Cyclic Organophosphorus Compounds. Part VIII.[1] Conformation in the 1,3,2-Dioxaphosph(v)orinan Series. Proton Magnetic Resonance Assignments to *gem*-5,5-Dimethyl groups, and Conformation at Phosphorus

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Chemical shifts for the *gem*-dimethyl groups in 5,5-dimethyl-1,3,2-dioxaphosph(v)orinans are reported for solutions in deuteriochloroform and benzene. Strong coupling between axial 4(6)-protons and the axial 5-methyl group is evident, and decoupling experiments further suggest that $^5J_{PH}$ is negligible or at least non-specific. For chloroform solutions of aralkyl phosphonates preferential shielding of the axial methyl group suggests that the aralkyl group and the phosphoryl bond lie in the equatorial and axial positions respectively.

In our considerations of the geometrical form of the isolated 1,3,2-dioxaphosphorinan ring system, boat and skew structures were eliminated for steric and ^{1}H n.m.r. spectral reasons. Our original conclusions regarding a further possibility, *i.e.* conformationally stable chair rings, were based on the recently reported ^{1}H n.m.r. spectra of some 5,5-disubstituted 2-oxo- (and 2-thiono-) 1,3,2-dioxaphosphorinans (I; X = O or S)[2] and have received support from recent structural determinations. We now present additional ^{1}H n.m.r. data pertaining to the compounds previously described by us, and also data for some new compounds prepared by conventional means (see Table).

We draw attention to two features of our results. The first is the measurable difference in the widths of the two methyl signals, which is dependent on the nature of the exocyclic group attached to phosphorus. The widths at half height ($W_{\frac{1}{2}}$) of the narrow and broad signals are 1·0—1·8 and 1·3—2·2 c./sec. (see, however, footnote to Table). Differences in band widths for the methyl signals from 5,5-dimethyl-1,3-dioxans have been commented upon recently;[3] bandwidths are similar (1·3 and 2·0 c./sec.) for the cyclic sulphite (II).[4]

The observed differences in $W_{\frac{1}{2}}$ for the methyl signals of our 1,3,2-dioxaphosph(v)orinans could be the result of either (or both) long-range ($^4J_{HH}$) interactions between non-equivalent methyl groups or of methyl–methylene interactions (also $^4J_{HH}$). Such long-range proton–proton couplings are well established for phosphorus-free ring systems[5] even extending through five bonds, *e.g.* in the cyclic orthoformate structures in the adamantane series for which $^4J_{HH}$ is 0·2 and $^5J_{HH}$ 1·25 c./sec.[6] In no case was actual splitting of the methyl signals for the 1,3,2-dioxaphosph(v)orinan series observed, although splitting of methyl signals has been reported for 2,2-dimethyl-1,3-dioxans ($^4J_{HH}$ 0·6 c./sec.) in which the two

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[2] K. D. Bartle, R. S. Edmundson, and D. W. Jones, *Tetrahedron*, 1967, **23**, 1701.
[3] J. E. Anderson, *J. Chem. Soc.* (*B*), 1967, 712.
[4] R. S. Edmundson, *Tetrahedron Letters*, 1965, 1649.
[5] S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15.
[6] E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1966, **88**, 1140.

N.m.r. data (δ values) for 5,5-dimethyl-1,3,2-dioxaphosph(v)orinans in deuteriochloroform and in benzene

