Nuclear Magnetic Resonance Studies of Isobutylene, Propylene, and 2,3-Butanediol Phosphites and Phosphates

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The nmr spectra of seven five-membered ring phosphites and three phosphates have been analyzed exactly in terms of chemical shifts and coupling constants. Both the proton and phosphorus spectra were utilized in the analysis. The phosphorus-proton coupling constants are consistent with a twist-envelope conformation for the five-membered ring. Data obtained from the isobutylene phosphites indicate that the twist in the five-membered ring increases with increasing alkyl substitution of the ring.

Our interests in the synthesis of cyclic five-membered ring phosphate esters from analogous phosphite precursors have led us to examine the stereochemical stability of trivalent phosphorus and the conformational preferences in these systems. All recent nmr studies[1-4] of cyclic phosphites have agreed that inversion at phosphorus is very slow. Haake, *et al.*,[3] have reported a detailed nmr analysis of ethylene sulfite and a series of ethylene phosphites and concluded that these systems exist in a twist–envelope conformation with a ring O–C–C–O dihedral angle of approximately 30°. We have examined a series of isobutylene and propylene phosphites and the corresponding phosphates by detailed nmr analysis and now report our findings in this paper.

Experimental Section

Spectra.—Proton and phosphorus nmr spectra were obtained using a Varian Associates HA-100 spectrometer operating at 100 and 40.5 MHz, respectively, with a probe temperature of 29°. Neat solutions containing 2% TMS as lock signal source and internal reference were used for the proton spectra of the phosphites. Identical solutions were used for the phosphorus spectra except that P_4O_6 was used as an external reference and lock signal source. ^{31}P chemical shifts were not corrected for bulk susceptibility differences. Spectra of the phosphates were obtained from 10% solutions in chloroform-*d*. All measurements were made in the frequency sweep mode. Calibration of the spectra was by the frequency difference technique. Line positions were obtained by averaging the results of two upfield and downfield scans. A scan width of 50 Hz was used with a sweep time of 1000 sec. Variable temperature experiments were performed on a Hitachi R-20 spectrometer.

Methyl Isobutylene Phosphite[5,6] **(Ia).**—The procedure described for preparation of this ester is typical for synthesis of esters Ib, Ic, and Id also. To a 250-ml three-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and dropping funnel was added 0.25 mol of isobutylene phosphorochloridite (If) dissolved in 90 ml of dry ether. The dropping funnel was charged with 0.25 mol of dry methanol and 0.25 mol of dry pyridine. The alcohol–pyridine solution was added dropwise over a period of 1 hr maintaining the temperature between 0 and 10°. After the addition was completed, the amine hydrochloride was removed by suction filtration and the solvent was evaporated under vacuum. The crude phosphite ester was distilled: bp 35° (4.3 mm), yield 65%.

Isopropyl isobutylene phosphite (Ib) had bp 33° (1.7 mm), yield 41%.

tert-**Butyl isobutylene phosphite** (Ic) had bp 30° (0.8 mm), yield 61%.

Phenyl isobutylene phosphite (Id) had bp 60° (0.2 mm), yield 75%.

Isobutylene Phenylphosphonite (Ie).—A procedure similar to that used for the preparation of isobutylene phosphorochloridite was employed with dichlorophenylphosphine replacing phosphorus trichloride, bp 61° (0.2 mm), yield 37%.

Isobutylene Phosphorochloridite (If).—The preparation followed the procedure given by Azubuzov and Azanovskaya[7] with modification. In a 1000-ml three-necked flask equipped with a mechanical stirrer, alcohol thermometer, nitrogen inlet, and two 250-ml dropping funnels was placed 400 ml of dry ether and 80 g (1 mol) of dry pyridine. The flask and its contents were cooled to −20 to −30° in an acetone–Dry Ice bath. 2-Methyl-1,2-propanediol (45 g, 0.5 mol), dried over potassium carbonate, was dissolved in 200 ml of dry ether and placed in one dropping funnel. Freshly distilled phosphorus trichloride (69 g, 0.5 mol) dissolved in 200 ml of dry ether was added to the remaining dropping funnel. Both solutions were added dropwise, simultaneously, over a period of approximately 6 hr. The temperature of the reaction was maintained between −10 to 0° during the addition. Upon completion of the addition, the solution was heated under reflux for 30 min. The pyridinium chloride was removed by suction filtration and the solvent was evaporated under vacuum. The crude material was then vacuum distilled, bp 33° (4.5 mm), yield 20 g (26%).

