Reversibility of Bromonium Ion Formation and Its Effect on Olefin Reactivity in Electrophilic Bromination. New Evidence from the 5*H*-Dibenz[*b*,*f*]azepine System

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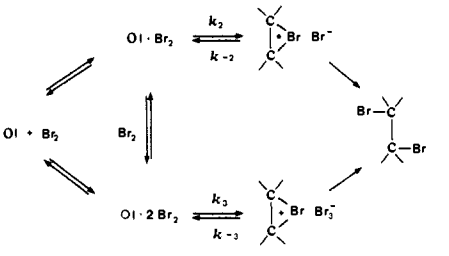
Abstract: It has been shown that the bromonium–bromide ion-pair intermediate generated from the reaction of *trans*-10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride (**3**) with HBr in 1,2-dichloroethane, chloroform, or carbon tetrachloride can either collapse to *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride (**4**) or release molecular Br_2 to give 5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride (**1**). The ratio of these two products changes from ca. 7:3 in 1,2-dichloroethane to ca. 3:7 in carbon tetrachloride. Olefin **1** is similarly obtained in 50% yield when bromohydrin **3** is reacted with BF_3·Et_2O in chloroform in the presence of resorcinol, which acts as a Br^+ scavenger and is transformed into its 4-bromo derivative. 5*H*-Dibenz[*b*,*f*]azepine-5-carbonyl chloride adds Br_2 in 1,2-dichloroethane at 50 °C according to a third-order rate law with a rate constant (k_3 = 1.9 (0.1) × 10^{-2} M^{-2} s^{-1}) that is 4 orders of magnitude lower with respect to that of the acyclic analogue *cis*-stilbene and gives only the *trans*-dibromide **4**. The latter is debrominated easily to olefin **1** at 25 °C in dimethylformamide without the addition of any specific reagent or slowly in acetonitrile in the presence of *cis*-stilbene as a Br_2 scavenger, through the same bromonium–bromide ion-couple intermediate involved in the reaction of bromohydrin **3** with HBr. The easy reversion of this intermediate back to olefin and Br_2 has been rationalized on the basis of the structural parameters obtained by X-ray diffraction of dibromide **4**, showing a highly strained C(10)–C(11)–C(11a) internal angle of 121° and strongly unequivalent bromine atoms, with a rather longer Br–C(11) bond.

Fifty years after the postulation of bromonium ions as the intermediates of the electrophilic bromination of olefins by Roberts and Kimball,[1] important features concerning the formation of these transient species are still under discussion. It is now generally accepted that more or less symmetrically bridged bromonium ions or open bromocarbenium ions, depending on the substrate structure, paired to bromide or tribromide counterions, according to the protic or aprotic nature of the solvent, are involved in olefin bromination under ionic conditions.[2-5] These ion pairs have been shown to arise by slow ionization of weak charge-transfer complexes formed in a preequilibrium step[3] and are assumed to collapse rapidly to dibromo adducts (Scheme I). Kinetics, product stereochemistry, and substituent effects have been rationalized on the basis of these mechanisms.[2-5]

Conclusive evidence for the bromonium ion pathway has been provided by the isolation of an unusually unreactive bromonium–tribromide salt from the reaction of Br_2 with adamantylideneadamantane and its recent structure determination by X-ray diffraction.[6] The capability of this particular salt of regenerating Br_2 and the starting olefin has also been established.[6,7] In general, however, the question of the occurrence and kinetic importance of the k_{-3}, as well as of the corresponding k_{-2} process of Scheme I, i.e., the question of the reversibility of bromonium ion formation and of its connection with the reactivity of olefins toward bromination, does not seem to have been sufficiently addressed. The reversibility of the electrophilic step has been assumed for brominations with complexes of Br_2,[4,5,8] where olefin–bromine charge-transfer complexes but not ionic intermediates appear to be involved, but was invoked only occasionally for addition of molecular Br_2.[9] The latter reactions have instead been almost generally considered to proceed by irreversible formation of ionic intermediates.[10]

