Organoborates: Carbonylation, Cyanoborate, and Alkynylborate Processes. Energetics of Sequential 1,2-Shifts from Boron to Carbon Calculated by ab Initio and MNDO Methods

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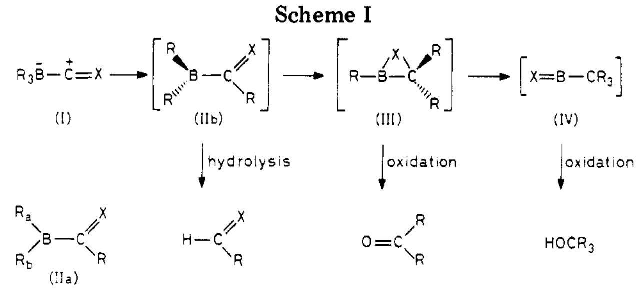
Molecular geometries of organoborates (BH_3CX, where X = O, NH, and CH_2) and their isomers are calculated by STO-3G (ab initio) and MINDO/3 and MNDO (semiempirical) molecular orbital theories. Isomerization energies for the three sequential rearrangements by 1,2-hydride shifts from boron to carbon are also calculated at 4-31G and 6-31G* ab initio levels. These calculations model carbonylation (X = O), cyanoborate protonation (X = NH), and alkynylborate protonation (X = CH_2) processes in which 1,2-alkyl shifts occur. For carbonylation the calculated energies and independent chemical evidence are consistent with a reversible reaction between borane or alkylborane and CO, followed by rate-limiting rearrangement by 1,2-shift. Subsequent rearrangements followed by dimerization or trimerization are predicted to be highly exothermic. The first 1,2-hydride shift for BH_3CNH is less endothermic than that for BH_3CO, and that for BH_3CCH_2 is highly exothermic. The relative ease of the second rearrangement follows the order: X = O ~ NH > CH_2; third rearrangements follow the order: X = O > NH > CH_2. Dissociation energies ($BH_3CX \rightarrow BH_3 + CX$) follow the reverse order. Calculated rotational barriers for planar compounds BH_2Z follow the order: Z = NH_2 > OH > $CHCH_2$ > CHNH > CHO > BH_2, using 6-31G*, MNDO, and (with reservations) MINDO/3; for the latter two the perpendicular conformation is preferred. Agreement between independent theoretical methods is satisfactory with some exceptions, particularly heats of formation; also MINDO/3 predicts some unlikely molecular geometries.

Sequential 1,2-shifts in organoborates (I) from boron to carbon provide versatile synthetic methods for carbon–carbon bond formation. Up to three such shifts can occur and products are formed after oxidation or hydrolysis of organoborane intermediates (Scheme I).[1] Little is known about the nature of the monomeric organoborane intermediates (II, III, IV), which have not been isolated or even observed spectroscopically. Dimers of III and trimers of IV can be isolated, and the monomeric intermediates have also been trapped by other reactions (e.g., with aldehydes, glycol, or water).[2–5] It seems likely that many of the monomeric species (II, III, IV) are highly reactive; so to aid understanding of the mechanisms of the reactions, we initiated a research program to predict by molecular orbital methods the structures, mechanisms, and energetics of rearrangement of organoborates. This provides a survey of a wide area and helps to indicate promising aspects for further experimental studies.

When this work began the GAUSSIAN 70 (ab initio)[6] and MINDO/3 (semiempirical)[7] molecular orbital computer programs were available, and extensive calculations of a wide variety of chemical phenomena had been published.[6,7]

Scheme I



Both computer programs permitted geometry optimization within reasonable sized budgets of computer time. As relatively little experimental data are available for organoboranes and the adjustable parameters for boron required by MINDO/3 were only preliminary,[7] we compared the two computational methods. Some serious deficiencies in MINDO/3 were found, but we were able to interpret the mechanism and stereochemistry of the alkynylborate process (I, X = CH_2) using MINDO/3 supported by selected ab initio calculations.[8] Later GAUSSIAN 76[6d] and MNDO[9] programs became available, and a comparison between various procedures (MINDO/3, MNDO, STO-3G, 4-31G, and 6-31G*) is now reported. Emphasis is given to energy changes (rotational barriers and isomerization energies) because these are most relevant to interpretation of mechanism and reactivity. In this report no allowance is made for solvent effects and all calculations refer to hydrogen as the substituent on boron (Scheme I, R = H). Other workers have examined the electronic structure of BH_3CO (I, R = H, X = O), because there is considerable interest in boron ylides (I), particularly in the bonding and dissociation energies of these donor–acceptor complexes.[10] Systematic studies of other organoboranes by MNDO[9b–d]

