Radical Addition of Iodoperfluoroalkanes to Vinyl and Allyl Monomers

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Vinyl acetate added a variety of iodoperfluoroalkanes including 1-iodoperfluoropropane and homologs, 1,6-diiodoperfluorohexane, and 2-bromo- or 2-chlorotetrafluoro-1-iodoethane (but not 1,2-diiodotetrafluoroethane) under the influence of azo free radical initiators. Addition did not take place using ultraviolet light or peroxide initiation. Reduction of the very reactive adducts gave 2-perfluoroalkyl-substituted ethanols, while coupling gave 1,4-bis(perfluoroalkyl)-2,3-butanediols. Azo-initiated addition to allyl acetate took place readily, and the adduct with alkali gave a perfluoroalkyl-substituted epoxide in good yield.

The free radical chain addition of iodoperfluoroalkanes to vinyl esters is one of the more interesting azonitrile-initiated reactions recently discovered.[1] There appears to be no previous record of success in this particular reaction although extensive reviews of related free radical chemistry have appeared.[2,3] Addition of bromotrichloromethane to vinyl acetate initiated by acetyl peroxide gave 1-bromo-3,3,3-trichloropropyl acetate in 90% yield.[4] The reaction induced by ultraviolet light or benzoyl peroxide at 60° has been studied to define the kinetic rate constants for the radical chain sequence.[5]

We found that 1-iodoperfluoropropane and vinyl acetate did not react when heated with benzoyl peroxide at 60° and that the mixture became black when irradiated at 50°; very little addition product was formed. Tar and black solid were obtained by heating these reactants in a sealed tube at 200°. The adduct was obtained however, in high yield when an azo compound such as azobisisobutyronitrile (ABN) was used as initiator in catalytic amounts below 80°. Iodine in high dilution acts as an extremely efficient inhibitor for vinyl acetate polymerization,[6,7] and had to be absent. Polymerization inhibitors such as hydroquinone also had to be carefully removed. A moderate increase in the amount of initiator used would not compensate for traces of inhibitor. A summary of reactions employing various iodoperfluoroalkanes and vinyl acetate is found in Table I. The mono adduct from vinyl acetate and 1-iodoperfluoropropane was 1-iodo-3,3,4,4,5,5,5-heptafluoropentyl acetate since reduction with zinc and acid or by lithium aluminum hydride gave the known 3,3,4,4,5,5,5-heptafluoropentan-1-ol[8] (Table II). The perfluoroalkyl radical, therefore, becomes attached to the terminal carbon of the vinyl group, as anticipated.[2,3]

$$R_f\cdot + CH_2{=}CHO_2CCH_3 \longrightarrow \underset{(A)}{R_fCH_2\underset{\cdot}{C}H{-}O_2CCH_3} \text{ (addition)}$$

Transfer of the radical A with iodoperfluoroalkane to give adduct B comprises the second step in the normal sequence of the chain reaction. Radical

$$A + R_fI \longrightarrow \underset{(B)}{R_fCH_2CHIO_2CH_3} + R_f\cdot \text{ (transfer)}$$

chains of about 100 in length were obtained using ABN with equimolar amounts of reactants, assuming an efficiency of about 70% for initiation by the azo compound, as found for vinyl acetate alone.[9]

An excess of vinyl acetate gave telomerization in contrast to bromotrichloromethane which gave only monoadduct with as much as a tenfold excess

$$A + CH_2{=}CHO_2CCH_3 \longrightarrow R_f[CH_2CH(O_2CCH_3)]_m\cdot \text{ (propagation)}$$

of vinyl acetate, because of the very high transfer constant of 40.[5] However, we obtained only low molecular weight telomers using a 6 to 50 mole ratio of vinyl acetate to 1-iodoperfluoroheptane.[1] Carbon tetrachloride and vinyl acetate also produce telomers[10] and the transfer constant[11] is near unity over a temperature range of 60–75°.

1,6-Diiodoperfluorohexane added two equivalents of vinyl acetate and the expected adducts were obtained from 1-iodo-2-bromotetrafluoroethane and 1-iodo-2-chlorotetrafluoroethane. 1,2-

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[1] N. O. Brace, to be published.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 247.

[3] A. Roedig; Houben-Weyl, "Methoden der organischen Chemie," 4th ed., Vol. V, Georg. Thieme Verlag, Stuttgart, 1960, pp. 653–657.

[4] M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

[5] W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **56**, 407 (1960); and references cited therein.

[6] P. D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, **72**, 1051 (1950).

[7] D. S. Trifan and P. D. Bartlett, *ibid.*, **81**, 5573 (1959).

[8] J. D. Park, E. R. Larson, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **23**, 1166 (1958).

