The Radiation-Induced Addition Reaction of Dialkyl Phosphonates to Chlorofluoroolefins

KAN INUKAI, TERUO UEDA, AND HIROSHIGE MURAMATSU

Government Industrial Research Institute, Nagoya Kita-ku, Nagoya, Japan

Received March 17, 1964

The radiation-induced addition reactions of dialkyl phosphonates (methyl, ethyl, and *n*-propyl) to chlorofluoroolefins such as 1,2,2-trichloro-1-fluoroethylene, 1,2-dichloro-1,2-difluoroethylene, and 1,1-dichloro-2,2-difluoroethylene were made to give the corresponding dialkyl chlorofluoroethylphosphonates. These phosphonates were hydrolyzed to the chlorofluoroethylphosphonic acids and converted to the chlorofluoroethylphosphonic dichlorides. The chlorofluoroethylphosphonic acids have an acidity similar to the ω-hydroperfluoroalkylphosphonic acids and perfluoroalkylphosphonic acids.

As part of a research program in this laboratory dealing with the radiation-induced addition reaction of organic molecules to chlorofluoroolefins,[1-3] a study has been made of the reactions of dialkyl phosphonates to chlorofluoroolefins under γ-ray irradiation.

The free-radical addition reactions of dialkyl phosphonates to ethylene and other polymerizable olefins were first reported by Hanford and Joyce[4] in a patent literature using peroxide as an initiator. Stiles and Rust[5] added dialkyl phosphonates to octene, tetradecene, and other olefins in organic solvents and Ladd and Harvey[6] added them to dodecyl allyl ether. The addition reactions to tetrafluoroethylene were carried out by Brittle and Joyce[7] to give $H(CF_2CF_2)_nPO(OR)_2$ where $n = 1-6$. The addition products of tetrafluoroethylene and their derivatives have been further intensively studied by Brace.[8]

The present paper is concerned with the γ-radiation-induced addition of $HPO(OR)_2$, where R is methyl, ethyl, or *n*-propyl, to 1,1,2-trichloro-2-fluoroethylene, 1,2-dichloro-1,2-difluoroethylene, and 1,1-dichloro-2,2-difluoroethylene, and the isolation of chlorofluoroethylphosphonic esters, acids, and dichlorides. The apparent reactivity of olefins and dialkyl phosphonates for the addition reaction and some properties of the 1:1 adducts and their derivatives as a function of chlorofluoroethyl group were also studied.

The reactants were irradiated in a glass tube at a rate of 0.6–0.7 × 10^5 r./hr. for a period of 2 weeks at room temperature. The irradiation conditions of each run are listed in Table I with yields based on the amounts of olefins added. Although the radiation-induced addition of 1,1,2-trichloro-2-fluoroethylene and 1,2-dichloro-1,2-difluoroethylene gave mainly 1:1 adducts in appreciable yields, 1,1-dichloro-2,2-difluoroethylene reacted with dialkyl phosphonates to give 1:1 adducts and telomers in rather poor yields. The general reaction is

$$HPO(OR)_2 + CFX{=}CX_2 \xrightarrow{\gamma\text{-ray}} CHX_2CFXPO(OR)_2$$

where X = F or Cl; R = CH_3, C_2H_5, or *n*-C_3H_7. The physical properties of the 1:1 adducts, the new fluorine-containing phosphonates, are shown in Table II. The trends[9] in apparent reactivity of chlorofluoroolefins and dialkyl phosphonates observed in the addition reaction were as shown.

TABLE I

γ-RADIATION-INDUCED ADDITION OF $HPO(OR)_2$ TO CHLOROFLUOROOLEFINS

R	Molar ratio of $HPO(OR)_2$ to olefin	Irradiation time, hr.	Total dosage, r. × 10^6	Yield[a] of 1:1 adduct, %
		$CFCl{=}CCl_2$		
CH_3	2.00	341	20	12
C_2H_5	2.00	341	20	20
n-C_3H_7	2.00	341	20	25
		$CFCl{=}CFCl$		
CH_3	3.00	230	16	48
C_2H_5	3.00	230	16	53
n-C_3H_7	3.01	230	16	68
		$CF_2{=}CCl_2$		
CH_3	2.10	390	22	3
C_2H_5	2.10	390	22	3
n-C_3H_7	2.10	390	22	2

