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Syntheses and Reactions of Fluorine-containing Aromatic Ketones

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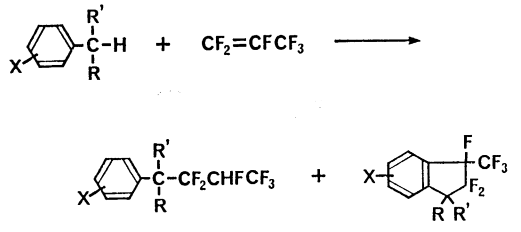
Phenyl 1,1,2,3,3,3-hexafluoropropyl ketone(I) and 2,2,3-trifluoro-3-(trifluoromethyl)indanone(II) were synthesized by the radical-addition reaction of benzaldehyde to hexafluoropropene. The reduction with $NaBH_4$ and the Grignard reaction with methylmagnesium iodide of these ketones gave the corresponding secondary and tertiary alcohols respectively. A Clemmensen reduction, alkaline hydrolyses, and reactions with hydroxylamine and with diazomethane were also carried out.

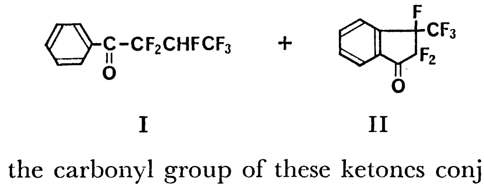
Fluorine-containing ketones have become of interest for their characteristic chemical properties due to the presence of an electron-deficient carbonyl group. Especially hexafluoroacetone and its chlorine-substituted derivatives have been widely studied and found to have unique reactivities.[1] However, few investigations of the syntheses and reactions of phenyl fluoroalkyl ketones are known.

In previous papers, we reported that the radical-addition reaction of alkylbenzenes to hexafluoropropene gave the 1 : 1 adducts, together with the cycloadducts,[2] and that the ratio of the products could be controlled by the reaction conditions.[3]



(R, R′=H, CH_3)

To ascertain the applicability of the above-mentioned radical reaction to the preparation of phenyl fluoroalkyl ketones, we attempted the addition of benzaldehyde to hexafluoropropene and obtained phenyl 1,1,2,3,3,3-hexafluoropropyl ketone(I) as a 1 : 1 adduct and 2,2,3-trifluoro-3-trifluoromethylindanone(II) as a cycloadduct.



I II

Since the carbonyl group of these ketones conjugates with the aromatic ring, and since its electron density is decreased by the adjacent highly electronegative fluorine atoms, these ketones seem to have a high reactivity toward the nucleophiles. Therefore, we attempted some reactions of these ketones.

Results and Discussion

Addition Reaction of Benzaldehyde to Hexafluoropropene. The addition reaction of benzaldehyde to hexafluoropropene (HFP) was carried out in the presence of di-*t*-butyl peroxide in a stainless steel autoclave. Four kinds (A—D) of reaction conditions were employed: to investigate the effect of dilution with a solvent, 1,1,2-trichlorotrifluoroethane was used as an inert solvent in Methods B and C, and to study the effect of the molar ratio, an excess of HFP was used in Methods A and B, whereas an excess of benzaldehyde was used in Methods C and D. The reaction conditions and product yields are given in Table 1.

TABLE 1. THE RADICAL ADDITION REACTION OF BENZALDEHYDE TO HEXAFLUOROPROPENE

Method		A	B	C	D
C_6H_5CHO (mol)		0.400	0.400	0.800	1.201
HFP (mol)		0.575	0.563	0.333	0.467
DTBP (mol)		0.410	0.410	0.100	0.041
$C_2Cl_3F_3$ (mol)		—	1.000	0.535	—
[I]/[II][a]		2.8	1.6	5.5	
Yield[b]	[I] (%)	21.5	18.5	8.8	trace
	[II] (%)	7.4	8.4	1.8	—
Higher boiling products (g)		59	56	22	2

a) Determined by the peak areas of GLC. b) Yields are calculated on the basis of the amounts of benzaldehyde consumed.

The I/II ratios could be controlled by changing the reaction conditions. As compared with Method A, Method B gave a smaller value of I/II due to the effect of dilution. As compared with Method B, Method C gave a larger value of I/II due to the excess of benzaldehyde. These results can be explained in the same manner as in the addition reaction of alkylbenzenes described previously;[3] the I/II ratio is determined by the competition between the intermolecular hydrogen abstraction and the intramolecular cycloaddition, followed by the loss of a hydrogen radical. Only a trace of I was obtained by Method D, although the alkylbenzenes gave the 1 : 1 adducts in good yields under the same conditions.[2] In the cases of the addition reaction of benzaldehyde, a relatively larger amount of the initiator was required because it was consumed by the reaction with benzaldehyde yielding *t*-butyl benzoate.

