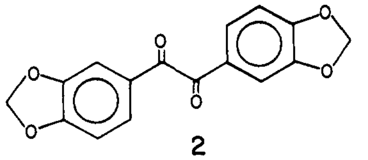
low solution was cooled to −78°, and isobutyronitrile (2.20 ml, 25 mmol) was added dropwise over a period of 5 min. The mixture was warmed at 0° for 15 min, cooled to −78°, and a solution of π-benzenechromium tricarbonyl (**1**) in 25 ml of THF was added dropwise over 5 min. The yellow solution was warmed at 0° for 30 min, cooled to −78°, and a solution of iodine (25 g, 98 mmol of I_2) in 75 ml of THF was added dropwise over 15 min. After the resulting mixture had been stirred at 24° for 3 hr (CO evolution), it was partitioned between ether (200 ml) and 5% aqueous sodium bisulfite solution (100 ml). The ether layer was washed successively with water and aqueous salt solution, dried over anhydrous magnesium sulfate, and concentrated to leave a yellow liquid. Flash distillation at 25° (0.001 Torr) afforded 3.562 g (98% yield) of a colorless liquid with spectral properties identical with phenylisobutyronitrile.[11]

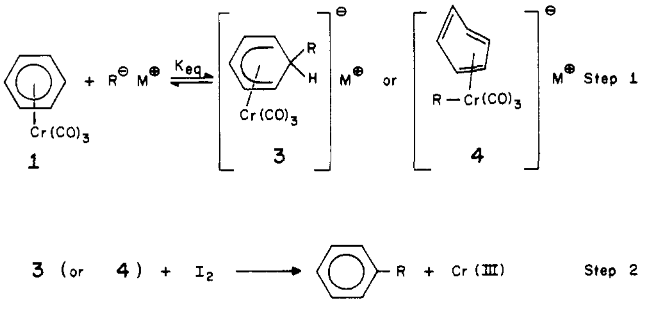
Several generalizations are clear from Table I. Very reactive organolithium reagents (entries 1-7) give efficient phenylation under mild conditions in THF. Organomagnesium halides (entries 13, 14) and lithium enolates of ketones and esters (entries 8, 16) do not give significant yields of phenylation products under these conditions. However, ester enolates undergo phenylation much more efficiently if a polar, aprotic solvent is added to the medium (entries 10-12) or if the potassium cation is used (entry 9). In contrast to phenylation using π-(chlorobenzene)chromium tricarbonyl,[6] secondary and primary ester enolates participate in the reaction just as well as tertiary ester enolates (entries 11, 12). Ketone enolates, even with potassium as the counterion and using high concentrations of hexamethylphosphoric triamide (HMPA), fail to give preparatively useful amounts of α-phenyl ketones (e.g., entry 15). The more stabilized cyanohydrinacetal anion of entry 17 also fails to undergo phenylation, even using the potassium counterion (from potassium hydride-THF) and HMPA. In this case the anion presumably is not interacting with the π-benzenechromium tricarbonyl (**1**); the observed product, the α-diketone **2**,[12] is obtained in 92% yield after iodine oxidation in the presence or absence of **1**.



2

The nature of the intermediate and the steps in the iodine oxidation procedure are not yet clear, but two reasonable alternatives (**3** and **4**) for the structure of the intermediate are suggested in Scheme I. Intermediate **3** results from carbanion attack at the π-arene ligand, a process with abundant precedent in the chemistry of ionic π-arenemetal complexes.[3-5] Intermediate **4** represents initial attack at chromium and is more easily reconciled with the apparent reversibility of the first step.[13]

Scheme I



The failure of the more stable anions (ketone enolates, aryl substituted cyanohydrin-acetal anions) to give efficient phenylation presumably arises from a low equilibrium constant, K_{eq}, for step 1. Similarly, using HMPA solvent or potassium counterions in phenylation of ester enolates may have the effect of raising K_{eq} and thus providing a high concentration of the intermediate (**3** or **4**) prior to quenching with iodine. Studies are underway to elucidate the structure and reactivity of the proposed intermediate.

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(12) The α-diketone exhibited ir, ^1H NMR, and mass spectral data consistent with the structure.
(13) Unpublished work by H. T. Hall, M. Yoshifuji, and J. Belasco in these laboratories.
(14) Fellow of the Alfred P. Sloan Foundation and recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant.

