC retention time from I, II, or IV, and is believed to be 1-ethoxy-2-chloro-3-keto-cyclobutene as the result of hydrolysis of II. The isomeric products II and IV

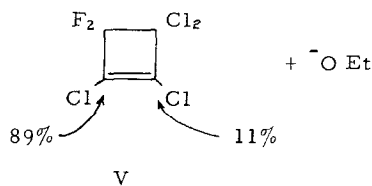
show differences in physical properties shown in the table below. Satisfactory analyses were obtained for both compounds.

Table I
Physical Properties of Compounds II and IV

	II	IV
b. p.	~130° C/629 mm dec. at ~112° C	125° C/629 mm
n_D^{20}	1.4192	1.4125
d_4^{25}	1.239	1.213
$\nu_c = c$	1680 cm^{-1}	1680 cm^{-1}
<u>NMR</u>		
Ring Methylene Triplet	2.91 ppm $J_{\text{HF}} =$ 1.8 cps	2.77 ppm $J_{\text{HF}} = 3.0$ cps
Ethoxy Methylene Quartet	4.33 ppm	4.20 ppm
Ethoxy Methyl Triplet	1.35 ppm	1.30 ppm

1, 2-Dichloro-3, 3-difluorocyclobutene (I) was obtained from a Zn/EtOH dechlorination of 1, 1, 2, 2-tetrachloro-3, 3-difluorocyclobutane.² 1-Chloro-2, 3, 3-trifluorocyclobutene (III) was prepared according to the method of Raasch, Miegel and Castle.⁶

In the previously reported reactions of 1, 2-dichlorotetrahalocyclobutenes⁵ with ethoxide ion, a mixture of products resulted from ethoxide attack at both ends of the double bond. Predominant attack at one end took place depending on the allylic or β -substituents. 1, 2, 3, 3-Tetrachloro-4, 4-difluorocyclobutene gave the following distribution.

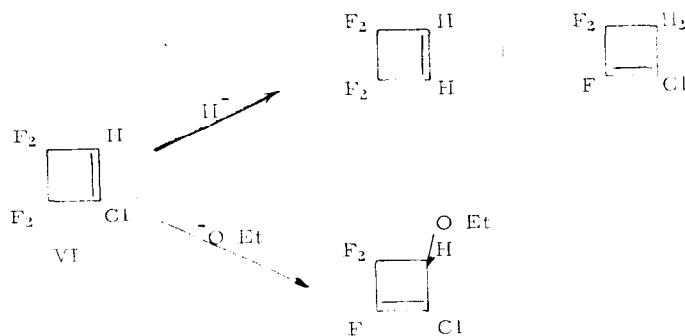


The influence of the allylic dichloro group in directing the etho-

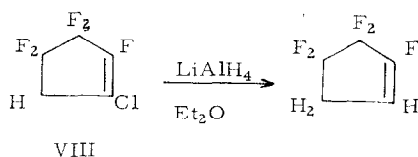
xide attack has been proposed as electronic^{2,5} and suggested as steric.² If the major directive influence were steric in nature then one would surely expect at least a distribution of products from the reaction of I with ethoxide ion. The fact that only II is formed is good evidence for the importance of the stabilizing effect of the fluorines β to the intermediate carbanion. Also, the reaction of I with ethoxide proceeds slowly at 25°C. and not at all at 0°C. The reactions of perhalocyclobutenes with ethoxide at 0°C. go rapidly to completion further indicating the importance of electron withdrawing effects of the β -halogens.

The reaction of Burton and Johnson of 1-chloro-3,3,4,4-tetrafluorocyclobutene (VI) with lithium aluminum hydride and sodium borohydride results in hydride substitution at both vinylic positions in ratios interpreted as being due to differences in steric bulkiness of the two metal hydride nucleophiles.³

Burton and Johnson also stated that there might be mechanistic differences in the nucleophilic attack of metal hydrides and alkoxides since Park, *et al.*,⁸ found that ethoxides attacked VI at one end of the double bond only.



This point finds support in the comparison of the reaction of III and ethoxide ion with that of 1-chloro-5H,5H-pentafluorocyclobutene (VII) and LiAlH₄ reported by Feast, Gerrard, and Stephens.⁷



They explained the specific attack at the chloro carbon as due to the allylic fluorines stabilizing the intermediate carbanion. The reaction of the analogous cyclobutene III with ethoxide ion yields just the opposite result: a specific attack at the vinylic fluoro carbon.

We reiterate our proposal^{2,5} that the alkoxide attack from a primary alcohol on halocyclobutenes is directed by the carbanion stabilization of the α -substituents (a secondary alkoxide is apparently the limiting case since isopropoxide did not react at all in the system of Dreier, Duncan and Mill⁴). When the α -substituents are the same or nearly the same at both ends of the double bond, then the products will arise as the result of influential stabilization by the β -substituents. Another mechanistic interpretation is needed for the reaction of halocycloolefins with metal hydrides³.

References

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