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Synthesis of Polyfluoroöxetanes by Photoinitiated Addition of Fluorocarbonyl Compounds to Fluoroölefins

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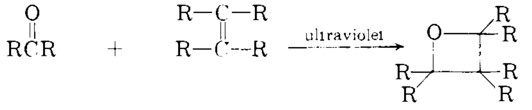
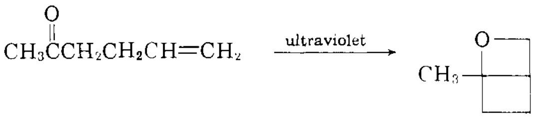
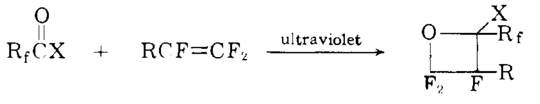
The ultraviolet irradiation of fluoroaldehydes, fluoroketones or fluoroacyl fluorides in admixture with fluoroölefins results in the formation of polyfluoroöxetanes.

Of the relatively few methods known for the preparation of oxetanes,[1] perhaps the most unusual is the photoinitiated cycloaddition of carbonyl compounds to olefins, first reported by Paterno and Chieffii[2] and subsequently studied by Büchi and co-workers[3] (equation 1) and by Srinivasan[4] (equation 2). Since polyfluoroöxetanes are virtually unknown,[5] an investigation of the applicability of the cycloaddition reaction for the preparation of these compounds has been made.


(1)


(2)

Ultraviolet irradiation of a reluxing mixture of a terminal fluoroölefin and either a fluoroaldehyde, a fluoroacyl fluoride or a fluoroketone has been found to result in the cycloaddition of the carbonyl function to the olefin to form a polyfluoroöxetane, often in excellent yield (equation 3)


(3)

X = H, F, R_f; R = R_f, Cl

The products of these reactions are all colorless liquids which exhibit considerable thermal stability. Examples of the reaction involving members of each class of carbonyl compound are discussed below. The details of individual experiments are listed in Tables I and II.

Results

Fluoroaldehydes and Fluoroölefins.—The 1:1 adduct fractions obtained by irradiating mixtures of a fluoroaldehyde and a terminal fluoroölefin were generally shown by gas chromatography to contain two components in about equal amounts. Since the infrared spectra indicated only trace amounts of carbonyl compounds, the two components were obviously isomeric oxetanes. Four such isomers are possible; for example trifluoroacetaldehyde with hexafluoropropene might form I (a and b) and II (a and b)


a, *cis*
b, *trans*
I


a, *cis*
b, *trans*
II

The fluorine nuclear magnetic resonance (n.m.r.) pattern (Table III) of each component isolated by prep-scale gas chromatography was of such simplicity as to indicate essentially a single compound. Based upon the following interpretation of these patterns, it is concluded that the two components are the *cis* (with respect to the 2 CF_3 groups) and *trans* isomers of 2-H-2,3-bis-(trifluoromethyl)-trifluoroöxetane (I-a and b).

The pattern of the lower boiling isomer (b.p. 38–39°) consists of four resonances in approximate ratio of 2:3:3:1. The chemical shifts of the resonances corresponding to the CF and the CF_2 groups (Table III) indicate the CF_2 to be next to oxygen (see footnote 6). Upon close examination of the CF_2 resonance (Fig. 1), it is evident that it is composed of a weak–strong–strong–weak pattern with the strong components so close that they actually overlap. The right hand weak component is hidden beneath one of the CF_3 resonances. The splittings of all of the peaks appear to be rather complicated and were not interpreted. Such a complicated splitting pattern is not surprising in view of the many possibilities for splitting, including cross-ring splitting. The fluorine n.m.r. pattern of the higher boiling isomer (b.p. 41–42°) is quite similar to that just discussed, and the chemical shifts of the CF and CF_2 resonances again indicate that the CF_2 group is next to oxygen. The components of the CF_2 resonance (Fig. 2), however, are spread out considerably more than in the pattern of the lower boiling isomer. These weak–strong–strong–weak patterns arise from the different

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[1] (a) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter I, p. 59. (b) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IV-A, Elsevier Publishing Co., New York, N. Y., 1957, p. 20.

[2] E. Paterno and G. Chieffii, *Gazz. chim. ital.*, **39**, 341 (1909).

[3] G. Büchi, C. G. Inman and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

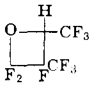
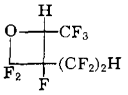
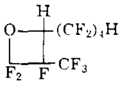
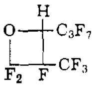
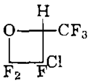
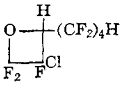
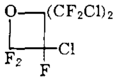
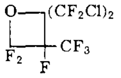
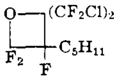
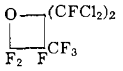
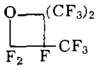
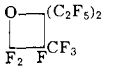
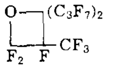
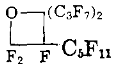
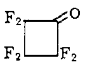
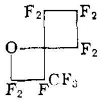
[4] R. Srinivasan, *ibid.*, **82**, 775 (1960).