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Computational Evidence for a Stable Intermediate in the Rearrangement of $1,2\text{-}C_2B_4H_6$ to $1,6\text{-}C_2B_4H_6$

Sir:

Few reaction pathways in rearrangements[1] of boron compounds are mechanistically well understood. The isomerization of $1,2\text{-}C_2B_4H_6$ to $1,6\text{-}C_2B_4H_6$ is a polyhedral rearrangement for which the cooperative twist dsd (diamond-square-diamond)[1a] mechanism has been suggested. This interconversion proceeds measurably[2] at 250°, but a CNDO/2 study[3] failed to find an energetically accessible pathway. We report here a PRDDO[4] study of this interconversion (see Figure 1) and of the analogous degenerate rearrangement of $B_6H_6^{2-}$ which utilizes and serves to introduce a new approach for computing reaction pathways.[5] A principal result is a subtle but energetically significant modification of the dsd mechanism which implicates a third stable geometry on the $C_2B_4H_6$ energy surface as an intermediate in the interconversion. A second focus is the effect—and predictability—of carbon substitution on the energetics of the parent $B_6H_6^{2-}$ rearrangement. Based on past experience,[4b] we expect the results presented here to be of essentially ab initio minimum-basis-set quality.

The reaction pathways approach we have developed and employ here will be fully described in a forthcoming paper;[5] for reasons of space, we give here only a brief introduction. First, we construct an initial *linear synchronous transit*

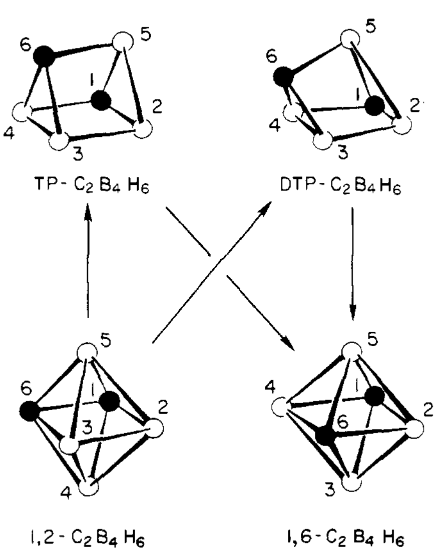

Figure 1. Possible pathways for rearrangement of 1,2-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$. The numbering convention for the 1,6-isomer is used.

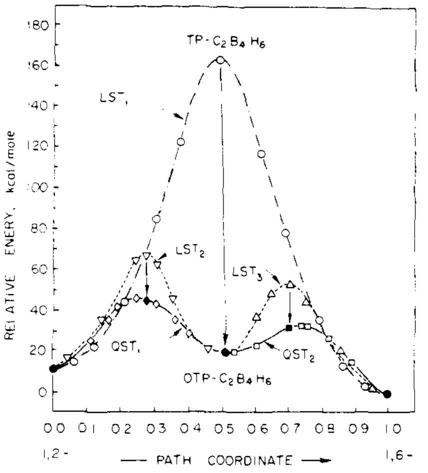

Figure 2. Synchronous transit pathways for the interconversion of 1,2- and 1,6-$C_2B_4H_6$. TP and DTP denote trigonal prism (C_2) and distorted trigonal prism (C_1) geometries.

pathway (LST) between two path-limiting structures, e.g., 1,2- and 1,6-$C_2B_4H_6$. The condition which defines this pathway is that *all* $N(N-1)/2$ internuclear distances vary essentially linearly between their path-limiting values.[6] Specifically, the calculated $N(N-1)/2$ internuclear distances, $r_{ab}(\mathrm{c})$ (usually greater than the $3N-6$ or $3N-5$ independent parameters), are fitted by least squares to a set of linearly interpolated trial values, $r_{ab}(\mathrm{i})$, by minimizing

$$\sum_{a<b}^{N}\frac{[r_{ab}(\mathrm{c})-r_{ab}(\mathrm{i})]^2}{r_{ab}(\mathrm{i})^4}+10^{-6}\sum_{w=x,y,z}\sum_{a}^{N}[w_{\mathrm{a}}(\mathrm{c})-w_{\mathrm{a}}(\mathrm{i})]^2$$

with respect to the $3N$ cartesian coordinates, $w_{\mathrm{a}}(\mathrm{c})$. The r^{-4} weighting gives priority to bonded distances, and the weak second term ensures sufficient conditions for a determinate fit.

Second, the *path coordinate, p,* of each intermediate structure is taken as $p = d_0/(d_0 + d_f)$, where d_0 (or d_f) is the *distance* of the intermediate structure from the first (or second) path-limiting structure. We define the distance, *d*, between two structures as the rms difference in Cartesian coordinates at maximum coincidence.[7]

Third, the initial pathway is refined by optimizing one or more key intermediate points (e.g., that of maximum energy) under the constraint that the relative position, *p*, along the path remain unchanged (*orthogonal optimization*). The usual result is that a three-point interpolation pathway (quadratic synchronous transit, QST) can be constructed whose maximum and whose orthogonally optimized central point are upper and lower energy bounds for the transition state (here, at the minimum-basis-set PRDDO[4] level). In this way, or through successive orthogonal optimizations, the energy and geometry of the transition state can be determined efficiently.