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Table I. Equilibrium Geometries and Energies for Boranes (Scheme I, R = H) Calculated by STO-3G

molecule	symmetry	geometrical parameters[a]	total energy[b]
I, X = O[c]	C_{3v}	BC = 1.631, CO = 1.144, BH = 1.162, HBC = 103.4	−137.33199
IIa, X = O	C_s	BC = 1.586, CO = 1.233, BH_a,BH_b = 1.161, CH = 1.103, H_aBC = 120.3, H_bBC = 119.2, BCH = 119.5, BCO = 122.1	−137.29624
IIb, X = O	C_s[d]	BC = 1.593, CO = 1.227, BH = 1.162, CH = 1.108, HBC = 120.2, BCH = 117.7, BCO = 123.7	−137.29479
III, X = O	C_s	BC = 1.508, CO = 1.465,[e] BO = 1.328, BH = 1.150, CH = 1.087, HCH = 113.1, CBH = 157.8, B-CHH[f] = 168.1	−137.34636
IV, X = O	C_{3v}	BC = 1.546, BO = 1.178, CH = 1.085, HCB = 110.8	−137.42579
I, X = NH[g]	C_{3v}	BC = 1.629, CN = 1.158, BH = 1.162, NH = 1.016, HBC = 104.3	−117.76771
IIa, X = NH	C_s	BC = 1.565, CN = 1.287, BH_a = 1.160, BH_b = 1.161, CH = 1.092, NH = 1.051, H_aBC = 119.9, H_bBC = 120.1, BCH = 119.4, BCN = 119.8, CNH = 110.0	−117.77031
IIb, X = NH	C_s[d]	BC = 1.578, CN = 1.279, BH = 1.163, CH = 1.095, NH = 1.048 HBC = 120.4, BCH = 117.2, BCN = 120.1, CNH = 109.5	−117.76575
III, X = NH	C_s	BC = 1.549, CN = 1.456,[h] BN = 1.327, BH = 1.150, CH = 1.087 NH = 1.017, HCH = 112.3, CBH = 153.4, BNH = 156.4, B-CHH[f] = 163.4	−117.80252
IV, X = NH	C_{3v}	BC = 1.549, BN = 1.197, CH = 1.085, NH = 1.007, HCB = 111.0	−117.85547
I, X = CH_2[i]	C_s	BC = 1.561, CC = 1.289, BH = 1.165, CH = 1.084, HBC = 105.5, CCH = 120.7	−101.93051
III, X = CH_2	C_{2v}	BC = 1.522, CC = 1.525, BH = 1.152, CH = 1.081, HCH = 112.3, CBH = 149.9, B-CHH[f] = 153.8	−102.01931
IV, X = CH_2	C_s	B-C = 1.547, B=C = 1.341, =CH = 1.078, CH = 1.086, HCB = 111.1, B=CH = 122.9	−102.01031
HOBO[l]	C_s	B=O = 1.187, B-O = 1.348, OH = 0.983, HOB = 110.3, OBO = 176.2[m]	−172.70490

[a] Bond lengths in angstroms, angles in degrees; assumed symmetry can be deduced from the geometry specified. [b] Hartrees; for selected molecules footnotes c, g, i, and l give 4-31 G and 6-31 G* values; energies for other molecules can be calculated from Tables III and IV. [c] Energies: −138.91633, −139.13660. [d] Dihedral angle HBCX = ±90°. [e] Actually optimized OBC = 61.8. [f] B-CHH specifies the angle between the plane of the CH_2 and the BC bond. [g] Energies: −119.09706, −119.27207. [h] Actually optimized NBC = 60.2. [i] Energies: −103.04938, −103.19682. [j] Local C_{3v} on boron. [k] Local C_{3v} on CH_3. [l] Energies: −174.81941, −175.07428. [m] B=O bent away from H.

and ab initio[11] methods have also been reported.

