Fluoroketenes. III. Reactions of Bis(trifluoromethyl)ketene with Unsaturated Compounds[1]

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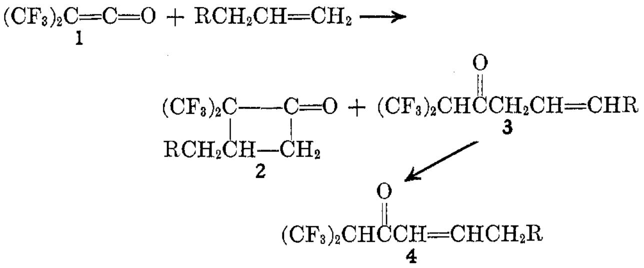
Bis(trifluoromethyl)ketene reacts with simple olefins to give cyclobutanones by cycloaddition to its carbon–carbon double bond and linear ketones by an ene reaction. Dienes react at the carbonyl group of bis(trifluoromethyl)ketene in Diels–Alder fashion to give dihydropyrans and related adducts. Implications of these findings on the mechanism of cycloadditions to ketenes are discussed.

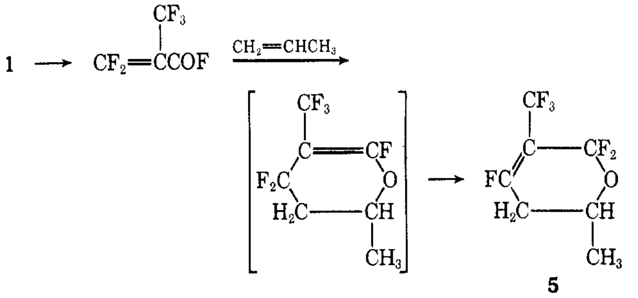
The first authenticated perfluoroketene, bis(trifluoromethyl)ketene (**1**), has become readily available from a simple process[2] and its chemistry is being studied.[2,3] The purpose of this paper is to report in detail on some previously communicated[2a] reactions of ketene **1** with olefins and dienes.

The electrophilic nature of the ketene group is greatly enhanced by the electron-withdrawing effect of the trifluoromethyl groups in **1**, and most of its reactions can be interpreted through polar intermediates. Previous work[2b] demonstrated the reactivity of **1** toward nucleophiles and the tendency of **1** to form an anion $[\overline{(CF_3)_2\overset{-}{C}\text{–}C(O)}B]$ with bases such as fluoride ion. The same type of stabilized anion has been shown to form by removal of a proton from the conjugate acid, $(CF_3)_2CHCOF$.[4] As will be discussed below and in subsequent publications, neutral unsaturated compounds also tend to react with ketene **1** to give polarized transition states or dipolar intermediates in which negative charge resides on the fluorinated segment of the intermediate. The products isolated are cycloadducts obtained by ring closure and/or linear adducts by proton transfer, depending on the reaction conditions and on the nature of the unsaturated coreactant.

Olefins.—Terminal olefins add to the carbon–carbon double bond of ketene **1** to form cyclobutanones (**2**) and acyclic β,γ-unsaturated ketones (**3**). Conjugated acyclic ketones (**4**) are formed from **3** in a slower secondary reaction.



Several attempted reactions of **1** with propylene in sealed glass tubes above the critical temperature of propylene (92°) gave no product under conditions where no liquid phase was present (100–200° and modest pressures). At 60–80° with the same loading density, however, products were slowly formed over a period of weeks. Higher pressure (~850 atm) at 150° gave higher yields in less time. A similar response was observed with butene-1. The products isolated from the reaction at 150° with excess propylene were cyclobutanone **2** (R = H, 13%), β,γ-unsaturated ketone **3** (R = H, 6%), and compound **5** (35%). Compound **5** resulted from the side reaction of isomerization of ketene **1** to perfluoromethacryloyl fluoride,[2] since it can be prepared under milder conditions directly from perfluoromethacryloyl fluoride.[5] The β,γ-unsaturated ketone **3** (R = H) isomerized to α,β-unsaturated ketone **4** (R = H) on long standing, but **4** was at best a very minor product in the original reaction.



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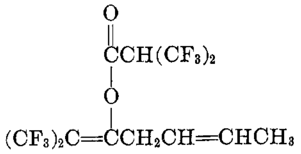
Ethylene (critical temperature 9°) did not react appreciably with **1** at 130–200° under moderate pressure. Since these conditions were successful for propylene, a much lower reactivity for ethylene is indicated.

Butene-1 (critical temperature 146°) gave no significant reaction with **1** in sealed tubes at 175° for 8 hr, but at the same loading density reacted to a moderate extent in 3 days at 100°. Products from a reaction with excess ketene at 100° for 37 days were the cyclic ketone **2** (R = CH_3, 16%), the β,γ-unsaturated ketone **3** (R = CH_3, 11%), and 34% product characterized as the vinyl ester **6**. Ester **6** is not formed in a secondary reaction of **1** with the enol of **3** (R = CH_3) since this reaction was shown separately not to occur. Several enol esters of this type were isolated from reactions of **1**.



$$(CF_3)_2C{=}\underset{\displaystyle |}{C}(OC(O)CH(CF_3)_2)CH_2CH{=}CHCH_3$$

6

Hexene-1 (critical temperature 243°) reacted appreciably with the ketene in a sealed tube at 150° for 8

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[1] Part II: D. C. England and C. G. Krespan, *J. Org. Chem.*, **33**, 816 (1968).

[2] (a) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 4019 (1965); (b) *ibid.*, **88**, 5582 (1966).

[3] Y. A. Cheburkov and I. L. Knunyants, *Fluorine Chem. Rev.*, **1**, 107 (1967).

[4] Y. A. Cheburkov, M. D. Bargamova, and I. L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 339 (1964).

[5] Reactions of perfluoromethacryloyl fluoride will be published separately.

hr giving the cyclic ketone **2** (R = C_3H_7, 12%) and the β,γ-unsaturated ketone **3** (R = C_3H_7, 8%), along with a small amount of higher boiling product, apparently an enol ester analogous to the above product from butene-1.

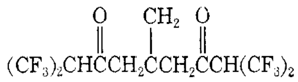
Isobutylene reacted more readily at 100° with **1** than the previously considered terminal olefins such as propylene, in keeping with an increased nucleophilicity because of the additional methyl group. Although conditions were milder (isobutylene reacts with **1** even at room temperature[3]), no cyclobutanone was formed. When isobutylene was used in 2:1 excess, the β,γ-unsaturated ketone **7** was obtained in 86% yield after 20 hr at 100°. When the reaction mixture was heated for 60 hr, the product was a mixture of **7** and the isomeric α,β-unsaturated ketone, **8**. From a reaction of **1** with **7**, a low yield of the 2:1 product **9** was isolated, the main product being a compound believed to have the structure **10**. **9** may arise from attack of a second molecule of **1** at the terminal olefinic bond of **7** in an "ene" reaction analogous to the formation of **7** from isobutylene. Attack of a third molecule of **1** on **9** or on the internal double-bond isomer of **9** followed by dehydration of an enol form would give **10**.

$(CF_3)_2CHCOCH_2C(CH_3){=}CH_2$

7

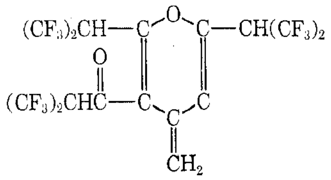
$(CF_3)_2CHCOCH{=}C(CH_3)_2$

8



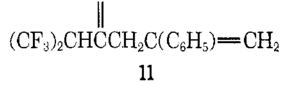
$(CF_3)_2CH\overset{O}{\overset{\|}{C}}CH_2\overset{CH_2}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH(CF_3)_2$

9



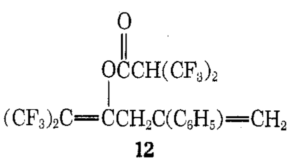
10

α-Methylstyrene, similar to isobutylene in being a disubstituted terminal olefin containing allylic hydrogen, reacts with **1** in 2 hr at 100° to give a 96% yield of products. Some enol ester **12** was formed along with linear adduct **11**, but here also it was not possible to react **11** with **1** to give **12**. However, **12** did decompose thermally to form **1** and **11** and could also be hydrolyzed under mild conditions to give the α,β-unsaturated ketone, **13**.



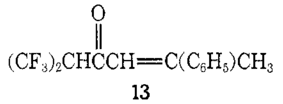
$(CF_3)_2CH\overset{O}{\overset{\|}{C}}CH_2C(C_6H_5){=}CH_2$

11



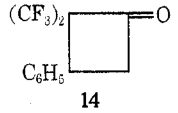
$(CF_3)_2C{=}\overset{O\overset{O}{\overset{\|}{C}}CH(CF_3)_2}{\overset{|}{C}}CH_2C(C_6H_5){=}CH_2$

12



$(CF_3)_2CH\overset{O}{\overset{\|}{C}}CH{=}C(C_6H_5)CH_3$

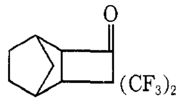
13



14

Styrene, with an activating substituent capable of stabilizing a positive charge but no allylic hydrogens, reacts readily with **1** at 100° to give cyclobutanone **14** in 87% yield.[6]

Norbornene did not react appreciably with **1** at 100°; at 175° norbornene added to the carbon–carbon double bond of **1** nearly quantitatively to give a cyclic ketone of structure **15**, but with unknown configuration. The rate of reaction of **1** with norbornene was much higher in nitroethane than in hexane, but formation of byproducts was a serious complication in both solvents.