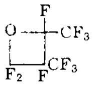
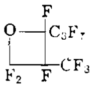
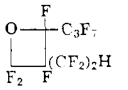
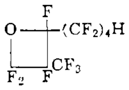
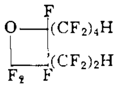
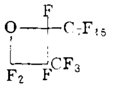
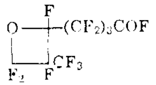
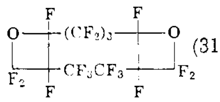
[5] Apparently only two polyfluoroöxetanes have been reported previously. They are hexafluoroöxetane itself, prepared by the electrolytic fluorination of oxetane (E. A. Kauck and J. H. Simons, U. S. Patent 2,594,272, April 29, 1952) and 2-H-*p*entafluoroöxetane, prepared by the reaction of oxygen with 1,1,2,2,3-pentafluoropropane at 500° (A. L. Henne, International Symposium on Fluorine Chemistry, Birmingham, England, July 14–17, 1959).

environments experienced by the two fluorines in the CF_2 group, and we interpret the more strongly split pattern as indicating that the environments of the corresponding fluorines differ to a larger degree than the environments of the two fluorines responsible for the less strongly split pattern. It is thus concluded that the higher boiling isomer with the more strongly split CF_2 resonance is the

TABLE I

ULTRAVIOLET RADIATION-INDUCED CYCLOADDITIONS OF POLYFLUOROCARBONYL COMPOUNDS TO POLYFLUOROOLEFINS

Carbonyl compound	Olefin	Period of irradiation (days)	Product (% yield)
		Aldehydes	
CF_3CHO 59 g. (0.602 m.)	$CF_2{=}CFCF_3$ 116 g. (0.724 m.)	8	 (32)[a] *cis* and *trans* (about 1:1)
CF_3CHO 20 g. (0.204 m.)	$CF_2{=}CF(CF_2)_2H$ 40 g. (0.22 m.)	3	 (66) *cis* and *trans*
$H(CF_2)_4CHO$ 24.9 g. (0.108 m.)	$CF_2{=}CFCF_3$ 35 g. (0.233 m.)	12	 (59)[a] *cis* and *trans* (about 1:1)
C_3F_7CHO 60.5 g. (0.306 m.)	$CF_2{=}CFCF_3$ 63 g. (0.420 m.)	12	 (37) *cis* and *trans* (about 1:1)
CF_3CHO 25 g. (0.255 m.)	$CF_2{=}CFCl$ 32 g. (0.274 m.)	1	 (14) + polymer
$H(CF_2)_4CHO$ 25 g. (0.109 m.)	$CF_2{=}CFCl$ 27 g. (0.232 m.)	3	 (15) + polymer
		Ketones	
$ClCF_2COCF_2Cl$ 38 g. (0.101 m.)	$CF_2{=}CFCl$ 15 ml. (liquid)	4	 (11) + polymer
$ClCF_2COCF_2Cl$ 242 g. (1.22 m.)	$CF_2{=}CFCF_3$ 135 g. (0.90 m.)	12	 (56)
$ClCF_2COCF_2Cl$ 91 g. (0.46 m.)	$CF_2{=}CFC_5F_{11}$ 113 g. (0.32 m.)	8	 (47)
$Cl_2CFCOCFCl_2$ 50 g. (0.216 m.)	$CF_2{=}CFCF_3$ 75 g. (0.50 m.)	7	 (39)
CF_3COCF_3 39 g. (0.235 m.)	$CF_2{=}CFCF_3$ 43 g. (0.286 m.)	7	 (50)
$C_2F_5COC_2F_5$ 43 g. (0.162 m.)	$CF_2{=}CFCF_3$ 35 g. (0.233 m.)	5	 (46)
$C_3F_7COC_3F_7$ 45 g. (0.131 m.)	$CF_2{=}CFCF_3$ 40 g. (0.267 m.)	8	 (62)
$C_3F_7COC_3F_7$ 45 g. (0.123 m.)	$CF_2{=}CFC_5F_{11}$ 45 g. (0.129 m.)	12	 (32)
 17 g. (0.133 m.)	$CF_2{=}CFCF_3$ 35 g. (0.233 m.)	4	 (33)

	Acyl fluorides		
CF_3COF 56 g. (0.483 m.)	$CF_2{=}CFCF_3$ 95 g. (0.633 m.)	8	 (38) *cis* and *trans* (65:35 ratio)
C_3F_7COF 35 g. (0.162 m.)	$CF_2{=}CFCF_3$ 68 g. (0.453 m.)	7	 (73)[a] *cis-trans* (about 1:1)
C_3F_7COF 20 g. (0.0925 m.)	$CF_2{=}CF(CF_2)_2H$ 20 g. (0.11 m.)	4	 (35)[a]
$H(CF_2)_4COF$ 25.1 g. (0.101 m.)	$CF_2{=}CFCF_3$ 30 g. (0.20 m.)	6	 (48)
$H(CF_2)COF$ 28 g. (0.113 m.)	$CF_2{=}CF(CF_2)_2H$ (0.110 m.)	6	 (61)
$C_7F_{15}COF$ 40 g. (0.0964 m.)	$CF_2{=}CFCF_3$ 50 g. (0.333 m.)	13	 (91)
$FOC(CF_2)_3COF$ 26 g. (0.107 m.)	$CF_2{=}CFCF_3$ 60 g. (0.40 m.)	7	 (34)  (31)

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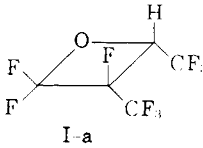
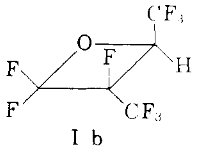
[a] No attempt was made to measure the excess volatiles; thus this is a minimum yield.

cis isomer (I-a) and that the other (lower b.p.) is the *trans* isomer (I-b)


I-a
(*cis*, b.p. 41–42°)


I b
(*trans*, b.p. 38–39°)