Results

Calculations relevant to carbonylation (I, X = O),[2,3] cyanoborate protonation (I, X = NH)[4,5] and alkynylborate protonation (I, X = CH_2)[12] are given in Table I. Initial estimates of geometrical parameters were based on standard bond lengths and bond angles,[13] and then each parameter was varied in sequence until the energy minimum was obtained. Final geometries were calculated by interpolation of three points on a parabola to the energy minimum, using increments of 0.01 Å for bond lengths and 1° for bond angles. All these calculations were carried out by using the STO-3G level (minimal basis set), and then to obtain improved calculations for energy changes,[6a] these STO–3G optimized geometries were used for single calculations at 4-31G and 6-31G* levels. Independent geometry optimizations for MINDO/3 and MNDO were carried out automatically, using the standard derivative procedures in these programs.[7,9a] Further optimization of the STO-3G geometries (Table I) by MNDO resulted in relatively small reductions in energy (<2.5 kcal/mol) for all molecules except the organoborates (I), which showed energy changes <6 kcal/mol. A comparison with the limited experimental data available is shown in Table II, which includes some geometry optimizations at the 4-31G level, using the three-point interpolation procedure.

Table II. Comparison of Experimental and Calculated Equilibrium Geometries

molecule and parameter	exptl	calcd 4-31G	calcd MNDO
BH_3CO	b	c	
BC	1.534	1.600	1.496
CO	1.135	1.122	1.163
BH	1.222	1.200	1.176
HBC	103.8	104.2	106.8
BH_3CNH		d	
BC		1.613	1.501
CN		1.148	1.176
BH_3CNCH_3	e	STO-3G[f]	
BC	1.566	1.629	
CN	1.155	(1.158)[g]	
NCH_3	1.416	1.453	
HBC	105.7	(104.2)[g]	

[a] Bond lengths in angstroms, angles in degrees. [b] Reference 14a. [c] Energy: −138.91965 hartrees, after complete C_{3v} geometry optimization. [d] Energy: −119.10073 hartrees, assuming NH = 0.996, BH = 1.199, and HBC = 104.2. [e] Reference 14b. [f] Energy: −156.36166 (STO-3G), −158.07862 (4-31G). [g] For BH_3CNH, Table I.

Discussion

Reliability of the Calculations. All of the theoretical methods used in this work have imperfections, many of which have been discussed elsewhere.[6,7,9] Therefore it is necessary to compare these independent theoretical methods with each other and with the limited experimental data available. Probably the most difficult geometrical parameter to calculate is the BC bond length in BH_3CX (I). The minimal basis set (STO-3G) calculations predict for BH_3CO a BC bond length 0.10 Å too long; the more extensive basis set (4-31G) predicts 0.07 Å too long (Table II), but changes of ±0.01 Å increase the energy by less than 0.03 kcal/mol, consistent with experimental evidence that

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Table III. Rotational Barriers ($E_{planar} \rightarrow E_{perp}$, kcal/mol) about the B-Z Bond in BH_2Z

	ab initio[a]			semiempirical[b]	
Z	STO-3G	4-31G	6-31G*	MNDO	MINDO/3
BH_2	-12.7[c]	-11.9[d]	-10.5[c]	-17.7	-21.4
NH_2[e]	35.6[c]	37.6[d]	29.4[c]	23.8	34.3
OH	21.7[c]	13.3[d]	14.4[c]	15.0	(~12)[f]
CHO	0.9	-1.6	-2.5	-4.9	(~-6)[g]
CHNH	2.9	1.8	1.3	-2.2	h
$CHCH_2$	5.8[i]	7.0[i]		1.2	(3.3)[j]

[a] Geometries are optimized STO-3G from Table I and ref 13. [b] Optimized geometry but the symmetry was assumed to be the same as that used for ab initio calculations. [c] Reference 13. [d] 4-31G total energies in hartrees of planar forms are the following: Z = BH_2, -51.53850; Z = NH_2, -81.37632; Z = OH, -101.17227. [e] Pyramidal nitrogen in perpendicular conformation. [f] Assuming HOB = 112° (from STO-3G), cf. MNDO 117.5 (planar) and 124.7° (perpendicular); MINDO/3 predicts 174° and 180°, respectively. [g] Assuming for the perpendicular conformation, BCO = 120° to prevent cyclization during geometry optimization to BCO = 69°. [h] Both planar and perpendicular conformations cyclized during geometry optimization. [i] K. Krogh-Jespersen, unpublished results (Erlangen). [j] Using STO-3G optimized geometries.

