The infrared spectrum of the compound, as determined on Beckman Models IR-5A and IR-10 spectrometers, has absorptions at the following wavenumbers (cm^{-1}) with the relative intensities given in parentheses: 1580 (7), 1540 (9), 1495 (7), 1450 (5), 1415 (2), 1385 (shoulder, 1), 1370 (10), 1310 (8), 1270 (9), 1210 (1), 1168 (2), 1129 (2), 1104 (8), 1052 (1), 1030 (3), 905 (7), 812 (8), 805 (7), 770 (8), 738 (5), 615 (8), 580 (2), 520 (6), 510 (3). This spectrum is similar to that reported between 4000 and 650 cm^{-1} for the thorium(IV) complex,[11] except near 3400 cm^{-1}, the OH stretch, and between 700 and 850 cm^{-1}, the CH deformation region.[12] No OH stretch was observed for the tungsten complex in the 3400-cm^{-1} region when the spectrum of a KBr pellet containing the complex was measured *vs.* a blank KBr disk of appropriate thickness. Traces of water in the KBr usually give bands in the 3400-cm^{-1} region if the pellets are measured single beam or against air; *cf.* ref 11. The differences in multiplicities and positions in the CH deformation region suggest different interactions in the solid state, such as might be obtained in going from antiprismatic to dodecahedral coordination, the two favored configurations for eight-coordination,[10] but a change in crystal structure might produce a similar effect. Since the sizes of central cations are different, no definite conclusions as to geometry can be drawn from the infrared spectrum alone.

Acknowledgment. The support of NSF GP-2938 and GP-5971 is gratefully acknowledged. Earlier support [Contract AF 33(615)-1043 and an NSF-URP stipend (to W. D. B.)] laid the groundwork for this discovery.

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(11) Sadtler Infra-red Spectrogram 10712.

(12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958, pp 280–281.

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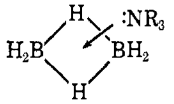
The Structure of B_2H_6–Base Complexes. Molecular Electron Deficiency and Acidity

Sir:

In a recent communication Shore and Hall reported[1] that trimethylamine and diborane at low temperature can form a specific complex whose stoichiometry was established as B_2H_6–NR_3 by titrimetry. With the only additional structural characterization being a boron-11 nmr spectrum, the authors report that this complex has the structure of a "singly hydrogen bridged borane," *i.e.*, R_3N–BH_2–H–BH_3. The spectrum shown for this unsymmetrical structure is a symmetrical multiplet. The two chemically different boron-11 atoms were assumed to give a seven-line nmr pattern, a superimposed triplet and quartet.[2]

Actually, the spectrum shown by Shore and Hall for the diborane–amine complex is that of a nine-line pattern, *i.e.*, the triplet of triplets expected of B_2H_6 itself. Their spectrum is, in fact, virtually superimposable on the first boron-11 nmr spectrum published for diborane 12 years ago by Ogg.[3,4] Each boron in the diborane unit is split by two proton pairs. The two J_{BH} values in the low-temperature diborane–amine spectrum (136 ± 2 and 44 ± 2 cps) are within the same experimental error that Gaines has found[5] with diborane etherate at low temperature. In short, the nmr spectrum of B_2H_6–NR_3 cannot be that of a "singly hydrogen-bridged borane."[6]

We propose that trimethylamine coordinates the electron-deficient borane dimer intact to yield a complex represented by **1**. In general, a Lewis base reacts with the intact dimer as represented in eq 1; additional base may or may not dissociate the complex, *e.g.*, as in eq 2. In addition to being consistent with the observed nmr spectrum, complex **1** is analogous to coordination complexes we have found for intact alkyllithium dimers with Lewis bases, *i.e.*, ethers and tertiary amines.[7] Ethers also may be seen to coordinate the intact borane dimer. Thus, as with the electron-deficient lithium reagents, ethereal solvents (relative to hydrocarbons or no solvent) effect the nmr chemical shift of diborane without at the same time interrupting the multicenter splitting of the dimer. With increasing temperature, this splitting pattern of boron-11 in ethereal diborane is modified, as first reported by Gaines.[5] From the usual triplet of triplets (each boron split by two distinct proton pairs), an intramolecular exchange process causes the pattern to become a regular septet, both borons equivalently split by all six protons.[6]



1

$$B_2H_6 + \text{base} \rightleftharpoons B_2H_6\text{–base} \quad (1)$$

$$B_2H_6 + 2\ \text{base} \rightleftharpoons 2\ \text{base–}BH_3 \quad (2)$$

The boron-11 splitting observed by Gaines[5] demonstrates the absence of fast intermolecular exchange of borane units from its dimer etherate in ethereal solvents, including the very basic glycol dimethyl ether, and thus demonstrates that the excess Lewis base

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(1) S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966).