The structures of I and II were elucidated by means of their IR, NMR, and mass spectra, which are shown in Table 2. The mass spectrum of I is very different from that of II. A large molecular ion peak was observed in II, whereas a very small one appeared in I. The large ions of I, *m*/*e*: 105 C_6H_5CO and *m*/*e*:

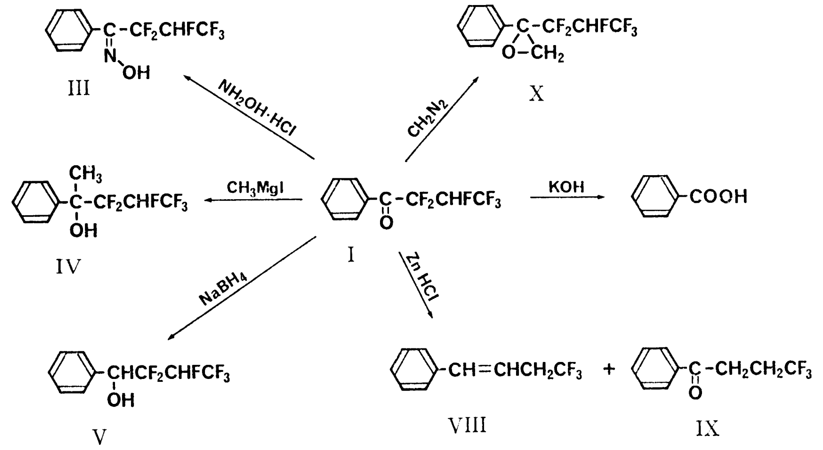


Fig. 1.

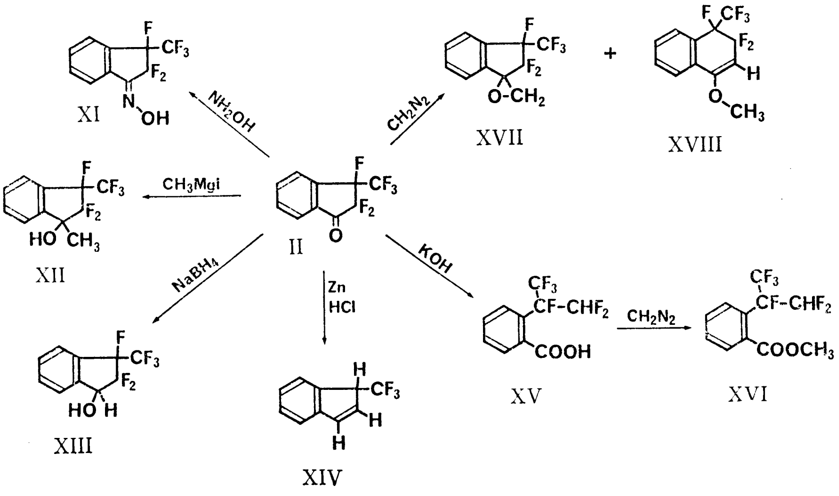


Fig. 2.

77 C_6H_5, are generated by the cleavage of the C–C bond connected to the carbonyl group.

In the NMR spectra, the signals of the fluorines of each CF_2 group on both I and II have AB patterns. For I, the non-equivalence is due to the adjacent asymmetric carbon atom. The configurations of the non-equivalent fluorines (^aF and ^bF) of II were estimated by means of the fluorine-fluorine coupling constants with a CF_3 group. From a consideration of the through-space coupling, it is assumed that the fluorine (^aF, $\delta=41.7$) with a smaller value ($J=3.6$ Hz) is on the opposite side of the indanone framework from the CF_3 group, whereas the fluorine (^bF, $\delta=47.1$) with a larger value ($J=14.0$ Hz) is on the same side.

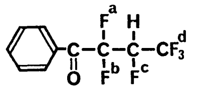
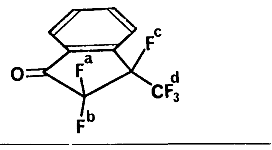
Some Reactions of Fluorine-containing Ketones. The reactions of I and II are summarized in Fig. 1 and Fig. 2 respectively. The corresponding ketoximes (III and XI) were prepared in high yields from I and II under acidic conditions, but under basic conditions haloform cleavages were competitive with the formation of oximes, III was not obtained, and the yield of XI fell to 45.3%.

Although the Beckmann rearrangement of these ketoximes was attempted under refluxing in trifluoroacetic acid or by heating at 100 °C in concentrated sulfuric acid, no corresponding acid amides were obtained; only ketoximes were recovered unchanged. In the reaction with 2,4-dinitrophenylhydrazine, II gave the corresponding hydrazone (mp 176 °C), but I did not yield the hydrazone under the same conditions. Some fluorinated ketones have been reported not to react with substituted hydrazines.[4]

The Grignard reaction of I with methylmagnesium iodide gave the corresponding tertiary alcohol (IV) in a 94% yield. GLC and the ^{19}F NMR spectrum indicated the presence of two diastereoisomers in the ratio of 65 : 35. On the other hand, the reaction of II with methylmagnesium iodide gave XII, which contained only one stereoisomer, in a 78% yield. The methyl group of XII seems to be on the opposite side of the trifluoromethyl group in the indane framework. In the reaction of cyclic fluoroketone(II), methylmagnesium iodide might attack the carbonyl carbon from a sterically favorable side, that is, opposite to the trifluoromethyl group.[5]

The reductions of I and II with sodium tetrahydroborate gave the corresponding secondary alcohols (V and XIII) in almost quantitative yields. The GLC of V indicated the formation of equal amounts of two diastereoisomers, whereas XIII consisted of two

