1), 87088-39-9; 11 (isomer 2), 87088-59-3; 12, 87088-40-2; 13, 87088-41-3; 14, 87088-42-4; 15, 87088-43-5; 16, 87088-44-6; (Z)-17, 87088-45-7; (E)-17, 87088-46-8; 18, 110-93-0; 19, 87088-47-9; 20, 87088-48-0; 21, 87088-49-1; 22, 4234-93-9; 23, 106-72-9; 24, 87088-50-4; 25, 87088-51-5; 26, 87088-52-6; 27, 87088-53-7; 30, 87088-54-8; 31, 87088-55-9; 32, 87088-56-0; triethyl 2-phosphonobutanoate, 17145-91-4; phenylselenyl chloride, 5707-04-0; triethyl 2-phosphono-2-(phenylseleno)butanoate, 87088-57-1; methylenecyclohexane, 1192-37-6; 2-methyl-2-butene, 513-35-9; (E)-3-methyl-2-pentene, 616-12-6; (Z)-3-methyl-2-pentene, 922-62-3; 2,3-dimethyl-2-butene, 563-79-1; 1-hexene, 592-41-6; paraformaldehyde, 30525-89-4; acetaldehyde, 75-07-0.

Hydroboration Kinetics. 9.[1] Kinetics and Mechanism of the Complex Formation of 9-Borabicyclo[3.3.1]nonane Dimer with Representative Amines. Effect of Steric Hindrance on the Reaction Mechanism

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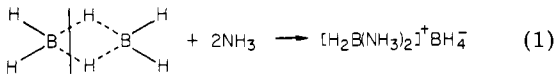
The complex formation of 9-borabicyclo[3.3.1]nonane dimer $(9\text{-BBN})_2$ with representative amines was studied. In all cases, symmetrical cleavage of the boron–hydrogen bridge bonds of $(9\text{-BBN})_2$ was observed. However, the symmetrical cleavage proceeds through a dissociation mechanism or a bimolecular direct attack mechanism, depending on the steric requirement and the nucleophilicity of the amine. With sterically unhindered amines such as pyrrolidine, piperidine, *n*-butylamine, etc., the reaction exhibits second-order kinetics, indicating that the rate-limiting step involves the direct reaction between the dimer and the amine. Sterically more hindered amines, such as *tert*-butylamine, di-*n*-butylamine, and quinuclidine, exhibit first-order kinetics, first order in $(9\text{-BBN})_2$. Obviously, in these cases the reaction proceeds by the dissociation of the dimer, followed by the reaction of the amine with the monomer. *sec*-Butylamine shows intermediate kinetic behavior. Thus, the mechanism of this reaction is strongly affected by moderate changes in the steric requirements of the amine.

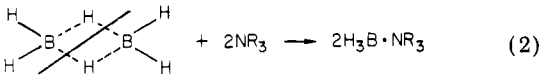
Complex formation between boron compounds and amines has been extensively studied. Studies of the thermodynamic stabilities of the borane–amine complexes have led to a quantitative understanding of steric effects as a factor in chemical behavior.[4] Synthetic applications of these addition compounds have also been investigated.[5]

The reaction mechanisms for the formation of complexes of amines with organoboranes have also been studied.[6] Two different mechanisms have been postulated for the reactions of diborane with amines. The reaction of ammonia with diborane results in the formation of the diammoniate of diborane (eq 1).[7] The reaction appears to



(1)

involve the unsymmetrical cleavage of the hydrogen bridge bonds in diborane. On the other hand, the reaction with mono-, di-, or trimethylamine produces monomeric adducts (eq 2).[8] Therefore, symmetrical cleavage of the hydrogen



(2)

R = H or CH_3

bridge bonds of diborane was postulated. The symmetrical cleavage may proceed through a unimolecular dissociation mechanism or through a bi- or termolecular direct attack mechanism.[9]

We recently investigated the kinetics and mechanism of the hydroboration of alkenes and alkynes with 9-borabicyclo[3.3.1]nonane dimer and found that the reaction proceeds through the prior dissociation of $(9\text{-BBN})_2$, followed by the reaction of the monomer with the unsaturated substrate[1a,c] (eq 3 and 4).

