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AN ELUCIDATION OF TWO MAJOR FACTORS IN THE REACTIONS OF 1,2-DICHLOROPERFLUOROCYCLOALKENES WITH TRIALKYL PHOSPHITES

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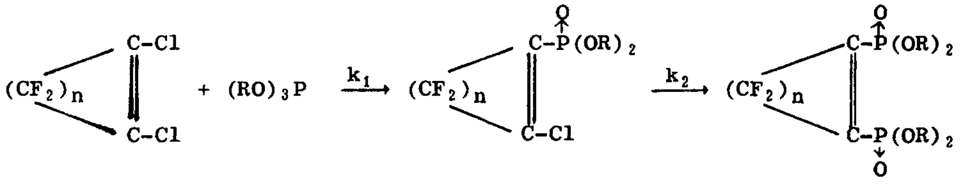
The reactions of 1,2-dichloroperfluorocycloalkenes with trialkyl phosphites(1) have led to the synthesis of a variety of diphosphonates, arising from displacement of both vinylic halogens. Frank(1) has been able to synthesize a variety of these compounds by varying the ring size of the olefin and the alkyl group of the phosphites. Monophosphonates were not isolated under these conditions.

The failure to isolate any monophosphonates must be a consequence of the unusually rapid rate of the second substitution.

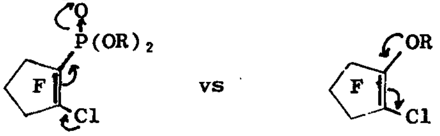


(A)

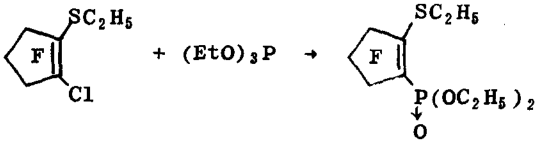
I

$n = 2,3,4.$ $\quad k_2 >> k_1$

Although the sequence, as shown, is over-simplified, the comparison of overall rates for each substitution should be valid. This phenomenon is quite anomalous since mono- and di-ethers have been reported when ethoxide ion is reacted with these alkenes. The product differences in these two cases have been attributed to a difference in the electronic effect of the ethoxy group relative to the dialkyl phosphonate group(1).

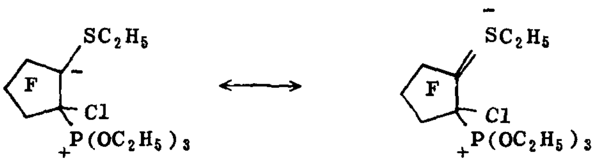


A kinetic acceleration of the second substitution (k_2) occurs in the phosphonate case whereas vinylic attack is deactivated by alkoxy. An alternative explanation exists, however; thermodynamic stabilization of an incipient carbanion could lead to the same phenomenon. This explanation is reasonable since the dialkyl phosphonate radical is one of the best carbanion stabilizers known(2). To test the latter hypothesis, 1-thioethoxy-2-chlorohexafluorocyclopentene was synthesized from 1,2-dichlorohexafluorocyclopentene and potassium thioethoxide. The monothioether gave an extremely high yield (63.7%) of vinylic substitution resulting in formation of II.

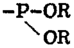


II

Since the thioethoxy radical is not able to accelerate vinylic substitution by electron withdrawal, kinetic acceleration is not possible. However, stabilization of an incipient carbanion is possible by d-π orbital overlap.



We have been able to synthesize a monophosphonate from the aforementioned olefins by reaction with triisopropyl phosphite. Diethyl-2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylene phosphonate was isolated from the reaction of 1,2-dichlorohexafluorocyclopentene-1 and triisopropyl phosphite. Although the yield (5.6%) was low, the significance of its formation cannot be neglected.

Since -R of I in sequence A is quite distant from the halogen substituted vinylic carbon, it's electronic effect should be almost negligible. Therefore, we believe that when R = isopropyl, effective steric bulk of  $-\overset{O}{\overset{\uparrow}{P}}(OR)OR$ is sufficiently large such that hindrance to the second substitution occurs.

The monophosphonate had a bp 73-75° (6 mm), and its infrared spectrum showed the following major absorptions: 1605, 1285, 1400-1100, 1020, and 895

cm^{-1}. The mass spectrum showed isotope peaks at m/e = 373 and 375 in the appropriate ratios for chlorine.

We feel, therefore, that thermodynamic stabilization of an incipient carbanion and steric hindrance play a major role in the reactions of halocycloalkenes and trialkyl phosphites.

(1) A. W. Frank, J. Org. Chem., **30**, 3663 (1965).

(2) W. S. Wadsworth and W. D. Emmons, J. Amer. Chem. Soc., **83**, 1733 (1961).