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The Addition Reactions of Dialkyl Phosphites to Polyfluorocyclobutenes

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The radiation-induced addition reactions of dialkyl phosphites to polyfluorocyclobutenes, such as perfluoro-, 1,2-dichlorotetrafluoro-, 1-chloro-2,3,3,4,4-pentafluoro-, 1,3,3,4,4-pentafluoro- and 1-chloro-3,3,4,4-tetrafluorocyclobutenes were carried out. In general, the corresponding dehydrohalogenated 1 : 1 adducts, polyfluorocyclobutenylphosphonates, were obtained as the main products instead of the expected 1 : 1 adducts. The direction of attack of the phosphonyl radical on the unsymmetrical double bond and reaction mechanism were discussed.

The syntheses of the polyfluorocycloalkenylphosphonates *via* ionic process have been investigated rather extensively. Knunyants and co-workers[1,2] prepared diethyl perfluorocyclobutenylphosphonate by the Arbuzov rearrangement of the phosphorane, which was obtained in the reaction between perfluorocyclobutene and triethyl phosphite. In the reactions between 1,2-dichloroperfluorocycloalkenes and trialkyl phosphites,[3] only the corresponding diphosphonates were obtained and no monophosphonates could be detected, regardless of the order of addition or the ratio of reactants.

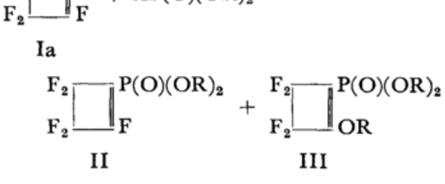
No paper has appeared so far on the syntheses of polyfluorocycloalkenylphosphonates by a free radical-induced addition reaction. As dialkyl chlorofluoroethylphosphonates were found to be produced in moderate yields by the radiation-induced addition reaction of dialkyl phosphites to chlorofluoroethylenes,[4] we extended the addition reaction under γ-ray irradiation to polyfluorocyclobutenes for syntheses of the polyfluorocyclobutyl- or polyfluorocyclobutenylphosphonates.

Results and Discussion

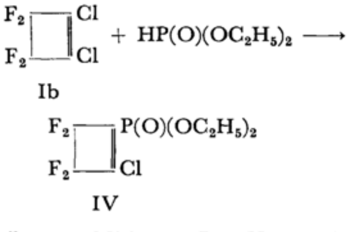
Perfluorocyclobutene (Ia), 1,2-dichlorotetrafluorocyclobutene (Ib), 1-chloro-2,3,3,4,4-pentafluorocyclobutene (Ic), 1,3,3,4,4-pentafluorocyclobutene (Id) and 1-chloro-3,3,4,4-tetrafluorocyclobutene (Ie) were prepared by conventional methods (see Experimental).

A mixture of polyfluorocyclobutene and dialkyl phosphite in a molar ratio of about 1 : 2 in a glass ampoule was irradiated at room temperature for a month. After unchanged reactants were recovered, products were separated by distillation and/or by preparative gas chromatography. The structure of the products was determined by elemental analysis, IR, NMR and mass spectroscopy. The reaction conditions and yields of products are shown in Table 1.

As a whole dehydrohalogenated 1:1 adducts were obtained as the main products instead of the expected simple 1:1 adducts. Addition of the dialkyl phosphites to Ia gave a mixture of dialkyl 2,3,3,4,4-pentafluoro - 1 - cyclobutenylphosphonate (II) and 2 - alkoxy-3, 3, 4, 4-tetrafluoro -1- cyclobutenylphosphonate (III) in total yields of 23—27%. Addition to Ib, however, resulted in only trace amounts of diethyl 2-chloro-3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate (IV), probably due to a steric interaction between the attacking phosphonyl radical and chlorine atoms on the double bond.



R = CH_3, C_2H_5, n-C_3H_7



In an addition to Ic, IV was also obtained along with III. The absence of II in the products in this case indicates that a phosphonyl radical attacked exclusively on the carbon bearing fluorine. Preferential attack of the phosphonyl radical on the

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[1] I. L. Knunyants, E. Ya. Pervova and V. V. Tyuleneva, *Dokl. Akad. Nauk SSSR*, **129**, 576 (1959).

