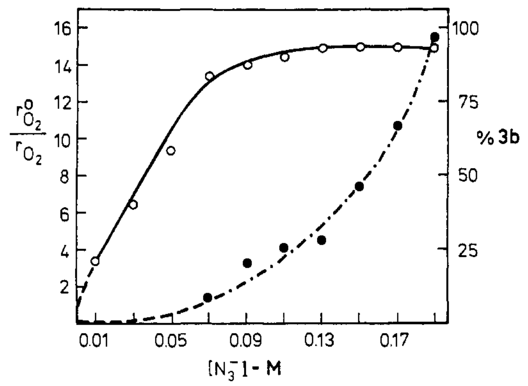
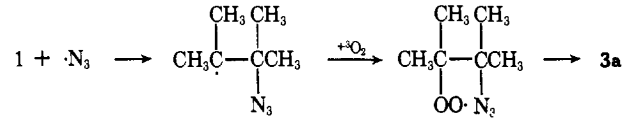


Figure 1. Ratio of rates of oxygen consumption by 1 in the absence ($r_{O_2}^0$) and presence of N_3^- (r_{O_2}) as a function of [N_3^-], and percentage of azido alcohol 3b formation as a function of [N_3^-] in 40% aqueous methanol: O—O, $r_{O_2}^0/r_{O_2}$ as f([N_3^-]); ●--●, % 3b as f([N_3^-]).

could be isolated without reduction with sodium sulfite increased. Reaction of hydroperoxide **2a** with **1** to give **2b** and the epoxide of **1**, which subsequently reacts with N_3^- to **3b**, is excluded since no **2b** was found at high N_3^- concentrations. In control experiments **3a** and **3b** were not formed from **2a** or **2b**, respectively, when treated with N_3^-.

Electrolysis (2.6 V, 50 mA) of 2 g of NaN_3 for 17 hr in 200 ml of oxygen-saturated methanol or aqueous methanol in the presence of 7 g of **1** yielded about 500 mg of **3b** and some polymeric material. So far, we have not isolated the azido hydroperoxide **3a**. However, that the oxygen in the azido alcohol stems from O_2 rather than from the solvent is concluded from the fact that in nitrogen-saturated solutions only 2,3-diazido-2,3-dimethylbutane[14] and some unidentified compounds were formed, but no **3b**.[15]

Thus, formation of **3b** occurs by addition of N_3 radicals to **1** to give **4**, which adds $^3O_2$ to give **5**, which



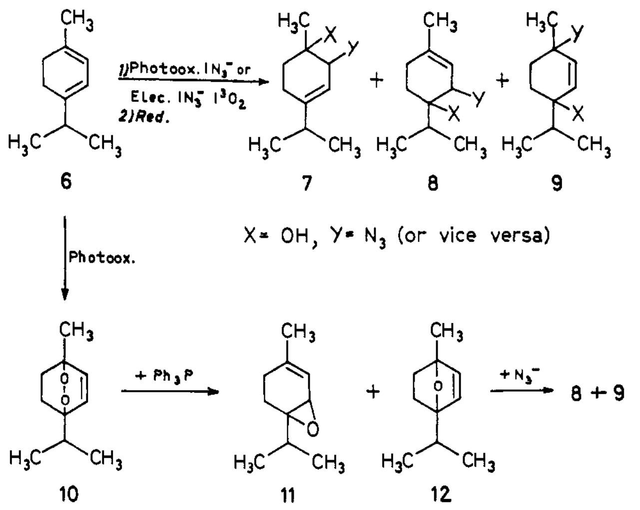
$$1 + \cdot N_3 \longrightarrow \underset{\cdot}{\overset{CH_3}{CH_3C}}-\underset{N_3}{\overset{CH_3}{CCH_3}} \xrightarrow{+^3O_2} \underset{OO\cdot}{\overset{CH_3}{CH_3C}}-\underset{N_3}{\overset{CH_3}{CCH_3}} \longrightarrow \mathbf{3a}$$

4 **5**

in turn abstracts hydrogen to form **3a**. By some unknown reduction reaction, **3a** is transformed to **3b**, as is the case in the photooxygenation reaction.[16]

These results support our view that in photooxygenation reactions in the presence of azide ions, azido radicals are formed that can produce azido hydroperoxides. To check this assumption further, α-terpinene (**6**) was photooxygenated as well as subjected to electrolytic treatment under similar conditions.