The fluorine n.m.r. patterns (Table III) of the products obtained from the analogous reactions of heptafluorobutyraldehyde and 5-H-octafluorovaleraldehyde with hexafluoropropene are similar to those discussed above, and analogous structures have been assigned (Table II). The reaction of trifluoroacetaldehyde and of 5-H-octafluorovaleraldehyde with chlorotrifluoroethylene led to formation of large quantities of polychlorotrifluoroethylene accompanied by small amounts of 1:1 adducts. On the basis of structure VIII (see a later section) assigned to the 1:1 adduct of chlorotrifluoroethylene with *sym*-dichlorotetrafluoroacetone, the products from trifluoroacetaldehyde and from 5-H-octafluorovaleraldehyde were assigned structures in which the CF_2 group is next to oxygen

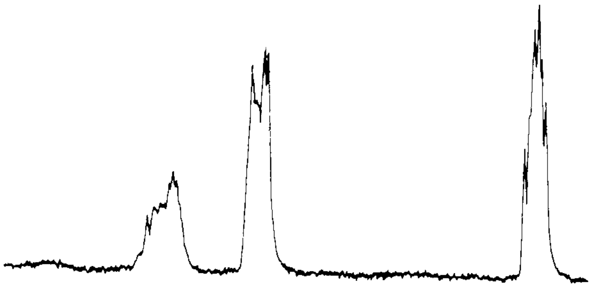


Fig. 1.—Detail of CF_3 region of fluorine n.m.r. pattern for the lower boiling isomer of 2-H-2,3-bis(trifluoromethyl)-trifluoroöxetane.

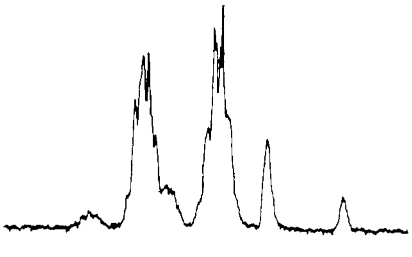
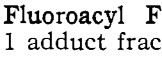
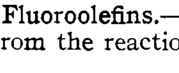


Fig. 2.—Detail of CF_3 region of fluorine n.m.r. pattern for the higher boiling isomer of 2-H-2,3-bis-(trifluoromethyl)-trifluoroöxetane.

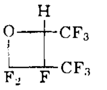
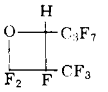
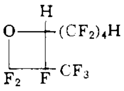
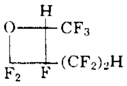
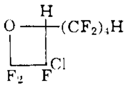
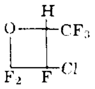
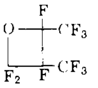
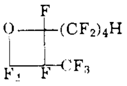
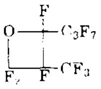
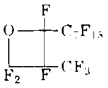
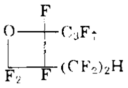
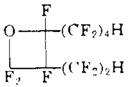
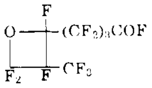
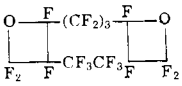
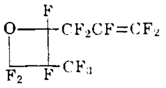




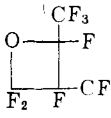
Fluoroacyl Fluorides and Fluoroolefins.—The 1:1 adduct fraction obtained from the reaction of

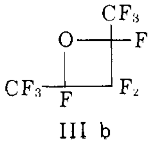
TABLE II

POLYFLUOROOXETANES

Compound		B.p. °C.	$n_{D/T}$	Formula	Carbon		Hydrogen		Fluoride		Chlorine	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
				From aldehydes								
	*trans*	38–39		C_5HF_9O	24.2	24.4	0.4	0.5	68.9	67.9		
	cis	41–42		C_5HF_9O	24.2	25.0	.4	.9	68.9	67.8		
	*trans*	83		$C_7HF_{13}O$	24.2	24.4	.3	.6	70.9	70.6		
	cis	86		$C_7HF_{13}O$	24.2	24.5	.3	.5	70.9	71.0		
	*trans*	124		$C_8H_2F_{14}O$	25.3	25.3	.5	.7	69.9	69.4		
	cis	128		$C_8H_2F_{14}O$	25.3	25.7	.5	.7	69.9	69.6		
	*trans*	72		$C_6H_2F_{10}O$	25.7	25.9	.7	1.0	67.9	67.8		
	cis	89		$C_6H_2F_{10}O$	25.7	25.7	.7	1.0	67.9	67.4		
		136	1.3204/25	$C_7H_2ClF_7O$					60.3	59.6	10.2	10.2
		53		C_4HClF_6O					53.2	52.7	16.5	16.5
				From acyl fluorides								
		25 (mixture)		$C_5F_{10}O$	(a) Less prevalent				71.4	71.8		
					(b) More prevalent				71.4	72.2		
		111–118.5		$C_8HF_{15}O$	24.2	24.6	0.3	0.5	71.5	72.2		
	(a)	80		$C_7F_{14}O$	22.9	23.4			72.7	73.5		
	(b)	78		$C_7F_{14}O$	22.9	23.2			72.7	72.7		
		161		$C_{11}F_{22}O$	23.3	23.6			73.8	74.1		
		109–115		$C_8HF_{15}O$	24.2	24.4	.3	.7	71.5	71.4		
		79–94/98 mm.		$C_9H_2F_{16}O$	25.1	25.4	.5	.5	70.7	71.2		
		102–104		$C_8F_{14}O_2$	24.4	24.7			67.5	65.8		
		153–155		$C_{11}F_{20}O_2$	24.3	24.7			69.8	69.7		
		79–82		$C_7F_{12}O$	25.6	26.3			69.5	69.5		

trifluoroacetyl fluoride with hexafluoropropene was, according to a gas chromatogram, composed of two materials in a ratio of about 65:35. The fluorine n.m.r. pattern of the less prevalent component indicated structure III-a rather than III-b


III-a


III b

Thus the pattern contains two CF resonances which are widely separated, consistent with *one* of them (the one responsible for the low field resonance) being next to oxygen.[6] In III-b both CF's are next to oxygen, and it would be expected that both resonances would occur in the low field CF

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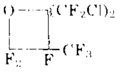
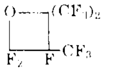
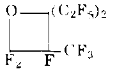
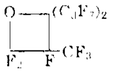
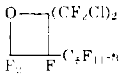
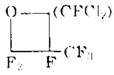
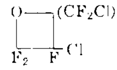
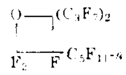
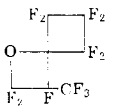
[6] The effect of adjacent oxygen in shifting fluorine resonances to lower field is well known. This pattern also has significance for the discussion of those oxetanes derived from aldehydes and ketones, since the resonance of the CF next to oxygen (+3525 c.p.s.) indicates where the CF resonance of these products would fall if the addition had occurred to give the structure with the CF next to oxygen.