TABLE 2. SPECTRAL DATA OF FLUORINE-CONTAINING KETONES

Compound				
IR				
$\nu_{C=O}$ (cm^{-1})	1708		1762	
NMR[a]				
Chemical shifts (ppm)				
$\tau_{C_6H_5(4)}$	1.9—2.9	m	2.0—2.2 broad	s
τ_{CH}	4.73	d-d-d-q		
δ_{CF^a}	33.1 } AB	m	41.7 } AB	q
δ_{CF^b}	38.4	m	47.1	d-q
δ_{CF^c}	137.0	d-t-q	90.9	d-q
$\delta_{CF_3{}^d}$	−3.5	d-d-d-d	−1.8	d-d-d
Coupling constants (Hz)				
$J_{F^a-F^b}$	306.0		283.4	
$J_{F^a-F^c}$	11.5		0.7	
$J_{F^a-F^d}$	11.2		3.6	
$J_{F^b-F^c}$	11.5		3.0	
$J_{F^b-F^d}$	9.0		14.0	
$J_{F^c-F^d}$	11.1		10.6	
J_{H-F^a}	6.8			
J_{H-F^b}	13.1			
J_{H-F^c}	43.6			
J_{H-F^d}	6.0			
Mass spectra				
m/e (relative abundance)	256(0.3)	M^+	254(100)	M^+
	237(2.0)	$C_{10}H_6F_5O$	235(22.8)	$C_{10}H_4F_5O$
	217(3.3)	$C_{10}H_5F_4O$	185(84.5)	$C_9H_4F_3O$
	105(100)	C_7H_5O	157(42.7)	$C_8H_4F_3$
	77(58.6)	C_6H_5		

a) Neat liquid; using TMS as an internal standard for ^1H and CF_3COOH as an external standard for ^{19}F. The signals being denoted by s(singlet), d(doublet), t(triplet), q(quartet), and m(multiplet).

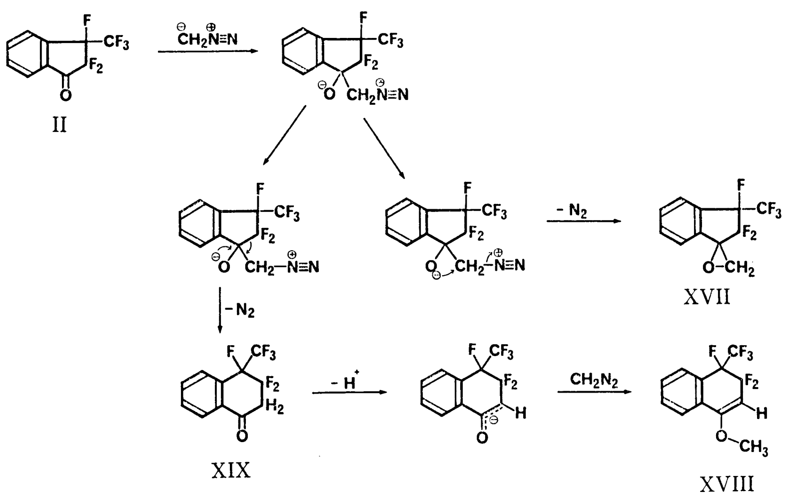
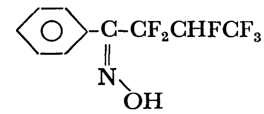
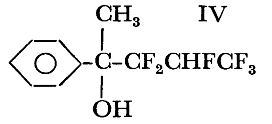
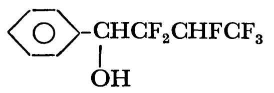
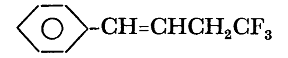
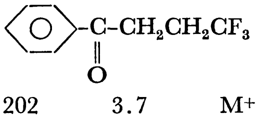
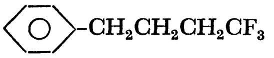
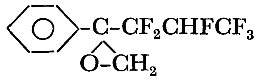
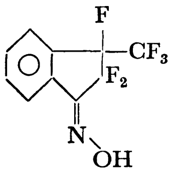
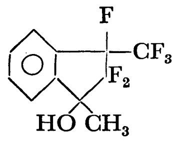
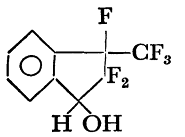
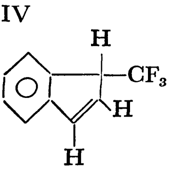
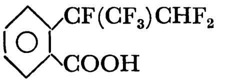
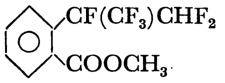
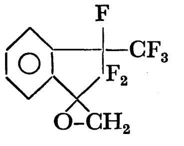
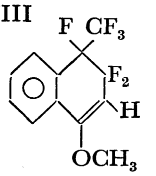


Fig. 3.

