

## Free-Radical Chain Addition Reactions of Aldehydes with Perfluoro Ketones and Chloro Perfluoro Ketones

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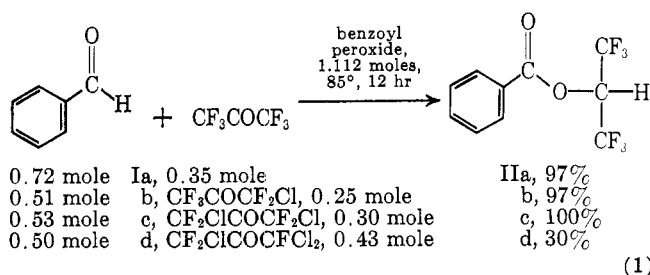
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Benzaldehyde reacts with hexafluoroacetone (Ia), or its chloro derivatives (Ib-d), in the presence of benzoyl peroxide at 80° to give good yields of 1,1,1,3,3,3-hexafluoro-2-propyl benzoate (IIa), or analogous chloro fluoro esters (IIb-d). Alkanals also give the corresponding esters (IVa-d) as well as carbon monoxide and bis(trihalomethyl)alkylcarbinols (Va-d). Hence, acyl radicals add to the oxygen atoms of these carbonyl functions while alkyl radicals from the decarbonylation of alkanoyl radicals undergo the alternative carbonyl addition. The nmr spectra of these esters show that the two fluorine atoms of chlorodifluoromethyl groups are nonequivalent. All structures are confirmed by mass spectrometry.

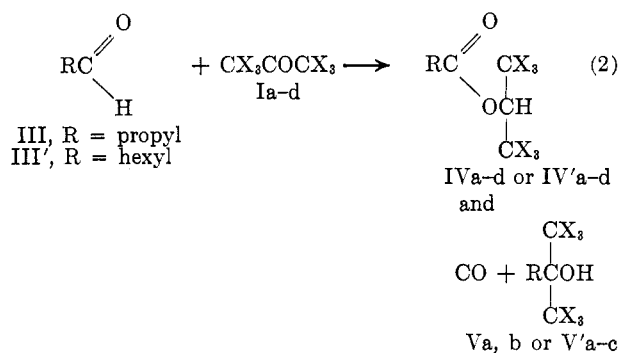
These reactions are analogous to the previously studied additions of aldehydes to olefins<sup>1</sup> and to azo compounds.<sup>2</sup> Many reactions are known in which the addition of radicals to the carbonyl group has been postulated,<sup>3</sup> but free-radical chain reactions involving this step are rare.

Aromatic aldehydes give such reactions with azo compounds<sup>2</sup> and with olefinic substances such as diethyl maleate (low yields).<sup>1c</sup> In attempts so to add benzaldehyde to alkenes,<sup>1a</sup> no addition product was observed and a small amount of the dibenzoate of 1,2-diphenyl-1,2-ethanediol was obtained. However, benzaldehyde reacts with these ketones Ia-d as shown.



The yields given are based upon ketone consumed. Conversions (with Ia, 50%; Ib, 91%; Ic, 75%; and Id, 12%) differed, and with Id a product of dehydrochlorination of IIId (20%) was also obtained.

With alkanals III and III', this reaction gives the analogous esters IVa-d and IV'a-d as well as the ter-



(1) (a) M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); (b) J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955); (c) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1009, 1269 (1952); (d) R. L. Huang, *J. Chem. Soc.*, 1749 (1956).

(2) (a) M. S. Kharasch, M. Zimmerman, W. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **18**, 1045 (1953); (b) R. Huisgen and F. Jacobs, *Ann.*, **590**, 37 (1954).

(3) (a) W. H. Urry, D. J. Trecker, and N. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964); for other examples, see ref 11-16 therein; (b) R. L. Huang, *J. Chem. Soc.*, 1750 (1956); (c) W. H. Urry, M. H. Pai, and C. Y. Chen, *J. Am. Chem. Soc.*, **86**, 5342 (1964).

tiary alcohols Va, b, and V'a-c. When a solution containing butanal (III, 75 g, 1.04 moles), hexafluoroacetone (Ia, 78.0 g, 0.47 mole), and benzoyl peroxide (0.021 mole) was held at 85° for 11 hr in a stainless steel bomb, 1,1,1,3,3,3-hexafluoro-2-propyl butanoate (IVa, 95.1 g, 0.39 mole, 83%, bp 107°, *n*<sub>D</sub><sup>20</sup> 1.3204, molecular ion 238) and 1,1,1-trifluoro-2-(trifluoromethyl)-2-pentanol (Va, 10.2 g, 0.049 mole, 10%, bp 98°, *n*<sub>D</sub><sup>20</sup> 1.3299, molecular ion 210) were obtained. Substance IVa gave N-(*p*-tolyl)butyramide (mp 75°), and its saponification gave 1,1,1,3,3,3-hexafluoro-2-propanol (distilled after reaction mixture was acidified; *pK*<sub>a</sub> = 9.3,<sup>4</sup> bp 51.2°; molecular ion 168; <sup>1</sup>H nmr in CCl<sub>4</sub> with TMS, 1 H septet at δ 4.35, *J* = 6.3 cps, and 1 H singlet at 3.67 changes with concentration). This alcohol gave its α-naphthylurethane (mp 161°). Substance Va (identical with the above, bp 98°, *n*<sub>D</sub><sup>20</sup> 1.3303, infrared and nmr) also was prepared by the hydrogenation of 1,1,1-trifluoro-2-(trifluoromethyl)-4-penten-2-ol (Pt, 0.98 mole of H<sub>2</sub> consumed) from the reaction of propene with Ia<sup>5</sup> at 155° for 16 hr.

Data for these reactions studied are summarized in Table I. Attempts to increase the yields of V'e,d with higher reaction temperatures (expt 8 and 9) were thwarted by side reactions probably catalyzed by acidic products from decomposition of the products IV and V. Aldehyde condensation products (2-ethyl-2-hexenal VI from III, and 2-pentyl-2-nonenal VII from III'), the ketone hydrates, some alkanolic acid, and high-boiling residues (probably higher condensation products from the alkenal) were obtained. Even at 85°, some of this reaction occurred with the more highly chlorinated ketones Ic and Id (expt 3 and 4).