TABLE II (*continued*)

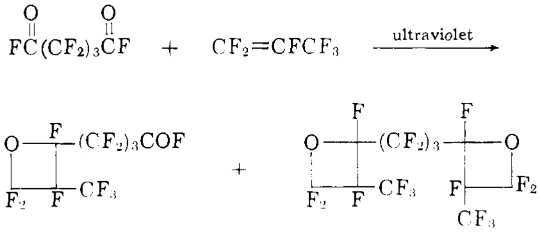
Compound	B.p., °C.	$n_{D/T}$	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found	Chlorine Calcd.	Chlorine Found
			From ketones								
	107.5	1.3259/26	$C_6Cl_2F_{10}O$			Mol. wt. 349	Mol. wt. 349 368	54.5	54.5	20.2	20.4
	51–52		$C_6F_{12}O$	22.8	23.5			72.1	71.4		
	97		$C_8F_{16}O$	23.1	23.8			73.1	72.9		
	136		$C_{10}F_{20}O$	23.3	23.8			73.6	73.4		
	182–184	1.3255–1.3258/25	$C_{10}Cl_2F_{18}O$	21.9	22.3			62.3	62.7	12.9	12.6
	171–172	1.3869	$C_6Cl_4F_8O$	18.9	19.4			39.9	39.7	37.1	36.9
	120	1.3613/24	$C_5Cl_3F_7O$					42.1	41.8	33.8	33.4
	199–201		$C_{14}F_{28}O$	23.5	23.9			74.3	74.7		
	68–69		$C_7F_{12}O$	25.6	26.0			69.5	69.7		

region. In addition, the pattern contains the characteristic CF_2 weak–strong–strong–weak pattern in the CF_3 region as seen in the aldehyde products, indicating that the CF_2 is next to the oxygen[6] as in III-a.

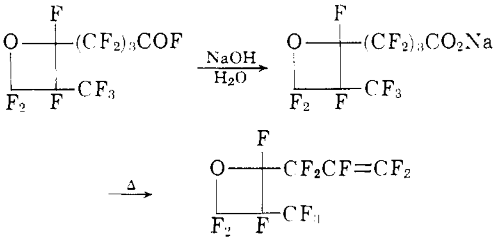
The fluorine n.m.r. pattern of the more prevalent component indicates the presence of impurities. However, the two CF resonances are apparent, and they are similar in positions to those of the previously discussed pattern. It is therefore concluded that this component is largely an oxetane of structure III-a, and thus both the *cis* and *trans* isomers corresponding to III-a were formed. Because of uncertainties in the pattern of the more prevalent component, a specific *cis-trans* assignment has not been made.

The reaction of heptafluorobutyryl fluoride with hexafluoropropene also yielded a 1:1 adduct fraction composed largely of two components in about equal amount. The fluorine n.m.r. patterns of the isolated components each contained two widely separated CF peaks indicative of structures with the CF_2's next to oxygen. Thus the two components are the *cis* and *trans* isomers of 2-heptafluoropropyl-3-trifluoromethyl tetrafluorooxetane. In the spectrum of one of the isomers, the ring CF_2 weak–strong–strong–weak pattern in the CF_3 region was readily apparent. In the other isomer, the weak components were evident, but the strong components were apparently hidden beneath the CF_3 resonances. In view of this latter uncertainty, no specific *cis–trans* assignment was made. The gas chromatogram of the reaction product from 5-H-octafluorovaleryl fluoride and hexafluoropropene indicated the presence of two materials, but the peaks were too close for separation. Only one peak was observed in the chromatogram of the product from the reaction of perfluoroöctanoyl fluoride and hexafluoropropene. By analogy with the structure III-a assigned to the products from the reaction of trifluoroacetyl fluoride with hexafluoropropene, it is assumed that these compounds and the others derived from acyl fluorides shown in Table II have the CF_2 group adjacent to oxygen.

The reaction of hexafluoroglutaryl fluoride with hexafluoropropene led to the formation of a 1:1 and a 2:1 adduct (equation 4). The fluorine n.m.r. patterns of these compounds were quite complicated, and the structures were assigned by analogy with the structure of the trifluoroacetyl fluoride–hexafluoropropene adducts. Conversion



