

196° (further recrystallization from chloroform did not raise the melting point); ir 5.8  $\mu$  (C=O); nmr (THF)  $^1\text{H}$  at  $\tau$  2.4 (broad multiplet, aromatic CH);  $^{19}\text{F}$  at 55.4 (doublet, 3,  $J_{\text{F}/\text{F}} = 37.0$  Hz,  $\text{CF}_3$ ), 111.2 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 37.0$  Hz, CF).

*Anal.* Calcd for  $\text{C}_{13}\text{H}_8\text{F}_6\text{O}$ : C, 68.41; H, 2.55; F, 24.05. Found: C, 68.56; H, 2.77; F, 24.36.

An attempt to repeat the reaction over new quartz chips gave a much lower yield, but the yield was improved by pyrolysis over sodium fluoride pellets.

**4,4-Bis(trifluoromethyl)-3-(*p*-tolyl)-2-cyclobutenone (2b).**—*p*-Tolylacetylene (3.0 g, 0.026 mol) and **1** (8.7 g, 0.049 mol) were heated 16 hr in a steam bath to give, after three crystallizations from petroleum ether, 3.0 g (39.5%) of the cyclobutenone: mp 44.5–45.5°; ir 5.58 (C=O), 6.20, 6.30, 6.42, and 6.64  $\mu$  (aromatic and conjugated C=C); nmr ( $\text{CDCl}_3$ )  $^1\text{H}$  at  $\tau$  2.27, 2.41, 2.61, and 2.75 (AB quartet, 4, *para*-aromatic  $\text{C}_6\text{H}_4$ ), 3.19 (singlet, 1, =CH), 7.60 (singlet, 3,  $\text{CH}_3$ );  $^{19}\text{F}$  at 64.6 ppm [singlet, ( $\text{CF}_3$ )<sub>2</sub>].

*Anal.* Calcd for  $\text{C}_{13}\text{H}_8\text{F}_6\text{O}$ : C, 53.11; H, 2.74; F, 38.78. Found: C, 52.66; H, 2.79; F, 39.11.

**4,4-Bis(trifluoromethyl)-3-(*p*-chlorophenyl)-2-cyclobutenone (2e).**—*p*-Chlorophenylacetylene (3.5 g, 0.026 mol) and **1** (8.7 g, 0.049 mol) were heated 16 hr in a steam bath to give, after two recrystallizations from petroleum ether, 5.0 g (62%) of **2e**: mp 55–60°; ir 5.57 (C=O), 6.25, 6.31, 6.43 and 6.71  $\mu$  (aromatic and conjugated C=C); nmr ( $\text{CDCl}_3$ )  $^1\text{H}$  at  $\tau$  2.38 (multiplet, 4, aromatic  $\text{C}_6\text{H}_4$ ), 3.08 (singlet, 1, =CH);  $^{19}\text{F}$  at 64.5 ppm [singlet, ( $\text{CF}_3$ )<sub>2</sub>].

*Anal.* Calcd for  $\text{C}_{12}\text{H}_6\text{F}_6\text{ClO}$ : C, 45.82; H, 1.60; F, 36.25; Cl, 11.28. Found: C, 46.63; H, 1.52; F, 35.10, Cl, 11.49.

**3-Phenyl-5-(*p*-chlorophenyl)-6,6-bis(trifluoromethyl)-2,4-cyclohexadienone (22).**—Cyclobutenone **2e** (2.0 g, 0.0064 mol) and excess phenylacetylene were heated in a steam bath for 60 hr. Distillation up to 160° (45  $\mu$ ) gave 1.3 g of oil which crystallized in petroleum ether and on recrystallization gave 1.0 g (38%) of

**22**: mp 105–107°; ir 5.97 (conj C=O), 6.09, 6.26, 6.36, 6.71, and 6.91  $\mu$  (aromatic and conj C=C); nmr ( $\text{CDCl}_3$ )  $^1\text{H}$  at  $\tau$  2.53 (multiplet, 5,  $\text{C}_6\text{H}_5$ ), 2.75 (multiplet, 4,  $\text{C}_6\text{H}_4$ ), 3.12 (doublet, 1,  $J_{\text{H}/\text{H}} = 1.4$  Hz, =CH), 3.60 (doublet, 1,  $J_{\text{H}/\text{H}} = 1.4$  Hz, =CH);  $^{19}\text{F}$  at 61.5 ppm [singlet, ( $\text{CF}_3$ )<sub>2</sub>].

*Anal.* Calcd for  $\text{C}_{20}\text{H}_{11}\text{F}_6\text{ClO}$ : C, 57.67; H, 2.66; F, 27.37; Cl, 8.51. Found: C, 57.04; H, 2.72; F, 27.14; Cl, 8.85.

**3-(*p*-Chlorophenyl)-5-phenyl-6,6-bis(trifluoromethyl)-2,4-cyclohexadienone (23).**—A 7.0-g (0.025 mol) sample of **2a** and 3.5 g (0.025 mol) of *p*-chlorophenylacetylene were heated in a steam bath for 50 hr. Rapid distillation gave an oil, bp ~120° (0.4 mm), which solidified. Recrystallization from petroleum ether gave 2.0 g (20%) of crystals. Further crystallization gave 0.6 g of **23**, mp 90–94°; ir 5.96 (conj C=O), 6.09, 6.25, 6.31, 6.40, and 6.66  $\mu$  (aromatic and conj C=C); nmr ( $\text{CDCl}_3$ )  $^1\text{H}$  at  $\tau$  2.45 (multiplet, 4,  $\text{C}_6\text{H}_4$ ), 2.57 (singlet, 5,  $\text{C}_6\text{H}_5$ ), 3.03 (doublet, 1,  $J_{\text{H}/\text{H}} = 1.4$  Hz, =CH), 3.48 (doublet, 1,  $J_{\text{H}/\text{H}} = 1.4$  Hz, =CH);  $^{19}\text{F}$  at 61.4 ppm [singlet, ( $\text{CF}_3$ )<sub>2</sub>].

*Anal.* Calcd for  $\text{C}_{20}\text{H}_{11}\text{F}_6\text{ClO}$ : C, 57.67; H, 2.66; F, 27.37; Cl, 8.51. Found: C, 57.83; H, 2.73; F, 27.43; Cl, 8.33.

**Registry No.**—**2a**, 4141-87-1; **2b**, 25631-73-6; **2c**, 25631-74-7; **2d**, 25631-75-8; **2e**, 25631-76-9; **2f**, 25631-77-0; **3**, 25631-78-1; **5**, 14203-12-4; **6**, *cis*, 25631-80-5; **6**, *trans*, 25798-19-0; **7**, 25631-82-7; **10**, 25631-83-8; **11**, 25631-84-9; **12**, 25631-85-0; **13**, 25631-86-1; **14**, 25631-87-2; **15**, 25631-88-3; **16**, 25631-89-4; **17**, 25631-90-7; **18**, 25631-91-8; **21**, 25631-92-9; **22**, 25631-93-0; **23**, 25631-94-1; 4,4-difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylic acid, 25679-32-7; 4,4-difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylic acid Me ester, 25631-95-2.

## Fluoroketenes. V. Cycloadditions to the Bis(trifluoromethyl)ketene Carbonyl Group<sup>1</sup>

DAVID C. ENGLAND AND CARL G. KRESPAN

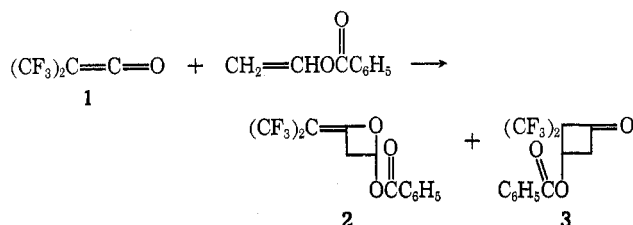
Contribution No. 1659 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received February 12, 1970

Cycloadditions of very nucleophilic olefins to bis(trifluoromethyl)ketene tend to occur at the carbonyl group to form oxetanes. The mechanism for this reversible cycloaddition involves a dipolar intermediate, as shown by isomerizations with *cis*- and *trans*-propenyl propyl ethers. Supporting evidence is the increase in rate and in products of proton transfer with increase in solvent polarity, an increasing reactivity with increasing nucleophilicity of olefinic coreactant, the orientation of substituents in product, and a cationic polymerization of vinyl ethers and styrenes as a side reaction. A second mode of cycloaddition to the ketene carbon-carbon double bond also occurs to give thermodynamically more stable cyclobutanones. The latter cycloaddition is also reversible in the vinyl ether case, and evidence that it proceeds through a second type of dipolar intermediate is presented.

**Vinyl Esters.**—Ketenes normally form cyclobutanones with very reactive olefins as well as with simple alkenes.<sup>2</sup> Aside from the special case of ketene dimerizations to give  $\beta$ -lactones, the only example of a 1,2 cycloaddition to a ketene carbonyl group to form an oxetane seems to be with bis(trifluoromethyl)ketene (**1**).<sup>3</sup> Reaction of **1** with vinyl benzoate neat at 100° was reported to form 2-benzoyloxy-4-hexafluoroisopropylidenoxyoxetane (**2**) and 2,2-bis(trifluoromethyl)-3-

benzoyloxycyclobutanone (**3**) in 34 and 42% yields, respectively.



(1) For parts III and IV on reactions at the double bond of bis(trifluoromethyl)ketene, see D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3300, 3308 (1970).

(2) For a review of the chemistry of ketenes, see R. N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 1161.

(3) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 4019 (1965).