The parts of the <sup>1</sup>H nmr spectra of these esters II or IV, owing to their benzoyl or alkanoyl groups, are as expected. Also, the expected septets are observed for the single hydrogen atoms of the hexafluoro-2-propyl groups of IIa (δ 6.04, *J* = 6.3 cps), IVa (δ 5.80, *J* = 6.5 cps), and IV'a (δ 5.56, *J* = 6.0 cps). However, the corresponding multiplets in the nmr spectra of IIb-d and IVb-d indicate that the two fluorine atoms of their chlorodifluoromethyl groups are not equivalent (IIb, four superimposed quartets centered at δ 6.07 with *J*<sub>HCF<sub>2</sub></sub> = 5.9 cps, *J*<sub>HFA</sub> = 9.0 cps, and *J*<sub>HFA'</sub> = 6.7 cps; IIc, three overlapping triplets at δ 6.08, probably *J*<sub>HFA</sub> = *J*<sub>HFA'</sub> = 9.8 cps and *J*<sub>HFB</sub> = *J*<sub>HFB'</sub> = 6.3 cps; and IId, eight peaks of nearly equal area cen-

(4) I. L. Knunyants, M. P. Gambarjan, C.-Y. Chen, and E. M. Rokhlin, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk*, **684**, 633 (1962).

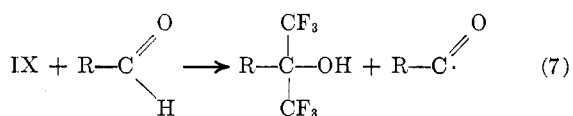
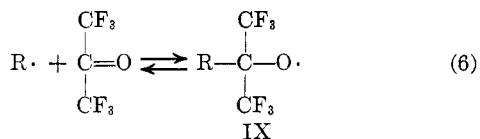
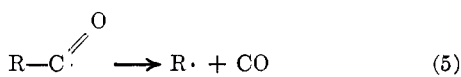
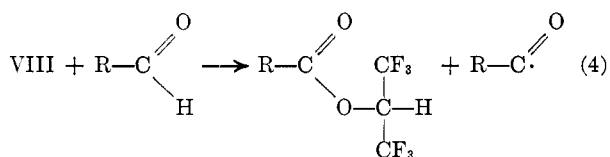
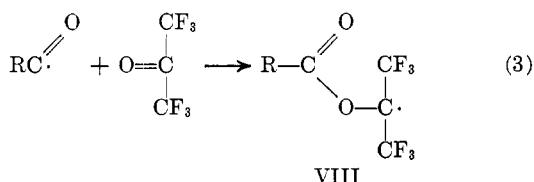
(5) H. R. Davis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 3-8, 1961, p 25M.



rearrangement ion (226 → 206, ms 187.8) is also a metastable process. With the butanoate esters, the base peak is butanoyl (71), but with the heptanoate esters, alkyl fragments provide the base peaks (with IV'a, 71; IV'b, 43; and IV'e, 71).

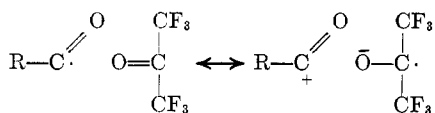
The molecular ions of the tertiary alcohols are as unstable as expected, and the  $M - 18$  peak systems are also weak. Loss by the molecular ions of the possible trihalomethyl groups is important, as well as subsequent loss of HF by metastable events. Also, various rearrangement processes apparently occur (for example, with Vb,  $\text{CH}_3\text{CHCl}$ , 63; and  $\text{CH}_3\text{CH}_2\text{CHCl}$ , 77).

This reaction probably has the chain-propagating steps shown in eq 3-7. With benzaldehyde, the inter-



mediate benzoyl radical does not decarbonylate (no reaction 5), and only the esters IIa-d are obtained. Apparently, hexanoyl radicals do not undergo reaction 5 to the extent that butanoyl radicals do, and products V' are obtained in lower yields in the reactions of III' (cf. expt 5 and 6 with 1 and 2). A careful study showed that no Vc is formed in the reaction of butanal with Ic. Presumably with this ketone, acyl radical addition to it (reaction 3) occurs too rapidly to permit significant decarbonylation (reaction 5).

This reaction demonstrates a striking difference between acyl and alkyl radicals. Addition of the former to the oxygen atom of the carbonyl group (reaction 3)<sup>3a</sup> probably involves stabilization of its transition state by the contributions of polar structures,<sup>7</sup> and possibly by developing carboxylate delocalization in it.



Other results suggest that such additions (reaction 3) are very rapid, and probably irreversible. This unit

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 277, 286.

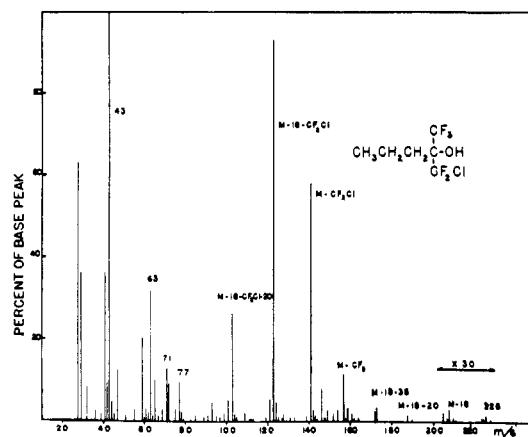
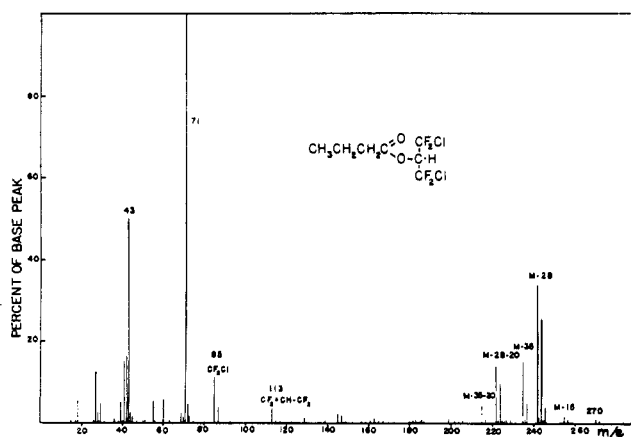
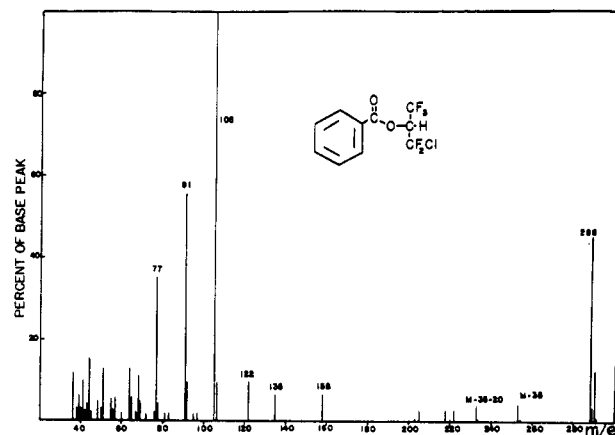


Figure 1.—Mass spectra of IIb (upper), IVc (middle), and Vb (lower).

