The Free Radical-Induced Addition Reaction of Aldehydes to Dichlorodifluoroethylenes

HIROSHIGE MURAMATSU AND KAN INUKAI

Government Industrial Research Institute, Nagoya, Japan

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The peroxide-induced addition of aldehydes to 1,2-dichloro-1,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene was carried out. While the reactions of acetaldehyde, propionaldehyde, and *n*-butyraldehyde with olefins gave the corresponding dichlorodifluoroethyl alkyl ketones, *i*-butyraldehyde gave both the ketones and dichlorodifluoro-3-methylbutanes. The direction of addition of the acyl radicals to the asymmetrical olefin was determined.

While the ionic reactions for the synthesis of fluorine-containing ketones have been studied extensively,[1] little attention has been paid to the free radical-induced addition reaction. The only data available hitherto were reported by LaZerte and Koshar[2] who carried out the addition of aldehydes to perfluoropropene and perfluorobutene-1.

The present work deals with the peroxide-induced addition of aldehydes to 1,2-dichloro-1,2-difluoroethylene and 1,1-dichloro-2,2-difluoroethylene using benzoyl peroxide as a catalyst. The main products were identified as dichlorodifluoroethyl alkyl ketones, which were thought to be formed by the addition of the acyl radicals to the haloolefins. The general reactions are

$$\mathrm{CFCl{=}CFCl + RCHO \longrightarrow CHFClCFClCOR}$$

and

$$\mathrm{CF_2{=}CCl_2 + RCHO \longrightarrow CHCl_2CF_2COR}$$
$$(\mathrm{R} = \mathrm{CH_3, C_2H_5}, n\text{- and } i\text{-}\mathrm{C_3H_7})$$

While the reactions of acetaldehyde, propionaldehyde, and *n*-butyraldehyde with olefins gave the corresponding ketones as principal products, *i*-butyraldehyde gave both the ketones and dichlorodifluoro-3-methylbutanes. The addition reaction of *i*-butyraldehyde to asymmetrical dichlorodifluoroethylene gave the ketone and 1,1-dichloro-2,2-difluoro-3-methylbutane in molar ratio of about 1:2. In the case of symmetrical olefin, however, 1,2-dichloro-1,2-difluoro-3-methylbutane was obtained predominantly. When benzaldehyde and furfural were used, the expected addition products were not obtained under the same reaction conditions.

The mechanism suggested by Kharasch[3] for the addition reaction of aldehyde to the nonhalogenated olefins may be applied to the formation of the ketone (equations 1) and halohydrocarbon (equations 2) as follows:

$$\mathrm{R\cdot}\ (\text{from peroxide}) + i\text{-}\mathrm{C_3H_7CHO} \longrightarrow \mathrm{RH} + i\text{-}\mathrm{C_3H_7CO\cdot}$$
$$i\text{-}\mathrm{C_3H_7CO\cdot} + \mathrm{CF_2{=}CCl_2} \longrightarrow i\text{-}\mathrm{C_3H_7COCF_2CCl_2\cdot} \quad (1)$$
$$\xrightarrow{i\text{-}\mathrm{C_3H_7CHO}} i\text{-}\mathrm{C_3H_7COCF_2CCl_2H} + i\text{-}\mathrm{C_3H_7CO\cdot}$$
$$i\text{-}\mathrm{C_3H_7CO\cdot} \longrightarrow i\text{-}\mathrm{C_3H_7\cdot} + \mathrm{CO}$$
$$i\text{-}\mathrm{C_3H_7\cdot} + \mathrm{CF_2{=}CCl_2} \longrightarrow i\text{-}\mathrm{C_3H_7CF_2CCl_2\cdot} \quad (2)$$
$$\xrightarrow{i\text{-}\mathrm{C_3H_7CHO}} i\text{-}\mathrm{C_3H_7CF_2CCl_2H} + i\text{-}\mathrm{C_3H_7CO\cdot}$$