[a] Based on the amounts of olefin added.

$$CFCl{=}CFCl > CFCl{=}CCl_2 > CF_2{=}CCl_2$$

$$\text{R in } HPO(OR)_2\text{:}\ n\text{-}C_3H_7 > C_2H_5 > CH_3$$

This order of reactivity of dialkyl phosphonates is consistent with the order of electron-donating effect of alkyl groups and the similar trends in the effect of alkyl groups on the reactivity of the substrates were observed in the radiation-induced addition of alcohols[1] and aldehydes.[2]

The direction of the additions of the $\cdot PO(OR)_2$ radical formed to the asymmetrical olefins was determined by the basic hydrolysis, β-chlorine elimination reaction,[10] of the acids of 1:1 adducts, chlorofluoroethylphosphonic acids, to give chlorofluoroolefins. The structures of the olefins formed were identified by comparing their infrared spectra and gas chromatograms with those of authentic samples.

$$CHCl_2CFClPO(OR)_2 \xrightarrow{H^+} CHCl_2CFClPO(OH)_2 \xrightarrow[H_2O]{OH^-} CHCl{=}CFCl + H_3PO_4 + Cl^-$$

The formation of 1,2-dichloro-1-fluoroethylene in the hydrolysis of trichlorofluoroethylphosphonic acid showed that the $\cdot PO(OR)_2$ radical added to the $=CFCl$ side in $CFCl{=}CCl_2$. In the same way, the $\cdot PO(OR)_2$ radical was found to attack on the $=CF_2$ side of $CF_2{=}CCl_2$.

---

(1) H. Muramatsu, *J. Org. Chem.*, **27**, 2325 (1962).

(2) H. Muramatsu and K. Inukai, *ibid.*, **27**, 1572 (1962).

(3) H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **29**, 2220 (1964).

(4) W. E. Hanford and R. M. Joyce, U. S. Patent 2,478,390 (1949).

(5) A. R. Stiles and F. F. Rust, U. S. Patent 2,724,718 (1955).

(6) E. C. Ladd and M. P. Harvey, U. S. Patent 2,664,438 (1953).

(7) J. A Brittle and R. M. Joyce, U. S. Patent 2,559,754 (1951).

(8) N. O. Brace, *J. Org. Chem.*, **26**, 3197 (1961).

(9) Based on the yields of 1:1 adducts obtained.

(10) J. A. Maynard and J. M. Swan, *Proc. Chem. Soc.*, 61 (1963).

TABLE II

DIALKYL CHLOROFLUOROETHYLPHOSPHONATES

R	B.p., °C.	mm.	n^{20}_D	d^{20}_4	MR Calcd.	MR Found	Chlorine, % Calcd.	Chlorine, % Found	Mol. wt. Calcd.	Mol. wt. Found
					$CHCl_2CFClPO(OR)_2$					
CH_3	93–94	4	1.4630	1.536	46.23	46.54	41.0	40.7	260	253
C_2H_5	100–102	4	1.4560	1.399	55.46	55.86	37.0	36.8	288	286
n-C_3H_7	105–108	4	1.4535	1.310	64.69	65.16	33.8	33.5	316	317
					$CHFClCFClPO(OR)_2$					
CH_3	91–92	6	1.4347	1.508	41.43	42.02	29.2	28.7	243	244
C_2H_5	100–102	6	1.4289	1.361	50.67	51.31	26.2	25.8	271	271
n-C_3H_7	110–112	6	1.4310	1.280	59.91	60.46	23.7	23.1	299	300
					$CHCl_2CF_2PO(OR)_2$					
CH_3	73–75	3	1.4270	1.495	41.43	41.72	29.2	28.5	243	246
C_2H_5	87–90	3	1.4265	1.350	50.67	51.50	26.2	25.3	271	275
n-C_3H_7	98–100	3	1.4257	1.263	59.91	60.64	23.7	23.0	299	295

