mixture of 10 ml. of saturated sodium bicarbonate solution, 10 ml. of distilled water and 75 ml. of C.P. acetone (red carotenoid color restored). After dilution to 200 ml. with hexane, the solution was allowed to stand until all ten portions were ready. The combined pigment was then transferred to hexane by careful addition of water, the epiphase was washed acetone-free, dried and evaporated; photometrically estimated pigment recovery, 99 mg. of "γ-carotene" (40%). The evaporation residue was dissolved in 100 ml. of hexane (with the initial aid of a few drops of chloroform) and developed on four 45 × 4.5 cm. columns with 500 ml. of hexane–4% acetone each.

92 seven "top zones"
24 pale pink (unchanged γ-carotene, 2 mg.)
12 colorless interzone
280 many yell.-orange zones and (in part) interzones

The combined "top zones" (containing 20% of the initial pigment) were eluted with ethanol, transferred to hexane, washed ethanol-free, dried, and developed for 2.5 hr. on two 45 × 4.5 cm. columns with 1 l. of acetone–hexane 1:9, for each.

28 a tan and a pink zone
17 orange (4-hydroxy-γ-carotene)
20 orange
15 pink
16 yellow
35 nearly colorless interzone
20 orange (4-keto-γ-carotene)
54 nearly colorless interzone
20 yellow
23 nearly colorless interzone
24 yellow

The corresponding zones of the two chromatograms were combined, eluted with acetone–ethanol 1:1, transferred to hexane, washed acetone-free, dried and rechromatographed on 20 × 3.5 cm. columns. Most zones not designated in the above chromatogram represented partially hydrogenated derivatives; some of them were crystallized.[5]

4-Hydroxy-γ-carotene.—The zone in the above chromatogram contained 6 mg. (2.4%) of this compound which yielded, from benzene–methanol, 0.5 mg. of nearly rectangular, deep orange plates (many with jagged ends), m.p. 144–145°; partition ratio, 82:18 in hexane–95% methanol and

92:8 in hexane–90% methanol; maxima at 438, *460*, 491 mμ (Fig. 5). A sharp OH band appeared at 2.78 μ (in CCl₄). On lime–Celite the compound was adsorbed above 4-hydroxy-β-carotene but below lycopene. The reaction with acid chloroform was positive and rapid. The spectrum of the dehydrated product thus formed showed a broad maximum at 467 mμ but no fine structure in the visible region.

Acetylation.—Into a solution of 2 mg. of 4-hydroxy-γ-carotene in 1 drop of anhydrous pyridine 1 drop of acetyl chloride (C.P.) was introduced. After an hour, 10 ml. of methanol and then 10 ml. of hexane were added. The pigment was transferred to hexane and developed with the same solvent on a 18 × 1.8 cm. column. The main zone, located below that of the unchanged hydroxy compound, contained 1.4 mg. of 4-acetoxy-γ-carotene and showed an unchanged spectrum; partition ratio, 95:5 in hexane–95% methanol. The esterification could be reversed by methanolic KOH.

Etherification.—To a solution of 2 mg. of 4-hydroxy-γ-carotene in 5 ml. of abs. ethanol, 3 drops of the acid chloroform reagent was added. After standing for 12 hr. the pigment was transferred to 10 ml. of hexane, dried, and developed on a 18 × 1.8 cm. column with hexane–2% acetone. The top orange zone included unreacted material, while the lower orange zone contained 0.9 mg. of 4-ethoxy-γ-carotene showing the γ-carotene spectrum; partition ratio, 99:1 in hexane–95% methanol. The compound was hydrolyzed to 4-hydroxy-γ-carotene by the method just described for the preparation of the ether, but using a water–acetone mixture 1:4 instead of ethanol.

Oxidation.—One mg. of 4-hydroxy-γ-carotene was dissolved in 5 ml. of reagent grade chloroform and air was bubbled through for 1 hr. The solution was then developed with hexane–5% acetone (column, 18 × 1.8 cm.). The upper zone (orange) contained unreacted substance, and the lower one (pink) 0.1 mg. (10%) of 4-keto-γ-carotene (see below).

