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Synthesis of Partially Fluorinated Oxetanes (I)

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The applicability of photosynthesis of oxetanes by cycloaddition of carbonyl compounds to olefins has recently been reported by Harris and Coffman (2). These workers found the synthesis successful with terminal fluoroolefins and either a fluoroaldehyde, a fluoroacyl fluoride, or a fluoroketone. More recently, Bissell and Fields (3) obtained low yields of oxetanes from several perhalogenated ethylenes and acetaldehyde.

With nonhalogenated olefins the reaction has been reported to take a different tack. Thus, from 1,3-dienes and perhalogenated acyclic ketones, 5,6-dihydro-2*H*-pyrans were obtained by a photo-initiated Diels-Alder reaction (4), while alkenes having an allylic hydrogen readily gave carbinols (5). Even ethylene was found to give a carbinol although in this case a catalyst was required (6).

We have found, however, that under actinic irradiation, hexafluoroacetone with ethylene, vinyl fluoride, or vinylidene fluoride gave good yields of oxetanes. With vinyl and vinylidene fluorides it was possible to isolate and identify both possible adducts (I and II) and also to determine the isomer distribution.

The two isomeric oxetanes from vinyl fluoride were found in a 1.6:1 (I:II) ratio; and with vinylidene fluorine in a 1.3:1 ratio. This low selectivity of cyclization stands in contrast to the results of several other workers, where only one direction of addition was observed in radical addition (7), although bidirectional attack has been observed in several other cases (8, 9).

It appears likely that the answer may lie with the relative energies of the attacking radical species. One would then expect that triplet hexafluoroacetone would show less selectivity towards the addend olefin than radicals generated under milder conditions.

Structural elucidation was accomplished by proton NMR spectroscopy. The assignments, tabulated in Table II, are self-explanatory and agree with the published spectrum of trimethylene oxide (10), with allowance for fluorine shielding and coupling.

EXPERIMENTAL

Oxetane synthesis and isolation.

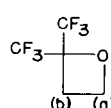
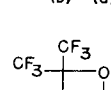
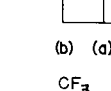
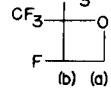
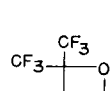
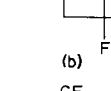
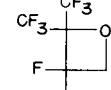
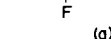
To an evacuated 3-necked 12 l. flask equipped with a manometer and a quartz well containing a 450 watt Hanovia high-pressure mercury lamp was charged 300 mm. of hexafluoroacetone and 300 mm. of the selected olefin. After about 15 minutes the pressure dropped to approximately one-half of the original value (300 mm.) and, if irradiation was not halted, would slowly increase. In all cases, the time required was approximately 12 hours. The flask was then pumped down through

TABLE I

Oxetane	b. p.	Formula	Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
I; X ₁ =X ₂ =H	85.7(761mm)	C ₆ H ₄ F ₆ O	30.95	31.12	2.08	2.35
I; X ₁ =H, X ₂ =F	78.8(764mm)	C ₆ H ₃ F ₇ O	28.32	28.50	1.42	1.50
II; X ₁ =H, X ₂ =F	88.6(764mm)	C ₆ H ₃ F ₇ O	28.32	28.48	1.42	1.64
I; X ₁ =X ₂ =F	58.0(761mm)	C ₅ H ₂ F ₈ O	26.10	26.32 (a)	0.88	1.08 (a)
II; X ₁ =X ₂ =F	65.2(761mm)					

(a) Mixture of isomers.

TABLE II
Proton NMR Assignments

	(a)	triplet τ 5.31 ($J = 8.0$ c/s)
	(b)	triplet τ 7.06 ($J = 8.0$ c/s)
	(a)	sextuplet τ 3.96 ($J_{AF} 70$ c/s; $J_{AB} 3.9$ c/s)
	(b)	multiplet τ 6.91
	(a)	multiplet τ 5.11
	(b)	sextuplet τ 4.37 ($J_{BF} 55$ c/s; $J_{AB} 6.0$ c/s)
	(b)	triplet τ 6.59 ($J = 7.0$ c/s)
	(a)	triplet τ 5.00 ($J = 12.2$ c/s)

a dry-ice cooled trap while infra-red lamps were played on the lower walls of the flask to insure removal of all volatile material. Separation and isolation of the isomers was effected with a Wilkins Instrument "Autoprep" employing a 20 ft. x 3/8 in. 30% tricresyl phosphate column. Other than the "non-volatile" in the flask, which was generally about 20% of the total product, there was no other material present in significant amounts in the oxetane mixtures. Physical data are presented in Table I.

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Received July 12, 1965

Princeton, New Jersey