of tetrakis(dimethylamino)diboron (**5**) from sodium and chlorobis(dimethylamino)borane,[17] and their ready recombination has been advanced as a possible explanation for the relatively high thermal stability of **5**.[18] Butyl(dimethylamino)boron radicals have been suggested as possible intermediates in the decomposition of 1,2-bis(dimethylamino)-1,2-di-*n*-butyldiborane(4).[19]

Although the observed cleavage of the boron–boron bond in 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) is a unique process in organoboron photochemistry, the similarity to the azine cases[6,7] and difference from the all-carbon diene case[5] are noteworthy. Despite the elucidation of the gross reaction mechanism, the precise nature of the reactive excited state of **1** and the scope of the boron–boron cleavage reaction remain undetermined. These detailed aspects of the reactions of bis(amino)diborons and related compounds are currently under investigation.

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(18) L. L. Petterson and R. J. Brotherton, *Inorg. Chem.*, 2, 423 (1963).
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A 1,3-Bromine Migration. The Deamination of 3-Bromo-2,2-bis(bromomethyl)propylamine

Sir:

The intermediacy of 1,2-halonium ions in the addition of halogen to double bonds has been known for many years.[1,2] Recently examples of 1,4-halonium ions[3–5] and 1,5-halonium ions[5] also have been reported. The intermediacy of 1,3-halonium ions has been postulated in the addition of bromine to bicyclo[2.1.0]pentane[6a] and to a substituted bicyclo[2.2.1]heptane.[6b] An unsuccessful attempt to observe 1,3-halogen shifts under identical conditions where 1,2- and 1,4-halonium ions could be generated was recently reported.[3]

We now wish to report the first example of a 1,3-bromine migration[7] which occurred during the deamination of 3-bromo-2,2-bis(bromomethyl)-*1*-d_2-propylamine perchlorate (**4**). The deuterated amine (**4**) was synthesized in three steps from 3-bromo-2,2-bis(bromomethyl)propionamide (**1**).[8] Dehydration of **1** with thionyl chloride in the presence of dimethylformamide as catalyst produced 3-bromo-2,2-bis(bromomethyl)-propionitrile (**2**)[9] in 75% yield, mp 43.5–46.5°. Reduction of **2** with B_2D_6[10] by a modified procedure of Brown,[11] followed by the addition of excess ethanol and hydrogen bromide, gave 3-bromo-2,2-bis(bromomethyl)-1-d_2-propylamine hydrobromide (**3**) in 49% yield, mp 233–236° dec. The nmr spectrum of **3** (DMSO-d_6, TMS internal standard) showed the absence of the CH_2–NH_3Br^- signal which appears at −3.05 ppm in the undeuterated amine hydrobromide. The perchlorate salt **4** was prepared by reaction of **3** with silver perchlorate. The nmr spectrum of **4** (DMSO-d_6–D_2O, TMS) exhibited a singlet at −3.67 ppm. Deamination of the perchlorate salt **4** in glacial acetic acid gave a total of 11 components by glpc analysis. The two major components were isolated by preparative glpc and identified[12] as 3-bromo-2,2-bis(bromomethyl)-1-propyl acetate (**5**, R = H, 45% yield)[12] and 3-bromo-2-(bromomethyl)-1-propene (**6**, 5.5% yield).[12]

A 1,3-bromine shift was demonstrated by the presence of a significant CH_2OAc signal at −4.21 ppm ($CDCl_3$) in the nmr spectrum of the deuterated acetate product **5** (R = H) (see Scheme I). The integrated ratio of the CH_2OAc signal (−4.21 ppm, $CDCl_3$) to the CH_2Br signal (−3.57 ppm, $CDCl_3$) in the nmr spectrum was 1:6.5. The expected ratios for possible mechanisms of bromine involvement are summarized in Table I.

