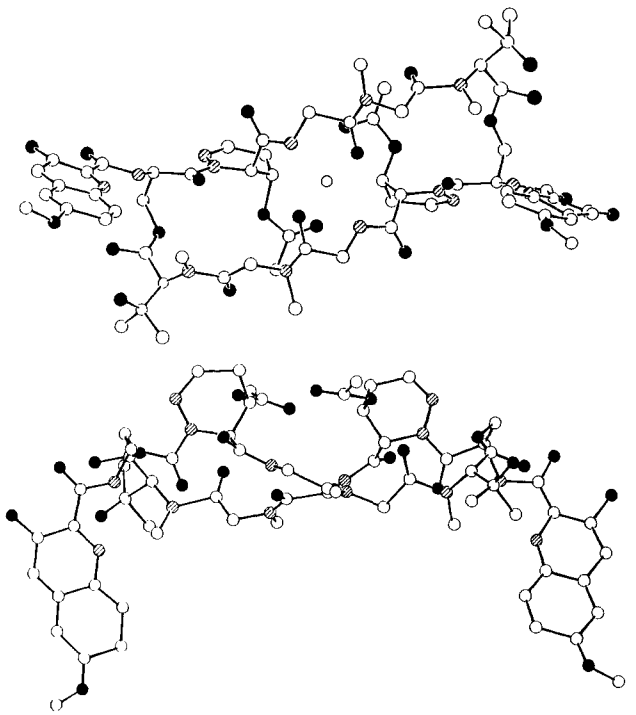

Figure 1. A computer-generated perspective drawing of two views of the current X-ray model of BBM-928 A. The top illustration is a view down the molecular twofold axis which is marked by the open circle at the center. The bottom illustration is at right angles to the first. Carbons are designated by open circles, oxygens by black circles, and nitrogens by stripes.

lustrated is based on the hydrolysis data.[6]

Two different views of the crystallographic model of BBM-928 A are given in Figure 1. The overall shape of the molecule is rectangular, with a molecular but noncrystallographic twofold axis. The long sides of the rectangle consist of twisted, antiparallel β-extended chains, and the short sides are lactone linkages from the hydroxyl group of serine to the carboxyl group of *N*-methylhydroxyvaline. The two unsubstituted amide nitrogens in the cycle are involved in weak (2.96 Å) hydrogen bonds of the 5→1 type that bridge the ring between the glycine amide hydrogen and the sarcosine carbonyl oxygen. This feature is also found in uncomplexed valinomycin.[13] There are two other intramolecular hydrogen bonds, one between the hydroxyl of *N*-methylhydroxyvaline and its own carbonyl (2.82 Å) and one between the aromatic 3-hydroxyl of the quinoline and its carbonyl (2.60 Å). There are no intermolecular hydrogen bonds. The serine residue at the corner is of the *R*(D) configuration, and this use of an "unnatural" amino acid to turn the corner is precedented in the cyclic peptide antibiotic gramicidin S.[14]

The unusual cyclic imino acid *trans*-(3*S*,4*S*)-4-acetoxy-2,3,4,5-tetrahydropyridazine-3-carboxylic acid is noteworthy. To the best of our knowledge, the only other report of a naturally occurring pyridazine ring system is the fully saturated hexahydropyridazine-3-carboxylic acid found in the monomycin series of antibiotics.[15] In the crystal the conformation of the tetrahydropyridazine ring is best described as a half-chair. β-Hydroxy-*S*(L)-valine has been previously reported,[16] but this is the first report of the *N*-methyl derivative.

One plausible model for the bisintercalation of BBM-928 A into double-helical DNA in the B form[17,18] may be constructed as follows. The geometry and symmetry are most plausible if we assume a bisintercalating mode where the quinoline rings are separated by two "sandwiched" base pairs. The simplifying assumptions we make are the following: (1) in the complex the twofold axis of BBM-928 A is coincident with that of DNA; (2) the conformation of the decadepsipeptide ring in the crystal is similar to that in the complex; (3) stacking distances are approximately 3.4 Å in both B DNA and the modification in which both quinoline systems have intercalated; (4) the quinoline systems from carboxamide to methoxy (9 Å) essentially overlap with their adjacent included base pair. It is reasonable to expect that most of the unwiding of the double helix that accompanies intercalation[19] occurs between the sets of base pairs that are being separated and that the twist angle of 36° between the two included base pairs is nearly maintained in the complex. On the basis of this model, one may calculate a serine-N to serine-N distance which ranges from 12 to 14.5 Å, depending on the exact quinoline-included base pair overlap; the observed distance in the crystal is 14.7 Å. The twisted conformation of the decadepsipeptide (see Figure 1) appears to be precisely complementary with the twisting nature of the included base pairs in a right-handed DNA double helix. Alternatively, if one relaxes the restriction in this model that the crystal conformation is conserved in the complex, at least one other bisintercalating mode is possible in which the β-extended chains are more nearly parallel to the Watson-Crick base pairs. In this second formulation, the twist angle between the included base pairs would probably be significantly less than 36°.