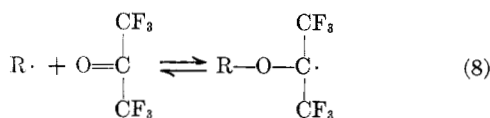
reaction is postulated in reactions of ketones with acid chlorides and triphenyltin hydride,<sup>8</sup> and it occurs so rapidly that no aldehyde is formed *via* reaction of the acyl radicals with the hydride. The rapidity of this reaction is further illustrated by the formation of esters as minor products in the reactions of organotin hydrides with acid chlorides<sup>9</sup> *via* acyl radical addition to product aldehydes.

The observed addition of alkyl radicals to the carbon atom of the carbonyl group<sup>10</sup> may be attributed to greater reactivity of radical IX even though both alternative modes of addition (reactions 6 and 8)

(8) L. Kaplan, *J. Am. Chem. Soc.*, **88**, 1833 (1966), and private communication.

(9) H. G. Kuivila and E. J. Walsh, Jr., *ibid.*, **88**, 571, 576 (1966).

(10) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *ibid.*, **70**, 4253 (1948).



probably occur. Certainly, radical X from reaction 8 should be more stable than radical IX. However, both reactions 6 and 8 are reversible. Decompositions of *t*-alkoxy radicals are well known,<sup>11</sup> and the reverse of reaction 6 would probably occur in preference to the alternative loss of a trifluoromethyl radical. Further, a reaction analogous to the reverse of reaction 8 is postulated in the free-radical chain rearrangements of  $\alpha$ -alkoxystyrenes.<sup>12</sup> However, even if both radicals IX and X are present in the reaction mixture with the latter at higher steady-state concentration, the reaction may take the observed course to give V if the rate of reaction of IX with aldehyde is much greater than that of the corresponding reaction of X.

### Experimental Section

**Procedures.**—Ketones Ia and Ib were distilled into an evacuated 1-l. stainless steel bomb containing a solution of initiator in the aldehyde at  $-80^\circ$ , and then the bomb and its contents were heated for the reaction period. With ketones Ic and Id, the reactants were placed in the bomb, and it was swept with nitrogen prior to heating. Part of the experimental details are given in reaction 1 and Table I, and others are described below.

**The Reaction of Ia with Benzaldehyde.**—After the bomb cooled to  $25^\circ$ , it was opened and part of the unreacted IIa (29 g, 0.175 mole) evolved. The remaining reaction mixture (110 g) was distilled to give a distillate [bp  $170^\circ$  (88 mm), 96.6 g] and a residue (8.2 g). Vpc analysis of this distillate (Aerograph A-700; Carbowax 20 M,  $3/8$  in.  $\times$  7 ft, isothermal  $198^\circ$ ; He flow rate, 3.33 ml/sec) showed that it contained IIa (retention time 1.8 min, 26.5 mole %, 46.3 g, 0.17 mole, 50% conversion of Ia, 97% yield) and unreacted benzaldehyde (retention time 6.4 min, 73.5 mole %, 40 g, 0.47 mole).

Since distillation was ineffective in separating these two substances, part of the IIa (24 g) present was obtained by chilling the distillate ( $-50^\circ$ , 1 hr), and IIa that precipitated was separated on a filter. Pure IIa (mp  $53.9^\circ$ ) was obtained by dissolving this precipitate in pentane, the pentane solution was extracted with sodium bicarbonate solution and water, and IIa was recrystallized from the dried pentane solution at  $-50^\circ$ .

*Anal.* Calcd for  $\text{C}_{10}\text{H}_6\text{F}_6\text{O}_2$ : C, 44.1; H, 2.2; F, 41.9. Found: C, 44.4; H, 2.4; F, 41.7.

The spectra of IIa ( $^1\text{H}$  and  $^{19}\text{F}$  nmr) were previously described. Mass spectrum, molecular ion at 272, 2.9%; 122, 12.9%; base peak at 105, 15.4%; 91, 6.6%; 77, 12.0%; 51, 3.9%; 44, 2.7%; and 36, 2.4%, all of  $\Sigma_{35}$ ; metastable peaks at 235.2 owing to loss of F by the molecular ion, 272  $\rightarrow$  253; at 214.5 owing to loss of HF by the latter ion, 253  $\rightarrow$  233; at 56.5, 105  $\rightarrow$  77; at 40.5, 272  $\rightarrow$  105; and at 33.8, 77  $\rightarrow$  51. Infrared,  $1765\text{ cm}^{-1}$  confirm the assigned structure.

The distillation residue (8.2 g) was dissolved in ether, and the ether solution was extracted with sodium carbonate solution (10%). Acidification of the aqueous extract gave benzoic acid (2.6 g, mp  $120.5\text{--}121^\circ$ ), and distillation of the ether extract gave an oil (2.7 g) that contained no IIa and only a trace of benzaldehyde.

**The Reaction of Ib with Benzaldehyde.**—Analysis (vpc, above) showed that this reaction mixture contained unreacted Ib (retention time 0.8 min, 4.3 mole %, 0.023 mole), IIb (retention time 3.6 min, 40.1 mole %, 62.8 g, 0.218 mole, 91% conversion, 97% yield), and unreacted benzaldehyde (retention time 6.4 min, 55.6 mole %, 0.302 mole).

Its distillation did not separate unreacted benzaldehyde and IIb. However, a distillate [bp  $109\text{--}130^\circ$  (82 mm), 72.7 g] and a distillation residue (17.9 g) were obtained while unreacted Ib (5.0 g) condensed in the ( $-80^\circ$ ) trap. A pentane solution of the distillate was cooled to  $-50^\circ$ , and crude IIb precipitated. Pure

IIb (mp  $35.8\text{--}35.9^\circ$ , bp  $203^\circ$ ) was obtained from two further such recrystallizations.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_6\text{ClF}_5\text{O}_2$ : C, 41.6; H, 2.1; Cl, 12.3; F, 32.9. Found: C, 41.3; H, 2.0; Cl, 12.2; F, 32.6.