[9] L. M. Arnett and J. H. Peterson, *J. Am. Chem. Soc.*, **74**, 2031 (1952).

[10] J. Harmon, U.S. Patent 2,396,261, March 12, 1946.

[11] J. T. Clarke, R. O. Howard, and W. H. Stockmayer, *Makromol. Chem.*, **44-46**, 427 (1961)(English).

TABLE I

RADICAL ADDITION OF R_fI TO VINYL ACETATE

				Conditions		$R_fCH_2CHOCOCH_3$											
										Calcd.				Found			
R_fI[a]	Moles	$CH_2{=}CHO_2CCH_3$, moles	Initiator, moles × 10^3	Temp., °C.	Time, hr.	Conversion, %	Yield, %	B.p. (mm.), °C.	n^{25}_D	C	H	F	I	C	H	F	I
$CF_3(CF_2)_2I$[b]	0.1	0.1	AVN[c] 1.2	50–80	7.0	87	96	32 (0.7)	1.3971	22.0	1.6	34.8	33.2	22.1	1.5	34.2	32.9
$CF_3(CF_2)_2I$[b]	.5	.5	ABN[d] 10.0	65–80	7.0	73	85	45 (1.2)	1.3978								
$CF_3(CF_2)_2I$[b]	.5	.54[e]	ABN 10.0 AVN 1.2	55–60	10.6	13.0	95	[f]	1.3904								
$CF_3(CF_2)_6I$[b]	.11	.1	ABN 1.2	70–93	6.0	95	95		1.3692	22.7	1.0	48.9	21.8	24.2	1.5	49.1	20.9
$CF_3(CF_2)_6I$[b]	.1	.1	ABN 0.61	80–90	2.0	90	95	[f]	...								
$CF_3(CF_2)_{10}I$[b]	.016	.035	ABN 1.2	74–81	7.0	90	90	[g]	...	23.0	0.8		16.2	23.1	1.1		13.3
$ClCF_2CF_2I$[h]	.1	.1	ABN 1.8	66–77	7.0	83	95	32 (0.1)	1.4404	20.7	1.7	10.2[i]	36.4	21.4	2.0	10.2	36.4
$BrCF_2CF_2I$[h]	.05	.05	ABN 0.6	70–83	6.0	50	90	42 (0.3)	1.4609	18.3	1.5		20.3[j]	19.0	1.9		20.3[j]
$H(CF_2)_4I$[k]	.1	.12	AVN .8 ABN .6	70–92	12.0	88	90	[f]	...	23.2	1.7	36.7	31.4	25.6	2.6	33.0	29.3
$I(CF_2)_2I$[l]	.05	.15	AVN 2.0	70–80	12.0	0	0[m]										
	.1	.25	ABN 3.5	80	8.0	0	0[n]										
$I(CF_2)_6I$[o]	.036	.1	ABN 0.6	87–130	3.0	100	[f]	[f]	...	23.1	1.7	31.3	34.9	24.5	2.4	30.2	33.5

[a] All R_fI were known compounds which were redistilled and colorless. $CF_3(CF_2)_nI$, $n = 2$, b.p. 41°, n^{25}_D 1.3250; $n = 6$, b.p. 70° (70 mm.), n^{25}_D 1.3270; $n = 10$, b.p. 105° (18 mm.), m.p. 77–79.5°.

[b] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, 1958, p. 48.

[c] Azobis-2,4-dimethylvaleronitrile; see ref. 19.

[d] Azobisisobutyronitrile; see ref. 19.

[e] Vinyl acetate redistilled without caustic treatment to remove hydroquinone inhibitor; low conversion resulted. When hydroquinone (5% by weight) was added to the vinyl acetate before redistillation, no reaction occurred under comparable conditions.

[f] See Table II for zinc reduction to alcohol.

[g] M.p. 75–83°.

[h] R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

[i] Chlorine.

[j] Bromine.

[k] C. G. Krespan, *J. Org. Chem.*, **23,** 2016 (1958).

[l] M. S. Raasch, U.S. Patent 2,424,667 (1947).

[m] The reaction mixture was distilled and reactants recovered unchanged; 1.5 g. of residue.

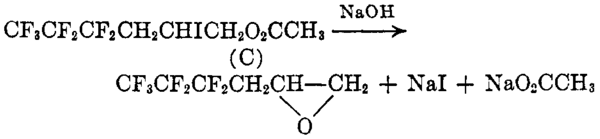
[n] Gas chromatographic analysis.

[o] R. N. Haszeldine, *Nature*, **167,** 139 (1951); b.p. 67–80 (10 mm.); m.p. 23–25°; n^{25}_D 1.4020.