$$(9\text{-BBN})_2 \overset{k_1}{\rightleftharpoons} 2\ 9\text{-BBN} \quad (3)$$

$$9\text{-BBN} + \text{alkene or alkyne} \rightarrow B\text{-alkyl-9-BBN} \quad (4)$$

These results significantly differed from those on the reaction of disiamylborane dimer with alkenes, which seemed to proceed through a direct attack of the alkene on the borane dimer.[10] We thought that a systematic study of the reaction of $(9\text{-BBN})_2$ with representative nucleophiles might help in understanding the general mechanism of hydroboration by $(R_2BH)_2$. Consequently, we studied the kinetics of the reduction of aldehydes and ketones with $(9\text{-BBN})_2$ and found that the dissociation mechanism operates[1h] (eq 3 and 5). We then studied the

$$9\text{-BBN} + \text{aldehyde or ketone} \rightarrow B\text{-alkoxy-9-BBN} \quad (5)$$

(1) For previous studies in this series see: (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698–702. (c) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306. (d) Wang, K. K.; Scouten, C. G.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 531–536. (e) Nelson, D. J.; Brown, H. C. *Ibid.* **1982**, *104* 4907–4912. (f) Nelson, D. J.; Blue, C. D.; Brown, H. C. *Ibid.* **1982**, *104* 4913–4917. (g) Wang, K. K.; Brown, H. C. *Ibid.* **1982**, *104*, 7148. (h) Brown, H. C.; Wang, K. K.; Chandrasekharan, J. *Ibid.* **1983**, *105*, 2340. (i) Brown, H. C.; Chandrasekharan, J.; Wang, K. K. *J. Org. Chem.* **1983**, *48*, 2901.

(2) Postdoctoral research associate on Grant CHE 79-18881 of the National Science Foundation.

(3) Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation.

(4) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.

(5) Lane, C. F. *Aldrichimica Acta* **1973**, *6*, 51–58.

(6) Onak, T. "Organoborane Chemistry"; Academic Press: New York, 1975; pp 183–186.

(7) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8–12.

(8) Parry, R. W.; Kodama, G.; Schultz, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 24–27.

(9) Bauer, S. H. *J. Am. Chem. Soc.* **1956**, *78*, 5775–5782.

(10) Brown, H. C.; Moerikofer, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2063–2065.

0022-3263/83/1948-3689$01.50/0

kinetics of protonolysis of $(9\text{-BBN})_2$ with representative alcohols.[1i] In THF, the dominant reaction pathway is via the solvent-assisted dissociation of $(9\text{-BBN})_2$. In CCl_4, however, the situation is different. Hindered alcohols such as *tert*-butyl alcohol reacted by the dissociation mechanism (eq 3 and 6). In the case of unhindered alcohols, such as

$$9\text{-BBN} + \text{ROH} \rightarrow B\text{-alkoxy-9-BBN} \quad (6)$$

methanol, in addition to this dissociation pathway, a direct reaction pathway involving the attack of the alcohol on the dimer is also observed (eq 7 and 8). It appeared that

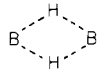
$$(9\text{-BBN})_2 + CH_3OH \rightarrow 9\text{-BBN} + B\text{-OMe-O-9-BBN} + H_2 \quad (7)$$

$$9\text{-BBN} + CH_3OH \rightarrow B\text{-}CH_3\text{-O-9-BBN} + H_2 \quad (8)$$

increasing the nucleophilicity of the substrate increases the possibility for the operation of a direct attack mechanism. It occurred to us that with amines, which are more powerful nucleophiles than alcohols, the direct attack mechanism should assume greater importance. Consequently, we studied the kinetics of complexation of $(9\text{-BBN})_2$ with representative amines.