4-Keto-γ-carotene.—The indicated zone in the chromatogram described above contained 1.2 mg. (0.5%) of this ketone; dark red, rhomboidal platelets (from benzene–methanol), m.p. 140–142°; partition ratio 89:11 in hexane–95% methanol and 98:2 in hexane–90% methanol; maximum at 468 mμ. On lime–Celite the compound is adsorbed above γ-carotene and 4-keto-β-carotene but below 4-hydroxy-γ-carotene; acid chloroform reaction, negative.
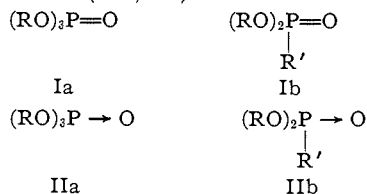
PASADENA, CALIFORNIA

Bond Refractions and the Nature of Phosphorus–Oxygen Bonds

BY R. G. GILLIS, J. F. HORWOOD AND G. L. WHITE

The P–O bond refraction was found to be 3.18 and the P → O bond refraction −1.22 from the experimentally determined molecular refractions of several trialkyl phosphites and phosphates. This supports the formulation of P → O as a coördinate bond. Absence of exaltation and the virtual constancy of the phosphorus–oxygen infrared stretching frequency in diethyl vinylphosphonate and diethyl allylphosphonate, also provide evidence for this view.

In phosphates and phosphonates the phosphorus–oxygen bond commonly represented as a double bond (Ia,Ib) may also be represented as a coördinate bond (IIa,IIb).[1]

$$(RO)_3P{=}O \qquad (RO)_2P{=}O$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad R'$$

Ia   Ib

$$(RO)_3P \rightarrow O \qquad (RO)_2P \rightarrow O$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad R'$$

IIa   IIb

(1) The notation X → Y is preferred to X⁺−Y⁻. The latter implies that the fractional charges on X and Y are equal, which is misleading. The former may be confused with the notation for inductive effect, but this is less likely to be troublesome.

The sulfur–oxygen bond in sulfoxides and sulfones may be similarly represented. In this case the double-bond structure has been supported by Phillips, Hunter and Sutton,[2] and by Cumper and Walker[3] on the basis of dipole moment measurements; by Barnard, Fabian and Koch,[4] and by Amstutz, Hunsberger and Chessick,[5] from a study of hydrogen bonding by infrared spectroscopy;

(2) G. M. Phillips, J. S. Hunter and L. E. Sutton, J. Chem. Soc., 146 (1945).

(3) C. W. N. Cumper and S. Walker, Trans. Faraday Soc., 52, 193 (1956).

(4) D. Barnard, J. M. Fabian and H. P. Koch, J. Chem. Soc., 2442 (1949).

(5) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, 73, 1220 (1951).

and by Koch and Moffitt,[6-8] who considered ultraviolet spectra and then made quantum mechanical calculations. Some of these conclusions have been attacked by Wells,[9] and by Vogel, Cresswell, Jeffery and Leicester.[10] Price and co-workers have supported the coördinate bond on evidence from copolymerization measurements,[11,12] by studies of conjugation by ultraviolet and infrared spectroscopy,[13,14] and by bond refractions.[15]

Less attention has been given so far to the phosphorus–oxygen bond. Vogel[10] has made a preliminary estimate of the coördinate bond refraction; Gore[16] has estimated the bond stretching frequency; and Muller, Lauterbur and Goldenson[17] concluded that no decision on the nature of the bond could be made from their nuclear magnetic resonance data. As part of a program of work on the nature of such bonds between atoms in Groups V and VI, we now report results on the bond refraction of P–O and P→O bonds, and on the conjugation of P→O.

Experimental

Densities were determined in a Hennion[18] pycnometer and refractive indices with an Abbe refractometer. In both cases temperature was controlled at $20.00 \pm 0.03°$.

Data used in calculating molecular refractions were concordant results from consecutive fractions obtained with a column 20 mm. internal diameter and 300 mm. long packed with helices of 4–6 turns of 27 B. & S. gauge stainless steel wire wound on a 5 mm. mandrel.