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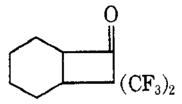
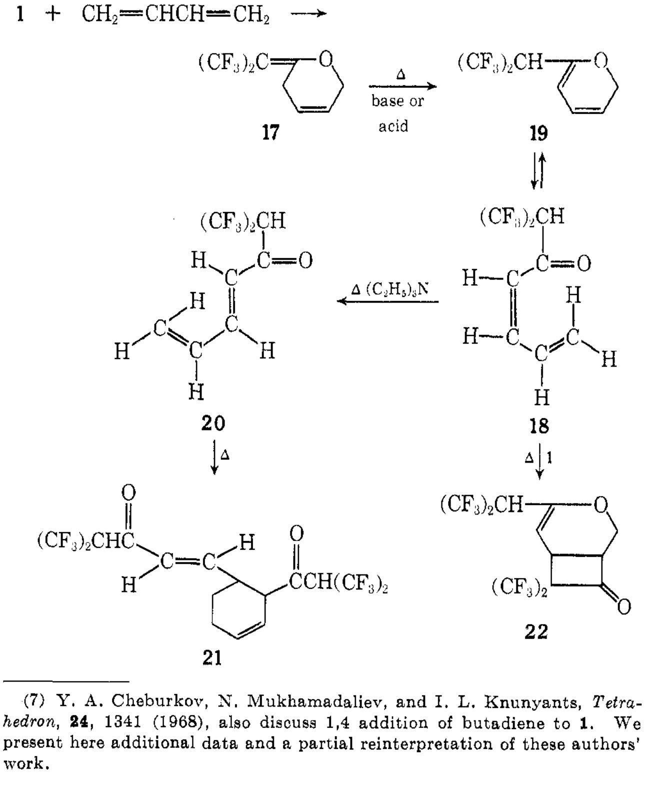


16

Although the strained double bond in norbornene is sufficiently reactive to undergo cycloaddition to ketene **1**, more normal internal olefins have resisted attempts to force reaction. No reaction was detected with *trans*-butene-2 at 100° overnight or with tetramethylethylene at 100° for 45 days. Cyclopentene gave little or no adduct in 8 hr at 175° and formed decomposition products at 250°. Cyclohexene reacted slowly at 100° over 2 months giving a low yield of cyclobutanone **16** and mixed acyclic ketones.

1,3-Dienes and Related Compounds.—Unlike ketenes in general, **1** reacts with conjugated dienes in the Diels–Alder manner and the addition occurs at the carbonyl group of ketene **1**. Reaction of **1** with butadiene has been studied most intensively and is at the same time one of the most sensitive to the precise conditions employed.[7] Reactions at 100° gave products which were easily decomposed. The use of acid-washed equipment helped stabilize the products, and even better yields of the initial adduct **17** were achieved by running the reaction with excess **1**. The conversion of **17** to acyclic *cis*-diene **18** is base catalyzed and apparently proceeds through a tautomerization to pyran **19** followed by an electrocyclic transformation of **19** to **18**. **17** is also sensitive to protic acids and will undergo isomerization to **18** on distillation from acid-washed equipment. With excess butadiene, **18** was obtained directly from the reaction, but in low yield, along with



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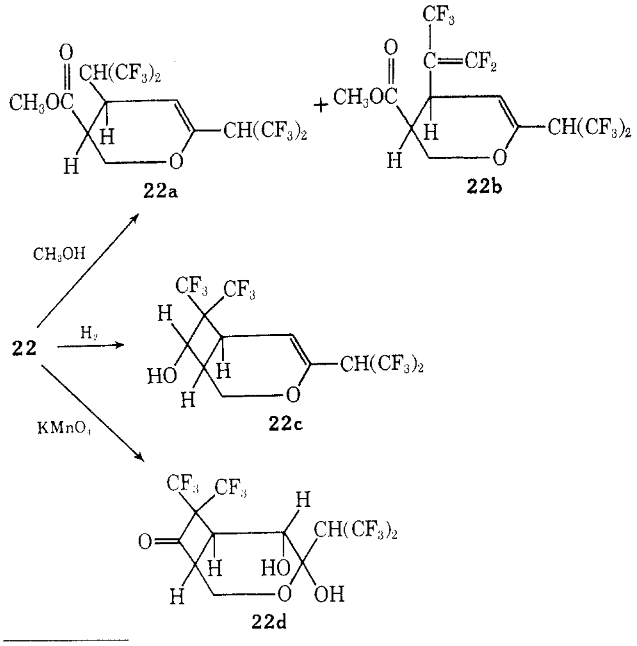
(6) Y. A. Cheburkov, N. Mukhamadaliev, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 384 (1966), also report this cycloadduct from styrene.

(7) Y. A. Cheburkov, N. Mukhamadaliev, and I. L. Knunyants, *Tetrahedron*, **24**, 1341 (1968), also discuss 1,4 addition of butadiene to **1**. We present here additional data and a partial reinterpretation of these authors' work.

its polymer. When the reaction of butadiene and **1** was conducted in hexane with phenothiazine present as inhibitor, it was possible to isolate 58% **18** containing an isomer, apparently the ring-closed form, **19**.[8] Although **18** polymerized easily, the *trans* isomer **20** preferentially formed an isomeric mixture of dimers (proposed to have general structure **21**) even at room temperature. **18** was converted to **20** by treatment with catalytic amounts of triethylamine. The behavior of **18** and **20** is analogous to that of *cis*-piperlyene, which polymerizes rather than form a Diels–Alder dimer, and *trans*-piperylene, which readily dimerizes. With the *cis*-dienes, the substituents presumably prevent the cisoid configuration of the diene necessary for a concerted Diels–Alder addition to give dimer.

Preparations of **17**, preferably carried out with excess **1**, gave varying amounts of a 2:1 1–butadiene adduct, especially in reactions at longer times or higher temperatures. The evidence best fits structure **22** for the 2:1 adduct, a product which would arise by cycloaddition of **1** to the unhindered but activated double bond of **19**. It was not possible to define conditions giving exclusively **17** or **22**, because results were not reproducible. Nevertheless, overall yields of **17** and/or **22** were consistently very good when excess **1** was used.

Chemical evidence for the structure of **22** was obtained as follows. Evidence for the cyclobutanone structure was provided by its reaction with alcohols which is analogous to the reaction of **14** with nucleophiles.[7] Reaction with methanol gave a mixture of saturated (**22a**) and unsaturated (**22b**) esters. The small-ring carbonyl group indicated by the ir spectrum was easily reduced to an alcohol (**22c**) by hydrogenation. Oxidation with permanganate occurred at the double bond, apparently to give the *cis*-glycol **22d**. Both the ^{19}F and ^{1}H spectra of the 2:1 product are in agreement with structure **22**. A cyclic 8-membered ring lactone structure which has been proposed[7] is unlikely in view of the above evidence. In addition the ^{1}H spectrum should have three instead of the one vinyl hydrogen observed, and the ^{19}F spectrum should be a doublet and singlet of equal areas instead of the doublet and pair of quartets observed.



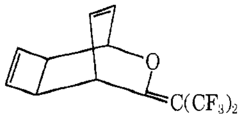
The reaction of **1** and butadiene was examined by nmr in hexane and in nitroethane. The results show the rate of reaction of **1** to increase with solvent polarity. Similarly, conversion of **17** to **18** and to polymeric products is favored in the polar solvent (Table I).

TABLE I
REACTION OF 1 WITH BUTADIENE[a]

Solvent	Temp, °C	Time, hr	Per cent of total: 1	17	18 + others
Hexane	100	1.25	100	0	0
	140	3.5	62	34	4
	140	13	18	73	9
	140	19	10	74	16
Nitroethane	50	0.25	84	2	14
	100	0.25	42	43	15
	100	1.25	7	76	17
	140	3.5	0	0	100

[a] Carried out in sealed tubes as described in part V: ref. 11.

Cyclooctatetraene, reacting in the bicyclic form at 100°, added slowly to the carbonyl group of **1** in Diels–Alder fashion to form **23**. Cycloheptatriene also added 1,4 to the carbonyl of **1**, the product of which contained a reactive double bond similar to that in norbornene; another mole of **1** appeared in the final product as a result of a cycloaddition to the carbon–carbon double bond of **1**. The 2:1 adduct actually obtained is formulated as structure **24** on the basis of minimized steric hindrance.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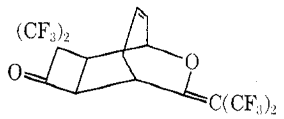
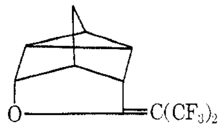

24

Bicycloheptadiene is known to react with dienophiles such as hexafluoro-2-butyne to give a homo-Diels–Alder addition.[9] Bicycloheptadiene added readily to the carbonyl of **1** at 100° to give adduct **25** in 81% yield.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Discussion

A monoalkylethylene containing allylic hydrogen will add to **1** with formation of two products, a cyclobutanone by cycloaddition and a β,γ-unsaturated ketone by an "ene" reaction.[10] The alkyl-substituted cyclobutanones are stable to the reaction conditions (80–175° and only moderately polar media); so the

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[8] Cyclization of such dienones to 2H-pyrans is generally a preferred reaction, so that compound **18** is a member of a class rarely isolated; *cf.*, P. Schiess, H. L. Chia, and C. Suter, *Tetrahedron Lett.*, 5747 (1968).