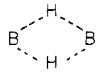
Results and Discussion

The kinetics of complexation of $(9\text{-BBN})_2$ with representative amines were followed by monitoring quantitatively the



absorption at 1570 cm^{-1} using an IR spectrometer.[1c]

Products. The reaction of $(9\text{-BBN})_2$ with amines proceeds by a symmetrical cleavage of the



bridge to yield 9-BBN–amine complexes. Many of these have been characterized earlier.[11] For example, the ^{11}B NMR spectrum of 9-BBN–pyridine is a clean doublet centered at –0.2 ppm (reference: $BF_3{\cdot}Et_2O$).[12] If an unsymmetrical cleavage had occurred, two peaks should appear in the ^{11}B NMR spectrum, one a singlet and the other a triplet. The ^{13}C NMR spectra of representative 9-BBN–amine complexes have also been recorded.[13]

Complex Formation with Second-Order Kinetics. Unlike hydroboration or reduction, the complex formation of pyridine (0.130 *M*) with $(9\text{-BBN})_2$ (0.065 *M*) in cyclohexane at 25 °C exhibits second-order kinetics, first order in $(9\text{-BBN})_2$ and first order in pyridine (eq 9). In addition,

$$\frac{-d[(9\text{-BBN})_2]}{dt} = k_2[(9\text{-BBN})_2][\text{pyridine}] \quad (9)$$

the rate of reaction is faster than the rate of dissociation of $(9\text{-BBN})_2$. The first half-life of the reaction is only 10.7 min ($k_2 = 1.20 \times 10^{-2}$ M^{-1} s^{-1}, Table I), which is about 8 times shorter than the half-life of the dissociation of $(9\text{-BBN})_2$ ($t_{1/2} = 78$ min, $k_1 = 1.50 \times 10^{-4}$ s^{-1}). Obviously, the complex formation of pyridine cannot proceed through the dissociation mechanism (eq 3 and 10). There must be

$$9\text{-BBN} + \text{amine} \overset{\text{fast}}{\rightleftharpoons} 9\text{-BBN–amine} \quad (10)$$

some additional reaction pathway to account for the faster reaction rate and the different kinetics. The bimolecular direct attack mechanism can well explain the observed kinetic behavior (eq 11 and 12). Since the complex for-

$$(9\text{-BBN})_2 + \text{amine} \underset{k'_{-2}}{\overset{k'_2}{\rightleftharpoons}} 9\text{-BBN–amine} + 9\text{-BBN} \quad (11)$$

$$9\text{-BBN} + \text{amine} \overset{\text{fast}}{\rightleftharpoons} 9\text{-BBN–amine} \quad (12)$$

mation of pyridine with $(9\text{-BBN})_2$ in cyclohexane is greater than 99% complete, the reverse reactions of eq 11 and 12 can be ignored.[14]

Although it is true that both the dissociation mechanism and the direct attack mechanism may act simultaneously, the latter one is the predominant pathway, as evidenced by the kinetic observation. Doubling the initial concentration of pyridine did not affect the second-order rate constant appreciably while the first-order rate constant changed very much.

initial concentration		rate constants	
$(9\text{-BBN})_2$	pyridine	10^2k_1, s^{-1}	10^2k_2, M^{-1} s^{-1}
0.065	0.260	0.209	1.13
0.065	0.130	0.069	1.20

The observance of second-order kinetics with pyridine encouraged us to study the complexation of $(9\text{-BBN})_2$ by several other amines. The results are given in Table I. Pyrrolidine, piperidine, *n*-butylamine, and neopentylamine all react faster than pyridine and exhibit second-order kinetics. Benzylamine and cyclohexyl-, cycloheptyl-, and cyclopentylamines also react with $(9\text{-BBN})_2$, exhibiting second-order kinetics.[15]

Reactions with First-Order Kinetics. The complexation by sufficiently hindered amines proceeds by the dissociation mechanism exhibiting clean first-order kinetics. Di-*n*-butylamine, *N*-methylpyrrolidine, 2-methylpyridine, quinuclidine, and *tert*-butylamine belong to this class. All of these compounds form complexes with $(9\text{-BBN})_2$ at essentially the same rate (Table I). The first-order rate constant is in good agreement with those