Recent, independent work by Brown's and our groups has, however, shown that Br_2 can be scavenged both from bromonium ions produced by solvolysis of trans bromohydrin brosylates in the presence of Br^-[11] and from bromonium–bromide ion pairs generated by reacting bromohydrins with HBr gas.[12] This, as well as the *cis*- to *trans*-stilbene isomerization observed during the bromination of the former olefin,[12] indicated that the reverse

Scheme I



k_{-2} and k_{-3} reactions of Scheme I cannot be neglected. In this paper we are reporting on unusually easy elimination reactions of *trans*-10-bromo-11-hydroxy- (**3**) and *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride (**4**),

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(10) See, for instance: Bartlett, P. D.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466–474. Dubois, J.-E.; Garnier, F. *Bull. Soc. Chim. Fr.* **1967**, 4512–4514. Ruasse, M.-F.; Dubois, J.-E. *J. Org. Chem.* **1972**, *37*, 1770–1778.
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Table I. Product Yields from the Reactions of *trans*-10-Bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b,f*]azepine-5-carbonyl Chloride (**3**) with Hydrogen Bromide and Boron Trifluoride Etherate

run	reagent	solvent	time, h	yields,[a] %		
				3	**4**	**1**
1a	HBr	$(CH_2Cl)_2$	1.5	25	36 (69)	16 (31)
1b	HBr	$(CH_2Cl)_2$	1.5	36	38 (73)	14 (27)
2a	HBr	$CHCl_3$	1.5	<1	38 (52)	35 (48)
2b	HBr	$CHCl_3$	1.5	40	21 (47)	24 (53)
3a	HBr	CCl_4	1.5	16	17 (29)	42 (71)
3b	HBr	CCl_4	1.5	44	15 (28)	39 (72)
4a–e[b]	$BF_3{\cdot}Et_2O$ + resorcinol	$CHCl_3$	1.5–7	<1		50 ± 5

[a] Figures in parentheses are the relative percentages of **4** and **1**. [b] Results of five runs carried out using 1:1–1:4 ratios of **3** to $BF_3{\cdot}Et_2O$ and 1:2 ratios of **3** to resorcinol. 4-Bromoresorcinol was also detected in molar amounts comparable with those of **1**.

which reveal an unexpectedly high propensity of the bromonium ion related to these compounds to undergo reversion to the corresponding olefin. The crystal and molecular structure of the *trans*-10,11-dibromide, pointing to a considerable angle strain as the driving force for this reaction, is also reported.[13]

Results

Elimination of HOBr from Bromohydrin 3. *trans*-10-Bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**3**) was obtained, as reported,[14] by opening of 1a,10b-dihydro-6*H*-dibenz[*b,f*]oxireno[*d*]azepine-6-carbonyl chloride (**2**), prepared by epoxidation of 5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**1**),[15] with aqueous HBr in tetrahydrofuran. Bromohydrin **3** was also obtained as the sole product of the reaction of **2** with gaseous HBr in $CHCl_3$ when the hydrogen halide was bubbled into a solution of **2** for a short time. The trans relationship of the 10,11-substituents had been established by the facile ring closure to 1a,10b-dihydro-6*H*-dibenz[*b,f*]oxireno[*d*]azepine-6-carboxamide (**2**, X = $CONH_2$) upon treatment with ammonia.[14] Their gauche orientation was shown by the NMR spectrum in $CDCl_3$, which exhibited an AB-type pattern, with some broadening of the two lower field lines and a coupling constant $J_{10,11}$ of 9.4 Hz, indicating anticoplanar α-protons.

