no unreacted enamine **3**. The 10.5- and 12.4-min peaks were trapped and their infrared spectra were essentially identical with authentic **4** and **5**, respectively. The drying agent was removed by filtration in a nitrogen drybox and the filtrate was concentrated under vacuum (20 mm). The resultant oil was distilled in a bulb-to-bulb apparatus with a free flame at 0.5 mm. Some water came over and then a reddish oil was collected, 0.657 g. A glpc of this oil indicated that compounds **4** and **5** were still the major constituents (*ca.* 51%), but a number of other peaks were present which were not present at the end of the reaction. Integration gave the following reaction yields: **4**, 9.4%, and **5**, 7.8%.

Oxidation of α-Pyrrolidinocyclohexanone (4).—α-Pyrrolidinocyclohexanone (4.09 g, 0.0244 mol) was injected into a mixture of 70 ml of ethyl acetate and 5 g of magnesium sulfate contained in a flask attached to an oxygen buret. Oxygen uptake commenced immediately and 353 ml (61%) had been absorbed in 18 min. After 117 min, 463 ml (78%) had been taken up. A glpc indicated three peaks: 4.5 min (X4 peak height), 10.5 min (X32), and 12.5 min (X4). The latter two had the same retention times as those of the starting ketone **4** and 6-oxo-1-pyrrolidinocyclohexene (**5**). The 12.5-min peak was trapped and its infrared spectrum was identical with that of authentic **5**. The reaction was allowed to proceed for an additional 18.5 hr during which an additional 310 ml of oxygen was absorbed (total uptake 773 ml or 1.3 molar equiv). A glpc indicated peaks at 4.5 min (X8), 10.5 min (X8), and 12.5 min (X4). There were now several minor peaks at longer retention times.

Preparation of α-Pyrrolidinocyclohexanone (4).—α-Hydroxycyclohexanone (11.41 g, 0.10 mol), pyrrolidine (8.35 ml, 0.10 mol), and benzene (50 ml) were placed in a flask connected to a Dean–Stark trap. The system was flushed with nitrogen and heated at reflux for 3 hr at which time 0.10 mol of water had collected in the trap. The benzene was removed under vacuum (20 mm) and the residue distilled to give 14.26 g (89%) of title compound: bp 91–93° (4.5 mm); $n^{20}\text{D}$ 1.4893; ir (neat) 1720 cm^{-1} (C═O); nmr (C_6H_6) δ 2.8–1.9 (m, 7), 1.9–1.2 (m, 10); mass spectrum (50 eV) *m/e* (rel intensity) 167 (23), 139 (53), 110 (284), 97 (38), 96 (101).

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.7; H, 10.4; N, 8.2.

Preparation of 6-Oxo-1-pyrrolidinocyclohexene (5).—Cyclohexa-1,2-dione (10.20 g, 0.091 mol) and pyrrolidine (6.47 g, 0.091 mol) were dissolved in 40 ml of benzene and heated at reflux for 4 hr. A total of 1.5 ml of water collected in a Dean–Stark trap (theory, 1.64). The benzene was removed at 20 mm and the dark oil remaining was distilled. A fraction was collected: 9.0 g; bp 70–71° (0.2 mm); ir (neat) 1680 and 1600 cm^{-1} [lit.[6] bp 70–72° (0.07 mm); ir 1681 and 1605 cm^{-1}].

Oxidation of 1-Morpholinocyclohexene (6) at 80°.—1-Morpholinocyclohexene (28.75 g, 0.172 mol) was dissolved in 150 ml of anhydrous benzene in an apparatus containing a Dean–Stark trap. The solution was heated at reflux while oxygen was bubbled through at 0.05 ft^3/hr. After 22 hr, no water had collected, the solution was red, and a dark film adhered to the reactor walls. A glpc (70° start, 10°/min program) indicated a number of peaks, among which the major peaks were at 3 min, 10.5 min, and 11.5 min. The latter two peaks were trapped and their infrared spectra were essentially identical with 1-morpholinocyclohexene **6** and α-morpholinocyclohexanone **7**, respectively.

Registry No.—**1**, 15431-00-2; **3**, 1125-99-1; **4**, 22003-63-0; **6**, 670-80-4.