More extensive work with this system has shown that the ratios of products vary erratically and that the presence of solvent encourages by-product formation. Table I summarizes the results obtained by  $^{19}\text{F}$  nmr for

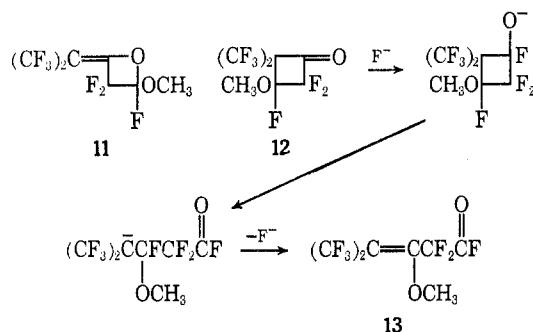


TABLE II  
 REACTIONS OF *cis*-PROPENYL PROPYL ETHER WITH BIS(TRIFLUOROMETHYL)KETENE<sup>a</sup>

Solvent	Temp, °C	Time	Products, per cent of total <sup>b</sup>						
			Oxetane			Cyclobutanone		Linear products <sup>c</sup>	Other products <sup>d</sup>
			<i>cis</i> 16	<i>trans</i> 19	Mix	<i>cis</i> 17	<i>trans</i> 20		
<i>n</i> -Hexane	-50	10 min	79	0		20	0	1	
		2 hr	79	0		19	0	2	
	25	30 min	78	0		20	0	2	
		1 hr	77	0		20	0	3	
		8 hr	75	0		22	0	3	
	25	20 hr	64	0		30	0	6	
	100	1 hr	5	0		88	0	7	
CH <sub>2</sub> Cl <sub>2</sub>	-50	2-3 weeks	90	0		5	0	5	
		1 hr	90	0		5	0	5	
	25	30 min			78	13	0	9	
		1 hr			71	18	0	11	
		8 hr			33	45	7	15	
	25	20 hr			17	56	9	18	
	CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	-50	2-3 weeks	92	0		0	0	8
1 hr					67	5	0	16	12
0		2 hr			64	5	0	18	13
25		30 min			51	9	0	20	20
25		1 hr			43	9	2	27	19
25		8 hr			13	13	5	59	10
25		20 hr			10	14	6	64	6
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	-50	10 min	100	0		0	0	0	0
		1 hr			83	13	0	4	0
	0	2 hr			80	15	0	5	0
	25	30 min			42	32	10	16	0
	25	1 hr			25	40	15	20	0
	25	4 hr			0	60	25	15	0
	25	20 hr			0	62	26	12	0

<sup>a</sup> Solutions were 1.0 *M* in *cis*-propenyl propyl ether, 0.50 *M* in bis(trifluoromethyl)ketene, and 0.50 *M* in reference compound, *o*-bis(trifluoromethyl)benzene. The reference compound was occasionally omitted since its presence as solid prevented complete mixing at temperatures below -50°. Reactions duplicate in each solvent were carried through the entire temperature range. <sup>b</sup> Ketene 1 completely reacted in all cases. <sup>c</sup> Largely or entirely linear ketone 18, varying amounts of unidentified products containing CF<sub>3</sub> groups attached to saturated carbon being present. <sup>d</sup> Unidentified products characterized by low-field CF<sub>3</sub> groups.

related cyclobutanones<sup>5,6</sup> and proceeds by addition of fluoride ion to the carbonyl carbon, ring opening to a stable carbanion, and elimination of fluoride ion. Under the same conditions, 11 did not react.



A proof of position of methoxy group in both 11 and 12 was obtained by hydrolysis with concentrated sulfuric acid. In both cases the product obtained after ring cleavage and decarboxylation was the expected difluoromethyl hexafluoroisopropyl ketone.

To provide further insight into the course of cycloadditions to ketene 1, a detailed study was made of reactions between *cis*- and *trans*-propenyl propyl ethers and 1. *cis*-Propenyl propyl ether (14) and *trans*-propenyl propyl ether (15) were prepared by a modified literature<sup>7</sup> procedure. The mixture of ethers

from this preparation was about 70% 14 and 30% 15; fractionation gave samples of 14 containing 3.5% 15 and of 15 containing 5.8% 14 by glpc. The ethers showed no tendency to interconvert during 8 days at 100° in sealed, alkali-washed glass tubes. Even in the presence of hexafluoroisobutyric acid, the acidic impurity generated in reactions of 1, equilibration was slow at 100°. The 96.5:3.5 mixture of 14 and 15 was converted to a 70.5:29.5 mixture after 8 days. The 94.2:5.8 mixture of 15 and 14 was slowly converted to a 44.5:55.5 mixture in 21 days. After 1 month, some polymerization had occurred; so the equilibrium point was not determined. However, the equilibrium mixture must contain between 55 and 70% *cis* ether 14. The rate of interconversion is sufficiently slow that acid catalysis did not influence the stereochemical results of reactions carried out in the temperature range -50 to 100°. Since light also effects interconversion between 14 and 15, reactions with 1 were carried out in the dark.

Reactions of 1 with ethers 14 and 15 followed the same general pattern as that with ethyl vinyl ether. Examination of the cycloaddition of 14 to 1 by <sup>19</sup>F nmr showed that 1 was consumed very rapidly, even at -50°, and that the major product area (79%) appearing at low temperature could be ascribed to *cis*-oxetane 16, while *cis*-cyclobutanone 17 was a minor product (20%). No change was observed after 2 hr at 0°, showing the absence of secondary reactions in hexane at low temperatures. At 25° a slow increase in proportion of 17 and linear ketone 18 at the expense of 16 was observed. This secondary reaction also proceeded

(6) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 5582 (1966).

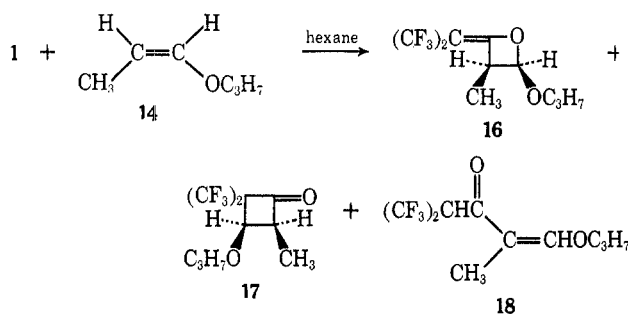
(7) W. Rottig and O. Liethen, German Patent 1,019,090 (1957); *Chem. Abstr.*, **54**, 10403 (1960).

TABLE III  
 REACTIONS OF *trans*-PROPENYL PROPYL ETHER WITH BIS(TRIFLUOROMETHYL)KETENE<sup>a</sup>

Solvent	Temp, °C	Time	Unreacted ketene 1	Products, per cent of total							
				Oxetane		Mix	Cyclobutanone		Linear product	Other products	
				<i>cis</i> 16	<i>trans</i> 19			<i>cis</i> 17			<i>trans</i> 20
Hexane	-50	10 min	100								
	0	15 min	21	0	26		0	51		2	
	0	1 hr	4	0	32		0	62		2	
	0	2 hr	0	0	34		0	63		3	
	25	30 min	0	0	31		0	67		2	
	25	24 hr	0	0	33		0	66		1	
	100	1 hr	0	0	15		4	78		3	
CH <sub>2</sub> Cl <sub>2</sub>	-50	2-3 weeks	0			37	15	33		15	
	0	15 min	0			36	12	34		18	
	0	2 hr	0			36	17	30		17	
	25	30 min	0			36	15	39		10	
	25	1 hr	0			34	12	41		13	
	25	8 hr	0			22	23	44		11	
	25	20 hr	0			11	31	46		12	
CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	-50	2-3 weeks	0			37	7	26		30	
	0	15 min	0			37	7	26		30	
	0	2 hr	0			30	9	28		33	
	25	30 min	0			37	6	30		27	
	25	1 hr	0			33	8	32		27	
	25	8 hr	0			12	18	34		27	9
	25	20 hr	0			9	22	39		27	3
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	-50	10 min	60			16	5	8		11	
	0	15 min	0			44	19	26		11	
	0	1 hr	0			41	17	27		15	
	0	2 hr	0			38	19	28		15	
	25	30 min	0			31	24	34		11	
	25	1 hr	0			13	32	36		19	
	25	4 hr	0			0	40	43		17	
	25	24 hr	0			0	43	43		14	

<sup>a</sup> Solutions 1.0 M *trans*-propenyl propyl ether, 0.50 M in 1, and occasionally 0.50 M in reference [*o*-bis(trifluoromethyl)benzene].

stereospecifically, and even at 100°, formation of 17 as the major product (88%) was stereospecific. These results are summarized in Table II. In accord with the spectral results, a reaction between 1 and 14 in hexane at 100° gave 89% isolated yield of 17 containing an amount of *trans*-cyclobutanone 20 corresponding to the *trans* isomer in the starting ether 14.



A check on the material balance in these reactions was obtained by incorporation of *o*-bis(trifluoromethyl)benzene, which provided a known, constant <sup>19</sup>F nmr absorption for reference. By this method a reasonable correspondence was shown between total amount of products observed from ketene 1 at various stages of reaction and the expected amount. The values obtained, however, are not very accurate, since the lower limit of detection by the nmr method in these systems represents a yield greater than 5%. That this is so can be seen, for example, from the lack of observed peaks for *cis* products in reactions in hexane of *trans* ether 15 (Table III), when starting 15 con-

tained 6% of the much more reactive *cis* ether 14 as impurity. Vpc analysis was frequently not satisfactory because of the mobile equilibria involved (see below).

Although the reaction of 1 and 14 is stereospecific in hexane even up to 100°, more polar solvents induce isomerization (Table II). Stereospecificity is preserved at 0° in methylene chloride, but lost rapidly from the oxetane 16 and slowly from cyclobutanone 17 at 25°. In both ethyl acetate and nitroethane, stereospecificity is lost from 16 but preserved with 17 at 0° and lost from 17 at 25° (more slowly in ethyl acetate). The trend is clearly one of increased isomerization with increased solvent polarity, although again ethyl acetate ( $\epsilon$  6.0) is anomalous in being more effective than methylene chloride ( $\epsilon$  9.1). Since the reactions are complicated and, in the case of ethyl acetate, lead to unusually large amounts of by-products, deviations from a simple ranking by polarity are not unexpected.<sup>8</sup>

Another striking feature of Table II is the increasing amount of oxetane 16 and decreasing amount of cyclobutanone 17 formed with increasing solvent polarity at -50°, *i.e.*, under conditions which give kinetically determined products. With increasing temperature and/or increasingly polar solvents the labile oxetane 16 is easily scrambled and, at 25° or over, also easily converted to cyclobutanones, the latter being the first isolable products. Cyclobutanone 17 is converted at still higher temperature and especially in the more polar

(8) S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Amer. Chem. Soc.*, **88**, 5254 (1966), observed a similar order in olefin cycloadditions involving dipolar intermediates.

