

the prediction of a positive change in  $^2J_{\text{HH}}$  is also associated with inductive withdrawal, so an additional comparison is needed. This is provided by cases 5 and 6. Comparison of cases 5 and 6 shows that the inductive differences are rather small. The value of  $J_{34}$  for set 6 is less than that for set 5, corresponding to the fact that the  $P_{2p_x,2p_z}$  value in 6 is larger than that for set 5. Similarly, the  $J_{33}$  value for set 6 is greater than that for 5, and this agrees with the fact that  $P_{2p_x,2p_z}$  is smaller in set 6 than for set 5. Thus the results in Table I convey a self-consistent picture of established patterns of experimental substituent effects.

Work is currently under way exploring further the use of the pseudo-atom approach in  $\text{CH}_3\text{X}$  and other systems to simulate common patterns of substituent effects with the aim of gaining insight into their fundamental nature.

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(15) Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

Gary E. Maciel,\*<sup>15</sup> Kim D. Summerhays  
Department of Chemistry, University of California  
Davis, California 95616

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## Phosphaundecaboranes

Sir:

During the last 3 years, several reports have appeared on the insertion of representative elements other than carbon into boron hydrides or carboranes. Boron hydrides containing sulfur,<sup>1</sup> nitrogen,<sup>1</sup> or phosphorus<sup>2</sup>

Deprotonation of decaborane(14) in diethyl ether with sodium hydride and then slow addition of a diethyl ether solution of  $\text{C}_6\text{H}_5\text{PCl}_2$  produce  $\text{B}_{10}\text{H}_{12}\text{PC}_6\text{H}_5$  (I) in moderate yield. Unreacted decaborane is removed by sublimation and the residues are dissolved in aqueous ammonia and precipitated with tetramethylammonium chloride solution. The crude salt is dried, dissolved in acetonitrile, and passed through strongly acidic ion exchange resin. Sublimation produces pure I, mp 82–84°. The low-energy mass spectrum cuts off at  $m/e$  230, corresponding to the parent ion  $^{11}\text{B}_{10}^{1}\text{H}_{17}^{12}\text{C}_6^{31}\text{P}^+$ . The ring protons appear in the proton nmr spectrum as a complex multiplet centered at  $-7.8$  ppm. Doublets in the boron-11 nmr spectrum at 32.1 MHz are badly overlapped, but can be interpreted as the 1:1:2:2:2:2 pattern expected for  $C_s$  symmetry. This does not distinguish between 7- $\text{B}_{10}\text{H}_{12}\text{PC}_6\text{H}_5$  and 2- $\text{B}_{10}\text{H}_{12}\text{PC}_6\text{H}_5$ .<sup>9</sup> Assuming, however, that the decaborane framework has not rearranged under the mild reaction conditions, 7- $\text{B}_{10}\text{H}_{12}\text{PC}_6\text{H}_5$  would be the product of simple phosphorus insertion.

Synthesis of 7- $\text{B}_{10}\text{H}_{12}\text{PCH}_3$  (II) (mp 86.5–88.5°) is carried out by the method cited above for I using  $\text{CH}_3\text{PCl}_2$ . The low-energy mass spectrum cuts off at  $m/e$  168, corresponding to the parent ion  $^{11}\text{B}_{10}^{1}\text{H}_{15}^{12}\text{C}^{31}\text{P}^+$ . The proton nmr spectrum at 60 MHz consists of a doublet ( $J_{\text{PCH}} = 11$  Hz) centered at  $-2.08$  ppm, assigned to  $\text{P}-\text{CH}_3$ . Boron-11 nmr at 70.6 MHz shows six different types of boron in 1:1:2:2:2:2 distribution, strongly suggesting that this molecule possesses  $C_s$  symmetry.

For I and II, one bridging proton can be removed by weak base, such as aqueous ammonia, and both "extra" protons can be removed by strong base, such as NaH. Addition of aqueous tetramethylammonium chloride to aqueous ammonia solutions of I and II precipitates

Table I. Analytical Data

Compound	Calculated, %						Found, %					
	C	H	B	P	Mn	Mol wt	C	H	B	P	Mn	Mol wt <sup>a</sup>
$\text{B}_{10}\text{H}_{12}\text{PC}_6\text{H}_5$	31.58	7.51	47.40	13.57		228.2	31.62	7.51	45.46	13.54		235
$(\text{CH}_3)_4\text{NB}_{10}\text{H}_{11}\text{PC}_6\text{H}_5$	39.85	9.36	35.86	10.36		301.4	39.67	9.42	35.74	10.17		
$\text{B}_{10}\text{H}_{12}\text{PCH}_3$	7.23	9.10	65.04	18.63		166.2	7.23	9.28	64.60	17.93		166
$(\text{CH}_3)_4\text{NB}_{10}\text{H}_{11}\text{PCH}_3$	25.09	10.95	45.17	12.94		239.3	25.19	10.76		13.28		
$(\text{CH}_3)_4\text{N}(\text{B}_{10}\text{H}_{10}\text{PC}_6\text{H}_5)\text{Mn}(\text{CO})_3$	35.53	6.19	24.62	7.05	12.50	439.3	35.04	6.53	24.40		12.28	

