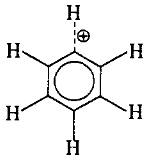
location of a π-electron to this σ-orbital before dissociation of the collision complex. The complex lifetime partially depends upon the depth of the potential well accessible to reactants: this potential well will be much shallower than is suggested by the heat of formation of ground-state $C_6H_6^{\bullet+}$. The threshold for the electronically forbidden ${}^2E_{2g}(\sigma-1) \leftarrow {}^2E_{1g}(\pi-1)$ transition has been assigned at 502 nm,[14] corresponding to an energy difference of 57 kcal mol^{-1}. The potential well depth of the collision complex IV thus cannot exceed 31 kcal mol^{-1}, leading to a substantially reduced complex lifetime consistent with the observed lack of association.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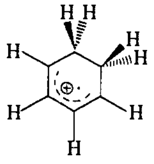
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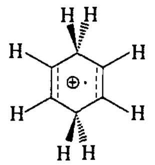
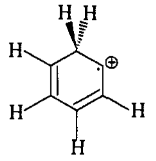
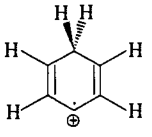

VI

The apparent saturation (as inferred by the lack of pressure dependence)[15] of the association reaction of $C_6H_6^{\bullet+}$ with $H^\bullet$ is consistent with conservation of spin in this reaction. The association is seen to occur at $k/k_c = 0.13 \pm 0.07$, reasonably close to that fraction ($^1/_4$) of the collision rate which would be expected for formation of singlet products. The lowest lying triplet state of $C_6H_7^+$, if bound, presumably is sufficiently far above the ground singlet state to render the triplet association channel much less efficient; alternatively, triplet association may fall upon a repulsive curve. H-atom transfer does not occur because essentially all collisions leading to the singlet potential surface result in association, while H-atom transfer on the triplet potential surface is presumably endothermic: the highest level theoretical calculation performed on the singlet–triplet separation in $C_6H_5^+$ places the B_1 level at 5 ± 15 kcal mol^{-1} above the ${}^1A_1$ level.[17] The uncertainty of this calculation is sufficient to permit the endothermicity of this channel. The lack of association of $C_6H_7^+$ with $H^\bullet$ is consistent with the shallower potential well for this reaction. The absence of H-atom transfer is more surprising, since the arguments presented above for $C_6H_5^+$ and $C_6H_6^{\bullet+}$ clearly do not apply to the reaction of $C_6H_7^+$ with $H^\bullet$. Two collision complexes, V and VI, can be formed corresponding to the dominant centers of charge localization in structure III. Loss of H_2 by 1:1 elimination from these complexes would give the isomers VII and VIII, respectively, whose heats of formation are not known but are probably sufficiently high that their production in this reaction is endothermic. (1,2)- and (1,4)-hydrogen shifts would convert VII and VIII, respectively, to II; the absence of H-atom transfer in $C_6H_7^+ + H^\bullet$ suggests that a barrier prevents their occurrence concomitantly with H_2 loss.[18]


VII


VIII

In summary, we have measured rate coefficients for reactions of $H^\bullet$ and H_2 with several hydrocarbon ions generated from benzene and have proposed mechanisms to account for the observed reactivities. These results appear to preclude a catalytic role in H-atom recombination for all three of the benzenoid hydrocarbon ions as well as the linear $C_6H_5^+$ isomer investigated in this study.

Acknowledgment. The authors thank Dr. A. Viggiano for his advice on the construction of the H-atom source and we are grateful to Dr. A. C. Hopkinson and Dr. E. Lee-Ruff for useful discussions on reaction intermediates. D.K.B. thanks the Natural Sciences and Engineering Research Council of Canada for the financial support of this research and the Canada Council for a Killam Research Fellowship.

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(14) Kodera, Y.; Hikida, T. *Spectrosc. Lett.* **1989**, *22*, 1229.

(15) The observation of apparent saturation suggests the occurrence of a saturated termolecular reaction in which the $C_6H_7^+$ is stabilized by collisions with the He buffer gas, but it does not rule out the possibility of bimolecular radiative association[16] or, indeed, the occurrence of a combination of the two.

(16) Dunbar, R. C. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 423.

(17) Bernardi, F.; Grandinetti, F.; Guarino, A.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *153*, 309.

(18) Several examples of simpler systems (e.g., $CHN^{\bullet+}$, CH_2N^+, CHO^+, and $CH_2O^{\bullet+}$) in which substantial barriers exist to isomerizations by (1,2)-shifts have been discussed in the literature. See, for example: (a) Schaefer, H. F. *Acc. Chem. Res.* **1979**, *12*, 288. (b) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95.