[9] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83**, 3428 (1961).

[10] J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187, (1966), use this convenient name for K. Alder's "indirect substitutive addition" in which acyclic products are obtained from thermal addition of olefins to dienophiles.

acyclic ketones or the corresponding enols are considered to be primary products. A preliminary cycloaddition to the ketene carbonyl group to give unstable oxetanes may in principle also occur, but we find no evidence that this possibility bears on formation of the ene products. No oxetanes have been detected in the reaction of **1** with simple alkenes, even though the oxetanes from **1** and more reactive olefins such as vinyl esters[11] have been isolated and can be stable at 100° and above in nonpolar media, but form α,β-unsaturated ketones in polar media.

Although oxetane formation may not be involved in reactions of **1** with simple olefins, an intermediate of some sort is indicated by the formation of enol esters as by-products. These enol esters are not obtainable from **1** and the related β,γ-unsaturated ketones under the reaction conditions. One interpretation in accord with the known facts is that the ene products from simple olefins arise at least in part *via* a cyclic transition state in which the enol of ketone **3** is formed as an intermediate with sufficient lifetime to react with another molecule of **1**.

The preference for a liquid phase in these reactions suggests a polarized transition state or perhaps even a dipolar intermediate stabilized by solvation. Orbital symmetries in ketenes are such that an analysis according to Woodward–Hoffmann methods has only recently been made.[12] Our results fit the idea that the less nucleophilic olefins cycloadd to the carbon–carbon double bond of **1** by way of an unsymmetrical, polarized transition state or perhaps a dipolar intermediate of very low stability. The reactions are accelerated in polar solvents and by substituents in the olefin capable of stabilizing a positive charge, but tend to be relatively slow even at elevated temperatures. On the other hand, extremely nucleophilic olefins have been shown to cycloadd thermally to both the C=C and C=C of **1** by a nonconcerted process involving dipolar intermediates.[11] Since cyclobutanone formation, in particular, seems to present an unusual instance in which the mechanism can vary all the way from nonconcerted to concerted, it appears that ketene **1** can act normally in cycloaddition to the C=C unless the stabilization of positive charge by substituents in the olefinic segment and by solvation is sufficient to favor a dipolar intermediate.

Wide variations in mechanism have also been reported for cycloadditions to dimethylketene and diphenylketene. At one extreme there is good evidence that enamines add to dimethylketene *via* an ionic intermediate.[13,14] On the other hand, strong support is available for a nearconcerted mechanism with relatively little charge separation in the transition state for cycloadditions of diphenylketene to vinyl ethers.[15,16] Therefore, there seems to be no single mechanism for cycloadditions to the C=C of ketenes. Rather, there exists a continuum of slightly to highly charge-separated intermediates or transition states, and bond formation can be stepwise or not symmetrical in the transition state.[17]

The ease of reaction of **1** with isobutylene and the absence of cyclobutanone as a product can be attributed to the presence of an additional methyl group. Reactivity is enhanced by increased nucleophilicity due to the added methyl, but steric hindrance prevents formation of a cyclobutanone containing adjacemt *gem*-substituted carbon atoms. Oxetane formation, which would imply capability of forming a dipolar intermediate with **1**, is not observed either. The presence of a methyl group with its reactive allylic hydrogen atoms in the ene product **7** promotes a second ene reaction to give **9**. We observed no enol ester formation with isobutylene, but low yields of this product were reported at 0°.[7]

Reactivity similar to that of isobutylene is observed with α-methylstyrene in formation of acyclic ketone **11** as the primary product. Lack of reactive allylic hydrogens in **11**, however, precludes formation of a 2:1 ene product, and enol ester **12** is formed in a manner similar to that with the monoalkylethylenes and **1**.

Conjugated dienes generally add to ketene, dialkylketenes, and diphenylketene in a 1,2 manner to give cyclobutanones.[18] Even the negatively substituted ketene, dichloroketene, cycloadds 1,2 to cyclopentadiene to form a cyclobutanone ring.[19] One example of a 1,4 addition is known with these various ketenes, that of 2-methoxybutadiene to the carbonyl bond of diphenylketene.[16] In contrast to the behavior of other ketenes, **1** adds dienes 1,4 in general to its carbonyl group.

Butadiene and **1** show pronounced acceleration of reaction rate in a polar solvent, unusual in a Diels–Alder reaction and presumably indicating a significant charge separation in the transition state. The fact that neither oxetane nor, in a nonpolar solvent, cyclobutanone was observed is an indication that a more or less concerted 4 + 2 addition has taken precedence. This interpretation and the results of other work[11] lead us to postulate that cycloadditions to the ketene carbonyl group, when they occur, are to the isolated π system and follow Woodward–Hoffmann rules.

Experimental Section[20]

Bis(trifluoromethyl)ketene and Ethylene.—No monomeric product could be isolated from attempted reactions of the ketene with ethylene at 950-atm pressure and 150–175° with or without 1,1,2-trichlorotrifluoroethane as solvent.

Bis(trifluoromethyl)ketene and Propylene.—No product could be isolated from attempted reactions in sealed glass tubes at 100–200°. However, a mixture of 34 g of the ketene and 14 g of propylene heated for 6 weeks in a water bath at 60–80° gave 5 g of a mixture of products. A similar mixture was obtained in higher yield at elevated pressure and temperature. A metal tube charged with 35 g (0.20 mol) of the ketene and 100 g of propylene was heated at 150° for 6 hr. The top pressure of 855 atm dropped to 730 atm. There was recovered 34 g of liquid boiling above room temperature. Distillation gave 8 g (19% yield on ketene

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[11] Part V, *J. Org. Chem.*, **35**, 3312 (1970), describes the formation of such oxetanes from **1** and very nucleophilic olefins. Such adducts are formed under comparatively mild conditions *via* a dipolar intermediate, a mechanism which also allows proton transfer to occur with formation of α,β- rather than β,γ-unsaturated acyclic ketones.

[12] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[13] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

[14] J. C. Martin, P. G. Gott, and H. U. Hostetter, *ibid.*, **32**, 1654 (1967).

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

[16] W. J. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

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

[18] See J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965), for recent extensive work in this area and for leading references.

[19] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

[20] Melting points and boiling points are uncorrected. ^{19}F nmr spectra are reported in parts per million upfield from external trichlorofluoromethane. ^{1}H nmr resonances are relative to external tetramethylsilane and were run at 60 MHz unless otherwise noted.

charged) of a mixture, bp 63–70° (100 mm); separation by glpc gave 30% 1,1,1-trifluoro-2-(trifluoromethyl)-5-hexen-3-one (**3**, R = H) and 70% 2,2-bis(trifluoromethyl)-3-methylcyclobutanone (**2**, R = H). In addition there was obtained 15 g (35%) of 2,2,4-trifluoro-5,6-dihydro-6-methyl-3-(trifluoromethyl)-2H-pyran (**5**), bp 102° (100 mm).

For the linear ketone **3**: ir 5.77 (C=O), 6.15 μ (C=C); nmr ^1H at about τ 5.00 (multiplet, 3, CH=CH$_2$), 5.98 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 6.95 (doublet, $J_{H/H}$ = 8.0 Hz, 2, CH$_2$); ^{19}F at 64.8 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_7H_6F_6O$: C, 38.21; H, 2.75; F, 51.82. Found: C, 38.44; H, 2.73; F, 51.93.

Reexamination of the above sample after storage in glass for about 4 years showed that it had been converted to the isomeric α,β-unsaturated ketone, 1,1,1-trifluoro-2-(trifluoromethyl)-4-hexen-3-one (**4**, R = H): ir 5.91 μ (C=O); nmr ^1H at τ 3.18 (doublet, $J_{H/H}$ = 16.0 Hz, to quartets, $J_{H/H}$ = 7.0 Hz, 1, COCH=CH–), 4.01 (doublet, $J_{H/H}$ = 16.0 Hz, to quartets, $J_{H/H}$ = 1.5 Hz, 1, COCH=CH–), 5.80 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 8.49 (doublet, $J_{H/H}$ = 7.0 Hz, to doublets, $J_{H/H}$ = 1.5 Hz, 3, CH$_3$); ^{19}F at 65.1 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

For the cyclic ketone **2** (R = H): ir 5.50 μ (C=O); nmr ^1H at τ 6.80 to 7.43 (multiplet, 3, ring CH), 8.88 (multiplet, 3, CH$_3$); ^{19}F at 64.9 (quartet, $J_{F/F}$ = 9.2 Hz, with fine structure, 3, CF$_3$), 70.2 ppm (quartet, $J_{F/F}$ = 9.2 Hz, C, CF$_3$).