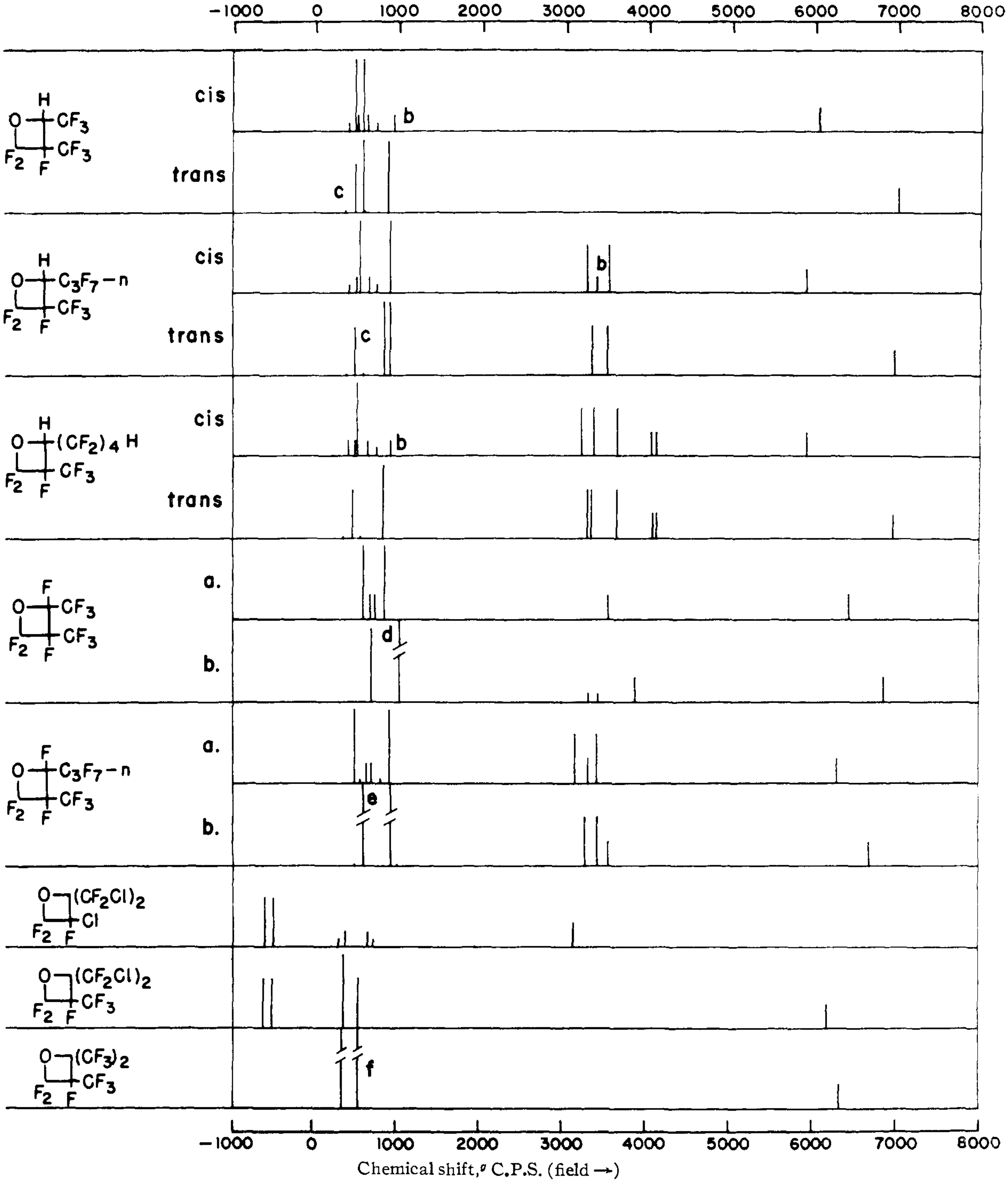
(4)



(5)

TABLE III

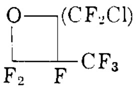
FLUORINE NUCLEAR MAGNETIC RESONANCE SPECTRA AT 56.4 MC.[a]



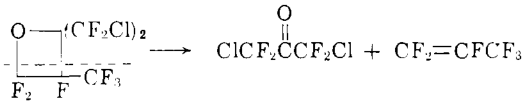
[a] Spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, California, operating at approximately 9395 gauss. Relative intensities are indicated by line heights. [b] Presumably extraneous. [c] This peak is composed of the two strong components of a weak–strong–strong–weak pattern. The weak components are represented by dots. [d] This resonance presumably contains the ring CF_2 resonance and one of the CF_3 resonances. [e] The strong components of the weak–strong–strong–weak pattern for the ring CF_2 are apparently hidden under the CF_3 resonances. [f] These CF_3 resonances presumably cover the components of the ring CF_2 resonance. [g] Spectra were measured in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of sym-difluorotetrachloroethane as an external standard.

of the 1:1 adduct (equation 4) to a sodium salt, followed by pyrolysis, resulted in the formation of perfluoro-(2-allyl-3-methyloxetane) (equation 5).

Fluoroketones and Fluoroolefins.—The 1:1 adduct fraction formed by irradiation of sym-dichlorotetrafluoroacetone in admixture with hexafluoropropene appeared to be essentially one compound which, because of the chemical shifts of the CF and the ring CF_2 groups observed in the fluorine n.m.r. pattern, is considered to be 2,2-bis-(chlorodifluoromethyl)-3-trifluoromethyltrifluoroöxetane (IV)

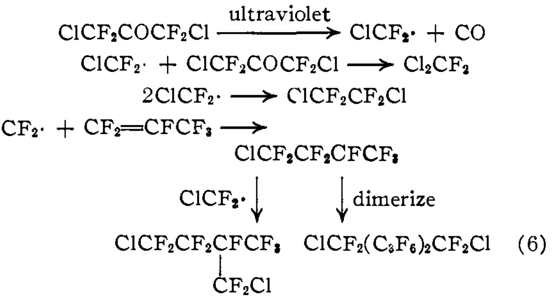

IV

Additional evidence that this product is an oxetane was provided by its pyrolysis at 650° to obtain the starting ketone and hexafluoropropene along with a small amount of carbonyl fluoride presumably from the alternative mode of ring cleavage.



$$\longrightarrow ClCF_2\overset{O}{\overset{\|}{C}}CF_2Cl + CF_2{=}CFCF_3$$

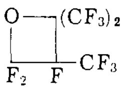
Examination of the volatile products from a reaction of hexafluoropropene and *sym*-dichlorotetrafluoroacetone revealed the presence of carbon monoxide, dichlorodifluoromethane and *sym*-dichlorotetrafluoroethane. In the liquid product, in addition to the 1:1 adduct, two other compounds (V and VI) were found. All of these products apparently result from photolysis of the ketone to give carbon monoxide and chlorodifluoromethyl radicals[7] (equation 6).