the force constant is considerably less than that for a good single bond.[14c] MNDO predicts a BC bond length 0.04 Å too short, and similar trends can be seen for BH_3CNH and BH_3CNCH_3. Despite the large differences in geometry predicted by STO-3G and MNDO, the energy difference between these two geometries for BH_3CO is calculated by MNDO to be only 5.1 kcal/mol (cf. STO-3G, 4.3 kcal/mol). In most cases much lower energy differences between the two different geometries were found with use of MNDO; e.g., for IIa, 0.9 kcal/mol, and calculated BC bond lengths agree within 0.02 Å. Consequently, emphasis will be given to predicted energy changes, which should not be markedly dependent on errors in the calculated geometries.

MNDO overestimates the stability of BH_3CO—the BC bond length is too short and the heat of formation is too low.[9b] In contrast a relatively inflexible minimal basis set STO-3G calculation should underestimate the stability of BH_3CO, consistent with the calculated BC bond length which is too long. By examination of energy differences between various rotamers or isomers, more reliable results should be obtained. Rotational barriers calculated for II and other substituted boranes (BH_2Z, Table III) show satisfactory agreement between ab initio and semiempirical methods including MINDO/3, although some unlikely equilibrium geometries were predicted by the latter method. The barrier to rotation in planar BH_2Z decreases in the order: Z = NH_2 > OH > $CHCH_2$ > CHNH > CHO > BH_2, paralleling ease of π-electron donation.[13] Allylborane (Z = $CHCH_2$ or II, X = CH_2, Scheme I) prefers a planar conformation[15] and BH_2CHO prefers a perpendicular conformation (IIb, X = O); the barrier to rotation for BH_2CHNH is so low that its sign is in doubt.

Energies of double bonds and small ring systems are difficult to calculate accurately[6a] and the isomerization energies vary with the method of calculation (Table IV); MINDO/3 predicted unlikely geometries and these results have been excluded. The more reliable ab initio calculations (6-31G*) are known to reproduce correctly the relative energies of propene and cyclopropane, whereas 4-31G calculations underestimate the stability of the small ring system by over 5 kcal/mol.[6a] This systematic error accounts for the discrepancies between the 4-31G and 6-31G* calculations for the second rearrangement with X = O and for the third rearrangements with X = O and X = NH (Table IV). Another systematic error in 4-31G calculations appears to be an overestimate of the strength of BN single bonds,[16] and these two systematic errors almost cancel for the second rearrangement with X = NH. Although suitable model reactions are not available to test the predicted energy changes for the first rearrangement of organoborates (I), the differences between 4-31G and 6-31G* calculations for X = O and CH_2 can be explained if 4-31G underestimates the stability of the organoborate. Therefore the energies in Table IV calculated by 6-31G* are considered to be more reliable than the 4-31G values. As the reactions in Table IV are not *isodesmic*,[6a] the 6-31G* calculations might be further refined by allowing for electron correlation. With use of Møller-Plesset second-order perturbation theory, it has recently been shown that the relative energies of small rings containing boron are significantly *but not markedly* affected by electron correlation.[11c]

Table IV. Isomerization Energies (kcal/mol) for Sequential Rearrangement of Organoborates (I → IIb → III → IV, Scheme I) for Carbonylation (X = O), Cyanoborate Protonation (X = NH), and Alkynylborate Protonation (X = CH_2)

(molecule) theoret procedure[a]	first rearrangement (I → IIb)	second rearrangement (IIb → III)	third rearrangement (III → IV)
(X = O)			
4-31G	10.2	-8.9	-69.6
6-31G*	17.2	-15.9	-56.5
MNDO	19.5	2.1	-64.7
(X = NH)			
4-31G	5.6	-11.6	-47.4
6-31G*	0.3	-9.2	-36.1
MNDO	2.3	0.6	-42.1
(X = CH_2)			
4-31G	-50.5	11.7	-13.5
6-31G*	-50[b]		
MNDO	-34.1	13.3	-8.1

[a] Geometries for 4-31G and 6-31G* calculations from Table I; separate geometry optimization for MNDO calculations. [b] Energy for (I → IIa) = 57.3 kcal/mol; *estimate* of barrier (IIa → IIb), ca. 7 kcal/mol (Table III).