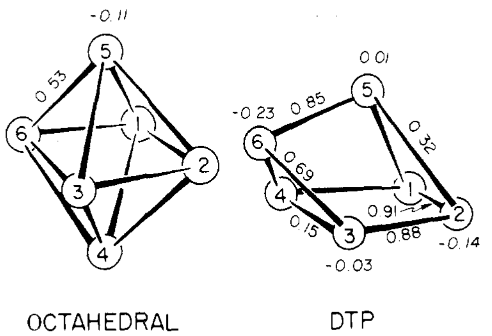

Figure 3. Mulliken[11] atomic charges (at atoms) and atomic overlap populations (along bonds) for optimized $B_6H_6^{2-}$ structures.

For the rearrangement of 1,2- to 1,6-$C_2B_4H_6$, the initial LST (LST_1, Figure 2) passes through a trigonal prism (TP) structure and at all points has the C_2 symmetry expected for the dsd cooperative-twist pathway.[1a] Optimization,[8] however, lowers the TP energy by fully 143 kcal/mol and yields a distorted TP (DPT) structure (Figure 1). The result is rather like the sagging of an improperly braced sawhorse. The linear paths[9] LST_2 and LST_3 connecting the DTP and octahedral structures have sufficiently large barriers to suggest that the DTP structure may be a true intermediate. Indeed, optimization[10] of the LST_2 and LST_3 maxima resulted in paths (QST_1, QST_2) having barriers of 27 and 14 kcal/mol, respectively. In each case, the QST maximum lies within 2 kcal/mol of the optimized point (solid symbol). Thus the respective transition states have been adequately located.[5] Although the estimated barrier for rearrangement of DTP-$C_2B_4H_6$ to 1,6-$C_2B_4H_6$ is small, its synthesis might be possible at low temperatures.

The DTP-$C_2B_4H_6$ structure lies about 8 and 20 kcal/mol above 1,2- and 1,6-$C_2B_4H_6$, respectively. The rate-determining step is the formation of the DTP from 1,2-$C_2B_4H_6$ (computed barrier, 35 kcal/mol). Available experiments[2] suggest a barrier of 42–45 kcal/mol, if we assume 0–6 eu for the entropy of activation. The computed pathway differs principally from the model dsd pathway in that the trigonal face (3,4,6) pivots first about one corner (B_3) to produce the DTP and then about B_4 to yield 1,6-$C_2B_4H_6$ (Figure 1), rather than rotating uniformly about the *pseudo*-C_3 axis.

Similarly, the LST pathway for the corresponding rearrangement of $B_6H_6^{2-}$ yields a TP structure (D_{3h}) which lies above octahedral $B_6H_6^{2-}$ by about 174 kcal/mol. Optimization within C_s symmetry gave the DTP structure (Figure 3) and lowered the energy by 91 kcal/mol. The symmetry-related LST pathways analogous to LST_2 and LST_3 in Figure 2 gave much smaller barriers of ~20 kcal/mol. If the DTP structure is not a true intermediate, the computed barrier to rearrangement is 83 kcal/mol, the difference in energy between octahedral and DTP $B_6H_6^{2-}$.

The effect of formal substitution of CH for BH^- on the computed activation barrier is in accord with the reasonable expectation that this substitution should occur preferentially at positions which are the most negative and which participate in the strongest two-center bonds. Thus, we find that 1,2- and 1,5-$C_2B_3H_5$ based on trigonal bipyramid $B_5H_5^{2-}$ (axial positions strongly negative) differ by 53 kcal/mol, as compared to just 12 kcal/mol for 1,2- and 1,6-$C_2B_4H_6$. In the optimized DTP-$B_6H_6^{2-}$ (C_s), the secondary apex, B_6, and two basal positions, B_1 and B_2, are especially favorable sites (Figure 3). The charges and overlap populations[11] imply that the DTP structure obtained above for $C_2B_4H_6$ should be the most stable of the several possible isomers. Hence, useful information concerning relative energies and favored rearrangement pathways in carboranes can be inferred from simpler computations on the parent boron hydride systems.

Further, a more electronegative substituent could invert the order of stability. Preliminary calculations on the hypothetical $N_2B_4H_4$ predict the 1,6-disubstituted DTP structure to lie 10 and 15 kcal/mol below 1,6- and 1,2-$N_2B_4H_4$, respectively. For $NB_5H_5^-$, however, the "octahedral" form is calculated as being the most stable, the 6-, 1-, 3-, and 5-substituted DTP structures lying higher in energy in the order expected from the $B_6H_6^{2-}$ atomic charges by 35, 48, ~90, and ~110 kcal/mol.[12] Finally, the attachment of electronegative substituents to carbon in the $C_2B_4H_6$ system may sufficiently stabilize the DTP structure to allow its experimental detection.