Diiodotetrafluoroethane, however, failed to react under analogous conditions.[12]

Radical addition of iodoperfluoroalkanes to allyl acetate, previously reported by Park and Lacher[13] and Moore[14] to give an 81% yield in five days using ultraviolet light, occurred smoothly in a few hours with azo initiator. A 90% yield at 78% conversion to 4,4,5,5,6,6,6-heptafluoro-2-iodo-hexan-1-ol acetate (C) and about 10% of higher boiling products was obtained. The 2-iodo-3-perfluoroalkyl esters were considerably more stable to heat, air, and light than the 1-iodo esters from vinyl acetate.

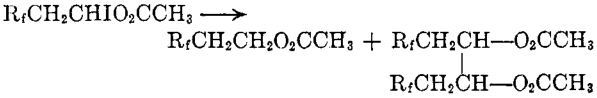
Reaction of C with sodium hydroxide in dry ether gave the epoxide in good yield.



Kinetics of polymerization in the iodoperfluoroalkane vinyl acetate system have not as yet been worked out in detail, but there is a strong constrast to the behavior of iodoperfluoroalkanes with other polymerizable compounds. At a 2 to 1 initial concentration (moles) of 1-iodoperfluoropropane to ethyl acrylate, reaction initiated by ABN at 70–80° gave telomer having an average of eight monomer units.[15] No monoadduct could be detected by gas chromatographic analysis in a competitive experiment in which the acrylate was run against heptene-1.

A second striking contrast is that with styrene very little addition or propagation was obtained under comparable conditions, and strong inhibition of addition of 1-iodoperfluoropropane to heptene-1 was observed. A total of only 1.64% reaction occurred in four (or twelve hours) at 70° with 1.00% of azonitrile initiator concentration and equimolar amounts of reactants.[1] A coupled product was isolated in low yield; its structure may be the anticipated 2,2′-bis-phenyl-4,4′-bis(perfluoropropyl butane. The resonance energy of the intermediate benzyl-type radical similar to A evidently favors addition of $R_f\cdot$ to the vinyl group, but abstraction of iodine from R_fI in a transfer step to give a product like B has to compete with coupling and with a degradative chain transfer mechanism similar to that proposed for polymerization of allyl acetate[16] which uses up initiator without carrying on a chain reaction. The vinyl acetate radical is about 1500–2000 times as reactive in chain transfer reactions as is the styrene radical, even though they are similar in polarity.[11] Butadiene-1,3- and 2-chloro-1,3-butadiene were similar in behavior to styrene in ABN-initiated reaction with 1-iodoperfluoropropane.

Properties of the Adducts B.—The 1-iodoalkyl acetates were difficult to handle because of their great sensitivity to light and air. Loss of iodine and conversion to tar occurred immediately at room temperature. Thermal decomposition gave a volatile unstable iodine compound, probably acetyl iodide, and undistillable residue. The adduct B from 1-iodoperfluoropropane could be obtained in pure condition only when distilled at a temperature below 50°. Microgram samples for analysis were loaded in ampules in an atmosphere of nitrogen, frozen, and immediately sealed. Other techniques failed. Gas chromatographic analysis was satisfactory only below 120° using a heavy flow of helium carrier gas. Infrared spectra in a sealed cell were recorded; however, some darkening of the sample occurred. The carbonyl absorption band was at 5.60 μ while that of the iodine–free ester was at 5.66 μ. Reduction occurred with lithium aluminum hydride or zinc in alcohol or acetic acid. Reduction with zinc dust in ether or a zinc–copper couple in tetrahydrofuran gave both reduced and coupled products for which analysis and properties agreed with the structures.



$$R_fCH_2CHIO_2CCH_3 \longrightarrow R_fCH_2CH_2O_2CCH_3 + \begin{array}{l} R_fCH_2CH{-}O_2CCH_3 \\ \quad\quad\quad\;\; | \\ R_fCH_2CH{-}O_2CCH_3 \end{array}$$

Further study of synthetic reactions employing these potentially useful iodoalkyl esters is being carried on.

The n.m.r. spectra (Fig. 1) of B taken at 56.4 megacycles showed a quadruplet centered at 2.82 τ,[17] a less well resolved multiplet at 7.13 τ and the methyl proton resonance at 7.91 τ. The interpretation which is due to Roberts[18] is that the splitting pattern is the result of unequal populations of the possible rotation conformations of the substituted ethane. The four lines spaced at 4–5

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[12] The reaction (either concerted with or subsequent to initiation):

$$ICF_2CF_2\cdot \longrightarrow I\cdot + CF_2{=}CF_2$$

may proceed at a rate much greater than addition of this particular R_f radical to vinyl acetate, and/or transfer of the radical A with this iodo compound may not occur at a rate sufficient to compete. 1,2-Diiodotetrafluoroethane decomposes to iodine and tetrafluoroethylene when irradiated even at −70°, or when heated above 80°, and radical addition to other unsaturated compounds such as heptene-1 was not observed either.[1] The reactions were all carried out under nitrogen. There was no apparent formation of molecular iodine, but it is possible that traces were present sufficient to inhibit the chain reaction.

