reaction. The use of cobalt and other metal carbonyls, as catalysts for other organoborane reactions, is under active investigation.

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Registry No. **3** (R = PhCO; R′ = R″ = Ph), 4198-95-2; **3** (R = p-$CH_3C_6H_4CO$; R′ = p-$CH_3C_6H_4$; R″ = Ph), 82537-51-7; **3** (R = p-$CH_3OC_6H_4CO$; R′ = p-$CH_3OC_6H_4$; R″ = Ph), 82537-52-8; **3** (R = PhCO; R′ = Ph; R″ = p-$CH_3OC_6H_4$), 4198-96-3; **3** (R = p-$CH_3OC_6H_4$; R′ = H; R″ = Ph), 836-41-9; **4** (R‴ = C_2H_5), 97-94-9; **4** (R‴ = n-C_4H_9), 122-56-5; **4** (R‴ = n-C_7H_{15}), 3244-73-3; **4** (R‴ = $PhCH_2CH_2$), 1883-35-8; **4** (R‴ = $PhCH(CH_3)CH_2$), 51136-87-9; **4** (R‴ = Ph), 960-71-4; **5** (R = PhCO; R′ = R″ = Ph; R‴ = C_2H_5), 80783-92-2; **5** (R = PhCO; R′ = R″ = Ph; R‴ = n-C_4H_9), 82537-53-9; **5** (R = PhCO; R′ = R″ = Ph; R‴ = n-C_7H_{15}), 82544-30-7; **5** (R = PhCO; R′ = R″ = Ph; R‴ = $PhCH_2CH_2$), 82537-54-0; **5** (R = PhCO; R′ = R″ = Ph; R‴ = $PhCH(CH_3)CH_2$), 82537-55-1; **5** (R = PhCO; R′ = R″ = R‴ = Ph), 81640-85-9; **5** (R = p-$CH_3C_6H_4CO$; R′ = p-$CH_3C_6H_4$; R″ = Ph; R‴ = n-C_4H_9), 82537-56-2; **5** (R = p-$CH_3OC_6H_4CO$; R′ = p-$CH_3OC_6H_4$; R″ = Ph; R‴ = C_2H_5), 82537-57-3; **5** (R = PhCO; R′ = Ph; R″ = p-$CH_3OC_6H_4$; R‴ = C_2H_5), 80783-96-6; **5** (R = p-$CH_3OC_6H_4$; R′ = H; R″ = Ph; R‴ = C_2H_5), 82537-58-4; **6** (R = PhCO; R′ = R″ = Ph), 5722-91-8; **6** (R = PhCO; R′ = Ph; R″ = p-$CH_3OC_6H_4$), 19339-72-1; **7**, 82537-59-5; dicobalt octacaronyl, 10210-68-1.

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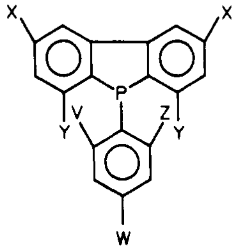
Preferred Geometry of the Through Space 2p-3d Overlap Effect

Summary: Six 5-aryldibenzophospholes have been prepared and the rates of their S_N2 reactions with benzyl chloride in chloroform solution measured.

Sir: In order to determine the preferred geometry of the 2p-3d overlap effect, [1-7] we have prepared the six dibenzophospholes listed in Table I. The essentially rigid geometrical relationship between the methoxy groups and phosphorus in compounds **1** and **2**, as against the variable geometrical relationships possible for **3**, **4**, and **5**, have enabled us to determine the geometrical requirement for the occurrence of maximum through space 2p-3d overlap effects. It is apparent from the relative rate data for the reactions of compounds **1**-**6** with benzyl chloride that the maximum acceleration results when the 5-aryl group containing an o-methoxy substituent can be orthogonal to the dibenzophosphole ring. Thus, the transition state that affords the maximum through space 2p-3d overlap is that shown in **7** or **7a**, in which an o-methoxy substituent of the orthogonal 5-aryl group occupies a quasi-apical position of an incipient trigonal-bipyramidal configuration.