In those reactions, a small amount of crotonaldehyde analogs, which were identified with authentic samples, was formed due to the condensation of the reactant aldehydes. For example, with propionaldehyde used as a reactant, the following condensation reactions occurred

$$\mathrm{2CH_3CH_2CHO \longrightarrow C_2H_5CH(OH)CH(CH_3)CHO \xrightarrow{-H_2O} C_2H_5CH{=}C(CH_3)CHO}$$

These reactions seemed to be catalyzed[4] by a trace of acids, hydrochloric and hydrofluoric, which might be produced by the decomposition of addition products. The similarity of boiling points of the crotonaldehyde analogs to those of the corresponding ketones made their separation by distillation difficult. Therefore, the ketones formed were separated from the corresponding crotonaldehyde analogs by oxidizing with aqueous potassium permanganate solution under cooling.

Inasmuch as the ketones formed were unstable in the presence of acid when heated, the acidic material was removed with sodium bicarbonate solution before distillation. The infrared spectra of the ketones exhibited strong absorption bands at 5.71–5.74 μ for $\mathrm{CHCl_2CF_2COR}$, and at 5.75 μ for $\mathrm{CHFClCFClCOR}$, attributable to carbonyl stretching modes with a shift of about 0.1 μ to shorter wave length resulting from the inductive effect of the substituted halogens.[5] The properties of the addition products of the aldehydes to the

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(1) For a recent review of the syntheses of fluorine containing ketones, see A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, 1958, p. 182.

(2) J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

(3) M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

(4) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, 3rd ed., 1956, p. 208.

(5) D. G. Weiblen, "Fluorine Chemistry," Vol. 2, J. H. Simons, ed., Academic Press, Inc., New York, 1954, p. 449.

TABLE I

1,2-DICHLORO-1,2-DIFLUOROETHYL ALKYL KETONE (CHFClCFClCOR) AND 1,2-DICHLORO-1,2-DIFLUORO-3-METHYLBUTANE

R	Yield, %	B.P.	Mm.	n^{20}_D	d_4^{20}	MR_D		Fluorine, %		Chlorine, %	
						Calcd.[a]	Found	Calcd.	Found	Calcd.	Found
CH_3	20	95–96	300	1.4062	1.417	30.58	30.69	21.47	21.57	40.07	39.99
C_2H_5	15	100–100.5	200	1.4122	1.340	35.20	35.48	19.89	19.79	37.13	37.18
n-C_3H_7	17	100–102	100	1.4159	1.264	39.81	40.70	18.53	18.47	34.59	33.18
i-C_3H_7	3	85–87	100	1.4108	1.263	39.81	40.29	18.53	19.15	34.59	35.12
$(CH_3)_2CHCFClCFClH$	15	73–74	100	1.4099	1.258	35.18	34.86	21.47	21.02	40.06	39.56

TABLE II

1,1-DIFLUORO-2,2-DICHLOROETHYL ALKYL KETONE ($CHCl_2CF_2COR$) AND 1,1-DIFLUORO-2,2-DICHLORO-3-METHYLBUTANE

R	Yield, %	B.P.	Mm.	n^{20}_D	d_4^{20}	MR_D		Fluorine, %		Chlorine, %	
						Calcd.[a]	Found	Calcd.	Found	Calcd.	Found
CH_3	38	96–96.5	300	1.4028	1.415	30.58	30.51	21.47	21.51	40.07	40.06
C_2H_5	42	101–101.5	200	1.4088	1.345	35.20	35.10	19.89	20.23	37.13	37.25
n-C_3H_7	43	100.5–101	100	1.4136	1.282	39.81	39.93	18.53	18.61	34.59	34.69
i-C_3H_7	15	91.5–92	100	1.4087	1.274	39.81	39.76	18.53	18.62	34.59	34.61
$(CH_3)_2CHCF_2CCl_2H$	26	77–78	100	1.4090	1.259	35.18	34.76	21.47	21.70	40.06	39.43

[a] Molecular refractions calculated by adding the customary increments of the pertinent elements AR_F[1,18].