[13] J. D. Park and J. R. Lacher, W.A.D.C.T.R. 56-590, Pt. II (1958), ASTIA No. 151014, "Photochemical Synthesis of Organic Fluorine Compounds."

[14] L. D. Moore, thesis, Purdue University (1959); *Dissertation Abstr.*, **20**, 96 (1959).

[15] *Cf.* R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953).

[16] P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, **67**, 812, 816 (1945).

[17] G. V. D. Tiers, "N.m.r. Spectroscopy," Minnesota Mining and Mfg. Co., St. Paul, Minnesota, 1960.

[18] I am indebted to Prof. J. D. Roberts for interpretation of the n.m.r. spectrum (Fig. 1). In B^1, B^2, and B^3, the coupling constants between *trans* hydrogens (α-β in B^1 and α-γ in B^2) was taken as 10 c.p.s., and the coupling between the gauche pairs (α-γ in B^1, α-β in B^2, and α-β and α-γ in B^3) was taken as 3 c.p.s. The summation of these constants is $(0.80 \times 10) + (0.20 \times 3) + (0 \times 3) = 8.6$ c.p.s. and $(0.80 \times 3) + (0.20 \times 10) + (0 \times 3) = 4.4$ c.p.s.

TABLE II

ZINC REDUCTION OF $R_fCH_2CHIOAc$ (B)

$R_fCH_2CHIOAc$		Reactants				Conditions		Products $R_fCH_2CH_2OH$		
R_f	Moles	Acid	Cc.	Zinc, moles	Solvent,[a] cc.	Temp., °C.	Time, hr.	Yield, %	B.p., °C. (mm.)	$n^{25}D$
$CF_3(CF_2)_2$	0.21	HCl	[a]	0.31	E 150	60–80	1.5	67	127 (160)	1.3123
$CF_3(CF_2)_6$	.095	36% aq. HCl	15	.31	E 250	60	2			
$CF_3(CF_2)_{10}$	.013	...	..	.15	A 50	95–100	1.25	62	[b]	
$ClCF_2CF_2$	.05	18% aq. HCl	25	.6	...	90–160	2.0			
$H(CF_2)_4$	.052	36% aq. HCl	10	.15	E 100	56–60	2.0	51[e]	71 (15)	1.3322
$—(CF_2)_6—$	.3	36% aq. HCl	20	.31	A 100	50–65	2.5			

[a] See Experimental for details; E is ethanol; A is 75% aqueous acetic acid. [b] Soluble in ether; m.p. 108–110° after sublimation; 1.5 g. of ether-insoluble solid also obtained. [c] The adduct B was added to zinc dust and acid and the product steam distilled; it was acetylated with acetic anhydride. [d] Chlorine. *Anal.* Calcd., 15.0. Found, 15.4. [e] A side-

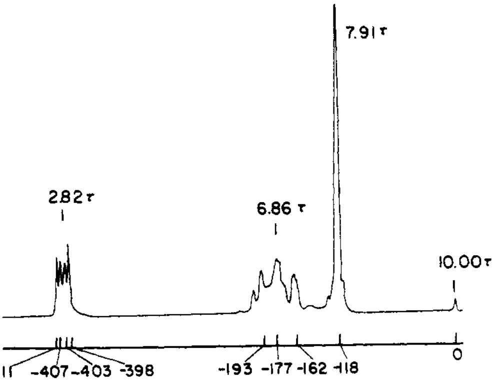
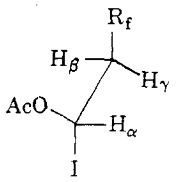
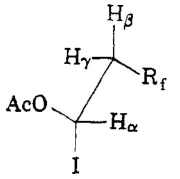


Fig. 1.—Proton magnetic resonance spectra obtained at 56.4 Mc. (spinning); *ca.* 50 mole % of $C_3F_7CH_2CHIO_2CCH_3$ in carbon tetrachloride or deuteriochloroform solution (under nitrogen). Abscissa is "c.p.s. relative to tetramethylsliane." No ordinate units.

