and fluoride ions. Distillation of the organic layer on spinning-band column separated the two main components, 1-heptafluoroisopropoxy-2-bromocyclohexane (**1**) and 1,2-dibromocyclohexane (**2**).[14] The purity of the products was checked by vpc analysis (Table X).

TABLE X

PHYSICAL CONSTANTS OF PURIFIED SAMPLES

Product	Bp, °C (mm)	$n^{25}D$	Yields, %
1	51–53 (7)	1.3949	22
2	41–41.5 (0.5)	1.5491	26
trans-Dibromocyclohexane	99.6–99.9 (13)[a]	1.5507	

[a] Literature boiling point: S. Winstein, *J. Amer. Chem. Soc.*, **69**, 2488 (1947).

Isolation of N-(2-Bromocyclohexyl)acetamide (3) and N-(2-Bromocyclohexyl)-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)-butyramide (4).—The reaction of $(CF_3)_2CO$–CsF adduct with cyclohexene and bromine was run in acetonitrile as described above. Emulsions formed on treatement of the acetonitrile solution with water. Methanol was added (*ca.* 250 cc of CH_3OH to 900 cc of water) giving good separation of the organic layer. The aqueous layer was stripped to remove all the methanol and some water, giving a white solid (10.1 g, 18%). Recrystallization from ethyl acetate or $CHCl_3$–CCl_4 gave N-(2-bromocyclohexyl)-acetamide (**3**): mp 105–108° (lit.[9] mp 109–110°) (the mixture melting point with authentic sample prepared according to Cairns[9] showed identity: mmp 105–108°); λ_{max} (KBr) 3.05, 6.05, 6.1, 6.4 μ; nmr[15] ($CDCl_3$), H^1, sharp singlet at δ 2.04 ppm (CH_3 protons), broad peak at 6.75 ppm (–NH–), multiplet at ~4.0 ppm (tertiary ring protons), multiplet at ~1.6 ppm (secondary ring protons).

The organic layer was distilled giving 1-heptafluoroisopropoxy-2-bromocyclohexane and 1,2-dibromocyclohexane. The brown distillation residue crystallized on standing (11.6 g). A 3-g sample of the solid was chromatographed on silica gel (80 g). Elution with 15% ethyl acetate in benzene gave a white solid, mp 119–121.5°. The crystals were dissolved in methanol and precipitated with water giving the pure N-(2-bromocyclohexyl)-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)butyramide (**4**): mp 124–125°; total yield, 12%; λ_{max} (KBr) 2.97, 3.08, 6.08, 6.2, 6.45, 8.35–8.45 μ. *Anal.* Calcd for $C_{11}H_{14}BrF_6NO_2$: C, 34.30; H, 3.63; N, 3.63; Br, 20.7; F, 29.7. Found: C, 34.2; H, 3.96; N, 4.1; Br, 20.8; F, 30.1.[16]

Nmr[15] analysis follows (DMSO-d_6): F^{19}, singlet at +77.4 cps (CF_3 groups); H^1, broad peak at δ 8.9 ppm (–OH and –NH), broad peak at 2.9 ppm (–CH_2–), multiplet at ~4.0 ppm (tertiary ring protons), multiplet at ~1.6 ppm (secondary ring protons).

Hydrolysis of 4.—Amide **4** (1.34 g, 0.0035 mol) in 25 cc of 25% H_2SO_4 was heated to reflux for 2 hr. The clear water layer was decanted from some decomposition products and extracted with ether. Evaporation of the dried ether layer gave 0.5 g (64%) of white crystals, mp 72–80°. Sublimation at 50° (0.02 mm) gave the pure 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)-butyric acid (**5**), mp 83–84°, mmp 83.5–84° with sample prepared from hydrolysis of β,β-bistrifluoromethyl-β-propiolactone.

Hydrolysis of β,β-Bistrifluoromethyl-β-propiolactone.[17]—The lactone (2.66 g, 0.013 mol) was treated with 60% H_2SO_4 at reflux for 30 min. The clear water solution was distilled under vacuum (~50 mm). The distillate was extracted with ether. Evaporation of the ether solution gave 2.18 g (76%) of white crystals, mp 83–84.5°. Recrystallization from CCl_4 and sublimation gave the pure acid (**5**): mp 87–88° (lit.[17] mp 87–88°); λ_{max}^{neat} 5.9 μ; nmr[15] (acetone-d_6), F^{19}, equivalent CF_3 groups at +78.5 cps, $J_{CF_3CH_2}$ = 1 cps; H^1, –OH and –COOH protons gave a very broad peak at δ 8.5 ppm, two aliphatic protons appeared at 2.96 ppm.