Confirmation of the structure of IIb was obtained from its spectra (infrared,  $1760\text{ cm}^{-1}$ ;  $^1\text{H}$  and  $^{19}\text{F}$  described before. Mass spectrum, Figure 1, with metastables at 214.5, 253  $\rightarrow$  233; at 56.5, 105  $\rightarrow$  77; at 38.3, 288  $\rightarrow$  105; and at 33.8, 77  $\rightarrow$  51). The residue was dissolved in ether, and the ether solution was extracted with sodium carbonate solution (10%). Distillation of the ether solution obtained gave an oil (9.3 g) that was shown to contain IIb (95 mole %, vpc) and unreacted benzaldehyde (5 mole %). Acidification of the aqueous extract gave benzoic acid (3.1 g, mp  $119.5\text{--}120^\circ$ ).

**The Reaction of Ic with Benzaldehyde.**—Vpc analysis of the reaction mixture showed that it contained unreacted Ic (retention time 0.8 min, 10.8 mole %, 15.0 g, 0.075 mole), unreacted benzaldehyde (retention time 6.4 min, 49.1 mole %, 29.2 g, 0.27 mole), and IIc (retention time 7.6 min, 40.1 mole %, 68.8 g, 0.226 mole, 75% conversion of Ic, 100% yield).

Vacuum distillation of this reaction mixture gave preliminary fractions containing unreacted benzaldehyde and IIc [bp  $83\text{--}122^\circ$  (25 mm), 48.8 g], pure IIc [29.0 g, bp  $233^\circ$ ,  $126^\circ$  (25 mm),  $n_D^{20}$  1.4632], and a residue (16.8 g). Unreacted Ic was condensed in the cold trap (14.5 g). The residue was shown as before to contain benzoic acid (2.0 g, mp  $121\text{--}122^\circ$ ), and IIc (10.5 g). Spectra of IIc ( $^1\text{H}$  and  $^{19}\text{F}$  nmr described above. Mass spectrum, molecular ions at 308, 0.9%; 306, 5.2%; and 304, 8.1%; 269, 2.6%; 249, 1.5%; 106, 4.4%; base peak at 105, 42.4%; 77, 13.4%; 51, 5.8%; 50, 1.9%, all of  $\Sigma_{35}$ ; metastable peaks at 230.5 and 232.5 owing to loss of HF from the M - 35 and M - 37 ions, 269  $\rightarrow$  249 and 271  $\rightarrow$  251; at 56.5, 105  $\rightarrow$  77; at 36.3, 304  $\rightarrow$  105; and at 33.8, 77  $\rightarrow$  51. Infrared,  $1760\text{ cm}^{-1}$ ) were taken.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_6\text{Cl}_2\text{F}_4\text{O}_2$ : C, 39.4; H, 2.0; Cl, 23.2; F, 24.9. Found: C, 40.0; H, 2.0; Cl, 23.7; F, 25.2.

**The Reaction of Id with Benzaldehyde.**—Distillation of the reaction mixture gave unreacted Id [82.0 g, bp  $22\text{--}24^\circ$  (42 mm), vpc as above—retention time 1.1 min], benzaldehyde [44.0 g, 71-73 $^\circ$  (18 mm), retention time 6.4 min], and residual reaction product. Extraction of the latter as above gave benzoic acid (3.8 g, mp  $122^\circ$ ). Vpc analysis and separation of the residual reaction product gave IIc (4.8 g, 0.015 mole, bp  $255^\circ$ ,  $n_D^{20}$  1.4864, retention time 15.0 min, infrared  $1760\text{ cm}^{-1}$ ), and a product of its dehydrochlorination (2.9 g, 0.010 mole, bp  $237^\circ$ ,  $n_D^{20}$  1.4901, retention time 9.9 min, infrared  $1790$  and  $1695\text{ cm}^{-1}$ ).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_6\text{Cl}_3\text{F}_3\text{O}_2$ : C, 37.4; H, 1.9; Cl, 33.1; F, 17.7. Found: C, 37.7; H, 2.0; Cl, 33.0; F, 17.9.

Spectrometry confirmed the structures of IIc ( $^1\text{H}$  nmr described above. Mass spectrum, molecular ions at 320, 2.2%; 322, 2.2%; and 324, 0.7%; 106, 6.0%; base peak 105, 22.1%; 78, 2.2%; 77, 22.0%; 51, 11.3%; 50, 3.4%; and 44, 2.3%, all of  $\Sigma_{28}$ ; metastables at 248.4, 287  $\rightarrow$  267; at 246.4, 285  $\rightarrow$  265; at 56.5, 105  $\rightarrow$  77; at 34.5, 320  $\rightarrow$  105; and at 33.8, 77  $\rightarrow$  51), and the product of its dehydrochlorination ( $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS: 5 H benzoate multiplet previously described only. Mass spectrum, small molecular ion system showing two chlorine atoms per molecule at 285, 287, and 289; and otherwise virtually identical with the mass spectrum of IIc except that peaks at 249 and 251 with relative heights indicating one chlorine atom in the fragment are relatively large).

**The Reaction of Ia with III.**—Vpc analysis of this reaction mixture (as above except isothermal,  $133^\circ$ ) showed that it contained IVa (retention time 1.2 min, 95.1 g, 0.39 mole, 83%), unreacted III (retention time 2.3 min, 44.4 g, 0.62 mole), and Va (retention time 7.1 min, 10.2 g, 0.049 mole, 10.4%). Fractional distillation (Nestor-Faust, 2-ft spinning band) gave only preliminary separation. Fractions rich in IVa and Va were separated by vpc to give pure IVa (bp  $107^\circ$ ,  $n_D^{20}$  1.3204.  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  1.01, *J*-7 cps; 2 H sextet at  $\delta$  1.73, *J*-7 cps; 2 H triplet at  $\delta$  2.48, *J*-7 cps; 1 H septet at  $\delta$  5.80, *J*-6.5 cps. Infrared  $1765\text{ cm}^{-1}$ ), and Va (bp  $98^\circ$ ,  $n_D^{20}$  1.3313.  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  1.01, *J*-6 cps; 4 H multiplet at  $\delta$  1.82; 1 H singlet at  $\delta$  3.07—changes with concentration. Infrared  $3350\text{ cm}^{-1}$ ).