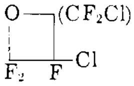
$$\begin{gathered}
ClCF_2COCF_2Cl \xrightarrow{\text{ultraviolet}} ClCF_2\cdot + CO \\
ClCF_2\cdot + ClCF_2COCF_2Cl \longrightarrow Cl_2CF_2 \\
2ClCF_2\cdot \longrightarrow ClCF_2CF_2Cl \\
ClCF_2\cdot + CF_2{=}CFCF_3 \longrightarrow ClCF_2CF_2\dot{C}FCF_3 \\
ClCF_2\cdot\downarrow \qquad \downarrow\text{dimerize} \\
ClCF_2CF_2\underset{\displaystyle CF_2Cl}{\underset{|}{C}}FCF_3 \qquad ClCF_2(C_3F_6)_2CF_2Cl \qquad (6)
\end{gathered}$$

V VI

The product of the reaction of hexafluoroacetone and hexafluoropropene was assigned the structure with the CF_2 group next to oxygen (VII) on the basis of the position of the CF resonance in the fluorine n.m.r. pattern. The components of the ring CF_2 pattern were not readily discernible due, apparently, to overlap with the CF_3 resonances.


VII

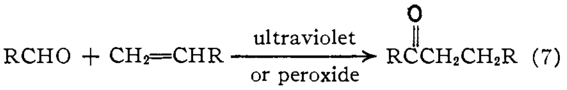
The structures of the products obtained from the reactions of decafluoro-3-pentanone with hexafluoropropene; from *sym*-dichlorotetrafluoroacetone with 4-H-heptafluoro-1-butene and with tetradecafluoro-1-heptene; from *sym*-tetrachlorodifluoroacetone with hexafluoropropene; from perfluoro-4-heptanone with hexafluoropropene and with tetradecafluoro-1-heptene; and from perfluorocyclobutanone with hexafluoropropene were all assigned on the basis of analogy with the structure of the *sym*-dichlorotetrafluoroacetone-hexafluoropropene adduct. The product from *sym*-dichlorotetrafluoroacetone and chlorotrifluoroethylene has been assigned structure VIII on the basis of the chemical shift of the ring CF_2 resonance (weak–strong–strong–weak) in the fluorine n.m.r. pattern.


VIII

Discussion

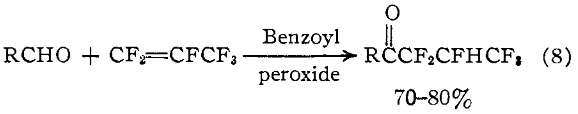
A striking feature of the cycloaddition reactions described herein is the high yield often obtained compared to the yields obtained in analogous preparations of oxetanes reported previously.[2-4]

It is somewhat surprising that the photoinitiated reaction of fluoroaldehydes with terminal fluoroolefins yields oxetanes (apparently almost exclusively) and not ketones since studies by Kharasch, Urry and Kuderna[8] have shown that the addition of aliphatic aldehydes to terminal olefins to yield ketones proceeds readily in the presence of ultraviolet radiation or peroxide catalysts: Similarly,



$$RCHO + CH_2{=}CHR \xrightarrow[\text{or peroxide}]{\text{ultraviolet}} R\overset{O}{\overset{\|}{C}}CH_2CH_2R \quad (7)$$

LaZerte and Koshar[9] have reported that the peroxide-initiated addition of aliphatic aldehydes to terminal fluoroölefins to give ketones proceeds in high yield (equation 8). These reactions are



$$RCHO + CF_2{=}CFCF_3 \xrightarrow[\text{peroxide}]{\text{Benzoyl}} R\overset{O}{\overset{\|}{C}}CF_2CFHCF_3 \quad (8)$$
$$70\text{–}80\%$$

no doubt chain reactions of considerable chain length. An attempted reaction of perfluorobutyraldehyde and hexafluoropropene under the conditions described by LaZerte and Koshar gave no detectable product. It thus seems that the radical abstraction of hydrogen from a polyfluoroaldehyde is much more difficult than from an aliphatic aldehyde, and it is apparently this behavior that allows the non-chain cycloaddition of the polyfluoroaldehyde to the fluoroölefin to proceed rather than ketone formation by a chain reaction. Similarly, one could postulate a radical chain addition of an acyl fluoride to a fluoroölefin to yield a ketone, but this would require abstraction of a fluorine atom, an event even less likely than the abstraction of aldehydic hydrogen.

The mechanism of olefin–carbonyl cycloadditions has not been studied. Büchi[3] has suggested a two-step process initiated by the carbonyl com-

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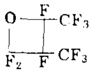
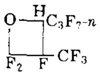
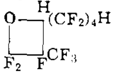
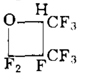
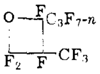
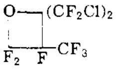
(7) The photolysis of *sym*-dichlorotetrafluoroacetone has been studied by R. Bowles, H. Derbyshire, J. R. Majer and C. R. Patrick, *Nature*, **185**, 683 (1960). It was postulated that all of the products identified, including CO and Cl_2CF_2, stemmed from an initial cleavage of the ketone to CO and $ClCF_2$· radicals.