	R in (I)	In deuteriochloroform Me_{eq}	In deuteriochloroform Me_{ax}	In benzene Me_{eq}	In benzene Me_{ax}	Δδ * Me_{eq}	Δδ * Me_{ax}
X = O							
1	OMe	0·90 (1·05)	1·24 (1·3)	0·30 (1·6)	0·91 (1·8)	0·60	0·33
2	OPh	0·97 (1·2)	1·29 (1·4)	0·29 (1·1)	0·94 [a] (1·6)	0·68	0·35
3	Cl	0·93	1·32	0·17 (1·3)	0·84 (1·8)	0·76	0·48
4	$NHCMe_3$ [b]	0·98 (1·2)	1·16 (1·5)	0·52 (1·7)	0·86 [c] (2·2)	0·46	0·30
5	Me [d]	1·01 (1·0)	1·11 (1·3)	0·60 (1·6)	0·74 [c] (1·8)	0·51	0·37
6	CCl_3	0·99	1·42	0·28 (1·3)	0·95 [a] (1·7)	0·71	0·47
7	Ph	1·09	1·12	0·54 (1·1)	0·74 (1·4)	0·55	0·38
8	CH_2Ph [e]	0·95 (1·0)	0·81 (1·4)	0·38 (1·2)	0·50 (1·4)	0·57	0·31
9	CHMePh	0·90 (1·1)	0·83 (1·3)	0·37 (1·0)	0·57 (1·4)	0·53	0·26
10	CPh_3	0·98 (1·3)	0·78 (1·5)	0·47 (1·4)	0·51 [a] (1·6)	0·51	0·27
11	CH(NHPr)Ph	0·98 (1·4)	0·77 (1·5)	0·47	0·43	0·51	0·34
12	$CH_2{\cdot}C_6H_2Me_3$-2,4,6 [f]	0·86 (1·1)	0·81 (1·6)	0·29 (1·4)	0·63 (1·9)	0·57	0·18
X = S							
13	OMe [h]	0·91	1·22	0·40 (1·3)	0·82 (1·4)	0·55	0·44
14	Cl	0·91 (1·8)	1·33 (2·2)	0·35 (1·5)	1·12 (2·2)	0·56	0·21
15	NMe_2	0·91 (1·3)	1·25 (1·8)	0·33 (1·6)	0·92 (2·3)	0·58	0·31

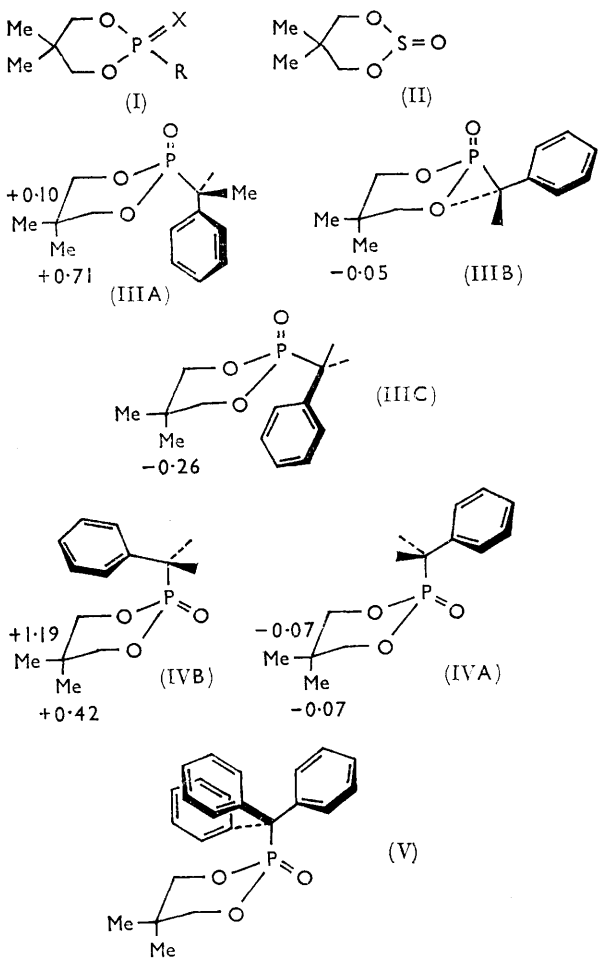
Chemical shifts in p.p.m.; $W_{\frac{1}{2}}$ (in parentheses) in c./sec. The spectra have not all been run under conditions of identical instrument resolution, but these conditions were as similar as possible for deuteriochloroform and benzene solutions of the same compounds; $W_{\frac{1}{2}}$ values are therefore relative ($CDCl_3$ *vs.* PhH) for each compound, and are not relative to a standard tetramethylsilane peak width. For all $W_{\frac{1}{2}}$ measurements, spectra were run at a sweep width of 100 c./sec. and radiofrequency power level of 0·03—0·05 mG.