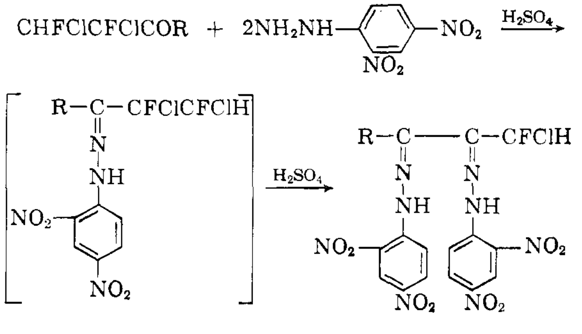
dichlorodifluoroethylenes are shown in Tables I and II.

Although no difficulty is involved in the assignments of the structures to the 1:1 addition products with the symmetrical olefins, in the case of asymmetrical olefins it is possible for addition of acyl radicals to take place either to $=CF_2$ or $=CCl_2$. Thus it would be possible to obtain either $CHCl_2CF_2COR$ or CHF_2CCl_2COR. It is described by Hudlicky[6] on the free radical-induced addition of halohydrocarbons to the haloolefins that the haloalkyl radicals formed add in general to the side having less steric hindrance.[7] Krespan and coworkers[8] reported that in heating a fluorinated acid chloride, nickel carbonyl, and 1,1-dichloro-2,2-difluoroethylene at 150° an intermediate fluoroalkyl radical $R_f\cdot$ added to the $=CF_2$ side to give $R_fCF_2CCl_2\cdot$. We observed also that α-hydroxyalkyl radicals attacked the $=CF_2$ side in the radiation-induced addition of alcohols.[9] Therefore, the formation of $CHCl_2CF_2COR$ is more probable. It is of considerable diagnostic value for determination of the direction of the additions that the wave lengths of the carbonyl bands for the adducts of asymmetrical olefins were slightly shorter than those for the adducts of symmetrical ones.

Furthermore, a direct proof is afforded from the following chemical reactions. Oxidation of the adduct of acetaldehyde to 1,1-dichlorodifluoroethylene gave dichlorodifluoropropionic acid. Pyrolysis of the sodium salt of the acid resulted in an olefin, which was found to be identical with 1-chloro-2,2-difluoroethylene from its infrared spectrum.[10] Thus, it was confirmed that the acyl radical added to the $=CF_2$ side.

$$CHCl_2CF_2COCH_3 \xrightarrow[\text{2. aq. NaOH}]{\text{1. KMnO}_4} CHCl_2CF_2COONa \xrightarrow{\Delta} CHCl{=}CF_2 + NaCl + CO_2$$

While 1,1-difluoro-2,2-dichloroethyl alkyl ketones gave only the corresponding 2,4-dinitrophenylhydrazones of the haloketones upon heating in an aqueous alcohol solution in the presence of sulfuric acid, 1,2-dichloro-1,2-difluoroethyl alkyl ketones did not give the corresponding hydrazones, but the intermediate hydrazones were converted very easily to the bis-2,4-dinitrophenylhydrazones of the halo-α-diketones with the same reaction conditions. There are several reports concerning with the reactions of α-halocarbonyl compounds. For example, the bis-2,4-dinitrophenylhydrazones were obtained from 2-chlorocyclohexanone[11] and chloropropanone-2,[12] and also chloroglyoxal- and glyoxalbis-2,4-dinitrophenylhydrazone from chloral[13] and dichloroacetal,[12] respectively. The 1,2-dichloro-1,2-difluoroethyl alkyl ketones would react in the same way as the above α-halocarbonyl compounds:



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(6) M. Hudlicky, "Chemie der organischen Fluorverbindungen," VEB Deutscher Verlag der Wissenschaften, Berlin, 1960, p. 219.

(7) There are exceptions in this statement. For example, R. N. Haszeldine, *J. Chem. Soc.*, 3565 (1953) and R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3005 (1955), reported that in the free radical additions of trifluoroiodomethane to $CF_2{=}CHCH_3$ and $CF_2{=}CHCF_3$ the attack of trifluoromethyl radical occurred at the $=CH—$ group. R. N. Haszeldine and B. R. Steele, *J. Chem. Soc*, 2800 (1957), demonstrated that the addition reaction of CBr_2CF_2 to $CF_2{=}CFH$ gave isomeric mixtures of $CF_2BrCFHCF_2Br$ and CF_2BrCF_2CFHBr, and this was confirmed by A. T. Coscia, *J. Org. Chem.*, **26**, 2995 (1961).

