

1, 2-Dihalofluorocycloalkenes 와 삼가 인과의 반응

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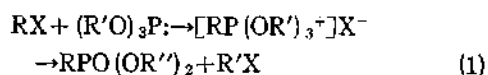
The Reactions of 1, 2-Dihalofluorocycloalkenes with Trivalent Phosphorus

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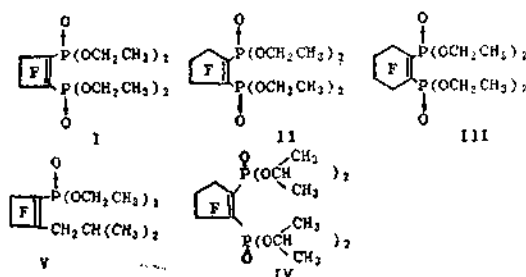
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The reactions of nucleophiles with halocycloalkenes have been studied in detail. Discussions of the mechanism and the characterization of the products from the reactions with alkoxide-ion and Grignard reagents have been reported. Studies of nucleophilic reactions of phosphorus compounds with halocycloalkenes, however, have not been studied to any extent.

Nucleophilic attack of trialkyl phosphites on alkyl halides has been known for many years and appears to be one of the most useful methods of preparing phosphonic acids and their derivatives. The reaction involves a nucleophilic substitution on the alkyl halide by the phosphorus atom. Subsequent elimination of alkyl halide leads to an alkyl-dialkyl phosphonate ester:



The success of the reactions depends on the reactivity of the alkyl halide (RX) toward nucleophilic substitution and on the volatility



of the alkyl halide eliminated (R'X).

We wish to report the first successful synthesis of analogous phosphonate esters with halogenated cycloalkenes:

The synthesis is accomplished by refluxing the

Table 1. Yield Data

Starting Olefin	Product	Yield (%)
Cl Cl	I	29.0
Cl Cl	II	31.0
Cl Cl	III	7.3
Cl Cl	IV	31.4
CH ₂ CH(CH ₃) ₂ F	V	41.9

(*) Yield based on trialkyl phosphite

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trialkyl phosphite with an excess of the appropriate olefin and a trace of toluene. The toluene is used as an internal standard as the progress of the reaction is followed by g.l.c. The reaction mixture is refluxed until the trialkyl phosphite is consumed. The yield data and spectra data are summarized in Tables 1 and 2.

5 (a) Yield based on trialkyl phosphite

The mass spectra of the diphosphonates show three modes of fragmentation. The two

major modes are by loss of an alkoxy radical and by loss of the diethyl phosphonate radical; the minor mode is by loss of the ethenyl radical with the transfer of two hydrogens. The latter mode has been previously reported for the hydrocarbon analogues⁴.

The nuclear magnetic resonance spectra for the diethyl phosphonate group consists of eleven lines: an unsymmetrical triplet for the $-\text{CH}_3$ and an eight line multiplet for the methylene

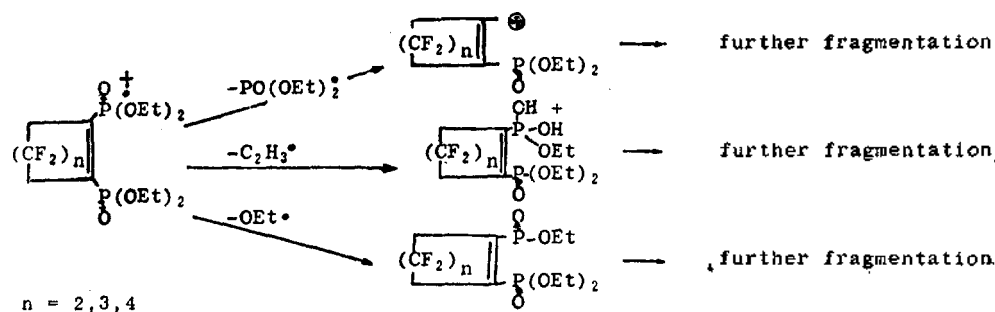
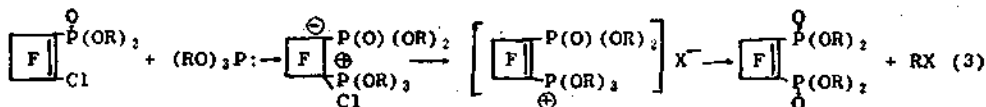
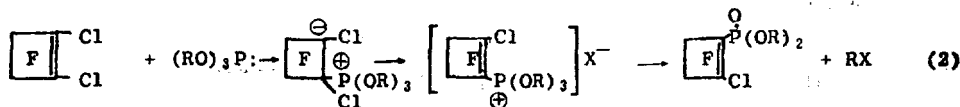


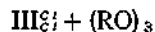
Table 2. Nuclear Magnetic Resonance and Mass Spectra

Compound	Mult.	J , vic (cps)	Group	Chem. Shift	Molec. Ion
I	$t(u)$	H-H=7.0	$-\text{CH}_3$	8.62	398
	m	H-H=7.0	$-\text{CH}_2$	5.78	
		$P-\text{OCH}_2=8.6$			
II	$t(u)$	H-H=7.1	$-\text{CH}_3$	8.63	448
	m	H-H=7.1	$-\text{CH}_2$	5.73	
		$P-\text{OCH}_2=9.0$			
III	$t(u)$	H-H=7.1	$-\text{CH}_3$	8.62	498
	m	—	$-\text{CH}_2$	5.73	
		Methylene-poorly resolve			
IV	m	—	$-\text{CH}_3$	—	504
	M	—	$-\text{CH}$	5.10	
		poorly resolved spectrum			
V	$d(u)$	H-H=6.0	$-\text{CH}_3$	8.96	318
	$t(u)$	H-H=7.1	$-\text{CH}_3$	8.61	
	m	—	$-\text{CH}$	7.91	
	m	—	$-\text{CH}_2$	7.46	
	m	HH-H=7.1	$-\text{CH}_2$	5.83	
		$P-\text{OCH}_2=9.0$			



protons.

The products can be rationalized by assuming carbanion formation, as in the case with the alkoxide ion and the Grignard reagents:



Continued work in the study of nucleophilic phosphorous reactions is in progress. Reactions with various halogens in the vinylic positions and with other phosphorous nucleophiles have been completed, and a more detailed discussion of reaction rates and mechanisms will be discussed in a later publication.

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synthesis of some of the compounds.

References

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