* δ(Deuteriochloroform) — δ(benzene).

[a] Containing *ca.* 10% (v/v) $CDCl_3$. [b] In $CDCl_3$ $\delta(CMe_3)$ 1·34 p.p.m., J_{PNCCH} *ca.* 0·7 c./sec.; in PhH the values are 1·36 p.p.m. and *ca.* 0·0 c./sec. [c] Containing *ca.* 20% (v/v) $CDCl_3$. [d] In $CDCl_3$, δ(Me) 1·58 p.p.m., and J_{PCH} 17·4 c./sec.; in PhH the values are 1·23 p.p.m. and 17·3 c./sec. [e] In $CDCl_3$, $\delta(PhCH_2)$ 3·28 p.p.m., and J_{PCH} 21·3 c./sec.; in PhH, the values are 3·04 p.p.m. and 21·5 c./sec. [f] In 1, 5, and 25% (v/v) PhH–$CDCl_3$, the Me_{ax} signals were at 0·83, 0·78, and 0·69 p.p.m., and the Me_{eq} signals at 0·90, 0·83, and 0·69 p.p.m. [g] In $CDCl_3$, $\delta(ArCH_2)$ 3·36 p.p.m., and J_{PCH} *ca.* 23 c./sec.; in PhH, the values are 3·23 p.p.m. and 22·5 c./sec. [h] In $CDCl_3$, δ(OMe) 3·78 p.p.m. and J_{POCH} 13·8 c./sec.; in PhH the values are 3·48 p.p.m. and *ca.* 13 c./sec. [i] In $CDCl_3$, δ(NMe) 2·83 p.p.m., and J_{PNCH} *ca.* 11·5 c./sec.; in PhH the values are 2·65 p.p.m. and *ca.* 11·5 c./sec.

methyl groups are non-equivalent.[7,8] Such splitting has not been observed for 2,2,5,5-tetramethyl-1,3-dioxan, where the spectrum is suggestive of rapid flipping, nor for 2-benzyl-5,5-dimethyl-1,3-dioxan [δ(Me) ($CDCl_3$) 0·70 ($W_{\frac{1}{2}}$ 1·15 c./sec.) and 1·20 p.p.m., ($W_{\frac{1}{2}}$ 1·85 c./sec.)]. Anderson cites additional data which suggest that *gem*-dimethyl groups relatively far from ring oxygens are coupled to a lesser extent than those which are closer to oxygen.[3]

Methyl–methyl interactions are therefore probably only slight, but there remains the possibility of long-range phosphorus–methyl couplings ($^5J_{PH}$). Some clarification of the present situation was obtained by means of proton decoupling experiments on 5,5-dimethyl-2-dimethylamino-2-thiono-1,3,2-dioxaphosphorinan (in deuteriochloroform solution), which gives a particularly well defined proton spectrum. Irradiation at the downfield methyl resonance frequency brought about resolution of each of the four broad signals due to the (two)



axial methylene protons (δ 4·32 p.p.m.) into well defined 1 : 2 : 1 triplets (cf. the broad peaks in Figure 1 of Anderson's paper,[3] although here axial and equatorial methylene proton peaks are reversed in position in comparison with those of our cyclic phosphorus esters) in addition to a further slight clarification of the groups of already clear 1 : 2 : 1 triplets due to equatorial 4- and 6-protons (δ 3·75 p.p.m.). The reverse experiment, *i.e.* irradiation at the downfield (axial) methylene signal frequency yielded two methyl peaks, identical within the limits of experimental error. More detailed studies on this particular compound are to be reported elsewhere. These results seem to indicate little or no specific coupling

[7] W. J. Mijs, *Rec. Trav. chim.*, 1967, **86**, 220, and refs. therein.
[8] J. E. Anderson, *Tetrahedron Letters*, 1965, 4713.