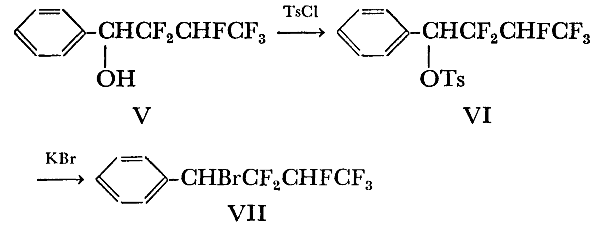
stereoisomers in the ratio of 90 : 10. The predominant isomer isolated by recrystallization was found to have a hydroxyl group on the same side of the trifluoromethyl group in the indane framework. The predominance of this isomer showed that the reduction proceeded mainly by the nucleophilic attack of the BH_4^- ion which, in effect, transferred H^- to the carbon[6] from the opposite side of the trifluoromethyl group.

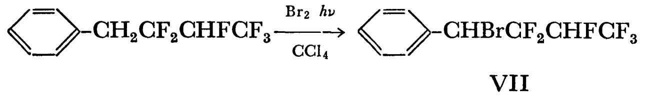
The substitution of the hydroxyl group of V for bromine was carried out *via* the formation of tosylate

Table 3. Main mass spectral bands

m/e	Abundance (%)	Ion	m/e	Abundance (%)	Ion	m/e	Abundance (%)	Ion	m/e	Abundance (%)	Ion
III			IV			V			VII		
											
271	33.0	M^+	272	0.5	M^+	258	0.8	M^+	320	9.8	M^+
120	33.7	C_7H_6NO	255	1.2	$C_{11}H_9F_6$	107	100	C_7H_7O	241	100	$C_{10}H_7F_6$
103	20.7	C_7H_5N	235	1.3	$C_{11}H_8F_5$	79	65.6	C_2HF_2O	221	21.4	$C_{10}H_6F_5$
77	100	C_6H_5	151	5.3	C_3HF_6	77	35.5	C_6H_5	171	24.0	$C_9H_6F_3$
69	15.1	CF_3	121	100	C_8H_9O	69	13.2	CF_3	159	44.7	$C_8H_6F_3$
51	23.0	C_4H_3	77	16.0	C_6H_5				140	77.1	$C_8H_6F_2$
VIII			IX						X		
											
186	25.9	M^+	202	3.7	M^+	188	4.6	M^+	270	25.2	M^+
147	9.2	$C_{10}H_8F$	183	2.4	$C_{10}H_9F_2O$	168	10.4	$C_{10}H_{10}F_2$	269	9.6	$C_{11}H_7F_6O$
117	100	C_9H_9	105	100	C_7H_5O	91	100	C_7H_7	151	23.6	C_3HF_6
115	58.5	C_9H_7	77	55.6	C_6H_5	65	11.0	C_5H_5	119	14.3	C_8H_7O
91	32.6	C_7H_7	51	23.8	C_4H_3	51	6.8	C_4H_3	91	100	C_7H_7
XI			XII			XIII			XIV		
											
269	60.1	M^+	270	7.9	M^+	256	25.3	M^+	184	67.2	M^+
200	49.7	$C_9H_5F_3NO$	255	50.9	$C_{10}H_5F_6O$	236	17.1	$C_{10}H_5F_5O$	165	4.2	$C_{10}H_7F_2$
183	41.3	$C_9H_4F_3N$	250	67.2	$C_{11}H_7F_5O$	167	100	$C_9H_5F_2O$	164	6.6	$C_{10}H_6F_2$
169	20.9	$C_9H_4F_3$	235	100	$C_{10}H_4F_5O$	107	34.3	C_7H_4F	133	9.1	C_9H_6F
152	100	$C_8H_4F_2N$	207	30.5	$C_9H_4F_5$	105	40.4	C_7H_5O	115	100	C_9H_7
XV			XVI			XVII			XVIII		
											
272	10.7	M^+	286	9.7	M^+	268	35.6	M^+	282	100	M^+
255	10.0	$C_{10}H_5F_6O$	266	20.4	$C_{11}H_7F_5O_2$	248	17.0	$C_{11}H_5F_5O$	239	30.6	$C_{10}H_5F_6$
204	45.8	$C_9H_4F_4O$	255	100	$C_{10}H_5F_6O$	219	14.1	$C_{10}H_4F_5$	219	23.4	$C_{10}H_4F_5$
151	100	C_3HF_6	235	20.3	$C_{10}H_4F_5O$	171	17.0	$C_9H_6F_3$	213	44.4	$C_{11}H_8F_3O$
			207	14.5	$C_9H_4F_5$	169	100	$C_9H_4F_3$	169	32.8	$C_9H_4F_3$
						151	76.3	$C_9H_5F_2$	151	40.0	$C_9H_5F_2$

(VI) as an intermediate. Bromide(VII) was obtained in a 60.2% overall yield. The same product was also synthesized by the photobromination of the 2,2,3,4,4,4-hexafluorobutylbenzene obtained by the radical addition of toluene to hexafluoropropene.²⁾





VII

The Clemmensen reduction of I gave several products, 1-phenyl-4,4,4-trifluorobutane, *trans*-1-phenyl-4,4,4-trifluoro-1-butene(VIII) and phenyl 3,3,3-trifluoropropyl ketone(IX), whose composition varied with the reaction conditions. Whereas the reduction at 70—80 °C for 2 h gave VIII as the main product in a 63.3% yield, the reduction at 0 °C gave IX in a 54.5% yield. The reduction of I in the presence of toluene at 90—100 °C gave a mixture of about equal amounts of four products,