Further studies will explore the relevance of this crystalline conformation to the mode of action of BBM-928 A.

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(13) Karle, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 4379-4386.
(14) Hull, S. E.; Karlsson, R.; Main, P.; Woolfson, M. M.; Dodson, E. J. *Nature (London)* **1978**, *275*, 207-208.
(15) Bevan, K.; Davies, J. S.; Hassall, C. H.; Morton, R. B.; Phillips, D. A. S. *J. Chem. Soc. C* **1971**, 514-522. Hassall, C. H.; Ogihara, Y.; Thomas, W. A. *Ibid.*, **1971**, 522-526.
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(17) See: Sarma, R. H. In "Nucleic Acid Geometry and Dynamics"; Sarma, R. H., Ed., Pergamon Press: Elmsford, NY, 1980 and references therein.
(18) Wing, R.; Drew, H.; Takano, T.; Broka, C.; Tanaka, S.; Itakura, K.; Dickerson, R.; *Nature (London)* **1980**, *287*, 755-758.
(19) See: Sobell, H. M. In "Nucleic Acid Geometry and Dynamics"; Sarma, R. H., Ed., Pergamon Press: Elmsford, NY, 1980 and references therein.

Cyclopropylidene Radical Anion and 1,4-Elimination-Type Remote Ionization Effect in the Reduction of Bi(*gem*-dihalocyclopropane) Systems

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It has commonly been held that the electron-transfer reduction of *gem*-dihaloalkanes (**1**) in protic media proceeds via halocarbanion **2** and its protonated product **3** according to eq 1.[1] If

$$\underset{\mathbf{1}}{R_2CX_2} \xrightarrow[-X^-]{e,\,e} \underset{\mathbf{2}}{R_2C(X)^-:} \xrightarrow{SH} \underset{\mathbf{3}}{R_2CHX} \xrightarrow[-X^-]{e,\,e} \xrightarrow{SH} \underset{\mathbf{4}}{R_2CH_2} \quad (1)$$

this is indeed the case, then in the reduction with a deficient amount of reductant, the intermediate **3** should remain as a product until **1** is consumed, since polarographic half-wave potentials specify that the ease of reduction of haloalkanes decreases in the order RCX_3, $RCHX_2$, RCH_2X.[2] We have found, however, that the reduction of bi(*gem*-dihalocyclopropane) compounds (**5**)

(1) M. M. Baizer, "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, 1973, pp 256 and 683.
(2) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

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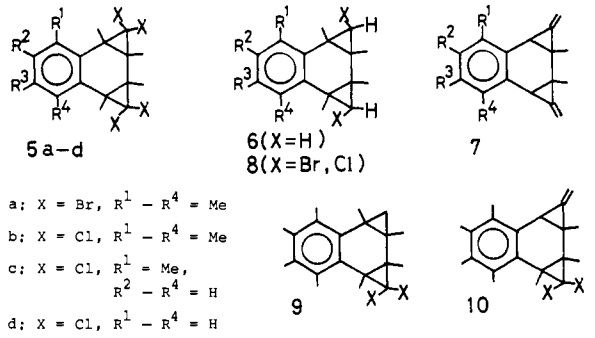
Table I. Reduction of 5 with Alkali Metal in NH_3 or with $C_{10}H_8^{\cdot-}$.[a]

compd (halogen)	reductant[b] (molar ratio to 5	solvent	Et-OH, molar ratio to 5	product yields, %[c] 5	6	7	8
5a (Br)	Na (6)	NH_3/THF[d]	20	32	68	0	0
5b (Cl)	Na (4)	NH_3/THF		57	43	0	0
5b (Cl)	Na (4)	NH_3/THF	20	50	50	0	0
5c (Cl)	Na (4)	NH_3/THF	20	57	43	0	0
5d (Cl)	Na (4)	NH_3/THF	20	62	38	0	0
5a (Br)	K-naph (6)	THF		15	30	45	0
5a (Br)	K-naph (6)	DME		24	38	16	0
5a (Br)	Na-naph (4)	THF		*e*	0	44	0
5a (Br)	Na-naph (4)	DME		*e*	5	40	0
5b (Cl)	K-naph (6)	THF		0	0	89	0