Table I. Kinetic Data for the Complex Formation of Amines with $(9\text{-BBN})_2$ in Cyclohexane at 25 °C[a,b]

amine	10^2k_2, M^{-1} s^{-1}	10^4k_1, s^{-1}
pyrrolidine	27.5[c]	
piperidine	5.63	
n-butylamine	1.73	
neopentylamine	1.40	
pyridine	1.20	
benzylamine	0.95	
cyclohexylamine	0.51	
cycloheptylamine	0.45	
cyclopentylamine[d]	0.44	
sec-butylamine[e]		
2-methylpyridine		1.46
N-methylpyrrolidine		1.40
di-*n*-butylamine		1.61
quinuclidine		1.37
tert-butylamine		1.42
aniline		1.37

[a] The initial concentration of $(9\text{-BBN})_2$ was kept at 0.065 M and that of the amine at 0.130 M. [b] The standard deviations of the rate plots were $\leq 1.5\%$ of the reported rate constants. [c] The rates were too fast to measure accurately. [d] Showed slight intermediate behavior. [e] The data did not fit the integrated rate expressions of either second or first order.

(11) Brown, H. C.; Kulkarni, S. U. *Inorg. Chem.* **1977**, *16*, 3090–3094.
(12) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846–849.
(13) Brown, H. C.; Wang, K. K. *J. Org. Chem.* **1980**, *45*, 1748–1753.
(14) Brown, H. C.; Wang, K. K. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 117–120.
(15) Cyclopentylamine showed slight intermediate behavior.

obtained for hydroboration and reduction.[1] Obviously, the rate-limiting dissociation of $(9\text{-BBN})_2$ is followed by the reaction of the monomer with the amine in these cases (eq 3 and 6). Aniline also reacts with $(9\text{-BBN})_2$ by dissociation mechanism.

Effect of Structure on the Rate and Mechanism of Complexation. The rate of complexation of $(9\text{-BBN})_2$ by amines is highly dependent on their structure. For example, branching of the alkyl group in an acyclic primary amine has a remarkable effect on the rate and mechanism of complexation: *n*-butylamine reacts by second-order kinetics; *tert*-butylamine shows first-order kinetic behavior, while *sec*-butylamine reacts with intermediate kinetics; the rate data do not fit the integrated rate expressions of either first or second order. Obviously, there is a simultaneous operation of direct attack and dissociation pathways in the case of *sec*-butylamine. The first half-life of complexation is 10 times shorter in the case of *n*-butylamine than that of *tert*-butylamine for the same initial concentration (0.130 *M*). The rate of complexation by *sec*-butylamine lies in between those of *n*- and *tert*-butylamine.

Branching of the alkyl group at the β-position to the nitrogen in an acyclic primary amine does not cause any change in the mechanism. For example, neopentylamine reacts only slightly slower than *n*-butylamine. Another interesting observation is the ease of complexation of cycloalkylamines. We were interested in studying the behavior of cyclopentyl-, cyclohexyl-, and cycloheptylamines. All of them react faster than *sec*-butylamine. In fact, they exhibit second-order kinetics while *sec*-butylamine reacts with intermediate kinetic behavior. That cycloalkylamines react faster than *sec*-butylamine is presumably due to the smaller *F* strain in the former ones since the alkyl groups are held back in the form of a ring.

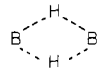
Pyrrolidine complexes with 9-BBN faster than piperidine does. It is probably due to the smaller steric requirements of the five-membered ring than those of the six-membered one.

Aniline reacts by the dissociation mechanism while benzylamine exhibits second-order kinetics in its reaction with $(9\text{-BBN})_2$.

Thus the mechanism of complexation of $(9\text{-BBN})_2$ by amines is highly dependent on the steric requirements and the nucleophilicity of the amine.

Complex Formation by Highly Hindered Amines. With highly hindered amines, the equilibrium for complex formation does not go to completion. For example, complex formation between diisopropylamine and $(9\text{-BBN})_2$ is only 36% complete. The reverse processes in eq 7 and 8 cannot be ignored, making the kinetics more complex. Consequently, the kinetics of complexation by very hindered amines were not studied.