Trialkyl phosphites were prepared by the reaction of phosphorus trichloride with a slight excess of alcohol in the presence of a tertiary base and an inert solvent. For trimethyl phosphite, the solvent was diethyl ether and for the others petroleum ether (b.p. 40–60°). Diethylaniline was used as the tertiary base with methyl and ethyl alcohol, triethylamine with the others. Yields of purified material were 60–70% based on phosphorus trichloride.

Trimethyl phosphite had b.p. 111°, n^{20}D 1.4089, d^{20}_4 1.0472 (lit.[19] n^{20}D 1.4095, d^{20} 1.0520).

Triethyl phosphite had b.p. 58° at 15 mm., n^{20}D 1.4126, d^{20}_4 0.9663 (lit.[19] n^{20}D 1.4135, $d^{20}\alpha$ 0.9687).

Tripropyl phosphite had b.p. 92° at 14 mm., n^{20}D 1.4282, d^{20}_4 0.9417 (lit.[19] n^{20}D 1.4265, d^{20}_0 0.9522).

Tri-isopropyl phosphite had b.p. 74° at 20 mm., n^{20}D 1.4110, d^{20}_4 0.9063 (lit.[20] $d^{18.5}_0$ 0.9187).

Tributyl phosphite had b.p. 104° at 4 mm., n^{20}D 1.4320, d^{20}_4 0.9174 (lit.[21] n^{16}D 1.4339, d^{20}_4 0.9259).

Diethyl ethylphosphonate was prepared from triethyl phosphite and ethyl iodide in 80% yield, b.p. 104° at 27 mm., 85° at 11 mm., n^{20}D 1.4168, d^{20}_4 1.0254 (lit.[19] n^{20}D 1.4165, d^{20}_4 1.0272).

Diethyl vinylphosphonate was prepared by the dehydrobromination of diethyl 2-bromoethylphosphonate with triethylamine in 68% yield, b.p. 92° at 12 mm., 60° at

2 mm., n^{20}D 1.4296, d^{20}_4 1.0529 (lit.[22] n^{20}D 1.4300, d^{20}_p 1.0526).

Diethyl allylphosphonate was prepared by adding allyl bromide to preheated triethyl phosphite. If the two reagents were mixed cold and then heated, the allyl bromide distilled out before the reaction began.

Eighty-three grams (0.5 mole) of triethyl phosphite was placed in a flask fitted with a fractionating column as above, dropping funnel and a thermometer to register internal temperature. The flask was heated by an oil-bath maintained at 165–175°. When the internal temperature reached 160°, addition of allyl bromide (61 g., 0.5 mole) was commenced, and maintained at the same rate as ethyl bromide distilled. The addition required one hour, the internal temperature rose to 175°, and the temperature at the head of the column fluctuated between 42–46°. The recovery of the ethyl bromide was 43 g. (79%). The residue was fractionated and gave 70 g. (79%) of diethyl allylphosphonate, b.p. 102° at 11 mm., n^{20}D 1.4339, d^{20}_4 1.0308 (lit.[23] b.p. 78–81° at 2 mm., n^{21}D 1.4320).

Ethyl vinylacetate was prepared from vinylacetic acid[24] in 75% yield, b.p. 123–124°, n^{20}D 1.4120 (lit.[25] n^{20}D 1.4105).

Ethyl acrylate (L. Light & Co.) was redistilled once, b.p. 100°, n^{20}D 1.4061 (lit.,[26] n^{25}D 1.4032).

Infrared spectra were determined in a Perkin–Elmer Model 12C spectrometer with a type 107 amplifier and rocksalt optics. Complete spectra of the phosphonates are presented in Table I, but ethyl acrylate and ethyl vinylacetate were examined only to determine the C—C and C—O stretching frequencies. Ultraviolet spectra were determined on freshly distilled fractions in a Unicam ultraviolet and visible spectrophotometer using heptane as solvent. All three phosphonates showed weak absorption and the vinylphosphonate exhibited no maximum down to 215 mμ. At this wave length, log ϵ for the vinyl-, allyl- and ethylphosphonates was 1.97, 1.11 and 0.78, respectively. A weak maximum at 257 mμ was shown by all in 95% alcohol; log ϵ_{max} increased with time, and this is attributed to free acid produced by hydrolysis.