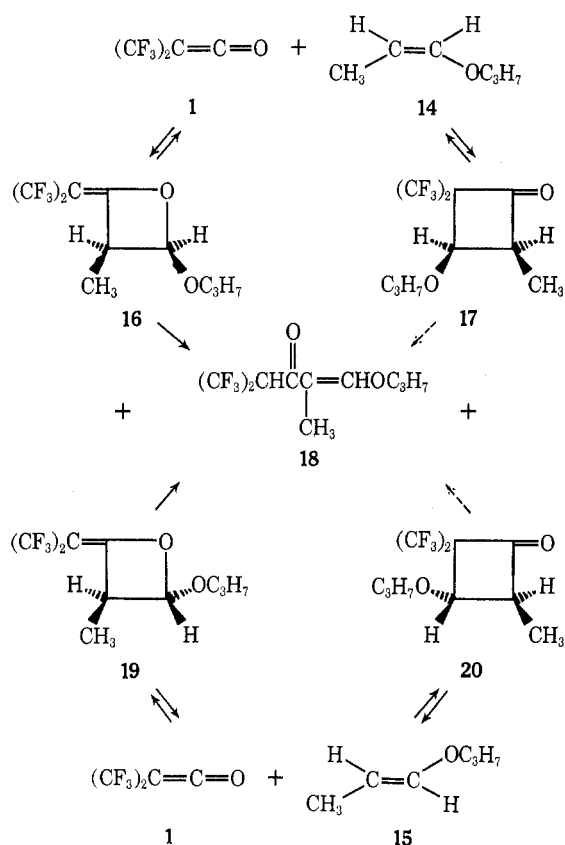


Figure 1.—Reaction scheme for *cis*- and *trans*-propenyl propyl ether.

solvents to isomeric cyclobutanone 20 and ring opened to linear ketone 18. The slow isomerization 17 → 20 + 18 has been carried out separately; a neat sample of 17 was converted in 60 hr at 100° to a mixture containing 80% 17 and 20 (13:87) and 20% 18. Under the same conditions, pure 20 was converted to essentially the same mixture.

Equilibration of 17 ⇌ 20 is quickly established with a trace of cesium fluoride in a small amount of glyme. Mixtures containing varying amounts of 17 and 20 equilibrated exothermically when shaken with the fluoride catalyst to give 10:90 mixtures of 17 and 20 with substantially no 18 present. Heating of the mixture at 100° for several hours in the presence of fluoride ion catalyst converted it entirely to linear ketone 18. The activity of the catalyst is apparently due to its ability to abstract a proton α to the carbonyl group, causing loss of stereochemistry at that position. At elevated temperatures the resulting anion undergoes irreversible ring opening to give 18 after protonation.

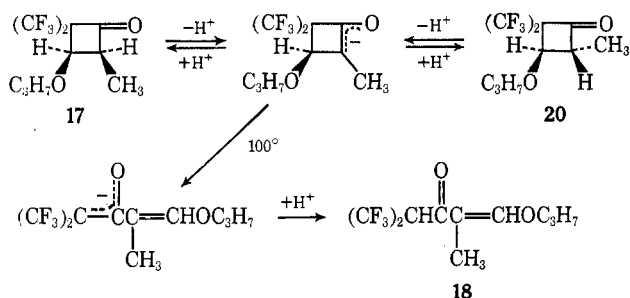


Table III summarizes the results with *trans* ether 15 and 1. Trends similar to those observed with ether 14

can also be seen to obtain with 15. Stereospecificity is preserved with 15 in hexane up to 25°, but slowly lost at 100°. With increasingly polar solvents, stereospecificity is more easily lost and mixed oxetanes and cyclobutanones are obtained in nitroethane even at -50°. With *trans* ether 15, the scrambling of oxetanes under milder conditions than for cyclobutanones was not observed (as it was with 14), perhaps because of the ease with which both were scrambled. The ratio of oxetanes to cyclobutanones in the primary reaction increased with solvent polarity, as did the rate of conversion of oxetanes to cyclobutanones and the formation of ring-opened products.

Additional points emerge from comparison of the results in Tables II and III. Ether 15 reacts much less rapidly than 14, even though the *trans*-substituted cyclic products are thermodynamically the more stable, so that at low temperatures unreacted 1 can be detected.<sup>9</sup> Since with 15 the reaction can be slowed sufficiently for observation while 1 is still present, a much slower rate of reaction of 1 with 15 in hexane than in nitromethane can be observed at -50°. The solvent dependence of rate of ketene 1 reaction is the same as that of the secondary reactions, increasing with increasing solvent polarity. Product from 15 are more easily scrambled, to the extent that in nitroethane, at -50°, mixed cyclobutanones and oxetanes are obtained. With 14 in nitroethane, on the other hand, stereochemistry is retained at -50°, and lost from oxetane but not cyclobutanone at 0°.

The ratios of oxetane:cyclobutanone mixtures formed at low temperatures can be used to indicate the dependence of product types formed in the primary reaction on solvent. These ratios of oxetane to cyclobutanone increased steadily for both 14 at -50° and 15 at 0°, but was larger for 14 (Table IV).

TABLE IV  
SOLVENT DEPENDENCE OF  
OXETANE-CYCLOBUTANONE RATIOS

ε (°C)	Solvent	Oxetane-cyclobutanone from	
		<i>cis</i> 14	<i>trans</i> 15
1.89 (20)	Hexane	4.0	0.53
9.08 (20)	CH <sub>2</sub> Cl <sub>2</sub>	18	0.77
6.02 (25)	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Very large	1.1
28.0 (30)	C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	Very large	1.0

The evidence indicates that the system 1:14:15 at 25° in a polar solvent can be a complicated pseudo-equilibrium in which first oxetanes and then cyclobutanones predominate, and from which components can go irreversibly to acyclic ketones and other unidentified products. The generalized scheme, parts of which can be isolated by the use of nonpolar solvents, is shown in Figure 1 with racemic partners omitted for simplification.

**Styrenes.**—Olefins with insufficient nucleophilicity to cycloadd to the carbonyl group of 1 give only cyclobutanones as cycloadducts.<sup>1</sup> One such olefin, styrene, showed no indication of oxetane formation with 1, even when the reaction was examined by nmr in the same manner as described above for the propenyl propyl ethers. The product, 2,2-bis(trifluoromethyl)-3-

(9) The same difference in reactivity has been reported in ref 4, wherein cyclobutanone formation with diphenylketene was found to be ca. 200 times faster with 14 than with 15.

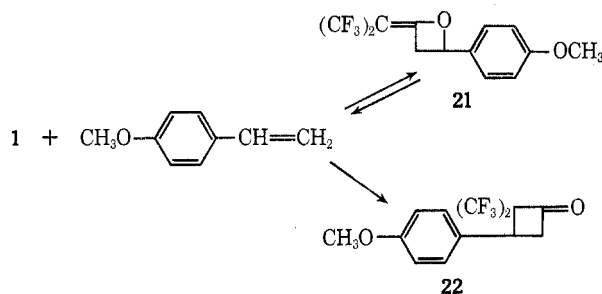
TABLE V  
 REACTION OF 1 WITH STYRENE<sup>a</sup>

Solvent	Unreacted ketene		Cyclobutanone		Linear products	
	80°, 14 hr	180°, 30 min	80°, 14 hr	180°, 30 min	80°, 14 hr	180°, 30 min
Hexane	100	80	0	20	0	0
CH <sub>2</sub> Cl <sub>2</sub>	31	13	51	67	18	20
CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	27	5	41	60	32	35
CH <sub>3</sub> NO <sub>2</sub>	0	0	36	36	64	64

<sup>a</sup> Solutions were 1.0 M in styrene, 0.50 M in 1, and 0.50 M reference [*o*-bis(trifluoromethyl)benzene]. Sealed tubes were heated at 80° for 14 hr, examined by nmr, and then heated at 180° for 30 min and reexamined. Values given are per cent of total products + ketene 1.

phenylcyclobutanone, is apparently the first and only cycloadduct formed in a reaction which requires elevated temperatures. Both reaction rate and amount of linear products increased markedly with increasing polarity of solvent. At 80° for 14 hr, no reaction was detected in hexane, whereas complete reaction had occurred in nitromethane. At 180° for 30 min, only cyclobutanone was found as product in hexane, in contrast to the 2:1 ratio of linear products to cyclobutanone formed at 80° in nitromethane and remaining unchanged at 180° (Table V).

Activation by a *p*-methoxy group is sufficient to allow reaction at 25° and below. Isolation of the product afforded a good yield of cyclobutanone 22, but an unstable oxetane, 21, was detected by nmr. The oxetane was the major product in the polar solvent, nitroethane, at low temperature and the minor product in hexane. The reaction was also much faster in nitroethane (Table VI).


 TABLE VI  
 REACTION OF 1 WITH *p*-METHOXYSTYRENE<sup>a</sup>

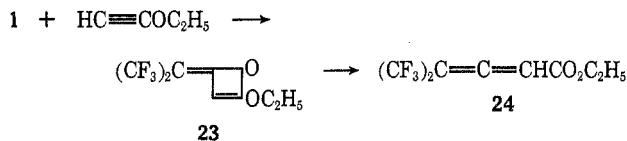
Solvent	Temp, °C	Time	Per cent of total			Linear products
			1	21	22	
Hexane	25	15 min	73	4	15	8
	25	18 hr	1	23	68	8
	100	30 min	1	2	89	8
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>	-50	15 min	27	56	2	17
	50	5 min	1	25	57	17
	25	18 hr	0	0	80	20

<sup>a</sup> Tubes loaded as described for the propenyl propyl ether runs, 1.0 M in *p*-methoxystyrene and 0.50 M in 1.