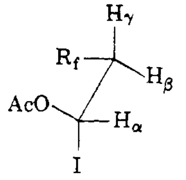
c.p.s. apart and centered on 2.82 τ correspond to the average chemical shift of H_α for the rapidly equilibrating conformation isomers as follows:



B^1



B^2



B^3

The equilibrium mixture of isomers present was estimated by Roberts (assuming reasonable values for the coupling constants in the separate conformations[18]) to be about 80% of B^1 (preferred conformation), 20% of B^2, and 0% of B^3. As the temperature of the liquid B was reduced gradually from 25° to *ca.* −180° where it became a glass, broadening of the proton resonance peaks at 2.82 τ gradually occurred. In a mixture of many slowly rotating isomers, several more coupling constants would be involved and the usual viscosity effect may also be invoked. In any case, the n.m.r. spectrometer was not able to resolve the several proton resonances in the cold mixture.

Experimental

Addition of 1-Iodoperfluoropropane to Vinyl Acetate Using ABN Initiator.—To a solution of 1.64 g. (0.01 mole; 2 mole %) of ABN in 150 g. (0.50 mole) of 1-iodoperfluoropropane was added 33 g. (0.38 mole) of vinyl acetate which had been treated with potassium hydroxide at 10° to remove inhibitor and distilled under nitrogen. The mixture was stirred and heated at reflux under nitrogen for 2 hr. at 65° (exothermic heat carried the temperature to 72° after 1.5 hr.) and 10.0 g. (the remainder of 0.5 mole) of vinyl acetate was added. The temperature rose to 80° as refluxing stopped and held at 80° a total of 5 hr. The adduct B (1-iodo-3,3-4,4,5,5,5-heptafluoropentyl acetate) was distilled in a Claisen flask, b.p. 45° (1.2 mm.); shielded from light and kept cold; n^{25}D 1.3978; 136.5 g.; a higher boiling fraction was also collected, b.p. 55–100° (0.5 mm.); n^{25}D 1.4098; 17.8 g. Nitrogen was admitted to the vacuum system at the end of the distillation in each case. Distillation of the cold trap liquid gave 18.7 g. of 1-iodoperfluoropropane and 10.2 g. of vinyl acetate. The higher boiling material was fractionated in a 16-in. platinum spinning band column (column A) giving an additional 3.0 g. of adduct B (total yield 85%). The higher boiling material (b.p. 54–77° (0.7 mm.); 9.9 g.) was extremely sensitive to light and air, and could not be obtained in pure condition.

Allyl Acetate.—A mixture of 1-iodoperfluoropropane (90 g.; 0.3 mole), allyl acetate (30.0 g.; 0.30 mole) and ABN (0.30 g.; 1.8 mole; 0.6 mole %) was heated in a bath under nitrogen at 71–80° for 5 hr. Distillation in a 3-ft.platinum spinning band column (column B) gave 16.1 g. of 1-iodoperfluoropropane (8.7 g. in trap); 9.0 g. of allyl acetate and 71.8 g. (60% conversion; 85% yield) of 4,4,5,5,6,6,6-heptafluoro-2-iodohexan-1-ol acetate, b.p. 78.5° (5.0 mm.), n^{25}D 1.4012. The residual oil (8.6 g.; n^{25}D 1.4312) amounted to 10% of the product. Gas chromatography showed the distilled ester was a single pure compound. A 78% conversion to product (90% yield) was obtained using 2 mole % of ABN initiator at 50–90° for 5 hr.

Anal. Calcd. for $C_8F_7H_8O_2I$: C, 24.2; H, 2.03; F, 33.6; I, 32.1. Found: C, 24.7; H, 2.0; F, 34.0; I, 32.0.

Ethyl Acrylate.—1-Iodoperfluoropropane (60.0 g.; 0.2 mole, redistilled, colorless) and ethyl acrylate (10.0 g.; 0.10 mole; treated with potassium hydroxide, distilled under nitrogen, b.p. 99.8°; n^{25}D 1.4036) and azobis-2,4-dimethylvaleronitrile[19] (AVN) (0.30 g.; 1.2 mmoles) were mixed in this order in a flask, magnetically stirred under nitrogen, using a −70° reflux condenser. The mixture refluxed at 47° for 12 hr. (bath at 63°). The unchanged iodide was distilled in column B, b.p. 41°, n^{25}D 1.3257; 44.4 g.; and the pressure reduced to 1.0 mm. of mercury. Liquid collected in the −70° trap (6.4 g.; n^{25}D 1.3336) which gas chromatography showed was principally 1-iodo-

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(19) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949). The rates of decomposition are: AVN, $k = 7.1 \times 10^4$ sec.$^{-1}$ at 80.2°; 1.98×10^4 sec.$^{-1}$ at 69.8°; ABN, $k = 1.7 \times 10^4$ sec.$^{-1}$ at 80.2°; 0.38×10^4 sec.$^{-1}$ at 69.8°.