Discussion

Bond Refractions in Phosphates.[27]—Vogel determined a value of 3.19 for (P–O) from data on three trialkyl phosphites, and then used this figure to estimate (P → O) as -1.26 from data on seven trialkyl phosphates.[10] It seemed preferable to determine (P → O) directly: R_D (phosphate) $- R_D$ (phosphite). For this purpose, the five trialkyl phosphites were prepared and purified under the same conditions. From these, (P–O) was determined using Vogel's values[10]: (C–H), 1.676; (C–C), 1.296; (C–O), 1.46. The results are shown in Table II. The mean value 3.18 for (P–O) is in good agreement with Vogel's earlier figure, as is the mean value for (P → O), -1.22. (P → O) is negative as is (S → O) in sulfates, about which Vogel[10] commented "no explanation can at present be offered for the negative value." Although molecular refractions are always positive, they are determined at an arbitrary temperature and wave length. By choosing other conditions, molecular refractions could be so changed that all bond refractions would be positive. As a corollary, differences between the refractions of related bonds are meaningful, whereas ratios are not.

(6) H. P. Koch, J. Chem. Soc., 408 (1949).

(7) H. P. Koch and W. Moffitt, Trans. Faraday Soc., **47**, 7 (1951).

(8) W. Moffitt, Proc. Roy. Soc. (London), **A200**, 409 (1950).

(9) A. F. Wells, J. Chem. Soc., 55 (1949).

(10) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, ibid., 514 (1952).

(11) C. C. Price and J. Zomlefer, This Journal, **72**, 14 (1950).

(12) C. C. Price and R. D. Gilbert, ibid., **74**, 2073 (1952).

(13) C. C. Price and H. Morita, ibid., **75**, 4747 (1953).

(14) C. C. Price and J. J. Hydock, ibid., **74**, 1943 (1952).

(15) C. C. Price and R. G. Gillis, ibid., **75**, 4750 (1953).

(16) R. C. Gore, Discussions Faraday Soc., **9**, 138 (1950).

(17) N. Muller, P. C. Lauterbur and J. Goldenson, This Journal, **78**, 3557 (1956).

(18) G. F. Hennion, Ind. Eng. Chem., Anal. Ed., **9**, 479 (1937).

(19) B. A. Arbuzov and V. S. Vinogradova, Izvest. Akad. Nauk S.S.S.R., o.kh.n., 459 (1947).

(20) A. E. Arbuzov, Ber., **38**, 1171 (1905).

(21) W. Gerrard, J. Chem. Soc., 1464 (1940).

(22) M. I. Kabachnik, Izvest. Akad. Nauk S.S.S.R., o.kh.n., 233 (1947).

(23) A. H. Ford-Moore and J. H. Williams, J. Chem. Soc., 1465 (1947).

(24) E. Reitz, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 851.

(25) P. Bruylants, Bull. soc. chim. Belg., **38**, 133 (1929); C. A., **23**, 4443 (1929).

(26) E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Publ. Corp., New York, N. Y., 1954, p. 8.

(27) We follow Vogel and use R_D to represent molecular refraction and (X–Y) to represent the contribution to the molecular refraction made by the X–Y bond, "bond refraction."