**Ethoxyacetylene.**—Acetylenes cycloadd to 1 with direct formation of cyclobutenones,<sup>1</sup> while other ketenes give cyclobutenones only with activated acetylenes such as with ethoxyacetylene<sup>10</sup> and various diethylaminoacetylenes.<sup>11</sup> Reaction of 1 with ethoxyacetylene

(10) (a) J. Druey, E. F. Jenny, K. Schenker, and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962); (b) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **27**, 3743 (1962).

at -80° follows an entirely different course; just as with the more nucleophilic olefins and 1, this very reactive acetylene appears to add to the carbon-oxygen bond of 1. Evidence for the oxete 23 so formed was obtained by low temperature nmr. This unstable oxete did not isomerize to a cyclobutanone, but rather underwent an electrocyclic transformation to allenic ester 24.<sup>12</sup>



## Discussion

Two modes of cycloaddition to compound 1 are available, across the carbon-oxygen and the carbon-carbon double bonds. The previously described<sup>1,5</sup> Diels-Alder addition of butadiene to the carbonyl group of 1 accords with the Woodward-Hoffmann selection rules<sup>13</sup> for concerted cycloadditions in carbon systems. The pronounced solvent effect<sup>1</sup> may be interpreted as resulting from a polarized transition state in which the oxygen atom and trifluoromethyl groups stabilize a partial negative charge. Evidence against a stepwise 4 + 2 cycloaddition, aside from possible violation of the selection rules, is the absence of 2 + 2 cycloadducts and the relatively stringent conditions required for the reaction, both indicative of a highly ordered transition state leading to product.

Concordant with the view that cycloadditions to the ketene carbonyl follow Woodward-Hoffmann rules, the present work demonstrates that 2 + 2 cycloadditions to carbonyl of 1 proceed through dipolar intermediates of finite lifetime. The isomerization reactions observed with propenyl ethers, 14 and 15, are direct evidence for such intermediates, 25a and 25b, formed as tight ion pairs in nonpolar solvents and as essentially a single solvent-separated dipolar species in polar solvents (Figure 2). However, intermediate 25 (from 1 and either 14 or 15) is not necessarily in equilibrium with the possible cyclobutanone precursor, 26, since mixtures of the isomeric oxetanes can be obtained with little or no indication of formation of mixtures of the isomeric cyclobutanones.<sup>14</sup> Another distinguishing characteristic is the increase in ratio of oxetane to cyclobutanone formed at low temperatures as solvent polarity increases, indicating an intermediate or transition state on the way to cyclobutanone of lower polarity than 25 (Table IV). These observations contrast with the assumption of Binsch, Feiler, and Huisgen that dipolar intermediates from dimethylketene and 14 or 15 would necessarily be identical and capable of closing to a cyclobutanone.<sup>15</sup>

We take our results as an indication that a significant barrier exists between 25 and 26. Formation of 25a or

(11) W. E. Truce, R. H. Bavry, and P. S. Bailey, Jr., *Tetrahedron Lett.* 5651 (1968).

(12) W. J. Middleton, *J. Org. Chem.*, **30**, 1307 (1965), reports a similar series of reactions with ethoxyacetylene and hexafluoroacetone.

(13) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(14) As examples, see the results in Table II for reactions of 14 in methylene chloride at 25° and in nitroethane at 0°. Cyclobutanone isomerization seems to require a somewhat higher temperature than that for oxetane.

(15) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968).

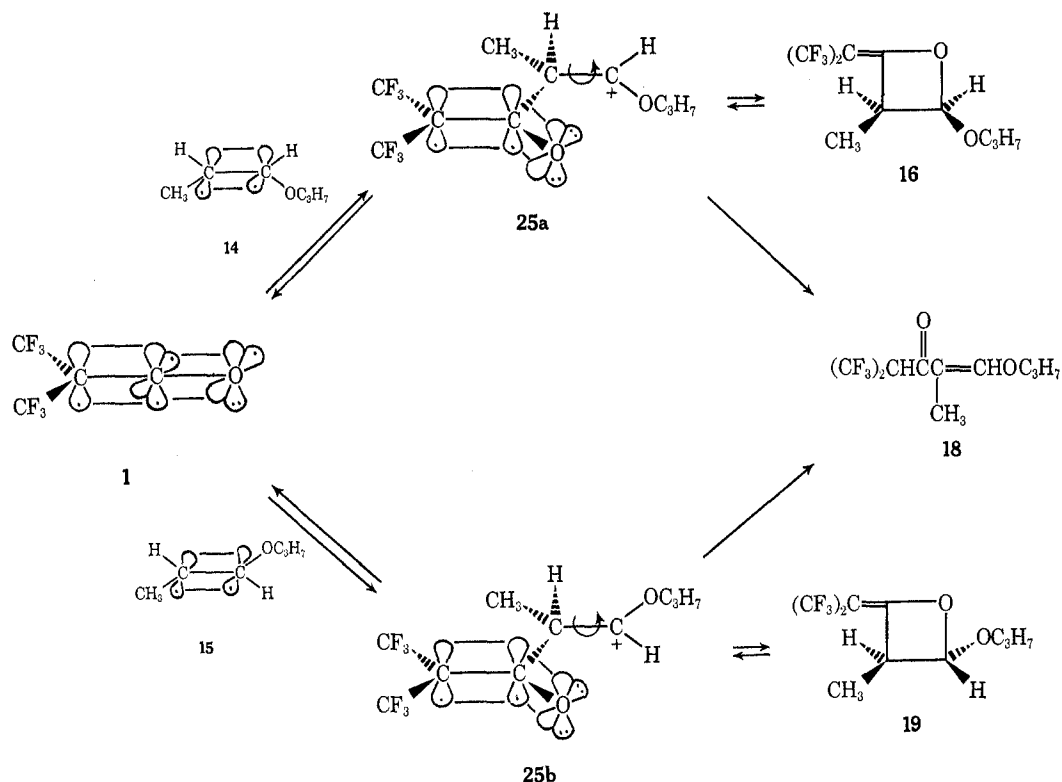


Figure 2.—Intermediates in a cycloaddition to the carbonyl of bis(trifluoromethyl)ketene.

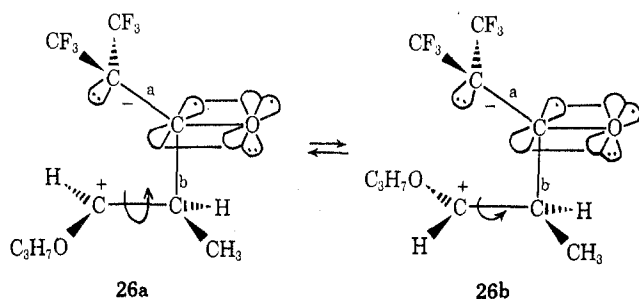


Figure 3.—Proposed intermediates in cycloaddition of propyl propenyl ether to the C=C of bis(trifluoromethyl)ketene.

**25b** as depicted in Figure 2 involves attack at the isolated carbonyl  $\pi$  system to give directly the delocalized, well-stabilized anionic portion of a dipolar intermediate which can ring close with minimum movement of nuclei. Attack on the olefinic bond to form **26** would involve approaching the other  $\pi$  orbital on the central carbon atom, leading to a presumably higher energy dipole with a stabilized (but not delocalized) negative charge in an  $sp^3$  orbital. Closure of **26** to cyclobutanones could occur directly, but equilibration with **25** would require not only solvation to reduce Coulombic attraction but also synchronous rotation about bonds a and b (Figure 3).

Although conditions have been found where **25** is not readily transformed to **26**, facile interconversion in other cases can by no means be ruled out, particularly at temperatures above  $25^\circ$ .

Because all the cycloadducts seem to dissociate to starting materials in the  $25$ – $100^\circ$  temperature range (see below), the observed equilibration between cyclobutanones **17** and **20** can occur indirectly. The dissociated ethers can isomerize *via* oxetane intermedi-

ate **25** and then re-form the mixed cyclobutanones without having to pass through intermediate **26**. However, the results with *trans* ether **15** at  $-50^\circ$ , where the reverse reaction is not seen even on long standing, provide evidence for the existence of **26a** and **26b** as rotational conformers. Stable mixtures (at low temperatures) of cyclobutanones as well as oxetanes are formed in all solvents but hexane (Table III).

The effect of solvent polarity on rate of cyclobutanone formation appears to be large and can also be attributed to the intermediacy of **26**, in which the negative charge is stabilized by trifluoromethyl groups.<sup>16</sup> Where positive charge is well stabilized, as by an alkoxy oxygen, the dipolar intermediate is favored.<sup>17</sup> With less nucleophilic coreactants, **1** appears to form cyclobutanones by a less polar mechanism, perhaps involving an unsymmetrical polarized transition state.<sup>1</sup> Similar concerted, though unsymmetrical, cycloadditions have been proposed or implied for other ketenes.<sup>15,18–22</sup>

In addition to *cis-trans* isomerization reactions, intermediates from **1** and **14** or **15** were found to initiate polymerization of the vinyl ethers. In these cationic polymerizations, ketene **1** is acting as a Friedel-Crafts catalyst to generate a dipolar species (presumably **25**,

(16) Cf. S. Andreades, *J. Amer. Chem. Soc.*, **86**, 2003 (1964).

(17) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963); J. C. Martin, P. G. Gott, and H. U. Hostettler, *ibid.*, **32**, 1654 (1967). Indications that cycloaddition of very nucleophilic olefins to nonfluorinated ketenes can also be stepwise were obtained from reactions of enamines with dimethylketene.

(18) R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964).

(19) W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

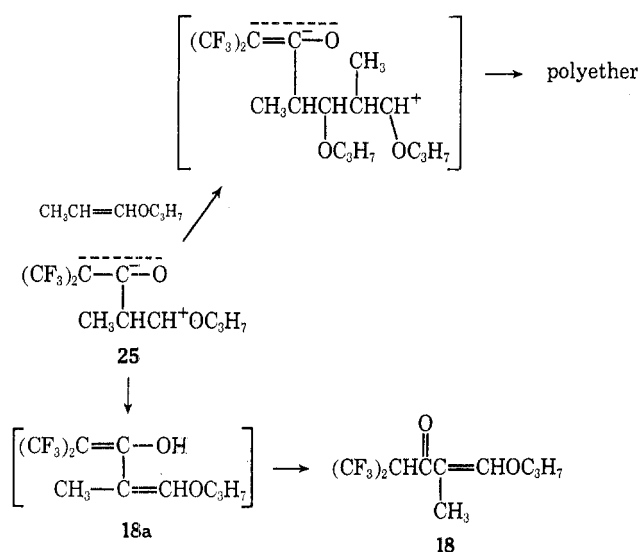
(20) T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963).