Effect of Solvent on the Rate of Complexation of $(9\text{-BBN})_2$ with Amines. The complexation by a few selected amines was studied in benzene and THF in order to understand the role of solvent on this reaction. The data are given in Table II. The reaction proceeds faster in benzene and THF irrespective of the mechanism. The effect of solvents on the rates of complexation by those amines which proceed by the dissociation mechanism is essentially the same as that observed in the hydroboration and reduction reactions involving $(9\text{-BBN})_2$.[1b,h] The rate of complexation is about 10 times higher in THF than in noncomplexing cyclohexane solvent. The role of THF is to assist in breaking up the



bonds of the reagent.[1g]

Table II. Effect of Solvent on the Complexation of Amines with $(9\text{-BBN})_2$ at 25 °C

amine	cyclohexane	benzene	THF
second-order kinetics, $k \times 10^2$ M^{-1} s^{-1}			
pyrrolidine	27.5	86.3	101.5
piperidine	5.63	10.2	15.7
pyridine	1.20	1.80	4.03[a]
first-order kinetics, $k \times 10^4$ s^{-1}			
2-methylpyridine	1.46	2.16	14.1
N-methylpyrrolidine	1.40	1.92	13.3
di-*n*-butylamine	1.61	2.37	14.2

[a] Shows some intermediate behavior.

There is also an increase in the rates of complexations proceeding by the direct attack mechanism on changing the solvent from cyclohexane to THF. The increase is about 4 times compared to cyclohexane. It may be noted that the rate increase is not as high as that observed in reactions proceeding through the dissociation mechanism. The rate increase observed in the case of unhindered amines may well be due to the greater stabilization of the charged transition state, involving the amine and $(9\text{-BBN})_2$, by the more polar THF solvent.

Conclusion

The systematic kinetic studies of the reactions of alkenes, alkynes, aldehydes and ketones, alcohols, and amines with 9-BBN_2 have revealed a spectrum of mechanistic pathways. It consists of the following:

(1) second-order kinetics

$$(9\text{-BBN})_2 + \text{N} \xrightarrow{k_2} 9\text{-BBN}\cdot\text{N} + 9\text{-BBN}$$

$$9\text{-BBN} + \text{N} \xrightarrow{\text{fast}} 9\text{-BBN}\cdot\text{N}$$

(2) first-order kinetics

$$(9\text{-BBN})_2 \xrightarrow{k_1} 2\ 9\text{-BBN}$$

$$9\text{-BBN} + \text{N} \xrightarrow{\text{fast}} \text{product}$$

(3) three-halves-order kinetics

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN}$$

$$9\text{-BBN} + \text{N} \xrightarrow{\text{slow}} \text{product}$$

Less hindered amines react by mechanism 1. More hindered amines react by mechanism 2. Reactive alkenes react by mechanism 2. Less reactive alkenes follow mechanism 3. Finally, in certain cases, it has also been possible to observe intermediate kinetic behavior.

Clearly, the nucleophilicity of the substrate plays a very important role in determining the reaction pathway.

Experimental Section

Materials. The purification of solvents and the preparation of $(9\text{-BBN})_2$ were carried out as described elsewhere.[16] Standard procedures were followed for handling the air-sensitive compounds.[16] The amines were obtained commercially and distilled from CaH_2 under nitrogen before use.

Kinetic Procedure. The kinetic studies of the complex formation of $(9\text{-BBN})_2$ with amines were carried out by monitoring quantitatively the rate of disappearance of the boron–hydrogen

(16) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

bridge bonds of 9-BBN dimer at 1570 cm^{-1} with an IR spectrometer.[1c] A detailed procedure has been described earlier. A typical example is as follows. Cyclohexane (1.3 mL), followed by $(9\text{-BBN})_2$ (36.8 mL of a 0.068 *M* solution), was added into a 100-mL round-bottom flask with the usual precautions of air protection. After the reaction mixture was equilibrated in a constant-temperature bath at 25.0 ± 0.1 °C, it was pumped through a 0.1-mm NaCl IR cell to determine the absorbance of

vibration at 1570 cm^{-1}. The reaction was initiated by adding pyridine (0.40 mL). The initial concentrations of $(9\text{-BBN})_2$ and pyridine were 0.065 *M* and 0.130 *M*, respectively. The initial absorbance increased slightly, due to a weak absorption of pyridine at 1570 cm^{-1}.