Anal. Calcd for $C_7H_6F_6O$: C, 38.21; H, 2.75; F, 51.82. Found: C, 38.34; H, 2.74; F, 51.71.

For the perfluoromethacryloyl fluoride derivative **5**: ir 5.85 μ (C=C); nmr ^1H at τ 5.85 (quartet, $J_{H/H}$ = 7.0 Hz, 1, –CH–CH$_3$), 7.70 (multiplet, 2, CH$_2$), 8.80 (doublet, $J_{H/H}$ = 7.0 Hz, 3, CH$_3$); ^{19}F at 84.5 (quartet, $J_{F/F}$ = 17.0 Hz with fine structure, 1, =CF), 59.5 (doublet, $J_{F/F}$ = 17.0 Hz, 3, CF$_3$), 56.4, 59.5, 71.0, and 74.1 ppm (AB, 2, CF$_2$).

Anal. Calcd for $C_7H_6F_6O$: C, 38.21; H, 2.75; F, 51.82. Found: C, 37.70; H, 2.61; F, 51.90.

The above compound is also the major product of the reaction of propylene with perfluoromethacryloyl fluoride.

Bis(trifluoromethyl)ketene and Butene-1.—There was no appreciable reaction in a sealed tube at 175° but appreciable reaction at 100°. A mixture of 9.5 g of **1** and 8.5 g of butene-1 sealed in a Carius tube was heated on a steam bath for 3 days. There was obtained 4.2 g of distilled product. The reaction was repeated on 9 g (0.05 mol) of **1** and 5 g (0.09 mol) of butene-1 for 37 days to give 7 g of distilled product, consisting of 3.5 g (27%) of 1:1 products, and 3.5 g (34%) of a 2:1 ketene–butene-1 product. The 1:1 mixture, bp 52–55° (20 mm), was separated by glpc into 36% 1,1,1-trifluoro-2-(trifluoromethyl)-5-hepten-3-one (**3**, R = CH$_3$) and 64% 2,2-bis(trifluoromethyl)-3-ethylcyclobutanone (**2**, R = CH$_3$).

For the linear ketone **3** (R = CH$_3$): n^{23}_D 1.3553; ir 5.75 (C=O) and 6.16 μ (C=C); nmr ^1H at τ 4.75 (multiplet, 2, CH=CH), 5.85 [septet, $J_{H/F}$ = 7.5 Hz, 1, $(CF_3)_2CH$], 6.90 (doublet, $J_{H/H}$ = 6.0 Hz, CH$_2$), 8.67 (doublet, $J_{H/H}$ = 5.0 Hz, 3, CH$_3$); ^{19}F at 63.1 ppm [doublet, $J_{H/F}$ = 7.5 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_8H_8F_6O$: C, 41.06; H, 3.45; F, 48.72. Found: C, 41.41; H, 3.64; F, 48.54.

After standing for 4 years the sample was about 40% converted to the α,β isomer **4** (R = CH$_3$): ir 5.90 (C=O) and 6.16 μ (C=C); mmr ^1H at τ 3.17 (doublet, $J_{H/H}$ = 16.0 Hz, to triplets, $J_{H/H}$ = 6.0 Hz, COCH=CH), 4.04 (doublet, $J_{H/H}$ = 16.0 Hz with fine structure, COCH=CH–), 5.85 [septet, $J_{H/F}$ = 7.5 Hz, 1, $(CF_3)_2CH$], 8.11 (fine peaks, overlapping quartets, $J_{H/H}$ = 7.0 Hz, and doublets, $J_{H/H}$ = 6.0 Hz, 2, CH$_2$), 9.34 (triplet $J_{H/H}$ = 7.0 Hz, 3, CH$_3$); ^{19}F at 62.9 [doublet, $J_{H/F}$ = 7.5 Hz, $(CF_3)_2CH$], 63.2 ppm (a similar doublet of one-fourth the intensity, possibly due to *cis–trans* isomers).

For the cyclic ketone **2** (R = CH$_3$): n^{25}_D 1.3545; ir 5.52 μ (C=O); nmr ^1H at τ 6.7–7.4 (multiplet, 3, ring CH), 8.40 (broad, 2, CH$_2$), 9.23 (triplet, $J_{H/H}$ = 7.0 Hz, 3, CH$_3$); ^{19}F at 64.1 (broad quartet $J_{F/F}$ = 9.4 Hz, 3, CF$_3$), 69.75 ppm (sharp quartet, $J_{F/F}$ = 9.4 Hz, 3, CF$_3$).

Anal. Calcd for $C_8H_8F_6O$: C, 41.06; H, 3.45; F, 48.72. Found: C, 40.84; H, 3.44; F, 48.94.

The 2:1 ketene–butene-1 product, bp 82° (20 mm), n^{24}_D 1.3492, was characterized as the enol ester **6**, 1,1,1-trifluoro-2-(trifluoromethyl)-2,5-heptadien-3-ol 3,3,3-trifluoro-2-(trifluoromethyl)propionate, based on analysis, ir, and nmr: ir 5.58 (C=O), 5.96 μ (C=C); the proton nmr was essentially the same as for the linear ketone **3** (R=CH$_3$) above—^1H at τ 4.4 to 5.3 (multiplet, 2, CH=CH), 6.18 [septet, $J_{H/F}$ = 7.0 Hz, 1, $(CF_3)_2CH$], 6.96 (doublet, $J_{H/H}$ = 6.0 Hz with fine structure, 2, CH$_2$), 8.65 (doublet, $J_{H/H}$ = 5.5 Hz, 3, CH$_3$); ^{19}F at 58.9 (quartet, $J_{F/F}$ = 9.5 Hz, 1, CF$_3$), 61.3 (broad quartet, $J_{F/F}$ = 9.5 Hz, 1, CF$_3$), 66.0 ppm [doublet, $J_{H/F}$ = 7.0 Hz to quartets, J = 2.0 Hz, 2, $(CF_3)_2CH$].

A 5-g sample of a mixture of cyclic and linear ketones, **2** and **3** (R = CH$_3$) (about 3:1 ratio), containing none of the enol ester **6** was sealed in a glass tube with 5.2 g of **1** and heated for 100 hr in a steam bath. Examination by glpc showed no change, and none of the enol ester **6** was detected. The materials were recharged with a trace of BF$_3$ and heated for 62 hr. There was recovered most of the ketene (4.5 g) and a viscous liquid. Glpc showed the presence of the cyclic ketone **2** (R = CH$_3$) and the absence of both the linear ketone **3** (R = CH$_3$) and the enol ester **6**.

1,1,1-Trifluoro-2-(trifluoromethyl)-5-nonen-3-one (3, R = C$_3$H$_7$) and 2,2-Bis(trifluoromethyl)-3-butylcyclobutanone (2, R = C$_4$H$_9$).—A mixture of 17 g (0.20 mol) of hexene-1 and 36 g (0.20 mol) of **1** was heated in a sealed glass tube at 150° for 8 hr. On distillation there was obtained 11 g (20%) of material boiling mostly at 70° (14 mm) which was separated by glpc into about 40% linear ketone **3** (R = C$_3$H$_7$) and 60% cyclic ketone **2** (R = C$_3$H$_7$). In addition, the distillation gave 1 g of material boiling at 94° (14 mm).

For the linear ketone **3** (R = C$_3$H$_7$): ir 5.73 (C=O), 6.15 μ (C=C); nmr ^1H at τ 4.3–5.2 (multiplet, 2, CH=CH), 5.90 [septet, $J_{H/F}$ = 7.5 Hz, 1, $(CF_3)_2CH$], 6.92 (doublet, $J_{H/H}$ = 5 Hz, 2, CH$_2$), 8.10–8.50 (multiplet, 2, CH$_2$), 8.60–9.30 (multiplet, 2, CH$_2$), 9.47 (triplet, $J_{H/H}$ = 6.0 Hz, 3, CH$_3$); ^{19}F at 64.6 ppm [doublet, $J_{H/F}$ = 7.5 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_{10}H_{12}F_6O$: C, 45.84; H, 4.62; F, 43.51. Found: C, 45.39; H, 4.59; F, 43.20.

After 4 years of storage, the vinyl protons of the α,β isomer were easily identified, one as a doublet (J = 16 Hz) to triplets (J = 6.5 Hz) centered at τ 2.93 and one as a doublet (J = 16.0 Hz) at 3.77: ^{19}F nmr at 64.7 ppm [doublet, J = 7.5 Hz, $(CF_3)_2CH$].

For the cyclic ketone **2** (R = C$_3$H$_7$): ir 5.50 μ (C=O); nmr ^1H at τ 7.10 (multiplet, 3, ring CH), 8.40 (broad peak, 2, CH$_2$), 8.88 (multiplet, 4, CH$_2$CH$_2$), 9.34 (multiplet, 3, CH$_3$); ^{19}F nmr consisted of a pair of quartets.

Anal. Calcd for $C_{10}H_{12}F_6O$: C, 45.84; H, 4.62; F, 43.51. Found: C, 46.58; H, 4.57; F, 41.78.