<sup>a</sup> Osmometric in benzene

and carboranes containing Be,<sup>3</sup> Al,<sup>4</sup> Ga,<sup>5</sup> Ge,<sup>6</sup> Sn,<sup>6</sup> Pb,<sup>6</sup> P,<sup>7</sup> As,<sup>8</sup> or Sb<sup>8</sup> have been reported. One polyhedral phosphaborane,  $\text{B}_{11}\text{H}_{11}\text{PC}_6\text{H}_5$ , was prepared in very low yield.<sup>2</sup> This communication is concerned with the preparation and some chemistry of 11-atom *nido*-phosphaboranes.

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$[(\text{CH}_3)_4\text{N}]7\text{-B}_{10}\text{H}_{11}\text{PC}_6\text{H}_5$  (III) or  $[(\text{CH}_3)_4\text{N}]7\text{-B}_{10}\text{H}_{11}\text{PCH}_3$  (IV), both of which are recrystallized from acetone-ethanol. A sharp singlet (12 H) and a broad multiplet (5 H) appear at  $-3.48$  and  $-7.65$  ppm, respectively, in the proton nmr spectrum of III. The proton nmr spectrum of IV consists of a sharp doublet (3 H,  $J_{\text{PCH}} = 9$  Hz) at  $-1.60$  ppm and a sharp singlet (12 H) at  $-3.50$  ppm. The boron-11 nmr spectrum of III at 32.1 MHz is very similar to that of the analogous thiaborane,<sup>1</sup>  $\text{B}_{10}\text{H}_{11}\text{S}^-$ .

By treating I in tetrahydrofuran with 2 equiv of NaH and 1 equiv of  $\text{BrMn}(\text{CO})_5$ , moderate yields of  $(\text{B}_{10}\text{H}_{10}\text{PC}_6\text{H}_5)\text{Mn}(\text{CO})_3^-$  may be obtained. The pale yellow [ $\lambda_{\text{max}}$ ,  $m\mu$  ( $\epsilon$ ): 219 (23,000), 309 (sh, 1060), 340 (sh, 901)] tetramethylammonium salt of this metallocene

(9) This numbering system conforms to the nomenclature rules published in *Inorg. Chem.*, **7**, 1945 (1968).

analog is air sensitive and must be crystallized from methylene chloride-hexane in an inert atmosphere. In the infrared spectrum (CH<sub>3</sub>CN solution) the characteristically sharp A mode is seen at 2008 cm<sup>-1</sup>. However, the E mode predicted by C<sub>3v</sub> local symmetry for Mn(CO)<sub>3</sub> is split into a broad doublet (1933 and 1919 cm<sup>-1</sup>). Splitting of the E mode<sup>10</sup> is also observed in the spectrum of (1,7-B<sub>9</sub>H<sub>9</sub>CHPCH<sub>3</sub>)Mn(CO)<sub>3</sub><sup>-</sup>. Analytical data for all compounds are given in Table I.

Further studies of phosphaborane chemistry are now in progress and will be reported later.

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John L. Little,\* Andrew C. Wong

Department of Chemistry, The University of Mississippi  
University, Mississippi 38677

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### Energy Barriers in Photochemical Reactions. A Case for the Relevance of Woodward-Hoffmann-Type Correlations<sup>1</sup>

Sir:

The Woodward-Hoffmann (W-H) rules<sup>2</sup> state that a reaction is photochemically allowed if the lowest excited state of the reactant correlates with the lowest excited state of the product. van der Lugt and Oosterhoff (V-O) have recently suggested<sup>3</sup> that the existence of such a correlation is irrelevant. Instead, they proposed a simple rule, "ground-state forbidden" = "excited-state allowed," based on the general quantum mechanical argument that whenever crossing (or avoided crossing) of potential energy curves leads to a potential energy barrier in the ground state, it will also lead to an excited-state energy minimum through which radiationless deactivation will proceed efficiently.

