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THE STEREOCHEMISTRY OF CERTAIN BICYCLIC PHOSPHONATES

THE MICHAELIS-ARBUZOV REARRANGEMENT WITH 1-PHOSPHA-2,8,9,-TRIOXAADAMANTANE—II[1,2]

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Abstract—Treatment of 1-phospha-2,8,9-trioxaadamantane (III) with benzyl chloride, benzhydryl chloride, and 1-(chloromethyl) naphthalene afforded a series of new bicyclic phosphonates which may be classified as derivatives of bicyclo[3.3.1]-nonane. Formation of 3-benzyl-7-chloro-2,4-dioxa-3-phosphabicyclo[3.3.1]nonane, 3-oxide (IV-a) by a stereospecific, intramolecular Michaelis-Arbuzov rearrangement is indicated by stereochemical data *via* IR and NMR analysis. Although multiple separation in the NMR spectrum of IVa at 60 Mc was insufficiently resolved, the determination at 100 Mc gave excellent line separation. The double resonance technique was employed to verify peak assignments of the protons in IVa. Conformational homogeneity of the cyclohexane ring in IVa is postulated in view of the nine line grouping for the proton in an axial position at C_1. Dipole moment measurements obtained on solutions of IVa in dioxane also support a boat-chair structure.

Since the discovery of the Michaelis-Arbuzov rearrangement in 1898,[7] the utility of the method for the synthesis of carbon-phosphorus bonds has been examined with simple phosphites[8–12] and phosphonites.[13–14] Mechanistically, the reaction involves initial formation of a quasiphosphonium salt which subsequently

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[1] We gratefully acknowledge the support of the National Institutes of Health, GM-10367-01. This paper was presented in part at the 144*th meeting of the American Chemical Society*, Los Angeles, California, April (1963).

[2] For the previous article in the series, see: K. D. Berlin, C. Hildebrand, J. G. Verkade and O. C. Dermer, *Chem. Ind.* 291 (1963).

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[4] Abstracted in part from the thesis of C. Hildebrand submitted in partial fulfillment of the Master of Science Degree, 1963.

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[6a] Varian Associates, Palo Alto, California. We thank Dr. J. Shoolery who suggested the NMR determination of IVa be made at 100 Mc.

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[7] A. Michaelis and R. Khan, *Chem. Ber.* **31**, 1048 (1898).

[8] A. E. Arbuzov, *J. Russ. Phys. Soc.* **38**, 687 (1906); *Chem. Zentr*, **77**, II 1639 (1906).

[9] G. M. Kosolapoff, *Organophosphorus Compounds*, J. Wiley, New York (1950).

[10] A. Y. Garner, E. C. Chapin and P. M. Scanlon, *J. Org. Chem.* **24**, 532 (1959).

[11] K. D. Berlin and G. B. Butler, *Chem. Revs.* **60**, 243 (1960).

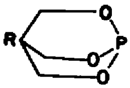
[12] H. J. Harwood and D. W. Grisley, Jr., *J. Amer. Chem. Soc.* **82**, 423 (1960).

[13] A. W. Frank, *Chem. Revs.* **61**, 389 (1961).

[14] G. O. Doak and C. D. Freedman, *Chem. Revs.* **61**, 31 (1961).

decomposes to a pentavalent phosphorous compound.[10,15–19] While our work was in progress, data was released on the stereochemical transformation which occurred when certain bicyclic phosphites (I) were treated with alkyl halides.[20] The inherently unstable boat conformer was presumably converted to the thermodynamically more stable chair form (II). The present work was undertaken in an effort to gain further insight into the breakage of oxygen-phosphorus bonds in cyclic systems and to determine the stereochemistry of the ring-opening process. It was anticipated that the tricyclic phosphite (III) should yield derivatives of the bicyclo[3.3.1]nonane class. In addition, there was considerable indication that such bicyclic phosphonates (IV) could be of biological significance in view of their structural similarity to the cyclic phosphorylated hexoses which are recognized intermediates in the metabolism of carbohydrates.[21]

A new bicyclic phosphonate, 3-benzyl-7-chloro-2,4-dioxa-3-phosphabicyclo-[3.3.1]nonane, 3-oxide (IVa), was recently announced from this Laboratory along with an improved procedure for the precursor (III).[2] Elemental and IR analyses as well as the molecular weight determination supported the monomeric structure (IVa). The successful preparation of two additional bicyclic phosphonates IVb and IVc are now reported. Moreover, an exhaustive study of the stereochemistry of IVa was made in an effort to elucidate the mechanism of the ring-opening process.