[2] I. L. Knunyants, V. V. Tyuleneva, E. Ya. Pervova and R. N. Sterlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1964**, 1797.

[3] A. W. Frank, *J. Org. Chem.*, **30**, 3663 (1965).

[4] K. Inukai, T. Ueda and H. Muramatsu, *ibid.*, **29**, 2224 (1964).

Table 1. Irradiation conditions and yields in addition reactions

Polyfluoro-cyclobutene	$HP(O)(OR)_2$ R	Molar ratio of $HP(O)(OR)_2$ to cyclobutene	Total dosage MR	Yield, %*				
				II	III	IV	VII	VIII
Ia	CH_3	3.0	31	16.8	11.5	—	—	—
	C_2H_5	2.0	31	14.8	14.0	—	—	—
	n-C_3H_7	2.0	31	19.5	7.2	—	—	—
Ib	C_2H_5	2.0	41	—	—	1.6	—	—
Ic	C_2H_5	2.0	40	—	10.5	9.3	—	—
Id	C_2H_5	2.0	40	—	—	—	8.1	9.5
Ie	C_2H_5	2.0	41	—	—	—	9.7	11.9

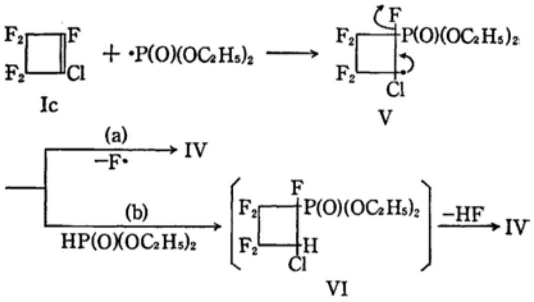
* Based on the amount of the polyfluorocyclobutenes added.

carbon bearing fluorine over on the carbon bearing chlorine of a double bond was observed in the addition to chlorofluoroethylenes.4) The direction of the radical attack may be explained both by the steric effect and by the stability of an intermediate radical.

The structure of III was confirmed by comparing its IR spectrum with that of an authentic sample, prepared by a reaction of II or IV with alcohol in the presence of potassium hydroxide. Since the dialkyl phosphites produced the corresponding alcohols even at room temperature in the presence of hydrochloric acid or hydrofluoric acid, which was always formed in γ-irradiation of a mixture of the polyfluorocyclobutene and the dialkyl phosphite, III seems to be formed by the reaction of the 1 : 1 adducts, II or IV, with the alcohols. The carbon to carbon double bond of dialkyl polyfluorocyclobutenylphosphonates are known3) to be reactive toward nucleophiles due to the electron-withdrawing effect of the P=O group.

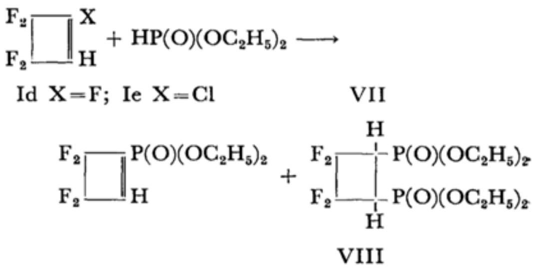
The reasons why only the dehydrohalogenated 1 : 1 adducts were obtained in the addition to polyfluorocyclobutenes whereas the addition to chlorofluoroethylenes4) produced the simple 1:1 adducts, may be the steric interaction between the substituted halogens and phosphorus atom, the conjugation of the P=O group with C=C group in the cyclobutenylphosphonates formed, and the instability of the 1 : 1 adducts.

Since a mixture of polyfluorocyclobutene and dialkyl phosphite gave no products upon standing in the dark at room temperature for a month, the reactions under radiation seem to proceed through a free radical mechanism. For formation of II or IV from Ia—c, two routes are conceivable. One of them (a) involves a radical elimination of fluorine from an intermediate radical (V). The other (b) is through formation of an unstable 1:1 adduct (VI), which is supposed to be readily dehydrofluorinated.



There are seveal papers5) on the chlorine elimination from an intermediate radical in addition reactions, but no example of fluorine elimination has been reported so far except one, in which removal of fluorine by a radical was assumed in a reaction of perfluorobenzene with trimethylsilane under UV irradiation to explain the formation of pentafluorophenyltrimethylsilane.6) Although it is difficult to obtain unambiguous evidence, the ionic elimination of hydrogen fluoride from VI seems to be the more probable route for the formation of IV.