(21) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968).

(22) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965).

since its charge separation is greater than that of 26), which is trapped by another molecule of vinyl ether in a propagation reaction which leads ultimately to polymer. The cycloaddition studies were carried out with excess 14 and 15 to ensure complete reaction of 1. Polymerization was most troublesome with *trans* ether 15. The unusual by-products formed in ethyl acetate as solvent may have originated in a similar attack of dipolar intermediate on ethyl acetate.

Acyclic products of proton transfer, such as 18, are easily explained through the dipolar intermediates. The generally increasing amounts of 18 with decreasing amounts of oxetanes, particularly in polar solvents (Tables II and III), indicate that 25 is capable of stabilizing itself by migration of a proton. The enol 18a is not necessarily an intermediate, since proton migration could give 18 directly.



According to Figure 1, the cycloadditions of 14 and 15 to 1 are reversible reactions from which acyclic products such as 18 may be withdrawn by essentially irreversible processes. Evidence for the reversibility of oxetane formation was obtained by reacting 1 and a twofold excess of 14 in hexane at 0° to convert 1 to oxetane 16 (65%) and cyclobutanone 17 (35%), then adding a sixfold excess of ethyl vinyl ether and warming to 25°. Reaction was slow, since no change in the <sup>19</sup>F nmr spectrum was observed after 2 and 6 hr. After 24 hr at 25°, the nmr spectrum of the mixture showed the presence of ethyl vinyl ether cycloadducts to 1. Integration of <sup>19</sup>F nmr peaks and comparison with a synthetic mixture of the two cyclobutanones (which had been isolated) indicated a mixture of 38% 16, 19% 7, 38% 17, and 5% 8. The conditions for generation and capture of 1 in this experiment correspond to the mildest conditions for conversion of oxetane 16 to cyclobutanone 17, further evidence that intermediates 25 and 26 are not easily interconverted.

Repetition of the above experiment in nitroethane resulted in conversion of all oxetane to cyclobutanones in 4 hr at 25° with peaks attributable to 8 present. Since both 17 and 20 were present, the amount of 8 could not be determined by integration, but was found to be greater than 20% by comparison with a synthetic mixture of known amounts.

Complete reversibility of cyclobutanone formation was also demonstrated by capture of dissociated 1 with ethyl vinyl ether. Pure samples of 17 and 20 were heated at 100° with a twofold excess of ethyl vinyl ether, conditions shown before to lead to slow isomerization of both 17 and 20. Increased viscosity showed polymerization of vinyl ethers had occurred. Examination by vpc at low temperature showed that 17 gave product composed of 11.5% 17, 13.5% 20, 29% 8, and 46% 9. Similarly, 20 was shown to give 9 as the major product.

A related series of experiments involving isomerization of 17 and 20 at 100° for 9 hr in the presence of 14 or 15 with and without solvents gave unexpected results. In all cases 17 or 20 was converted to mixtures of 17, 20, and 18. With *cis* ether 14 present, regardless of whether the cyclobutanone was 17 or 20 and regardless of the solvent, only the *cis* ether 14 (no 15) could be detected after heating. However, if *trans* ether 15 was used, mixtures of 14 and 15 were detected after heating. Our explanation of these results is that 26a and 26b, although rotamers which can be interconverted at 25–100°, have appreciable differences in energy and in stability. Rotamer 26a, derived from 14, is least stable and dissociates preferentially to form 1 and 14. This rationalization would, of course, not be available if the concerted mechanism for cycloaddition of vinyl ethers to 1 were assumed.

### Experimental Section<sup>23</sup>

**2-Benzoyloxy-4-hexafluoroisopropylidenoxetane (2) and 2,2-Bis(trifluoromethyl)-3-benzoyloxycyclobutanone (3).**—Vinyl benzoate (8.0 g, 0.054 mol) containing 0.5 g of phenothiazine and 1 (9.0 g, 0.05 mol) were sealed in an evacuated Carius tube and heated on a steam bath overnight. The low boiler (1 g) was evaporated and the solid residue was recrystallized from hexane to give 5.6 g (34%) of 2, mp 99–100°. Another recrystallization from hexane gave 5.35 g: mp 100–101°; ir 5.72 (ester C=O), 5.82 μ (exocyclic C=C); nmr <sup>1</sup>H at τ 2.17 (multiplet, area 2, phenyl H), 2.68 (multiplet, area 3, phenyl H), 3.09 (triplet, area 1, J<sub>H/H</sub> = 3.7 Hz, ring C-H), 6.32 (complex multiplet, area 2, ring CH<sub>2</sub>); <sup>19</sup>F at 58.7 (multiplet, area 1, CF<sub>3</sub>), 59.3 ppm (multiplet, area 1, CF<sub>3</sub>).

The filtrates from recrystallization of 2 were distilled to give 1.7 g of recovered vinyl benzoate and 6.9 g (42%) of 3, bp 86° (1 mm), n<sub>D</sub><sup>25</sup> 1.4464. The product solidified on standing; recrystallization from hexane gave 3.5 g: mp 45–46°; ir 5.50 (ring C=O), 5.74 μ (ester C=O); nmr <sup>1</sup>H at τ 1.85 (multiplet, 2, phenyl H), 2.40 (multiplet, 3, phenyl H), 3.93 (triplet, 1, J<sub>H/H</sub> = 8.0 Hz, with further fine structure, ring CH), 6.23 (doublet, 2, J<sub>H/H</sub> = 8.0 Hz, with further fine structure, ring CH<sub>2</sub>); <sup>19</sup>F at 64.8 (quartet, 1, J<sub>F/F</sub> = 9.0 Hz, CF<sub>3</sub>), 68.6 ppm (quartet, 1, J<sub>F/F</sub> = 9.0 Hz, CF<sub>3</sub>).

*Anal.* Calcd for C<sub>13</sub>H<sub>5</sub>F<sub>6</sub>O<sub>3</sub>: C, 47.89; H, 2.47; F, 34.97. Found for 2: C, 48.09; H, 2.67; F, 35.23. Found for 3: C, 47.91; H, 2.70; F, 34.79.

**2-Acetoxyvinyl Hexafluoroisopropyl Ketone (6).**—A mixture of 9.0 g (0.05 mol) of 1 and 6.0 g (0.07 mol) of vinyl acetate was heated overnight in a sealed tube at 100°. Near the end of the heating cycle, rapid darkening occurred; so the reaction mixture was distilled to give 13.3 g (99%) of mixed products, bp 30–90° (1 mm). (A similar complete reaction was obtained in only 4 hr at 100° in a separate experiment.) Fractions totaling 5.3 g (40%), bp 55–57° (1 mm), solidified and two recrystallizations from CCl<sub>4</sub> gave 1.1 g of pure 6, mp 49–50°. Lower boiling cuts

(23) Melting and boiling points are uncorrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer. Peak center positions for <sup>1</sup>H are reported τ = 10 - δ<sub>H</sub> ppm. Fluorine nmr spectra were obtained with a Varian A56-60 spectrometer using CFCl<sub>3</sub> as an external standard. Peak center positions for <sup>19</sup>F are reported in parts per million upfield from CFCl<sub>3</sub>. Solid samples were dissolved in acetone-d<sub>6</sub> (20% solutions) for nmr determinations.



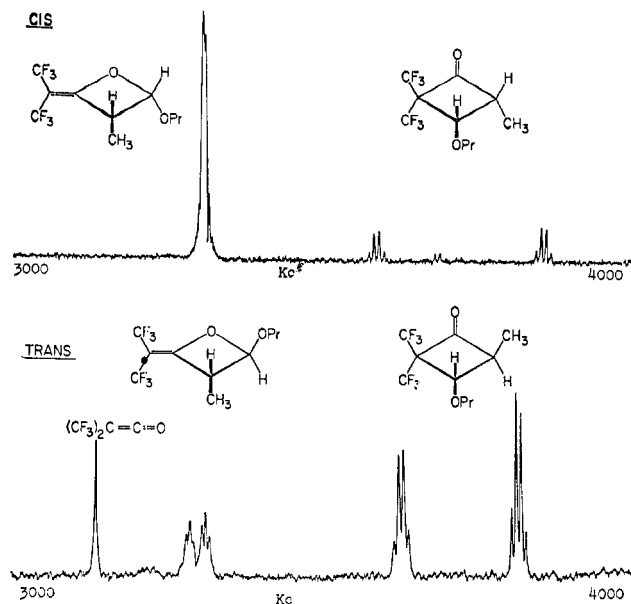


Figure 4.— $^{19}\text{F}$  spectra observed for  $(\text{CF}_3)_2\text{C}=\text{C}=\text{O}$  plus *cis*- and *trans*-propenyl propyl ethers in hexane at  $-50^\circ$ .

were shown to contain 5 and higher boiling cuts 4 along with more 6. For 6: ir 5.58 (ester  $\text{C}=\text{O}$ ), 5.86 (ketone  $\text{C}=\text{O}$ ), 6.09  $\mu$  ( $\text{C}=\text{C}$ ); nmr  $^1\text{H}$  at 486, 473, 359, and 346 Hz (AB, 2,  $J_{\text{H}/\text{H}} = 13$  Hz, *trans*  $\text{CH}=\text{CH}$ ),  $\tau$  5.20 [septet, 1,  $J_{\text{H}/\text{F}} = 8.0$  Hz,  $(\text{CF}_3)_2\text{CH}-$ ], 8.23 (singlet, 3,  $\text{CH}_3$ );  $^{19}\text{F}$  at 64.7 ppm [doublet,  $J_{\text{F}/\text{F}} = 8.0$  Hz,  $(\text{CF}_3)_2\text{CH}-$ ].

*Anal.* Calcd for  $\text{C}_8\text{H}_8\text{F}_6\text{O}_3$ : C, 36.39; H, 2.29; F, 43.18. Found: C, 36.49; H, 2.68; F, 43.00.

**2-Acetoxy-4-hexafluoroisopropylidenoxetane (4) and 2,2-Bis(trifluoromethyl)-3-acetoxycyclobutanone (5).**—The reaction above of vinyl acetate and 1 without solvent gave largely the linear product 6 and was complete in 4 hr at  $100^\circ$ . The same reactants in hexane gave very little reaction after 5 hr at  $100^\circ$ . Long reaction times are required in a nonpolar solvent such as hexane, but the stabilizing influence of hexane allows retention of the products with cyclic structures.