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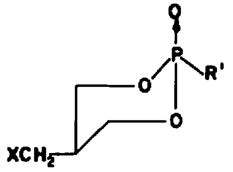
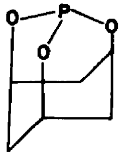
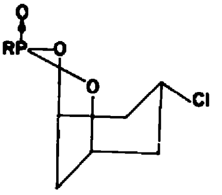


II



III



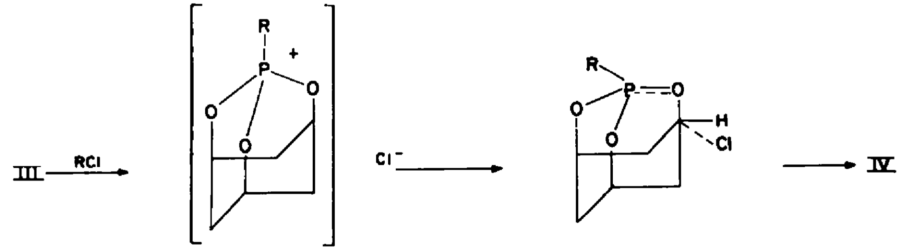
IVa = $C_6H_5CH_2$
IVb = $(C_6H_5)_2CH$
IVc = $1\text{-}C_{10}H_7CH_2$

When III was heated at 110° over forty-eight hours with benzhydryl chloride or 1-(chloromethyl)naphthalene, IVb and IVc were obtained in yields of 63% and 20%, respectively. As in the previous case with IVa,[2] purification of the two phosphonates was tedious. Several recrystallizations from a petroleum ether–methylene

[15] S. R. Landauer and H. N. Rydon, *Chem. Ind.* 313 (1951).
[16] W. Gerrard and G. J. Jeacocke, *J. Chem. Soc.* 3647 (1954).
[17] T. C. Meyers, S. Pries and E. V. Jensen, *J. Amer. Chem. Soc.* **76**, 4172 (1954).
[18] J. I. G. Cadogan, *Quart. Revs.* **16**, 208 (1962).
[19] F. C. Buck and J. T. Yoke, *J. Org. Chem.* **27**, 3675 (1962).
[20] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.* **84**, 610 (1962).
[21] H. G. Khorana, *Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest*, J. Wiley, New York (1961).

chloride system followed by vacuum sublimation were required to give analytically pure IVb. Chromatography of the crude rearrangement product on alumina and recrystallization of the major fraction yielded pure IVc. Although the bicyclic esters did not appear hygroscopic, samples exposed to the atmosphere melted over a range and were best preserved in a vacuum desiccator. Table 1 contains pertinent data on the new compounds.

Kinetic data made available recently support a two-step process for the Michaelis-Arbuzov rearrangement in simple phosphites.[19] Rapid formation of an ionic intermediate which slowly decays to a phosphonate is believed to occur. Relief of compressional strain might be anticipated in the ionic intermediate leading to IVa since bonding to phosphorus is altered from trigonal to near tetrahedral. At the same time suspected distortion of the COP angle of the intermediate could induce collapse of the salt. Initiation of such a decomposition would be expected to involve an intramolecular, nucleophilic attack of chloride ion at a bridgehead carbon atom. However, two alternative pathways are apparent for rupture of the carbon-oxygen bond. Cleavage to create a carbonium ion at C_1 would be expected to yield two cyclohexyl derivatives, one with chlorine in the equatorial conformation and the other possessing an axial chlorine atom. Product analysis of the reaction mixture containing IVa revealed III as the only other component. It is reasonable to postulate that a nucleophilic attack by chloride ion occurs, *via* an S_N2 mechanism, with simultaneous carbon-oxygen bond severance. This sequence obligates the chlorine atom to the equatorial position since the hydrogen atom at C_1 would be forced into an axial conformation. Assumption is made that the bridge connecting C_3 and C_5 does not allow total inversion of the cyclohexane ring in the molecule during the ring-opening step.[22] Conformer-1 is a reasonable structure and is favoured from studies with models. The chair-chair conformer-2 possesses seemingly intolerable repulsive forces between proton *a* and the phosphoryl oxygen atom O_8 while considerable 1,4-interaction is indicated between chlorine and proton *f* in conformer-3. Comparable to this structural ambiguity is the severe *trans*-annular interaction between C_3 and C_7 in bicyclo[3.3.1]nonane (V).[23] Apparently the boat-chair conformer is favoured although an X-ray analysis of a crystal could not be found in