(TABLE II *Continued*)

$R_fCH_2CH_2OAc$			$R_fCH_2CH_2OH$						$R_fCH_2CH_2OAc$					
			Calcd.			Found			Calcd.			Found		
Yield, %	B.p., °C. (mm.)	$n^{25}D$	C	H	F	C	H	F	C	H	F	C	H	F
6.2	38–49 (10)	1.3282												
50	84 (10)	1.3241							28.9	1.55	62.4	29.2	1.55	63.3
			25.4	0.82	71.2	25.8	1.4	70.6						
60[c]	93 (100)	1.3658							32.4	3.2	34.1	32.4	3.2	33.1[d]
			29.3	2.5	62.1	29.7	2.7	61.9						
55[f]	104 (0.1)	1.3696							35.4	2.98	48.1	35.4	2.9	47.8

product, b.p. 88–102°/0.6 mm.; $n^{25}D$ 1.3678; 3.3 g. also obtained. [f] A 1.1-g. sample of liquid, b.p. 56–77°/0.6 mm.; $n^{25}D$ 1.3472 [probably $H(CF_2)_6CH_2CH_2OH$] and a higher boiling point oil also obtained. The mixture was acetylated with acetic anhydride.

perfluoropropane with a trace of an unknown compound. The residual tan gum (14.5 g.; $n^{25}D$ 1.4523; 100% conversion) was a telomer of ethyl acrylate, DP *ca.* 8.

Anal. Calcd. for $C_{43}H_{64}F_7IO_{16}$: C, 47.0; H, 5.88; F, 12.1; I, 11.6; mol. wt. 1095.5. Found: C, 49.4; H, 6.5; F, 10.5; I, 9.7; mol. wt. (ebullioscopic) 1083, 1078.

Styrene.—1-Iodoperfluoropropane (29.6 g.; 0.10 mole), styrene (13.5 g.; 0.13 mole, redistilled), and ABN (0.1 g.; 0.006 mole) were heated as above for 5 hr. at 60°; an additional 12 g. (0.03 mole) of iodide and 0.1 g. of ABN were added and heating continued for 2 hr. The colorless mixture was distilled in column B; 36.1 g. (87.6%) of 1-iodoperfluoropropane, 9.3 g. (71.6%) of styrene (b.p. 52° (21 mm.); $n^{25}D$ 1.5433), and a residue of 2.2 g. were obtained. The residue appeared to be a mixture of 31% of 1:1 adduct and 69% of coupled product, 4,4-bisphenyl-1,1-bis(perfluoropropyl)butane according to molecular weight and iodine content.

Anal. Calcd. for $C_{11}H_8F_7I$; mol. wt. 400.1; I, 31.7; for $C_{22}H_{16}F_{14}$: mol. wt. 534.2. Found: mol. wt. (ebullioscopic 509, 503); I, 10.0.

Zinc Reduction of 1-Iodoalkyl Esters.—A solution of 1-iodo-3,3,4,4,5,5,5-heptafluoropentyl acetate (81.0 g.; 0.21 mole) in cold alcohol (100 ml.) was added over a period of 1 hr. to a rapidly stirred slurry of zinc dust (20 g.; 0.31 mole) in alcohol (50 ml.) heated at 60–80°. The solution was saturated with dry hydrogen chloride at 15-min. intervals. An additional 10 g. of zinc dust was added after 0.75 hr. and refluxing was continued for 0.5 hr. after the addition was complete. Alcohol was removed by distillation at 300 mm.; the residue poured into water and extracted three times with ether (or with chloroform). The organic solution, after drying over anhydrous magnesium sulfate, was distilled in column B giving 3,3,4,4,5,5,5-heptafluoropentan-1-ol,[8] b.p. 125° or 75° (100 mm.), $n^{25}D$ 1.3123, 28.7 g. (67% conversion), and its acetate, b.p. 38–49° (10 mm.), $n^{25}D$ 1.3282, 3.3 g. (6.2% conversion).

Lithium Aluminum Hydride Reduction of 1-Iodo-3,3- to 9,9,9-Pentadecafluorononyl Acetate.—The title compound B (53.7 g., 0.092 mole; 92% conversion, 100% yield on recovered reactants) was obtained by reaction of 0.1 mole each of vinyl acetate and 1-iodoperfluoroheptane with 1.2 mole % of ABN at 80° for 2 hr. Unchanged materials (88%) were recovered by distillation at 7 to 2 mm. in the same ratio as original mixture according to gas chromatographic analysis. (Perkin-Elmer Vapor Fractometer, 80° column temperature; 10-ft. "Apiezon" M on 60–80 mesh alkaline-washed "Chromosorb W" column; helium carrier gas at about 40 cc./min.). A slurry of 5.0 g. (0.131 mole; an excess) of lithium aluminum hydride in 50 cc. of anhydrous ether was stirred rapidly while the adduct B, dissolved in 50 cc. of anhydrous ether, was added over a 0.75 hr. period at a gentle boil. The thick mixture was refluxed 1 hr., cooled to 10° and 15 cc. of ethyl acetate added, followed by cautious addition of 50 cc. of 30% aqueous sulfuric acid. The gray slurry became clear when heated for 3–4 hr. Hydrogen was evolved during addition of the ether and during hydrolysis. The ether layer was drawn off, extracted two times with 25 cc. of 5% aqueous sodium bisulfite, and dried over magnesium sulfate. Distillation in a Claisen flask gave 30.5 g. (80% conversion) of 3,3- to 9,9,9-pentadecafluorononan-1-ol, b.p. 84° (10 mm.); $n^{25}D$ 1.3164 and 3.5 g. of a higher boiling residue.