tert-**Butyl Propylene Phosphite (II).**—Propylene phosphorochloridite was prepared in a manner similar to that given for If, using 1,2-propanediol in place of 2-methyl-1,2-propanediol. The chloridite was then treated with *tert*-butyl alcohol to produce the corresponding *tert*-butyl ester. The crude product was vacuum distilled, bp 32° (3.6 ml), quantitative yield (based on the phosphorochloridite).

tert-**Butyl (*dl*)-2,3-Butanediol Phosphite (III).**—A mixture of meso and *dl* isomers of methyl 2,3-butanediol phosphite was prepared by the method of Denney, *et al.*[8] A solution of 20 g of the mixture of esters in a large excess of *tert*-butyl alcohol was heated under reflux for about 12 hr in a dry nitrogen atmosphere. The alcohol solvent was removed by distillation and the resulting isomeric mixture of *tert*-butyl 2,3-butanediol phosphites was separated by vacuum distillation on a Teflon spinning band column. The *dl* phosphite distilled at 38° (10 mm) and the meso at 42° (10 mm).

Preparation of the Phosphate and Phosphonate Esters (IVa–c).—The appropriate phosphite or phosphonite ester was dissolved in 50 ml of petroleum ether (bp 30–60°) and the solution was cooled in an ice bath. Nitrogen dioxide was bubbled through the mixture until a light green color was observed in the solution. The solvent was removed under vacuum and the phosphate was purified on a modified Hickman still at 0.15 mm. Yields were about 90–95% of theory.

Results

The numbering used in this paper corresponds to the following structure.

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(2) D. Gagnire, J. B. Robert, J. Verrier, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3719 (1966).

(3) P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, **90**, 715 (1968).

(4) H. Goldwhite, *Chem. Ind.* (*London*), 495 (1964).

(5) For an alternative method of preparation, see ref 8.

(6) We have chosen to use the nomenclature system which emphasizes the phosphorus portion of the molecule rather than the more exact, yet more cumbersome, heterocyclic nomenclature. Thus, the alkyl isobutylene phosphite esters correspond to 2-alkoxy-4,4-dimethyl-1,3,2-dioxaphospholanes, the alkyl propylene phosphites to 2-alkoxy-4-methyl-1,3,2-dioxaphospholanes, and the alkyl 2,3-butanediol phosphites to 2-alkoxy-4,5-dimethyl-1,3,2-dioxaphospholanes.

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TABLE I

^{1}H NMR PARAMETERS FOR THE ISOBUTYLENE PHOSPHITES AND PHOSPHATES[a]

Compd	ν_1[b]	ν_2	ν_3	ν_4	J_{34}[c]	J_{35}	J_{45}
Methyl isobutylene phosphite (Ia)	1.447	1.248	3.796	3.802	−8.45	13.43	0.29
Isopropyl isobutylene phosphite (Ib)	1.437	1.228	3.738	3.826	−8.32	12.99	0.27
tert-Butyl isobutylene phosphite (Ic)	1.440	1.206	3.714	3.874	−8.25	13.20	0.32
Phenyl isobutylene phosphite (Id)	1.479	1.336	3.723	3.803	−8.32	13.12	0.31
Isobutylene phenylphosphonite (Ie)	1.215	1.211	3.726	3.331	−8.80	13.95	0.39
Isopropyl isobutylene phosphate (IVa)	1.487	1.524	4.114	4.036	−8.75	14.26	9.28
Phenyl isobutylene phosphate (IVb)	1.383	1.485	4.108	3.965	−9.08	11.35	11.01
Isobutylene phenylphosphonate (IVc)	1.472	1.618	4.286	4.095	−8.99	13.55	8.05

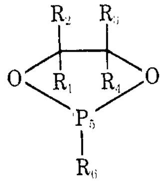
[a] Numbering used is that given in the text. [b] In parts per million downfield from internal TMS. [c] In hertz.