When a vigorous stream of HBr was bubbled through a chloroform solution of epoxide **2** for a sufficiently long time, no bromohydrin **3** but only olefin **1** and a dibromide identified as **4** (see text below) were detected by HPLC. Similar product mixtures were obtained when the primary product of ring opening of **2**, bromohydrin **3**, was reacted with gaseous HBr. These reactions were carried out in three nonprotic solvents of different polarity, 1,2-dichloroethane (ϵ 10.7), chloroform (ϵ 4.6), and carbon tetrachloride (ϵ 2.2), and the products were separated by preparative TLC and identified by comparison with authentical samples of **1** and **4**. All crude reaction mixtures were also subjected to HPLC after addition of an appropriate standard in order to determine the product yields. The results obtained in pairs of typical runs are reported in Table I.

Only **1** and **4** were always found in the HBr reactions, besides the unreacted bromohydrin **3**, in amounts that changed from run to run depending on the gas flow rate through the reaction mixtures. The overall yields of detected products and starting material ranged between 73 and 98%, the lowest value being found at complete conversion and the highest one at the lowest conversion. The ratios between **4** and **1** obtained in duplicate runs were, however, well reproducible independent of the amount of unreacted **3**. These facts indicated that both **1** and **4** were stable under the reaction conditions and suggested that some bromohydrin **3** was consumed in unidentified side reactions, giving at most about 25% of products that escaped detection. This conclusion was checked by exposing both olefin **1** and dibromide **4** to HBr under the conditions of runs 1–3 of Table I. Both products were quantitatively recovered. A substantial increase in the **1** to **4** ratio was observed when the reaction of **3** with HBr was carried out in solvents of decreasing polarity. The use of carbon tetrachloride led to the unprecedented result of an elimination of the elements of HOBr largely prevailing over the substitution of the hydroxyl.

Table II. NMR Parameters of Dibromide **4**

solvent	protons α to Br		
	δ	δ	J, Hz
chloroform-*d*	5.6	6.1	4.5
acetone-d_6	6.0	6.5	4.5
acetonitrile-d_3	5.8	6.3	4.4
methanol-d_4	5.9	6.35	4.4
dimethylformamide-d_7	5.85	6.3	4.4

Furthermore, olefin **1** was found in about 50% yield in the reaction of **3** with an excess of $BF_3{\cdot}Et_2O$ in chloroform in the presence of resorcinol (runs 4a–e of Table I). 4-Bromoresorcinol, the product of bromination of resorcinol in $CHCl_3$, was also detected by HPLC in an amount roughly equivalent to that of **1**. The yield of this reaction remained practically unchanged on increasing the reaction time from 1.5 to 7 h, thus showing that **1** was not further transformed under the reaction conditions and again suggesting that a part of the starting bromohydrin was undergoing some unidentified side reaction.

Bromination of Olefin 1 and Debromination of Dibromide 4. 5*H*-Dibenz[*b,f*]azepine-5-carbonyl chloride (**1**) added Br_2 in 1,2-dichloroethane at a surprisingly slow rate. At 50 °C the reaction was found to follow cleanly the third-order rate law (second order in Br_2) usually observed for olefin bromination in this solvent,[3-5] with a k_3 = 1.9 (0.1) × 10^{-2} M^{-2} s^{-1}. Under the same conditions a third-order rate constant k_3 = 2.31 (0.05) × 10^2 M^{-2} s^{-1} was measured for the acyclic analogue *cis*-stilbene.[16] In contrast to other olefins scarcely reactive toward molecular Br_2,[5] **1** did not react with tetrabutylammonium tribromide in 1,2-dichloroethane. [A large excess of Br_2 was needed in preparative brominations in order to obtain a product completely free from olefin.] HPLC analysis of the bromination product revealed the formation of a single dibromo derivative.[17] An approximately antiperiplanar orientation of the bromine atoms was determined in this product by the X-ray diffractometric study reported below. The same conformation was deduced in solution by the NMR spectra in several solvents, where the C(10) and C(11) protons appeared as an AB system with a coupling constant typical for gauche protons (Table II). The preference for this conformation with anti-oriented bromine atoms can be attributed to the repulsive C–Br dipole–dipole interaction, which is also responsible for the

(13) Preliminary communications on this subject were presented at: Giornate di Chimica Organica Fisica e Meccanicistica, Catania, Oct 22–25, 1986, abstracts p 59; 5th Italian–Yuogoslav Crystallographic Congress, Padova, June 3–6, 1986, abstracts C 26.

