of pure A and B (*vide infra*). Thin layer chromatography[31] verified that the total, crude, solid product of reaction was composed primarily of equal parts of the diketones A and B.

Fractional crystallization of a 5-g. portion of this product from ethyl acetate by the "pyramid scheme" of combining filtrates, gave 1.1 g. (22%) of A as plates, m.p. 267–269°, as the least soluble component of the mixture, and 1.9 g. (38%) of B as star clusters, m.p. 190–192°. The n.m.r. spectra of A and B in deuteriochloroform verified the absence of hydrogen.

Anal. Calcd. for $C_{10}Cl_8O_2$: C, 27.56; H, 0.00; Cl, 65.09; mol. wt. 436. Found for isomer A: C, 27.44; H, 0.26; Cl, 64.76; mol. wt. (ebullioscopic in dioxane), 481. Found for isomer B: C, 27.13; H, 0.24; Cl, 64.88; mol. wt. (freezing point in dioxane), 422, 446.

In a subsequent preparation of A and B it was found convenient, though less efficient, to separate these isomers by crystallizing the total, crude, reaction product (49 g.) from the minimum amount of boiling ethyl acetate (300 ml.), giving A as crystals, m.p. 260–265°, which after recrystallization from fresh ethyl acetate melted at 270–271° (6.83 g.). Evaporation of the filtrate from the first crystallization and three recrystallizations of the residue from boiling amyl acetate gave moderately pure B (17 g.), m.p. 185–186°.

Partial Resolution of Diketone B.—To a solution of diketone B (1.74 g., 0.002 mole) in ethyl acetate (100 ml.) was added brucine (0.79 g., 0.002 mole), and the mixture was heated at reflux temperature for 12 hr. After being kept 1 day at room temperature, the black reaction mixture was filtered, and the filtrate was evaporated to dryness *in vacuo*. The black residue obtained was sublimed at 130° (0.05 mm.) giving 0.8 g. (46%) of a light yellow sublimate which was recrystallized from ethyl acetate and resublimed, giving white needles of B, m.p. 192.0–193.0°, $\nu_{\max}^{\mathrm{CHCl_3}}$ 1760 and 1587 cm.$^{-1}$ (*cf.* Table II). A solution of 0.403 g. of B in 2.0 ml. of chloroform had $[\alpha]^{24}\mathrm{D}$ −0.5°. Rotatory dispersion in dioxane (*c* 0.30), *ca.* 25° showed $[\alpha]_{374}$ −25°, $[\alpha]_{363}$ −20°, $[\alpha]_{356}$ −25°, $[\alpha]_{343}$ −2°, $[\alpha]_{338}$ −3°.

Anal. Calcd. for $C_{10}Cl_8O_2$: C, 27.56; H, 0.00; Cl, 65.09. Found: C, 27.76; H, 0.30; Cl, 64.73.

Trichloronitroethylene.—Trichloroethylene (26 g., 0.2 mole) and nitrogen dioxide[38] (27 g., 0.6 mole) in an 80-ml. Hastelloy-lined autoclave were heated slowly (3–4 hr.) to 80° and held at that temperature for 6 hr. The vessel was cooled to room temperature and vented slowly, giving 19 g. of a light brown, mobile liquid. Flash distillation of one-half of this liquid through a short Vigreux column gave 6 ml. of a light yellow liquid, b.p. 48–65° (20 mm.), which was refractionated through an 8-in. spinning-band column[39] and gave 5.6 g. (32%) of trichloronitroethylene, b.p. 64° (33 mm.) [lit. b.p. 55° (4 mm.),[33a] 59° (18 mm.)[33b]]. The infrared spectrum of this yellow liquid exhibited nitro bands at 1550 and 1325 cm.$^{-1}$ and a band at 1639 cm.$^{-1}$ assignable to the olefinic linkage. The presence of unsaturation was verified by the rapid oxidation of its solution in acetone by aqueous potassium permanganate.

Anal. Calcd. for $C_2Cl_2NO_3$: N, 7.95; Cl, 60.2. Found: N, 8.09; Cl, 60.2.

Reaction of Trichloronitroethylene with Diaminodurene.—To 0.1769 g. (1.0 mmole) of trichloronitroethylene in 10 ml. of benzene was added dropwise and with stirring 0.1572 g. (0.86 mole) of pure diaminodurene in 15 ml. of benzene. The green solid that formed was centrifuged, washed with 20 ml. of benzene, centrifuged, and dried *in vacuo*, giving 0.17 g. (89%) of a dark green salt, soluble in alcohol or water. The infrared spectrum (KBr) of this salt was similar to that of an authentic sample[41] of the Würster salt,[35] diaminodurene chloride, having in common bands at 3333, 3175, 1739, 1650, 1600, 1471, and 1379 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}ClN_2$: N, 14.0; Cl, 17.80. Found: N, 14.23; Cl, 17.86.