A mixture of vinyl acetate (17.0 g, 0.20 mol), 1 (36.0 g, 0.20 mol), 0.5 g of phenothiazine, and 25 ml of hexane in a sealed tube was heated for 63 hr in a steam bath. By distillation there was isolated 21.8 g (41%) of a mixture, bp  $60\text{--}80^\circ$  (14 mm), and 23.2 g (44%) of 4, bp  $98^\circ$  (14 mm). The lower boiling material could be separated by vpc into nearly equal amounts of 5 and an unknown compound plus a trace of 6. The unknown product gave a single broad  $^{19}\text{F}$  nmr peak and on standing was converted to 6; the unknown and 6 may therefore be *cis* and *trans* isomers, respectively. For 4: ir 5.61 (ester  $\text{C}=\text{O}$ ), 5.83  $\mu$  (exocyclic  $\text{C}=\text{C}$ ); nmr  $^1\text{H}$  at  $\tau$  3.48 (triplet, 1,  $J_{\text{H}/\text{H}} = 3.6$  Hz,  $\text{CH}$ ), 6.62 (broad, 2,  $\text{CH}_2$ ), 8.18 (singlet, 3,  $\text{CH}_3$ );  $^{19}\text{F}$  at 59.1 (quartet, 1,  $J_{\text{F}/\text{F}} = 6.5$  Hz,  $\text{CF}_3$ ), 59.9 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 6.5$  Hz, plus fine structure,  $\text{CF}_3$ ). For 5: ir 5.49 (ring  $\text{C}=\text{O}$ ), 5.65  $\mu$  (ester  $\text{C}=\text{O}$ ); nmr  $^1\text{H}$  at  $\tau$  4.45 (broad triplet, 1,  $J_{\text{H}/\text{H}} = 7.6$  Hz,  $\text{CH}$ ), 6.61 (doublet, 2,  $J_{\text{H}/\text{H}} = 7.6$  Hz,  $\text{CH}_2$ ), 8.22 (singlet, 3,  $\text{CH}_3$ );  $^{19}\text{F}$  at 65.5 (quartet, 1,  $J_{\text{F}/\text{F}} = 8.5$  Hz,  $\text{CF}_3$ ), 68.6 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 8.5$  Hz,  $\text{CF}_3$ ).

*Anal.* Calcd for  $\text{C}_8\text{H}_8\text{F}_6\text{O}_3$ : C, 36.39; H, 2.29; F, 43.18. Found for 4: C, 36.38; H, 2.19; F, 43.67. Found for 5: C, 36.63; H, 2.48; F, 43.07.

**2-Ethoxyvinyl Hexafluoroisopropyl Ketone (9).**—A mixture of 9.0 g (0.05 mol) of 1 and 4.0 g (0.055 mol) of ethyl vinyl ether in a sealed tube was allowed to warm from a liquid nitrogen temperature. Reaction occurred immediately on melting, and direct distillation gave 0.6 g (5%) of 8 (characterization below), bp  $38^\circ$  (5 mm), and 11.6 g (92%) of 9, bp  $77^\circ$  (5 mm),  $n_D^{25}$  1.3912. The latter solidified on cooling and could be recrystallized from hexane: mp  $27^\circ$ ; ir 5.92 (conj  $\text{C}=\text{O}$ ), 6.30  $\mu$  (conj  $\text{C}=\text{C}$ ); nmr  $^1\text{H}$  at 463.8, 451.2, 345.0, and 332.4 Hz (AB, 2,  $J_{\text{H}/\text{H}} = 12.6$  Hz, *trans*  $\text{CH}=\text{CH}$ ),  $\tau$  5.85 [septet, 1,  $J_{\text{H}/\text{F}} = 8.1$  Hz,  $(\text{CF}_3)_2\text{CH}-$ ], 6.22 (quartet, 2,  $J_{\text{H}/\text{H}} = 7.4$  Hz,  $\text{CH}_2\text{CH}_2$ ), 9.00 (triplet, 3,  $J_{\text{H}/\text{H}} = 7.4$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{19}\text{F}$  at 65.1 ppm [doublet,  $J_{\text{H}/\text{F}} = 8.1$  Hz,  $(\text{CF}_3)_2\text{CH}-$ ].

*Anal.* Calcd for  $\text{C}_8\text{H}_8\text{F}_6\text{O}_2$ : C, 38.43; H, 3.23; F, 45.60. Found: C, 38.61; H, 3.38; F, 45.52.

**2,2-Bis(trifluoromethyl)-3-ethoxycyclobutanone (8).**—Ethyl vinyl ether (20.0 g, 0.28 mol), 1 (40.0 g, 0.22 mol), and 25 ml of hexane in a sealed, evacuated tube were allowed to warm to  $25^\circ$  and stand overnight. Distillation of the reaction mixture gave 33.7 g (67%) of 8, bp  $47^\circ$  (10 mm), and 6.7 g (13%) of 9, bp  $77^\circ$  (5 mm). For 8: ir 5.50  $\mu$  (ring  $\text{C}=\text{O}$ ); nmr  $^1\text{H}$  at  $\tau$  5.57 (triplet, 1,  $J_{\text{H}/\text{H}} = 8.0$  Hz with fine structure,  $\text{CH}$ ), 6.76 (doublet, 2,  $J_{\text{H}/\text{H}} = 8.0$  Hz, ring  $\text{CH}_2$ ), 6.59 (quartet, 2,  $J_{\text{H}/\text{H}} = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ ), 9.05 (triplet, 3,  $J_{\text{H}/\text{H}} = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{19}\text{F}$  at 64.8 (quartet, 1,  $J_{\text{F}/\text{F}} = 8.6$  Hz,  $\text{CF}_3$ ), 68.5 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 8.6$  Hz,  $\text{CF}_3$ ).

*Anal.* Calcd for  $\text{C}_8\text{H}_8\text{F}_6\text{O}_2$ : C, 38.43; H, 3.23; F, 45.60. Found: C, 38.57; H, 3.15; F, 45.05.

Essentially the same experiment using nitromethane in place of hexane gave 21.3 g (43%) of 8 and 20.2 g (40%) of 9. Examination of the reaction products in hexane and in nitromethane at  $-50^\circ$  by fluorine nmr showed low-field  $^{19}\text{F}$  resonances as multiplets at 58.8 and 59.4 ppm, respectively, for oxetane 7, which disappeared on warming while resonances for 8 and 9 appeared.

**1,1-Bis(trifluoromethyl)-4-ethoxybuta-1,3-dien-2-yl Hexafluoroisobutyrate (10).**—Products from 1 and ethyl vinyl ether depend on conditions. Uncontrolled neat reactions tend to form 9 and reactions in nonpolar solvents give 8 as the main product isolated, but numerous by-products may also appear. One such product is the 2:1 adduct 10 formed with excess 1 and heat.

A mixture of 15.7 g (0.063 mol) of 9 and 21.0 g (0.12 mol) of 1 was heated in a sealed tube at  $100^\circ$  overnight. Distillation afforded 25 g (93%) of 10: bp  $73^\circ$  (1 mm);  $n_D^{25}$  1.3575; ir 5.53 (vinyl ester  $\text{C}=\text{O}$ ), 5.82 (vinyl ester  $\text{C}=\text{C}$ ), 6.07  $\mu$  ( $\text{C}=\text{C}$ ); nmr  $^1\text{H}$  at 357, 352, 265, and 260 Hz (AB, 2,  $J_{\text{H}/\text{H}} = 5.0$  Hz,  $\text{CH}=\text{CH}$ ),  $\tau$  6.48 [septet, 1,  $J_{\text{H}/\text{F}} = 8.0$  Hz,  $(\text{CF}_3)_2\text{CH}$  overlapping with quartet, 2,  $J_{\text{H}/\text{H}} = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ ], 9.02 (triplet, 3,  $J_{\text{H}/\text{H}} = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{19}\text{F}$  at 63.5 (quartet, 3,  $J_{\text{F}/\text{F}} = 11.1$  Hz,  $=\text{CCF}_3$ ), 67.2 (quartet, 3,  $J_{\text{F}/\text{F}} = 11.1$  Hz,  $=\text{CCF}_3$ ), 66.9 ppm [doublet, 6,  $J_{\text{H}/\text{F}} = 8.0$  Hz,  $(\text{CF}_3)_2\text{CH}$ ].

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{12}\text{F}_{12}\text{O}_3$ : C, 33.67; H, 1.89; F, 53.27. Found: C, 34.32; H, 2.04; F, 52.88.

**2-Methoxy-2,3,3-trifluoro-3-hexafluoroisopropylidenoxetane (11) and 2,2-Bis(trifluoromethyl)-3-methoxy-3,4,4-trifluorocyclobutanone (12).**—A mixture of 36 g (0.20 mol) of 1 and 11.2 g (0.10 mol) of methyl trifluorovinyl ether containing some phenothiazine as inhibitor was heated in a sealed tube for 60 hr at  $100^\circ$ . Distillation gave 6.0 g (20%) of 12, bp  $94\text{--}96^\circ$ , and 15.1 g (55%) of 11, bp  $110\text{--}112^\circ$ . A sample of 12, bp  $95^\circ$ , was purified by vpc: ir 5.42  $\mu$  (ring  $\text{C}=\text{O}$ ); nmr  $^1\text{H}$  at  $\tau$  6.52 (multiplet,  $\text{CH}_3$ );  $^{19}\text{F}$  at 64.1 ppm [unresolved structure, 6,  $(\text{CF}_3)_2\text{C}$ ], 6473, 6733, 6948, and 7208 Hz (AB with fine structure, 2,  $J_{\text{F}/\text{F}} = 260$  Hz, ring  $\text{CF}_2$ ), 134.1 ppm (multiplet, 1,  $\text{CF}$ ).

