alcohols with ethylene sulfide.[10,11a] Thioalkoxy mercaptans have been prepared by the last method from mercaptans and ethylene sulfides.[11] An authentic sample of cyclohexyl β-mercaptoethyl ether was, in fact, obtained in 36% yield from cyclohexyl β-hydroxyethyl ether[7] *via* the chloride and thiocyanate; it corresponded in boiling point (89–91° (10 mm)), refractive index (n^{18}D 1.4868), and infrared spectrum to the sample listed in Table I.

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[10] R. Oda, *Mem. Fac. Eng. Kyoto Univ.*, 14, 195 (1952); *Chem. Abstr.*, **48**, 1935*c* (1954).

[11] *E.g.*, (a) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2675 (1947); (b) E. M. Meade and F. N. Woodward, *J. Chem. Soc.*, 1894 (1948); C. C. J. Culvenor, W. Davies, and N. S. Heath, *ibid.*, 282 (1949); E. P. Adams, *et al.*, *ibid.*, 2649 (1960).

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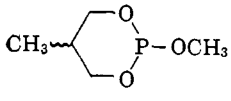
Geometric Isomerism in Six-Membered Ring Phosphites[1]

Sir:

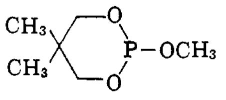
Several groups have shown that unsymmetrically substituted phosphines can be isolated in their enantiomorphic forms.[2] These substances have been of considerable value in studying the mechanisms of many reactions of phosphines. The situation with respect to other trisubstituted phosphorus compounds is much different in that no optical or geometric isomers have been available. There is a report that five-membered ring cyclic phosphites are configurationally stable about the phosphorus atom. This conclusion is based on nmr evidence alone, and no separation of these substances has been achieved.[3] It is the purpose of this report to describe the preparation of several six-membered ring phosphites. The data indicate that these materials exist as *cis* and *trans* isomers, and it has been found that these isomers can be prepared, in some cases, relatively free of each other.

Condensation of 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, *meso*-2,4-pentanediol, and a mixture of *meso*- and *dl*-2,4-pentanediol with trimethyl phosphite yielded the cyclic phosphites I–V.[4]

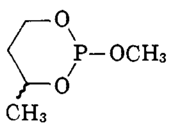
The phosphite I showed two doublets for C–CH$_3$ absorption at 0.69 ($J = 6$ cps) and 1.28 ($J = 6$ cps) ppm; their relative areas were 4:1. These absorptions are very similar indeed to those of II which occur at 0.70 and 1.18 ppm. Glpc analysis of I under several conditions has only given one major peak. Oxidation of I by *t*-butyl hydroperoxide gave a mixture of two phosphates which could be separated by glpc. The ratio of the two phosphates was essentially the same as that of the two phosphites. These phosphates had C–CH$_3$ absorptions at 0.84 ($J = 7$ cps) and 1.17 ($J = 7$ cps) ppm. The phosphate from II has C–CH$_3$ at 0.89 and 1.23 ppm.



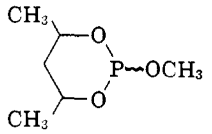
Ia,b



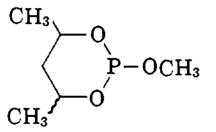
II



IIIa,b



IVa,b



V

The phosphite, III, showed C–CH$_3$ absorption at 1.15 ($J = 6$ cps) ppm. Oxidation by *t*-butyl hydroperoxide gave two phosphates, 95:5; oxidation by mercuric oxide gave the same phosphates but in different relative amounts, *ca.* 7:3. These two phosphates can be separated by distillation and glpc. They show C–CH$_3$ absorptions at 1.34 ($J = 7$ cps) and 1.39 ($J = 7$ cps) ppm; each doublet is further split by coupling to phosphorus ($J = 2$ cps). Reaction of 1,3-butanediol with phosphorus trichloride yielded the cyclic phosphorochloridite, C–CH$_3$, at 1.30 ($J = 6$ cps) ppm. Treatment of this material with sodium methoxide in ether gave IIIa and a new material, IIIb, C–CH$_3$ 1.36 ($J = 6$ cps) ppm. Glpc analysis gave two peaks which were incompletely separated. Treatment of this mixture with a trace of methanol caused rapid isomerization of IIIb to IIIa as evidenced by nmr and glpc. The relative amounts of IIIa and b obtained by this method varies rather considerably from experiment to experiment. The highest percentage of IIIb obtained to date is 72, as determined by nmr. Oxidation of this mixture with cumene hydroperoxide gave the two phosphates obtained by mercuric oxide oxidation of IIIa. The ratio of isomers in this case was 3:7, which is in agreement with that predicted by the nmr analysis of the phosphite mixture.[5]