*Anal.* Calcd for  $\text{C}_7\text{H}_5\text{F}_6\text{O}_2$ : C, 35.3; H, 3.4; F, 47.9. Found: C, 35.1; H, 3.2; F, 47.6.

*Anal.* Calcd for  $\text{C}_6\text{H}_5\text{F}_5\text{O}$ : C, 34.3; H, 3.8; F, 54.3. Found: C, 34.2; H, 3.5; F, 54.1.

Mass spectra taken with the Associated Electrical Industries, Ltd., Type MS9 mass spectrometer confirmed the assigned struc-

(11) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

(12) K. B. Wiberg and B. I. Rowland, *ibid.*, **77**, 1159 (1955).

tures of IVa (molecular ion, 238, 0.1%; 210, 1.4%; 71, 7.1%; base peak 69, 11.8%; 55, 2.2%; 51, 1.9%; 43, 10.5%; 42, 6.2%; 41, 9.6%; 39, 8.4%; 29, 2.7%; 28, 2.8%; 27, 13.6%; 26, 2.1%, all of  $\Sigma_{14}$ ; metastables at 209, 238  $\rightarrow$  223; at 185.3, 238  $\rightarrow$  210; at 180.8, 219  $\rightarrow$  199; at 171.9, 210  $\rightarrow$  190; at 165, 203  $\rightarrow$  183; and at 152.1, 190  $\rightarrow$  170) and of Va (molecular ion, 210, 0.1%; 192, 0.1%; 123, 2.9%; 103, 3.2%; base peak 69, 8.9%; 43, 5.5%; 41, 8.9%; 39, 6.8%; 29, 6.8%; 28, 3.1%; and 27, 11.5%, all of  $\Sigma_{14}$ ).

Substance IVa was converted to N-(*p*-tolyl)butyramide (mp 74.6–74.8°).<sup>13</sup> Saponification of IVa (10% potassium hydroxide solution, 1 hr) gave 1,1,1,3,3,3-hexafluoro-2-propanol (bp 51.2°);<sup>4</sup> reaction mixture was acidified before this alcohol could be distilled since its  $pK_a$  is 9.3.<sup>14</sup> The spectra of this alcohol (<sup>1</sup>H nmr given above. Mass spectrum, molecular ion, 168, 0.04%; 149, 2.1%; 129, 8.4%; 101, 5.6%; 99, 6.0%; 79, 5.2%; 69, 13.7%; base peak 51, 16.7%; 50, 3.7%; 49, 9.8%; 31, 4.5%; and 29, 10.8%, all of  $\Sigma_{17}$ ; metastable at 111.7, 149  $\rightarrow$  129) confirmed its structure. This alcohol when treated with  $\alpha$ -naphthyl isocyanate in ligroin with pyridine gave its  $\alpha$ -naphthyl urethan (mp 160.5–161° from methanol; <sup>1</sup>H nmr in perdeuterioacetone with TMS, 1 H singlet at  $\delta$  2.98; 1 H septet at 6.31,  $J = 7$  cps; and 7 H multiplet 7.50–8.40).

*Anal.* Calcd for  $C_{14}H_9F_6NO_2$ : C, 49.9; H, 2.7; N, 4.2; F, 33.8. Found: C, 50.1; H, 2.9; N, 4.4; F, 33.6.

Substance Va was prepared by an alternative synthesis.<sup>5</sup> In the stainless steel bomb, Ia (108.0 g, 0.65 mole) and propylene (24.0 g, 0.58 mole) were heated at 135° for 16 hr. After the bomb and its contents had cooled, unreacted reactants were allowed to evaporate. The residual reaction product (31 g) was distilled to give 1,1,1-trifluoro-2-(trifluoromethyl)-4-penten-2-ol [25 g, bp 98°, 42° (100 mm),  $n_D^{20}$  1.3343. <sup>1</sup>H nmr in  $CCl_4$  with TMS; 2 H doublet at  $\delta$  2.61,  $J = 6.5$  cps; 1 H singlet at 3.02, changes with concentration; and 3 H vinyl multiple 5.03–6.23]. This substance (20.3 g, 0.0975 mole) in ethanol (15 g, was hydrogenated (25–45°, 2 hr, 0.096 mole of  $H_2$  absorbed,  $PtO_2$ , 0.2 g). Vapor phase chromatography (above column conditions, isothermal 137°) gave ethanol (retention time 1.7 min) and Va (retention time 4.3 min, 19.3 g, 94%, bp 98°,  $n_D^{20}$  1.3313; infrared and nmr identical with the above).

**The Reaction of Ib with III.**—Distillation of this reaction mixture (122 g) gave unreacted III (42.5 g, 0.73 mole), a mixture of IVb and Vb [46.0 g, bp 58–61° (55 mm)], and a distillation residue (12.0 g, shown to contain benzoic acid as above). The cold trap condensate (6.3 g) consisted of mostly unreacted ketone Ib.

Vpc analysis and separation of this product mixture as above showed that it contained IVb (retention time 2.0 min, 85 mole %, 39.7 g, 0.156 mole, 63% yield, bp 132°,  $n_D^{20}$  1.3517) and Vb (retention time 13.8 min, 15 mole %, 6.26 g, 0.028 mole, 11%, bp 127°,  $n_D^{20}$  1.3672).

*Anal.* Calcd for  $C_7H_5ClF_3O_2$ : C, 33.0; H, 3.2; Cl, 13.9; F, 37.3. Found: C, 33.0; H, 3.5; Cl, 13.9; F, 37.6.

*Anal.* Calcd for  $C_8H_5ClF_3O$ : C, 31.8; H, 3.6; Cl, 15.6; F, 41.9. Found: C, 32.3; H, 3.5; Cl, 15.7; F, 42.6.