A sample of 11, bp  $112^\circ$ , was analyzed: ir 5.72  $\mu$  (exocyclic  $\text{C}=\text{C}$ ); nmr  $^1\text{H}$  at  $\tau$  6.58 (doublet,  $J_{\text{H}/\text{F}} = 0.7$  Hz,  $\text{CH}_3$ );  $^{19}\text{F}$  at 61.5 (multiplet, 3,  $\text{CF}_3$ ), 62.5 (multiplet, 3,  $\text{CF}_3$ ), 117.5 (multiplet, 2,  $\text{CF}_2$ ), 90.1 ppm (multiplet, 1,  $\text{CF}$ ).

*Anal.* Calcd for  $\text{C}_7\text{H}_8\text{F}_9\text{O}_2$ : C, 28.99; H, 1.04; F, 58.97. Found for 12: C, 29.25; H, 0.85; F, 59.34. Found for 11: C, 30.15; H, 1.80; F, 58.68.

As proof of structure, both 11 and 12 were hydrolyzed with sulfuric acid.

An immiscible mixture of 15.0 g of 12 and 30 ml concentrated  $\text{H}_2\text{SO}_4$  was heated in a sealed tube at  $175^\circ$  for 8 hr. When the tube was opened, carbon dioxide (characterized by ir) was evolved. Distillation of the clear top layer afforded 4.9 g (41%) of difluoromethyl hexafluoroisopropyl ketone: bp  $67^\circ$ ; ir 5.62  $\mu$  ( $\text{C}=\text{O}$ ); nmr  $^1\text{H}$  at  $\tau$  4.49 (triplet, 1,  $J_{\text{H}/\text{F}} = 53.5$  Hz,  $\text{CF}_2\text{H}$ ), 5.67 [septet, 1,  $J_{\text{H}/\text{F}} = 7.3$  Hz,  $(\text{CF}_3)_2\text{CH}$ ];  $^{19}\text{F}$  at 130.3 (doublet, 1,  $J_{\text{H}/\text{F}} = 53.5$  Hz into septets,  $J_{\text{F}/\text{F}} = 2.6$  Hz,  $\text{CF}_2\text{H}$ ), 65.6 ppm [doublet, 3,  $J_{\text{H}/\text{F}} = 7.3$  Hz into triplets,  $J_{\text{F}/\text{F}} = 2.6$  Hz,  $(\text{CF}_3)_2\text{CH}$ ].

*Anal.* Calcd for  $\text{C}_5\text{H}_2\text{F}_8\text{O}$ : C, 26.11; H, 0.88; F, 66.09. Found: C, 26.56; H, 1.30; F, 65.81.

In like manner, a mixture of 16.7 g of 11 and 30 ml of concentrated  $\text{H}_2\text{SO}_4$  was heated at  $175^\circ$  for 8 hr. Similarly, carbon dioxide was evolved and a clear layer obtained, which gave on distillation 1.9 g (14%) of difluoromethyl hexafluoroisopropyl ketone.

**3-Methoxy-2,2,5,5,5-pentafluoro-4-(trifluoromethyl)-pent-3-enyl Fluoride (13).**—Compound 12 (4.4 g) was mixed in a sealed tube with 0.1 g of  $\text{CsF}$ , 0.1 g of tetraethylammonium chloride,

TABLE VII  
NMR DATA FOR *cis*- AND *trans*-PROPENYL PROPYL ETHERS

$$\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---O---CH}_d\text{=CH}_e\text{---CH}_f$$

Ether	Chemical shifts, $\tau$						Coupling constants, Hz				
	a	b	c	d	e	f	a/b	b/c	d/e	d/f	e/f
14	9.22	8.49	6.56	4.32	5.92	8.63	6.4	6.3	6.2	1.7	6.8
15	9.26	8.51	6.68	4.04	5.51	8.68	6.5	6.2	12.4	1.5	6.4

TABLE VIII  
NMR DATA FOR *cis*- AND *trans*-CYCLOBUTANONES 17 AND 20<sup>a</sup>

$$\begin{array}{c} \text{CF}_3 \\ | \\ \text{H} \text{---} \text{C} \text{---} \text{C} \text{=O} \\ | \quad | \\ \text{CH}_3\text{---CH}_2\text{---C} \text{---} \text{O---C} \text{---} \text{CHCH}_3 \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$

	Chemical shifts						Ppm			
	a	b	c	d	e	f	g	h	i	
17	8.82	8.12	6.11	6.25	5.15	5.97	8.49	68.7	63.6	
20	8.95	8.25	6.26	6.40	5.68	5.95	8.61	68.0	64.3	

	Coupling constants, Hz						
	a/b	b/c + b/d	c/d	e/f	e/h	f/g	h/i
17	7.5	6.4	8.9	9.4	1.0	7.8	8.8
20	7.5	6.4	8.7	7.2	<1.0	7.3	8.6

<sup>a</sup> Proton spectra taken on a Varian 220-MHz instrument, using 10% solutions in CDCl<sub>3</sub> with TMS as internal standard.

and 5 ml of methylene chloride. After the mixture was heated overnight- at 100°, 13 was essentially the only product present. The crude product was purified by vpc to give 2.6 g (59%) of 13: ir 5.30 and 5.34 (COF), 6.04  $\mu$  (C=C); nmr <sup>1</sup>H at  $\tau$  6.24 (singlet, CH<sub>3</sub>); <sup>19</sup>F at -16.0 (triplet, 1,  $J_{F/F}$  = 10.9 Hz, COF), 59.1 (triplet, 3,  $J_{F/F}$  = 13.6 Hz into quartets,  $J_{F/F}$  = 9.0 Hz, CF<sub>3</sub>), 61.2 (quartet, 3,  $J_{F/F}$  = 9.0 Hz, CF<sub>3</sub>), 105 ppm (5 lines, 2, overlapping quartet,  $J_{F/F}$  = 13.6 Hz, into doublet  $J_{F/F}$  = 10.9 Hz, CF<sub>2</sub>).

Anal. Calcd for C<sub>7</sub>H<sub>9</sub>F<sub>3</sub>O<sub>2</sub>: C, 28.99; H, 1.04; F, 58.97. Found: C, 29.31; H, 1.38; F, 58.53.

*cis*- and *trans*-Propenyl Propyl Ethers (14 and 15).—An adaptation of the literature procedure<sup>7</sup> was used. A mixture of 574 g of hexane, 386 g of propionaldehyde, 976 g of *n*-propyl alcohol, and 4 g of *p*-toluenesulfonic acid was refluxed with a water separator and 125 ml of water was removed in 1 day. Slow distillation gave the desired ethers, bp 88–90°. Too rapid distillation gave the high boiler (ca. 140°), apparently the acetal, while slow distillation allowed propanol to split out. The distillate was washed with 2% potassium hydroxide to remove propanol, and the remaining *cis*- and *trans*-propenyl ethers were fractionated. From two such runs and fractionation through a Podbielniak column there was obtained 265 ml of 14, bp 94° (96.5% *cis*, 3.5% *trans* by glpc), and 101 ml of 15, bp 101° (94.2% *trans*, 5.8% *cis* by glpc). Nmr data are given in Table VII.

*cis*- and *trans*-2,2-Bis(trifluoromethyl)-3-propoxy-4-methylcyclobutanones (17 and 20).—Examination of the reaction between 1 and 14 or 15 by <sup>19</sup>F nmr (see Tables II and III) showed that ketene was consumed very rapidly even at -50° and that initially large amounts of oxetane were formed along with cyclobutanone (Figure 4). When warmed to room temperature, oxetane was converted to cyclobutanone. It was, therefore, not possible to isolate oxetane, but cyclobutanone could be isolated in good yield. Further heating caused isomerization and opening of the cyclobutanone ring to give a linear ketone (see below).

In a typical experiment, 10 g (0.10 mol) of 14, 25 ml of hexane, and 18.0 g (0.10 mol) of 1 were sealed in a Carius tube, warmed to room temperature, and then heated 1 hr in a steam bath. After the tube was opened and solvent removed, the crude product examined by analytical vpc indicated that the reaction was essentially stereospecific. During a slow fractionation, the isomers apparently equilibrated somewhat. One initial fraction, bp 63–64° (13 mm), was 89% 20 and 11% 17 while a final cut, bp 69–70° (13 mm), was 99% 17 and 1% 20 (Table VIII). Total recovery of distilled fractions was 25 g (89%). An attempt to separate the isomers by preparative vpc resulted in some equilibration and ring opening on the column. A similar experiment

starting with 15 and 1 gave predominantly 20. For 17, ir 5.51  $\mu$  (ring C=O). For 20, ir 5.50  $\mu$  (ring C=O).

Anal. Calcd for C<sub>10</sub>H<sub>12</sub>F<sub>6</sub>O<sub>2</sub>: C, 43.20; H, 4.35; F, 41.01. Found for 17: C, 43.39; H, 4.22; F, 41.39. Found for 20: C, 43.08; H, 4.35; F, 41.41.

1-Methyl-2-propoxyvinyl Hexafluoroisopropyl Ketone (18).—A 5-g mixture of 17 and 20 (over 80% 17), when shaken with a source of fluoride ion (trace of cesium fluoride in 1 ml of glyme), became warm. Examination by vpc showed that the isomer mixture had changed to 90% 20 and 10% 17. Similarly a 5-g mixture which was 80% 20 changed to 90.7% 20 and 9.3% 17. Warming of the mixture in the presence of fluoride ion catalyst on a steam bath for several hours converted it entirely to 18: bp 60° (0.1 mm); mp 45–46° (from petroleum ether); ir 5.72 and 5.79 (C=O doublet), 6.01 and 6.11  $\mu$  (C=C); nmr <sup>1</sup>H at  $\tau$  2.38 (singlet, 1, =CH), 5.38 (septet, 1,  $J_{H/F}$  = 7.5 Hz, (CF<sub>3</sub>)<sub>2</sub>CH), 5.78 (triplet, 2,  $J_{H/H}$  = 6.4 Hz, OCH<sub>2</sub>), 8.09 (quartet, 2,  $J_{H/H}$  = 7.2 Hz, into triplets,  $J_{H/H}$  = 6.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 8.10 (singlet, 3, =CCH<sub>3</sub>), 8.93 (triplet, 3,  $J_{H/H}$  = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>19</sup>F at 63.6 ppm [doublet,  $J_{H/F}$  = 7.5 Hz, (CF<sub>3</sub>)<sub>2</sub>CH].