TABLE III

CHLOROFLUOROALKYLPHOSPHONIC DICHLORIDES

Compounds	B.p., °C.	mm.	n^{20}_D	d^{20}_4	MR Calcd.	MR Found	Chlorine, % Calcd.	Chlorine, % Found
$CHCl_2CFClPOCl_2$	87–88	8	1.5025	1.786	43.43	44.41	66.1	65.4
$CHFClCFClPOCl_2$	67–68	8	1.4695	1.761	38.65	39.88	56.4	55.9
$CHCl_2CF_2POCl_2$	67–68	8	1.4690	1.751	38.65	40.08	56.4	55.9
$H(CCl_2CF_2)_2POCl_2$[a]	120–125	8	1.4812	1.778	57.78	61.66	55.3	53.9

[a] Calcd. for $C_4HCl_6F_4OP$ (crude sample): mol. wt., 385. Found: mol. wt., 398.

After distillation of addition products, appreciable amounts of viscous liquid residues remained. These residues were treated with phosphorus pentachloride to give the products which were identified to be the chlorofluoroethylphosphonic dichlorides from their infrared spectra. The authentic dichlorides were prepared by hydrolysis of the 1:1 adducts in the presence of hydrochloric acid, followed by the treatment with phosphorus pentachloride. Thus, the residues were found to be chlorofluoroethylphosphonic acids, which seem to be formed by the hydrolysis of the 1:1 adducts with the atmospheric moisture. In order to get better yields of 1:1 adducts, therefore, the exclusion of atmospheric moisture seemed to be important in the addition reaction of dialkyl phosphonates to chlorofluoroolefins. The orders[11] of effects of chlorofluoroethyl groups and alkyl groups in dialkyl chlorofluoroethylphosphonates on apparent ease of hydrolysis with moisture follow.

$$CHCl_2CF_2 > CHFClCFCl > CHCl_2CFCl;\ CH_3 > C_2H_5 > n\text{-}C_3H_7$$

Table III shows the physical properties of chlorofluoroethylphosphonic dichlorides.

The chlorofluoroethylphosphonic acids are hygroscopic crystalline solids and their pH titration exhibited the enhanced acidity of the dibasic phosphonic acid groups as compared with unfluorinated alkylphosphonic acid.[12] The enhancement of acidity due to the inductive effect of substituted fluorine atoms in the polyfluoroalkylphosphonic acids have been reported for the perfluoroalkyl analogs[13,14] and ω-hydroperfluoroalkyl analogs.[8] The chlorofluoroethylphosphonic acids have the pK_a values close to those of ω-hydroperfluoroalkyl analogs. The calculated pK_a values taken from the titration data are listed in Table IV together with the reported data.

TABLE IV

APPARENT DISSOCIATION CONSTANTS FOR CHLOROFLUOROETHYLPHOSPHONIC ACIDS[a]

Phosphonic acids	pK_a (1st break)	pK_a (2nd break)
$CHCl_2CFClPO(OH)_2$	2.4	5.2
$CHFClCFClPO(OH)_2$	2.2	4.9
$CHCl_2CF_2PO(OH)_2$	2.2	4.9
$CH_3CH_2PO(OH)_2$[b]	2.43	8.05
$CHF_2CF_2PO(OH)_2$[c]	2.2	4.7
$CF_3PO(OH)_2$[d]	1.16	3.93

[a] The pK_a values were taken directly from the titration curves obtained with a pH meter at 0.01 *M* concentration. [b] Ref. 12. [c] Ref. 8. [d] Ref. 13.

Experimental[15]

Materials.—The chlorofluoroolefins used in the experiments were prepared by the dechlorination of the corresponding chlorofluoroethanes with zinc dust in ethanol or n-butanol according to the method of Henne, *et al.*[16] The dialkyl phosphonates were synthesized from phosphorus trichloride and the corresponding alcohols using ether as a solvent by the method of Combie, *et al.*[17]

Irradiation by γ-Ray.—A mixture of the chlorofluoroolefins and dialkyl phosphonate in a molar ratio of about 1:2–3 was sealed into a Pyrex tube of *ca.* 300-ml. capacity. The reaction tube was then irradiated by γ-ray from Co^{60} for a period of 2 weeks at a dose rate of 0.6–0.7 × 10^5 r./hr. at room temperature.