TABLE II

^{1}H NMR PARAMETERS FOR *tert*-BUTYL PROPYLENE AND *tert*-BUTYL (*dl*)-2,3-BUTANEDIOL PHOSPHITE[a]

Compd	ν_1[b]	ν_2	ν_3	ν_4	J_{12}[c]	J_{13}	J_{14}	J_{24}	J_{34}	J_{15}	J_{25}	J_{35}	J_{45}
tert-Butyl propylene phosphite (II)	4.486	1.217	3.368	4.167	6.17	6.57	6.53		−8.22	0.40	0.74	8.17	1.94
tert-Butyl (*dl*)-2,3-butanediol phosphite (III)	1.328	3.593	1.279	4.027	6.09			8.20	6.07	0.72	4.20	0.48	0.72

[a] Numbering used is that given in the text. [b] In parts per million downfield from internal TMS. [c] In hertz.



Ia, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = OCH_3
Ib, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = $OCH(CH_3)_2$
Ic, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = $OC(CH_3)_3$
Id, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = OC_6H_5
Ie, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = C_6H_5
If, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = Cl
II, R_1, R_3, R_4 = H; R_2 = CH_3; R_6 = $OC(CH_3)_3$
III, R_1, R_3 = CH_3; R_2, R_4 = H; R_6 = $OC(CH_3)_3$
IVa, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = O, $OCH(CH_3)_2$
IVb, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = O, OC_6H_5
IVc, R_1, R_2 = CH_3; R_3, R_4 = H; R_6 = O, C_6H_5
V, R_1, R_2, R_3, R_4 = H; R_6 = OCH_2CH_3

Spectra were analyzed in terms of chemical shifts and coupling constants using the computer program LAOCN3.[9] Both the ^{1}H and ^{31}P spectra were utilized in the analysis. Results obtained for the proton parameters are given in Tables I and II. Chemical shifts and coupling constants for the methyl protons on the five-membered ring and for the alkoxyl groups of all compounds are those obtained from a first-order analysis. A typical spectrum is that of *tert*-butyl isobutylene phosphite (Ic) shown in Figure 1. Results obtained at 60 MHz confirm that the appearance of the spectrum is not due to an unusually large phosphorus coupling constant but is due to the magnetic nonequivalence of the two methylene hydrogens and of two methyl groups. The methylene protons show a typical AB pattern when the spectrum is obtained while decoupling phosphorus.

The protons of the isobutylene phosphites were assigned from comparison of the parameters of the various compounds and from considerations of models of the compounds. All the isobutylene phosphites studied, with the exception of Ie, have similar chemical shifts and coupling constants. In Ie, one methyl group and methylene proton are shifted upfield considerably, whereas the other methyl group and methylene proton have shifts similar to one of the methyl and methylene protons in Ia–d. Inspection of a model of Ie in the envelope conformation reveals that the methyl and methylene protons cis to the phenyl ring are located in a position such that they should be upfield due to the anisotropic effect of the phenyl substituent.[10] The phenyl substituent should have little effect on the shifts of the methyl and methylene protons trans to the substituent. Therefore, those protons shifted upfield in Ie are assigned to those cis to the phenyl ring and those protons unaffected are assigned as being trans to the phenyl substituent. Thus, the methyl and methylene protons trans to the substituent on phosphorus in Ia–d are assigned as those appearing at highest field. Similar conclusions are reached on the basic of steric arguments. The assignment of II and III follows from the above arguments. This assignment is in complete agreement with that of Gagnaire, *et al.*,[2] who assigned the proton with the largest P–H coupling in the *meso*- and *dl*-2,3-butanediol phosphorochloridites as cis to the electron pair on phosphorus.