Acknowledgment.—It is a pleasure to acknowledge helpful discussions during the preparation of this paper with Professor Richard C. Lord, Professor John D. Roberts, and Dr. Howard E. Simmons. Dr. Victor E. Shashoua kindly provided the optical rotatory dispersion data. Thanks are due Miss Naomi E. Schlichter, Miss Ellen Wallace, Dr. Carl E. Willoughby, and Mr. John Myers for their expert and generous assistance in making physical measurements.

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[41] Supplied by Dr. L. R. Melby of these laboratories, who prepared it by the action of chlorine on diaminodurene in chloroform.

Compounds of Phosphorus and Fluorine. II. Reaction of Phosphite, Phosphonite, and Phosphinite Esters with 1,2-Dichloroperfluorocycloalkenes[1]

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Trialkyl phosphites, unlike other nucleophilic reagents, react with 1,2-dichloroperfluorocycloalkenes with the displacement of both chlorine atoms, regardless of the order of addition or the ratio of reactants. The products are tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates. Similar reactions take place with phosphonous and phosphinous esters giving the corresponding diphosphinates and bis(phosphine oxides). The reason for the difference in mechanism is discussed.

In part I of this series we showed that trialkyl phosphites abstract vicinal halogen atoms from saturated chlorofluorocarbons without forming C–P bonds, the products being fluoro olefins, dialkyl phosphorochloridates (or -fluoridates), and alkyl chlorides.[1] The fluoro olefins thus formed are capable of reacting further with trialkyl phosphites giving products which do contain C–P bonds. Knunyants,[2] *et al.*, described the preparation of numerous dialkyl perfluoroalkenylphosphonates from perfluoro olefins by the displacement of vinylic fluorine, but fluoro olefins containing chlorine substituents have not hitherto been examined, with the sole exception of chlorotrifluoroethylene.[2c] The present paper deals with the reactions of trialkyl phosphites with 1,2-dichloroperfluorocycloalkenes (I), which proceed with the displacement of both chlorine atoms giving tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates (II).

The stoichiometry was established in a reaction between 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene

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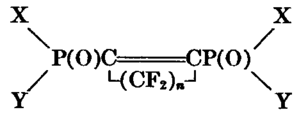
[1] Part I: A. W. Frank and C. F. Baranauckas, *J. Org. Chem.*, **30**, 3970 (1965).

[2] (a) I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva, *Dokl. Akad. Nauk SSSR*, **129**, 576 (1959); (b) I. L. Knunyants and E. Ya. Pervova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1409 (1962); (c) I. L. Knunyants, R. N. Sterlin, V. V. Tyuleneva, and L. N. Pinkina, *ibid.*, 1123 (1963); (d) I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva, *ibid.*, 1576 (1963); (e) I. L. Knunyants, V. V. Tyuleneva, E. Ya. Pervova, and R. N. Sterlin, *ibid.*, 1797 (1964).