(2) These seven lines were said to generate a symmetrical spectrum which "established the presence of a BH_2 (triplet) and BH_3 (quartet) unit."[1] Our initial observations were that the structure reported by Shore and Hall could not be established by such a spectrum, for a variety of reasons. For example, if the assumption of a superimposed BH_2 triplet and BH_3 quartet were correct, a remarkable rearrangement mechanism must average out the chemical shift between two protonic environments but not at the same time cause equivalent splitting by these protons. The point here is, considering the large chemical shifts observed between boron-11 atoms in subtly different environments, that one could certainly not expect such different B atoms as assumed[1] would show superimposed absorption unless their signals were averaged; *cf.*, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1966, p 970 ff.

(3) R. A. Ogg, *J. Chem. Phys.*, 22, 1933 (1954).

(4) The third and seventh lines in a triplet of triplets can be difficult to resolve and therefore easy to miss. For some reason, resolution of those two particular lines requires precise phasing adjustment of the spectrometer. Also, excess amine beyond that required to form the complexed dimer causes line broadening of the dimer nmr signals, presumably by some exchange process; we have observed the same effect with trialkylaluminum dimers complexed by amines at low temperature (unpublished work with S. C. Watson).

(5) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

(6) Certainly a singly bridged species might exist as a metastable intermediate, *e.g.*, in allowing intramolecular exchange processes, as Gaines has pointed out.[5]

(7) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

does not dissociate (*e.g.*, eq 2) the B_2H_6–base complex. This demonstrable stability of diborane etherates, as well as the titrimetric observation of diborane aminates,[1] shows that the borane dimer *per se* is acidic. Complexed alkyllithium dimers are even more resistant to dissociation analogous to eq 2.[8] That various electron-deficient dimers *per se* are intrinsically acidic (eq 1) seems rational on theoretical grounds. Previous workers have apparently been forced to write singly bridged species or dissociation of dimers (eq 2) because of their assumption that base only coordinates by σ-bonding directly to the metal atom, which furnishes an unoccupied AO. It is logical to assume that base could also coordinate by π-bonding the intact dimer, which furnishes an unoccupied MO.

Since at least six AO's are available in the four-centered dimer, an ordinary LCAO could be expected to make at least three MO's available for occupancy, but the four atoms of the uncomplexed dimer can furnish only four bonding electrons. An insufficiency of bonding electrons to fill all available MO's of the dimeric species must be the most logical basis of describing this species as electron deficient and as therefore acidic, *i.e.*, susceptible to complexation by an electron donor. As a generalization, Longuet-Higgins suggested[9] that if there are fewer than $2(n - 1)$ electrons bonding an n-centered oligomer, it is electron deficient.[10] Specifically for the four centers of the diborane system, the six possible energy levels estimated (by SCF equations in their LCAO form)[11] suggest that in the three lowest levels only two are strongly bonding and one is approximately nonbonding, and that, among these three, two are σ MO's and one has π symmetry. From considerations of both symmetry and energy levels in such a system, it appears that bonding overlap could occur with a donor furnishing $2p\pi$ electrons either from the nonbonding orbital of a simple Lewis base or from a π MO of an unsaturated system.

It is suggested that oligomeric metal alkyls and hydrides that associate as electron-deficient reagents are appropriately characterized as π acids. Recognition of this characteristic provides a basis for rationalizing the distinctive ability of these reagents to undergo various reactions with nonpolar, unsaturated hydrocarbons, an ability not shared by similar metal organics and hydrides that are not π acids. For example, diborane, aluminum trialkyls, dialkylaluminum hydrides, magnesium dialkyls, and lithium alkyls, all of which can be characterized as oligomeric π acids, all undergo addition to simple olefins, but this addition is not observed with sodium borohydride, dialkylaluminum halides, heavy metal alkyls, and Grignard reagents, none of which are electron-deficient oligomers.