[a] Temperature −70 to −78 °C. [b] Reductant was added to the solution of 5 at such a rate that the blue color of the reductant was maintained. [c] Determined by NMR and VPC. [d] Solvent ratio: NH_3/THF = 60/40. [e] Not determined.

by alkali metal in liquid ammonia in the presence of alcohol gives the parent hydrocarbon **6** together with unreacted **5** but none of the expected intermediates such as **8**. This result deserves attention because it affords evidence that the protonation of the intervening α-halocarbanion does not constitute the reaction process. In this regard we would like to present the first evidence of the intermediacy of a cyclopropylidene radical anion as the rational species that can account for the formation of **6** directly from **5**.

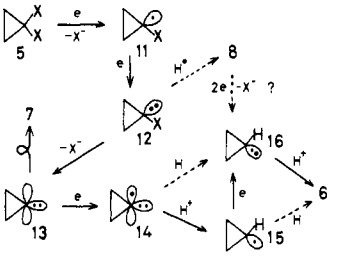
The reduction of 1,2;3,4-bis(dibromomethano)-1,2,3,4-tetrahydrooctamethylnaphthalene (**5a**)[3] in liquid ammonia at −70 °C



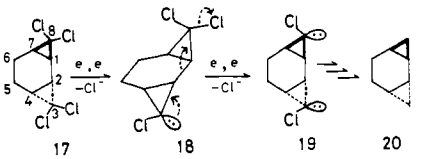
(THF was used as cosolvent) with 6 equiv of alkali metal (K or Na) and 20 equiv of ethanol gave a very simple product mixture which solely consisted of **6** (68%) and unreacted **5a** (32%). The same results were obtained from dichloromethano derivatives **5b**, **5c**, and **5d** (see Table I). Careful analyses (NMR and VPC) of these Birch-type products denied the formation of such half-reduction products as **8**, **9**, or rearranged products **7** and **10**.[4] In ammonia the methylene hydrogens of **6** are donated as proton from not only alcohol but also ammonia, because the same results were obtained even in the absence of alcohol.

Analogous reduction of **5a** with 6 equiv of potassium naphthalenide in THF at −78 °C, in which the reductant was added to the solution of **5a**,[5] yielded only two products **6** (30%) and **7** (45%) besides unreacted **5a** (15%).[6] Thus, a certain carbanionic species should be formed which is entirely different from α-halocyclopropyl anion but has a basicity strong enough to accept proton from such a weak acid as THF or ammonia in the absence of hydroxylic compounds. The results in Table I seem to imply

Scheme I



Scheme II



that, in naphthalenide reduction, the generation of this species depends upon the reducing power of the reductant: the yield of **6** increased more in DME than in THF,[7] more with K than with Na, and more from **5a** (X = Br) than from **5b** (X = Cl).[8]

First of all, what chemical species or reaction mechanism can simultaneously explain the exclusive formation of **6** and the absence of **8** in protic ammonia? Although the predominant involvement of α-halocyclopropyl anion in the reduction channel is indisputable, a repeating stepwise mechanism shown in eq 1 is ruled out on the basis of the electrochemical data.[2] However, there are two possible routes for the fate of the halocarbanion: the rearrangement to give **7**[4] and the generation of cyclopropylidene radical anion, a novel species in this category.[9,10] Scheme I illustrates the reaction channel which involves cyclopropylidene radical anion **14** as the indispensable intermediate to produce **6** not accompanied by the formation of **8**. The generation of **14** from carbanion **12** via carbene **13** will require the following conditions: (1) a strong reducing power of the reductant, (2) the use of a solvent which strongly solvates cations and reinforces the departure of halide anion from **12**, (3) as nonnegative a reduction potential as possible of the C–X bond, and (4) as noncovalent a nature as possible of the C–metal bond. These requirements seem to be consistent with our observations. Thus, when the halide elimination from **12** giving **13** is fast in a polar medium, the protonation producing **8** cannot take place. In ammonia the solvated electron transfers to the intervening **13** so much faster than naphthalenide,[11] giving rise to the generation of **14**, that the skeletal rearrangement from **13** to **7** cannot compete with it. With naphthalenide, however, the electron transfer slows down relative to the rate of rearrangement. Thus formed, **14** must have enough basicity to be protonated by such a weak carbon acid as THF followed by further reduction leading to **6** through the sequence in Scheme I.