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(15) Bellucci, G.; Berti, G.; Chiappe, C.; Lippi, A.; Marioni, F. *J. Med. Chem.* **1987**, *30*, 768–773.

(16) A similar k_3 value of 2.7 (0.1) × 10^2 M^{-2} s^{-1} had been obtained for the bromination of *cis*-stilbene in 1,2-dichloroethane at 25 °C.[12] The rates of olefin bromination in low-polarity solvents are known to exhibit often very low or negative temperature coefficients (see ref 3 and references cited therein).

(17) A 10,11-dibromide obtained by free-radical bromination of 10,11-dihydro-5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride has been reported, without further delucidation, in patents: Findeisen, C.; Doff-Sotta, M.; Conrad, W.; Graul, K. H.; Koehler, I. Ger. (East) Patent 108 535, 1974; *Chem. Abstr.* **1975**, *83*, 97062w. Jpn. Kokai 74 56 990, 1974; *Chem. Abstr.* **1976**, *85*, 21151v.

Table III. Time Course of the Debromination of *trans*-10,11-Dibromo-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carbonyl Chloride (**4**) at 25 °C

[4], M	solvent	added *cis*-stilbene, M	time, h	1, %
9×10^{-2}	DMF-d_7[a]		4	3
			8	8.5
			24	37
			32	60
2×10^{-1}	DMF-d_7[a]		16	29
			20	50
			24	65
6×10^{-2}	$(CH_2Cl)_2$	1.8	225	<0.5
6×10^{-2}	CH_3CN[b,c]	0.3	75	4
			150	9.5
			200	11
			270	14
6×10^{-2}	CH_3CN[b,c]	0.6	75	3.5
			150	8.5
			200	12.5
			270	16
			310	18
6×10^{-2}	CH_3CN[b,c]	1.8	75	4.5
			150	9.5
			200	11
			270	15
			310	20

[a] Reaction followed by NMR. The reported percentages of **1** were accurate to ±2%. [b] Reaction followed by HPLC. The reported percentages of **1** are averages of three experiments, which were reproducible within ±10% of the quoted figures. [c] Total amounts of *meso*- and *d*,*l*-1,2-dibromo-1,2-diphenylethane equivalent to those of the formed **1** were also detected in these reactions. The ratios between these *d*,*l*- and *meso*-dibromides were around 9:1.

diaxial conformation preferentially adopted by cyclohexane vicinal *trans*-dibromides in nonpolar solvents.[18] This repulsion is, however, considerably relieved in the six-membered system on passing to more polar solvents. This change appears, instead, to have no effect on the relative orientation of the two halogen atoms in dibromide **4**. The same approximately anti relationship of the bromine atoms has also been found by X-ray diffraction of *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carboxamide (**4**, X = $CONH_2$)[19] and seems to be a typical feature of these systems.

When stored in the open air at room temperature, the crystalline dibromide **4** tended to slowly lose Br_2, giving olefin **1**. Typically, a pure sample of **4** contained about 5% of **1** after 3 weeks.

In dimethylformamide solution **4** was debrominated fairly quickly even at 25 °C (Table III). The debromination did not follow a simple kinetic law, the rate being apparently accelerated during the course of the reaction. At 30 °C practically complete debromination was achieved within 24 h. Although examples of debromination of vicinal dibromides in this solvent without the addition of any specific reagent have been reported,[20] they required heating and were limited only to vicinal dibromides having at least one bromine bonded to a tertiary carbon. In particular, *meso*- and *d*,*l*-1,2-dibromo-1,2-diphenylethane, the acyclic analogues of **4**, were debrominated to a negligible extent at 60 °C, and only in refluxing dimethylformamide was 80% debromination of the meso dibromide reported after 10 h.[21]