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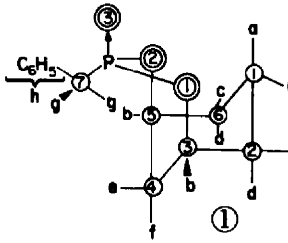
[22] Obviously, C_1 could invert after the decomposition to give conformer-3. Models favor conformer-1 since there is virtually no interference between protons *e* and *f* and phosphorus. Protons *g* appear sufficiently removed from the system that potential restricted rotation by proton *e* is monor. More serious nonbonded interaction between proton *e* and the benzene ring is apparent if the ring is rotated 180° from its position in conformer-1.

[23] For a discussion of the bicyclo[3.3.1]nonanes, see: E. L. Eleil, *Stereochemistry of Carbon Compounds*, chap. 10. McGraw-Hill, New York (1962).

TABLE 1. BICYCLIC PHOSPHONATES

R	Reaction		M. P. (C°)	Yield (%)	Analysis							
					Calculated				Found			
	Temp (C°)	Time (hr)			C	H	P	Cl	C	H	P	Cl
$C_6H_5CH_2$ IVa	110	24	199·5–200·5	66	54·46	5·63	10·80	12·37	54·26	5·57	10·84	12·20
$(C_6H_5)_2CH$ IVb	110	48	219·5–220·5	63	62·90	5·56	8·54	9·77	62·60	5·77	8·68	9·42
1-$C_{10}H_7CH_2$ IVc	110–140	28	179–180	20	60·63	5·40	9·21	10·55	60·58	5·54	8·96	10·47



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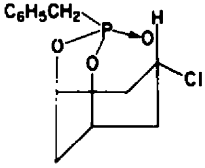

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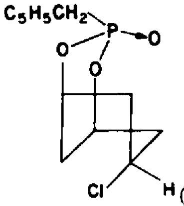
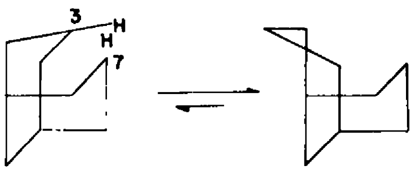
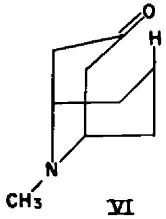


③

the literature. In pseudopelletierene (VI) the methylene group is replaced by a carbonyl function which supposedly allows for a chair-chair form[23] although some disagreement has been expressed on this point from considerations of models.[24] Courtauld models demonstrate that the chair-chair conformer-2 is not a good candidate because of the spatial requirements of the phosphoryl oxygen atom (O_3) and proton *a*. The O_3—H_I distance was calculated to be 0·90 Å in conformer-2 assuming a perfect chair-chair model. In contrast conformer-1 in a perfect boat-chair arrangement would have a value of 4·04 Å for the O_3—H_I separation.[25]



V



VI

IR analysis of IVa,[2] IVb and IVc support the postulated structures of the bicyclic esters. Principal absorption for IVb occurred at 1257 (phosphoryl group), 1014 (P—O—C linkage),[26] 734 (equatorial chlorine),[27–29] and 703 cm^{-1} (monosubstituted benzene).[28] Peaks are exhibited by the naphthylmethyl analog IVc at 1256 (phosphoryl group), 1017 (P—O—C), 742 (equatorial chlorine), and at 779 and 759 cm^{-1} (naphthalene ring).[28] In contrast only very weak bands appear below 700 cm^{-1} in IVa and IVc while strong absorption is normally expected near 688 cm^{-1} for axial chlorine in cyclohexane compounds.[27] The absence of any band below 700 cm^{-1} in the spectrum is considered evidence against the presence of axial chlorine in the

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[24] For a critical evaluation of this stereochemical enigma, see; N. J. Leonard, D. F. Morrow and M. T. Rogers, *J. Amer. Chem. Soc.* **79**, 5476 (1957).