(8) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

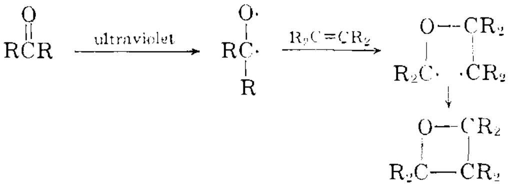
(9) J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

TABLE IV

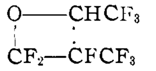
GAS CHROMATOGRAPHY ANALYSES

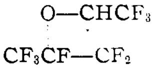
Reaction product	Column packing	Column temp., °C.	Helium flow rate, ml./min.	Retention time, min.
	20% Ethyl ester of Kel-F Acid 8114—"Columpak" 12′ × 1/4″	0	60	(1) 6.25 (2) 7.15
	30% DC703-Firebrick 12′ × 3/4″	Room	475	(1) 7.8 (2) 11.0
	30% DC703-Firebrick 12′ × 3/4″	50	500	(1) 26.0 (2) 36.5
	20% Diglyceride of ω-trifluorohexanoic acid—"Columpak" 6′ × 1/4″	25	117	(1) 2.1 (2) 2.6
	20% Ethyl ester of Kel-F Acid 8114—"Columpak" 6′ × 1/4″	25	61	(1) 6.4 (2) 7.3
	20% Ethyl ester of Kel-F Acid 8114—"Columpak" 2 meter × 1/4″	75	25	14.1

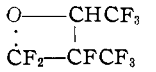
pound in a diradical triplet state[10]

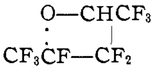


Another possibility is that reaction occurs by a four - center concerted type mechanism.[11] As pointed out by Büchi,[3] the concept of the two-step diradical process is useful in predicting the product by assuming that the intermediate radical is the most stable of those possible. For example, of the four possibilities (IX–XII) in the reaction of trifluoroacetaldehyde with hexafluoropropene, the diradical IX would be predicted to be the most stable. This intermediate is congruent with the structure of the oxetane (I) formed. Similar


IX


X


XI


XII

considerations, when applied to the products of the reactions involving the other aldehydes, ketones and acyl fluorides, lead to the assigned structures which are supported by the n.m.r. data in each case.

Experimental

I. Reactions of Fluorocarbonyl Compounds with Fluoroolefins. A. Reactions at Atmospheric Pressure.—All of these reactions were carried out in approximately the same manner. The reactor consisted of a vertical quartz tube (2″ × 10″) fitted with a magnetic stirrer, a gas inlet adapter and a large acetone–solid carbon dioxide cooled condenser vented through a trap, also cooled by acetone–solid carbon dioxide, the exit of which was fitted with a T-tube through which a slow stream of nitrogen passed. The ultraviolet radiation source consisted of a helix-shaped (4″ × 2-1/2″) low-pressure mercury lamp constructed of 37 mm. quartz tubing and powered by a 5000 volt, 60-milliamp. transformer. The lamp was fitted around the quartz reaction tube so that its radiation impinged primarily upon the liquid portion of the reaction mixture. The details of a typical experiment involving reaction of *sym*-dichlorotetrafluoroacetone with hexafluoropropene follow.

Dry nitrogen was passed through the assembled apparatus for several minutes, and then both the condenser and trap were filled with coolant. One hundred thirty-five grams (0.90 mole) of hexafluoropropene and 242 g. (0.122 mole) of *sym*-dichlorotetrafluoroacetone were loaded in the tube. Frosting on the outside of the reactor was prevented by allowing methanol to drip down the side of the reactor. The mixture was irradiated for 12 days. Upon distillation of the reaction mixture through a spinning band still, there was obtained 176.4 g. (56%) of crude 2,2-bis-(chlorodifluoromethyl)-3-trifluoromethyltrifluoroöxetane distilling at 105–109°. This material was further purified by distillation through a small Podbielniak still: b.p. 107.5°, n^{26}_D 1.3259, d^{25} 1.7424. The analytical data for this compound are given in Table II. Considerable quantities of higher and lower boiling material were also obtained, but no clear-cut fractions were separated.

The other experiments carried out in this manner are tabulated in Table I.

B. Reaction in a "Vycor" Shaker Bottle.—Fifteen grams of *sym*-dichlorotetrafluoroacetone was placed in a 300-ml. "Vycor" shaker bottle attached to a Parr hydrogenation assembly. The bottle was briefly evacuated and was then pressured to 30 p.s.i. with hexafluoropropene. While being shaken, the bottle and its contents were irradiated for 2 days with two General Electric H-85 C-3 lamps placed as close to the bottle as possible. The reaction was repeated, and the two reaction mixtures were combined. An infrared examination of the volatile products indicated the presence of $CF_2{=}CFCF_3$ (20%), $ClCF_2CF_2Cl$ (10%), CF_2Cl_2 (1%) as well as CO, CO_2 and SiF_4.

Distillation of the liquid portion of the reaction mixture resulted in the isolation of the cyclic ether (12%) and two other compounds

V. $ClCF_2CF_2CF(CF_3)CF_2Cl$—(15%) b.p. 91°, n^{25}_D 1.3135

Anal. Calcd. for $C_5Cl_2F_{10}$: F, 59.2; Cl, 22.1; mol. wt., 321. Found: F, 57.9; Cl, 22.1; mol. wt., 305, 307.

VI. $ClCF_2[CF_2CF(CF_3)]_2CF_2Cl$—(11%)

b.p. 150°, n^{25}_D 1.3271

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[10] Decision as to whether an excited singlet or triplet state is involved can probably not be made at the present time but must await a detailed study similar to that made by Hammond and Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959), on the photoreduction of benzophenone by alcohols in which it was found that the triplet state of the ketone was involved.