Agreement between the 6-31G* and MNDO calculations (Table IV) is within 9 kcal/mol except for three cases. The first rearrangement of (I, X = CH_2) is much less exothermic by MNDO than by 6-31G*; MNDO predicts a short BC bond length (1.455 Å) and, as discussed above, may overestimate the stability of the organoborates (I). However this error in MNDO should also occur for (I, X = O and NH; see Table II). If MNDO also overestimated the stability of IIb (X = O and NH), agreement between MNDO and 6-31G* for the first rearrangements and the two discrepancies for the second rearrangements could be explained; for the second rearrangements (X = O and NH), MNDO predictions are substantially less exothermic than 6-31G*. The latter two discrepancies do not appear to be due to errors associated with three-membered rings;

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(16) Hydrogenation energies for small boron molecules (BH_2BH_2, BH_2CH_3, BH_2NH_2, BH_2OH) have been reported for STO-3G optimized geometries at the 6-31G* level;[13] 4-31G energies agree within 4 kcal/mol except for BH_2NH_2 which differs by over 9 kcal/mol from that predicted by 6-31G*.[17]

Table V. Trends in Dissociation Energies (kcal/mol) of Boron Ylides ($BH_3CX \rightleftharpoons BH_3 + CX$)

molecule	STO-3G[a]	4-31G[a]	exptl
BH_3CO	22.5	10.2	22[b]
BH_3CNH	33.0	20.7	
BH_3CCH_2	44.7	31.0	

[a] Total energies of dissociated molecules CO, HNC, and CH_2C having STO-3G geometry from ref 6b; energies for BH_3 from ref 13 (STO-3G) and ref 18b (4-31G). [b] Reference 10a.

MNDO correctly reproduces the energy differences between propene and cyclopropane and between acetaldehyde and its isomeric epoxide.[9a] Also the third rearrangement involves opening of the three-membered ring and agreement between MNDO and 6-31G* is much better.

For the first rearrangement of I, the average of 6-31G* and MNDO energies varies from +18.3 kcal/mol for X = O to −42 kcal/mol for X = CH_2, remarkable considering the formal similarity between these processes. MNDO and ab initio calculations predict a huge variation in heats of reaction for the third rearrangement, which strongly reflects the differences in bond energies between B=O, B=N, B=C, and corresponding single bonds.[13]

Dissociation of BH_3CO occurs readily and trends in dissociation energies can be calculated (Table V). Although the STO-3G results appears to be satisfactory, the absolute values are not meaningful, because dissociation involves a change in the number of bonds and effects due to electron correlation must be taken into account.[10] The calculations refer to formation of CX from BH_3CX (I) and do not allow for the possible rearrangement of CNH to HCN or of CCH_2 to HCCH. Alkyl groups attached to boron should stabilize trivalent boron,[13] so lowering dissociation energies (Table V) and the energy for the first rearrangement (Table IV).

The effect of solvent is more difficult to predict. Coordination between ether solvents and trivalent boron would be expected, but carbonylation occurs in solvents having a wide range of polarities as well as in the gas phase.[2a] The species I–IV are neutral overall and extensive delocalization of charge in the ylides (I) is expected.[8] Therefore these calculations may provide helpful insights into the mechanisms of the reactions (Scheme I, R = alkyl; X = O, NH, CH_2)[19] in solution. For simplicity it will be assumed that trends in heats of reaction, for these related series, parallel activation energies. There are such differences in the calculated heats of reaction for the three series (X = O, NH, CH_2) that it would require unexpectedly large changes in the shapes of the potential energy surfaces to invalidate this simple assumption.

Mechanistic Considerations. The available experimental evidence and the calculations (Tables IV and V) for carbonylation are consistent with a reversible reaction between trialkylborane and carbon monoxide, followed by rate-limiting rearrangement to give (II, X = O).[3a] In the presence of complex metal hydrides the rate of carbonylation increases, and the product of one rearrangement (RCHO) can be isolated.[20a] These results supported a possible alternative mechanism, involving reversible formation of II;[3a] this requires a rate-limiting step after formation of II, presumably rate-limiting rearrangement to III. It is now known that the metal hydride reduces the organoborate I, and there is no evidence for the trapping of the acylborane (II, X = O) by metal hydrides.[20b] Acylboranes have not yet been characterized,[21] and they probably rearrange rapidly. The bora epoxide (III, X = O) can be trapped by dimerization, or by reactions with water, glycol or aldehyde.[2,3] These processes must compete with a highly exothermic rearrangement to CR_3BO (Table IV).