Table I. Rate Data for the Reactions of Dibenzophospholes with Benzyl Chloride in Chloroform Solution at 31.0 °C



compd	rel rate	$\Delta H^{\ddagger}$, kcal/m	$\Delta S^{\ddagger}$, eu
1, X = OMe; V = W = Y = Z = H	3.92	12.8	−41
2, Y = OMe; X = W = V = Z = H	15.6	12.0	−43
3, Z = OMe; X = Y = V = W = H	13.3	14.9	−32
4, W = OMe; X = Y = V = Z = H	1.77	12.0	−46
5, V = Z = OMe; X = Y = W = H	77.7	16.3	−24
6, X = Y = Z = V = W = H	1.00[a]	13.8	−41

[a] $k = 1.78 \times 10^{-6}$ L mol^{-1} s^{-1} at 26.0 °C; $k = 2.50 \times 10^{-6}$ L mol^{-1} s^{-1} at 31.0 °C; $k = 3.56 \times 10^{-6}$ L mol^{-1} s^{-1} at 36.0 °C. Each value of k derived from three independent experiments; average deviation ±3%. Estimates of precision measures are ±1.2 kcal/mol for $\Delta H^{\ddagger}$ and ±5.0 eu for $\Delta S^{\ddagger}$.

It is of importance to point out that the crystal and molecular structure of 5-(p-bromophenyl)-5-phenyldibenzophospholium bromide has been determined by Allen et al.,[8] who have found that the endocyclic C-P-C bond angle is only 93.9°. (In fact, the transition state depicted in **7** or **7a** is modeled on Allen's crystal structure for the salt.) This indicates significant deformation of bond angles for the quaternary phosphonium moiety compared with an acyclic phosphonium salt and helps to explain why 5-aryldibenzophospholes undergo quaternization reactions much more slowly than the corresponding triarylphosphines.[1-8] Furthermore, Allen et al. point out that the bond angle strain (and accompanying ring strain) "would be relieved on formation of a quinquecovalent trigonal bipyramidal phosphorane, in which the endocyclic C-P-C bond angle would be 90°, assuming that the five-membered ring occupies apical-equatorial positions as is generally found". This does much to explain why dibenzophospholium salts undergo alkaline cleavage (*with ring opening*) very rapidly in comparison with the normal hydrolysis of their acyclic analogues.[8] This observation is pertinent to the present study because a possible through space 2p-3d interaction of the type shown in the transition-state **7a** (with the consequent quasi-trigonal-bipyramidal configuration about phosphorus) would help to alleviate the angle strain that otherwise grows as quaternization proceeds.

The reactions were carried out at three different temperatures, and the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined. It is apparent from the data that a large decrease in $\Delta S^{\ddagger}$ arises only when an o-methoxy group is present on the 5-aryl group, as in the reactions of compounds **3** and **5**. At the same time, the interaction of the methoxy groups of **3** with the phosphorus compensates to a large degree for any possible loss of stabilization of the transition state by interaction with the solvent, and, therefore, the value

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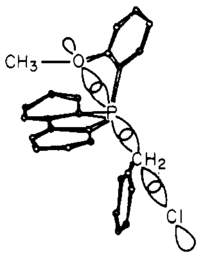
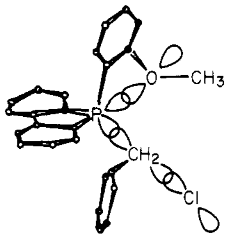


7



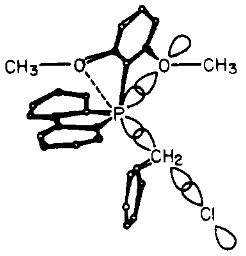
7a

of $\Delta H^{\ddagger}$ for the reaction of **3** with benzyl chloride is not significantly greater than that for the reaction of **6** with the same halide.

As pointed out previously,[1] intramolecular solvation of the type depicted in **7** or **7a** frees a solvent molecule, in contrast to the state of affairs for the dibenzophosphole system itself or for the transition states of the reactions of **1**, **2**, or **4**. The decrease in bonding to the solvent in the transition states for **3** and **5** leads to an increase of mobility of some solvent molecules, and this, in turn, causes an increase in the entropy of activation (i.e., this leads to a less negative value of $\Delta S^{\ddagger}$). Other factors have been considered previously.[3]

The small acceleration observed for the reactions of **1** and **4**, respectively, with benzyl chloride is undoubtedly attributable mainly to an inductive effect; i.e., the *p*-methoxy group causes an increase in the electron density of the attached aryl ring by a resonance effect, but this increase in electron density is felt by the phosphorus mainly through the inductive effect. There is convincing evidence, which we have cited previously,[7] that p_π–d_π overlap between carbon and phosphorus is at best of minor importance only. As evident from the data on the reactions of **1** and **4**, respectively, with benzyl chloride, the small rate acceleration is attributable mainly to a small decrease in $\Delta H^{\ddagger}$.