Table I. Nuclear Magnetic Resonance Signal Ratios of the Deamination Products for Possible Mechanisms of Bromine Involvement

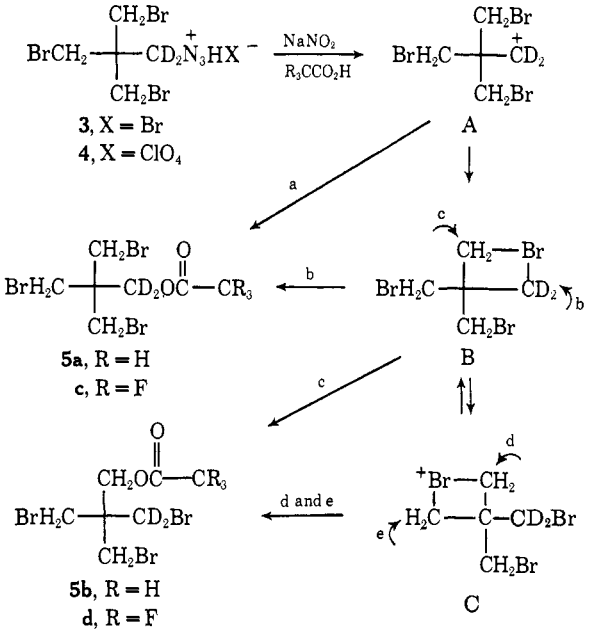
	Acetate **5** CH_2OR : CH_2Br	Olefin **6** $=CH_2$: CH_2Br
No 1,3-bromine shift	0	0
Single bromonium ion (B)	1:5	1:4 or 3
Equilibrating Br ion (B and C)	1:3	1:2
Actual ratio (HOAc)[a]	1:6.5	1:2
Actual ratio (CF_3CO_2H)[a]	1:3.9	*b*

[a] Accuracy of integration ±5%. [b] Not determined.

These ratios assume that any secondary deuterium isotope effects are small and would not be detected by nmr integration of the signals.[13] The low 1:6.5 ratio

(1) Credit for the idea of 1,2-halonium ions is generally given to I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).
(2) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); **90**, 947, 2587 (1968), and references therein.
(3) P. E. Peterson and F. J. Slama, *ibid.*, **90**, 6516 (1968).
(4) (a) P. E. Peterson and E. V. P. Tao, *ibid.*, **86**, 4503 (1964); (b) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966); **85**, 2865 (1963); (c) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. M. Curran, D. E. Dillard, and R. J. Kamat, *ibid.*, **89**, 5902 (1967); (d) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968); (e) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968); (f) P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1283 (1967); (g) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *ibid.*, **92**, 2834 (1970).
(5) P. E. Peterson and J. E. Coffey, *Tetrahedron Lett.*, 3131 (1968).
(6) (a) R. T. LaLonde, *J. Amer. Chem. Soc.*, 87, 4217 (1965); (b) M. M. Avram, I. Pogany, F. Badea, I. G. Dinulescu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 3851 (1969).
(7) The phenomenon of internal return, where allylic halides undergo a 1,3-halogen shift simultaneously with double bond migration, is known, but quite different from a 1,3-halogen shift in a saturated system. See E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, pp 286–289.
(8) F. Nerdel, A. Heymons, and H. Croon, *Chem. Ber.*, **91**, 938 (1958).
(9) Satisfactory analyses were obtained on all new compounds.
(10) The precursor for B_2D_6 was $NaBD_4$ (>96% D) obtained from Alfa Inorganics.
(11) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **82**, 681 (1960).
(12) Yields were calculated from the integrated glpc peak areas relative to an internal standard that was precalibrated with the identified components. Identifications were first carried out on the products from deamination of the undeuterated amine perchlorate. The minor components have not yet been fully characterized, but are possible bromomethyl migration products.