Addition Reactions of Dialkyl Phosphonates to Chlorofluoroolefins.—A mixture of 190 g. (1.14 moles) of di-n-propyl phosphonate and 50 g. (0.38 mole) of 1,2-dichloro-1,2-difluoroethylene was sealed in a glass tube and irradiated to a total dosage of 1.6 × 10^7 r. for a period of 230 hr. Distillation of the irradiation products under reduced pressure, after the removal of the unchanged olefin and dialkyl phosphonate, gave 76 g. (0.24 mole, 68% yield) of di-n-propyl 1,2-dichloro-1,2-difluoroethylphos-

---

[11] These orders were determined from the amounts of chlorofluoroethylphosphonic acids formed, when the dialkyl chlorofluoroethylphosphonates were exposed to the atmosphere.

[12] P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3379 (1953).

[13] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954).

[14] H. J. Emeléus and J. D. Smith, *ibid.*, 375 (1959).

[15] All temperature readings are uncorrected.

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

[17] H. M. Combie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

phonate, b.p. 110–112° (6 mm.), and 16 g. of a residue. The residue was treated with 30 g. (0.14 mole) of phosphorus pentachloride to yield 8 g. of the dichlorodifluoroethylphosphonic dichloride, which was confirmed with the authentic sample prepared as mentioned below.

Using the same procedure, other dialkyl phosphonates were added to 1,2-dichloro-1,2-difluoroethylene. The addition reactions to other chlorofluoroolefins were carried out under similar conditions. In the case of 1,1-difluoro-2,2-dichloroethylene, the telomers were obtained with the 1:1 adduct. The dichloride of 1:2 adduct was isolated by distillation after the treatment of dialkyl ω-hydroperhaloalkylphosphonates with phosphorus pentachloride.

The irradiation conditions and yields based on the amounts of olefins added for each run are shown in Table I.

Chlorofluoroethylphosphonic Acids.—The hydrolysis of chlorofluoroethylphosphonates was carried out by the procedure of Brace.[8] In a flask fitted with a reflux condenser were added 25 g. (0.09 mole) of diethyl 1,2,2-trichloro-1-fluoroethylphosphonate and 60 ml. of concentrated hydrochloric acid. The mixture was refluxed at 80–110° for 5 hr. In 1 hr., a homogeneous solution was obtained. After ether extraction of the unchanged phosphonate, the aqueous solution was distilled under reduced pressure to remove hydrogen chloride and water. A trace of water remained and was removed by the azeotropic distillation with benzene. The liquid residue, 1,2,2-trichloro-1-fluoroethylphosphonic acid, 18.5 g. (0.08 mole, 92% yield), crystallized on standing. It was hygroscopic and liquefied on absorbing moisture in the air at room temperature. 1,2-Dichloro-1,2-difluoroethylphosphonic acid and 1,1-difluoro-2,2-dichloroethylphosphonic acid were prepared in an analogous fashion.

Chlorofluoroethylphosphonic Dichlorides.—To 16 g. (0.07 mole) of 1,1,2-trichloro-2-fluoroethylphosphonic acid in a flask with a reflux condenser was added 15 g. (0.07 mole) of phosphorus pentachloride in portions. A mixture was heated mildly and, in 0.5 hr., phosphorus oxychloride began to reflux. After heating for 1 hr., phosphorus oxychloride was distilled. To the residue, 15 g. (0.07 mole) of an additional phosphorus pentachloride was added and heated for 1 hr. Distillation of the products, after the removal of phosphorus oxychloride, gave 13 g. (0.05 mole) of 1,2,2-trichloro-1-fluoroethylphosphonic dichloride, b.p. 85–88° (8 mm.), and 3 g. of a solid residue.

Using the same procedure, 1,2-dichloro-1,2-difluoroethyl- and 1,1-difluoro-2,2-dichloroethylphosphonic dichlorides were prepared. Table III summarizes the physical properties of chlorofluoroethylphosphonic dichlorides.