Registry No.—**2,** 5401-62-7; **3,** 16003-42-2; **4,** 16003-43-3; **5,** 1547-36-0.

Acknowledgments.—We are indebted to Drs. J. P. Sibilia and R. Ettinger for the nmr analyses, to Mrs. L. S. Komarowski for recording the ir spectra, and to Mr. S. Roth for technical assistance.

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[14] The absence of an absorption in the ir spectrum at 7.75 μ reported for the *cis* compound showed that the addition was predominantly *trans*.

[15] TMS was used for the H^1 and CCl_3F for the F^{19} spectra as standards.

[16] Nitrogen value is high owing to the formation of CF_4.

[17] I. L. Knunyants and Yu. A. Cheburkov, *Bull. Acad. Sci. SSSR, Div. Chem. Sci.*, 640 (1960).

Addition of Hexafluoroacetone to Ketenimines

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Received December 27, 1967

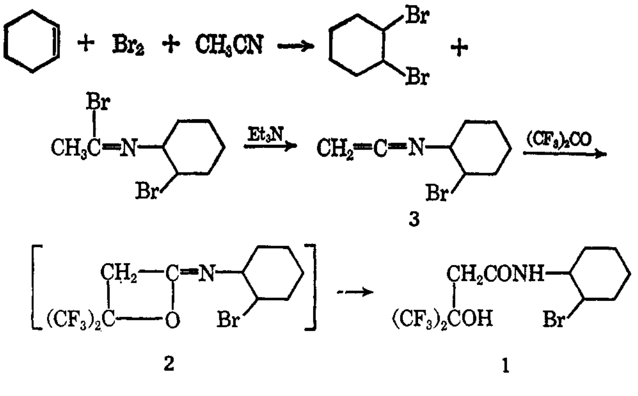
The ionic addition of hexafluoroacetone to ketenimines to give oxetanes was demonstrated in the reaction of diphenylketene-*p*-tolylimine and hexafluoroacetone. The structure of the very unreactive cyclic addition product was determined by mass spectroscopy. The same 1,2-addition mechanism was postulated in a reaction of cyclohexene, bromine, and acetonitrile with hexafluoroacetone. However, in this system, the hydrolysis product, a hydroxy amide, was isolated.

Recently we described the formation of a fluorine-substituted, secondary amide (**1**) in a reaction of the metal fluoride adduct of hexafluoroacetone with cyclohexene and bromine in acetonitrile.[1] An oxetane (**2**) was postulated as the intermediate, formed by the addition of hexafluoroacetone to a ketenimine (**3**).

Results and Discussion

In order to study the formation of **1** a reaction was run as described in Scheme I. Bromine was combined with cyclohexene in acetonitrile; triethylamine was added; and the precipitated hydrobromide was removed from the system. Subsequent reaction with hexafluoroacetone gave, after hydrolysis, 1,2-dibromocyclohexane and the amide (**1**) as the only products; no N-(2-bromocyclohexyl)acetamide was formed.

SCHEME I



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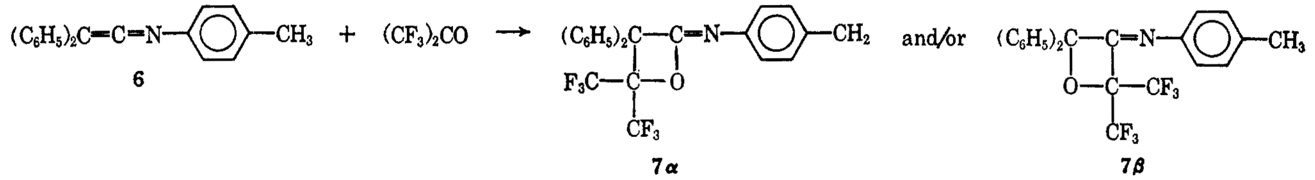
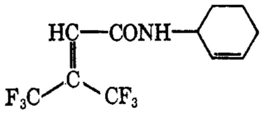
[1] F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1839 (1968).