The spectra of the isobutylene phosphates (IVa–c) also show two nonequivalent methylene protons and methyl groups. However, the two P-O-C-H coupling constants are quite different in IVa and IVc and approximately equal in IVb. Ramirez, *et al.*,[11] have also observed a large difference between the phosphorus–proton coupling constants of a similar compound and attributed this to a difference in the dihedral angle between phosphorus and the ring protons. The methyl group and methylene proton appearing a lower field in IVa–c are assigned as those cis to the phosphoryl oxygen. It is reasonable that a reversal in chemical shifts should occur between I and IV as a result of the phosphoryl–oxygen bond in IV. This assignment of the protons in IV is consistent with the assignment in I in that the larger phosphorus–proton coupling constant results from the proton trans to the

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(11) F. Ramirez, A. V. Patwardham, N. B. Desai, and S. R. Heller, *J. Amer. Chem. Soc.*, **87**, 549 (1965).

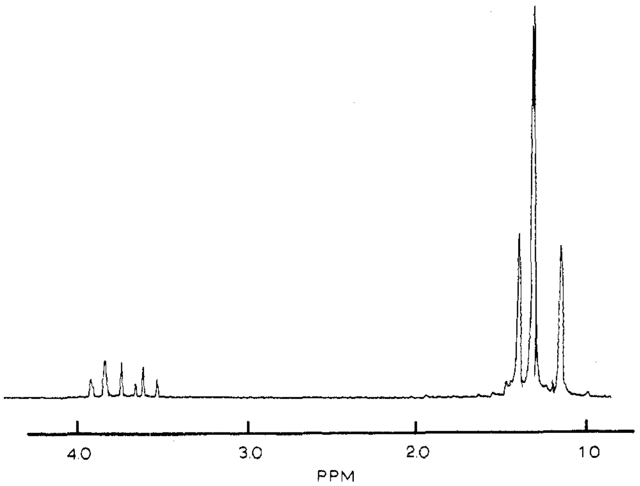

Figure 1.—The 100-MHz nmr spectrum of *tert*-butyl isobutylene phosphite (Ic).

alkoxyl group on phosphorus. A long-range coupling $^4J_{\text{H-H}}$ of 0.35 and 0.55 Hz is observed between the methyl protons cis to the alkoxyl substituent and the methylene proton trans to the substituent on phosphorus in IVa and IVc, respectively.

Discussion

Conformation of the Five-Membered Ring.—The complete analysis of the nmr spectra of compounds I–IV clearly demonstrates the nonequivalence of the methyl and methylene protons. Earlier studies on alkyl pinacol phosphites,[1] ethylene phosphites, ethylene chlorophosphites,[2,3] and propylene chlorophosphite[10] have shown that these compounds also possess nonequivalent protons. However, two explanations of the different magnetic environments in these compounds have been offered: (1) a stable pyramidal stereochemistry at phosphorus with an essentially planar five-membered ring[1,2,4] and (2) a twist-envelope conformation of the five-membered ring with a O–C–C–O dihedral angle of ~30°.[3] While it is true that a stable pyramidal configuration at phosphorus would account for the nonequivalence of the methyl and methylene protons in I–IV, there are other factors which require a nonplanar five-membered ring. Furthermore, earlier investigations of ethylene phosphorochloridites[2,3] have resulted in two explanations of the different P–O–C–H coupling constants observed in compounds of this type. It has been suggested that the different couplings arise from a dependence of the coupling on dihedral angle[3] and from the influence on the lone pair on phosphorus.[2]