Both Id and Ie gave diethyl 3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate (VII) together with the diphosphonate (VIII) in the addition reaction with diethyl phosphite.



Though the directions of phosphonyl radical attack are not clear in these cases, in the addition reaction to 1,1-difluoroethylene the phosphonyl radical was found to attack exclusively on the $=CH_2$ side, yielding diethyl 2,2-difluoroethylphosphonate (IX) and

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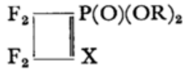
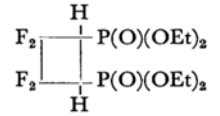
5) C. Walling, "Free Radical Rearrangements," in "Molecular Rearrangements," Vol I, ed. by P. de Mayo, Interscience Publishers, New York (1963), p. 423; H. Muramatsu, K. Inukai and T. Ueda, *J. Org. Chem.*, **30**, 544, 2546 (1965).

6) J. M. Birchall, W. M. Daniewski, R. N. Haszeldine and L. S. Holden, *J. Chem. Soc.*, **1965**, 6702.

Table 2. Dialkyl polyfluorocyclobutenylphosphonates,



X	R	Bp °C(mmHg)	n_D^{20}	d_4^{20}	MR_D		P, %		MW		$\nu_{C=C}$ cm^{-1}	$\nu_{P=O}$ cm^{-1}
					Found	Calcd	Found	Calcd	Found	Calcd		
F	CH_3	80—81 (5)	1.3773	1.476	39.3	39.0	12.0	12.3	260	252	1645	1280
F	C_2H_5	73—74 (1)	1.3829	1.359	48.1	48.2	10.5	11.1	284	280	1643	1276
F	n-C_3H_7	82—83 (1)	1.3910	1.298	56.4	57.4	9.5	10.1	308	308	1640	1278
CH_3O	CH_3	100—101 (5)	1.4058	1.441	45.0	45.2	11.7	11.7	264	264	1658	1295
C_2H_5O	C_2H_5	92—95 (1)	1.4057	1.282	58.6	59.0	9.3	10.0	306	306	1647	1294
n-C_3H_7O	n-C_3H_7	106—107 (1)	1.4139	1.204	72.2	72.9	8.7	8.9	348	348	1646	1292
Cl	C_2H_5	77—80 (1)	1.4098	1.337	54.9	53.0	10.0	10.4	297	297	1603	1280
H	C_2H_5	60—63 (1)	1.3957	1.291	48.7	48.1	11.2	11.8	263	262	1583	1277
		122—125 (1)	1.4162	1.341	75.0	78.0	14.8	15.5	400	400		1262

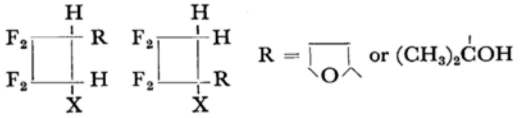
2,2,4,4-tetrafluorobutylphosphonate (X).

$$CF_2{=}CH_2 + HP(O)(OC_2H_5)_2 \longrightarrow$$

$$\underset{\text{IX}}{CHF_2CH_2P(O)(OC_2H_5)_2}$$

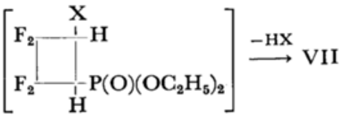
$$+ \underset{\text{X}}{H(CF_2CH_2)_2P(O)(OC_2H_5)_2}$$

Furthermore, in the addition of tetrahydrofuran and 2-propanol to Id (X=F) and Ie (X=Cl) under similar conditions,[7] the 1 : 1 adduct formed was exclusively XI in the case of Ie and a mixture of two isomers, XI and XII, was obtained in a ratio of about 80 : 20 in the case of Id.



XI XII

From these observations, it may be reasonable to assume that the phosphonyl radical attacked preferentially on the double bond carbon bearing a hydrogen atom and the 1 : 1 adduct (XIII) formed by hydrogen abstraction from diethyl phosphite evolved readily hydrogen halide to give VII. Further addition of diethyl phosphite to VII would produce VIII. This was confirmed by the irradiation of a mixture of VII and diethyl phosphite, which yielded VIII. Dehydrofluorination of VIII with powdered potassium hydoxide gave tetraethyl 2,3,3-trifluoro-1-cyclobutenyl-1,4-diphosphonate (XIV).