Spectrometry gave structural confirmation for IVb (<sup>1</sup>H nmr in  $CCl_4$  with TMS, 3 H triplet at  $\delta$  1.03,  $J = 7$  cps; 2 H sextet at 1.78,  $J = 7$  cps; 2 H triplet at 2.52,  $J = 6.5$  cps; and 1 H multiplet at 5.80 with four overlapping quartets,  $J_{CF_3H} = 6.0$  cps,  $J_{FAH} = 9.0$  cps, and  $J_{FBH} = 6.5$  cps. Mass spectrum, molecular ion system at 254, 0.23%; and 256, 0.08%; 228, 3.5%; 226, 11.1%; 219, 2.8%; 206, 3.7%; base peak 71, 20.6%; 69, 3.9%; 43, 5.2%; 42, 4.6%; 41, 5.1%; 29, 2.5%; and 27, 4.2%, all of  $\Sigma_{15}$ ; metastable peaks at 200.8 and 202.8, 256  $\rightarrow$  228 and 254  $\rightarrow$  226; at 189.8 and 187.8, 228  $\rightarrow$  208, and 226  $\rightarrow$  206; and at 181.0, 219  $\rightarrow$  199), and Vb (<sup>1</sup>H nmr in  $CCl_4$  with TMS; 3 H triplet at  $\delta$  0.98,  $J = 7.5$  cps; 4 H multiplet 1.22–2.22 with large peak at 1.86, probably middle peak of triplet,  $J = 7.5$  cps; and 1 H singlet at 2.94, changes with concentration. Mass spectrum, Figure 1, with metastables at 107.3, 141  $\rightarrow$  123; at 103.8, 141  $\rightarrow$  121; and at 86.3, 123  $\rightarrow$  103).

Substance IVb became pink on exposure to light, and slowly darkened. A similar reaction without benzoyl peroxide under identical conditions gave the same mixture of IVb and Vb (15 g, 20%).

When a solution of Ib (55.0 g, 0.30 mole), III (72.0 g, 1.0 mole), and azobisisobutyronitrile (4.0 g, 0.024 mole) was held at 70° for 8 hr, IVb (36.0 g, 0.151 mole) was obtained.

**The Reaction of Ic with III.**—This reaction mixture (135 g) was analyzed (vpc as above, isothermal 155°). It contained unreacted Ic (retention time 0.8 min, 2.6 g, 0.013 mole), unreacted III (retention time 1.7 min, 39.9 g, 0.55 mole), IVc (retention time 3.0 min, 81.1 g, 0.30 mole, 97%), 2-ethyl-2-hexenal VI (retention time 8.0 min, 5.3 g, 0.042 mole), and butanoic acid (retention time 13.8 min, 1.04 g, 0.012 mole).

Vpc separation gave pure IVc (bp 162°,  $n_D^{20}$  1.3511. Infrared 1800  $cm^{-1}$ . <sup>1</sup>H nmr in  $CCl_4$  with TMS; 3 H triplet at  $\delta$  1.02,  $J = 7$  cps; 2 H sextet at 1.77,  $J = 7$  cps; 2 H triplet at 2.51,  $J = 6.5$  cps; and 1 H multiplet at 5.85 with three superimposed triplets  $J_{FAH} = J_{FBH} = 9.0$  cps, and  $J_{FAH} = J_{FBH} = 6.0$  cps. Mass spectrum, Figure 1, with metastables at 203.6 and 205.6, 244  $\rightarrow$  224 and 242  $\rightarrow$  222).

*Anal.* Calcd for  $C_7H_8Cl_2F_4O_2$ : C, 31.0; H, 3.0; Cl, 26.2; F, 28.0. Found: C, 31.2; H, 3.1; Cl, 25.0; F, 27.8.

The VI (2,4-dinitrophenylhydrazone mp 119–120°. <sup>1</sup>H nmr in  $CCl_4$  with TMS, 6 H system of two overlapping triplets one at  $\delta$  0.96,  $J = 7.5$  cps; and the other at 1.00,  $J = 6$  cps; 2 H sextet at 1.55,  $J = 7$  cps; 4 H multiplet at 1.93–2.58,  $J = 7.5$  cps; with principal peak at 2.30, 1 H triplet at 6.33,  $J = 7.5$  cps; and 1 H singlet at 7.95), and butanoic acid (*p*-toluidide mp 75°; infrared and nmr spectra identical with those of authentic substance) were also so isolated.

Careful search failed to reveal any of the expected Vc. A similar reaction without benzoyl peroxide under identical conditions with no precautions taken to remove air gave the same product IVc (8 g, 11%).

**The Reaction of Id with III.**—This reaction of Id gave even more of the side reaction products, 2-ethyl-2-hexenal and butanoic acid, than the previous reaction of Ic with III. The product IVd was obtained in low yield since it is probably less stable than IVc, and its decomposition gives hydrogen halides that catalyze condensation and hydrolysis. These side reactions also are more important with Ic at higher temperatures (with *t*-butyl peroxide, 130–150°; expt 8, Table I).

Distillation of this brown reaction mixture gave a distillate [bp 25–116° (120 mm), 53.7 g], and a residue (16.3 g) that solidified to a dark brown tar upon cooling. Analysis of the distillate (vpc as above, isothermal 155°) showed that it contained III (retention time 1.6 min, 20 mole %), 1,1,3-trichloro-1,3,3-trifluoro-2,2-dihydroxypropane (retention time 3.2 min, 27 mole %), VI (retention time, 7.7 min, 40 mole %, same infrared, nmr, and 2,4-dinitrophenylhydrazone as above), IVd (retention time 8.0 min, 10 mole %, 8.5 g, 0.03 mole), and butanoic acid (retention time 19 min, 3.1 mole %, 1.1 g, 0.013 mole). Apparently, the residue contained predominantly aldehyde-derived material (10.9 g) and little ketone-derived material (5.0 g).

The IVd and VI could not be separated by vapor phase chromatography and their relative amounts were estimated from the vpc fraction containing them. Its nmr spectrum showed the triplet owing to the olefinic hydrogen atom in VI at  $\delta$  6.32, and the multiplet owing to the 2-propyl hydrogen of IVd at 5.92 (integrated areas showed 4:1 molar ratio). Butanoic acid isolated (vpc) was converted to its *p*-toluidide (mp 74.7–74.8° after two recrystallizations from methanol–water). The hydrate of Id (<sup>1</sup>H nmr in  $DCCl_3$  with TMS, singlet at  $\delta$  5.12, changes with concentration) had the same retention time as authentic material.

**The Reaction of Ia with III'.**—Rapid preliminary distillation gave four fractions, [50.1 g, bp 25–115° (38 mm)], and a residue (28.8 g). The  $-80^\circ$  trap used contained a condensate (2.8 g). Since the distillation gave little separation, each fraction was analyzed (vpc as above except isothermal 225°, and He flow rate 2.50 ml/sec) to show unreacted Ia (retention time 0.9 min, 9.0 g) and its hydrate (3.8 g, total 0.007 mole), IV'a (retention time 1.2 min, 33.8 g, 0.121 mole, 55%), unreacted III' (retention time 1.8 min, 11.9 g, 0.104 mole), and V'a (retention time 1.9 min, 1.7 g, 0.007 mole, 3.2%).