Decision between the two rules is difficult because they most often give identical predictions. However, we have recently observed<sup>4</sup> that the ground-state-forbidden ring opening I → II does not occur in the first excited singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) states, but proceeds from one of the higher triplets (T<sub>x</sub>). This clearly shows that the V-O rule is overgeneralized. We have also pointed out<sup>4</sup> that the pattern of triplet reactivities agrees with the W-H rule by symmetry arguments alone, but that it is not immediately obvious that S<sub>1</sub> of I does not correlate with S<sub>1</sub> of II (both are of the same symmetry).

Therefore, we have worked out the correlation diagrams in greater detail using the simple PPP method<sup>5</sup>

(1) Presented at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, Switzerland, July 12-18, 1970.

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(5) Pariser-Parr-Pople self-consistent-field calculations (interaction of singly excited configurations), using the parametrization suggested by J. Koutecký, J. Paldus, and R. Zahradnik, *J. Chem. Phys.*, **36**, 3129 (1962), which reproduces S → S spectra well but predicts generally too

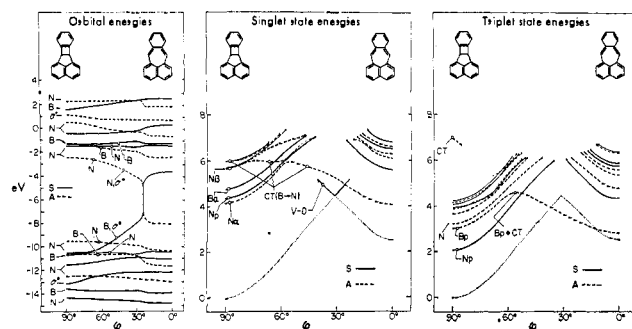
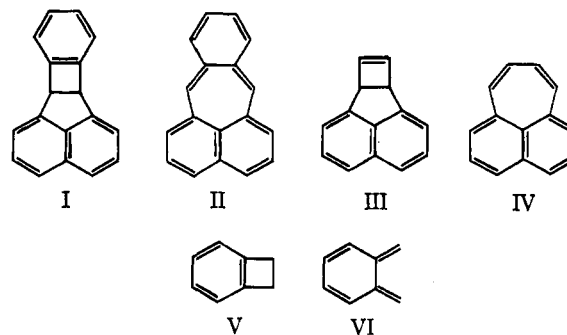


Figure 1. Correlation diagrams for I → II (schematic, based on PPP calculations<sup>5</sup>):  $\phi$ , angle of (dis) rotation; S and A, symmetric and antisymmetric with respect to the molecular plane of symmetry, respectively; dotted line, ground state; V-O, the van der Lugt-Oosterhoff minimum (the crossing with the ground state is actually avoided when multiply excited configurations are included in the calculation); N, B,  $\sigma$ , states (orbitals) localized mostly on naphthalene, benzene, and the originally single bond, respectively; CT, charge-transfer state;  $p, \alpha$ , Clar's notation for excited states. Numerous higher states are not shown.

(Figure 1): energy barriers are imposed both for S<sub>1</sub> and T<sub>1</sub> of I, since both attempt to correlate with very highly excited states of II, while S<sub>1</sub> and T<sub>1</sub> of II originate in highly excited states of I (corresponding to transfer of an electron from the benzene chromophore to the



naphthalene chromophore). The course of the state correlations is easily understood in terms of the orbital correlation diagram, also shown in Figure 1:<sup>6</sup> to remove the ground-state forbiddenness of the reaction, one needs to remove an electron from that orbital which becomes antibonding as the reaction proceeds and place it in that empty orbital which becomes bonding during the reaction. The excited state of I formed in this manner is just the above "charge-transfer" state. On the other hand, excitations such as 1 → -1, 1 → -2, 2 → -1, 2 → -2, etc., important in the lowest excited singlets and triplets of I, do not help to remove the energy barrier present in the ground state.

We conclude that allowedness in the W-H sense is important if a photochemical reaction is to proceed under usual conditions. Barriers imposed by the course

low energies for triplets relative to singlets. To obtain the correlation curves we repeat the calculations for about ten points along the reaction coordinate. The latter is approximated roughly by assuming that 2p orbitals on carbon atoms 6b and 10b in planar I, originally pointing toward each other and forming a localized  $\sigma$  bond, rotate symmetrically in a disrotatory fashion by 90° to give II. The results are insensitive to the details of the assumptions needed to perform the calculations (value of the resonance integral for  $\sigma$  overlap, etc.).

(6) Simple HMO method gives a virtually identical diagram. The value of closed-shell SCF procedure is actually questionable for values of  $\phi$  near 30°.