Scheme I



may be the result of some attack of solvent on A, or a species similar to A, before formation of B.[14] These results, therefore, do not demonstrate whether a symmetrical bromonium ion (B) is formed (which would give a 1:1 mixture of **5a**:**5b**) or whether such a bromonium ion is rapidly equilibrating (B and C). Such an equilibrating ion would lead to a 1:3 mixture of **5a** to **5b**. However, nmr analysis of the other main product, 3-bromo-2-(bromomethyl)-1-propene (**6**), indicated that this product is formed only after an equilibrating bromonium ion has formed. As seen from Scheme II, if only B was present when a 2 + 2 cycloreversion occured,[16,17] then a 1:1 mixture of **6a** and **6b** would result, giving a 1:4 nmr signal ratio for $=CH_2$ to CH_2Br. Likewise, if B were to undergo β cleavage, then a 1:1 mixture of **6a** and **6c** would result, giving a 1:3 nmr signal ratio for $=CH_2$ to CH_2Br. A ratio of 1:1:2 of **6a**, **6b**, and **6c** would be present in the olefinic product if B and C are equilibrated before olefin formation (*via* either mechanism), and a 1:2 nmr signal ratio for $=CH_2$ to CH_2Br would result (see Table I). The latter nmr signal ratio was adhered to exactly. It should be noted that no olefinic hydrogens would be present in the nmr spectrum if a bromonium ion intermediate or transition state did not occur and result in bromine migration, and that the $=CH_2$ to CH_2Br nmr signal ratio would be greater than 1:2 if A was even partially involved in the olefin formation process. It would seem that β scission could occur just as readily on the carbonium ion (A) as on the bromonium ions (B and C). It is therefore tempting to invoke the 2 + 2

(13) J. March, "Advanced Organic Chemistry: Reaction, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, pp 215–216.

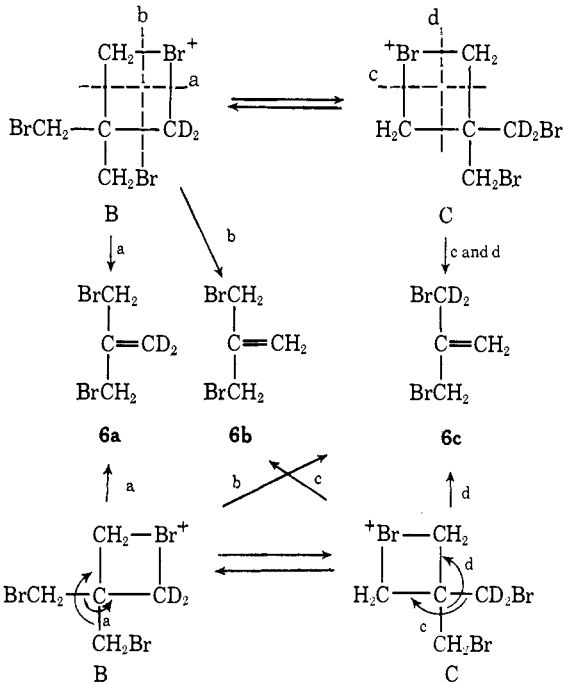
(14) The possibility that A exchanged deuterium for hydrogen from solvent *via* a diazoalkane intermediate[15] was eliminated by a field ionization spectrum of **5** (R = H). The spectrum showed a parent ion for the dideuterated species only. We are indebted to Dr. Lewis Shadoff for the mass spectra.

(15) J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968).

(16) See footnote *a*, Scheme II.

(17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Gemany, 1970, pp 65–75.

Scheme II. Formation of Olefin **6** by Either a 2 + 2 Cycloreversion[a] or a β Cleavage



[a] We wish to thank Dr. Paul D. Bartlett for suggesting that olefin **6** may arise from a 2 + 2 cycloreversion.

cycloreversion mechanism for the olefin formation. This is not an unattractive hypothesis, since the positive charge in the fission product ($CH_2{=}Br^+$ or $CD_2{=}Br^+$) must be on the bromine, so why should this not be on the ring bromine that already carried the charge? It should also be noted that the antibonding π orbital of $(BrCH_2)^+$ should be of relatively low energy.[16]