XIII

The physical properties and results of analyses of new dialkyl polyfluorocyclobutenylphosphonates prepared are listed in Table 2.

Experimental[8]

Materials. 1,2-Dichlorotetrafluorocyclobutene (Ib) was obtained from the Peninsular ChemResearch, Inc., and used without further purification. Perfluorocyclobutene (Ia)[9] and 1-chloro-2,3,3,4,4-pentafluorocyclobutene (Ic)[10] were prepared by dechlorination with zinc dust from 1,2-dichlorohexafluoro- and 1,1,2-trichloropentafluorocyclobutenes, respectively. 1,3,3,4,4-Pentafluorocyclobutene (Id)[11] was synthesized from 1,2-dichlorohexafluorocyclobutane by reduction with lithium aluminum hydride in dibutyl ether, followed by dehydrofluorination with aqueous potassium hydroxide. 1-Chloro-3,3,4,4-tetrafluorocyclobutene (Ie)[12] was prepared from Ib by reduction with sodium borohydride in diglyme.

Addition Reactions of Dialkyl Phosphites to Perfluorocyclobutene (Ia). A mixture of 85 g (0.62 mol) of diethyl phosphite and 50 g (0.31 mol) of Ia was sealed in a glass tube and irradiated from ^{60}Co to a total dosage of 30.5 MR for a period of 480 hr. Distillation of the irradiation products under reduced pressure and nitrogen atmosphere, after removal of

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[7] H. Muramatsu, K. Inukai and T. Ueda, unpublished.

[8] All temperature readings are uncorrected.

[9] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[10] E. L. Kropa and J. J. Padbury, U. S. Pat. 2590019 (1952).

[11] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, **1956**, 61.

[12] D. J. Burton and R. L. Johnson, *J. Am. Chem. Soc.*, **86**, 5361 (1964).

the unchanged diethyl phosphite and cyclobutene, gave 12.8 g (0.045 mol, 14.8% yield) of diethyl perfluoro-1-cyclobutenylphosphonate (II), bp 73—74°C/1 mmHg, 13.2 g (0.043 mol, 14.0% yield) of diethyl 2-ethoxy-3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate (III), bp 92—95°C/1 mmHg, and 5 g of a tarry material.

Using the same procedures, the addition reactions of other dialkyl phosphites to perfluorocyclobutene were carried out. The irradiation conditions and yields based on the amounts of the cyclobutene charged for each run are shown in Table 1.

Addition Reaction of Diethyl Phosphite to 1-Chloro-2,3,3,4,4-pentafluorocyclobutene (Ic). In a glass tube were sealed 135 g (0.98 mol) of diethyl phosphite and 88 g (0.49 mol) of Ic. After the content in the tube was irradiated to a total dosage 40 MR at room temperature, it was washed with aqueous sodium carbonate to remove the unchanged diethyl phosphite and extracted with ether. Distillation of the extract under reduced pressure and a nitrogen atmosphere gave 12.5 g of diethyl fluorophosphate, bp 75—77°C/45 mmHg,[13] 13.6 g (0.046 mol, 9.3% yield) of diethyl 2-chloro-3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate (IV), bp 77—80°C/1 mmHg, and 15.9 g (0.052 mol, 10.5% yield) of III, bp 92—95°C/1 mmHg.

In a similar way, diethyl phosphite was added to the other polyfluorocyclobutenes, Ib, Id and Ie.

Dialkyl 2-Alkoxy-3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate (III). To 0.7 g (0.013 mol) of potassium hydroxide in 1-propanol in a flask, 3.7 g (0.012 mol) of di-*n*-propyl perfluoro-1-cyclobutenylphosphonate was added. The reaction mixture was stirred at 40°C for 3 hr and, after addition of 50 m*l* of ether, poured into water. The organic layer was separated and distilled to give 2.0 g (0.005 mol, 48% yield) of di-*n*-propyl 2-propoxy-3,3,4,4-tetrafluoro-1-cyclobutenylphosphonate, bp 106—107°C/1 mmHg, whose IR spectrum and retention time of gas chromatogram were identical with those of III ($R=n\text{-}C_3H_7$) obtained in the addition of di-*n*-propyl phosphite to Ia.