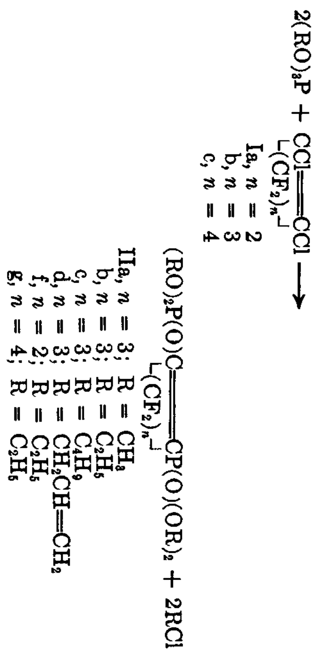
TABLE I

PERFLUORO-1-CYCLOALKEN-1,2-YLENEDIPHOSPHONATES, -PHOSPHINATES, AND -PHOSPHINE OXIDES



Compd.	X	Y	n	Procedure	B.p., °C. (mm.)	n^{25}_D	Yield, %	Calcd., % C	Calcd., % H	Calcd., % F	Calcd., % P	Found, % C	Found, % H	Found, % F	Found, % P
IIa	OCH_3	OCH_3	3	B	132–134 (0.4)	1.4159[a]	40	27.56	3.09	29.07	15.80	27.53	3.24	28.90	15.7[b]
IIb	OC_2H_5	OC_2H_5	3	B	111–112 (0.1)[c]	1.4167[a]	74[d]	34.83	4.50	25.43	13.82	35.09	4.59	25.27	13.3[b]
IIc	OC_4H_9	OC_4H_9	3	A	90–105 (0.004)[e]	1.4261[f]	93	45.00	6.48	20.34	11.05	45.22	6.61	20.7	10.9
IId	$OCH_2CH{=}CH_2$	$OCH_2CH{=}CH_2$	3	B	Undistd.	1.4521[g]	92				12.48				13.5[b]
IIe	OC_2H_5	OC_6H_5	3	B	Undistd.	1.4897	62[h]				11.38				11.5[b]
IIf	OC_2H_5	OC_2H_5	2	C	Undistd.	1.4208	100	36.21	5.06	19.08	15.55	36.20	5.20	18.95	15.2[b]
IIg	OC_2H_5	OC_2H_5	4	C	120–135 (0.5)	1.4140	51[j]				12.45				12.5[k]
III	OC_2H_5	C_6H_5	3	C	174–176 (0.45)		34[l]				12.09				12.6
IV	C_6H_5	C_6H_5	3	C	176–177[m]		75	60.42	3.50	19.78	10.75	60.46	3.81	19.03	11.1

[a] At 20°. [b] *Anal.* Found: Cl, 0.0. [c] F.p. between −55 and −60°. [d] Also 20% of diethyl ethylphosphonate. [e] Bath temperature. [f] d^{20}_4 1.1964. [g] d^{20}_4 1.2040. [h] Also 34% of ethyl phenyl ethylphosphonate, b.p. 108–109° (0.5 mm.), n^{24}_D 1.4897. *Anal.* Calcd. for $C_{10}H_{15}O_3P$: P, 14.5. Found: P, 13.5. A. E. Arbuzov and L. V. Nesterov [*Dokl. Akad. Nauk SSSR*, **92**, 57 (1953); *Chem. Abstr.*, **48**, 10538 (1954)] gave b.p. 142.5–143.5° (12.5 mm.), n^{20}_D 1.4922, for ethyl phenyl ethylphosphonate. [i] The product decomposed on attempted distillation at 0.3 mm. [j] Also 37% of diethyl ethylphosphonate. [k] *Anal.* Found: Cl, 0.14. [l] The distillation left a large tarry residue. [m] Melting point after recrystallization from ethyl acetate.



$$2(RO)_3P + \underbrace{CCl{=\!=}CCl}_{(CF_2)_n} \longrightarrow (RO)_2P(O)\underbrace{C{=\!=}C}_{(CF_2)_n}P(O)(OR)_2 + 2RCl$$

Ia, $n = 2$
b, $n = 3$
c, $n = 4$

IIa, $n = 3$; $R = CH_3$
b, $n = 3$; $R = C_2H_5$
c, $n = 3$; $R = C_4H_9$
d, $n = 3$; $R = CH_2CH{=}CH_2$
f, $n = 2$; $R = C_2H_5$
g, $n = 4$; $R = C_2H_5$

(Ib) (0.1 mole) and tributyl phosphite (0.3 mole). When a mixture of the two reagents was heated in a sealed pressure bottle in a boiling-water bath for 6 hr. (procedure A), the consumption of phosphite, measured by iodine titration, was 0.18 mole. The excess (0.10 mole) was recovered by distillation, together with 0.18 mole of butyl chloride, leaving a chlorine-free residue whose analysis corresponded to tetrabutyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (IIc). The properties of the distilled ester are given in Table I.

The trialkyl phosphites which formed gaseous byproducts (methyl chloride or ethyl chloride) were allowed to react with the fluoro olefins at atmospheric pressure in the stoichiometric 2:1 ratio, either by heating a mixture of the reagents to reflux (procedure B) or by adding the phosphite slowly to the gently boiling fluoro olefin (procedure C). In either case the reaction was allowed to proceed until the gas evolution subsided and a test for unreacted phosphite was negative. Procedure B was used for the preparation of IIa, IIb, IId, and for the preparation of the symmetrical diethyl diphenyl ester (IIe) from diethyl phenyl phosphite (Table I). Procedure C was used for the preparation of IIf and IIg (Table I) and for the larger scale preparations of IIb. This procedure was more time-consuming but enabled the reaction to be more easily controlled, particularly in the large-scale runs, and helped to repress the self-isomerization of the phosphite. It was noted, incidentally, that each fluoro olefin reacted at its boiling point but not below. The boiling points of Ia, Ib, and Ic are 67.1, 90.7, and 113°, respectively.[3]