The evidence that the olefinic product arises from an equilibrating bromonium ion unfortunately does not prove that even part of acetate **5** (R = H) is produced from the same intermediate. It was anticipated that deamination of the deuterated amine perchlorate **4a** in the less nucleophilic solvent trifluoroacetic acid[4c,18,19] would result in significantly less attack on A (or a species similar to A), thus bringing the nmr signal ratio of CH_2Br to $-CH_2OCOCF_3$ closer to 3:1 or 5:1. Deamination of **4a** in trifluoroacetic acid gave trifluoroacetate **5** (R = F) in 50% yield.[12,20] This product exhibited an nmr signal ratio of 1 (CH_2OCOCF_3) to 3.9 (CH_2Br) (Table I). This result rules out bromonium ion B as a single intermediate and indicates that approximately 80% of **5** (R = F) is formed by attack of trifluoroacetic acid on the equilibrated bromonium ions B and C. The other 20% of trifluoroacetate product is probably formed either by attack of trifluoroacetic acid on a species such as A or by nucleophilic displacement on the diazonium group. Either reaction would result exclusively in **5c** and consequently decrease the $-CH_2OCOCF_3$ to $-CH_2Br$ nmr signal ratio from that expected from attack solely on equilibrated bromonium ions B and C.

(18) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

(19) W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, **90**, 6876 (1968).

(20) The deamination in trifluoracetic acid produced only three minor products in addition to **5** (R = F). One was identified as olefin **6** (1.8% yield).[12]

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Deidaclin: A Natural Glucoside of Cyclopentenone Cyanohydrin

Sir:

The classical cyanogenetic glycosides are nearly all derivatives of valine, isoleucine, leucine, phenylalanine, and hydroxylated phenylalanines.[1,2] An exception is gynocardin, recently proved[3,4] to be the β-D-glucopyranoside (**1**) of 3σ-cyano-3ρ,4σ,5ρ-trihydroxycyclopentene.[5] The original sources of gynocardin belong to the tribe Pangieae of the dicotyledon family Flacourtiaceae. The Pangieae and adjacent cyanogenetic tribe Oncobeae of Flacourtiaceae[6] are the producers of chaulmoogra fatty acids having structure **2**, where *n* runs over even numbers from 12 down apparently to as low as 4 and the side chains are all σ oriented.[8,9] Chromatographic evidence[10] now indicates gynocardin to occur also in the closely related family Passifloraceae. Barterin, isolated[11] from a genus on the border between Flacourtiaceae and Passifloraceae, is the β-D-glucopyranoside of a 3-cyano-3,5σ-dihydroxycyclopentene.[11,12] Another new cyanogenetic glycoside was discovered by Hegnauer and coworkers[10] in *Deidamia clematoides* (Passifloraceae). They called the substance (mp 127–128°) deidamin, which we are altering to deidaclin with Professor Hegnauer's gracious consent in order to avoid the suggestion of basic properties. Enzymatic hydrolysis of deidaclin gave glucose, hydrogen cyanide, and a volatile carbonyl compound, isolated as a 2,4-dinitrophenylhydrazone.[10] In a color test[13] the hydrazone reacted like a conjugated unsaturated derivative. Having received deidaclin samples from Professor Hegnauer for additional study, we find it to be the β-D-glucopyranoside (**3**) of an enantiomer of 2-cyclopenten-1-one cyanohydrin.

The structure of deidaclin (*Anal.* Calcd for $C_{12}H_{17}NO_6$: C, 53.13; H, 6.32; N, 5.16. Found: C, 52.95; H, 6.03; N, 5.11) was revealed by its pmr spectrum [100 MHz, D_2O, external[14] $(CH_3)_4Si$]. The spectrum showed a multiplet representing four protons [$(CH_2)_2$] at δ 3.0 and an **AB** pair of doublets (each line apparently an unresolved triplet) at δ 6.40 and 6.87 (J = 6 Hz) for the two vinylic protons.[3] It also contained a doublet at δ 5.25 (J = 7.5 Hz) for the anomeric proton of a β-glucopyranoside[3,15] and signals from δ 3.6 to 4.5 for the six other unexchanged protons of the glucopyranosyl group. The 70-eV mass spectrum of deidaclin (probe temperature 130°) was consistent with the spectra of barterin and gynocardin (all had peaks at m/e = M − 49) and showed a strong doublet at m/e 92 and 93 ($ROC_6H_{11}O_5 \rightarrow R^+, RH^+$) corresponding to the barterin doublet[12] at m/e 108–109 and the single intense gynocardin peak[3] (R^+) at m/e 124.