TABLE I

INFRARED FREQUENCIES (CM.$^{-1}$) AND ASSIGNMENTS FOR DIETHYL ALKYLPHOSPHONATES

Ethyl	Vinyl	Allyl	Assignment[a]
743w	719m	727m	P–O–(C) stretching, sym.
785m	787s	777m	P–O–(C) stretching, asym. ?
795s		804m	
		828m	
		848m	
		910w	Terminal =CH₂ out-of-plane deformation
962s	966s	962s	C–C stretching coupled with C–O
	988m	994m	C–H out-of-plane deformation —CH=C<
1009s			
1027s	1026s	1030s	(P)–O–C stretching, in-phase
1049s	1055s	1050s	(P)–O–C stretching, out-of-phase
1060m			
1101m	1098m	1099m	CH₃ rocking, in-plane
1164m	1166m	1166m	CH₃ rocking, out-of-plane
		1218m	
1227s			
1253s	1249s	1253s	P→O stretching
1285m(sh)	1277m(s)	1280w(sh)	P–alkyl ?
1374w	1368w	1370w	C–CH₃ deformation, sym.
1395m	1397m	1397m	CH₂ wagging
	b	1422w	Terminal =CH₂ in-plane deformation
1449w	1445w	1455w	C–CH₃ deformation, asym.
1460m			
1481w	1479w	1479w	CH₂ deformation
	1618w		C=C stretching, conjugated
		1642m	C=C stretching, unconjugated
1658w	1656w		
1754w	1757w	1754w	
1845w	1852w	1845w	
1988 vw	1980w		
		2049w	
2123vw	2128w	2132vw	
	2203w		
2882m	2899m		C–H stretching in CH₃, sym.
2967s	2950s	2914s	C–H stretching in CH₃, asym.
		2994m	
		3067m	

[a] Assignments based on F. S. Mortimer, *Spectrochim. Acta*, **9**, 270 (1957), and L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1954. [b] Not observed in vinylphosphonate.

TABLE II

MOLECULAR AND BOND REFRACTIONS OF PHOSPHITES AND PHOSPHATES

R	Molecular refractions		Bond refractions	
	(RO)₃P[a]	(RO)₃PO[b]	(P–O)	(P→O)
Methyl	29.03	27.74	3.19	−1.29
Ethyl	42.84	41.77	3.15	−1.07
Propyl	56.94	55.66	3.19	−1.28
Isopropyl	57.07	55.79	3.23	−1.28
Butyl	70.76	69.57	3.16	−1.19
		Mean	3.18	−1.22

[a] This work. [b] A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943).

Price and Gillis[15] drew attention to the fact that (B ← O) is negative, −1.75, which is the mean of two values from published data on boron trifluoride etherate. This is one coördinate bond for which the bond refraction of the normal covalence is also available. From literature data[28] on triethyl, tributyl, triamyl and tri-isoamyl borates, (B–O) is

(28) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956). Data for tripropyl and tri-isobutyl borates at 25° are in agreement, but from those for trimethyl borate at 20° (B–O) was found to be 1.54; this result was neglected.

found to be 1.70. It is rather higher than might be expected from the position of the elements in the periodic table; nevertheless the coördinate bond refraction is 3.4 units *less* than the normal single bond refraction. Since (P → O) is 4.4 units less than (P–O), the inference is that the P → O bond is also coördinate.

Bond Refractions in Phosphonates.—Price and Gillis[15] found a small difference between (S → O) in sulfates (−0.2) and sulfones (+0.4). To check whether a similar difference exists between (P → O) in phosphates and phosphonates it was required to know also (C–P), which may be obtained from R_D for trialkylphosphines. For tripropyl-, tributyl- and triamylphosphine at 25°, R_D is 53.94, 67.83 and 81.67, respectively.[29] These values may be used if a temperature correction is applied, which can be obtained by differentiating the expression for molecular refraction.[30] For phosphines, the temperature coefficients of density and refractive index are both unknown, but a conservative estimate based on published data for amines[31] is −0.001 and −0.0005 unit per degree, respectively. Using these values, the corrected R_D's become 53.86, 67.73 and 81.55 from which the mean (C–P) at 20° is 3.60.[32]

Molecular refractions calculated using (C–P) 3.60 and (P → O) −1.22 (shown in parentheses) may now be compared with the experimental values for diethyl ethylphosphonate 40.73 (40.69), diethyl vinylphosphonate 40.24 (40.19) and diethyl allylphosphonate 45.01 (44.84). The agreement is sufficiently good for the same bond refraction to be used for P → O in phosphonates as in phosphates.[33]

The molecular refraction of diethyl vinylphosphonate may also be calculated from that of diethyl allylphosphonate by subtracting [(C–C)+2(C–H)], giving 40.37. Direct comparison with the experimental value, 40.24, shows that there is no exaltation. The same absence of exaltation was noted in methyl vinyl sulfide, sulfoxide and sulfone by Price and Gillis,[15] and was considered to support the formulation of S → O as a coördinate bond.