between phosphorus and the methyl groups, while axial methyl–axial proton couplings are of greater consequence than other proton–proton combinations. In systems with rigid 1,3,2-dioxaphosph(v)orinan chair rings, *e.g.* the 2,8,9-trioxa-1-phospha-adamantane oxides, values of $^3J_{PH}$ (18·0) and $^4J_{PH}$ (2 c./sec.) have been recorded; for the 4-alkyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane 1-oxides with boat rings, $^5J_{PH}$ was not detectable.[6]

We therefore conclude that for 5,5-dimethyl-1,3,2-dioxaphosph(v)orinans, long range phosphorus–proton coupling ($^5J_{PH}$) is negligible, or at least non-specific, and we assign narrow signals (δ 0·86—1·09) and broad signals (δ 0·77—1·42 p.p.m.) to equatorial and axial methyl groups respectively on the basis of stronger, planar zig-zag couplings. This conclusion is in keeping with those based on ^{1}H n.m.r. data for the conformationally rigid, methyl-substituted *cis*- and *trans*-decalins [9] and steroids.[9,10] Values recorded elsewhere for the chemical shifts of *gem*-dimethyl groups similarly placed in cyclic phosphites [11] and cyclic sulphites [4] are in keeping with the ranges mentioned.

The second noteworthy feature is the relative positions of the two methyl resonances in the spectra (deuteriochloroform) of compounds 8–12 (see Table) in comparison with the relative positions for the other compounds. In contrast to compounds 1—7 and to the thione series 13—15, the remainder, which are all aralkyl phosphonates, show the broader signal (Me_{ax}) upfield of the narrow signal (Me_{eq}). For these phosphonates, in solution at least, we assign the phosphoryl bond to the axial position on the basis of the following arguments.

The first concerns the steric acceptability of aralkyl groups. Attempts to obtain two isomers of 5-chloromethyl-5-methyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan failed, though 2-benzyl or -α-phenylethyl isomers could be obtained; moreover, the triphenylmethyl compound is (^{1}H n.m.r.) spectroscopically similar to one of the isomers of the benzyl or of the α-phenylethyl phosphonate.[12] The triphenylmethyl ester (compound 10) is also spectroscopically similar to the other aralkyl phosphonates listed, and we conclude that compounds 8—12 are conformationally the same, with the triphenylmethyl group equatorial.

Electronic interaction between the phosphoryl group and benzene rings is minimised in the phosphonates by the side-chain methylene group, a situation which contrasts with the case of the geometrically similar phenyl phosphate, for example, and allows first-order calculations based on the Johnson–Bovey models for benzene ring anisotropies to be made.[13] The results for certain highly idealised rotameric situations for the possible conformers of 2-benzyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan are indicated in structures (III) and (IV), where positive figures indicate shielding, and negative values (in p.p.m.) indicate deshielding relative to a similar compound without the benzene ring. Only in structure (IIIA) is there specific shielding of the axial methyl group relative to the equatorial one; all other structures indicated lead either to deshielding of both methyl groups, or to specific shielding of the equatorial methyl. A comparison between the benzyl phosphonate and the methyl phosphonate (compound 5) shows relative shielding of the axial and equatorial methyls by 0·30 and 0·06 p.p.m. respectively; similar values hold for the α-phenylethyl phosphonate (0·28 and 0·11 p.p.m.) and the triphenylmethyl phosphonate (0·33 and 0·03 p.p.m.).

Coupled with the patterns just described would be similar effects relating to the axial 4- and 6-protons. If substituents at phosphorus are axial then a triphenylmethyl group would shield [cf. structure (V)] the axial protons relative to the most probable benzyl situation [*i.e.* (IVA)], and any effect of the benzyl group would be more pronounced than that of a methyl group. This is in fact not the case, indeed it is the reverse for the axial protons, while the equatorial protons are shielded in the presence of a benzene ring.[2]