(8) C. G. Krespan, R. J. Harder, and J. J. Drysdale, *J. Am. Chem. Soc.*, **83**, 3424 (1961).

(9) H. Muramatsu, unpublished.

(10) J. R. Nielsen, C. Y. Liang, and D. C. Smith, *J. Chem. Phys.*, **20**, 1090 (1952).

In the attempted hydrolysis of 1,2-dichloro-1,2-difluorobutanone-3 in the presence of the same amount of sulfuric acid as above to yield 1-chloro-1-fluorobutadione-2,3, the expected α-diketone was not isolated, although a small amount of fluoride and chloride ions was detected. When the ethanol solution of the 2,4-dinitrophenylhydrazone of 1,2-dichloro-1,2-difluorobutanone-3 was heated under reflux with 2,4-dinitrophenylhydrazine in the presence of sulfuric acid, it changed very easily to the bis-2,4-dinitrophenylhydrazone of 1-chloro-1-fluorobutadione-2,3.

The melting points and results of the analyses of 2,4-dinitrophenylhydrazones of the ketones are shown in Table III. The preparation of the hydrazones of $CH_3(CH_2)_2COCFClCFClH$ and $(CH_3)_2CHCOCFClCFClH$ failed because they were very easily changed to the hydrazones of halo-α-diketones.

TABLE III

2,4-DINITROPHENYLHYDRAZONES OF THE KETONES

R	M.P.	Nitrogen, %	
		Calcd.	Found
$CHFClCFClCOR$			
CH_3	116–118	15.69	15.63
C_2H_5	104–106	15.09	15.02
$CHCl_2CF_2COR$			
CH_3	125–126	15.69	15.55
C_2H_5	103–105	15.09	15.08
n-C_3H_7	69–70	14.55	14.46
i-C_3H_7	98–100	14.55	14.52

Experimental[14]

Materials.—1,2-Dichloro-1,2-difluoroethylene was prepared by the dechlorination of 1,2-difluorotetrachloroethane with zinc dust in ethanol and purified by distillation. Difluorotetrachloroethane available commercially was found to contain 10–30% 1,1-difluorotetrachloroethane.[15] Therefore, difluorotetrachloroethane, which contained less than 1% 1,1-difluorotetrachloroethane, was prepared by the fluorination of hexachloroethane with antimony trifluoride and antimony pentachloride.[16] Symmetrical dichlorodifluoroethylenes used in the experiments were checked by gas chromatography and found to contain less than 1% asymmetrical dichlorodifluoroethylene.

1,1-Dichloro-2,2-difluoroethylene was prepared by the dechlorination of 1,1-difluorotetrachloroethane.[17]

All of the aldehydes and benzoyl peroxide used were reagent grade or purified by distillation.

Additions of Aldehydes to Dichlorodifluoroethylenes.—To a stainless steel autoclave were added 93 g. (0.70 mole) of 1,2-dichloro-1,2-difluoroethylene, 57 g.(1.29 moles) of acetaldehyde, and 12 g. (0.05 mole) of benzoyl peroxide. The mixture was agitated at 105–110° for 20 hr., and cooled, and then the unchanged materials were removed by distillation. About 100 ml. of ether was then added to the reaction mixture. The mixture was washed with aqueous sodium bicarbonate solution and then ether was removed. Potassium permanganate solution was added to the reaction mixture dropwise under cooling, until the red color appeared. The precipitated manganese dioxide was filtered off, and the lower organic layer of the filtrate was separated and dried with anhydrous sodium sulfate. Fractionation gave 24.4 g. (0.14 mole, 20% yield) of 1,2-dichloro-1,2-difluorobutanone-3, b.p. 95–96° (300 mm.). The infrared spectrum of the ketone exhibited a characteristic carbonyl absorption band at 5.75 μ.