Dibromide **4** was stable for days in 1,2-dichloroethane or acetonitrile solution at 25 °C. In the former solvent the addition of a large excess of *cis*-stilbene as a Br_2 scavenger failed to promote debromination. In contrast, **4** underwent slow debromination to **1** in acetonitrile solution at 25 °C in the presence of *cis*-stilbene. The amounts of **1** detected by HPLC at different times in the presence of increasing amounts of the scavenger olefin are shown in Table III. An increase in the concentration of *cis*-stilbene did not produce a proportional enhancement in the debromination rate. Total amounts of *meso*- and *d*,*l*-1,2-dibromo-1,2-diphenylethane equivalent to those of olefin **1** were also detected in all these reactions. Furthermore, the ratios of the *d*,*l* to the meso diastereomer were very similar to the 9:1 obtained by independent experiments for the addition of molecular Br_2 to *cis*-stilbene in acetonitrile.[22]

All these results showed that *cis*-stilbene was able to scavenge Br_2 from dibromide **4** at room temperature in a polar solvent like acetonitrile, but not in the less polar 1,2-dichloroethane. To the best of our knowledge, this is the first reported example of a transfer of Br_2 from a dibromide to a more reactive olefin. It is also noteworthy that this transfer occurs under the mild conditions usually employed for olefin bromination.

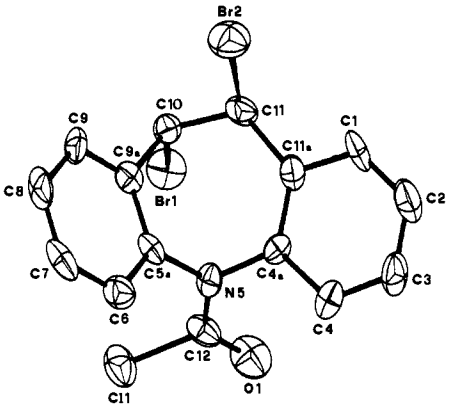

Figure 1.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters (Esd's in Parentheses)[a]

	x	*y*	*z*	B_{eq}
Br(1)	0.4259 (1)	0.0535 (1)	0.0000	3.84 (3)
Br(2)	0.7607 (2)	−0.373 (2)	−0.1744 (3)	4.82 (5)
Cl(1)	0.4541 (3)	0.3437 (3)	0.1296 (5)	4.1 (1)
O(1)	0.5166 (9)	0.207 (1)	0.313 (1)	4.5 (3)
C(1)	0.769 (1)	−0.055 (1)	0.161 (2)	3.3 (3)
C(2)	0.827 (1)	−0.033 (1)	0.276 (2)	4.1 (4)
C(3)	0.816 (1)	0.062 (1)	0.340 (2)	3.8 (3)
C(4)	0.746 (1)	0.140 (1)	0.287 (1)	3.3 (3)
C(4a)	0.6878 (8)	0.1194 (9)	0.168 (1)	2.1 (2)
N(5)	0.6156 (8)	0.2050 (8)	0.118 (1)	2.3 (2)
C(5a)	0.6300 (8)	0.2418 (8)	−0.019 (1)	2.1 (2)
C(6)	0.673 (1)	0.346 (1)	−0.042 (2)	3.2 (3)
C(7)	0.684 (1)	0.379 (1)	−0.178 (2)	3.5 (3)
C(8)	0.658 (1)	0.311 (1)	−0.283 (1)	3.6 (3)
C(9)	0.618 (1)	0.206 (1)	−0.255 (1)	3.4 (3)
C(9a)	0.6002 (8)	0.1740 (9)	−0.124 (1)	2.3 (2)
C(10)	0.561 (1)	0.0585 (9)	−0.098 (1)	2.6 (3)
C(11)	0.646 (1)	−0.0150 (9)	−0.028 (1)	3.1 (3)
C(11a)	0.700 (1)	0.0186 (9)	0.103 (1)	2.7 (3)
C(12)	0.536 (1)	0.238 (1)	0.198 (1)	2.9 (3)
H(1)	0.778 (1)	−0.128 (1)	0.117 (2)	3.3
H(2)	0.877 (1)	−0.090 (1)	0.314 (2)	4.1
H(3)	0.859 (1)	0.077 (1)	0.424 (2)	3.8
H(4)	0.738 (1)	0.212 (1)	0.334 (1)	3.3
H(6)	0.695 (1)	0.394 (1)	0.034 (2)	3.2
H(7)	0.712 (1)	0.454 (1)	−0.198 (2)	3.5
H(8)	0.667 (1)	0.336 (1)	−0.378 (1)	3.6
H(9)	0.603 (1)	0.154 (1)	−0.330 (1)	3.4
H(10)	0.548 (1)	0.0282 (9)	−0.190 (1)	2.6
H(11)	0.605 (1)	−0.0800 (9)	0.006 (1)	3.1