The higher boiling product was characterized only by ir data [5.50 (C=O) and 5.88 μ (C=C)], which were consistent with an enol ester analogous to that obtained with the ketene and butene-1 (**6**).

1,1,1-Trifluoro-2-(trifluoromethyl)-5-methyl-5-hexen-3-one (7).—A mixture of 16 g (0.09 mol) of **1** and excess isobutylene (10 g, 0.18 mol) in a Carius tube was heated overnight in a steam bath. There was obtained 18 g (86%) of the β,γ-unsaturated ketone **7**: bp 76° (100 mm); n^{25}_D 1.3505; ir 5.75 (C=O), 6.05 μ (C=C); nmr ^1H at τ 5.38 and 5.50 (multiplets, 2, CH=CH), 5.93 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 7.00 (singlet, 2, CH$_2$), 8.70 (doublet, $J_{H/H}$ = 1.8 Hz, to doublets, $J_{H/H}$ = 1.0 Hz, 3, CH$_3$); ^{19}F at 65.2 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_8H_8F_6O$: C, 41.06; H, 3.45; F, 48.72. Found: C, 41.67; H, 3.89; F, 47.87.

1,1,1-Trifluoro-2-(trifluoromethyl)-5-methyl-4-hexen-3-one, (8).—The above reaction was repeated, doubling the quantities and heating on the steam bath for a longer time (60 hr). There was obtained 21 g (50%) of the above β,γ-unsaturated ketone (**7**) and 15.5 g (37%) of the higher boiling α,β-unsaturated ketone (**8**): bp 90° (100 mm); n^{25}_D 1.3760; ir 5.91 (C=O), 6.20 μ (C=C); nmr ^1H at τ 3.83 (broad, 1, CH=), 5.87 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 8.07 (doublet, $J_{H/H}$ = 1.3 Hz, 3, CH$_3$), 8.30 (doublet, $J_{H/H}$ = 1.4 Hz, 3, CH$_3$); ^{19}F at 65.1 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_8H_8F_6O$: C, 41.06; H, 3.45; F, 48.72. Found: C, 40.89; H, 3.64; F, 48.00.

2,8-Bis(trifluoromethyl)-1,1,1,9,9,9-hexafluoro-5-methylenenonane-3,7-dione (9) and 4-Methylene-2,6-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-3-[3,3,3-trifluoro-2-(trifluoromethyl)propionyl]-4H-pyran (10).—In another experiment designed to prepared products containing more of the ketene, a mixture of the β,γ-unsaturated ketone **7** (18 g, 0.077 mol) and 16 g (0.09 mol) of **1** was heated in a Carius tube in a steam bath for 60 hr.

There was obtained by distillation 8 g (50%) of recovered β,γ-ketone mixed with its α,β-unsaturated isomer (**8**). In addition 1 g (3%) of white solid was collected which was recrystallized from carbon tetrachloride, mp 81–83°, as well as 7.9 g (46%) of higher boiling material which solidified, mp 114–142°. After two recrystallizations of the latter from carbon tetrachloride there remained 5.5 g, mp 142–143°.

The material melting at 81–83° was characterized as **9**: ir 5.74 (C=O), 6.07 μ (C=C); nmr ^{1}H at τ 5.07 (singlet, 1, $=CH_2$), 5.28 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 6.58 (singlet, 2, CH_2); ^{19}F at 64.8 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_{12}H_8F_{12}O_2$: C, 34.98; H, 1.95; F, 55.34. Found: C, 35.00; H, 1.89; F, 55.56.

The material melting at 142–143° was characterized as **10**: ir 5.88 (C=O) and 6.07, 6.16, 6.44 μ (C=C); nmr ^{1}H at τ 2.05 (doublet, $J_{H/H}$ = 2.0 Hz, 1, =CHH), 3.48 (doublet, $J_{H/H}$ = 2.0 Hz, 1, =CHH), 4.19 (singlet, 1, =CH), 5.40 [3 overlapping septets, $J_{H/F}$ = 8.0 Hz, 3, $(CF_3)_2CH$]; ^{19}F at 65.1 [doublet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 66.2 ppm [triplet of overlapping doublets, $J_{H/F}$ = 8.0 Hz, 2, $(CF_3)_2CH$].

Anal. Calcd for $C_{16}H_6F_{18}O_2$: C, 33.59; H, 1.40; F, 59.79. Found: C, 33.39; H, 1.29; F, 59.28.

2,2-Bis(trifluoromethyl)-3-phenylcyclobutanone (14).—A mixture of 10 g (0.056 mol) of **1** and 6.0 g (0.058 mol) of styrene containing phenothiazine as polymerization inhibitor sealed in a Carius tube was immiscible at room temperature. After being heated 4 hr in a steam bath, the homogeneous reaction mixture distilled to give 12.6 g (80%) of **14**: bp 72° (1 mm); $n^{25}D$ 1.4420; ir 5.48 μ (C=O); nmr ^{1}H at τ 3.03 (singlet, 5, C_6H_5), 5.90–7.41 (multiplet, 3 CH); ^{19}F at 54.9 (quartet, $J_{F/F}$ = 8.6 Hz, 1, CF_3), 59.7 ppm (quartet, $J_{F/F}$ = 8.6 Hz, 1, CF_3).

Anal. Calcd for $C_{12}H_8F_6O$: C, 51.11; H, 2.86; F, 40.43. Found: C, 50.73; H, 2.85; F, 40.14.

1,1,1-Trifluoro-5-phenyl-2-(trifluoromethyl)-5-hexen-3-one (11) and 1,1,1-Trifluoro-5-phenyl-2-(trifluoromethyl)-2,5-hexadien-3-ol 3,3,3-Trifluoro-2-(trifluoromethyl)propionate (12).—A mixture of 6.5 g (0.055 mol) of α-methylstyrene, 0.5 g of phenothiazine, and 8.0 g (0.045 mol) of **1** sealed in a Carius tube formed two layers at room temperature. After being warmed 15 min on a steam bath, the mixture was homogeneous and crystallized at room temperature. After 2-hr heating, the product was distilled at ~82° (1 mm) (12.8 g, 96%). In spite of a nearly constant boiling point, it was a mixture of the β,γ-unsaturated ketone **11** and its enol ester **12**. Recrystallization from petroleum ether (bp 30–60°) gave 4.6 g (35%) of purified **11**: mp 68–70°; ir 5.78 μ (C=O); nmr ^{1}H at τ 3.1 (multiplet, 5, C_6H_5), 4.75 (singlet, 1, =CHH), 5.12 (singlet, 1, =CHH), 5.23 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH-$], 6.33 (singlet, 2, CH_2); ^{19}F at 64.5 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH-$].

Anal. Calcd for $C_{13}H_{10}F_6O$: C, 52.75; H, 3.41; F, 38.51. Found: C, 52.68; H, 3.54; F, 38.45.

A pure sample of the enol ester **12** was prepared as follows. A mixture of 11.8 g (0.10 mol) of α-methylstyrene, 36 g (0.2 mol) of **1**, and 0.1 g of phenothiazine (polymerization inhibitor) was heated in a sealed tube in a steam bath for 46 hr. Recovered was 8 g of ketene and 33.5 g (70%) of enol ester boiling mostly at 65° (0.1 mm): $n^{25}D$ 1.4150; ir 5.58 (C=O), 5.96 μ (C=C); nmr ^{1}H at τ 6.54 [septet, $J_{H/F}$ = 7.4 Hz, $(CF_3)_2CH$], 6.47 (multiplet, 2, CH_2), 5.17 (singlet, 1, =CH), 4.84 (singlet, 1, =CH), 2.99 (singlet, 5, C_6H_5); ^{19}F at 58.8 (quartet, $J_{F/F}$ = 9.2 Hz, 1, CF_3), 60.6 (broad quartet, $J_{F/F}$ = 9.2 Hz, 1, CF_3), 65.0 ppm [doublet, $J_{F/H}$ = 7.4 Hz, to quartets, $J_{F/F}$ = 2.5 Hz, 2, $(CF_3)_2CH$].

Anal. Calcd for $C_{17}H_{10}F_{12}O_2$: C, 43.07; H, 2.12; F, 48.10. Found: C, 44.19; H, 2.27; F, 47.13.

A sample of the above enol ester **12** (4.5 g) was heated in a sealed tube with water (5 ml) in a steam bath for 20 hr. It was immiscible and remained unchanged; so 15 ml of tetrahydrofuran was added and the heating continued for 1 week. Removal of the solvents gave a gelatinous polymer and an oil which was characterized by ir as being largely the α,β-unsaturated ketone **13** (see below).

A sample of the enol ester **12** when added to 10% sodium hydroxide solution became warm and gave a tar. A similar result was obtained with the β,γ-unsaturated ketone **11** and dilute alkali.

Passage of a sample of the enol ester **12** through a preparative gas chromatography column at 147° gave **1**, which was collected and characterized by ir, as well as the β,γ-unsaturated ketone **11**, characterized by ir and mixture melting point.