In none of the foregoing experiments was any monophosphonate isolated. Attempts to prepare a monophosphonate from Ib and triethyl phosphite by changing the ratio of reactants or the order of addition were fruitless. When the reagents were taken in a 1:1 ratio, half of the fluoro olefin was recovered unchanged. The monophosphonate, if formed, is evidently more reactive toward triethyl phosphite than the fluoro olefin itself.[4]

An unusual feature of the diphosphonates IIa–g was the total absence of C=C stretching absorption in the infrared, with the exception of IIf, which showed a weak C=C band at 1595 cm.$^{-1}$, and, of course, of IId and IIe which contained allyl or phenyl groups. This absence cannot be explained by symmetry, nor, in the case of the cyclopentene derivatives, by a *trans* configuration of the phosphonate groups, because the

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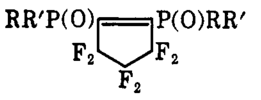
[3] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 126, 127.

[4] The preparation of this monophosphonate by other routes will be described in later papers in this series.

cyclopentene ring is considered to be planar, or almost so, with the substituents on the double bond extending outward in the same plane as the ring.[5] Moreover, the C=C stretching band was missing in all of the hexafluorocyclopentene diphosphonate derivatives described in the following paper in this series. The two P=O groups evidently exert a strong dampening effect on the stretching vibration of the C=C bond.

Further experiments were performed with other phosphorus esters and fluoro olefins to extend the scope of this reaction. Diethyl phenylphosphonite and ethyl diphenylphosphinite reacted smoothly with Ib, following procedure C, giving diethyl P,P′-diphenyl-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphinate (III) and 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylene-P,P,P′,P′-tetraphenylbis(phosphine oxide) (IV), respectively.



III, R = C_6H_5; R′ = OC_2H_5
IV, R = R′ = C_6H_5

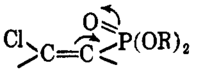
The reaction of triethyl phosphite with 2,2′,3,3′-tetrachloro-4,4,4′,4′,5,5,5′,5′-octafluorobi-2-cyclopenten-1-ylidene[6] gave only a small fraction identified as diethyl phosphorofluoridate.

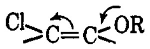
The reaction of triethyl phosphite with 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene, an acyclic fluoro olefin, appeared to proceed in a normal manner, but the product, though free of chlorine, was high in phosphorus and showed fluorinated C=C absorption at 1745 cm.$^{-1}$ in the infrared spectrum. Similar results were obtained with tributyl phosphite. The products were evidently not as stable as those derived from the cyclic fluoro olefins.

Mechanism.—The displacement of both chlorine atoms from a 1,2-dichloroperfluorocycloalkene is a departure from the usual pattern of nucleophilic reactions with these compounds. In most cases the chlorine atom at C-2 is preserved, the products being either C-1 monosubstituted or C-1,3,3 trisubstituted, depending on the reactivity of the nucleophile.[7,8] Obviously, a new factor is introduced when the nucleophile is a trialkyl phosphite.

The conventional reaction sequence has been clearly demonstrated in the reactions of Ia and Ib with methoxide ion.[9] The first mole of methoxide displaces a chloride ion at C-1. The second mole of methoxide again attacks at C-1, inducing an allylic shift of the double bond and displacing a fluoride ion at C-3. With careful work the dimethoxy derivative can be isolated, but in most cases it reacts further with a third mole of methoxide with the displacement of the remaining fluoride ion at C-3.

In order for displacement of chloride ion to occur at C-2 it is necessary that the attack of the nucleophile also be at C-2. The most obvious way to accomplish this is to place an electron-withdrawing substituent on C-1. *The new factor which is introduced when the nucleophile is a trialkyl phosphite is the placement of an electron-withdrawing P=O substituent on C-1.* The difference can be depicted as follows. The function





of the phosphonate group is to effect a reversal of the polarization of the double bond. Further support for this hypothesis will be presented in the subsequent papers.

Metal Extractants.—A cursory evaluation of one of the diphosphonates (IIb) as a metal extractant was made on the hypothesis that the rigid spatial configuration of its phosphorus atoms might give it a high selectivity for a narrow band of elements in the periodic table. The results are given in Table II, where the diphosphonate is compared with tributyl phosphate, a fair extractant, and tri-*n*-octylphosphine oxide, a good extractant. The diphosphonate proved to be a good extractant for only the heaviest elements, Th(IV) and U(VI).