The absorbance was continuously recorded on chart paper. After 3 h, the absorbance ceased to decrease. The residual absorbance was measured as the background absorbance. The concentration of $(9\text{-BBN})_2$ at a particular reaction time was calculated as described previously and the second-order rate constants were calculated on a Hewlett-Packard 9820 calculator. The best straight line was fitted to this set of data by using the method of least squares. The rate constant was obtained numerically as the slope of the line.

Acknowledgment. We thank the National Science Foundation for Grants CHE 76-20846 and CHE 79-18881.

Registry No. $(9\text{-BBN})_2$, 70658-61-6; pyrrolidine, 123-75-1; piperidine, 110-89-4; *n*-butylamine, 109-73-9; neopentylamine, 5813-64-9; pyridine, 110-86-1; benzylamine, 100-46-9; cyclohexylamine, 108-91-8; cycloheptylamine, 5452-35-7; cyclopentylamine, 1003-03-8; *sec*-butylamine, 13952-84-6; 2-methylpyridine, 109-06-8; *N*-methylpyrrolidine, 120-94-5; di-*n*-butylamine, 111-92-2; quinuclidine, 100-76-5; *tert*-butylamine, 75-64-9; aniline, 62-53-3; cyclohexane, 110-82-7; benzene, 71-43-2; tetrahydrofuran, 109-99-9.

Photoelectron Spectra of *syn*- and *anti*-Sesquinorbornene. Evidence for Vertical σ-π Delocalization in Bicyclo[2.2.1]heptene

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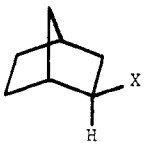
Received May 27, 1983

The photoelectron spectra of *syn*- and *anti*-sesquinorbornene show the π IP's to be 8.12 and 7.90 eV, respectively. Comparison of these IP's with those of other tetraalkylethylenes having the same number of carbon atoms indicates that both isomers are easier to ionize than expected for a C_{12} tetraalkylethylene. This is attributed to σ-π closed shell–closed shell repulsions between the ethano and methano bridges and the π bond. The difference of 0.2 eV in the π IP between the two is surprisingly large for two geometric isomers and is related to the molecular symmetry. The π IP of norbornene, when compared with those of a series of cis olefins, is 0.12 eV easier to ionize than is expected for a *cis*-dialkylethylene containing seven carbons. This small reduction in π IP which is attributable to vertical electronic factors may account for an increased reactivity of norbornene in processes involving electrophilic addition to the π bond.

Few systems have attracted more interest than the bicyclo[2.2.1]heptyl (norbornyl) skeleton.[1] The bulk of the controversy pertains to the high exo/endo selectivity both of its saturated derivatives (**1**) under solvolytic conditions and in additions (either electrocyclic or electrophilic) to the unsaturated norbornene (**2**).[2-5]



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2

Although it is generally accepted that norbornene itself exhibits unusual chemical properties, insofar as we are aware no incontrovertable analysis of extant data has been made which would indicate that its π IP[6,7] is substantially different from those of other olefins which do not incorporate the bicyclo[2.2.1] framework. Indeed, norbornene has been referred to as belonging to a well-behaved series of molecules in which an ethylene π level is affected by alkyl substitution.[8] If vertical σ-π interaction[9] were

(1) (a) For leading literature citations see: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 413-428. (b) Brown, H. C. *Tetrahedron* **1976**, *32*, 179-204. (c) Schleyer, P. V. R. In "The Non-Classical Ion Problem"; Brown, H. C., Ed.; Plenum: New York, 1977. (d) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41-52. (e) Sargent, G. D. In "Carbonium Ions"; Olah G. A., Schleyer, P. V. R., Eds.; Wiley: New York, 1972; Vol. III, Chapter 24. (f) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87-96.

(2) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439-490. (b) Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152-160.

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