Table VI. Heats of Formation for Boron-Containing Molecules

molecule	exptl[a]	6-31G*[b]	MNDO	MINDO/3
BH_3	23.8	23[c]	11.7[d]	46.5
BH_2BH_2		58	13.7	72.1
CH_3BH_2		15	−7.5	18.0[e]
NH_2BH_2		−14	−25.7	−27.5
$HOBH_2$	−69.4	−64	−78.2[d]	−60.1[f]
CH_2BH		76	45.2	53.4
NHBH		31	1.6	−10.6
OBH		−48	−68.6	−40.6
OBOH	−134.1	−121[g]	−133.1[d]	−147.5[h]
$(CH_3)_3B$	−29.2		−40.1[d]	−13.2
B_2H_6	8.4	[i]	−1.8	12.9

[a] Reference 22. [b] Reference 13; *estimated*, using calculated hydrogenation energies and experimental ΔH_f° (g) values for the hydrogenation products BH_3, CH_4, NH_3, and H_2O. [c] Assumed. [d] Reference 9b. [e] Assuming symmetrical CH_3, otherwise one hydrogen atom bridges B and C, giving $\Delta H_f^\circ = 10.6$. [f] Restricted geometry; see Table III, footnote *f*. [g] Data from Table I. [h] Linear HOB predicted. [i] Excluded because dissociation rather than hydrogenation is required.

Cyanoborate and alkynylborate processes differ from carbonylation in that reactions are usually initiated by electrophilic attack on organoborates $[R_3BCN]^-$ and $[R_3BCCR]^-$, respectively.[5,8,12] Thus there is an extra step to consider mechanistically and this is probably rate determining for alkynylborates.[8] Rearrangement of the organoborate ylide (I, X = CH_2) may occur spontaneously in a highly exothermic process and, in accord with the calculations (Table IV), the second rearrangement is relatively unfavorable. Adducts between boranes and isocyanides provide independent routes to the ylides (I, X = NH or NR′), and for derivatives of trialkylboranes rearrangement appears to occur readily.[3,4] The first isolable intermediates are dimers of II, which require heating at about 100 °C to induce the second rearrangement.[3,4] Therefore the latter step is rate determining in the current synthetic-scale reactions.[5] The calculations for monomeric species (Table IV) could model reactions occurring at much lower concentrations when, because the barrier to the first rearrangement is probably low, alkylation or protonation of $[R_3BCN]^-$ could become rate determining if weak electrophiles were used.

Conclusions

The calculations (Table IV) correctly reproduce the trends observed experimentally for carbonylation, cyanoborate protonation, and alkynylborate protonation processes. The organoborates (I, X = O, NH, CH_2; Scheme I) dissociate in the order X = O > NH (probably) > CH_2 and rearrange by the first 1,2-shift (I → IIb) in the reverse

(17) For 4-31G energies, see Table III (footnote *d*) and ref 18a.

(18) (a) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663. (b) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Radom, L. *Ibid.* **1976**, *98*, 3436.

(19) The calculations (Tables IV, V) should also model reactions having X = NCH_3 or $C(CH_3)_2$ or other alkyl derivatives.

(20) (a) Brown, H. C.; Coleman, R. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 499. (b) Brown, H. C.; Hubbard, J. L. *J. Org. Chem.* **1979**, *44*, 467.

(21) Smith, K.; Swaminathan, K. *J. Chem. Soc., Chem. Commun.* **1975**, 719.

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order. The ease of second rearrangement (IIb → III) is X = O ~ NH > CH_2 and third rearrangements (III → IV) follow the order X = O > NH > CH_2. Carbonylation proceeds by a rate-limiting first rearrangement after which two more rearrangements can occur readily. The first rearrangement for (I, X = CH_2) occurs very readily and protonation or alkylation of $[R_3BCCH]^-$ is probably rate determining in the alkynylborate processes. The cyanoborate process could proceed via several possible rate-determining steps and is probably more dependent on reaction conditions than carbonylation or alkynylborate processes.

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Appendix

During the course of this work heats of formation of small boron-containing molecules were calculated (Table VI). A few large discrepancies between the various methods are observed, partly because the 6-31G* results require a vibrational correction.[6a,6c] Clearly absolute values are more difficult to calculate than the energy differences (rotations and isomerizations) discussed above.