TABLE II

EVALUATION OF IIB AS A METAL EXTRACTANT

Metal	$(C_4H_9O)_3PO$	$(C_8H_{17})_3PO$	IIb
	% extracted from 6 *N* HNO_3		
Cr(III)	0	0	1
Fe(III)	0	0	17
Ni(II)	2	1	10
Cu(II)	1	0	4
Sr(II)	9	1	0
Ag(I)	0	1	0
Cd(II)	1	1	1
Hg(I)	27	20	3
Pb(II)	0	4	0
Bi(III)	2	1	1
Th(IV)	60	96	100
U(VI)	72	98	91
	% extracted from 6 *N* HCl		
Mn(II)	6	7	2
Fe(II)	2	21	24
Fe(III)	46	100	7
Co(II)	0	40	0
Ni(II)	2	3	2
Cu(II)	0	51	1
Zn(II)	0	96	0
Zr(IV)	7	92	Ppt.
Cd(II)	6	35	0
Hg(II)	9	82	3

The diphosphinate III and the bis(phosphine oxide) IV were also found to be good extractants for thorium and uranium, the per cent extraction being 99 (Th), 99 (U) for III, and 90 (Th), 100 (U) for IV.

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[5] C. B. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948).

[6] S. Gelfand, U. S. Patent 2,951,097 (Aug. 30, 1960); *Chem. Abstr.*, **55**, 4391 (1961).

[7] See C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959), and references therein for the cyclopentenes.

[8] See J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963), and references therein for the cyclobutenes.

[9] (a) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962); (b) J. D. Park, J. R. Dick, and J. R. Lacher, *J. Org. Chem.*, **28**, 1154 (1963); (c) F. Dreier, W. Duncan, and T. Mill, *Tetrahedron Letters*, 1951 (1964).

Experimental Section[10]

Reagents.—Diethyl phenylphosphonite[11] and ethyl diphenylphosphinite[12] were prepared from the corresponding chlorides by reaction with ethanol in the presence of dimethylaniline. Triethyl phosphite, triallyl phosphite, and Ib were Hooker products. The remainder of the reagents were obtained from other commercial sources and used without further purification.

Preparation of Perfluoro-1-cycloalken-1,2-ylenediphosphonates, -phosphinates, and -phosphine Oxides.—Each of the nine compounds described in Table I was prepared by one of the following procedures.

Procedure A.—A pressure bottle was charged with 24.5 g. (0.1 mole) of Ib and 75.0 g. (0.3 mole) of tri-*n*-butyl phosphite, sealed and heated in a water bath for 4 hr. at 60° followed by 6 hr. at 90°. The consumption of phosphite, followed by titration of an aliquot with 0.1 *N* iodine in benzene, was 0.04 mole after the first heating period and 0.18 mole after the second. The product was distilled, giving 16.5 g. (0.18 mole) of butyl chloride,[13] b.p. 81–83°, $n^{25}\text{D}$ 1.3981, and 25.2 g. (0.10 mole) of tri-*n*-butyl phosphite[14] in two fractions, 21.4 g., b.p. 86–87° (0.3 mm.), $n^{25}\text{D}$ 1.4290, and 3.8 g., b.p. 88–123° (0.3 mm.), $n^{25}\text{D}$ 1.4288. The remainder, 51.9 g., $n^{25}\text{D}$ 1.4262, was a viscous liquid which could not be distilled at 0.3 mm. without decomposition.

Anal. Calcd. for $C_{21}H_{36}F_6O_6P_2$: P, 11.05; Cl, 0.0. Found: P, 11.4; Cl, 0.0.

The product gave a negative iodine test for P(III). A permanganate test for unsaturation was positive, with the formation of a brown precipitate of manganese dioxide. A bromine test was negative, but Ib itself does not decolorize bromine. These tests, together with the analyses and the stoichiometry established above, served to identify the product as **tetra-*n*-butyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate** (IIc). An analytical sample (Table I) was prepared by distilling a portion of the ester at 0.004 mm. in a Hickman molecular still.

Procedure B.—A solution of 24.5 g. (0.1 mole) of Ib and 24.8 g. (0.2 mole) of trimethyl phosphite was heated slowly to reflux and maintained at reflux until the gas evolution subsided and a test for unreacted phosphite was negative (7.5 hr.). The gas evolution (methyl chloride) and refluxing both began at 90°. The product was then distilled, giving 11.1 g. (45%) of unreacted Ib, b.p. 34–37° (75 mm.), $n^{20}\text{D}$ 1.3672; 13.8 g. (56%) of crude dimethyl methylphosphonate,[15] b.p. 65–94° (11 mm.), $n^{20}\text{D}$ 1.4122, identified by analysis (*Anal.* Calcd. for $C_3H_9O_3P$: P, 25.0. Found: P, 23.3.) and by comparison of its infrared spectrum with an authentic sample; and 15.5 g. (40%) of **tetramethyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate** (IIa). The yield of IIa was considerably reduced by the self-isomerization of the phosphite.