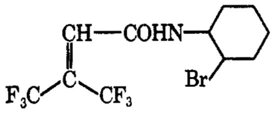
SCHEME II



The best evidence for the formation of an iminooxetane (**2**) would be the isolation of this intermediate. The hydrolysis step was thus excluded and the acetonitrile solution was distilled directly under vacuum; however, when the temperature was raised, decomposition took place (probably by the loss of hydrogen bromide) and a white compound was sublimed on the spinning-band column. This was isolated in a low yield and identified as N-(3-cyclohexenyl)hexafluoroisopropylideneacetamide (**4**). Also, a very small amount of the corresponding bromine-substituted amide (**5**) was found.



4



5

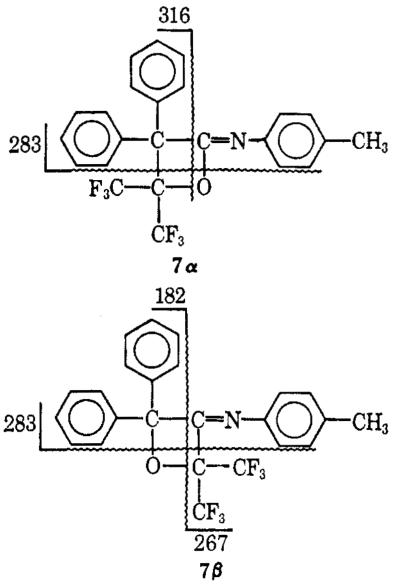
These amides could have been formed by proton abstraction and ring opening of the oxetane intermediate (**2**).

The infrared spectrum of the acetonitrile solution after the addition of hexafluoroacetone showed absorptions at 5.6 and 5.8 μ, as well as a strong absorption at 6.05 μ, and there was no sign of an -OH group. It thus appeared that the iminooxetane (**2**) was formed, but was too unstable to be isolated under these conditions.

We therefore decided to use a disubstituted ketenimine, which should not have the same tendency to rearrange after reaction with the fluoro ketone. Thus diphenylketene-*p*-tolylimine (**6**) was prepared[2] and its reaction with hexafluoroacetone was studied (Scheme II). At room temperature and atmospheric pressure, no reaction with hexafluoroacetone was observed, but, upon heating the acetonitrile solution of the two reactants in a closed vessel to 110°, reaction took place and a white crystalline compound was isolated in good yield. It showed a strong infrared absorption at 5.69 μ which could be attributed to a highly strained imine structure.[3] The high intensity of the absorption indicated the presence of a strongly electronegative substituent on the double bond as in an imino ether.[4] However, also a $-C(CF_3)_2-$ substituent might have given the same effect. On the other hand addition of hexafluoroacetone across the $-C{=}N-$ bond would leave a $-C{=}C-$ structure, which would not be expected to give such a strong absorption at 5.7 μ.[5] Similarly, the data from the uv spectrum as well as from the nmr spectrum were inconclusive.

However, in the mass spectrum a fragment was observed from an olefin (*m/e* 316) which could only have been obtained from structure (**7α**) (Chart I). Furthermore, no fragments at *m/e* 182 or *m/e* 267 were found as would be expected from structure (**7β**). The molecular ion peak was observed at *m/e* 449, as well as the base peak at *m/e* 283, assigned to the ketenimine fragment which is formed by the loss of hexafluoroacetone.

CHART I



7α

7β

The addition compound (**7α**) was soluble in alcohol and acetone, and in strong acid (85% H_2SO_4). Thus it could not be methylated (CH_3I), and attempted cleavage with 48% HBr gave only starting material. Acid or basic hydrolysis left the compound unchanged, and it was not reduced catalytically (Adams catalyst), or by lithium aluminum hydride. However, in a strongly acidic medium under severe conditions (75% sulfuric acid at reflux for 2 hr) the compound lost hexafluoroacetone. In addition to unreacted iminooxetane, N-(*p*-tolyl)diphenylacetamide was isolated as the hydrolysis product of the ketenimine. The absence of cleavage to form an isocyanate, as observed for compounds with a structure of type α,[6] can be understood in view of the well-known difficulty of cleaving a $-C(CF_3)_2-O-$ bond.

The ready addition of hexafluoroacetone to a ketenimine is expected in view of its analogous addition to olefins and ketene under mild conditions to give oxetanes.[7] Formation of the more crowded α isomer shows that the reaction is kinetically controlled, with the difference in energy between the possible resonance forms of the ketenimine being the most important factor in determining the structure of the product.