Acknowledgment. The author appreciates financial support from the Petroleum Research Fund, administered by the American Chemical Society.

(8) *Cf.* C. G. Screttas and J. F. Eastham, *J. Am. Chem. Soc.*, **88**, 5668 (1966).

(9) H. C. Longuet-Higgins, *Quart. Rev.* (London), 11, 121 (1957).

(10) For some consideration of electron deficiency in valence-bond terms, see H. A. Bent, *Chem. Rev.*, 61, 275 (1961).

(11) W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

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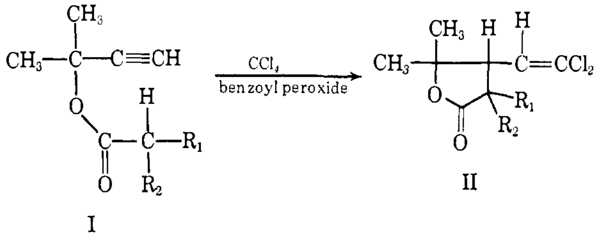
Vinyl Radical Isomerization. II. A New Free-Radical Synthesis of γ-Lactones with Retention of Optical Activity

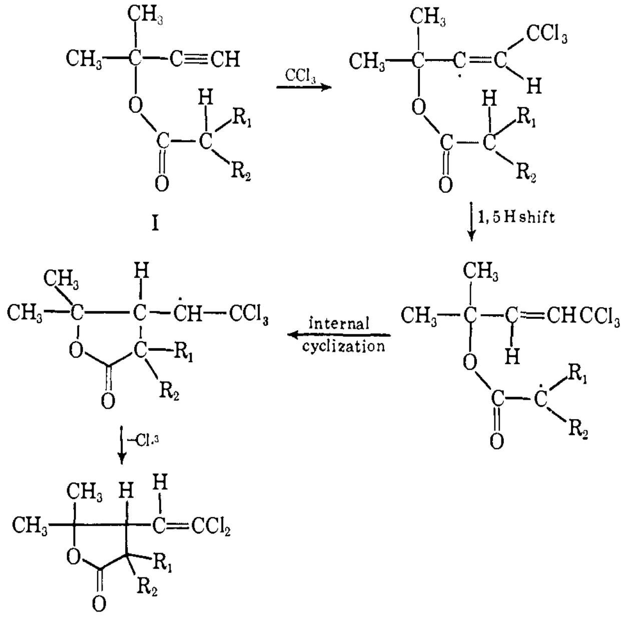
Sir:

We wish to report a new synthesis of γ-lactones from propargyl esters by free-radical means. The peroxide-initiated addition of CCl_4 to various propargyl esters yielded, besides the normal 1:1 CCl_4:acetylene adducts, γ-butyrolactone derivatives. The assigned structure of the lactone II was based on the following evidence. It was soluble in warm KOH solution and could be recovered upon acidification. It showed an infrared band at 5.62 μ characteristic of γ-lactones, as well as a band at 6.17 μ indicative of the vinylidene chloride group.[1] The nmr spectrum contained a doublet at τ 4.15 with a coupling constant between 9.1 and 10.9 cps, depending on the nature of the R groups. Elemental analyses indicated a compound which corresponded to an addition of CCl_2 to the original ester.



I

The formation of γ-lactones can best be explained by the following mechanism, which is similar to that proposed for the rearrangement of terminal acetylenes to vinylcyclopentanes.[2]



II

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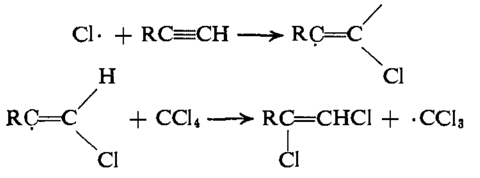
(1) R. Dowbenko, *Tetrahedron*, 21, 1647 (1965).

(2) E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, **88**, 1589 (1966).

(3) $CCl_3\cdot$ radical can be regenerated by the following mechanism



$$Cl\cdot + RC{\equiv}CH \longrightarrow R\dot{C}{=}C(H)Cl$$

$$R\dot{C}{=}C(H)Cl + CCl_4 \longrightarrow RC(Cl){=}CHCl + \cdot CCl_3$$

Such chlorine-addition products have been observed with alkylacetyl-