TABLE 4. NMR SPECTRA

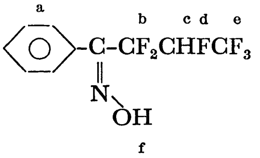
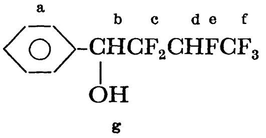
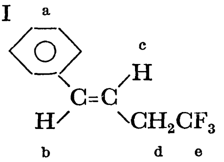
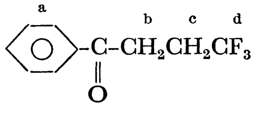
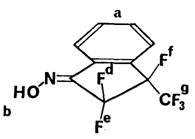
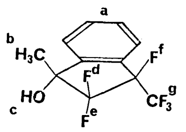
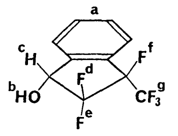
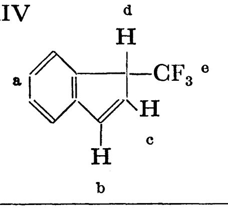
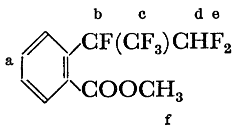
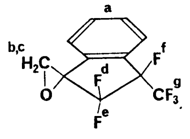
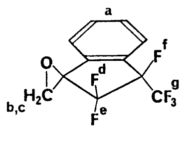
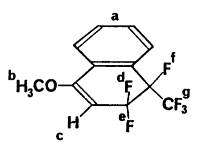
Compound	Absorption type	τ	δ (ppm)		Splitting	J (Hz)	
III 	a (5H)	2.7			broad s	H_c-F_d	42
	b (1F)		27.1	AB	d-d-q	F_b-$F_{b'}$	282
	b' (1F)		32.9		t-q	H_c-F_e	6
	c (1H)	4.68			d-m	F_b-F_e	12
	d (1F)		131.4		d-m	$F_{b'}$-F_e	9
	e (3F)		−4.9		d-d-d-d	F_d-F_e	18
	f (1H)	2.7			overlapped with a		
V 	a (5H)	2.77			s	H_b-F_c	12
	b (1H)	5.20			t-m	H_d-F_c	10
	c (2F)		44.7		m	H_d-F_e	44
	d (1H)	5.31			d-m	H_d-F_f	6
	e (1F)		134.9		d-d-q	F_c-F_f	11
	f (3F)		−4.0		d-d-t	F_e-F_f	11
	g (1H)	6.63			broad s		
VIII 	a (5H)	2.82			s	H_b-H_c	16
	b (1H)	3.55		AB	s	H_c-H_d	6
	c (1H)	4.03			t	H_d-F_e	11
	d (2H)	7.12			d-q		
	e (3F)		−12.3		t		
IX 	a (5H)	1.9—2.8			m	H_c-F_d	11
	b (2H)	6.0—6.9		A_2B_2	m		
	c (2H)	7.0—7.9			m		
	d (3F)		−12.1		t		
XI 	a (4H)	2.2—2.4			m	F_d-F_e	261
	b (1H)	1.4—1.5			m	F_d-F_f	3
	d (1F)		31.3	AB	d-q	F_d-F_g	4
	e (1F)		36.5		d-q	F_e-F_f	2
	f (1F)		89.0		q-m	F_e-F_g	14
	g (3F)		−2.4		d-d-d	F_f-F_g	11
XII 	a (4H)	2.50			broad s	F_d-F_e	240
	b (3H)	8.45			broad s	F_d-F_g	6
	c (1H)	6.93			broad s	F_e-F_g	11
	d (1F)		48.4	AB	m	F_f-F_g	10
	e (1F)		46.1		q-m		
	f (1F)		77.9		q-m		
	g (3F)		−4.7		d-d-d		
XIII 	a (4H)	2.4—2.9			m	H_c-F_d	8
	b (1H)	5.17			broad s	H_c-F_e	8
	c (1H)	4.80			t	F_d-F_g	3
	d (1F)		41.4	AB	m	F_e-F_g	14
	e (1F)		51.2		m	F_f-F_g	11
	f (1F)		82.6		d-q	F_d-F_e	241
	g (3F)		−3.9		d-d-d		
XIV 	a (4H)	2.81			broad s	H_b-H_c	6
	b (1H)	3.16		AB	broad s	H_c-H_d	2
	c (1H)	3.73			d	H_d-F_e	9
	d (1H)	6.00			q-m		
	e (3F)		−11.2		d-d-d		