Endocyclic Restriction Test: Experimental Evaluation of the Transition Structure Geometry of a Nucleophilic Substitution at Trivalent Phosphorus

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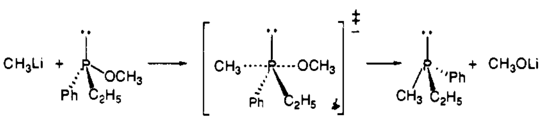
Received July 20, 1992

The generally accepted mechanism for nucleophilic substitution at trivalent phosphorus is the S_N2 in-line process.[1,2a,b,3] The reaction of **1** with methyllithium to give **2** is illustrative of these reactions, which have been found to proceed with inversion of configuration at phosphorus.[1-4] We wish to report an evaluation of the transition structure geometry for a nucleophilic substitution of an alkoxyl group by an aryllithium at trivalent phosphorus. Our results rule out a classic S_N2 in-line mechanism for the system we have studied.



1 2

In an application of the endocyclic restriction test, we have investigated the conversion of **3** to **4**.[5] If a geometry is required for substitution in which the entering and leaving groups are simultaneously in the apical positions of a trigonal bipyramid about phosphorus, this conversion would be intermolecular because a 180° disposition of the entering and leaving groups would not be possible within the five-membered endocyclic ring required for an intramolecular reaction. However, if the reaction can proceed by a different pathway, an intramolecular process could be observed.

3 4

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(1) Mikolajczyk, M. *Pure Appl. Chem.* **1980**, *52*, 959. Mikolajczyk, M.; Omelanczuk, J.; Perlikowska, W. *Tetrahedron* **1979**, *35*, 1531. Omelanczuk, J.; Mikolajczyk, M. *J. Chem. Soc., Chem. Commun.* **1976**, 1025.

(2) (a) Kyba, E. P. *J. Am. Chem. Soc.* **1976**, *98*, 4805; **1975**, *97*, 2554. Kyba, E. P.; Hudson, C. W. *Tetrahedron Lett.* **1975**, 1869. (b) Nielsen, J.; Dahl, O. *J. Chem. Soc., Perkin Trans. 2* **1984**, 553. Dahl, O. *Phosphorus Sulfur* **1983**, *18*, 201. (c) Smith, D. J. H.; Trippett, S. *Chem. Commun.* **1969**, 855. Corfield, J. R.; Oram, R. K.; Smith, D. J. H.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 713.

(3) For a study of free radical displacement at trivalent phosphorus, see: Bentrude, W. G.; Moriyama, M.; Mueller, H.; Sopchik, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 6053 and references cited therein.

(4) Cases with partial or complete retention of configuration at phosphorus have been reported for a few cyclic chlorophosphine systems; see: Keglevich, G.; Quin, L. D. *Phosphorus Sulfur* **1986**, *26*, 129. Hall, C. D.; Inch, T. D. *Tetrahedron Lett.* **1976**, 3645. Märkl, G.; Alig, B. *J. Organomet. Chem.* **1984**, *273*, 1.

(5) Beak, P. *Acc. Chem. Res.* **1992**, *25*, 215 and references cited therein.

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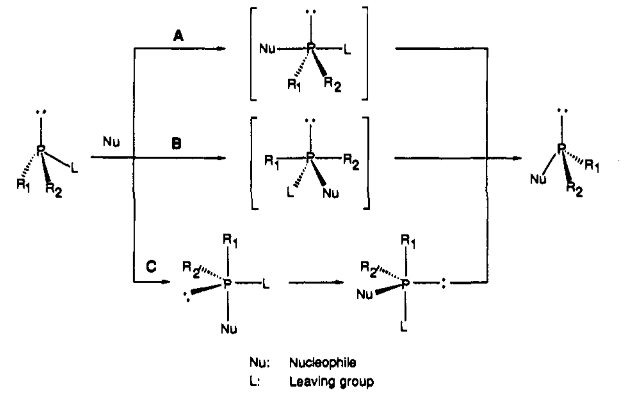
Table I. Isotopic Ratios of Reactants **5** and **5-D_2D_{10}** and Products **6** and **6-D_2D_{10}** (%)[a]

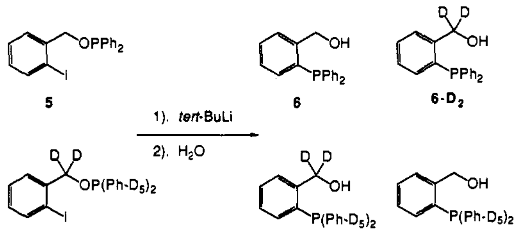
	M	M + 1	M + 2	M + 10	M + 11	M + 12
reactants[a,b]						
5 and **5-D_2D_{10}**	42	0	0	4	12	43
products						
6, **6-D_2**, **6-D_{10}**, and **6-D_2D_{10}** (intermolecular reaction)[c]	19	5	18	27	7	25
6 and **6-D_2D_{10}** (intramolecular reaction)[c]	42	0	0	4	12	43
experimental value[a]	48	0	1	1	9	42

[a] Determined by FIMS (±6%). [b] A mixture of **5** and **5-D_2D_{10}** with minor amounts of reactant containing 1 or 2 fewer deuteriums. [c] Calculated based on the ratios of reactant.