Benzoic acid (0.7 g, mp 122°) was recovered from the residue by acidification of its basic extract, and the residual oil (21.3 g) gave an nmr spectrum that suggested it was a mixture of higher condensation products derived from III'.

IV'a (bp 162°,  $n_D^{20}$  1.3523) and V'a (bp 167°,  $n_D^{20}$  1.3651) were obtained pure by large-scale vapor phase chromatography.

*Anal.* Calcd for  $C_{10}H_{14}F_6O_2$ : C, 42.9; H, 5.0; F, 40.7. Found: C, 43.1; H, 5.2; F, 40.9.

(13) C. F. Koelsch and D. Tennebaum, *J. Am. Chem. Soc.*, **55**, 3049 (1933).

(14) I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 923 (1964).

*Anal.* Calcd for  $C_9H_4F_6O$ : C, 42.9; H, 5.6; F, 45.2. Found: C, 43.1; H, 5.8; F, 45.0.

Their spectra confirmed the assigned structures: IV'a (infrared  $1790\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.88,  $J = 5$  cps; 8 H multiplet 1.06–1.96; 3 H triplet at 2.39,  $J = 6.5$  cps; and 1 H septet at 5.56,  $J = 6$  cps. Mass spectrum, molecular ion at 280, 1.3%; 237, 3.6%; 223, 5.4%; 210, 7.2%; 113, 4.4%; base peak 71, 12.5%; 69, 3.1%; 68, 3.0%; 55, 4.8%; 43, 6.3%; 41, 7.7%; 29, 5.0%; and 27, 4.0%, all of  $\Sigma_{25}$ ; metastables at 200.8, 280  $\rightarrow$  237; and at 184.8, 223  $\rightarrow$  203; and V'a (infrared  $3500\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.87,  $J = 4$  cps; 10 H multiplet 1.02–2.05 with peaks at 1.27 and 1.72; and 1 H singlet at 2.85, changes with concentration. Mass spectrum, molecular ion at 252, 0.13%; 234, 0.24%; 223, 3.4%; 209, 9.0%; 86, 6.7%; 70, 4.9%; 57, 8.0%; 55, 5.9%; parent mass 43, 16.3%; 42, 6.0%; 41, 8.0%; and 29, 5.1%, all of  $\Sigma_{25}$ ; metastables at 197.2, 252  $\rightarrow$  223; at 184.8, 223  $\rightarrow$  203; at 173.3, 252  $\rightarrow$  209; at 170.9, 209  $\rightarrow$  189; at 147.2, 185  $\rightarrow$  165; at 133.4, 252  $\rightarrow$  183; and at 127.5, 165  $\rightarrow$  145).

**The Reaction of Ib with III'.**—Rapid distillation of this reaction mixture gave one fraction of pure IV'b [37.3 g, bp  $187^\circ$ , 111.2–111.6° (55 mm),  $n_D^{20}$  1.3763], three other fractions (total, 88.9 g), a residue (21.1 g), and a cold trap condensate (1.1 g). Analysis (vpc) of the various fractions as in the previous experiment gave unreacted Ib (retention time 1.0 min, 13.6 g, 0.074 mole) and its hydrate (retention time 1.3 min, 5.8 g, 0.029 mole), benzene (0.39 g, 0.005 mole), IV'b (retention time 1.7 min, 78.1 g, 0.264 mole, 68%), unreacted III' (retention time 2.2 min, 4.6 g, 0.040 mole), and 2-pentyl-2-nonenal VII (retention time 9.5 min, 0.4 g).

*Anal.* Calcd for  $C_{10}H_{14}ClF_2O_2$ : C, 40.5; H, 4.8; Cl, 11.9; F, 32.0. Found: C, 40.9; H, 4.9; Cl, 11.9; F, 33.4.

The spectra of IV'b (infrared  $1775\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.88,  $J = 4$  cps; 8 H multiplet 1.05–2.00 with peak at 1.31, 2 H triplet at 2.41,  $J = 6.5$  cps; and 1 H multiplet at 5.58 with four superimposed quartets,  $J_{CF_2H} = 5.0$  cps,  $J_{FAH} = 9.0$  cps, and  $J_{FBH} = 6.7$  cps. Mass spectrum, molecular ions at 296, 0.41%; and 298, 0.13%; 226, 2.7%; 123, 3.9%; 113, 4.0%; 109, 3.7%; 107, 3.9%; 71, 6.8%; 70, 3.5%; 69, 1.9%; 68, 1.9%; 55, 4.6%; 52, 3.7%; 44, 3.0%; base peak 43, 9.3%; 42, 2.9%; 41, 6.8%; 29, 4.3%; and 27, 3.5%, all of  $\Sigma_{25}$ ; metastables at 218.2 and 216.2, 298  $\rightarrow$  255, 296  $\rightarrow$  253; at 202.6 and 200.6, 241  $\rightarrow$  221, 239  $\rightarrow$  219; at 189.8 and 187.8, 228  $\rightarrow$  208, 226  $\rightarrow$  206; and at 182.9 and 180.8, 221  $\rightarrow$  201, 219  $\rightarrow$  199) were in accord with the structure assigned.

From the residue, benzoic acid (mp  $122^\circ$ ) was obtained, and the residual oil (12.3 g) again gave nmr spectrum expected for products of condensation of III'.

**The Reaction of Ic with III'.**—Vacuum distillation of this reaction mixture gave IV'c [61.9 g, bp  $216^\circ$ , 111–112° (24 mm),  $n_D^{20}$  1.4009], four other fractions [bp 25–137° (24 mm), 23.1 g], a residue (17.4 g), and cold-trap condensate (7.5 g). Vpc analysis of all of these fractions as before showed that unreacted Ic (retention time 1.2 min, 18.3 g, 0.092 mole), unreacted III' (retention time 2.2 min, 14.7 g, 0.13 mole), IV'c (retention time 2.8 min, 62.2 g, 0.99 mole, 65%), and a trace of V'c (retention time 6.1 min) were obtained.

*Anal.* Calcd for  $C_{10}H_{14}Cl_2F_4O_2$ : C, 38.4; H, 4.5; Cl, 22.6; F, 24.3. Found: C, 38.8; H, 4.8; Cl, 22.0; F, 24.0.