The properties of the diphosphonates prepared by this procedure are given in Table I. In the case of triallyl phosphite the allyl chloride was distilled off as it formed, as it tended to slow down the reaction.

Procedure C.—Ib (490 g., 2.0 moles) was heated to gentle reflux and to it was added triethyl phosphite (664 g., 4.0 moles) at a rate sufficient to maintain a steady evolution of ethyl chloride. The addition was completed in 4.5 hr., but the evolution of gas continued for another 2.5 hr. The product then gave a negative test for unreacted phosphite. Distillation gave 60.2 g. (10%) of crude diethyl ethylphosphonate,[15] b.p. 57–62° (0.5 mm.), $n^{25}\text{D}$ 1.4069, identified by analysis (*Anal.* Calcd. for $C_6H_{15}O_3P$: P, 18.6. Found: P, 17.4.) and by comparison of its infrared spectrum with an authentic sample; and 730 g. (84%) of **tetraethyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate** (IIb), b.p. 111–113° (0.1 mm.), $n^{25}\text{D}$ 1.4148.

Anal. Calcd. for $C_{13}H_{20}F_6O_6P_2$: P, 13.82. Found: P, 13.7.

This product was identical with that of procedure B, whose properties are given in Table I.

The properties of the other diphosphonates, diphosphinates, and bis(phosphine oxides) prepared by this procedure are given in Table I. The reaction of triethyl phosphite with Ic was first attempted at 90–100°, but when no ethyl chloride evolution was observed, the temperature was raised to reflux.

Attempted Preparation of a Monophosphonate.—Two attempts were made to prepare the monophosphonate, diethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate, using equimolar amounts of the reagents. Triethyl phosphite (33.2 g., 0.2 mole) was added dropwise to boiling Ib (49.0 g., 0.2 mole) over a 14-min. period, followed by refluxing until the ethyl chloride evolution subsided (1 hr.). Distillation of the product gave 49% of unreacted Ib, 8% of diethyl ethylphosphonate, and 37% of IIb. When the order of addition was reversed, the products were 54% of unreacted Ib, 10% of diethyl ethylphosphonate, and 35% of IIb.

Bromination of the Tetraallyl Ester.—A solution of 640 g. (4.0 moles) of bromine in 1000 ml. of carbon tetrachloride was added dropwise to a refluxing solution of 454 g. (0.92 mole) of tetraallyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (IId) in 2000 ml. of carbon tetrachloride. A heat lamp was used to speed the reaction. The addition was completed in 4 hr. After an additional hour the reaction mixture was allowed to cool and was then stripped of solvent under reduced pressure, giving 1047 g. (100%) of **tetrakis(2,3-dibromopropyl) 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate** (II, $n = 3$; R $= CH_2CHBrCH_2Br$) as a dark colored, heavy oil.

Anal. Calcd. for $C_{17}H_{20}Br_8F_6O_6P_2$: Br, 56.3; P, 5.46. Found: Br, 56.1; P, 5.45.

The uptake of bromine corresponded to 1 mole for each allyl group, the cyclopentene double bond being preserved.

Infrared Spectra.—The spectra were taken on a Beckman IR-4 instrument, the liquids neat and the solid (IV) in a Nujol mull.

The seven tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates (IIa–g) all contained a strong P=O stretching band at 1282 ± 7 cm.$^{-1}$. In the diphosphinate (III) the band was shifted to 1252 cm.$^{-1}$, and in the bis(phosphine oxide) (IV) to 1222, 1230 cm.$^{-1}$. Compound IV was the only one which showed a doublet. These frequencies were higher than the norm[16a] by about 40 cm.$^{-1}$, reflecting the high electronegativity of the CF_2 groups.

All of the compounds contained a strong band due to P–O–(C) at 1020 cm.$^{-1}$ except IIa, in which it was centered at 1040 cm.$^{-1}$, and IV, which was not an ester.

The tetramethyl ester IIa showed a weak CH_3–O–(P) band at 1187 cm.$^{-1}$, but in the other esters the –CH_2–O–(P) band[16b] was masked by the strong C–F absorption.