It is not certain which factors are mainly responsible for the modest rate enhancement observed in the reaction of compound **2** with benzyl chloride. As mentioned previously,[4] a different type of through space 2p–3d overlap from that operative in the case of the reaction of **3** or **5** with benzyl chloride (e.g., overlap with an incipient d_{xy} orbital of phosphorus rather than a d_{z^2} orbital), or an inductive effect, or a field effect, or a combination of these may be involved. In like manner, the fundamental basis of the effect of the second methoxy group of compound **5** in its reaction with benzyl chloride is not certain; a double overlap effect, an inductive effect superimposed on the through space 2p–3d overlap effect of the first methoxy group, or a field effect superimposed on the overlap effect of the first methoxy group may be involved. The fact that the value of $\Delta S^{\ddagger}$ for the reaction of **5** with benzyl chloride is the least negative of all of the values shown in the table is consistent with the transition-state **8**, in which a favorable intramolecular backside solvation is superimposed on the "normal" through space interaction depicted in **7a**. It is also possible that the multiple repulsive interactions of the lone pairs of electrons on the methoxy groups and the phosphorus atom of 5-(2,6-dimethoxyphenyl)dibenzophosphole, **5**, are decreased as quaternization proceeds, which would be another rate-enhancing effect. At the same time, unfavorable steric interactions of the second methoxy group with the dibenzophosphole ring might account for the relatively high value of $\Delta H^{\ddagger}$ in this reaction.



8

5-Phenyldibenzophosphole, **6**, mp 95.7–96.2 °C, was prepared by the method of Nesmeyanov, et al.[9] 5-Phenyl-2,8-dimethoxydibenzophosphole, **1**, mp 137–138 °C, was prepared by the procedure of Allen et al.[10] 5-Phenyl-4,5-dimethoxydibenzophosphole, **2**, mp 230 °C (dec) was prepared by an adaptation of the method of McEwen et al.,[4] in which 3,3′-dimethoxybiphenyl was dilithiated by the action of *n*-butyllithium in ether and the dilithio derivative then treated with dichlorophenylphosphine. 5-(*p*-Methoxyphenyl)dibenzophosphole, **4**, mp 98–99 °C, was prepared by treatment of 2,2′-dilithiobiphenyl[11] with dichloro(*p*-methoxyphenyl)phosphine[12] in ether. Dichloro(*o*-methoxyphenyl)phosphine was prepared by treatment of bis(isopropylamino)(*o*-methoxyphenyl)phosphine with anhydrous hydrogen chloride in an adaptation of the method developed by Burg and Slota.[13,14] Reaction of the dichlorophosphine with 2,2′-–dilithiobiphenyl[11] gave 5-(*o*-methoxyphenyl)dibenzophosphole, **3**, mp 142–144 °C. Reaction of 2-lithio-1,3-dimethoxybenzene[4] with chlorobis(isopropylamino)phosphine gave bis(isopropylamino)(2,6-dimethoxyphenyl)phosphine, which was converted to dichloro(2,6-dimethoxyphenyl)phosphine, mp 65 °C, by the action of dry hydrogen chloride.[13,14] Reaction of the dichloro compound with 2,2′-dilithiobiphenyl[11] afforded 5-(2,6-dimethoxyphenyl)dibenzophosphole, **5**, mp 168–170 °C.

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Registry No. 1, 34938-20-0; 2, 82614-77-5; 3, 82614-78-6; 4, 82614-79-7; 5, 82614-80-0; 6, 1088-00-2; benzyl chloride, 100-44-7; 3,3′-dimethoxybiphenyl, 6161-50-8; dichlorophenylphosphine, 644-97-3; 2,2′-dilithiobiphenyl, 16291-32-0; dichloro(*p*-methoxyphenyl)phosphine, 19909-85-4; dichloro(*o*-methoxyphenyl)phosphine, 58325-49-8; bis(isopropylamino)(*o*-methoxyphenyl)phosphine, 82614-81-1; 2-lithio-1,3-dimethoxybenzene, 2785-97-9; chlorobis(isopropylamino)phosphine, 82614-82-2; bis(isopropylamino)(2,6-dimethoxyphenyl)phosphine, 82614-83-3; dichloro(2,6-dimethoxyphenyl)phosphine, 82614-84-4.

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