[25] Atomic radii for oxygen and hydrogen have been reported as 0·60 and 0·37 Å, respectively; M. C. Neuburger, *Z. Krist.* **93**, 1 (1936). The total of 0·97 Å would surely not permit a perfect chair-chair conformer to exist.

[26] L. W. Daasch and D. C. Smith, *Analyt. Chem.* **23**, 853 (1951).

[27] M. Larnandie, *C.R. Acad. Sci. Paris.* **235**, 154 (1952); **236**, 909 (1953). For a review of the stretching frequencies of C-halogen substituents in the axial and equatorial positions of cyclohexane, see reference 23, pp. 216–219.

[28] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley, New York (1958).

[29] The synthesis of *cis*- and *trans*-4-t-butylcyclohexyl chloride was recorded by Dr. F. D. Greene and coworkers, F. D. Greene, C. C. Chu, and J. Wolia, *J. Amer. Chem. Soc.* **84**, 2463 (1962). A private communication with these investigators included the designation of the carbon-chlorine stretching frequency for the axial and equatorial bonds at 692 and 762 cm^{-1}, respectively. This system is assumed to be conformationally homogeneous and therefore provides an adequate model for support of the equatorial assignment for the chlorine atom in the bicyclic phosphonates.

molecule IVb. Chlorocyclohexane has been examined carefully by IR and Raman spectroscopy, and the liquid halide displays absorption at 684·5 and 731 cm^{-1} for the axial and equatorial carbon-halogen bonds, respectively.[30] Since only the peak at 731 cm^{-1} was observed on the solid compound, it was assigned to the equatorial substituent. Noteworthy is the position of the phosphoryl group which occurs at nearly the same frequency in all three bicyclic phosphonates, namely at 1252, 1257 and 1256 cm^{-1} in IVa,[31] IVb, and IVc, respectively. Comparable is the peak (1260 cm^{-1}) recorded for the same group in *cis*-2-chloromethyl-2-ethyl-1,3-propanediol benzylphosphonate.[20] Similarly, a strong band at 1255 cm^{-1} is observable in the spectrum of dimethyl benzylphosphonate. The implication is that intramolecular hydrogen bonding in the bicyclic phosphonates is negligible.[32] Consequently, the conclusion is that the phosphoryl group in the bicyclic phosphonates is essentially free and in molecular environment similar to that found in the model compounds cited. This situation is more probable in the boat-chair conformer-1. Correlations of IR spectra and strain in a few bicyclo[3.3.1]nonane derivatives are available although conformational differences were not critically evaluated.[33]

Dipole moment measurements were obtained on anhydrous solutions of IVa in dioxane at 25°.[34] The value of 5·91 D agrees more closely with the calculated figure of 5·6 D for conformer-1 as contrasted with 4·64 D for conformer-2. Calculation of the dipole moment for any of the sixteen possible conformers of IVa obligates a selection of vector directions for the individual atoms. Although on rare occasions tentative assignments have been made,[35,36] a P—C directional is not well established but for our purpose it was assumed to be toward phosphorus. The involved calculations (see Experimental) were made on the basis of a perfect boat-chair arrangement in conformer-1 and a perfect chair-chair orientation in conformer-2.

NMR was most instructive in the structural determination of IVa. At 60 Mc the spectrum of IVa in deuterochloroform (Fig. 1) shows peaks assignable to hydrogens *b*, *c*, *d*, *g*, and *h*. Unfortunately, protons *a*, *e*, and *f* are obscured due to peak overlap at this frequency. Slightly improved line separation was observed using formic acid as solvent with a noteworthy diamagnetic shift for proton *a* to a field position higher than that of protons *b*. This suggests decreased hydrogen bonding of proton *a*, perhaps with the phosphoryl oxygen atom (O_3) or possibly with O_1 and O_2 which may undergo protonation in formic acid.[37] Hydrogen *a* (5·3 τ) in

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[30] K. Kajima and K. Sakaskita, *Bull. Chem. Soc., Japan* **31**, 796 (1958); *Chem. Abst.* **53**, 14689 (1959).