The mechanism rationalized above seems satisfactory so far as one-half of the molecule **5** divided along its C_2 axis of symmetry is concerned; it does not explain the absence of inevitably expected unsymmetrical products **9** and **10** as well. A priori, there should exist a specific effect of the initially reduced cyclopropane ring which somehow enhances the reactivity of the other intact ring

(3) For preparation, see A. Oku, T. Hino, and K. Matsumoto, *J. Org. Chem.*, **40**, 695 (1975).

(4) For the mechanism of producing **7**, see A. Oku and K. Yagi, *J. Am. Chem. Soc.*, **96**, 1966 (1974).

(5) See footnote *b* of Table I.

(6) In this reaction, 0.6 *d* was incorporated on the methylene of **6** by immediate quenching with D_2O, none was incorporated after 30 min, but 2.75 *d* was incorporated by quenching in situ with 2-propanol-*O*-*d*. This also indicates that the methylene hydrogens are donated as proton.

(7) M. Szwarc, *Acc. Chem. Res.*, **5**, 167 (1972).

(8) The difference in half-wave potentials between alkyl chlorides and bromides usually ranges between 0.5 and 0.9 V; C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, 1970, pp 226–241.

(9) (a) G. D. Sargent, C. M. Tatum, Jr., and S. M. Kastner, *J. Am. Chem. Soc.*, **94**, 7174 (1972); (b) G. D. Sargent, C. M. Tatum, Jr., and R. P. Scott, *ibid.*, **96**, 1602 (1974).

(10) (a) R. N. McDonald, J. R. January, K. J. Borhani, and M. Dale Hawley, *J. Am. Chem. Soc.*, **99**, 1268 (1977); (b) R. N. McDonald, K. J. Borhani, and M. Dale Hawley, *ibid.*, **100**, 995 (1978); (c) R. N. McDonald and K.-W. Lin, *ibid.*, **100**, 8028 (1978).

(11) F. J. You and L. M. Dorfman, *J. Chem. Phys.*, **58**, 4715 (1973); see also ref 2.

more than that of the starting **5**. First, for an examination of the role of a π bond existing between the two cyclopropane rings of **5**, the reduction of 3,3,8,8-tetrachlorotricyclo[5.1.0.0^{2,4}]octane (**17**) with sodium was carried out in a mixed solvent of ammonia and THF at -95 °C (**17**/Na/EtOH = 1/8/8) or in HMPA at -35 °C. Only the parent hydrocarbon **20** was obtained besides unreacted **17** (in ammonia, 92% and 8%, respectively). Thus, the π bond is not a requisite, and the effect should be exerted only in the bicyclopropane system.

In addition, a framework examination on **17**[12] reveals that the cyclopropane ring orbitals at positions C-1 and C-2 meet at approximately right angles, and therefore the conjugative effect through p orbitals, which might have explained the difference in reactivity between **5** and **9**, could not have been exerted. Consequently, it seems most rational that the initially formed α-halocyclopropyl anion **18** (or radical) weakens the C-X bond of the other ring by orbital interaction through bonds of this rigid tricyclic system in a fashion similar to an 1,4-elimination mechanism (Scheme II).[13] Depiction of **18** illustrates this idea in which the elimination of halide and the electron transfer at C-8 of **18** are occurring almost simultaneously.

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Supplementary Material Available: Additional data on the reduction of **5** and **17** (7 pages). Ordering information is given on any current masthead page.

(12) The stereochemistry of the two cyclopropane rings of **5** is determined as anti by X-ray crystallography.

(13) The partial cleavage of the C_1-C_2 bond of **18** may be involved in the transition state in which the dicyclopropenyl structure emerges to some extent. However, all processes including electron transfer will take place almost simultaneously.

Photoinduced Electron-Transfer Reactions. Radical Cations of Norbornadiene and Quadricyclene

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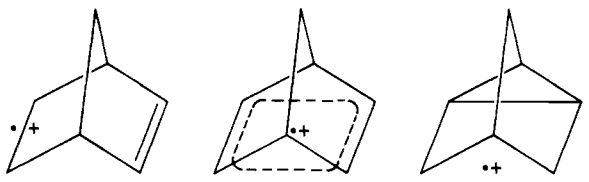
We have observed different nuclear spin polarization patterns during the photoreaction of electron acceptors with norbornadiene (**1**) and with quadricyclane (**2**). These results are incompatible with the concept of a single intermediate, **4**, for both reactions. Instead, they indicate that two discrete radical cations, **3** and **5**, respectively, with lifetimes greater than several nanoseconds are derived from the two hydrocarbons.[1]



3 4 5

(1) The structures **3** and **5** are meant to conveniently designate the valence isomeric radical cations of **1** and **2**, respectively. They are not meant to represent the actual geometry of these intermediates.