Conjugation of the P–O Bond.—The effect of conjugation of P → O with C=C may be seen by comparing the infrared stretching frequencies of these bonds in diethyl allylphosphonate (III) and diethyl vinylphosphonate (IV) and by making a cross-comparison with the analogous compounds

(29) W. J. Jones, W. C. Davies and W. J. C. Dyke, *J. Phys. Chem.*, **37**, 583 (1933).
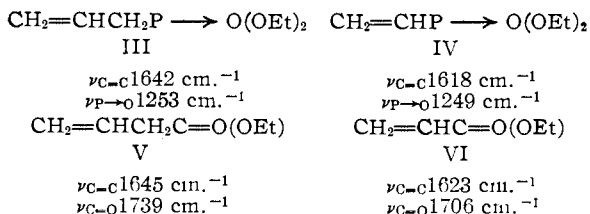
(30) N. Bauer and K. Fajans in "Physical Methods of Organic Chemistry," 2nd ed., edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1949, Part 2, Chap. 20.

(31) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950.

(32) From the properties of triethylphosphine at 18.6° given by Zecchini (*Gazz. chim. ital.*, **23**, I, 97 (1893)), (C–P) corrected to 20° is 3.76. The discrepancy is so great that this result has been disregarded.

(33) It has been pointed out by a referee that atomic refractions are not interchangeable between phosphates and phosphonates, and that the agreement found for bond refractions may be due to compensating errors. It is true that (C–P) is assumed to be the same in phosphonates as in phosphines, and any error here will be reflected in (P→O). The same assumption that (C–S) is constant was made for sulfides, sulfoxides and sulfones, where differences in (S→O) *were* found. Further theoretical deductions would be improper, but the figures may be used validly to calculate the expected R_D for new compounds.

containing the C=O group, ethyl vinylacetate (V) and ethyl acrylate (VI).

CH$_2$=CHCH$_2$P ⟶ O(OEt)$_2$　　CH$_2$=CHP ⟶ O(OEt)$_2$

III　　　　　　　　　　　　　　　　　IV

ν_{C-C}1642 cm.$^{-1}$　　　　　　　　ν_{C-C}1618 cm.$^{-1}$

$\nu_{P\to O}$1253 cm.$^{-1}$　　　　　　　　$\nu_{P\to O}$1249 cm.$^{-1}$

CH$_2$=CHCH$_2$C=O(OEt)　　CH$_2$=CHC=O(OEt)

V　　　　　　　　　　　　　　　　　VI

ν_{C-C}1645 cm.$^{-1}$　　　　　　　　ν_{C-C}1623 cm.$^{-1}$

ν_{C-O}1739 cm.$^{-1}$　　　　　　　　ν_{C-O}1706 cm.$^{-1}$

There is a shift of 33 cm.$^{-1}$ in $\nu_{C=O}$ from V to VI, but there is no comparable shift in $\nu_{P\to O}$ from III to IV; the difference, 4 cm.$^{-1}$, is just outside the limit of experimental error. The shift in ν_{C-C} is of the same order in both pairs of compounds.

Moffitt[8] has demonstrated mathematically that if the sulfur–oxygen bond in sulfones is a four-electron bond, the second pair of electrons will occupy an orbital formed by hybridization of a 2p oxygen orbital and a 3d sulfur orbital. He also demonstrated that this hybrid orbital can interact in conjugation with the π-orbital in a carbon–carbon double bond. If the same argument applies to phosphorus, and if conjugation does occur, it would be expected that $\nu_{P\to O}$ would be substantially

shifted. The small observed change in $\nu_{P\to O}$ is more in accord with the type of resonance postulated by Price and Gillis for methyl vinyl sulfone.[15] The π-electrons of the carbon–carbon double bond may occupy a vacant 3d orbital affecting $\nu_{C=C}$ to about the same extent as in full conjugation. The P → O bond as a two-electron bond is incapable of conjugation so that there is no major change in $\nu_{P\to O}$. The conjugation of C=C with the vacant 3d orbital will reduce slightly the fractional positive charge on the phosphorus atom, leading to a correspondingly small decrease in $\nu_{P\to O}$. In agreement with this explanation, the ultraviolet spectrum indicates weak conjugation in IV, and Ford-Moore and Williams report that nucleophilic addition to the double bond in this compound is negligibly slow.[23]