[31] The phosphoryl peak was inadvertently recorded in paper 1 (ref. 2) as being at 1247 cm^{-1} in IVa.

[32] For discussions of hydrogen bonding in phosphoryl groups, see: L. C. Thomas and R. A. Chittenden, *Chem. Ind.* 1913 (1961): and C. E. Griffin, *Ibid.* 1058 (1960).

[33] H. K. Hall and R. Zbinden, *J. Amer. Chem. Soc.* **80**, 6428 (1960).

[34] We thank Dr. Max T. Rogers, Department of Chemistry, Michigan State University for the determinations. The method and manner of calculation is found in: M. T. Rogers, *J. Amer. Chem. Soc.* 77, 3681 (1955). Since the compound IVa does pick up moisture slowly, two other checks were made on the dipole moment, one by Dr. J. Verkade, Iowa State University, and the other by Dr. T. L. Brown and R. Palmer, University of Illinois. The values obtained were 6·00 D and 6·05 D, respectively, which agree reasonably well with the value found by Dr. Rogers.

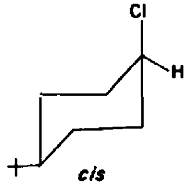
[35] G. M. Kosolapoff, *J. Chem. Soc.* 3222 (1954).

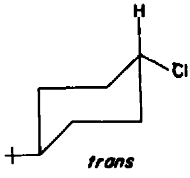
[36] B. A. Arbuzov and T. G. Shavska-Tolkacheva, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.* 812 (1954); *Chem. Abstr.* **49**, 4352 (1955).

[37] The phosphoryl group is probably similar to the carbonyl function in shielding effects (see: L. M. Jackman, *Applications of NMR in Organic Chemistry*, p. 57. Pergamon Press, N.Y. (1959).

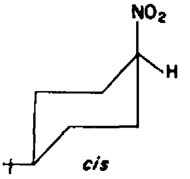
conformer-1 (Fig. 1) is sandwiched between O_1 and O_2, and consequently, a high field position of proton *a* might be expected although the effect may be offset by influence of the phosphoryl group. Increased magnetic shielding of C_1 protons by axial substituents at C_3 and C_5 has been predicted.[38]

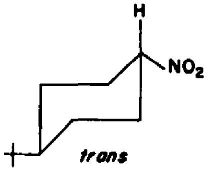
Conformational homogeneity was assumed in the recent study of the chemistry of *cis* and *trans*-4-t-butylcyclohexyl chloride.[29] A lone assignment in the NMR spectra of both isomers was made for the proton geminal to the chlorine atom.





Field positions at 5·63 and 6·36 τ were recorded for the C_1 hydrogens in the *cis*- and *trans*-isomers, respectively. A more elaborate analysis by NMR was made of the related *cis*- and *trans*-4-t-butylnitrocyclohexane.[39] Hydrogen-1 in the *cis*-isomer displays a signal at 5·57 τ with a small amount of spin-spin splitting by four adjacent protons. Analogous to the bicyclic phosphonate IVa, proton 1 (axial) in *trans*-4-t-butylnitrocyclohexane is resolved into the predicted nine-line spectrum with its center at 5·77 τ.[39] The spectrum of proton *a* in IVa centered at 5·3 τ, although obscured at 60 Mc (Fig. 1), at 100 Mc (Fig. 2) shows that the resonance is split into





a triplet of triplets, $J_{a,a} = 12{\cdot}1$ c.p.s. and $J_{a,e} = 5{\cdot}1$ c.p.s. Interactions of various hydrogens within the molecule IVa were clarified by decoupling at 100 Mc using the double resonance technique.[40] To examine proton *a*, irradiation of proton *c*, 205 c.p.s. up field, caused a collapse of the center triplet of *a* to a singlet.[41] A differential in irradiation frequency of 15 c.p.s. affects the two triplets at lower field where the lowest triplet has nearly coalesced to a singlet. Decoupling proton *a* from proton *d*, 306 c.p.s. up field, resulted in near total disappearance of the two outside triplets of *a* with marked reinforcement of the central triplet. That protons *c* and *d* are in turn coupled with *a* can be seen when *c* is decoupled from *a* 221 c.p.s. down field. Proton *d* was decoupled from *a* 325 and 307 c.p.s. down field in addition to the results of decoupling other protons.