The Reaction of Hexafluoroacetone with Olefins

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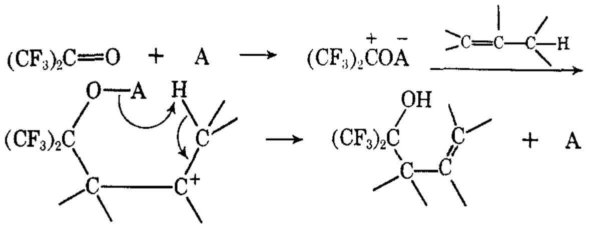
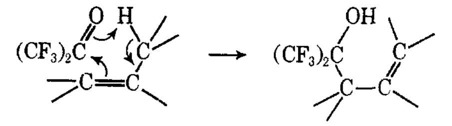
Several papers have recently discussed the reactions of hexafluoroacetone or fluoral with olefins.[1] These reactions may be carried out in good yield either by heating olefin and hexafluoroacetone or by treating them with a Lewis acid catalyst at low (−10°) temperature in hydrocarbon solvent. Both methods are reported to yield a single product, 1,1-bis(trifluoromethyl)-3-alken-1-ol. Mechanisms proposed to account for the single product and the double bond position are shown below.

catalyzed reaction



(1)

thermal reaction



(2)

In connection with other studies, we have recently had occasion to apply the $AlCl_3$-catalyzed reaction of hexafluoroacetone to a complex olefin system. In view of the intractable mixture of products obtained, the simpler alkenes propylene and 1-butene were reexamined.

A cold (−30°) mixture of olefin, hexafluoroacetone, and $AlCl_3$ catalyst in pentane was allowed to warm slowly. At *ca.* −15° there was an exothermic reaction, after which the mixture was stirred at 0° for 2 hr. The product mixture from either propylene or 1-butene was primarily *cis*- and *trans*-1,1-bis(trifluoromethyl)-2-alken-1-ols, with lesser amounts of the reported[1] 3-alken-1-ols. These products were isolated by preparative scale glpc methods and characterized by elemental analysis as well as nmr and infrared spectroscopy.

The thermal reaction of hexafluoroacetone with these olefins was carried out for comparison; and in these cases, as reported,[1] the only materials isolated were the isomeric 1,1-bis(trifluoromethyl)-3-alken-1-ols.

Products and yields for these reactions are shown in Table I.

In order to determine if the spectrum of compounds obtained from the $AlCl_3$-catalyzed reaction represents primary products or a secondarily rearranged mixture, each of the available isomers was treated with the catalyst in pentane solution. Treatment of **1**, *trans*-**3**, and *trans*-**4** yielded only the unchanged starting material, while *trans*-**2** was converted to 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran. From the absence of double-bond isomerization, it must be concluded that the observed products are formed in a primary reaction.

These results indicate that, while the cyclic concerted process (eq 2) is probably appropriate for the thermal reaction, the $AlCl_3$-catalyzed process is better thought of in terms of a Friedel–Crafts type of reaction involving

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[1] (a) N. P. Gambaryan, El. M. Rokhlina, and Yu. V. Zeifman, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.), **8**, 1425 (1965); (b) H. R. Davis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 25M; (c) I. L. Knunyants and B. L. Lyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.), **2**, 329 (1962); (d) R. L. Adelman, *J. Org. Chem.*, **33**, 1400 (1968); (e) R. Poutral, J. Marteau, and R. Cheritat, *Bull. Soc. Chim. Fr.*, 1182 (1968).

TABLE I

REACTIONS OF HEXAFLUOROACETONE WITH OLEFINS

$$\begin{array}{lcl} (CF_3)_2C{=}O & & HO(CF_3)_2CCH_2CH{=}CHR \\ + & \longrightarrow & \mathbf{1}, R = H \quad \mathbf{2}, R = CH_3 \\ RCH_2CH{=}CH_2 & & + HO(CF_3)_2CCH{=}CHCH_2R \\ & & \mathbf{3}, R = H \quad \mathbf{4}, R = CH_3 \end{array}$$

$AlCl_3$-catalyzed reaction

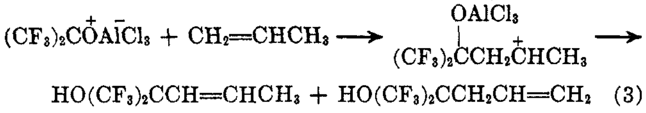
R	Product, % conversion			
	1	*trans*-**3**	*cis*-**3**	
H	27	43	2	
	trans-**2**	*cis*-**2**	*trans*-**4**	*cis*-**4**
CH_3	26	6	47	0[a]

Thermal reaction

R	Product, % conversion			
	1	*trans*-**3**	*cis*-**3**	
H	82	0	0	
	trans-**2**	*cis*-**2**	*trans*-**4**	*cis*-**4**
CH_3	59	15	0	0[a]

[a] No standard was available, but there was no evidence for the presence of these compounds.