Our conclusion that the aralkyl phosphonates possess an equatorial aralkyl group contrasts with structural determinations carried out on *cis*-2-bromo-5-bromomethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan [14] and 2-oxo-2-phenoxy-1,3,2-dioxaphosphorinan; [15] in both cases an equatorial phosphoryl bond is present. Elsewhere, no attempt has been made to define bond arrangements at C-5 or around phosphorus in 1,3,2-dioxaphosphorinans.[16,17] Nevertheless, these results are not necessarily inconsistent, since there is no reason to suppose that *gem*-5,5-dimethyl groups cannot allow equatorial substituents at phosphorus, and Wadsworth has claimed that 5-methyl-5-bromomethyl substituents can allow either axial or equatorial groups at phosphorus.[18] The possibility that the relative positions of the ^{1}H n.m.r. methyl signals are determined only by differences in configuration at phosphorus may be disregarded since both stable and unstable conformers of 5,5-dimethyl-2-oxo-2-piperidino-1,3,2-dioxaphosphorinan [12] show the same relative positions of the methyl peaks as do compounds 1—7.

The Table also includes data for benzene solutions [pure, or, because of solubility problems, containing deuteriochloroform (10—20% v/v)]. In general, resonances are moved upfield in comparison with those for

[9] K. L. Williamson, T. Howell, and T. A. Spencer, *J. Amer. Chem. Soc.*, 1966, **88**, 325.
[10] C. W. Shoppee, F. P. Johnson, R. E. Lack, J. S. Shannon, and S. Sternhell, *Tetrahedron*, 1966, Suppl. 8, Part II, 421.
[11] D. Z. Denny and D. B. Denny, *J. Amer. Chem. Soc.*, 1966, **88**, 1830; D. Gagnaire and J. Robert, *Bull. Soc. chim. France*, 1967, 2240.
[12] R. S. Edmundson and E. W. Mitchell, unpublished work.
[13] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
[14] T. A. Beineke, *Chem. Comm.*, 1966, 860.
[15] H. J. Geise, *Rec. Trav. chim.*, 1967, **86**, 362.
[16] J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, 1965, **4**, 83.
[17] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, 1962, **84**, 610.
[18] W. S. Wadsworth, *J. Org. Chem.*, 1967, **32**, 1603.

solutions in deuteriochloroform. For example, 5,5-dimethyl-2-dimethylamino-2-thiono-1,3,2-dioxaphosphorinan in deuteriochloroform exhibits chemical shifts for the axial and equatorial methylene protons of 3·77 and 4·30 p.p.m. respectively, whereas for a solution in benzene the corresponding values are 3·39 and 4·09 p.p.m. However, the most pronounced changes are those of the positions of the methyl signals. The changes for equatorial and axial methyl groups are 0·51—0·76 and 0·18—0·48 p.p.m. respectively; these ranges include some exceptional values shown by compounds 3, 6, and 12. For the aralkyl phosphonates the relative positions of the two methyl signals are now reversed, and their positions now correspond with the arrangement for the remaining compounds listed. This was shown to be a true reversal in positions of peaks and not merely an interchange of peak widths by measurements on solutions in deuteriochloroform containing increasing amounts of benzene.

The effect of aromatic solvents on proton chemical shifts has recently been recorded for cyclic sulphites [19] and for 2-alkyl-5,5-dimethyl-1,3-dioxans.[8] In the latter case, the explanation was based on association of benzene with the ring C–O bonds. In spite of probable differences in anisotropies of C–O bonds between such dioxans and the 1,3,2-dioxaphosph(v)orinans, this phenomenon seems to afford an explanation in our case, since those compounds possessing the much less polar P=S bond behave in exactly the same way as do those with the P=O bond.

EXPERIMENTAL

General experimental details are as outlined in previous papers in this series. I.r. spectra were recorded for potassium bromide discs except where indicated, with a Perkin-Elmer Infracord 237 spectrometer. ^{1}H N.m.r. spectra were recorded at 60 Mc./sec. with a Varian A60 spectrometer for *ca.* 10% (w/v) solutions at room temperature. Chemical shifts were measured with respect to internal tetramethylsilane.