Recent nmr data from six-membered ring phosphites,[12] phosphates,[12,13] and phosphonates[14] indicate a dependence of vicinal proton–phosphorus coupling constants on dihedral angle similar to that observed for proton–proton coupling constants.[15] The different values observed for J_{PH_3} and J_{PH_4} (13 and 0.3 Hz, respectively) in Ia–e could be taken to indicate different dihedral angles (~180 and 90°, respectively, based on models[3]). The observed coupling constants necessitate an important contribution of the envelope conformation, since different P–O–C–H dihedral angles would be found only when the five-membered ring is in an envelope conformation. Since the above arguments have been based on the different phosphorus–proton coupling constants observed in Ia–e, one cannot rule out the possibility that the different coupling constants arise from the orientation of the protons with respect to the lone pair on phosphorus.[2] While this interpretation has been shown for the different P–C–H couplings in phosphines,[16,17] the influence of the phosphorus lone pair on the coupling constants has been shown to be negligible in six-membered ring phosphites. There are at least two factors which necessitate some contribution from twisting of the five-membered ring. (1) If the five-membered ring were either planar or in an envelope conformation, expected P–O–C–H couplings in the isobutylene phosphites, I, would be of similar magnitude to those observed for the ethylene phosphites.[2,3] The larger P–O–C–H couplings observed in I (13.0 *vs.* 9.0 Hz) are therefore incompatible with a planar five-membered ring. (2) Considering the propylene phosphite (II) as a model, replacement of a proton trans to the phosphorus lone pair with a methyl group, as in the isobutylene phosphites Ia–e, should not alter the influence of the phosphorus lone pair on the coupling constant between the remaining cis proton (H-3) and phosphorus. However, significantly different P–O–C–H coupling constants are observed in I compared to II.

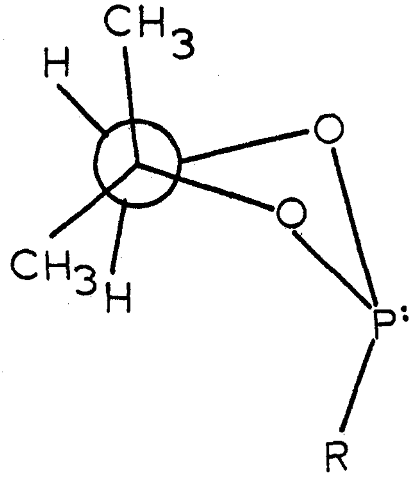

Figure 2.—Twist-envelope conformation of five-membered ring phosphites.

The different P–O–C–H coupling constants (Table I) observed for IVa–c most likely arise from different phosphorus–proton dihedral angles, as suggested by Ramirez, *et al.*[11] Different dihedral angles would be obtained if the five-membered ring were in twist–envelope conformation. The data for IVa and IVc indicate that the degree of twist is similar to that in I. For IVb, however, the phosphorus–proton coupling constants indicate that the ring is closer to being planar on the average than in IVa and IVc. The long-range $^4J_{\text{H-H}}$ coupling constants also support this

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[17] H. Goldwhite and D. G. Rowsell, *ibid.*, 1665 (1968).

view. In the sterically more favorable twist conformation of IV, the methyl group trans to the alkoxyl group on phosphorus and the cis methylene proton have a dihedral angle of ~180°. Couplings of 0.35 and 0.55 Hz are observed in IVa and IVc, respectively. As the ring becomes more planar, the CH_3–C–C–H dihedral angle decreases towards 90°. The $^4J_{HH}$ long-range coupling was not observed in IVb. Therefore, both the phosphorus–proton and proton–proton coupling constants support the view that IVa and IVc exist in a twist–envelope conformation similar to I while in IVb the twist in the five-membered ring is, on the average, smaller.

Thus, the nmr data for Ia–e and IVa–c are not consistent with a planar ring but are in accord with a twist–envelope conformation of the five-membered ring similar to that proposed for methyl ethylene phosphite[3] (Figure 2). Haake, *et al.*,[3] have proposed a value of ~30° for the twist in the ring based on considerations of the vicinal H–H coupling constants. The coupling constants in II and III are consistent with this value, whereas the larger P–O–C–H couplings in I and IV suggest a somewhat larger degree of twist.[18] Increased twisting of the ring is not unexpected, since the steric interactions of ring substituents with the alkyl group on phosphorus are greater for isobutylene phosphites and phosphates than for the ethylene phosphites.