[a] $B_{eq} = {}^4/_3\sum_j\sum_i\beta_{ji}a_ja_i$

X-ray Structure of Dibromide 4. A perspective drawing with atom labeling of compound **4** is shown in Figure 1. Final atomic coordinates and isotropic thermal parameters with standard deviations are listed in Table IV. Interatomic bond lengths and angles are reported in Tables V and VI. The torsion angle

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(22) Unpublished results from this laboratory.

Table V. Bond Lengths (Å) (Esd's in Parentheses)

Br(1)–C(10)	1.92 (1)	N(5)–C(5a)	1.45 (2)
Br(2)–C(11)	2.04 (1)	N(5)–C(12)	1.32 (2)
Cl(1)–C(12)	1.77 (1)	C(5a)–C(6)	1.40 (2)
O(1)–C(12)	1.23 (2)	C(5a)–C(9a)	1.38 (2)
C(1)–C(2)	1.37 (2)	C(6)–C(7)	1.41 (2)
C(1)–C(11a)	1.36 (2)	C(7)–C(8)	1.37 (2)
C(2)–C(3)	1.33 (2)	C(8)C(9)	1.41 (2)
C(3)–C(4)	1.39 (2)	C(9)–C(9a)	1.38 (2)
C(4)–C(4a)	1.40 (2)	C(9a)–C(10)	1.52 (2)
C(4a)–N(5)	1.46 (1)	C(10)–C(11)	1.54 (2)
C(4a)–C(11a)	1.40 (2)	C(11)–C(11a)	1.52 (2)

Table VI. Bond Angles (deg) (Esd's in Parentheses)

C(2)–C(1)–C(11a)	122 (1)	C(8)–C(9)–C(9a)	120 (1)
C(1)–C(2)–C(3)	120 (1)	C(5a)–C(9a)–C(9)	119 (1)
C(2)–C(3)–C(4)	119 (1)	C(5a)–C(9a)–C(10)	121 (1)
C(3)–C(4)–C(4a)	120 (1)	C(9)–C(9a)–C(10)	118 (1)
C(4)–C(4a)–N(5)	117 (1)	Br(1)–C(10)–C(9a)	112.9 (8)
C(4)–C(4a)–C(11a)	119 (1)	Br(1)–C(10)–C(11)	109.8 (9)
N(5)–C(4a)–C(11a)	123 (1)	C(9a)–C(10)–C(11)	113 (1)
C(4a)–N(5)–C(5a)	117.9 (9)	Br(2)–C(11)–C(10)	103.2 (9)
C(4a)–N(5)–C(12)	118 (1)	Br(2)–C(11)–C(11a)	110.1 (8)
C(5a)–N(5)–C(12)	123 (1)	C(10)–C(11)–C(11a)	121 (1)
N(5)–C(5a)–C(6)	118 (1)	C(1)–C(11a)–C(4a)	117 (1)
N(5)–C(5a)–C(9a)	119.2 (9)	C(1)–C(11a)–C(11)	116 (1)
C(6)–C(5a)–C(9a)	121 (1)	C(4a)–C(11a)–C(11)	125 (1)
C(5a)–C(6)–C(7)	117 (1)	Cl(1)–C(12)–O(1)	118 (1)
C(6)–C(7)–C(8)	121 (1)	Cl(1)–C(12)–N(5)	114 (1)
C(7)–C(8)–C(9)	119 (1)	O(1)–C(12)–N(5)	126 (1)