A heptad of strong sharp bands due to C–F in Ib at 1005, 1109, 1163, 1205, 1250, 1280, and 1330 cm.$^{-1}$ was found to be present in all of the cyclopentene derivatives, in which they appeared at 1010, 1100, 1155 ± 3, 1200 ± 5, 1239 ± 4 and 1255 (doublet), 1293, and 1345 ± 2 cm.$^{-1}$. The 1010-cm.$^{-1}$ band was in some cases a shoulder on the strong P–O–(C) band, and the 1293-cm.$^{-1}$ band was masked by the strong P=O band, being distinguishable only in III and IV in which the P=O band was shifted. The splitting of the 1250-cm.$^{-1}$ band was observed in all of the diphosphonates. The cyclobutene derivative IIf contained bands in this region at 1096, 1130, 1183, 1242, and 1325 cm.$^{-1}$, and the cyclohexene derivative IIg at 1117, 1170, 1199, 1220, and 1352 cm.$^{-1}$.

Absorption in the C=C region due to the cycloalkene double bond was conspicuously absent in all but the cyclobutene derivative IIf, which contained a weak band at 1595 cm.$^{-1}$. The tetraallyl ester IId contained a band at 1642 cm.$^{-1}$, and the three compounds containing phenyl substituents (IIe, III, and IV) showed a band at 1590 cm.$^{-1}$.

Ultraviolet Spectra.—The spectra were taken on methanol solutions with a Cary Model 14 instrument. None showed any

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(10) Melting points were determined using a Fisher-Johns apparatus and are corrected. The C, H, and F microanalyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

(11) G. Kamai, *Zh. Obshch. Khim.*, **18**, 443 (1948); *Chem. Abstr.*, **42**, 7723 (1948).

(12) (a) G. Kamai, *Dokl. Akad. Nauk SSSR*, **66**, 389 (1949); *Chem. Abstr.*, **44**, 127 (1950); (b) B. A. Arbuzov and N. P. Grechkin, *Zh. Obshch. Khim.*, **20**, 107 (1950); *Chem. Abstr.*, **44**, 5832 (1950).

(13) A. I. Vogel [*J. Chem. Soc.*, 636 (1943)] gave b.p. 78.0° (762 mm.), $n^{20}\text{D}$ 1.40223, for butyl chloride.

(14) W. Gerrard [*ibid.*, 1464 (1940)] gave b.p. 127–128° (18 mm.), $n^{19}\text{D}$ 1.4321, for tri-*n*-butyl phosphite.

(15) B. A. Arbuzov and V. S. Vinogradova [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 459 (1947); *Chem. Abstr.*, **42**, 3312 (1948)] gave b.p. 67° (12 mm.), $n^{20}\text{D}$ 1.4105, for dimethyl methylphosphonate and b.p. 85° (12 mm.), $n^{20}\text{D}$ 1.4165, for diethyl ethylphosphonate.

(16) (a) L. C. Thomas and B. A. Chittenden, *Spectrochim. Acta*, **20**, 467 (1964); (b) *ibid.*, **20**, 489 (1964).

significant absorption above 260 mμ. For compound IV, λ_{max} 223 mμ (ε 37,880).

Metal Extractions.—For each extraction 20.00 ml. of a 6 *N* acid solution containing 200 p.p.m. of the metal as the nitrate or chloride was shaken for 5 min. on a mechanical shaker with 20.00 ml. of a solution of IIb (0.05 *M*), III (0.05 *M*), tri-*n*-butyl phosphate (0.1 *M*), or tri-*n*-octylphosphine oxide (0.1 *M*) in cyclohexane. Compound IV was used as a 0.05 *M* solution in chloroform as it was insoluble in cyclohexane. The phases were then separated, and the aqueous phase was analyzed for the metal by X-ray fluorescence. The results (Table II) are expressed as per cent metal salt extracted from the aqueous phase, using solutions extracted with cyclohexane alone as blanks.