[38] See reference 37, p. 118, for a discussion of this effect.

[39] A. C. Huitric and W. F. Trager, *J. Org. Chem.* **27**, 1926 (1962).

[40] See M. Karplus, *J. Amer. Chem. Soc.* **84**, 2458 (1962) for a review, and R. Freedman and D. H. Whiffen, *Mol. Phys.* **4**, 321 (1961) for a theoretical treatment.

[41] If either the observed multiplet or the multiplet from which the observed multiplet is being decoupled is more than ~10 c.p.s. wide, instrumental limitations often make it impossible to decouple completely. The lines in an incompletely decoupled multiplet are often not predictable from first order considerations. However, to demonstrate spin-spin interactions it is generally sufficient to note changes in the spectrum when $|H_1 - H_2|$ = chemical shift difference of the interacting nuclei.

The tertiary hydrogens *b* geminal to the oxygen atom display a doublet with J = 17·5 c.p.s. and are located at 5·22 τ at 60 Mc. Comparable is the tricyclic phosphate whose tertiary protons exhibit a doublet centered at 4·78 τ, J = 19·5 c.p.s.[42] Improved separation of the resonances from *a* and *b* is obtained at 100 Mc (Fig. 2).

Dimethyl benzylphosphonate proved to be an excellent model compound for location of the methylene protons *g* and the aromatic protons *h* in IVa. A doublet (J = 22 c.p.s.) with a chemical shift of 6·83 τ appears for protons *g* while aromatic hydrogens *h* have a field position of 2·77 τ (Fig. 1). The model phosphonate exhibits a doublet at 6·75 τ (J = 21·7 c.p.s.) and a singlet at 2·75 τ for the corresponding methylene and aromatic protons, respectively.

Integration of the areas assigned to hydrogens *c* and *d* in IVa revealed a total of four protons. It is generally believed that in cyclohexane systems axial protons are more highly shielded than the equatorial counterpart.[43] Consequently, the doublet at 7·27 τ (J = 15 c.p.s.) was designated for protons *c*, and the triplet at 8·12 τ (J = 13 c.p.s.) represented the axial protons *d*. The separation (64 c.p.s.) of *c* and *d*- in IVa in deuterochloroform approximates $J_{a,e}$ = 68·6 c.p.s. in the tricyclic phosphite III. Unfortunately, solubility limitations of the tricyclic phosphate in the same solvent did not permit a similar comparison of the corresponding resonance frequencies.[44]

A single hydrogen was discovered under the areas assigned to protons *e* and *f*. Enhanced chemical shift at 100 Mc clarifies the two doublets (J = 15 c.p.s.) with the axial hydrogen *f* given the higher field position.[43] Increased shielding is indicated for these protons (8·79 and 9·33 τ) as compared to the corresponding methylene protons in III or the tricyclic phosphate. Decoupling *f* from *e*, 51 c.p.s. down field produced a singlet. A sharpening of peaks in the doublet of *e* was noted when it was decoupled from *b* 307 or 325 c.p.s. down field.

In chloroform solution the heterocyclic nonane IVa seemingly is composed of a cyclohexane system restricted to the chair conformation as implied by the NMR examination. It is conceivable that internal hydrogen bonding between proton *a* and the oxygen atoms O_1 and O_2 may increase the lifetime of a specific orientation in which the arrangement of C_3, C_4, C_5, O_1, O_2, and P resembles a boat configuration. Single crystal analysis by X-ray is now in progress on a monoclinic crystal and will be reported in the near future.[45]

Several compounds in this study were examined for growth inhibition of certain microorganisms, *Escherichia coli*, *Pseudomonas aerginosa*, *Bacillus cerus*, *Staphylococcus aureus*, and *Brevi fusicum*. At 37° on solutions of Difco nutrient and/or agar,

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[42] Line assignments for this phosphate were published recently, see: J. G. Verkade and R. W. King, *Inorg. Chem.* **1**, 948 (1962).