1,1,1-Trifluoro-5-phenyl-2-(trifluoromethyl)-4-hexen-3-one (13).—In a reaction of excess α-methylstyrene with **1** heated for only a short time it was possible to isolate the α,β-unsaturated ketone **13**. The α-methylstyrene (23.6 g, 0.2 mol), 20 g (0.11 mol) of **1**, and 0.1 g of phenothiazine were charged into a Carius tube and heated in a steam bath for 20 min. Distillation of the product gave 17.5 g of material, bp 65° (0.3 mm). By crystallization of these fractions from petroleum ether it was possible to isolate 3 g of the α,β-unsaturated ester **13**: mp 42–42.5°; ir 5.92 (C=O) and 6.25, 6.35, 6.69 (conjd linear and aromatic C=C); nmr ^{1}H ($CDCl_3$) at τ 7.37 (doublet, $J_{H/H}$ = 1.3 Hz, 3, CH_3), 5.90 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 3.38 (broad singlet, 1, =CH), 2.53 (singlet, 5, C_6H_5); ^{19}F at 64.0 ppm [doublet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_{13}H_{10}F_6O$: C, 52.75; H, 3.41; F, 38.51. Found: C, 53.14; H, 3.48; F, 39.00.

Samples of the above α,β-unsaturated ketone, **13**, mp 42°, and the β,γ-unsaturated isomer, **11**, mp 70°, were each sealed in nmr tubes with equimolar amounts of bis(trifluoromethyl)ketene and heated in a steam bath for 18 hr. No reaction occurred as evidenced by crystallization and separation of the ketene on cooling. Addition of BF_3 to the tube containing the β,γ-unsaturated isomer and continued heating caused darkening and some tar formation but only starting ketone and no enol ester **12** could be detected by infrared absorption.

8,8-Bis(trifluoromethyl)bicyclo[4.2.0]octan-7-one (16).—A mixture of cyclohexene (8 g, 0.1 mol), **1** (18 g, 0.1 mol), and 0.1 g of phenothiazine was sealed in a Carius tube and heated in a steam bath for 7 weeks. There was recovered 15 g of crude product. From about 5 g boiling around 45° (0.25 mm) there was collected by glpc 0.6 g of **16** and two less pure fractions (0.7 and 0.5 g) which appeared to be hexafluoroisobutyryl cyclohexenyl ketones. From another run using double quantities of cyclohexene and ketene at 175° for 8 hr, there was obtained only 1.6 g of a mixture similar to the above and a higher boiling mixture.

For the cyclobutanone **16**: ir 5.54 μ (C=O); nmr ^{1}H at τ 6.51 (multiplet, 1), 7.19 (multiplet, 1), 8.55 (multiplet, 8); ^{19}F at 62.7 (quartet, $J_{F/F}$ = 9.7 Hz, 1, CF_3), 69.4 ppm (quartet, $J_{F/F}$ = 9.7 Hz, 1, CF_3).

Anal. Calcd for $C_{10}H_{10}F_6O$: C, 46.19; H, 3.88; F, 43.85. Found: C, 45.61; H, 3.90; F, 43.23.

4,4-Bis(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]nonan-3-one (15).—An equimolar (0.05 mol) mixture of **1** (9.5 g) and norbornene (5 g) sealed in a Carius tube remained immiscible at room temperature after being heated overnight in a steam bath. However, heating at 175° for 8 hr gave 13.3 g (97%) of **15**: bp 79° (10 mm); $n^{25}D$ 1.4086; ir 5.53 μ (small-ring ketone C=O); nmr ^{1}H at τ 6.30 (multiplet, 1) 7.30 (multiplet, 3), 8.53 (multiplet, 6); ^{19}F at 63.2 (quartet, 1, $J_{F/F}$ = 10.2 Hz, CF_3), 68.7 ppm (quartet, to doublets, 1, $J_{F/F}$ = 10.2 Hz, $J_{F/H}$ = 2.0 Hz, CF_3).

Anal. Calcd for $C_{11}H_{10}F_6O$: C, 48.57; H, 3.71; F, 41.91. Found: C, 48.53; H, 3.64; F, 42.15.

Hexahydro-6-(hexafluoroisopropylidene)-1,2,4-methenopentalen-5(6H)-one (25).—A mixture of 9.0 g (0.05 mol) of **1** and 5.0 g (0.054 mol) of bicycloheptadiene in a Carius tube was miscible at room temperature but immiscible on cooling. After being heated for 1 hr in a steam bath, the mixture no longer separated on cooling. After 2 hr, there was obtained 11 g (81%) of **25**, bp 62° (1 mm), $n^{25}D$ 1.4297. Recrystallization from cold petroleum ether gave 7.6 g: mp 32–33°; ir 6.04 μ (C=C); nmr ^{1}H at τ 5.20 (1), 6.64 (quartet, 1, $J_{H/F}$ = 2.0 Hz), 7.77 (1), 8.28 (2), 8.48 (3) (all of the peaks had some fine structure); ^{19}F at 55.8 (quartet to doublets, 1, $J_{F/F}$ = 8.8 Hz, $J_{F/H}$ = 2.0 Hz, CF_3), 57.7 ppm (quartet, 1, $J_{F/F}$ = 8.8 Hz, CF_3).

Anal. Calcd for $C_{11}H_8F_6O$: C, 48.93; H, 2.99; F, 42.22. Found: C, 49.18; H, 3.11; F, 41.87.

10-Hexafluoroisopropylidene-9-oxatricyclo[4.2.2.0^{2,5}]deca-3,7-diene (23).—Cyclooctatetraene (7.0 g, 0.067 mol) with 0.5 g of phenothiazine added and **1** (9.5 g, 0.053 mol) in a Carius tube were immiscible at room temperature. After the mixture was heated overnight in a steam bath, strong cooling was necessary to separate two layers. Heating for 3 days in a steam bath gave 4 g of the ketene, 3.3 g of cyclooctatetraene, and 5.4 g (36%) of product, bp 70° (1 mm), which solidified: mp 78–79° (petroleum ether); ir 6.08 and 6.15 μ (C=C); nmr ^{1}H at τ 4.00 (multiplet, 4), 5.83 (multiplet, 1), 5.84 (multiplet, 1), 6.82 (multiplet, 1), 7.17 (multiplet, 1); ^{19}F at 53.1 (quartet, 1, $J_{F/F}$ = 9.8 Hz, CF_3), 56.7 ppm (quartet, 1, $J_{F/F}$ = 9.8 Hz, CF_3).

Anal. Calcd for $C_{12}H_8F_6O$: C, 51.11; H, 2.86; F, 40.43. Found: C, 50.97; H, 2.79; F, 39.83.

3,3-Bis(trifluoromethyl)-11-hexafluoroisopropylidene-10-oxatricyclo[4.3.2.0^{2,5}]undec-8-en-4-one (24).—A mixture of 20 g (0.2 mol) of cycloheptatriene (91% pure), 0.1 g of phenothiazine, and 37 g (0.2 mol) of **1** sealed in a Carius tube was immiscible at room temperature, but homogeneous after being heated overnight in a steam bath. Distillation gave 30 g (68%) of a 2:1 ketene–cycloheptatriene product: bp 90° (9 mm); ir 5.55 (C═O), 5.90 μ with 6.00 μ sh (C═C); nmr ^{1}H at τ 2.15 (singlet, 1), 3.55 (multiplet, 2), 4.05 (multiplet, 2), 4.80 (multiplet, 2), 7.80 (triplet, 1, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 6.0 Hz); ^{19}F at 61.3 (quartet, 1, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 6.4 Hz, CF$_3$), 63.5 [singlet, 2, C(CF$_3$)$_2$], 64.6 ppm (quartet to doublets, 1, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 6.4 Hz, $J^{\mathrm{F}}/_{\mathrm{H}}$ = 1.5 Hz, CF$_3$).

Anal. Calcd for $C_{15}H_8F_{12}O_2$: C, 40.21; H, 1.80; F, 50.89. Found: C, 40.84; H, 2.05; F, 51.07.

6-Hexafluoroisopropylidene-5,6-dihydro-2H-pyran (17).—A Carius tube was charged with 41 g (0.23 mol) of **1**, 5.0 g (0.09 mol) of butadiene, and 0.1 g of phenothiazine and heated 60 hr in a steam bath. There was recovered 25 g of the ketene and 21 g (98%) of crude **17** which was 94% pure by glpc. Distillation gave 16.7 g (78%): bp 65° (9 mm); n^{25}D 1.3957; ir 6.10 μ (C═C); nmr (220 MHz, 20% in CDCl$_3$, internal TMS) ^{1}H at τ 3.98 (multiplet, 1, ═CH), 4.12 (multiplet, 1, ═CH), 5.38 (multiplet, 2, CH$_2$), 6.80 (multiplet, 2, CH$_2$); ^{19}F at 57.2 (quartet, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 9.8 Hz, to triplet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 2.2 Hz, 1, CF$_3$), 58.7 ppm (quartet, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 9.8 Hz, to triplet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 1.8 Hz, 1, CF$_3$).

Anal. Calcd for $C_8H_6F_6O$: C, 41.41; H, 2.61; F, 49.14. Found: C, 40.82; H, 2.74; F, 48.82.