[11] Both a two-step radical mechanism and a concerted mechanism have been proposed for the formation of cyclobutanes from olefins by thermal cycloaddition, but thus far no decision between them has been made (J. D. Roberts and C. M. Sharts, forthcoming chapter in "Organic Reactions").

Anal. Calcd. for $C_8Cl_2F_{16}$: F, 64.5; Cl, 15.1; mol. wt., 471. Found: F, 64.5; Cl, 14.6; mol. wt., 437, 458.

II. **Preparation of Perfluoro-(2-allyl-3-methyloxetane).**—Perfluoro-2-(3-fluoroformylpropyl)-3-methyloxetane (11.16 g.) was mixed with 60 ml. of water, and a solution of 4 g. of sodium hydroxide in 25 ml. of water was added until the solution was just alkaline as indicated by phenolphthalein. The solution was then evaporated to dryness on the steam bath, and the resulting salt was dried at 95° in a vacuum oven.

The dried salt was placed in a flask connected through an acetone–solid carbon dioxide cooled trap to a water pump. The system was evacuated, and the flask was heated at 220–265° for several hours. Upon distillation of the trap contents (7.96 g., 86%), there was obtained 6.19 g. (66%) of perfluoro-(2-allyl-3-methyloxetane) distilling at 79–82°.

Anal. Calcd. for $C_7F_{12}O$: C, 25.6; F, 69.5. Found: C, 26.3; F, 69.5.

Purification of Products.—The products, the infrared spectrum of which revealed the presence of small amounts of carbonyl-containing impurities, were shaken with methanolic potassium hydroxide, then with water, dried over anhydrous magnesium sulfate and redistilled.

Many of the products were analyzed by gas chromatography. The details of these analyses are given in Table IV. Preparative scale separations of isomers, such as obtained in the aldehyde-olefin and acyl fluoride-olefin reactions, were carried out in the usual way, generally with 6′ × 3/4″ columns packed with the same materials as used in the analytical column.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Anchimerically Accelerated Bond Homolysis. II.[1] Neighboring Iodide and Sulfide Groups in *t*-Butyl Perester Decompositions

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Very large accelerations of the first-order thermal decompositions of *o*-substituted *t*-butyl perbenzoates are provided by certain substituents. Relative rates of decomposition in chlorobenzene at 60° vary with *o*-substituent in the order: C_6H_5S– 2.45×10^4; CH_3S–, 1.41×10^4; I–, 54.1; $(CH_3)_3C$–, 3.8; H–, 1.0. The tremendous rate enhancements observed with the first two of these peresters and the lesser effects accompanying the decomposition of the *o*-iodoperbenzoate are ascribed to neighboring-group participation in a homolytic bond cleavage, the O–O bond cleavage being accompanied by simultaneous O–S (or O–I) bond formation, probably involving an expansion of the sulfur (or iodine) valence octet. The free-radical nature of these decompositions is attested to by product composition and by the results of radical scavenging studies using stable free radicals as scavengers.

The effects of substituents upon rates of the thermal first-order decompositions of substituted benzoyl peroxides and of *t*-butyl perbenzoates have received considerable attention. The influence of *meta* or *para* substituents upon these rates has been shown[3–6] to be well correlated by the Hammett $\sigma\rho$ relationship. For the decompositions[4] of substituted benzoyl peroxides in dioxane, $\rho = 0.374$[5] at 80°. The perbenzoates decompose[5,6] in diphenyl ether with rates correlated with σ-constants by a ρ of -0.678 at 110.1°. These relatively small substituent effects, the largest differences in rate within a series corresponding to a factor of approximately ten, have been explained on the basis of an inductive effect. The ground state free energy of the molecules is increased or decreased by changing the magnitude of an unfavorable dipole–dipole interaction between the two fragments joined by the O–O bond.

The effect of *o*-substituents on decomposition rates has been known[7] for some time to be, at least in some cases, much larger than the effect of the corresponding *m*- or *p*-substituent. In general *o*-substituted benzoyl peroxides decompose more rapidly than the corresponding *p*-isomers by factors in the range 2–20. Cooper[7] observed an increase in rate of approximately 1000 when he compared the rate of decomposition of bis-(*o*-iodobenzoyl) peroxide with that of its *p*-isomer. On observing an increase in rate with the size of the *o*-substituent in a series of bis-(*o*-halobenzoyl) peroxides, Cooper postulated that the acceleration reflected a steric effect depending on the space-filling properties of the substituent.

Leffler,[8,9] in a careful study of the decomposition of the same iodo-substituted peroxide, confirmed the magnitude of the rate enhancement observed by Cooper[7] and suggested that its origin lay in the operation of a "heavy atom" effect,[9] the inhomogeneous magnetic field around the iodine nucleus enhancing the probability of an electronic singlet–triplet transition in the nearby O–O bonding electrons. Alternative explanations involving "trapping, by a concerted process or otherwise, of a nascent intermediate" were also suggested by Leffler.[9]

In a previous communication,[1] we presented preliminary evidence that the thermal decompositions of *t*-butyl *o*-iodoperbenzoate and of *t*-butyl *o*-(methylthio)-perbenzoate are actually *anchimerically*[10] *accelerated* through the action of the *ortho* groups. Decomposition through a singlet transition state (represented for *t*-butyl *o*-(methylthio)-perbenzoate by canonical forms I and II) stabilized

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[1] For Part I see J. C. Martin and W. G. Bentrude, *Chemistry & Industry*, 192 (1959).

[2] Taken from the Ph.D. thesis of W. G. Bentrude, University of Illinois, June, 1961. Presented in part before the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 46-O of Abstracts.

[3] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).

[4] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

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[8] J. E. Leffler, C. C. Petropoulos and R. D. Faulkner, *Chemistry & Industry*, 1238 (1956).

[9] J. E. Leffler, R. D. Faulkner and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

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