Basic Hydrolysis of Chlorofluoroethylphosphonic Acids.—1,2,2-Trichloro-1-fluoroethylphosphonic acid, 10 g. (0.04 mole), and 30 ml. of 10% aqueous sodium hydroxide solution were added to a flask fitted with a reflux condenser, which was in turn connected to a trap cooled in Dry Ice–acetone. The mixture was heated at 50–100° for 30 min. to yield 1 g. (0.009 mole) of an olefin. The infrared spectrum and gas chromatogram of the olefin were compared with those of 1,2-dichloro-1-fluoroethylene which was prepared by the dechlorination of 1,1,2,2-tetrachlorofluoroethane.[16]

The Reaction of Ethyl Azodicarboxylate with Monoolefins

WARREN A. THALER AND BORIS FRANZUS

The Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

Received February 28, 1964

The reaction of monoolefins with ethyl azodicarboxylate has been investigated. Acyclic monoolefins react by a nonradical process to give additive-substitution products with a shift of the double bond. Cyclic olefins, on the other hand, react predominantly by a free-radical process. The relative reactivity of C_4 and C_5 olefins (with ethyl azodicarboxylate) and the structure of the resultant products are all consistent with a concerted "addition–abstraction" mechanism involving a six-membered transition state. The data have been interpreted in terms of charge stabilization and steric interactions in the transition state.

The additive-substitution reaction of azodiformic acid esters with olefins was first observed in 1927 but received little attention[1,2] until recently.

Huisgen and Pohl were the first to present evidence for the mechanism of azo ester–olefin reactions. They demonstrated that aromatically conjugated olefins, such as 1,2- and 1,4-dihydronaphthalene and unsymmetrically substituted 1,3-diarylpropenes, underwent substitution in the allylic position with a shift of the double bond. Free-radical initiators and inhibitors had no effect on the rate or course of the reaction with these conjugated olefins; however, the reactions of azoformate ester with cyclopentene and cyclohexene were initiated by peroxide and retarded by radical inhibitors. The authors concluded that aromatically conjugated olefins react by a multicenter process involving a cyclic electron shift while nonconjugated olefins react by a free-radical chain process.

Levina, *et al.*,[4] reported that 1,1-disubstituted 1,3-dienes, whose steric hindrance precluded the usual Diels–Alder reaction, also underwent allylic substitution. However, they did not locate the positions of the double bond in the products and assumed that it occupied the same position as in the parent diene.

Cinnamon and Weiss[5] found that the reaction of cycloheptatriene with ethyl azodicarboxylate gave the diethyl ester of cycloheptatrienylbicarbamic acid instead of the customary Diels–Alder adduct which is roduced by reaction with other dienophiles such as aleic anhydride. They suggested that the driving rce for this reaction was the stability of the tropylium radical or tropylium ion which could be formed through hydrogen abstraction or hydride ion abstraction, respectively, followed by collapse to the allylic-substituted cycloheptatriene.

Franzus and Surridge[6a] demonstrated that 1,3- and 1,4-cyclohexadiene, which were neither sterically hindered nor capable of producing an unusually stable species, underwent substitution at the allylic position with a corresponding shift of double bond instead of the anticipated Diels–Alder reaction which is observed with cyclopentadiene. They also demonstrated the insensitivity of this reaction to radical initiators and inhibitors. Gillis and Beck[6b] found that the reaction of sterically hindered dienes such as 2,5-dimethyl-2,4-hexadiene, which was studied previously by Russian

---

[1] O. Diels and K. Alder, *Ann.*, **450**, 237 (1927).

[2] K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943).

[3] R. Huisgen and H. Pohl, *ibid.*, **93**, 527 (1960).

[4] R. Y. Levina, U. S. Shabarov, and M. G. Kuzmin, *Dokl. Akad. Nauk SSSR*, **131**, 1080 (1960).

[5] J. M. Cinnamon and K. Weiss, *J. Org. Chem.*, **26**, 2644 (1961).

[6] (a) B. Franzus and J. H. Surridge, *ibid.*, **27**, 1951 (1962); (b) B. T. Gillis and P. E. Beck, *ibid.*, **27**, 1947 (1962).