The addition reactions of propionaldehyde and *n*- and *i*-butyraldehydes to 1,2-dichloro-1,2-difluoroethylenes and 1,1-dichloro-2,2-difluoroethylenes were carried out under the similar conditions and treated the same way as above mentioned. The infrared spectra of the 1,2-dichloro-1,2-difluoroethyl alkyl ketones showed the strong carbonyl bands at 5.75 μ those of 1,1-difluoro-2,2-dichloroethyl alkyl ketones at 5.71–5.74 μ.

Tables I and II summarize the yields based on the olefins and physical properties of the adducts.

Oxidation of 1,1-Dichloro-2,2-difluorobutanone-3.—A mixture of 18 g. (0.10 mole) of 1,1-dichloro-2,2-difluorobutanone-3, 32 g. (0.20 mole) of potassium permanganate, and 50 ml. of reagent grade acetone was heated under reflux for 2 hr. The reaction mixture was diluted with water and filtered to remove manganese dioxide. The organic layer of the filtrate was separated, and 3 g. of unchanged ketone was recovered. The aqueous layer of the filtrate was acidified and extracted with diethyl ether. Neutralization of the extracts with aqueous sodium hydroxide yielded 9 g. of sodium 1,1-difluoro-2,2-dichloropropionate.

Pyrolysis of Sodium 1,1-Difluoro-2,2-dichloropropionate.—Nine grams (0.05 mole) of dried sodium 1,1-difluoro-2,2-dichloropropionate was heated on a sand bath at about 250° to give 4 g. (0.04 mole) of 1-chloro-2,2-difluoroethylene which was identified by its infrared spectrum.[10]

Preparation of 2,4-Dinitrophenylhydrazones of the Ketones.[18]—To 1 g. of 2,4-dinitrophenylhydrazine were added 1 g. of the ketone, 4 ml. of concd. sulfuric acid, 6 ml. of water, and 20 ml. of ethanol. The resulting mixture was allowed to stand at room temperature. In a few minutes, orange-colored precipitates were formed. Recrystallization of the crude hydrazones (1.7–1.9 g.) from ethanol gave the orange crystals whose melting points and analyses of nitrogen are shown in Table III.

Bis-2,4-dinitrophenylhydrazones of the Halo-α-diketones.—The ethanol solution of 1,2-dichloro-1,2-difluoropentanone-3 (1 g.) and 2,4-dinitrophenylhydrazine (1 g.) prepared the same was as above was heated under reflux for 1 hr. The orange-red precipitates appeared in about 10 min. After hot filtration, the precipitates (0.7 g.) were washed with ethanol several times, and air-dried. Bis-2,4-dinitrophenylhydrazone of 1-chloro-1-fluoropentadione-2,3 melted at 237–240° dec.

Anal. Calcd. for $C_{17}H_{14}ClFN_8O_8$: Cl, 6.91; F, 3.71; N, 21.85. Found: Cl, 6.95; F, 3.91; N, 22.01.

Using the above procedure, 1,2-dichloro-1,2-difluorohexanone-3 gave 0.6 g. of bis-2,4-dinitrophenylhydrazone of 1-chloro-1-fluorohexadione-2,3 which melted at 230–232° dec.

Anal. Calcd. for $C_{18}H_{16}ClFN_8O_8$: Cl, 6.73; F, 3.61; N. 21.27. Found: Cl, 6.60; F, 3.68; N, 21.15.

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(11) R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

(12) L. A. Jones, C. K. Hancock, and R. B. Seligman, *J. Org. Chem.*, **26**, 228 (1961).

(13) K. Yamaguchi, S. Fukushima, T. Tabata, and M. Ito, *J. Pharm. Soc. Japan*, **74**, 1327 (1954).

(14) All temperature readings are uncorrected.

(15) The isomers in the mixture could not be separated from each other by distillation.

(16) E. G. Locke, W. R. Brode, and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934).

(17) A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

(18) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," J. Wiley & Sons, Inc., New York, 4th ed., 1956, p. 219.