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[2] C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).

[3] L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.*, 1887 (1964).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

[5] Even if the structure where hexafluoroacetone had added across the C=N double bond could be definitely excluded only by the mass spectrum results, it was considered quite unlikely, owing to the known mode of addition of hexafluoroacetone to ketene structures. Furthermore a negative ozonization experiment spoke against a $-C{=}C-$ structure.

[6] L. A. Singer, and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 598 (1967); *ibid.*, **99**, 941 (1967).

[7] N. P. Gambaryan, E. M. Rokhlin, Yu. V. Zeifman, C. Ching-Yun, and I. L. Knunyants, *Angew. Chem.*, 1008 (1967), and references therein.

Experimental Section

The nmr spectra were recorded with a Varian A-56-60 spectrometer with TMS (H^1) or CCl_3F (F^{19}) as internal standards. The mass spectrum was taken on a spectrometer from Consolidated Electrodynamics Corp., Model 21-103 (modified) at an ionizing current of 52.5 μA and an inlet system (stainless steel) temperature of 150°.

Preparation of N-(2-Bromocyclohexyl)-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)butyramide (1) (Scheme I).—Dry acetonitrile, distilled from P_2O_5 (50 cc), was placed in a 500-cc flask with stirrer, Dry Ice condenser, thermometer, and gas inlet. Cyclohexene (chromatographic grade) (21.6 g, 0.25 mol), and then bromine, (40.0 g, 0.25 mol) were added slowly at 5–10° over a period of 1 hr. All bromine had reacted at the end of the addition. Dry diethyl ether (200 cc) and 17.5 g (0.17 mol) of triethylamine (redistilled) were added at 10°. A white precipitate was immediately formed. The solution was pressed with nitrogen through a filter to another flask. The precipitate was collected and dried (14.0 g) corresponding to 31% reaction with acetonitrile. To the solution was added hexafluoroacetone, (41.5 g 0.25 mol) at 5–15° over a period of 1.5 hr. The solution was stirred at room temperature for 30 min. It was poured on ice and water and made weakly acidic with dilute HCl. The organic layer was separated and the water layer was extracted with methylene chloride. The combined organic layers were washed with water, dried, and evaporated, leaving an oil which gave crystals of **1** on standing in the refrigerator (5.2 g, 6%), mp 112–118°. The remaining oil was distilled under vacuum giving 22.0 g (36%) of 1,2-dibromocyclohexane, bp 43–44° (0.5 mm). From the distillation residue an additional 16% of the amide **1** was isolated through chromatography on silica gel (elution with 15% ethyl acetate in benzene). The total yield of **1** was 22%. The pure amide crystallized from $CHCl_3$–CCl_4: mp 123–124°; λ_{max} (KBr) 2.98, 3.08, 6.1, 6.2, 6.45, 8.35–8.45 μ. *Anal.* Calcd for $C_{11}H_{14}F_6NO_2$: C, 34.20; H, 3.63; Br, 20.7; F, 29.7. Found: C, 34.25; H, 3.89; Br, 20.9; F, 30.1. A mixture melting point determination with the amide prepared by another method[1] gave no depression, and their nmr spectra were identical.

Isolation of N-(3-Cyclohexenyl)hexafluoroisopropylideneacetamide (4) and N-(2-Bromocyclohexyl)hexafluoroisopropylideneacetamide (5) in an Attempt to Isolate the Iminooxetane Intermediate (2).—The reaction of hexafluoroacetone, cesium fluoride, cyclohexene, and bromine was run as described earlier.[1] In this run, however, the hydrolysis at the end was omitted. Instead, the acetonitrile solution was filtered to remove precipitated cesium bromide, and the solution was flash evaporated at 5–10°. The oily residue was distilled under vacuum (0.2 mm) giving acetonitrile, 1-bromo-2-heptafluoroisopropoxycyclohexane, and 1,2-dibromocyclohexane. On further heating, decomposition took place and a white solid sublimed in the column. The crystals were dissolved in methanol, and water was added to give white crystals, mp 93–96°, in low yield (<5%). Recrystallization from hexane gave the pure N-(3-cyclohexenyl)hexafluoroisopropylideneacetamide (**4**): mp 96.5–97.5°; nmr ($CDCl_3$), F^{19}, two signals at +60.5 and +65.9 cps assigned to nonequivalent CF_3 groups ($J_{CF_3-CF_3}$ = 7.0 cps, J_{CF_3-CH} = 1.5 cps); H^1, one vinylic proton appeared at 7.0 split by six fluorines, two vinylic ring protons appeared at 5.7 and 5.9, –NH– appeared at approximately 6, the tertiary ring proton appeared at 4.6, and a group of signals in the region 1.75–2.0 ppm (δ) was assigned to the remaining ring protons. *Anal.* Calcd for $C_{11}H_{11}F_6NO$: C, 45.99; H, 3.86; F, 39.69; N, 4.88. Found: C, 45.84; H, 3.77; F, 38.3; N, 5.20.[8]