a free carbonium ion (or equivalent associated species). Electrophilic attack of the hexafluoroacetone–$AlCl_3$ complex on olefin yields an adduct as shown. This may lose a proton from either adjacent carbon to yield the mixtures of products observed.



$$(CF_3)_2C\overset{+}{O}A\overset{-}{l}Cl_3 + CH_2{=}CHCH_3 \longrightarrow (CF_3)_2\underset{}{\overset{OA\overset{-}{l}Cl_3}{\overset{|}{C}}}CH_2\overset{+}{C}HCH_3 \longrightarrow$$
$$HO(CF_3)_2CCH{=}CHCH_3 + HO(CF_3)_2CCH_2CH{=}CH_2 \quad (3)$$

Experimental Section[2]

$AlCl_3$-Catalyzed Reactions. Propylene.—The procedure is essentially the same as that in the literature.[1c] A cold (−30°) mixture of 166 g (1 mol) of hexafluoroacetone, 84 g (2 mol) of propylene, and 2 g of $AlCl_3$ in 1 l. of pentane was allowed to warm slowly. At *ca.* −15°, there was a gentle exotherm, after which the reaction mixture was stirred at 0° for 2 hr. Treatment with dilute (5%) hydrochloric acid and distillation yielded 150 g (72%) of product boiling at 97–100°. Glpc analysis showed the following product composition (yield, retention time): 1,1-bis(trifluoromethyl)-3-buten-1-ol (**1**) (37%, 9.0 min); *trans*-1,1-bis(trifluoromethyl)-2-buten-1-ol (*trans*-**3**)(60%, 13.2 min); and *cis*-1,1-bis(trifluoromethyl)-2-buten-1-ol (*cis*-**3**) (3%, 10.5 min). Compounds **1** and *trans*-**3** were isolated by preparative scale glpc techniques, but *cis*-**3** was not recoverable because of its low concentration.

Analytical Data. Compound 1 [$CH_{a2}{=}CH_bCH_{c2}C(CF_3)OH_d$].—Infrared spectrum: 1650 (C=C stretch) and 3500 cm^{-1} (OH stretch); ^1H nmr ($CDCl_3$) δ 5.8 (H_a, complex), 5.3 (H_b, complex), 2.70 (d, J_{cb} = 7 HzH_c), and 3.35 (H_d). The ^{19}F nmr spectrum showed a single peak at 0.0 ppm.

Anal. Calcd for $C_6H_6F_6O$: C, 34.62; H, 2.90. Found: C, 34.82; H, 3.23.

Compound *trans*-3 [$CH_{a3}CH_b{=}CH_cC(CF_3)_2OH_d$].—Infrared spectrum: 1680 (C=C stretch) and 3500 cm^{-1} (OH stretch); ^1H nmr δ 1.93 (d, J_{ab} = 7 Hz, H_a), 6.27 (q, 2, J_{ba} = 7 Hz, J_{bc} = 16 Hz, H_b), 5.58 (d, J_{cb} = 16 Hz, H_c), and 3.40 (H_d). The ^{19}F nmr spectrum showed a single peak at −0.1 ppm. The *trans* stereochemistry is dictated by the 16-Hz coupling constant for the vinyl protons. For the *cis* isomer, a value of *ca.* 11 Hz would be expected (see *cis*-**2**).

1-Butene.—The procedure is the same as that with propylene, using 166 g (1 mol) of hexafluoroacetone, 112 g (2 mol) of 1-butene, and 2 g of $AlCl_3$. Distillation yielded 175 g (79%) of product boiling at 114–117°. Glpc analysis showed the following product composition (yield, retention time): *trans*-1,1-bis(trifluoromethyl)-3-penten-1-ol (*trans*-**2**) (33%, 10.0 min); *cis*-1,1-bis(trifluoromethyl)-3-penten-1-ol (*cis*-**2**) (8%, 11.0 min); and *trans*-1,1-bis(trifluoromethyl)-2-penten-1-ol (*trans*-**4**) (59%, 13.0 min). Compounds were isolated by preparative scale glpc methods.

Analytical Data. Compound *trans*-2 [$CH_{a3}CH_b{=}CH_cCH_{d2}$-$C(CF_3)_2OH$] had ^1H nmr δ 1.70 (d, J_{ba} = 7 Hz, H_a); 5–6 (complex, H_b and H_c), and 2.60 (d, J_{cd} = 7 Hz, H_d). Spin decoupling shows H_b to be centered at 5.70 ppm and H_c to be at 5.35 ppm. Each shows a 16-Hz coupling constant, indicating the *trans* stereochemistry about the double bond. The ^{19}F nmr spectrum shows a single peak at −1.6 ppm.