In the absence of NaN_3, **6** was photooxygenated to ascaridole (**10**).[2b] In the presence of NaN_3, however, a mixture was obtained that contained azido alcohols **7**, **8**, and **9**. According to gas chromatography,



elemental analysis, and ir and nmr spectra, the *same* mixture was formed during electrolysis of N_3^- in the presence of **6** and $^3O_2$.[17] Ascaridole (**10**) did not react with NaN_3 under the experimental conditions.[18]

From these results it seems unlikely that in photooxygenation of monoolefins in the presence of N_3^- azido products are formed by interception of dioxetane or perepoxide intermediates.[10,11] In our opinion, the results are compatible with the assumption that in photooxygenation reactions, interaction between N_3^- and one intermediate (presumably the triplet excited sensitizer) gives rise to a decrease of the oxygen uptake rate, whereas the interaction between N_3^- with another intermediate (presumably singlet oxygen) results in electron transfer producing N_3 radicals that ultimately yield the azido compounds. The proposed refutation of the "ene" mechanism as a route to allylic hydroperoxides in $^1\Delta_g$ O_2 reactions with olefins is thus rendered doubtful.

Acknowledgments. We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der deutschen Industrie who supported our work done at Munich.

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[14] Satisfactory elemental analysis for the diazide was obtained: nmr one sharp singlet at τ 8.72 ($CDCl_3$).

[15] For studies on the electrolytic formation of N_3 radicals and on their reactions with olefins, see: H. Schäfer, *Angew. Chem.*, **81**, 940 (1969); **82**, 134 (1970), and references cited therein.

[16] In the meantime, using **2a** as a model compound, we found that organic hydroperoxides slowly react with N_3^- in aqueous methanolic solutions to give the corresponding alcohols and some molecular nitrogen.

[17] Satisfactory elemental analysis ($C_{10}H_{17}N_3O$) for the isomeric mixture was obtained, although we have not yet separated the components. Analysis of the nmr spectra of the mixtures, aided by europium shift reagents, showed that **7**, **8**, and **9** are present in a ratio of about 38:17:25.

[18] By reduction of **10** with triphenylphosphine to a mixture of oxides **11** and **12** (identified by elemental analysis and nmr spectra) followed by treatment with N_3^-, we were able to obtain **8** and **9** in a ratio of about 1:1.

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Fractional Three-Center Bonds in Carboranes

Sir:

The objective Edmiston–Ruedenberg procedure[1,2] for obtaining localized orbitals from accurate self-consis-

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[1] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1963).

[2] E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).

Table I

Molecule[e]	Atom	Terminal H	Bridge H	Framework bonds[a]	Populations[b]
$C_2B_4H_8$	B_2	1	2	2	0.50, 0.50
B_5H_9, I[c]	B_2	1	2	2	0.42, 0.55
	B_3	1	2	2	0.72, 0.23
1,6-$C_2B_4H_6$	C_1	1	0	4	0.83, 0.85, 0.79, 0.59
	B_3	1	0	4	0.54, 0.56, 0.46, 0.32
	B_4	1	0	4	0.56, 0.58, 0.54, 0.21
$C_2B_5H_7$	B_2	1	0	4	0.53, 0.54, 0.39, 0.37
B_5H_9, II[c]	B_2	1	2	2	0.63, 0.33
	B_3	1	2	2	0.65, 0.31
B_4H_{10}	B_1	1	2	1	0.81 (0.19,[d] 0.19[d])