The phosphite IVa, prepared from *meso*-2,4-pentanediol by transesterification, has C–CH$_3$ absorption at 1.15 ($J = 6$ cps) ppm. The phosphite V, from the *dl*-glycol, has C–CH$_3$ at 1.19 ($J = 6$ cps) and 1.42 ($J = 6$ cps) ppm. Treatment of a mixture of *meso*- and *dl*-glycols, *ca.* 4:1, with phosphorus trichloride gave a mixture of cyclic phosphorochloridites. This mixture was treated with sodium methoxide in ether. The product had C–CH$_3$ absorption for IVa and V. There was also C–CH$_3$ absorption at 1.25 ($J = 6$ cps) ppm. The integrated nmr spectrum indicated that the original mixture consisted of 25% IVa, 19% V, and 56% of the new material, IVb. Treatment of this mixture with a trace of methanol led to the loss of the 1.25 ppm absorption and an increase in the absorptions due to IVa.

Glpc analysis of the mixture showed that IVa and V were present. A third material was also present, as evidenced by a broadening of the IVa peak. This

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[1] Research supported by the National Institutes of Health under GM 12625.

[2] (a) W. E. McEwen, "Topics in Phosphorus Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1965, pp 1–41; (b) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

[3] H. Goldwhite, *Chem. Ind.* (London), 494 (1964).

[4] Satisfactory analyses were obtained for all compounds described here. Their integrated nmr spectra were in accord with the assigned structures. The nmr spectra were recorded on solutions in carbon tetrachloride except for those of IVa and b which were taken on benzene solutions. Tetramethylsilane was used as an internal standard throughout.

[5] See D. B. Denney and J. W. Hanifin, *Tetrahedron Letters*, No. 30, 2177 (1963), for arguments concerning the stereospecificity of hydroperoxide oxidations of trisubstituted phosphorus compounds.

broadening disappeared after treatment with methanol.[6] Qualitative oxidation experiments confirm these conclusions; thus three phosphates were obtained by cumene hydroperoxide oxidation of the mixture. These three phosphates were also obtained by oxidation of a mixture of IVa and V with mercuric oxide.

The results of these experiments are most readily explained by assuming that Ia,b, IIIa,b, and IVa,b represent pairs of geometric isomers.[7] Preparation of these materials by transesterification apparently yields the thermodynamic equilibrium mixture of each pair. This is not unreasonable; however, it is very interesting that in the pairs IIIa,b and IVa,b there is such a strong preference for one isomer. This is further evidenced by the rapid conversion of IIIb and IVb into IIIa and IVa on treatment with methanol.

The preparation of IIIb and IVb *via* the cyclic phosphorochloridites most probably involves an inversion about the phosphorus atom during the displacement by methoxide ion. Apparently the phosphorochloridites are formed in the main in one preferred configuration and this corresponds to that of the most stable phosphites. The fact that pure or nearly pure IIIb and IVb have not been obtained as yet is probably due to their isomerization under the reaction conditions.

It is clear that these geometric isomers will be of considerable value in studying the stereochemistry and mechanisms of phosphite reactions. Furthermore, it has already been observed that IIIb and IVb are considerably more reactive in the oxidation reactions than their counterparts and thus some interesting structure–reactivity effects may be in the offing.

(6) Analysis of all of these cyclic phosphites by glpc is quite difficult. Conventional instruments are totally inadequate and success when obtained has been with an instrument with glass injection ports and very low column temperatures. Even with these precautions resolution often varies from day to day in a nonpredictable manner.

(7) It could be argued that these are pairs of noninterconverting conformers. At the moment there seems to be no reason for adopting this extreme view. There are some very interesting conformational problems in this series and these will be considered when more information becomes available.