Structure **3** was established for deidaclin by identification of the carbonyl compound formed on hydrolysis with gynocardase[10] as 2-cyclopenten-1-one. The 2,4-dinitrophenylhydrazone that we obtained in a Conway diffusion dish[10] or by treatment of a chloroform extract of the hydrolysis mixture with dinitrophenylhydrazine consisted of red needles, mp 167.5–169°, which were identical as judged by mixture melting point, ir spectrum, and tlc with the dinitrophenylhydrazone (lit.[16] mp 168–170°) of authentic 2-cyclopenten-1-one (Aldrich).

Although the enantiomers of cyclopentenone cyanohydrin should have substantial, predictable rotations,[9] the molecular rotation of deidaclin [$[\alpha]^{27}D$ −20.4° (c 1, H_2O)] is near values for β-D-glucopyranosides of achiral aglucones. The configuration of deidaclin next to the cyano group, like that of barterin, stands unknown at present. Nevertheless, deidaclin can be regarded as a structural prototype of the series comprising barterin, gynocardin, and possible isomers[10] of these, linking them to the cyclopentenoid fatty acids. A logical biosynthetic precursor[1,2] of deidaclin is a 2-cyclopentene-1-glycine. The hydroxylation step of the biosynthesis may be expected to proceed with retention of configuration.[17,18] A plausible though not a necessary conjecture is that the cyano groups of deidaclin and barterin are σ oriented like their counterpart in gynocardin and the side chains of the chaulmoogra acids and that the precursor of the whole cyanogenetic series is L-2-cyclopentene-1σ-glycine (**4**).

Fowden has emphasized steric analogies between protein and nonprotein plant amino acids.[19] Mixed stereoisomers of 2-cyclopentene-1-glycine form a metabolic antagonist of both valine and isoleucine toward *Escherichia coli*, owing to steric likeness.[20] The im-

(1) E. E. Conn and G. W. Butler in "Recent Advances in Phytochemistry," J. B. Harborne and T. Swain, Ed., Academic Press, New York, N. Y., 1969, Chapter 2.
(2) E. E. Conn, *J. Agr. Food Chem.*, 17, 519 (1969).
(3) R. A. Coburn and L. Long, Jr., *J. Org. Chem.*, **31**, 4312 (1966).
(4) H. S. Kim, G. A. Jeffrey, D. Panke, R. C. Clapp, R. A. Coburn, and L. Long, Jr., *Chem. Commun.*, 381 (1970).
(5) In cyclopentenes bearing directly attached carbon atoms at only one allylic position, consider the specified allylic carbon atom of the ring (imagined planar) to be replaced by oxygen, and disregard substituents elsewhere. Call the face of the cyclopentene corresponding to the *re–re* face [K. R. Hanson, *J. Amer. Chem. Soc.*, 88, 2731 (1966); D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969)] of the double bond in the resulting molecule of 2,3-dihydrofuran ρ, and the other face σ.
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(12) M. G. Ettlinger and R.-R. Paris, in preparation.
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(14) The standard signal fell *ca.* 0.4 ppm higher in field than that of internal $(CH_3)_4Si$.
(15) R. C. Clapp, F. H. Bissett, R. A. Coburn, and L. Long, Jr., *Phytochemistry*, **5**, 1323 (1966).
(16) H. Koch, J. Kotlan, and H. Mohar, *Monatsh. Chem.*, **95**, 1257 (1964).
(17) F. H. Bissett, R. C. Clapp, R. A. Coburn, M. G. Ettlinger, and L. Long, Jr., *Phytochemistry*, **8**, 2235 (1969).
(18) L. J. Morris and C. Hitchcock, *Eur. J. Biochem.*, 4, 146 (1968).
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