[a] Numbers of orthogonal orbitals contributing to bonds involving B or C atoms other than the indicated atom (fractional and whole). [b] Contributions to boron–carbon framework localized orbitals attributed to all atomic orbitals on the indicated atom. [c] Structures I and II were obtained from different initial random starting guesses. [d] Atom B_1 is primarily singly bonded to B_3, but there are small contributions from bonding of B_1 (or B_3) to B_2 and B_4 as indicated. [e] Valence structure I for B_5H_9 has a single bond B_1–B_4 and fractional three-center bonds $B_1B_3B_2$ and $B_1B_5B_2$ dotted toward B_2. Extrapolation to $B_{10}H_{14}$ would replace the B_2–B_6 single and $B_5B_2B_7$ open three-center bonds with fractional three-center central bonds $B_7B_2B_6$ and $B_5B_2B_6$, both dotted toward B_2; a similar replacement may be made at the symmetry-equivalent other side of $B_{10}H_{14}$.

tent field wave functions has yielded unique two-center, three-center hydrogen bridge and central three-center BBB bonds in B_2H_6, B_4H_{10},[3] B_5H_{11},[3] and B_6H_{10}.[4] However, open three-center BCB bonds occur[5] in 1,2-$C_2B_4H_6$. In these examples, the localized orbitals clearly indicate preferred topologically[6,7] allowed valence structures, even when it is possible to have many nearly equivalent resonance hybrids.

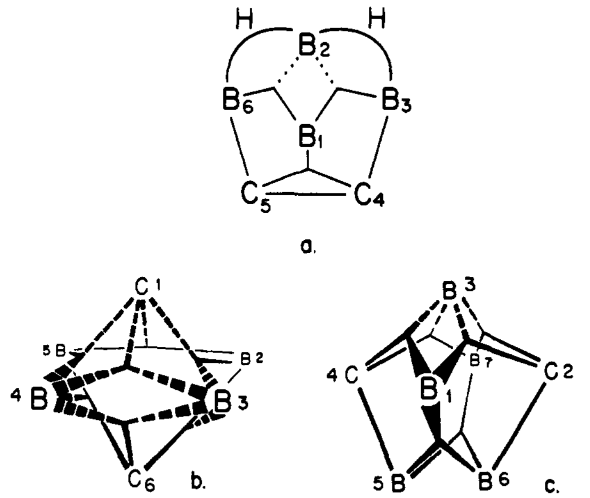

Figure 1. Bonding to BH units and CH units, represented by B and C, in $C_2B_4H_8$, in 1,6-$C_2B_4H_6$, and in 2,4-$C_2B_5H_7$. Dotted legs of three-center bonds are used to indicate fractional localized bonds. The localized framework orbitals of 1,6-$C_2B_4H_6$ (b) consist of central three-center bonds in each face of the distorted octahedron except for the $B_2B_5C_6$ face.

Localizations of molecular orbitals by successive unitary transformations[1,8–12] of a randomized set[3,13] of molecular orbitals in 4,5-$C_2B_4H_8$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have yielded a total of five atoms, four borons, and one carbon, which show a consistent new kind of localization. In representing this situation we have used a dotted component of each central three-center bond when there *appear* to be five bonds to B or C including the external bond to hydrogen, at B_2 in $C_2B_4H_8$, at C_1, B_3, and B_4 in 1,6-$C_2B_4H_6$, and at B_3 in 2,4-$C_2B_5H_7$ (Figure 1). We emphasize that only four valence orbitals are used for each B or C and that all localized orbitals are orthogonal.