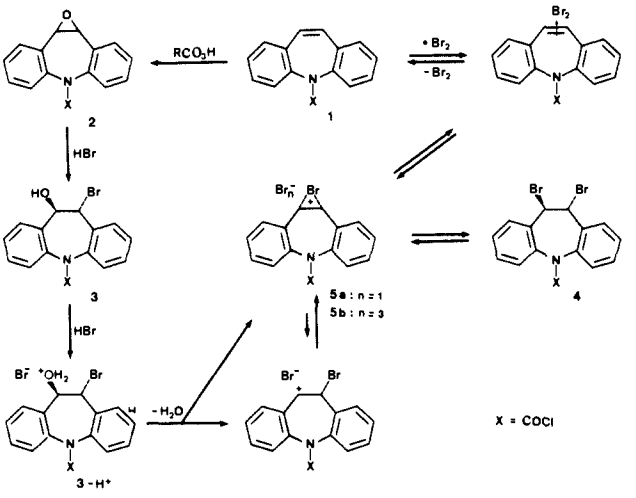
Br(1)–C(10)–C(11)–Br(2) is 162.4 (5)°. The C–C, C–N, C–O, and C–Cl bond lengths are in agreement with the accepted values. The two Br–C bonds are significantly different, 1.91 (1) and 2.04 (1) Å for Br(1)–C(10) and Br(2)–C(11), respectively. The normal sp^3 C–Br single bonds fall in the range 1.93–2.03 Å,[6] mean values being around 1.97.[23,24] The Br(2)–C(11) bond is at the high end of the range and is a little shorter than both values, 2.116 (6) and 2.194 (6) Å, reported for Br–C in a structure where a bromine ion forms a three-membered ring with two carbon atoms.[6] The internal angles at the bromine-substituted carbon atoms are 113 (1) and 121 (1)° for C(9a)–C(10)–C(11) and C(10)–C(11)–C(11a), respectively. The last value, together with the high value of the Br(2)–C(11) bond length, suggests considerable sp^2 character at C(11).

The two benzene rings and the chlorocarbonyl group are at dihedral angles of 38.2, 18.1, and 59.8°, respectively, with the central seven-membered ring. The four planes are defined as the best squares planes: (1) through the atoms C(5a), C(6), C(7), C(8), C(9), C(9a); (2) through the atoms C(1), C(2), C(3), C(4), C(4a), C(11a); (3) through the atoms N(5), C(12), Cl(1), O(1); (4) through the atoms C(4a), N(5), C(5a), C(9a), C(10), C(11), C(11a). The N(5), C(10), and C(11) atoms are apart from the best plane through the atoms C(5a), C(9a), C(11a), C(4a) by 0.58, 0.82, and 0.21 Å, respectively, showing that the maximum puckering occurs at C(10).

Discussion

The *trans*-10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b*,*f*]azepine system was chosen for the present investigation of the occurrence of the reverse k_{-2} process of Scheme I in bromonium–bromide ion pairs produced by reaction of bromohydrins with HBr in view of the structural relation of compounds of this type and of their 5*H*-dibenz[*b*,*f*]azepine precursors to the *threo*-2-bromo-1,2-diphenylethanol–*cis*-stilbene system, for which the process under discussion had already been examined.[12] The closure of a seven-membered ring through a nitrogen bridge between the ortho positions of the two phenyl rings was expected to remove the complications arising, in the acyclic system, from

Scheme II



the rearrangement of the cis to the more stable trans bromonium ion by rotation around the C–C bond of an open benzylic bromocarbenium ion. This cis to trans rearrangement, followed by loss of molecular Br_2 from the *trans*-bromonium–bromide ion pair, had allowed us to establish the reversibility of bromonium ion formation during the bromine addition to *cis*-stilbene.[12] It prevented, on the other hand, a direct evaluation of the intrinsic propensity of the *cis*-bromonium–bromide ion pair to revert to the *cis*-olefin, information that could instead be expected from the investigation of a tricyclic system like the 5*H*-dibenz[*b*,*f*]-azepine one.