The solid, consisting mainly of cesium bromide, which had been removed by filtration, was dissolved in 250 cc of water. A white solid precipitated from the solution, giving 0.9 g, mp 140–150°. Recrystallization from hexane gave the pure N-(2-bromocyclohexyl)hexafluoroisopropylideneacetamide (**5**): mp 157–158°; λ_{max} (KBr) 3.03, 6.07, 6.4 μ; nmr (DMSO-d_6), F^{19}, two CF_3 groups at +59.5 and +63.5 cps ($J_{CF_3-CF_3}$ = 7.0 cps, J_{CF_3-CH} = 1.0 cps); the H^1 nmr spectrum showed one vinylic proton at 7.47 split by six fluorines, an –NH proton at 8.7, two tertiary protons at 4.0, and eight secondary protons at 1.6–2.0 ppm (δ). *Anal.* Calcd for $C_{11}H_{12}F_6NOBr$: C, 35.89; H, 3.29; F, 30.96; N, 3.81; Br, 21.72. Found: C, 35.74; H, 3.15; F, 31.6; N, 4.04;[8] Br, 21.9.

Other attempts, in which the hydrolysis in Scheme I was omitted and the mixture was chromatographed on silica gel column, in order to isolate the intermediate **2**, were unsuccessful, even when the reaction was run at low temperature (below −25°).

Addition of Hexafluoroacetone to Diphenylketene-*p*-tolylimine.—Diphenylketene-*p*-tolylimine (**6**) was prepared from N-(*p*-tolyl)diphenylacetamide by the dehydration with P_2O_5 and alumina in pyridine.[2]

Diphenylketene-*p*-tolylimine (8.5 g, 0.03 mol) was dissolved in 250 cc of dry acetonitrile in a pressure bottle and the solution was cooled to −20°. A large excess of hexafluoroacetone was added, and the system was closed and slowly heated to 110° to give a pressure of 70 psig. The temperature was kept at 110° for 6 hr and then at 70° (40 psig) overnight. The solution was evaporated to dryness to give a crystalline residue (mp 110–130°). It was extracted with petroleum ether (40–60°) at reflux twice; the insoluble portions collected on the filter were combined to give 2.4 g (26%) of a white solid, mp 173.5–176°, identified as N-(*p*-tolyl)diphenylacetamide by mixture melting point and spectral data.

The petroleum ether solutions were combined and cooled to give a white crystalline product (10.0 g, 74%). Recrystallization from methanol or petroleum ether gave the pure N-(*p*-tolyl)2,2-diphenyl-3,3-bistrifluoromethyliminooxetane (**7a**): mp 119.5–120.5°; λ_{max} (KBr), 5.69, 8.0, 8.35 μ; λ_{max} (MeOH) 255 mμ (log ϵ 2.11); nmr ($CDCl_3$), F^{19}, broad signal at +69.5 assigned to the two CF_3 groups; the nmr H^1 spectrum showed aromatic and –CH_3 protons. The aromatic protons of the toluene ring appeared at 7.8 ppm (δ, band center), which indicated that the ring was very electron deficient.

Anal. Calcd for $C_{24}H_{17}F_6NO$: C, 64.18; H, 3.81; F, 25.37. Found: C, 64.11; H, 3.80; F, 25.2.

Acknowledgments.—Thanks are due Dr. J. P. Sibilia and Dr. R. Ettinger for the nmr analyses and to Mrs. L. Komarowski for the infrared analyses. The mass spectrum was recorded by Mr. E. R. McCarthy. Technical assistance by Mr. S. Roth is gratefully acknowledged.

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[8] The nitrogen value is high owing to the formation of CF_4.