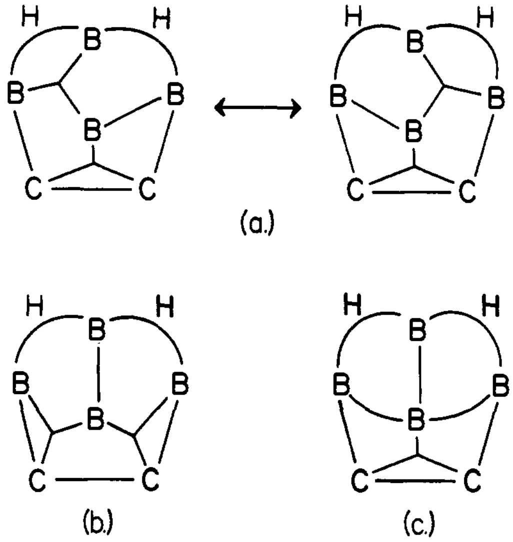

Figure 2. (a) A resonance hybrid for bonding in $C_2B_4H_8$. Similar structures can be drawn for the other carboranes in this paper. (b and c) Other symmetrical localized structures for $C_2B_4H_8$. All of these structures place only three bonds to each B–H or C–H unit, but Figure 1a more accurately depicts the valence structure of this molecule.

We have listed (Table I) the orbital populations at the indicated atom for a near-continuum of cases from the well-localized, unique fractional three-centered bonds

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(3) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(4) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **10**, 171 (1971).

(5) D. S. Marynick, I. R. Epstein, and W. N. Lipscomb, unpublished results.

(6) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(7) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).

(8) J. E. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, **198**, 1, 14 (1949).

(9) G. G. Hall and J. E. Lennard-Jones, *ibid.*, *Ser. A*, **202**, 155 (1950).

(10) J. E. Lennard-Jones and J. A. Pople, *ibid.*, *Ser. A*, **202**, 166 (1950).

(11) J. E. Lennard-Jones and J. A. Pople, *ibid.*, *Ser. A*, **210**, 190 (1951).

(12) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, 597 (1965).

(13) M. D. Newton, E. Switkes, and W. N. Lipscomb, *ibid.*, **53**, 2645 (1970).

of $C_2B_4H_8$ to the unique but somewhat delocalized B–B single bond in B_4H_{10}. Also included in Table I are previous results[3] for B_5H_9 which we may now interpret in terms of fractional three-center bonds. We introduce the notation of a dotted component of the bond at the appropriate atom in order to distinguish this new bonding situation from the earlier notations for bonds in boron hydrides and carboranes. It is interesting, and somewhat unexpected, that the molecular bonding localizes symmetrically to a structure containing fractional three-center bonds, instead of to the very nearly equivalent resonance hybrid shown, for example, for the $C_2B_4H_8$ molecule in Figure 2a, or to one of the previously considered[4] symmetrical structures shown in Figure 2b and c. Of course, similar structures can be written for 2,4-$C_2B_5H_7$ and 1,6-$C_2B_4H_6$.

Recognition of these fractional three-center bonds allows unique, or symmetry equivalent, single valence structures to be drawn for at least these carboranes, in such a way that a common feature of bonding is preserved. These results, together with the uniquely localized bonds in the boron hydrides listed above, suggest that similar simplified bonding diagrams may emerge from more complex boranes, carboranes, carbonium-like compounds, and their metal derivatives.

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A Remarkably Facile Reductive Opening of Tetrahydrofuran and Related Ethers by Lithium Tri-*tert*-butoxyaluminohydride in the Presence of Triethylborane

Sir:

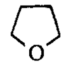
Lithium tri-*tert*-butoxyaluminohydride is stable indefinitely in tetrahydrofuran at 25°.[1,2] The addition of 1 mol equiv of triethylborane induces a rapid opening of the tetrahydrofuran ring, essentially complete within 3 hr, with the formation of 1-butanol. Even a catalytic quantity of triethylborane (10 mol %) is effective. With this new reagent 2,5-dihydrofuran is readily converted into *cis*-crotyl alcohol and the bicyclic ring system of 7-oxabicyclo[2.2.1]heptane is readily opened to form cyclohexanol. Consequently, it appears that this reducing system is one of the most active currently available.