Anal. Calcd for C<sub>10</sub>H<sub>12</sub>F<sub>6</sub>O<sub>2</sub>: C, 43.20; H, 4.35; F, 41.01. Found: C, 43.46; H, 4.71; F, 39.46.

Method for the <sup>19</sup>F Nmr Study of the Reaction of 1 with 14 and 15 in Solvents of Different Polarity.—The nmr tubes were first necked down with a neck large enough to permit insertion of a hypodermic needle, but small enough to allow easy sealing with a flame under vacuum. By means of a hypodermic syringe, the tubes were charged with 64  $\mu$ l (0.05 g, 0.0005 mol) of the propenyl propyl ether, 370  $\mu$ l of solvent, and 37  $\mu$ l (0.0535 g, 0.00025 mol) of *o*-bis(trifluoromethyl)benzene. The latter was used as a standard for integration of fluorine peaks since it gave a single peak which did not interfere with product peaks. However, its melting point prevented mixing at low temperature, and it was sometimes omitted. The tube was then placed on a manifold system to which was also attached a vacuum pump, manometer, and supply of 1. The tube was cooled in liquid nitrogen, evacuated, and cut off from the system by a stopcock. The system was then pressured with 1 so that a calibrated amount (measured by pressure drop to an accuracy of  $\pm 1.5\%$ ) was delivered when the stopcock to the liquid nitrogen cooled tube was opened. The tube, now containing 0.5 M ketene, 0.5 M reference, and 1.0 M propenyl ether (excess to allow for some polymerization), was sealed and mixed while completely submerged in a Dry Ice-acetone bath at -80°. For tubes containing the *o*-bis(trifluoromethyl)benzene reference, it was necessary to warm to about -50°. After mixing, the tubes were stored in a Dry Ice-acetone bath. They were examined by <sup>19</sup>F nmr with the

probe cooled to  $-50^{\circ}$ . The nmr spectra were taken after heating at different temperatures for varying times followed by quenching in Dry Ice-acetone. The heating schedules were 0.25, 0.5, 1, and 2 hr at  $0^{\circ}$  (wet ice bath) and 0.25, 0.5, 1, 2, 4, 8, 16, 20, and 24 hr at  $25^{\circ}$  (refluxing  $\text{CFCl}_3$  bath).

**2,2-Bis(trifluoromethyl)-3-(*p*-methoxyphenyl)cyclobutanone (22).**—*p*-Methoxystyrene (27.0 g, 0.20 mol), **1** (43.0 g, 0.24 mol), 25 ml of benzene, and 0.1 g of phenothiazine were heated overnight at  $100^{\circ}$  in a sealed tube. After removal of volatiles, the resulting solid was recrystallized from  $\text{CCl}_4$  to give 49 g (79%) of **22**, mp  $84-86^{\circ}$ . Another recrystallization gave an analytical sample, mp  $85-87^{\circ}$ . In other experiments, it was found that the reaction goes at  $25^{\circ}$  and the product can be distilled: bp  $96^{\circ}$  (1 mm); ir  $5.53 \mu$  (ring C=O); nmr [ $(\text{CD}_3)_2\text{CO}$ ]  $^1\text{H}$  at  $\tau$  3.2 (AA'BB', 4, aromatic CH), 6.3 (overlapping multiplets, 3,  $\text{CHCH}_2$ ), 6.7 (singlet, 3,  $\text{CH}_3$ );  $^{19}\text{F}$  at 64.3 (quartet, 1,  $J_{\text{F}/\text{F}} = 8.6 \text{ Hz}$ ,  $\text{CF}_3$ ), 68.6 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 8.6 \text{ Hz}$ ,  $\text{CF}_3$ ).

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{10}\text{F}_6\text{O}_2$ : C, 50.04; H, 3.23; F, 36.54. Found: C, 49.82; H, 3.16; F, 36.49.

In hexane at  $25^{\circ}$ , oxetane **21** was also formed, causing an nmr signal for  $^{19}\text{F}$  at 58.9 ppm (multiplet).

**Ethyl 5,5,5-Trifluoro-4-(trifluoromethyl)penta-2,3-dienoate (24).**—A sealed tube containing 14 g (0.20 mol) of ethoxyacetylene and 39 g (0.22 mol) of **1** was held at  $-80^{\circ}$  overnight in an attempt to control the exothermic reaction. Distillation gave

19.5 g (39%) of **24**: bp  $68^{\circ}$  (50 mm);  $n_D^{20}$  1.3580; ir 5.03 ( $\text{C}=\text{C}$ ),  $5.77 \mu$  (ester  $\text{C}=\text{O}$ ); nmr  $^1\text{H}$  at  $\tau$  3.77 (septet, 1,  $J_{\text{H}/\text{F}} = 2.5 \text{ Hz}$ ,  $=\text{CH}$ ), 6.12 (quartet, 2,  $J_{\text{H}/\text{H}} = 7.2 \text{ Hz}$ ,  $\text{CH}_2$ ), 9.10 (triplet, 3,  $J_{\text{H}/\text{H}} = 7.2 \text{ Hz}$ ,  $\text{CH}_3$ );  $^{19}\text{F}$  at 62.6 ppm (doublet,  $J_{\text{H}/\text{F}} = 2.5 \text{ Hz}$ ).

*Anal.* Calcd for  $\text{C}_8\text{H}_6\text{F}_6\text{O}_2$ : C, 38.74; H, 2.44; F, 45.97. Found: C, 39.10; H, 2.72; F, 46.31.

Evidence for oxete **23** was  $^{19}\text{F}$  nmr signals obtained at ca. 57.0 (quartet, 1,  $J_{\text{F}/\text{F}} = 7.0 \text{ Hz}$ ,  $\text{CF}_3$ ), 59.8 ppm (quartet, 1,  $J_{\text{F}/\text{F}} = 7.0 \text{ Hz}$ ,  $\text{CF}_3$ ), along with the doublet at 62.6 ppm when rapidly scanned while warming from  $-80^{\circ}$  in the probe at  $30^{\circ}$ . These quartets rapidly disappeared as the doublet signal became stronger.

**Registry No.**—**1**, 684-22-0; **2**, 4233-20-9; **3**, 4141-80-4; **4**, 25636-21-9; **5**, 25636-22-0; **6**, 25631-65-6; **8**, 25636-23-1; **9**, 25631-66-7; **10**, 25631-67-8; **11**, 25636-24-2; **12**, 25636-25-3; **13**, 25636-95-7; **14**, 143360-78-2; **15**, 21087-24-1; **17**, 25631-70-3; **18**, 25679-31-6; **20**, 25631-71-4; **22**, 25636-96-8; **24**, 25636-97-9; difluoromethyl hexafluoroisopropyl ketone, 25636-98-0.

## Fluoroketenes. VI. Cycloadditions of Cumulenes to Bis(trifluoromethyl)ketene<sup>1</sup>

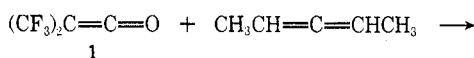
DAVID C. ENGLAND AND CARL G. KRESPAN

Contribution No. 1663 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

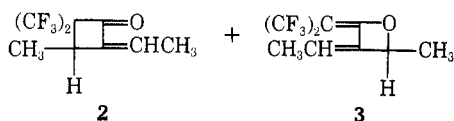
Received February 12, 1970

Dimethylallene cycloadds to bis(trifluoromethyl)ketene to form both oxetane and cyclobutanone, but tetramethylallene forms only products of an ene reaction because of steric hindrance to ring closure. Cycloadditions of ketene and methylketene to bis(trifluoromethyl)ketene proceed easily and in good yield to form  $\beta$  lactones derived only from addition across the  $\text{C}=\text{C}$  of the nonfluorinated ketene. A dipolar intermediate is proposed for this reaction. Dimethylketene cycloadds to bis(trifluoromethyl)ketene to form both cyclobutanedione and  $\beta$  lactone, a change presumably induced by increased steric hindrance. The direction of this latter reaction is strikingly dependent on solvent polarity.

**Allenes.**—The reactions of bis(trifluoromethyl)ketene (**1**) with allenes and with simple olefins are somewhat analogous, indicating that some factors governing the reaction courses are similar. As with ethylene, allene itself has not been made to react with **1** up to  $165^{\circ}$ . 1,3-Dimethylallene showed reactivity like that of a vinyl ester<sup>1</sup> in that it gave an unusual cycloaddition to **1** (apparently unique for an allene-ketene combination) at  $100^{\circ}$  to form both cyclic ketone **2** and oxetane **3**. The orientation of substituents in the adducts is that expected from bond formation at the central allene carbon atom to form stabilized dipolar intermediates and/or polar transition states.



**1**

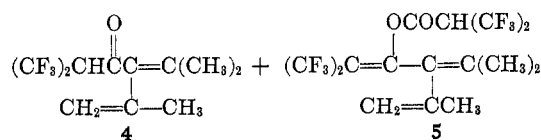
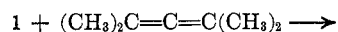


**2**

**3**

Tetramethylallene resembled isobutylene in its slow reaction with **1** at  $25^{\circ}$  to form only open-chain products of an ene reaction. Steric hindrance to closure of

either the normally stable cyclobutanone ring or the oxetane ring resulted in preferential formation of products of hydrogen migration. Even when equimolar amounts of reactants were used, the enol ester **5** was the major product (79%). The ketodiene **4** was isolated in only 9% yield and could not be reacted in a separate step with **1** to give **5**. This is analogous to the formation of enol esters through intermediates not isolated in the reactions of **1** with butene-1 and with  $\alpha$ -methylstyrene.<sup>2</sup>



**Ketenes.**—Mixed ketene dimers have seldom been studied, presumably because of a tendency to form in low yield along with simple dimers.<sup>3</sup> Since ketene **1** does not dimerize thermally but is extremely reactive toward unsaturated nucleophiles, mixed dimers of **1** with various other ketenes form easily and in high yield. Dimers of both the 1,3-dione type **6** and  $\beta$ -lac-

(1) Part V: D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3312 (1970).

(2) D. C. England and C. G. Krespan, *ibid.*, **35**, 3300 (1970).

(3) Cf. W. E. Hanford and J. C. Sauer, *Org. React.*, **3**, 129 (1946).