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The Insertion of Halocarbenes into the Mercury–Halogen Bond

Sir:

In 1960 Reutov and Lovtsova[1] reported a useful synthesis of trihalomethyl derivatives of mercury by the reaction of an organomercuric halide with haloform and potassium *t*-butoxide. A mechanism involving dihalocarbene insertion into the Hg–X linkage was suggested for this reaction by these authors. Our subsequent work provided strong evidence that this reaction did not occur by a dihalocarbene insertion mechanism, but rather that the trihalomethylmercury products were formed by nucleophilic attack of initially generated CX_3^- at mercury.[2] Similarly, the preparation of trichloromethylmercury compounds by the decarboxylation of sodium trichloroacetate in the presence of mercuric chloride or arylmercuric chlorides does not proceed *via* dichlorocarbene insertion into the Hg–Cl linkage.[3] Razuvaev and Vasileiskaya[4] recently have reported the formation of CCl_3HgCl by photolysis of chloroform in the presence of mercuric chloride and pyridine. A mechanism in which dichlorocarbene inserted into the Hg–Cl bond was claimed by these workers (eq 1). Convincing experimental verification of this postulated mechanism was, however, lacking, and alternative polar or radical mechanisms could well be operative in this case.

$$CHCl_3 \xrightarrow{h\nu} [\cdot CHCl_2 + \cdot Cl] \longrightarrow HCl + :CCl_2 \xrightarrow{HgCl_2} CCl_3HgCl \qquad (1)$$

Our previous studies have shown that phenyl(bromodichloromethyl)mercury reacts rapidly with olefins at 80° in benzene solution to produce phenylmercuric bromide and *gem*-dichlorocyclopropanes in high yield.[5] Evidence which strongly suggests that this CCl_2 transfer reaction involves the intermediacy of dichlorocarbene—either free or complexed with phenylmercuric bromide—has been obtained.[5–7] Consideration of preliminary kinetic data[7,8] suggested to us that the extrusion of CCl_2 from $C_6H_5HgCCl_2Br$ might be a reversible process, *i.e.*, that dichlorocarbene might insert into the Hg–X bond under *neutral* conditions. This has been found to be the case.

A mixture of 10 mmoles each of phenylmercuric chloride and phenyl(bromodichloromethyl)mercury in 25 ml of benzene was heated at reflux for 2 hr. Filtration produced a flaky, white solid which was identified by thin layer chromatography and melting behavior as phenylmercuric bromide with admixed smaller amounts of phenylmercuric chloride. The filtrate was distilled under vacuum; glpc showed the distillate to contain tetrachloroethylene (4% yield, based on $C_6H_5HgCCl_2Br$). The solid distillation residue, mp 105–109°, was recrystallized from hexane–chloroform to give 2.46 g (62%) of phenyl(trichloromethyl)mercury, mp 115.5–116.5°, whose identity was confirmed by its mixture melting point and infrared spectrum. Thus the reaction shown in eq 2 had occurred. In an identical reaction the crude, benzene-soluble solid was treated with bromine in carbon tetrachloride. Glpc analysis of the volatile cleavage products showed the presence of bromotrichloromethane (70%), dibromodichloromethane (3%), and bromobenzene (72%). Such bromine cleavage has been shown to serve well in the analysis of phenyl(trihalomethyl)mercurials.[2]

$$C_6H_5HgCl + C_6H_5HgCCl_2Br \longrightarrow C_6H_5HgCCl_3 + C_6H_5HgBr \qquad (2)$$

In a similar experiment, *p*-tolylmercuric chloride was converted to *p*-tolyl(trichloromethyl)mercury, mp 120–122°, in 57% yield. Reaction of 10 mmoles of mercuric chloride with 25 mmoles of phenyl(bromodichloromethyl)mercury in benzene at 80° gave a mixture of bis(trichloromethyl)mercury, mp 141–143°, lit.[3] mp 140–

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(1) O. A. Reutov and A. N. Lovtsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1716 (1960); *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961).

(2) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962); *J. Organometal. Chem.*, **4**, 127 (1965).

(3) T. J. Logan, *J. Org. Chem.*, **28**, 1129 (1963).

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(5) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(6) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

(7) D. Seyferth in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. IX. Organometallic Compounds," Robert A. Welch Foundation, Houston, Texas, in press.

(8) D. Seyferth and J. Y.-P. Mui, to be published.