Registry No. I (R = H; X = O), 13205-44-2; I (R = H; X = NH), 60048-47-7; I (R = H; X = CH_2), 51220-37-2; II (R = H; X = O), 32375-83-0; II (R = H; X = NH), 5844-50-8; III (R = H; X = O), 79723-20-9; III (R = H; X = NH), 71720-68-8; III (R = H; X = CH_2), 39517-80-1; IV (R = H; X = O), 79723-21-0; IV (R = H; X = NH), 79723-22-1; IV (R = H; X = CH_2), 79723-23-2; HOBO, 13460-50-9; BH_3CNCH_3, 79723-24-3; BH_2BH_2, 18099-45-1; BH_2NH_2, 14720-35-5; BH_2OH, 35825-58-2; BH_2CHCH_2, 5856-70-2; BH_3, 13283-31-3; CH_3BH_2, 12538-96-4; CH_2BH, 56125-75-8; NHBH, 15119-97-8; OBH, 20611-59-0; $(CH_3)_3B$, 593-90-8; B_2H_6, 19287-45-7.

Hydrogen Bonded Complexes. 3. Some Anomalous Acid Salts of Dibasic Acids[1]

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A large number of salts of dibasic acids, H_2Y, with amines and quaternary ammonium hydroxides are reported. These include the normal neutral salt (R_2Y), the normal acid salt (RHY), and two series of anomalous salts (RH_3Y_2 and $R_2H_4Y_3$), in all of which R^+ represents the cation formed from the neutralizing base. Infrared spectroscopy has been used to draw some inferences about the structures of the anomalous salts.

Our continuing interest in conducting systems for electrolytic capacitors has occasioned the preparation of many substituted ammonium and quaternary ammonium salts of dibasic acids. The dibasic acids form two series of normal salts, the neutral or disalts (R_2Y) and the acid or monosalts (RHY), in both of which H_2Y represents the dibasic acid and R^+ the cation formed from the neutralizing base. In addition, the dibasic acids form two types of anomalous salts, RH_3Y_2 and $R_2H_4Y_3$, but only with selected neutralizing cations. The neutral salts are readily preparable when both dissociation constants of the acid are of sufficient magnitude (e.g., as with fumaric acid). The structures of the salts that result present no problems and are of little interest.

The acid salts are the most readily available and most easily prepared. Some interest is attached to the structures of these salts because of the structure of the hydrogen maleate anion, in potassium hydrogen maleate for example. For this anion there is evidence from infrared spectroscopy,[2] from a two-dimensional neutron-diffraction study,[3] and from a three-dimensional structure analysis with X-rays[4] to indicate that the two carboxyl groups of the monoionized anion are crystallographically equivalent and linked by a "very short" and probably symmetrical hydrogen bond. Similar, symmetrical hydrogen bonds also occur in some acid salts, RHX_2, of monobasic acids, HX.[5]

Of present interest are the anomalous acid salts of dibasic acids.[5] In almost every case we have obtained the anomalous salt in a serendipitous manner while trying to prepare a normal salt. Moreover, we have encountered two types of anomalous salts, one with two dibasic acid molecules per cation and the other with three dibasic acids per two cations. It is our present purpose to record the properties of the salts that we have prepared and to discuss such structural considerations as are permitted by infrared spectroscopy.

Results and Discussion

As already noted the neutral disalts of dibasic acids are of minimal interest. The few that were prepared and analyzed to verify the stoichiometry are given in Table I.

The acid monosalts of dibasic acids are useful as solutes in organic electrolyte systems, and we have had occasion to prepare a large number of them. In fact, our first encounters of anomalous, acid salts of dibasic acids resulted from attempts to prepare the normal monosalts. In Table

(1) For the previous paper in this series, see J. E. Barry, N. E. Cipollini, M. Finkelstein, and S. D. Ross, *Tetrahedron*, 37, 1669 (1981).
(2) H. M. E. Cardwell, J. D. Dunitz, and L. E. Orgel, *J. Chem. Soc.*, 3740 (1953).
(3) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, 29, 948 (1958).
(4) S. F. Darlow and W. Cochran, *Acta Crystallogr.*, 14, 1250 (1961).
(5) For an excellent review article on acid salts of both monocarboxylic acids and dicarboxylic acids and a discussion of the anomalous acid salts, see J. C. Speakman, *Struct. Bonding (Berlin)* 12, 141 (1972).

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