[43] R. U. Lemieux, R. R. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.* **80**, 6098 (1958). It is also of interest to note that Huitric and Trager (ref. 39) observed a doublet (J = 11·6 c.p.s.) in *cis*-4-t-butylnitrocyclohexane centered at 7·42 τ which they attributed to equatorial protons at C_2 and C_6 each being split by a geminal axial hydrogen. Insufficient resolution with the *trans*-isomer obscured the patterns of resonance frequencies assignable to ring protons. The large spin-spin coupling of protons on the same carbon has been observed with methylene groups in certain steroids, see J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.* **80**, 5121 (1958).

[44] A discussion of gem coupling has been made available recently, see: M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.* **85**, 1899 (1963).

[45] K. D. Berlin, C. McKinney, C. Hildebrand and D. M. Hellwege, Unpublished results.

III and IVa (80% concentration), respectively, did not inhibit the growth of any of the organisms over a twenty-hour period.[46]

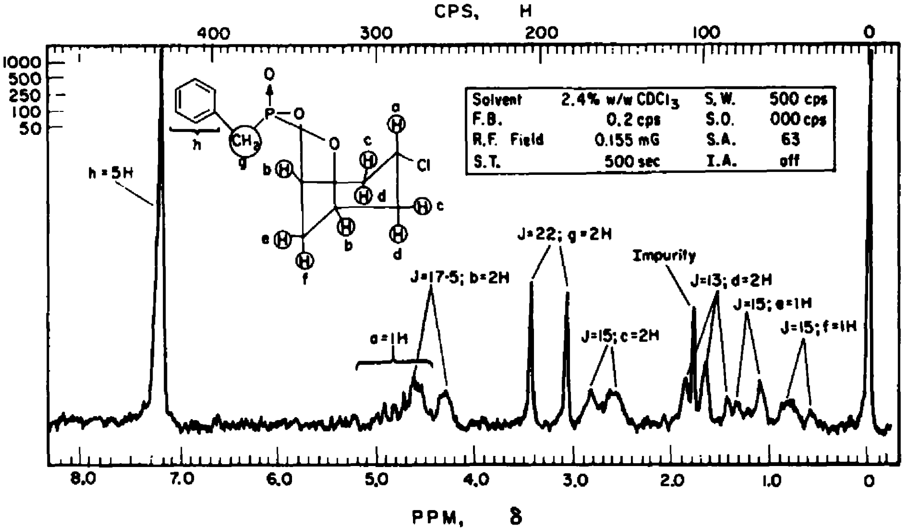

FIG. 1

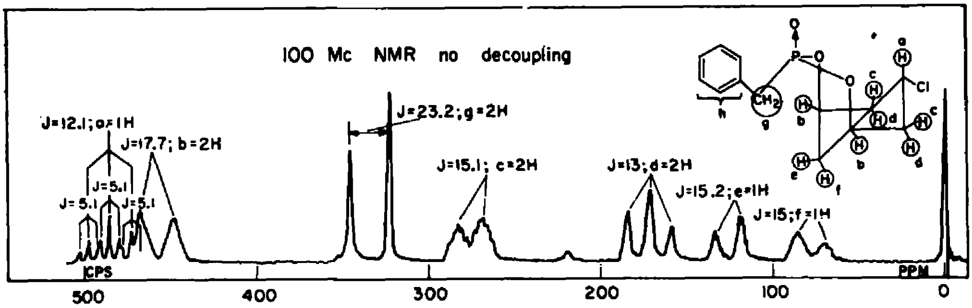

FIG. 2. Except in the case of Jac = 5·1 c.p.s., only the large (axial-axial) couplings are indicated. However, most of the lines are broadened by small axial-equatorial and equatorial-equatorial coupling.

EXPERIMENTAL[47]

cis-Phloroglucitol. An improvement in the purification of this compound was achieved by dissolving the crude product in slight excess of boiling methanol.[2] Decolorizing charcoal was added,

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[46] We thank Dr. N. Durham and J. Martin of the Microbiology Department for aiding in the growth studies.