TABLE 4. Continued

Compound	Absorption type	τ	δ	Splitting	J (Hz)	
		(ppm)				
XVI	a (4H)	2.1—2.7		m	H_d-F_e	52
	b (1F)		101.3	d-q	H_d-F_b	8
	c (3F)		−4.7	d-t	F_b-F_c	6
	d (1H)	3.35		d-t	F_b-F_e	9
	e (2F)		52.6	d-d-q	F_c-F_e	9
	f (3H)	6.18		s		
XVII	a (4H)	2.0—3.1		m	H_b-H_c	5
	b (1H)	6.46 AB		s	F_d-F_e	279
	c (1H)	6.80		d	F_d-F_g	5
	d (1F)		41.9 AB	d-q	F_e-F_g	12
	e (1F)		45.6	t-q	F_f-F_g	10
	f (1F)		94.9	q-m		
	g (3F)		−0.8	d-d-d		
XVII	a (4H)	2.0—3.1		m	H_b-H_c	5
	b (1H)	6.50 AB		s	F_d-F_e	281
	c (1H)	6.74		d	F_d-F_g	4
	d (1F)		41.3 AB	d-q	F_e-F_g	13
	e (1F)		46.2	t-q	F_f-F_g	11
	f (1F)		84.6	q-m		
	g (3F)		−3.2	d-d-d		
XVIII	a (4H)	2.4—3.1		m	H_c-F_d	3
	b (3H)	6.21		s	H_c-F_e	5
	c (1H)	4.37		d-d	F_d-F_e	281
	d (1F)		30.3 AB	m	F_d-F_f	15
	e (1F)		55.3	d-d-q	F_d-F_g	5
	f (1F)		115.6	d-d-q	F_e-F_f	10
	g (3F)		−2.6	d-d-d	F_e-F_g	18
					F_f-F_g	7

50% CCl_4 solution; using TMS as an internal standard for ^1H and CF_3COOH as an external standard for ^{19}F.

TABLE 5. PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Bp (°C)	n_D^{20}	d_4^{20}	Formula	Elemental analysis			
					C (%)		H (%)	
					Found	(Calcd)	Found	(Calcd)
[I]	194	1.4298	1.418	$C_{10}H_6F_6O$	46.51	(46.89)	2.41	(2.36)
[II]	205	1.4485	1.502	$C_{10}H_4F_6O$	47.48	(47.26)	1.74	(1.59)
[III]		Mp 79—84 °C		$C_{10}H_7F_6NO$	44.34	(44.29)	2.63	(2.60)
[IV][a]	214	1.4374	1.401	$C_{11}H_{10}F_6O$	48.37	(48.54)	3.46	(3.70)
[V][a]	213	1.4325	1.434	$C_{10}H_8F_6O$	46.61	(46.53)	3.00	(3.12)
[VII][a]	62—64/4[b]	1.6475	1.456	$C_{10}H_7F_6Br$	37.23	(37.41)	2.20	(2.20)
[VIII]	polymel. (180 °C)	1.4807	1.196	$C_{10}H_9F_3$	64.34	(64.51)	4.70	(4.87)
[IX]		Mp 59.8 °C		$C_{10}H_9F_3O$	59.63	(59.41)	4.57	(4.49)
[X][a]	208	1.4311	1.392	$C_{11}H_8F_6O$	48.99	(48.90)	3.04	(2.98)
[XI]		Mp 118.1 °C		$C_{10}H_5F_6NO$	44.52	(44.63)	2.05	(1.87)
[XII]		Mp 99.8 °C		$C_{11}H_8F_6O$	48.95	(48.90)	3.15	(2.98)
[XIII][a]		Mp 36—39 °C		$C_{10}H_6F_6O$	47.13	(46.89)	2.63	(2.36)
[XIV]	187	1.4859	1.280	$C_{10}H_7F_3$	65.32	(65.22)	3.76	(3.83)
[XVI]	226	1.4372	1.480	$C_{11}H_8F_6O_2$	46.58	(46.17)	2.84	(2.82)
[XVII][a]	decomp. (180 °C)	1.4493	1.483	$C_{11}H_6F_6O$	49.03	(49.27)	2.16	(2.26)
[XVIII]		Mp 75.7 °C		$C_{12}H_8F_6O$	50.92	(51.08)	2.85	(2.86)

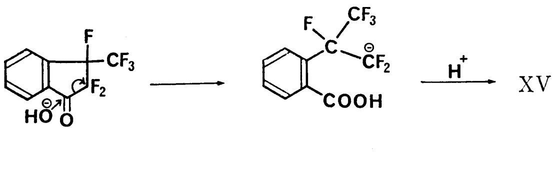
a) Mixture of stereoisomers.

b) °C/mmHg; decomposed at 200 °C and atmospheric pressure.

1-phenyl-4,4,4-trifluorobutane, VIII, IX, and an unidentified compound. The reduction of cyclic ketone (II) at 60—70 °C gave 1-trifluoromethylindene(XIV) in a 42.3% yield.

Both the elimination of α-halogen and the formation of olefin are known to be side reaction in the Clemmensen reduction.[7] The formation of olefin was especially enhanced when a double bond formed conjugated with a phenyl group. In the treatment of the fluorinated ketones, I and II, with zinc amalgam and hydrochloric acid, the reduction of the fluorines on the α- and β-carbons of the ketones seemed to occur first, followed by the reduction of the carbonyl or olefin formation, which were dependent on the reaction conditions.