Although the interconversion of norbornadiene and quadricyclane is well characterized in the excited singlet and triplet states,[2] the energy surface of the radical cations derived from the pair of valence isomers is not fully understood. The photoelectron specta of **1** and **2** reveal the existence of two discrete radical cation states,[3] an assignment which is supported by MINDO/3 calculations.[3c] On the other hand, γ irradiation of frozen solutions containing either **1** or **2** gives rise to the same species to which the structure of a norbornadiene radical cation has been assigned.[3c] Similarly, the observation that the mass spectra of **1** and **2** have nearly identical fragmentation patterns led to the conclusion that their molecular ions are identical with regard to energy and structure.[4] We have applied the CIDNP technique in an attempt to elucidate this energy surface.

Chemically induced nuclear spin polarization (CIDNP) effects are exceedingly useful for studying reactions proceeding via radical ion pairs and, particularly, involving the recombination of these pairs in the triplet state.[5] Successful applications of the CIDNP technique include the identification of aminium radical ions and aminoalkyl radicals in the photoreduction of keto compounds by tertiary amines,[6] the elucidation of several mechanisms underlying the electron-transfer induced isomerization of several classes of the electron-transfer induced isomerization of several classes of olefins,[7] and the elucidation of the structure of the diphenylcyclopropane radical cation.[8]

The study reported here was undertaken to elucidate the structure(s) of the radical cation(s) of **1** and **2** and, particularly, to ascertain whether they are two discrete species or whether they are best represented by a single, homoallylic structure (**4**). Ultraviolet irradiation of electron acceptors, such as chloranil (**6**) or cyanonaphthalene (**7**), in the presence of **1** or **2** gives rise to characteristic CIDNP effects which allow an insight into the structure of the intermediates and into the energy surface connecting them.

The irradiation of **6** in acetonitrile-d_3 solutions containing **1** (1 kW high-pressure Hg lamp) gives rise to strongly enhanced absorption (A) for the olefinic protons (6.6 ppm) of the reactant and weak emission (E) for its bridge protons (2.0 ppm) but does not produce any polarization for the rearranged hydrocarbon (Figure 1, top). The observed signal direction is compatible with a mechanism involving electron-transfer quenching of triplet **6** by **1** and regeneration of the reactants by reverse electron transfer after intersystem crossing. In analogy to other olefin radical cations[5,7] the "olefinic" protons of the norbornadiene radical cation (**3**) are assumed to have a negative hyperfine coupling constant (hfc) and the g factor of **3**, like that of other hydrocarbon radical ions very likely close to the free electron value,[9] should be much smaller than that of the chloranil radical anion (**8**, g = 2.0057).[9] Radical ion pairs not reacting by reverse electron transfer diffuse apart, allowing their polarization to decay by spin-lattice relaxation.

In contrast to the reaction of **6** the irradiation of **7** in solutions containing **1** gives rise to polarization for the rearranged product, **2** (cyclobutane protons, A; bridge protons, E) as well as for the reactant (olefinic protons, E; bridge protons, A; Figure 1, center). This polarization pattern is once again indicative of the radical cation **3**, this time paired with the cyanonaphthalene radical anion (**9**) generated by electron transfer from **1** to the excited singlet

(2) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7399 and references cited therein.

(3) (a) Taylor, G. N. *Chem. Phys. Lett.* **1971**, *10*, 355. (b) Heilbronner, E.; Martin, H. D. *Helv. Chim. Acta* **1972**, *55*, 1490. (c) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Ibid.* **1979**, *62*, 583.

(4) Dolejsek, Z.; Hanus, V.; Prinzbach, H. *Angew. Chem.* **1962**, *74*, 902.

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(6) (a) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270. (b) Roth, H. D.; Manion, M. L. *Ibid.* **1975**, *97*, 6886.

(7) (a) Roth, H. D.; Schilling, M. L. M. *Proc. IUPAC Symp. Photochem., 7th* **1978**, 281. (b) *J. Am. Chem. Soc.* **1979**, *101*, 1898. (c) *Ibid.* **1980**, *102*, 4303.

(8) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956.

(9) Blois, M. S., Jr.; Brown, H. W.; Maling, J. E. *Proc. Colloq. AMPERE* **1960**, 243.

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