Spectra confirmed the identity of IV'c (infrared  $1780\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.88,  $J = 5$  cps; 8 H multiplet 1.07–1.95 with peak at 1.32; 2 H triplet at 2.40,  $J = 6.5$  cps; and 1 H multiplet at 5.61, three overlapping triplets with  $J = 9.4$  cps between them and  $J = 5.8$  cps within each triplet. Mass spectrum, molecular ion system at 312, 0.92%; 314, 0.55%; and 316, 0.10%; 244, 2.3%; 242, 3.4%; 113,

7.9%; 85, 2.3%; 84, 3.9%; 71, 8.8%; 70, 2.3%; 69, 2.3%; 55, 3.5%; base peak 43, 9.5%; 42, 3.0%; 41, 5.7%; 29, 2.4%; and 27, 2.5%, all of  $\Sigma_{25}$ ; metastables at 231.8 and 233.9, 312  $\rightarrow$  269, 314  $\rightarrow$  271; at 216.6 and 218.6, 255  $\rightarrow$  235, 257  $\rightarrow$  237; and at 203.7 and 205.6, 242  $\rightarrow$  222, 244  $\rightarrow$  224).

Benzene (0.64 g, 0.008 mole) was observed in the cold-trap condensate, and the residue gave benzoic acid (1.6 g, mp  $122^\circ$ ) and an oil (13.1 g).

This reaction studied at higher temperature gave a higher yield of V'c, but the combined yields of IV'c and V'c were low. Accordingly, a solution containing Ic (27.2 g, 0.137 mole) and *t*-butyl peroxide (3.0 g, 0.021 mole) was added dropwise to III' (57.0 g, 0.50 mole) held at  $150^\circ$ . Soon after this addition was begun, the reaction mixture began to boil, and after 5 hr its reflux temperature had dropped to  $130^\circ$ . Preliminary distillation gave a distillate [bp  $25^\circ$  (77 mm) to  $109^\circ$  (3 mm), 52.0 g] and a residue (21.0 g). The  $-80^\circ$  trap contained *t*-butyl alcohol (1.35 g). Analysis (Aerograph A-700; Carbowax 20 M,  $\frac{3}{8}$  in.  $\times$  7 ft; isothermal  $225^\circ$ ; He flow rate, 3.33 ml/sec) of the distillate showed that it contained IV'c (retention time 2.2 min, bp  $218^\circ$ ,  $n_D^{20}$  1.4009, infrared  $1780\text{ cm}^{-1}$ , 6.4 g, 0.021 mole, 15%).  $^1\text{H}$  nmr and mass spectrum were the same as above), V'c (retention time 6.6 min, bp  $215^\circ$ ,  $n_D^{20}$  1.4205, 1.36 g, 0.0048 mole, 3.5%, infrared  $3500\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.91,  $J = 5$  cps; 10 H multiplet envelope 1.08–2.25 with peaks at 1.36 and 1.92; and 1 H singlet at 3.32, changes with concentration. Mass spectrum, weak molecular ion system at 284, 286 and 288, 0.027%; M – 18 system at 266, 268 and 270; and M – 29 system at 255, 257 and 259, all of relative peak heights to indicate two Cl atoms; 199, 3.1%; 85, 4.1%; 71, 4.5%; 70, 5.6%; 69, 4.1%; 57, 5.1%; 55, 5.8%; base peak 43, 8.6%; 42, 4.3%; 41, 6.8%; and 29, 5.3%, all of  $\Sigma_{25}$ ), and 2-pentyl-2-nonenal VII (retention time 11.2 min, parent mass 210, infrared and nmr spectra identical with authentic substance, 5.2 g, 0.025 mole, 2,4-dinitrophenylhydrazone mp  $128.6$ – $128.9^\circ$ ).<sup>15</sup>

*Anal.* Calcd for  $C_{10}H_{14}Cl_2F_4O_2$ : C, 38.4; H, 4.5; Cl, 22.6; F, 24.3. Found: C, 38.0; H, 4.5; Cl, 22.4; F, 25.0.

*Anal.* Calcd for  $C_9H_4Cl_2F_4O$ : C, 37.9; H, 4.9; Cl, 24.9; F, 26.7. Found: C, 38.0; H, 4.6; Cl, 24.7; F, 26.4.

**Reaction of Id with III'.**—A solution of *t*-butyl peroxide (1.0 g, 0.0077 mole) in Id (34.0 g, 0.16 mole) was added dropwise to III' (57.0 g, 0.50 mole) at  $150^\circ$ . The reaction mixture soon began to reflux, and after 5.5 hr that temperature had decreased to  $130^\circ$ . Preliminary distillation gave a distillate [56.5 g, bp  $25^\circ$  (65 mm) to  $107^\circ$  (1 mm)] and a residue (16.0 g). The attached  $-80^\circ$  trap contained a condensate (10.0 g). This distillate was analyzed as above (vpc isothermal  $223^\circ$ ). It contained unreacted Id (retention time 0.9 min, 14.3 g), unreacted III' (retention time 1.8 min, 29.7 g), IV'd (retention time 4.6 min; 7.04 g, 0.021 mole, 13%; infrared  $1785\text{ cm}^{-1}$ .  $^1\text{H}$  nmr in  $\text{CCl}_4$  with TMS, 3 H triplet at  $\delta$  0.92,  $J = 5$  cps; 8 H multiplet at 1.08–2.05 with peak at 1.33; 2 H triplet at 2.53; and 1 H multiplet at 5.91 described above. Mass spectrum, molecular ion system at 328, 0.13%; 330, 0.14%; 332, 0.04%; 334, 0.007%; 129, 2.3%; base peak at 113, 10.0%; 84, 4.2%; 71, 5.5%; 55, 3.1%; 43, 9.2%; 41, 4.6%; 29, 2.5%; and 28, 2.4%, all of  $\Sigma_{18}$ ; metastables, pairs at 219.5 and 221.5, 258  $\rightarrow$  238 and 260  $\rightarrow$  240; at 232.5 and 234.5, 271  $\rightarrow$  251 and 273  $\rightarrow$  253; and at 212.5 and 214.5, 251  $\rightarrow$  231, 253  $\rightarrow$  233), and 2-pentyl-2-nonenal VI (retention time 11.2 min, 5.51 g, 0.026 mole, infrared and nmr identical with those of an authentic sample).

*Anal.* Calcd for  $C_{10}H_{14}Cl_3F_3O_2$ : C, 36.4; H, 4.3; Cl, 32.3; F, 17.3. Found: C, 36.2; H, 4.2; Cl, 32.6; F, 17.1.

(15) A. T. Fuller and H. King, *J. Chem. Soc.*, 966 (1947).