***cis*-1,1,1-Trifluoro-2-trifluoromethyl-4,6-heptadien-3-one (18) and 6-[2,2,2-Trifluoro-1-(trifluoromethyl)ethyl]-2H-pyran (19).**—By contrast to the above experiment, when excess ketene was not used, usually only polymeric oils were obtained from such long heating periods. By using hexane as solvent and less heating the open chain *cis* isomer **18** was obtained and the possible presence of the cyclic isomer **19** was indicated by ^{1}H nmr.

A mixture of 21 g (0.39 mol) of butadiene, 35 g (0.20 mol) of **1**, 25 ml of hexane, and 0.1 g of phenothiazine was heated in a Carius tube 16 hr at 70°. Recovered was 27 g (58%) of 1:1 products, bp 41–46° (20 mm), n^{25}D 1.3910, and 6 g of higher boiling mixture. The material boiling at 42–46° appeared pure by glpc, but ^{1}H nmr of different fractions showed it to be a mixture. There were varying amounts of peaks not present in either the pure *cis* (**18**) or *trans* (**20**) isomer. These peaks included a well-separated septet which was at about 0.8-ppm higher field with a slightly larger (0.4 Hz) J value and may have been due to the presence of cyclic isomer **19**. Its presence diminished in the higher boiling cuts and in all cuts on standing.

The *cis* isomer **18** was distinguished from *trans* **20** (see below): ^{1}H nmr (220 MHz, 20% in CDCl$_3$, internal TMS) τ 5.82 [septet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 7.9 Hz, 1, (CF$_3$)$_2$C**H**], 4.30 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz, 1, $-\mathrm{C}{=}\underset{\mathrm{H}}{\mathrm{C}}{<}^{\mathrm{H}}_{\mathbf{H}}$), 4.27 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 18.0 Hz, 1, $-\mathrm{C}{=}\mathrm{C}{<}^{\mathbf{H}}_{\mathrm{H}}$), 3.89 [doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz, 1, (CF$_3$)$_2$CHCO-C**H**═], 3.34 [doublet $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz as apparent triplet, 1, (CF$_3$)$_2$CHCO–CH═C**H**–], 2.39 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 18.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz as overlapping pattern, 1, –C**H**═CH$_2$); ir 5.89 (C═O) and 6.18, 6.37 μ (C═C).

Anal. Calcd for $C_8H_6F_6O$: C, 41.41; H, 2.61; F, 49.14. Found: C, 41.46; H, 2.40; F, 48.70.

***trans*-1,1,1-Trifluoro-2-trifluoromethyl-4,6-heptadien-3-one (20).**—A sample (10.6 g) of the above material, bp 43–45° (20 mm), which by ^{1}H nmr was largely *cis* isomer **18** containing some **19** was mixed with three drops of triethylamine and slowly fractionated. The first fraction had about the same boiling point [43–50° (20 mm)] as the starting material, but glpc now showed a definite shoulder on the starting material peak and a small, well-separated peak which eluted later (*trans* isomer **20**). Later fractions (3.4 g, 32%) were nearly pure *trans* isomer **20**, bp 61° (20 mm), n^{25}D 1.4088. These fractions became crystalline because of dimer formation (see below) after standing at room temperature for 60 hr. The first fraction remained liquid even after 2 months, but became viscous because of polymer formation. The *trans* isomer **20** was further characterized as follows: ir 5.90 doublet (C═O) and 6.15, 6.30 μ (C═C); nmr (220 MHz, 20% in CDCl$_3$, internal TMS) τ 5.73 [septet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 7.9 Hz, 1, (CF$_3$)$_2$C**H**], 4.30 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz, 1, ${}_{\mathrm{H}}{>}\mathrm{C}{=}\mathrm{C}{<}^{\mathrm{H}}_{\mathbf{H}}$), 4.23 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 17.0 Hz, 1, ${}_{\mathrm{H}}{>}\mathrm{C}{=}\mathrm{C}{<}^{\mathbf{H}}_{\mathrm{H}}$), 3.64 [doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 15.0 Hz, 1, (CF$_3$)$_2$CHCO-C**H**═], 3.40 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 17.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 11.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 10.0 Hz, 1, –C**H**═CH$_2$), 2.64 [doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 15.0 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 11.0 Hz, 1, (CF$_3$)$_2$CHCOCH═C**H**–].

Dimer 21.—A sample (1.8 g) of the *trans* isomer **20** mixed with excess **1** (6.8 g) and 0.1 g of hydroquinone was heated in a sealed tube in a steam bath 16 hr. Removal of the unreacted ketene gave an oily solid which crystallized from hexane gave 0.9 g (50%) of dimeric **20**, mp 95–99°. Repeated recrystallizations raised the melting point to 107–108°, giving a relatively pure isomer of unknown structure represented by formula **21**: ir 5.75 (C═O), 5.90 (conjugated C═O), 6.13 μ (C═C); nmr ^{1}H at about τ 5.10 [two overlapping septets, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.0 Hz, 2, (CF$_3$)$_2$CH], 2.9 to 4.5 (complex pattern, 4, vinyl H), 6.4 to 8.6 (complex patterns, 6, CH); ^{19}F at 64.5 [doublet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.0 Hz, 1, (CF$_3$)$_2$CH], 64.8 ppm [doublet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.0 Hz, 1, (CF$_3$)$_2$CH]. Each of these doublets was overlapped slightly by a smaller doublet (J = 8.0 Hz), probably due to an isomer.

Anal. Calcd for $C_{16}H_{12}F_{12}O_2$: C, 41.41; H, 2.61; F, 49.14; mol wt, 464. Found: C, 41.81; H, 2.63; F, 48.67; mol wt, 482 (cryoscopic in benzene).

8,8-Bis(trifluoromethyl)-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-4-oxabicyclo[4.2.0]oct-2-en-7-one (22).—A sample (1.7 g) of the *cis* isomer **18** mixed with 0.1 g of hydroquinone was treated with excess **1** (6.8 g) in a sealed tube in a steam bath for 16 hr exactly as described above for the *trans* isomer **20**. In this case no solid was isolated but removal of unreacted ketene gave an oil which was shown by glpc to be **22**, containing 2 mol of **1** per mol of butadiene. Product **22** could be prepared in high yield by long heating of butadiene with excess **1**. The use of excess **1** gave excellent overall yields of cyclic products **17** and **22**, but conditions for obtaining one to the exclusion of the other were not well defined. The following conditions are essentially those described above for preparation of **17**, but in this case a high yield of **22** was obtained.

A mixture of 28 ml (47 g, 0.26 mol) of **1**, 7.1 g (0.13 mol) of butadiene, and 0.1 g of phenothiazine was heated for 60 hr in a sealed tube in a steam bath. There was distilled 41.4 g (77%) of the product **22**: bp 64° (0.4 mm); n^{25}D 1.3687; ir 5.50 (small ring, C═O), 5.95 μ (C═C); nmr ^{1}H (220 MHz, 20% in CDCl$_3$, internal TMS) at τ 6.40 [doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 12 Hz to doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 5 Hz, 1, (CF$_3$)$_2$C–C**H**], 6.43 [septet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.0 Hz, 1, (CF$_3$)$_2$C**H**], 6.18 (doublet, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 12.0 Hz, to doublets, $J^{\mathrm{H}}/_{\mathrm{H}}$ = 5.0 Hz, 1, –OC**H**H), 5.98 (unresolved broad peak, 1, O═C–C**H**), 5.55 (doublet, J = 12.0 Hz, to doublets, J = 2.0 Hz, 1, –COH**H**), 4.55 (doublet, J = 5.0 Hz, 1, C═C**H**); ^{19}F at 62.2 (quartet with fine structure, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 9.0 Hz, 1, ring CF$_3$), 64.2 [doublet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.0 Hz to quartets, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 2.0 Hz, 2, (CF$_3$)$_2$CH], 66.9 ppm (quartet, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 9.0 Hz, 1, ring CF$_3$).

Anal. Calcd for $C_{12}H_6F_{12}O_2$: C, 35.15; H, 1.48; F, 55.61. Found: C, 35.33; H, 1.64; F, 55.53.

8,8-Bis(trifluoromethyl)-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-4-oxabicyclo[4.2.0]oct-2-en-7-ol (22c).—Product **22** (20 g, 0.05 mol) in 100 ml of ethanol with 5 g of Raney nickel catalyst was shaken 4 hr at 125° under 2000 psi of hydrogen. There was isolated 13.9 g of material boiling mainly at 82° (0.9 mm). It was shown by glpc to be a 7:3 mixture of solid hydrogenation product (49% yield) and liquid products of reaction with ethanol (analogous to methanol reaction below). The first distillation cut (1.5 g) solidified and after four recrystallizations from petroleum ether there was obtained 0.7 g of **22c**: mp 63–65° [both mass spectrum (parent peak 412) and ^{1}H nmr indicated additions of two hydrogen atoms to **22**, and ir and ^{1}H nmr (one exchangeable proton) indicated formation of an alcohol; ir also showed hydroxyl and loss of the small-ring carbonyl group]; ir broad 2.82 (OH), 5.95 μ (C═C); nmr ^{1}H (220 MHz, 20% in CDCl$_3$, internal TMS) τ 7.29 (broad, exchangeable with D$_2$O, 1, –OH), 6.77 (multiplet, 2, CH$_2$), 6.41 [septet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.1 Hz, 1, (CF$_3$)$_2$CH], 5.99 (multiplet, 1, CH), 5.53 (multiplet, 1, CH), 5.14 (broad, 1, CHOH), 4.66 (multiplet, 1, C═CH); ^{19}F at 60.9 (quartet, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 10.1 Hz, 1, CF$_3$), 65.5 [doublet, $J^{\mathrm{H}}/_{\mathrm{F}}$ = 8.1 Hz, 2, (CF$_3$)$_2$CH], 72.5 ppm (quartet, $J^{\mathrm{F}}/_{\mathrm{F}}$ = 10.1 Hz, 1, CF$_3$).

