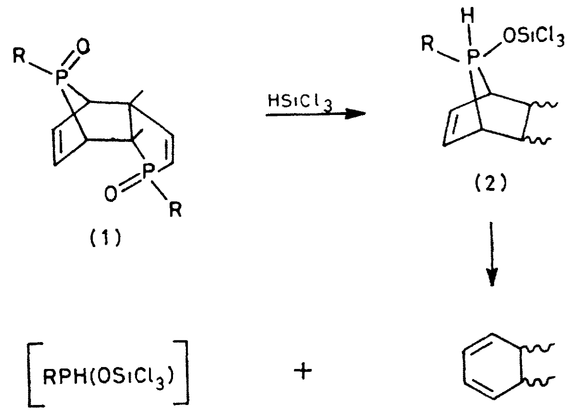
# Extraordinary Deshielding of $^{31}P$ in Phosphines of the *syn*-7-Phosphanorbornene System

By LOUIS D. QUIN* and KEITH A. MESCH
(*Gross Chemical Laboratory, Duke University, Durham, North Carolina* 27706)

*Summary* Deoxygenation of phosphole oxide dimers with $HSiCl_3$–$C_5H_5N$, but not $HSiCl_3$ alone, gives stable diphosphines whose phosphorus atoms in the *syn*-7-phosphanorbornene position have the most deshielded $^{31}P$ n.m.r. shifts ever reported for tertiary phosphines.

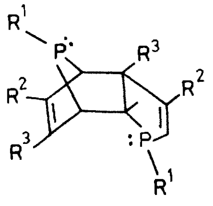
ALTHOUGH the 7-phosphanorbornene system has been known for a number of years[1] in compounds where the phosphorus is in the oxide, sulphide, or quaternary salt state, no tertiary phosphines in this system are known. Attempts to deoxygenate *P*-oxides in the related 7-phosphanorbornadiene system have always resulted in loss of the P bridge.[2] We have now found that, if deoxygenated under the proper conditions, loss of the P bridge can be avoided and the phosphine oxides of 7-phosphanorbornenes are ready sources of the tertiary phosphines. While these phosphines do have some unusual properties, they are quite stable at room temperature and require no unusual care in their handling.

Our studies have employed the 7-phosphanorbornene system as contained in the dimers of phosphole oxides (**1**).



We have found that the conventional technique of deoxygenation with $HSiCl_3$ in benzene can lead to extensive, or even complete, loss of the P bridge This is not due to a property of the phosphines, however, but to the formation of a $P^V$ intermediate (*e g* , **2**) which, as deduced from the nature of the isolated reaction products, undergoes retro-McCormack cycloaddition[3] to form a diene unit (**3**) and a $P^{III}$ molecule (**4**)

Details of this reaction will be reported in due course, of more synthetic importance is its *avoidance*, which we have accomplished by conducting the $HSiCl_3$ reduction in the presence of pyridine (reaction conditions refluxing benzene, molar ratio of oxide: $HSiCl_3$: $C_5H_5N$ 1 : 5 : 15) Apparently, competition for hydrogen interferes with the formation of the $P^V$ form, and allows normal deoxygenation to proceed The phosphines that have been prepared from the corresponding *P*-oxides are shown in the Table They were converted into their disulphides for elemental analysis The diphosphines are converted back into the dioxides with $H_2O_2$ (retention[4]) proving that the $HSiCl_3$–$C_5H_5N$ reduction, as usual,[5] proceeded with retention The $^{13}C$ n m r spectra are also convincing in showing that the phosphines had *syn* geometry at P, $^2J_{PC}$ values of phosphines are well known to be influenced by the proximity of the carbon to the lone-pair (greater coupling with closer proximity[6]), and compound (**5**) illustrates the presence of this effect in a typical diphosphine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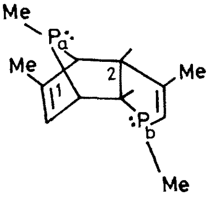
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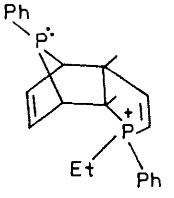
C-1 δ 142 4, $^2J(P_aC)$ 4 2 Hz
C-2 δ 59 6, $^2J(P_aC)$ 28 1 Hz
$^2J(P_bC)$ 4 2 Hz

The phosphines gave the totally unexpected result of displaying $^{31}P$ n m r signals in the *downfield region* of δ 100—120 p p m No other tertiary phosphine has signals close to this region[7] and current thinking would even suggest that the contracted C–P–C angle would be associated with strong *shielding*[8] The downfield shift is even more dramatic in mono-quaternary salts such as (**6**) where the bridging phosphorus appears at δ +147 1 p p m (with the 2-phospholen P at δ +56 1 p p m , $^3J$ 44 0 Hz) Two structural features appear essential for the unusual deshielding of these phosphines (i), the double bond, since the corresponding saturated diphosphines [*e g* , (**7**), prepared by hydrogenation of the dioxide and then deoxygenation with $HSiCl_3$] gave quite normal $^{31}P$ shifts for phospholan moieties,[9] (ii) the *syn* geometry at P, since the corresponding *anti* isomers [*e g* , (**8**), whose synthesis and n m r properties will be reported elsewhere[10]] lack the extraordinary deshielding of the *syn* isomer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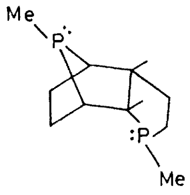
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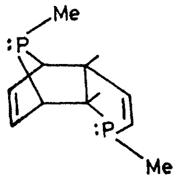
(**7**) δ −18 0 and −21 7 p p m (AB spectrum)
$^3J_{PP}$ 22 0 Hz

TABLE Diphosphines (**9**) and their properties

| $R^1$ | $R^2$ | $R^3$ | % Yield | M p or b p ($T$/°C) | δ $^{31}P$/p p m ($^3J_{PP}$/Hz)[a] | Sulphide, m p , °C |
|---|---|---|---|---|---|---|
| Ph | H | H | 83 | 124—127 | +114 2, +15 7 (24 4) | 181—183[b] |
| Ph | Me | H | 84 | Oil | +119 8 +15 0 (24 4) | 206—208[c] |
| Me | H | H | 80 | 75—78 (0 03 mmHg) | +96 5 −2 3 (24 4) | 198—199 |
| Me | Me | H | 80 | 80—83 (0 02 mmHg) | +100 7, −1 9 (24 4) | 226—228 |
| Me | Me | Me | 78 | 77—80 | +98 8, −14 4 (29 3) | 158—159 |

[a] Fourier transform proton decoupled, positive shifts are downfield, negative upfield of 85% $H_3PO_4$ as reference [b] Lit m p 183—184 °C G Markl and R Potthast, *Tetrahedron Lett* , 1968, 1755 [c] Lit m p 206 °C F Mathey and R Mankowski-Favelier, *Bull Soc Chim Fr* , 1970, 4433



(8)

δ +30·2 and −7·9 p.p.m.

Since the C–P–C bond angles should be very similar in the *syn* and *anti* isomers, and in the saturated form as well, this parameter, novel as it must be for a bridging P, can be dismissed as a direct cause of the $^{31}$P effect for the *syn* isomer. The nature of the orbital or steric interactions that must be responsible for the effect remains to be identified, but it is obvious that the effect is of very large magnitude and appears to result from an influence not previously recognized in $^{31}$P n.m.r. studies of phosphines.

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[8] For a recent discussion, see C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

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