Scheme I

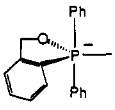


When a 0.1 M solution of 2-iodobenzyl diphenylphosphinite (**5**) in dry THF was treated with 2.2 equival of *tert*-butyllithium at −78 °C to generate the intermediate aryllithium **3** in situ, a 65% yield of the rearranged product **6** was obtained after hydrolysis at −78 °C and purification by MPLC. A double-labeling experiment was carried out with a 0.01 M solution of a mixture of **5** and **5-D_2D_{10}** to distinguish between the intermolecular and intramolecular pathways. For an intermolecular process, the product would be a mixture of **6**, **6-D_2**, **6-D_{10}**, and **6-D_2D_{10}**, whereas an intramolecular reaction would give only **6** and **6-D_2D_{10}**. Comparison of the isotopic ratios of reactants and products as summarized in Table I clearly shows that the conversion of **3** to **4** proceeds by an intramolecular pathway.[6]



The mechanisms which are plausible for substitution at trivalent phosphorus are shown in Scheme I for inversion of configuration. A is the classic S_N2 in-line process.[1,2a,b] B involves an equatorial attack of nucleophile followed by an equatorial loss of the leaving group;[2c,7] either of these processes could involve a transition state or an intermediate. C is an apical attack of the nucleophile to form a hypervalent intermediate, followed by either two Berry pseudorotations (BPR) or a type 2 turnstile rotation (TR^2).[8,9]

The S_N2 in-line process of pathway A is ruled out for the conversion of **3** to **4** by the intramolecularity of the reaction. Pathway B with the nucleophile and leaving group occupying the diequatorial positions would involve **7** or **8** as an intermediate and give an inverted product. Since these structures are inconsistent with the generally accepted apical–equatorial positions for a five-membered ring, this pathway may be considered unfavorable but cannot be excluded.[10]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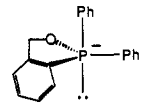
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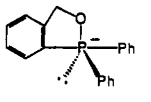
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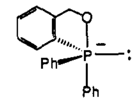
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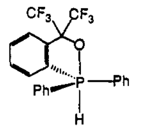
11

Displacement via pathway C would involve initial formation of **9** followed by either two BPR or a TR^2 process to give **10** which could undergo apical loss of the alkoxyl group to give an inverted product.[1,2,11] The proposed intermediate **10** finds analogy in **11**, a compound reported by Martin and Ross.[12] Alternatively, one BPR of **9** using the lone pair as the pivot position followed by the loss of an apical group could give a retained product.

In summary, the present results establish that the geometry of a classic S_N2 in-line pathway is not required for nucleophilic substitution at trivalent phosphorus. Further work will be required to determine the relationship of this result to the general case.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for the support of this work.

Supplementary Material Available: Listings of preparation and characterization data of compounds **5** and **5-D_2D_{10}** and details of the procedure of the double-labeling experiment (6 pages). Ordering information is given on any current masthead page.

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(6) This result is in contrast to the comparable reactions at nitrogen, see: Beak, P.; Li, J. *J. Am. Chem. Soc.* **1991**, *113*, 2796. Beak, P.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc.* **1986**, *108*, 6016. Beak, P.; Selling, G. W. *J. Org. Chem.* **1989**, *54*, 5574.

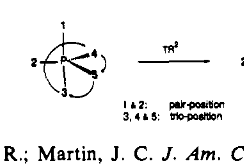
(7) Trippett's claim of this mechanism[2c] has been reinterpreted as an S_N2 reaction by Hudson, Holmes, and Luchenbach; see: (a) Hudson, R. F.; Brown, C. *Acc. Chem. Res.* **1972**, *5*, 204. (b) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monograph 1976; American Chemical Society: Washington, DC, 1980; Vol. II, pp 163–165. (c) Luckenbach, R. *Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements*; Georg Thieme Publishing: Stuttgart, 1973; pp 149–151.

(8) For a discussion of Berry pseudorotation (BPR), see: Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70.

(9) For a discussion of turnstile rotation (TR), see: (a) Gillespie, P.; Ramirez, F.; Ugi, I.; Marquarding, D. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 91. (b) Gillespie, P.; Hoffman, P.; Klusacek, H.; Marquarding, D.; Pfohl, S.; Ramirez, F.; Tsolis, E. A.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 687. (c) Davies, B.; McNeish, A.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 7573.

(10) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; John Wiley & Sons: New York, 1976; pp 65–72. Reference 7b, p 88. Trippett, S. *Pure Appl. Chem.* **1974**, *40*, 595.

(11) The type 2 turnstile rotation (TR^2) refers to no exchange in the pair positions, but rotation of trio positions as shown below.



(12) Ross, M. R.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1234.