Zinc Reduction and Coupling of 1-Iodo-3,3,4,4,5,5,5-heptafluoropentyl Acetate.—A slurry of zinc dust (27.0 g.; 0.42 mole) in ether was converted to the zinc–copper couple by the procedure of Shank and Schechter,[20] and the ether exchanged by tetrahydrofuran (60 cc.) in the final extraction. The zinc slurry was stirred rapidly under a nitrogen atmosphere in a 500-cc. round bottom flask fitted with a large-bore, water-cooled condenser while 75 g. (0.20 mole; 40 cc.) of 1-iodo-3,3,4,4,5,5,5-heptafluoropentyl acetate (distilled product; light yellow color changed to dark orange when transferred to addition funnel) dissolved in 25 cc. of tetrahydrofuran was added at 23° in a slow stream during 5 min. The reduction occurred with great vigor while the compound was being added. The mixture was stirred and refluxed at 61° for 1.5 hr., cooled and the gray slurry was filtered into a separatory funnel containing 100 cc. of water. A yellow solid sludge of amphoteric zinc salts formed in the aqueous layer, which dissolved when a small amount of concentrated hydrochloric acid was added. The aqueous layer was shaken three times with ether, and the orange ether layer evaporated off. The dark red oil (36.7 g.) was shaken three times with saturated aqueous sodium sulfite. The aqueous extracts were shaken with methylene chloride, the organic material dried with magnesium sulfate and fractionated in column A. 3,3,4,4,5,5,5-Heptafluoropentyl acetate, b.p. 51° (25 mm.); $n^{25}D$ 1.3261, 16.0 g. (31%); 1,2-bis-(2,2,3,3,4,4,4-heptafluorobutyl)-ethane-1,2-diol diacetate, b.p. 90° (2.0 mm.); $n^{25}D$ 1.3463; 11.0 g. (23% conversion); and a residue of 1.6 g. were obtained. The coupled product was examined by infrared spectroscopy. There was a strong carbonyl band at 5.60 μ, the C—CH_3 absorption band at 7.25 μ, and no absorption band near 3.00 μ of an hydroxyl group.

Anal. Calcd. for $C_{14}H_{12}F_{14}O_4$: C, 33.0; H, 2.35; F, 52.1. Found: C, 33.7; H, 2.4; F, 52.1.

The same products were obtained in about the same yield from reaction carried out in moist ether with zinc dust.

Hydrolysis of Allyl Acetate-1-iodoperfluoropropane Adduct to 4,4,5,5,6,6,6-Heptafluoro-1,2-epoxyhexane.[21]—Sodium hydroxide (8.0 g., 0.2 mole) was added over a period of 0.5 hr. (while protected from the atmosphere) to a stirred solution of 4,4,5,5,6,6,6-heptafluoro-2-iodo-hexan-1-ol acetate (41 g., 0.1 mole) in 100 ml. of ether at 24° (some heat produced). When the addition was complete the mixture was stirred and heated under reflux for 5 hr. The solid material (22.8 g.) was collected by filtration and washed with ether. Distillation in column B gave 4,4,5,5,6,6,6-

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(20) R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1827 (1959).

heptafluoro-1,2-epoxyhexane[21] (10.8 g.), b.p. 62–63° (131 mm.), n^{25}_{D} 1.3150. An intermediate fraction, 13.9 g., b.p. 65–140.5° (131 mm.) was shown to contain 80% epoxide by gas chromatography. Unchanged ester (10.0 g.), b.p. 98–99° (20 mm.), n^{25}_{D} 1.4004, was also recovered. The yield of epoxide was 78% at 61% conversion.

Anal. Calcd. for $C_6F_7H_5O$: C, 31.9; H, 2.2; F, 58.8. Found: C, 32.5; H, 2.5; F, 58.8.

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[21] After the completion of this work, the preparation of this compound was described by J. D. Park, F. E. Rogers, and J. R. Lacher, *J. Org. Chem.*, **26**, 2089 (1961).