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Methylene Derivatives as Intermediates in Polar Reactions. XII. Isopropoxyfluoromethylene[1]

BY JACK HINE AND KOZO TANABE

The reaction of chlorodifluoromethane with potassium isopropoxide has been found to produce isopropyl difluoromethyl ether, triisopropyl orthoformate and about 5% of fluoroform with a total yield in excess of 93%. This reaction is shown to involve the initial dehydrochlorination of the haloform to the reactive intermediate, difluoromethylene. All of the plausible paths for the transformation of this intermediate to triisopropyl orthoformate go through either isopropoxyfluoromethylene or isopropyl difluoromethyl ether. Thus, the observation that isopropyl difluoromethyl ether is quite stable under the reaction conditions shows that the triisopropyl orthoformate must be formed via the intermediate isopropoxyfluoromethylene. The yield of orthoformate falls from more than 30% at potassium isopropoxide concentrations around 0.5 M and approaches zero at zero isopropoxide ion concentration. From the nature of the variation in orthoformate yield with base concentration, additional details about the reaction mechanism are learned.

Introduction

Methylene is formed by such *homolytic* reactions as the photolysis of ketene and the photolysis and pyrolysis of diazomethane[2] and it appears very likely that methylene derivatives are formed by the decomposition of other diazo compounds and perhaps also in certain other homolytic processes.[3] Many of the *polar* reactions for which methylene-type intermediates have been suggested,[4] such as the formation of stilbene derivatives from benzyl

halides and alkali,[5] have been disproved,[6,7] or seem very unlikely, or at best can be explained reasonably without the hypothesis of methylene intermediates. The suggestion that the basic hydrolysis of haloforms involves the intermediate formation of dihalomethylenes still seems plausible, however.[8] The hypothesis that alkoxyhalomethylenes are intermediates in the reactions of haloforms with

(1) For part XI see ref. 15. This work was supported in part by the Office of Naval Research.

(2) H. Staudinger and co-workers, *Ber.*, **44**, 2197 (1911); **45**, 501 (1912); **46**, 1437 (1913); F. O. Rice and A. L. Glasebrook, THIS JOURNAL, **56**, 2381 (1934); T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).

(3) L. Wolff, *Ann.*, **394**, 23 (1912); B. Eistert, *Ber.*, **68**, 208 (1935); J. Dacey and J. Hodgins, *Can. J. Research*, **28B**, 90, 173 (1950); J. L. Margrave and K. Wieland, *J. Chem. Phys.*, **21**, 1552 (1953); R. K. Brinton and D. H. Volman, *ibid.*, **19**, 1394 (1951); G. B. Kistiakowsky and B. H. Mahan, *ibid.*, **24**, 922 (1956).

(4) J. U. Nef, *Ann.*, **270**, 267 (1892); **280**, 291 (1894); **287**, 265 (1895); **298**, 202 (1897); H. Scheibler, *Ber.*, **59B**, 1022 (1926); **60B**, 554 (1927).

(5) A. Michael, THIS JOURNAL, **42**, 870 (1920); E. Bergmann and J. Hervey, *Ber.*, **62B**, 893 (1929).

(6) F. Adickes, *ibid.*, **60B**, 272 (1927); **63B**, 3012 (1930); A. E. Arbusow, *ibid.*, **64B**, 698 (1931); D. Wood, Jr., and F. W. Bergstrom, THIS JOURNAL, **55**, 3314 (1933); F. Beyerstadt and S. M. McElvain, *ibid.*, **58**, 529 (1936); S. M. McElvain and R. L. Clarke, *ibid.*, **69**, 2661 (1947).

(7) E. Kleucker, *Ber.*, **62B**, 2587 (1929); C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956); cf. M. S. Kharasch, W. Nudenberg and E. K. Fields, *ibid.*, **66**, 1276 (1944).

(8) A. Geuther, *Ann.*, **123**, 121 (1862); J. Hine, THIS JOURNAL, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956); J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis Hokkaido Univ.*, **3**, 119, 147 (1955).