The haloform cleavage of these ketones was observed. The reaction of I with aqueous potassium hydroxide gave benzoic acid, whereas the reaction of the cyclic ketone(II) gave *o*-(hexafluoroisopropyl)benzoic acid (XV), which was isolated as the methyl ester(XVI) in a 50.3% yield. The mechanism of the alkaline degradation of II is as follows:



The reaction of I with diazomethane gave only the epoxide (X) in a 75.9% yield. On the other hand, the reaction of II gave ring-expanded enol ether(XVIII), together with the epoxide (XVII). The postulated mechanism of the formation of XVII and XVIII is shown in Fig. 3. The reaction of ketones with diazomethane has been extensively studied; non-fluorinated ketones react in three alternative ways, yielding epoxide and/or ketones in which a methylene group has been inserted.[8] The presence of electronegative substituents on ketones has been reported to enhance the reactivity with diazomethane and to give mainly oxides instead of the expanded ketones. α-Fluoroketones have been reported to give only epoxides in high yields.[9] In agreement with the information in the literature, the linear ketone(I) gave only epoxide. The cyclic fluorinated ketone(II), however, gave the ring-expanded product (XVIII) together with the epoxide(XVII). The reaction of II and diazomethane, with the migration of the difluoromethylene carbon, seems to lead to the ring-expanded ketone(XIX). Since the methylene group of XIX is adjacent to the electron-withdrawing difluoromethylene and carbonyl group, the acidic hydrogen dissociates as a proton and an enolate anion is generated. Another molecule of diazomethane reacts with the enolate anion to give enol ether(XVIII). The intermediate ketone (XIX) was not isolated. The NMR showed that both epoxides, X and XVII, were mixtures of two stereoisomers, in the ratios of 50 : 50 and 60 : 40 respectively.

The mass and NMR spectral data of the products are shown in Table 3 and Table 4 respectively. The physical properties and analytical data are shown in Table 5.

Experimental

The IR and mass spectra were measured using a Hitachi Model EPI-G3 grating spectrometer and a Model RMU-7 double-focussing mass spectrometer at 70 eV respectively. The NMR spectra were obtained on a Hitachi Model R-20B (^{1}H : 60 MHz; ^{19}F : 56.45 MHz), using TMS as an internal standard for ^{1}H and trifluoroacetic acid as an external standard for ^{19}F. The analytical GLC was carried out in a stainless steel column (3 m long × 3 mm diameter) packed with 20% Silicone DC550-Celite 545 or 20% Silicone DCQF-1-Chromosorb W on a Shimadzu GC-3AH. In the preparative scale work, an aluminum column (6 m long × 10 mm diameter) was used on a Varian Model 920.

Addition Reactions of Benzaldehyde to Hexafluoropropene. General Procedure: A mixture of benzaldehyde, HFP, DTBP, and 1,1,2-trichlorotrifluoroethane in the molar ratio shown in Table 1 was heated in a stainless steel autoclave at temperatures gradually rising from 130 °C to 160 °C. The products were separated by vacuum distillation. Phenyl 1,1,2,3,3,3-hexafluoropropyl ketone(I) and 2,2,3-trifluoro-3-trifluoromethylindanone(II) were obtained as colorless liquids, together with a large amount of a tarry residue.

Preparation of Oximes. Phenyl 1,1,2,3,3,3-Hexafluoropropyl Ketone Oxime (III): To a solution of I (2.5 g, 0.01 mol) in 4 ml of ethanol, 2 ml of a 50% aqueous hydroxylamine hydrochloride solution was added; the mixture was then refluxed for 8 h. After the ethanol had then been allowed to evaporate, 20 ml of water was added and the organic products were extracted with ether. After the solvent had been removed, III was obtained as an oily residue (1.9 g, 70.1%), which crystallized on standing overnight. Recrystallization from chloroform gave pale yellow needles (mp 84 °C).

2,2,3-*Trifluoro*-3-*(trifluoromethyl)indanone Oxime (XI)*: In a similar proceddre, II (1.25 g, 0.005 mol) gave XI (1.3 g, 98.2%) as colorless needles (mp 118 °C).

Grignard Reactions with Methylmagnesium Iodide. 2-Phenyl-3,3,4,5,5,5-hexafluoro-2-pentanol (IV): Methylmagnesium iodide was prepared from methyl iodide (1.5 g, 0.011 mol) and magnesium turnings (0.25 g, 0.010 atom) in 20 ml of ether. Then a solution of I (2 g, 0.008 mol) in 10 ml of ether was added, drop by drop, with cooling in an ice bath. The mixture was stirred for one hour at room temperature and then poured into dilute hydrochloric acid. The ether layer was separated and dried over magnesium sulfate. After the removal of the solvent, the residue was distilled *in vacuo*; IV (2.0 g, 94.2%) was thus obtained as a colorless liquid.

1-Methyl-2,2,3-trifluoro-3-(trifluoromethyl)-1-indanol (XII): By a similar procedure, XII (1.0 g, 78.4%) was obtained from II (1.2 g, 0.005 mol). Recrystallization from chloroform gave colorless prisms (mp 100 °C).