We recently reported that the reaction of B-alkyl-9-BBN derivatives with carbon monoxide in the presence of lithium trimethoxyaluminohydride (LTMA) provides a major new route from olefins to the corresponding aldehydes.[3] In extending this synthesis to olefins containing reducible functional groups it proved advantageous to shift to the milder reducing agent, lithium tri-*tert*-butoxyaluminohydride[4] (LTBA). However, we observed a puzzling feature in applying this last reagent. To obtain a good yield it was important that the reagent be added concurrently with the uptake of carbon monoxide. If the reagent were added to the organoborane prior to the introduction of carbon monoxide, the yield decreased sharply.

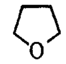
Investigation soon revealed that such solutions of LTBA and organoboranes rapidly lost active hydride with the concurrent formation of 1-butanol from reductive opening of the tetrahydrofuran (THF), utilized as solvent. For example, a 0.5 *M* solution of LTBA in THF appears to be stable indefinitely at 25°. Addition of an equimolar amount of triethylborane to such a solution results in a very rapid loss of hydride, with 72% of the active hydride disappearing in 5 min. Upon hydrolyzing the reaction mixture, an equivalent quantity of 1-butanol is found.

A catalytic quantity of triethylborane is also effective. Thus, the addition of 10 mol % of triethylborane causes the loss of 60% of the active hydride in 30 min, with the formation of 55% of 1-butanol. The reactions are essentially complete in 3 hr (Figure 1).

Thus triethylborane induces a rapid, essentially quantitative opening of the tetrahydrofuran ring at 25° (eq 1). To our knowledge no reducing system currently available is capable of achieving the reductive cleavage of THF so rapidly and cleanly. For example, diborane has been recommended for this purpose, but it requires 64 hr at 60° to achieve a 64% conversion to 1-butanol (eq 2).[5]



$$+\ \mathrm{LiAlH(O\text{-}\mathit{tert}\text{-}Bu)_3} \xrightarrow[25°,\ 3\ \mathrm{hr}]{\mathrm{Et_3B}} \mathrm{Li[\mathit{n}\text{-}BuOAl(O\text{-}\mathit{tert}\text{-}Bu)_3]} \tag{1}$$



$$+\ \mathrm{BH_3} \xrightarrow[64\ \mathrm{hr}]{60°} \underset{64\%}{(\mathit{n}\text{-}\mathrm{BuO})_3\mathrm{B}} \tag{2}$$

Surprisingly, triethylborane fails to induce a similar reductive cleavage of THF by the otherwise more powerful reducing agent, lithium trimethoxyaluminohydride.[6]

It would, of course, be very desirable to have an understanding of the mechanism of this reaction which would provide a reasonable explanation for the remarkable reducing capability exhibited by the system and for the marked difference in behavior of the methoxy and *tert*-butoxy derivatives. However, it appeared more timely to explore the utility of this new reduction for desired tranformations in synthetic operations.

Monoglyme dissolves LTBA and the addition of triethylborane results in a rapid evolution of a gas, presumably methane. In 1 hr at 25° there was identified the formation of 47% of 2-methoxyethanol. The reagent is also soluble in tetrahydropyran (THP). However, reductive cleavage of this ether is much slower. We found only 17% of 1-pentanol after 24 hr. Consequently, we adopted this solvent for a survey of certain interesting possibilities for reductive cleavages.

The reaction of cyclohexene oxide with LTBA is very slow.[2] Yet the addition of triethylborane causes

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[1] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958).

[2] H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963).

[3] H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Amer. Chem. Soc.*, **91**, 2144 (1969).

[4] H. C. Brown and R. A. Coleman, *ibid.*, **91**, 4606 (1969).

[5] J. Kollonitsch, *ibid.*, **83**, 1515 (1961).

[6] H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965).