Tetraethyl 3,3,4,4-Tetrafluorocyclobutenyl-1,2-diphosphonate (VIII). A mixture of 1.0 g (6 mmol) of diethyl phosphite and 0.5 g (1.9 mmol) of VII was irradiated to a total dosage of 40 MR. After treatment with aqueous sodium carbonate, the irradiation product was extracted with ether and dried. Upon evaporation of ether, there remained 0.65 g (1.5 mmol, 81% yield) of crude tetraethyl 3,3,4,4-tetrafluorocyclobutyl-1,2-diphosphonate, whose IR spectrum was identical with that of VIII produced in the addition of diethyl phosphite to Id or Ie.

Dehydrofluorination of VIII. To 0.5 g (12.5 mmol) of VIII, 0.7 g (12.5 mmol) of potassium hydroxide was added and stirred at room temperature for 2 hr. After addition of 50 m*l* of ether, the reaction mixture was poured into water and the organic layer was separated and dried. Distillation gave 2.7 g (7.1 mmol, 57% yield) of tetraethyl 2,3,3-trifluoro-1-cyclobutenyl-1,4-diphosphonate (XIV), bp 122—125°C/1 mmHg, n_D^{20} 1.4173, d_4^{20} 1.333, $\nu_{C=C}$ 1683 cm^{-1}, $\nu_{P=O}$ 1265 cm^{-1}.

Found: P, 16.4%; mol wt, 380. Calcd for $C_{12}H_{21}F_3O_6P_2$: P, 16.3%; mol wt, 380.

Addition Reaction of Diethyl Phosphite to 1,1-Difluoroethylene. To 138 g (0.1 mol) of diethyl phosphite in an autoclave cooled in a dry ice - acetone bath, 3.2 g (0.05 mol) of 1,1-difluoroethylene was condensed. The mixture was irradiated to a total dosage of 35 MR. Distillation of the irradiation products under reduced pressure and a nitrogen atmosphere gave 6.4 g (0.032 mol, 63.4% yield) of diethyl 2,2-difluoroethylphosphonate (IX), bp 73—76°C/5 mmHg, and 2.0 g (0.008 mol, 15% yield) of diethyl 2,2,4,4-tetrafluorobutylphosphonate (X), bp 100—103°C/1 mmHg. The orientation of the addition was established by means of the NMR spectra[14] of IX and X, which are presented below. The splitting pattern and coupling constants of the protons clearly indicated that the phosphonyl radical attacked the CH_2 group of 1,1-difluoroethylene.

IX: n_D^{20} 1.3990, d_4^{20} 1.194, τ_{CH_3} 8.69 ppm (triplet), J_{CH_3,CH_2} 7.2 cps, $\tau_{\underline{CH_2}CF_2H}$ 7.46 ppm (doublet of triplet), J_{CH_2,CF_2} 19.5 cps, $J_{CH_2,P}$ 4.9 cps, $\tau_{\underline{CH_2}CH_3}$ 5.86 ppm (doublet of quartet), $J_{CH_2,P}$ 8.2 cps, τ_{CHF_2} 3.78 ppm (triplet of quartet), $J_{H,F}^{gem}$ 56.1 cps.

Found: P, 14.9%. MR_D 41.0. Calcd for $C_6H_{13}F_2O_3P$: P, 15.3%; MR_D 40.9.

X: n_D^{20} 1.4002, d_4^{20} 1.287, τ_{CH_3} 8.65 ppm, $\tau_{\underline{CH_2}CF_2H}$ 7.20 ppm, $\tau_{\underline{CH_2}CH_3}$ 5.80 ppm, τ_{CHF_2} 3.72 ppm, $J_{H,F}^{gem}$ 54.3 cps.

Found: P, 11.0%; MR_D 50.2. Calcd for $C_8H_{15}F_4O_3P$: P, 11.6%; MR_D 50.3.

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13) The structure was determined by comparing its IR spectrum with that of an authentic sample reported in the literature: L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

14) The NMR spectra were obtained using a JNM-C-60 high resolution spectrometer (60 Mc for ^1H and 56.4 Mc for ^{19}F).