Reduction with NaBH$_4$. 1-Phenyl-2,2,3,4,4,4-hexafluoro-1-butanol (V): Sodium borohydride (4.0 g, 0.106 mol) and 60 ml of anhydrous ether were placed in a 200 ml Erlenmeyer flask; a solution of I (20.5 g, 0.08 mol) in 30 ml of ether was then added, drop by drop at room temperature. After the addition had been completed, stirring was continued for 3 h. The mixture was then poured into ice water, and the ether layer was separated and dried. After the removal of the solvent, the residue was distilled *in vacuo*; V was thus obtained as a colorless liquid (16.6 g, 80.4%).

2,2,3-Trifluoro-3-(trifluoromethyl)-1-indanol (XIII): By a similar procedure, XIII (3.6 g, 89.5%) was obtained from II (4.0 g, 0.015 mol) as a colorless liquid. Crystallization from chloro- form gave colorless prisms (mp 39 °C).

Clemmensen Reductions. trans-*1-Phenyl-4,4,4-trifluoro-1-butene (VIII)*: Zinc ribbon (20 g, 0.306 atom) was added to a 10 ml aqueous solution of mercuric chloride (2 g, 0.007 mol). After 5 minutes' shaking, the water layer was decanted and 5 ml of water and 20 ml of concentrated hydrochloric acid were added. A solution of I (5 g, 0.020 mol) in 10 ml of ethanol was then added, drop by drop, the temperature rose to 70—80 °C, after which stirring was continued for 2 h. The mixture was extracted with 20 ml of toluene, and then the organic layer was washed with water and dried. Vacuum distillation gave VIII (2.3 g, 63.3%) as a colorless liquid which was proved by GLC to contain small amounts of 1-phenyl-4,4,4-trifluorobutane and phenyl 3,3,3-trifluoropropyl ketone.

Phenyl 3,3,3-trifluoropropyl ketone (IX): A reduction similar to that described above was carried out at 0 °C under cooling in an ice bath. IX (2.2 g, 54.5%) was thus obtained as the main product from I (5 g, 0.020 mol).

1-*Trifluoromethylindene (XIV)*: By a procedure similar to that described above, II (2.6 g, 0.010 mol) gave XIV (0.8 g, 42.3%) as a colorless liquid.

Alkaline Hydrolysis. *Benzoic Acid*: Powdered potassium hydroxide (2 g, 0.036 mol) and 10 ml of hexane were placed in a 50 ml Erlenmeyer flask, and then a solution of I (3 g, 0.012 mol) in 10 ml of hexane was added. After 1 hour's stirring, the mixture was acidified with dilute hydrochloric acid. Benzene (30 ml) was then added, and the organic layer was separated. The solvent was allowed to evaporate to give a white solid (1.5 g). Recrystallization from hexane gave benzoic acid (1.0 g) as colorless needles (mp 123 °C).

o-*(Hexafluoroisopropyl)benzoic Acid (XV) and Its Methyl Ester (XVI)*: By a similar procedure, II (3 g, 0.012 mol) gave a pale yellow oil XV (1.9 g, 59.2%). A solution of XV in 20 ml of absolute ether was cooled in an ice bath, and then a freshly prepared diazomethane solution in ether was added. After the mixture had stood for 30 min, the solvent was removed. The vacuum distillation of the residue gave XVI (1.7 g, 50.3%) as a pale yellow liquid.

Reaction with Diazomethane. *2-Phenyl-3,3,4,5,5,5-hexafluoro-1,2-epoxypentene (X)*: A solution of I (2.0 g, 0.008 mol) in 20 ml of absolute ether was cooled in an ice bath; subsequently a freshly prepared diazomethane ether solution was added until the yellow color was no longer discharged. After the mixture had stood at room temperature for 3 h, the solvent was removed to give a pale yellow oily residue (1.6 g, 75.9%). Further purification was done by preparative GLC.

2,2,3-Trifluoro-1,1-methyleneoxy-3-trifluoromethylindane (XVII) and 1,2,2-Trifluoro-1-trifluoromethyl-4-methoxy-1,2-dihydronaphthalene (XVIII): By a similar procedure, II (2.0 g, 0.008 mol) gave a pale yellow residue (1.5 g) which contained XVII and XVIII in a ratio of 3 : 4 (GLC). They were separated by preparative GLC. Recrystallization from ethanol gave XVIII as colorless prisms (mp 76 °C).

Bromine Substitution of the Alcohol (V). *4-Bromo-1,1,1,-2,3,3-hexafluoro-4-phenylbutane (VII)*: To a mixture of V (10.4 g, 0.04 mol) and *p*-toluenesulfonyl chloride (10 g, 0.05 mol), 20% aqueous sodium hydroxide (15 ml) was added, drop by drop. After the reaction mixture had been heated at 100 °C for 6 h, it was poured into 100 ml of water and extracted with dichloromethane. The evaporation of the solvent gave tosylate(VI) (12.1 g, 73.4%) as colorless prisms (mp 106 °C), which were then recrystallized from ethanol.

A solution of VI (10 g, 0.024 mol) and potassium bromide (12 g, 0.10 mol) in ethylene glycol (20 ml) was heated at 160 °C for 6 h. The reaction mixture was poured into water and extracted with dichloromethane. After the solvent had been removed, the oily residue was distilled *in vacuo*. Bromide (VII) (6.4 g, 82.1%) was obtained as a colorless oil.

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