Anal. Calcd for $C_7H_8F_6O$: C, 37.85; H, 3.62. Found: C, 38.39; H, 3.63.

Compound *cis*-2 [$CH_{a3}CH_b{=}CH_cCH_{d2}C(CF_3)_2OH$] had nmr δ 1.64 (d, J_{ba} = 7 Hz, H_a), 5–6 (complex, H_b and H_c), and 2.70 (d, J_{cd} = 7 Hz, H_d). Spin decoupling showed H_b to be centered at 5.40 ppm and coupled with the *cis* vinyl proton showing an 11-Hz splitting constant.

Compound *trans*-4 [$CH_{a3}CH_{b2}CH_c{=}CH_dC(CF_3)_2OH$] had ^1H nmr δ 0.97 (t, J_{ba} = 6 Hz, H_a), 2.1 (complex, H_b), 6.28 (t, 2, J_{cb} = 6 Hz, J_{cd} = 16 Hz, H_c), 5.60 (d, J_{cd} = 16 Hz, H_d). The ^{19}F nmr spectrum showed a single peak at 0.6 ppm.

Anal. Calcd for $C_7H_8F_6O$: C, 37.85; H, 3.62. Found: C, 37.78; H, 3.71.

Thermal Reactions. Propylene.—The procedure followed is essentially the same as that in the literature.[1c] A mixture of 21 g (0.5 mol) of propylene and 83 g (0.5 mol) of hexafluoroacetone was heated in a sealed tube at 150° for 16 hr. Distillation of the contents gave 85 g (82%) of **1**, bp 94–95° (lit.[1c] bp 95–98°). Glpc analysis showed no other isomer to be present.

1-Butene.—The reaction was carried out in the same manner as with propylene, using 2.8 g (0.05 mol) of 1-butene and 8.3 g (0.050 mol) of hexafluoroacetone. Distillation of the residue yielded 7.7 g (74%) of product boiling at 117–119°. Glpc analysis shows this to consist of 80% *trans*-**2** and 20% *cis*-**2**.

Treatment of Alkenols with Aluminum Chloride in Pentane.—The pure alcohol (0.25 g), 25 ml of pentane, and 0.050 g of $AlCl_3$ were stirred for 3 hr at room temperature. After washing with 5% hydrochloric acid, the reaction mixture was examined by glpc. With **1**, *trans*-**3**, and *trans*-**4**, only starting material was observed. With *trans*-**2**, however, the only product that was observed was a material with a retention time of 1.5 min. A sample obtained by preparative scale glpc methods was identified as 2,2-bis(trifluoromethyl)-5-methyltetrahydrofuran. The infrared spectrum shows no hydroxyl absorption, while the ^1H nmr spectrum may be described as follows: δ, 1.30 (d, J = 6 Hz, CH_3), 4.3 (complex, HCO), and 1.5–2.5 [complex, $(CH_2)_2$]. The ^{19}F nmr spectrum shows two quartets at −0.9 and 1.6 ppm (J = 9 Hz).

Anal. Calcd for $C_7H_8F_6O$: C, 37.85; H, 3.62. Found: C, 37.97; H, 3.65.

Registry No.—**1**, 646-97-9; *cis*-**2**, 16223-66-8; *trans*-**2**, 16203-00-2; *trans*-**3**, 21308-76-9; *trans*-**4**, 21308-77-0; 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran, 21297-53-0; hexafluoroacetone, 684-16-2.

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[2] All boiling points are uncorrected. Infrared spectra were obtained as films using the Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were obtained with a Varian Associates Model HA 100 spectrometer using chloroform as solvent and TMS as internal standard. For fluorine spectra, trifluoroacetic acid was used as an external standard. Spectra were run using field frequency lock at 94.1 MHz using a modification described by Douglas.[3] Spectra at both frequencies are accurate to ±0.02 ppm. Glpc analyses were run on an F & M Model 720 gas chromatograph using a 9-ft column filled with a 20% Carbowax 20M on Chromosorb P packing. Preparative work was done on an F & M Model 775 Prepmaster gas chromatograph using a similar column (column temp 110°, helium flow 100 ml/min). Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Col.

[3] A. W. Douglas, Abstracts of papers presented at the 7th Experimental Nmr Conference, Feb 1966.

1-Triptycyl Radical Stability

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1-Triptycyl radical should be destabilized both by its considerable angle strain (triptycene has about 63° of "total angle strain" compared with 75° for norbornane)