Anal. Calcd for $C_{12}H_8F_{12}O_2$: C, 34.98; H, 1.96; F, 55.34. Found: C, 35.61; H, 2.40; F, 55.13.

Methyl 4,6-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-3,4-dihydro-2H-pyran-3-carboxylate (22a) and Methyl 4-[2,2-Difluoro-1-(trifluoromethyl)vinyl]-6-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-3,4-dihydro-2H-pyran-3-carboxylate (22b).—Compound **22** (42 g) in 50 ml of methanol containing a trace of sodium methoxide (probably unnecessary) was heated in a sealed tube in a steam bath 16 hr. After removal of methanol there was distilled in ten fractions 35 g of oil boiling mostly at 58–60° (0.05 mm). This product was shown by glpc to consist of two compounds, and when separated by preparative glpc, one of them crystallized. Early fractions were richer in the liquid product, which proved to be a methanol adduct assigned structure **22a**. Later fractions were richer in the solid product and could be recrystallized (petroleum ether) to mp 46–48°. The solid product, a methanol adduct minus HF, was assigned structure **22b**. Attempts to convert **22a** to **22b** were unsuccessful under the reaction conditions (methanol containing $NaOCH_3$ at 100°), in methanol saturated with hydrogen chloride at 100°, in glyme saturated with cesium fluoride at 100°, or in aqueous sodium hydroxide at 100°. Therefore it appears that nucleophilic attack of **22** with methanol or methoxide ion gives a carbanionic center which either loses fluoride ion to give **22b** or adds a proton to give **22a**, and **22b** is not formed from **22a**.

Compound **22a** was characterized as follows: ir 5.72 ($C{=}O$), 5.91 μ ($C{=}C$); nmr ^1H (220 MHz, 20% in $CDCl_3$, internal TMS) τ 6.84 (multiplet, 1, $CH_3O_2C{-}CH$), 6.75 [multiplet, 1, $(CF_3)_2CH{-}CH$], 6.48 [septet, $J_{H/F}$ = 8.0 Hz, $(CF_3)_2CHC{=}C$], 6.35 [multiplet, 1, $(CF_3)_2CHCH$], 6.26 (singlet, 3, OCH_3), 5.70 (doublet, $J_{H/H}$ = 6.0 Hz, 2, CH_2), 4.84 (broad, 1, $C{=}CH$); ^{19}F at 61.2 (broad quintet, presumably quartet, $J_{F/F}$ = 10.0 Hz, to doublet, $J_{H/F}$ = ~8 Hz, 1, CF_3), 65.2 (broad quintet, presumably quartet, $J_{F/F}$ = 10.0 Hz, to doublet, $J_{H/F}$ = ~8 Hz, 1, CF_3), 65.7 ppm [doublet, $J_{F/F}$ = 8.0 Hz, $(CF_3)_2CHC{=}C$].

Anal. Calcd for $C_{13}H_{10}F_{12}O_3$: C, 35.32; H, 2.28; F, 51.58; mol wt, 442.0437 (high resolution mass spectrum). Found: C, 35.48; H, 2.23; F, 51.54; mol wt, 442.0432.

Compound **22b** was characterized as follows: ir 5.78 ($C{=}O$), 5.95 μ ($C{=}C$); nmr ^1H (220 MHz, 20% in $CDCl_3$, internal TMS) τ 6.84 (multiplet, 1, CH), 6.44 [septet, $J_{H/F}$ = 8.0 Hz, 1, $(CF_3)_2CH$], 6.39 (multiplet, 1, CH), 6.30 (singlet, 3, OCH_3), 5.85 (multiplet, 1, CH), 5.70 (multiplet, 1, CH), 4.91 (doublet, $J_{H/H}$ = 4.5 Hz, 1, $C{=}CH$); ^{19}F at 58.7 (doublet, J_{F/CH_3} = 22.0 Hz to doublet, $J_{F/F}$ = 10.8 Hz, 3, CF_3), 69.7 (quartet, J_{F/CF_3} = 22.0 Hz, to doublet, $J_{F/F}$ = 10.8 Hz, to doublet, $J_{H/F}$ = 2.5 Hz, 1, $C{=}CF$), 72.1 (overlapping quartet, J_{F/CF_3} = 10.8 Hz, to doublet, $J_{F/F}$ = 10.8 Hz, 1, $C{=}CF$), 66.0 ppm [doublet, $J_{H/F}$ = 8.0 Hz, to doublet, $J_{H/F}$ = 2.0 Hz, 6, $(CF_3)_2CH$].

Anal. Calcd for $C_{13}H_9F_{11}O_3$: C, 37.00; H, 2.15; mol wt, 422.0376 (high resolution mass spectrum). Found: C, 37.38; H, 2.47; mol wt, 422.0381.

Compound **22** was treated with ethanol and with water (in equal amount of tetrahydrofuran) at 100° to give in each case a mixture of two products (adduct and adduct minus HF) analogous to the above methanol reaction. The mixtures were characterized only by nmr and not separated.

7,7-Bis(trifluoromethyl)-4,5-dihydroxy-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-3-oxabicyclo[4.2.0]octan-8-one (22d).—Starting material was recovered in an attempt to oxidize **22** (15 g, 0.037 mol) with acid permanganate at room temperature. It was redissolved in 50 ml of acetone, 50 ml of water, and 10 ml of concentrated sulfuric acid. While this solution was refluxed, a total of 36 g of potassium permanganate was added in small portions giving a vigorous reaction. After cooling, the mixture was decolorized with SO_2 and water added to dissolve inorganic salt. A heavy oil (12 g) separated and partly crystallized. Filtration gave 3.4 g (21%) of white crystals, mp 167–168°, and 6 g of oil. Recrystallization from xylene gave 3.0 g white needles, mp 167–168°. Structure **22d** is proposed for this product [mass spectrum (parent peak 444) indicated the addition of two hydroxyls to **22**, and ir showed loss of double bond, gain of hydroxyl and retention of the small ring carbonyl]: ir 2.78 (OH), 5.60 μ ($C{=}O$); nmr ^1H (220 MHz, 20% in acetone-d_6, internal TMS) τ 7.17 (broad multiplet, 1, CH), 6.93 (singlet, exchangeable with D_2O, 1, OH), 6.77 (broad multiplet, 1, CH), 5.86 [multiplet, 1, $(CF_3)_2CH$], 5.76 (multiplet, 1, CH), 5.63 (multiplet, 1, CH), 5.48 (multiplet, 1, CH), 4.09 (multiplet, exchangeable with D_2O, <1, OH); ^{19}F at 61.0 (quartet, $J_{F/F}$ = 9.0 Hz, 1, CF_3), 61.5 (quartet, $J_{F/F}$ = 9.0 Hz, 1 CF_3), 62.8 (quintet, presumably quartet, $J_{F/F}$ = 10.0 Hz, to doublet, $J_{H/F}$ = ~10 Hz, CF_3), 65.7 ppm (quintet, presumably quartet, $J_{F/F}$ = 10.0 Hz, to doublet, $J_{H/F}$ = ~10 Hz, 1, CF_3).

Anal. Calcd for $C_{12}H_8F_{12}O_4$: C, 32.46; H, 1.81; F, 51.35. Found: C, 32.97; H, 1.95; F, 51.19.

Registry No.—**1,** 684-22-0; **2** (R = H), 25636-67-3; **2** (R = CH_3), 25679-30-5; **2** (R = C_3H_7), 25636-68-4; **3** (R = H), 4141-85-9; **3** (R = CH_3), 25636-70-8; **3** (R = C_3H_7), 25636-71-9; **4** (R = H), 25636-72-0; **4** (R = CH_3), 25636-73-1; **4** (R = C_3H_7), 25636-74-2; **5,** 25636-75-3; **6,** 25636-76-4; **7,** 5548-89-0; **8,** 5548-91-4; **9,** 25636-79-7; **10,** 25636-80-0; **11,** 25636-81-1; **12,** 25636-82-2; **13,** 25636-83-3; **14,** 5604-68-2; **15,** 25636-85-5; **16,** 25636-86-6; **17,** 17698-59-8; **18,** 7108-74-9; **19,** 25636-87-7; **20,** 10253-48-2; **21,** 25631-63-4; **22,** 25636-88-8; **22a,** 25636-89-9; **22b,** 25636-90-2; **22c,** 25636-91-3; **22d,** 25631-64-5; **23,** 25636-92-4; **24,** 25636-93-5; **25,** 25636-94-6.