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(12) Based on $B_6H_6^{2-}$ framework geometries, plus optimization of the nitrogen-atom position except in the 3- and 5-substituted DTP isomers.

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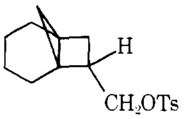
Conformationally Controlled Solvolysis. Ion Conformation as the Determining Factor in the Ring Expansion of Bicyclo[2.1.0]pentane Derivatives[1]

Sir:

Recently, we described the solvolytic behavior of the tosylates, **1** and **2**.[2] These epimeric compounds exhibited extremely diverse behavior on solvolysis in 90:10 v/v acetone–water buffered with 2,6-lutidine. Although product studies indicated that **1** and **2** gave dramatically different ions, the cause of this unique behavior was not established. In order to determine the mechanistic basis for our earlier observations, it was necessary to establish whether the tetramethylene bridges (and the associated tricyclic structures) of **1** and **2** were responsible for the presence of two divergent mechanistic paths or whether the observed behavior was a direct function of the stereochemical relationship between the cyclopropyl group and the carbinol moiety. In order to resolve this problem, we have prepared the tosylates **3** and **4**



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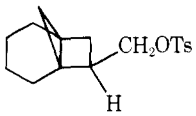

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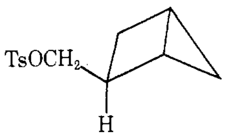

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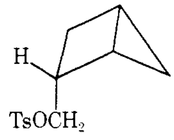

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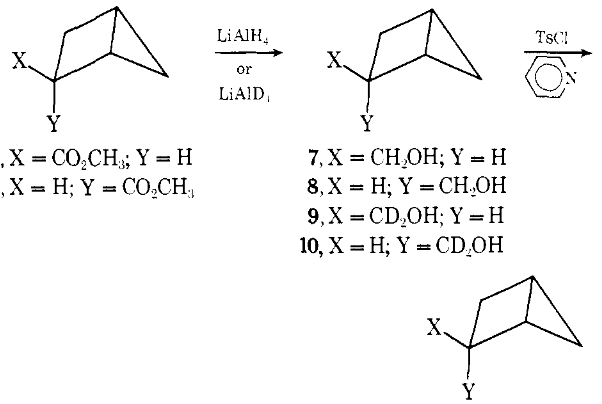
and studied their solvolyses. We now wish to report that our previously described results were not dependent on any interactions of the tetramethylene bridges of **1** and **2**. Furthermore, we wish to suggest that ion conformation is the determining factor in the diverse mechanistic paths followed by **3** and **4** (and through analogy by **1** and **2**).

Lithium aluminum hydride reduction of the known[3] esters **5** and **6** gave the carbinols **7** and **8**, while reduction with lithium aluminum deuteride gave the labeled carbinols **9** and **10** (>99% d_2 as determined by NMR spectroscopy). Treatment of **7**, **8**, **9**, and **10** with *p*-toluenesulfonyl chloride in pyridine gave the corresponding esters **3**, **4**, **11**, and **12**, respectively. Solvolysis of **3** and **4** in 90:10 v/v acetone–water buffered with 2,6-lutidine gave excellent pseudo-first-order kinetics. However, little difference in the rates of ionization was observed: $k_3 = 3.17 \times 10^{-7}$ (25°) and $k_4 = 1.92 \times 10^{-7}$ (25°).



5, X = CO_2CH_3; Y = H
6, X = H; Y = CO_2CH_3

7, X = CH_2OH; Y = H
8, X = H; Y = CH_2OH
9, X = CD_2OH; Y = H
10, X = H; Y = CD_2OH

3, X = CH_2OTs; Y = H
4, X = H; Y = CH_2OTs
11, X = CD_2OTs; Y = H
12, X = H; Y = CD_2OTs

While kinetic studies failed to indicate any major differences between **3** and **4**, product studies established that **3** and **4** ionized to produce species which were very different. The solvolysis of **3** gave a mixture of **13** (5%), **14** (13%), **15** (55%), **16** (4%), **17** (7%), and **18** (7%).[4] In stark contrast to the complex mixture of products obtained from **3**, **4** gave **19** as the only product in 91% yield.

The very diverse nature of the products obtained from **3** and **4** indicated the formation of two distinct ions. Mechanistically, it appeared that **3** ionized with accompanying migration of the C_2–C_3 bond (b) to give the cyclopropyl carbinyl cation **20**. Shifting of the C_1–C_2 bond (a) of **3** would give the boat conformer **21**, in which the cyclopropyl ring