Elimination Reactions of α-Halogenated Ketones. IX.[1a] A Comparison of the Reactions of 2-Bromo-2-(α-bromobenzyl)-1-indanone with Those of 2-Bromo-2-(α-bromobenzyl)-3,3-dimethyl-1-indanone

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2-Bromo-2-(α-bromobenzyl)-1-indanone reacts with piperidine and morpholine to give 3-piperidino(and 3-morpholino)-2-benzal-1-indanone and not the β-amino-α,β-unsaturated ketones, 2-(α-piperidinobenzal)-and 2-(α-morpholinobenzal)-1-indanone, as was previously reported.[1c] Thermal elimination of hydrogen bromide from 2-bromo-2-(α-bromobenzyl)-1-indanone similarly gives 3-bromo-2-benzal-1-indanone and not as previously reported 2-(α-bromobenzal)-1-indanone. The mechanisms of these eliminations and rearrangements are discussed. When the 3-positions are blocked, as in 2-bromo-2-(α-bromobenzyl)-3,3-dimethyl-1-indanone, elimination with piperidine and morpholine does give the β-amino-α,β-unsaturated ketones and these compounds are readily hydrolyzed to 2-benzoyl-3,3-dimethyl-1-indanone. With cyclohexylamine the last mentioned dibromo compound gave 2-(α-bromobenzal)-3,3-dimethyl-1-indanone.

The elimination of hydrogen bromide from 2-bromo-2-benzyl-1-tetralones yields predominantly the endocyclic elimination product 2-benzyl-1-keto-1,4-dihydronaphthalenes.[2] The elimination of hydrogen bromide from the related 2-bromo-2-benzyl-1-indanones was expected to give mainly exocyclic elimination because of steric differences. This indeed is the case, but the reaction of 2-bromo-2-(α-bromobenzyl)-1-indanone (IV) with piperidine or morpholine does not give the β-amino-α,β-unsaturated ketones (Xa, Xb) as was previously reported.[1c] Instead the exocyclic ketones VIIa and VIIb are produced wherein rearrangement has taken place during the elimination-substitution. Also thermal elimination of hydrogen bromide from the same dibromo compound IV does not yield 2-(α-bromobenzal)-1-indanone (IX) as was previously reported but instead forms 2-benzal-3-bromo-1-indanone (II). The same bromo compound II can also be prepared in high yield by the bromination of 2-benzal-1-indanone (I) with *N*-bromosuccinimide.

The β-amino-α,β-unsaturated ketone structures were considered to be correct for products from the reaction of the dibromo compound IV with amines because their ultraviolet and infrared spectra were somewhat different in an expected fashion from those of 2-benzal-1-indanone (I). However, it was observed[1c] that these amino products could not be hydrolyzed under the conditions normally successful with β-amino-α,β-unsaturated ketones.[3] Thus, as a final check on these amino products, it was considered desirable to carry out amine reactions with 2-bromo-2-(α-bromobenzyl)-3,3-dimethyl-1-indanone because only exocyclic elimination can occur from this compound.

3,3-Dimethyl-1-indanone was prepared in high yield, by the ring closure of β-phenylisovaleric acid with polyphosphoric acid, and condensed with benzaldehyde to give 2-benzal-3,3-dimethyl-1-indanone (XI). The latter with bromine in carbon tetrachloride solution readily formed 2-bromo-2-(α-bromobenzyl)-3,3-dimethyl-1-indanone (XV) in 72% yield. Piperidine and morpholine eliminated hydrogen bromide from this dibromo compound XV to give the β-amino-α,β-unsaturated ketones XVIIa and XVIIb, respectively. These strongly conjugated amino ketones had high melting points (180° and 214°, respectively) like amides and showed pronounced shifts of their carbonyl stretching frequencies (1640 and 1647 cm.$^{-1}$, respectively) when compared with the value for the parent 2-benzal-3,3-dimethyl-1-indanone (1705 cm.$^{-1}$). The strong conjugation between the electron donating amino group and the electron accepting carbonyl group results in the formation of an intense charge-transfer band in the visible spectrum of these compounds (406 and 401 mμ for XVIIa and XVIIb, respectively; $\epsilon \times 10^{-3}$, 19.6 and 21.0—ethanol solutions). This spectral data suggests that compounds XVIIa and XVIIb both have the same β-amino-α,β-unsaturated ketone structure, and to confirm this 2-(α-piperidinobenzal)-3,3-dimethyl-1-

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[1] (a) For paper VIII, see G. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962). (b) To whom communications concerning this paper should be addressed. (c) N. H. Cromwell and R. P. Ayer, *J. Am. Chem. Soc.*, **82**, 133 (1960).

[2] A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 and 901 (1958).

[3] N. H. Cromwell, *J. Am. Chem. Soc.*, **62**, 2897 (1940).