[47] All m.ps are corrected; all b.ps are uncorrected. The microanalyses were performed by Midwest Laboratories, Indianapolis, Indiana. The 60 Mc PMR spectra were determined with a Varian Model A-60 high resolution NMR spectrometer with field frequency stabilization. The concentration and solvent are indicated on each spectra. The 100 Mc PMR spectra and double resonance (decoupling) spectra were determined by Varian Associates, Palo Alto, California. All IR spectra were determined on a Beckman IR-5 as KBr discs. Because of space limitations the decoupling spectra of IVa at 100 Mc and the spectra of IVb and IVc at 60 Mc were omitted. Xerox copies may be obtained from the senior author. The spectra of IVb and IVc resembled that of IVa at 60 Mc and tentative assignments of proton frequencies were made by comparison.

and the mixture was boiled for a few min. and filtered. An equal volume of anhydrous carbon tetrachloride was added, and the solution chilled to 0° for 30 min. White crystals were filtered off and dried at 110° for 3 hr. A repeat of the above procedure resulted in the isolation of crystals melting at 185–186°. With only moderate care very little material loss was noted.

1-*Phospha*-2,8,9-*trioxaadamantane* (III). Reported in reference 2.

Synthesis of 3-*benzyl*-7-*chloro*-2,4-*dioxa*-3-*phosphabicyclo*[3.3.1]*nonane*, 3-*oxide*. Benzyl chloride (3·95 g, 0·031 mole) and 4·00 g (0·025 mole) III were mixed (under N_2) and heated at 110° for 24 hr, resulting in a melt containing a small amount of white solid. When cooled to room temperature, the melt solidified and was recrystallized from low boiling pet ether–methylene chloride or from methanol as white plates; yield 4·68 g. Concentration of the mother liquors resulted in the isolation of a solid, the IR spectrum of which was identical with that of the starting material.

3-*Benzhydryl*-7-*chloro*-2,4-*dioxa*-3-*phosphabicyclo*[3.3.1]*nonane*, 3-*oxide* (IVb). The phosphite III (1·59 g, 0·0099 moles) and 2·02 g (0·0099 mole) benzhydryl chloride were mixed and heated (under N_2) for 48 hr. Sublimation of impurities (100° at 0·1 – 0·3 mm for 5 hr and 160°/0·1 mm for 1·5 hr) was required to provide an analytical sample, m.p. 219–220°; yield 2·27 g.

3-(1-*naphthylmethyl*)-7-*chloro*-2,4-*dioxa*-3-*phosphabicyclo*[3.3.1]*nonane*, 3-*oxide* (IVc). A mixture of III (2·76 g, 0·017 mole) and 3·10 g (0·017 mole) 1-(chloromethyl)napthalene (b.p. 88–92/10·2 mm; n_D^{25} 1·6357) were heated (under N_2) at 110° for 16 hr followed by an additional 12 hr at 140°. Various combinations of solvents were ineffectual in providing a pure sample by recrystallization techniques. Chromatography on alumina using benzene–ether solution for elution resulted in the isolation of a semi-solid. Purification was achieved by dissolving the material in methylene chloride from which white needles were precipitated by the addition of excess CCl_4; yield 1·81 g.

Calculations of interatomic distances and dipole moments for isomers-1 *and* -2. At the request of the referee and editor, calculations of the dipole were omitted but Xerox copies may be obtained from the senior author.

Synthesis of dimethyl benzylphosphonate. To a reaction system similar to that employed for the preparation of the bicyclic esters were added 4·4 g (0·034 mole) benzyl chloride and 10·5 g (0·084 mole) trimethyl phosphite. One drop of triethylamine was added as catalyst, and the solution was heated at 110° for 24 hr. Vacuum distillation of the reaction solution yielded a sample, b.p. 100°/0·7 mm; 3·5 g, 50%.[48] The IR spectrum shows bands characteristic of the phosphoryl group (1255 cm^{-1}), the P-O-methyl group (1187 cm^{-1}), the P-O-alkyl linkage (1030, 1055 cm^{-1}) and mono-substituted benzene (698 cm^{-1}). Found: C, 53·70; H, 6·64; P, 14·72; Calcd. for $C_9H_{13}PO_3$: C, 54·00; H, 6·55; P, 15·47%).

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[48] This procedure was reported recently but no conditions were given: R. Rabinowitz, *J. Amer. Chem. Soc.* **82**, 4564 (1960).