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Azasteroids. V. The Direct Conversion of 1-(Carboethoxymethyl)-1,2,3,4-tetrahydroisoquinolines and Cyclic Ketones into Benzo[*a*]cycloalkano[*f*]quinolizinones. An Example of Enamine Acylation by an Ester Function[1,2]

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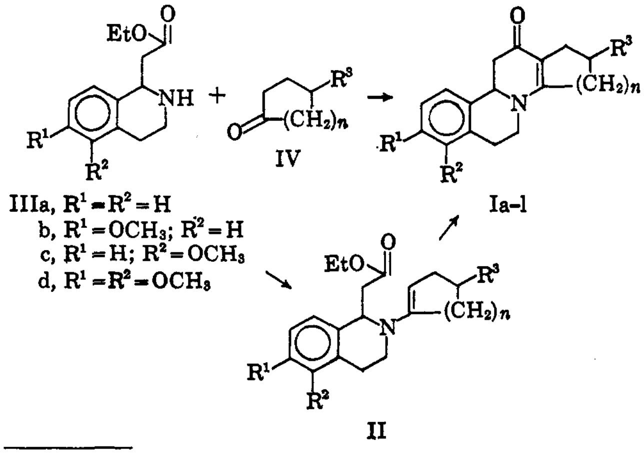
The intramolecular cyclization of N-(cycloalkenyl)-1-carbethoxymethyl-1,2,3,4-tetrahydroisoquinolines (II) in hot ethylene glycol has been re-examined and found not to require the latter solvent. The formation of benzo[*a*]cycloalkano[*f*]quinolizinones (I) is described under the conditions which are commonly expected to lead only to the enamines. The reaction proceeds with or without the use of acid catalysts, although the yields are higher and the reaction time shorter when they are employed. The perchlorate salts of these enamino ketones (I) were prepared and found to be O-protonated.

As part of a general program to synthesize totally azasteroids, various approaches to the construction of the steroidal skeleton have been considered.[5] In a recent communication,[6] a model for the 8- and 9-azasteroids was described employing as starting materials the tetracyclic enamino ketones (benzo[*a*]-cycloalkano[*f*]quinolizinones), Ie ($R^1 = OCH_3$; $R^2 = R^3 = H$; $n = 1$) and Ij ($R^1 = H$; $R^2 = OCH_3$; $R^3 = OCH_2CH_2O$–; $n = 2$). The former was considered to be a useful precursor to 8-azasteroids whereas the latter could provide a pathway to 9-azasteroids. Both of these starting compounds were prepared by condensing the appropriate tetrahydroisoquinoline esters (III) and cyclic ketones (IV) to give II according to the usual enamine procedures.[7] Replacement of the toluene solvent with ethylene glycol, and heating overnight at 170–180° gave I. The structure of Ie and Ij were supported by the infrared spectra which exhibited two strong bands in the region of 6.0–6.5 μ, typical of β-amino α,β-unsaturated ketones[8] and ultraviolet maxima in the 300–310-mμ region consistent with the N—C=C—C=O chromophore.[9] The position of the carbon–carbon double bond is established by the absence of any vinyl proton n.m.r. signal and the chemical shift of the lone proton adjacent to nitrogen and the phenyl group at τ 5.3.

Although these two compounds are considered extremely useful for further studies on azasteroids, the poor yields (Ie, 26%, and Ij, 18%) obtained by this method left much to be desired in view of the fact that many subsequent synthetic steps would be necessary before the final goal was reached. It was felt that a more detailed examination of the enamine cyclization in ethylene glycol was necessary before proceeding to seek out alternative procedures. Since the tetrahydroisoquinoline esters, IIIb and IIIc, were both difficult and costly to come by, studies were carried out using the readily available IIIa (*cf.* Experimental Section). Treatment of the latter with cyclopentanone in toluene with azeotropic removal of water gave the



IIIa, $R^1 = R^2 = H$
b, $R^1 = OCH_3$; $R^2 = H$
c, $R^1 = H$; $R^2 = OCH_3$
d, $R^1 = R^2 = OCH_3$

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[2] Presented before the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

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[4] Institute of Chemistry, "Alonso Barba," Madrid, Spain.

[5] A. I. Meyers, N. K. Ralhan, and J. Schneller, *J. Org. Chem.*, **28**, 2944 (1963); A. I. Meyers and N. K. Ralhan, *ibid.*, **28**, 2950 (1963); A. I. Meyers, N. K. Ralhan, B. J. Bertus, and K. Baburao, *J. Heterocyclic Chem.*, **1**, 13 (1964).

[6] A. I. Meyers, G. G. Munoz, W. Sobotka, and K. Baburao, *Tetrahedron Letters*, **No. 4**, 255 (1965).

[7] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[8] (a) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Franck, and D. J. Wallace, *ibid.*, **71**, 3337 (1949); (b) G. O. Dudek, *J. Org. Chem.*, **30**, 548 (1965).

[9] F. Bohlmann, E. Winterfeldt, O. Schmidt, and W. Reusche, *Ber.*, **94**, 1774 (1961); F. Bohlmann and O. Schmidt, *ibid.*, **97**, 1354 (1964).