The question of the orientation of the alkoxyl group attached to phosphorus with respect to the five-membered ring is significant. X-Ray analysis of methyl ethylene phosphate[19] shows the methyl group to be centered over the ring between the two ring oxygen atoms, whereas in methyl pinacol phosphate[20] the methyl group is directed away from the ring because of steric crowding by the ring methyl groups. If the phenyl group in Id were folded back over the ring, some shielding of the methyl and methylene protons cis to the phenyl group should be observed, since they would be located directly over the plane of the phenyl ring.[10] Such a conformation would result in considerable steric crowding. Since the chemical shifts in Id are similar to those in Ia–c, II, III, and IVa–c, the alkyl groups must be directed away from the five-membered ring in these phosphites and phosphates.

The spectra of all compounds reported here were examined at various temperatures up to 150°. No significant changes were observed in any of the spectra, indicating that inversion at phosphorus is extremely slow within this temperature range relative to the nmr time scale. For *tert*-butyl propylene phosphite, both cis and trans isomers are present. The ratio of trans to cis isomers is 2.03:1, a value slightly larger than that found for methyl propylene phosphite (1.55:1).[4]

Nmr Parameters.—The magnitude of the geminal H–H coupling constants (Tables I and II) agree with those obtained from other five-membered ring compounds and are in accord with the theory of geminal coupling constants.[15] Although little data is available on the dependence of P–O–C–H coupling constants on dihedral angle in phosphites, recent work with rigid six-membered ring compounds indicates values of 6 and 2 Hz for the trans and gauche coupling,[12] respectively. In ethylene phosphites, P–O–C–H coupling constants of 9.0 and 1.8 Hz were observed.[3] It appears that J_{trans} is larger in five-membered rings than in six-membered ring phosphites.[12] Slight differences in hybridization at phosphorus and carbon and in bond angles in the two systems could be responsible for this difference in coupling constants. It seems that the increase in one of the coupling constants results in a decrease in the other coupling constant. For example, in II the $J_{P-O-C-H}$ values are 8.17 and 1.94 Hz, in ethylene phosphites 9.0 and 1.8 Hz, and in Ia–e ~13.0 and 0.3 Hz. This observation would seem to support the suggestion[3] that the cyclic phosphites have P–O–C–H dihedral angles of ~180 and 90°, respectively. However, it is doubtful that the value of J_{trans} of 13 Hz is a limiting value.

The ^{31}P chemical shifts for Ia–e are given in Table III along with that of ethyl ethylene phosphite (V) for comparison.[21] With the exception of Ie, the shifts agree with those predicted from "group shift" values.[22] Jones and Katritzky[21] have pointed out the limitations of the additivity relationship; other investigators[23] have noted anomalous ^{31}P chemical shifts when an aromatic ring is attached directly to phosphorus. Although this and similar shifts[23] cannot be explained in terms of ring currents, some probable factors are a change in hybridization at phosphorus and a change in the O–P–O bond angle.

TABLE III

^{31}P CHEMICAL SHIFTS OF CYCLIC FIVE-MEMBERED RING PHOSPHITES

Compd	$\phi^{31}P^a$
Ia	−28.88
Ib	−30.55
Ic	−29.55
Id	−23.60
Ie	−57.50
II	−25.11
III	−27.42
V^b	−18.5

[a] In parts per million downfield from P_4O_6 external reference. [b] Reference 21.

Registry No.—Ia, 26964-02-3; Ib, 33835-20-0; Ic, 33835-21-1; Id, 33835-22-2; Ie, 33835-23-3; If, 31539-64-7; II, 33835-25-5; (±)-III, 33835-63-1; *meso*-III, 33835-64-2.

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