α-Phenylethylphosphonic Dichloride.—α-Phenylethyl chloride (70 g.) was added dropwise to a suspension of aluminium chloride (134 g.) in phosphorus trichloride (300 g.) stirred at *ca.* 40° during 2 hr. Volatile materials were removed *in vacuo* and the residue was taken up in dichloromethane (1 l.). This solution was cooled to −20° and treated dropwise with stirring with water (162 g.). The mixture was filtered rapidly, and the organic layer was separated and dried. Removal of the solvent left the crude phosphonic dichloride (97 g.). Pure *α-phenylethylphosphonic dichloride* (47 g., 43%) distilled at 116—120°/0·4 mm., n_D^{20} 1·5557, $\nu_{max.}$ 1275 cm.$^{-1}$ (P=O) (Found: C, 42·95; H, 4·0; P, 14·2. $C_8H_9Cl_2OP$ requires C, 43·05; H, 4·05; P, 13·9%).

NN'-Dicyclohexyl-α-phenylethylphosphonic Diamide.—This was obtained from the phosphonic dichloride and cyclohexylamine in chloroform. The product was recrystallised repeatedly from aqueous ethanol, but the solvent was retained tenaciously and the compound required prolonged drying (P_2O_5) *in vacuo*. The *phosphonic diamide* had m.p. 126—127°, $\nu_{max.}$ 1198 and 1182 (P=O) cm.$^{-1}$ (Found: C, 69·35; H, 9·5; P, 8·5. $C_{20}H_{33}N_2OP$ requires C, 68·95; H, 9·5; P, 8·9%).

5,5-Dimethyl-2-oxo-2-α-phenylethyl-1,3,2-dioxaphosphorinan.—This was obtained by addition of a solution of 2,2-dimethylpropane-1,3-diol and pyridine in ether to an ethereal solution of the phosphonic dichloride. The *ester* (92%) had m.p. 120—122° (from ether), $\nu_{max.}$ 1264 (P=O), 1064, and 1016 (P–O–C) cm.$^{-1}$ (Found: C, 61·7; H, 7·1; P, 12·4. $C_{13}H_{19}O_3P$ requires C, 61·4; H, 7·5; P, 12·2%). The compound sublimed without decomposition (m.p., mixed m.p., i.r. spectrum) when heated in a stream of nitrogen at 220°.

5,5-Dimethyl-2-oxo-2-(α-propylamino)benzyl-1,3,2-dioxaphosphorinan.—A mixture of *N*-benzylidene propylamine (2·95 g.) and 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan (3·0 g.) was warmed over steam for ½ hr., until solidification occurred. The *ester* (3·4 g., 91%) had m.p. 126—126·5° (from benzene), $\nu_{max.}$ 1258 (P=O), 1061, and 1009 (P–O–C) cm.$^{-1}$ (Found: C, 60·9; H, 7·95; P, 10·45. $C_{15}H_{24}NO_3P$ requires C, 60·6; H, 8·15; P, 10·4%).

5,5-Dimethyl-2-oxo-2-(2,4,6-trimethylbenzyl)-1,3,2-dioxaphosphorinan.— 5,5-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinan (3·2 g.) and chloromethylmesitylene (3·4 g.) were heated together at 170° (bath temp.) for 3 hr. The semisolid residue was crystallised from cyclohexane. The *ester* (3·8 g., 68%) had m.p. 131—131·5° (after chromatography on silica gel with 50% benzene–ether and recrystallisation from cyclohexane), $\nu_{max.}$ 1262 (P=O), 1060, and 1011 (P–O–C) cm.$^{-1}$ (Found: C, 63·8; H, 8·2; P, 10·8. $C_{15}H_{23}O_3P$ requires C, 63·8; H, 8·2; P, 11·0%).

2-Benzyl-5,5-dimethyl-1,3-dioxan.—A mixture of phenylacetaldehyde (6·0 g.), 2,2-dimethylpropane-1,3-diol (5·1 g.), and anhydrous toluene-*p*- sulphonic acid (0·5 g.) in benzene (50 ml.) was heated and the water produced was removed azeotropically. The solution was washed with potassium hydrogen carbonate solution, dried, and distilled, to yield the *dioxan* (6·3 g., 63%), b.p. 97°/0·5 mm., n_D^{24} 1·5080 (Found: C, 76·1; H, 8·8; $C_{13}H_{18}O$ requires C, 75·7; H, 8·8%).

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[19] G. Wood and M. Miskow, *Tetrahedron Letters,* 1966, 4433.