The electron-withdrawing carbonyl chloride group was introduced on nitrogen in order to prevent the stabilization of a carbocation center at a benzylic carbon on loss of water from the protonated bromohydrin **3**. Carbocationic intermediates of this type are known to be involved, for instance, in reactions of acids with 5*H*-dibenz[*b*,*f*]azepine 10,11-oxides bearing hydrogen or alkyl or even a carbamoyl group on N(5) and are responsible for ring restriction to acridane derivatives.[14,25,26] In contrast, the corresponding reactions of the 5-carbonyl chloride derivative **2** occur by an exclusive anti opening of the oxirane ring,[14,15] pointing to the involvement of the protonated epoxide and not of a β-hydroxycarbenium ion. This suggested, by analogy, that a bridged bromonium ion, and not a β-bromocarbenium ion, should be involved as the cationic intermediate in the transformation of bromohydrin **3** into the corresponding dibromide **4** by HBr, as well as in the addition of Br_2 to olefin **1**. The formation of the anti adduct **4** as the sole dibromide product and the lack of products of ring restriction in both these reactions are in agreement with this anticipation.

The competition of elimination versus substitution in the reaction of bromohydrin **3** with HBr and the bromination–debromination of the **1**–**4** pair can therefore be accommodated by the unique mechanistic picture of Scheme II, involving the formation of the same bromonium intermediate in all these reactions. It could be argued that the bromine and hydroxyl group, which are held in a trans–gauche relationship in bromohydrin **3**, are not favorably disposed for anchimeric assistance by the bromine atom to the leaving of a water molecule from the protonated bromohydrin. If the same conformation is maintained, as it seems probable, in the protonated form, this could mean that the first formed ionic species is a benzylic β-bromocarbenium ion. An increased stability can, however, be gained on passing to the bridged species, particularly in the low polarity solvent employed in the reaction under discussion.

It can also be observed that the gauche arrangement of the 10,11-substituents should disfavor a E2 bromide-promoted con-

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certed elimination of water and Br_2 from the oxonium bromide intermediate **3**-H^+, of the type often reported for the dehalogenation of vicinal *trans*-dihalides,[27] since this process also requires an anti orientation. This mechanism, on the other hand, had been excluded for the analogous HBr-promoted eliminations from *erythro*- and *threo*-2-bromo-1,2-diphenylethanol,[12] as well as for the elimination accompanying the solvolysis of alicyclic bromohydrin brosylates,[11] in favor of the stepwise bromonium ion mechanism of Scheme II. Further evidence for the latter mechanism is provided by the extensive elimination occurring in the reaction of **3** with boron trifluoride etherate: in this case the only reasonable mechanism goes through the formation of a bromocarbenium or bromonium ion, which then transfers electrophilic Br^+ to resorcinol to give its 4-bromo derivative.

Dibromide **4**, on the other hand, has the correct anti orientation of the two bromine atoms required for a bromine-assisted breaking of a benzylic C–Br bond to give directly the bromonium–bromide ion pair **5a**. The same bridged species ion paired to a Br_3^- anion (**5b**) should be formed during the bromination of olefin **1**, presumably by Br_2-assisted cleavage of a bromine–bromine bond in an olefin-Br_2 CTC.[3] Nucleophilic attack of the counterion at either of the bromonium carbons of intermediate **5** leads again to the *trans*-dibromide **4**, while attack at Br^+ can produce molecular Br_2 and olefin **1**, probably passing through the same charge-transfer complex likely involved in the bromination of **1**. The mechanism of debromination should thus be the reverse of that of olefin bromination, in agreement with the principle of microscopic reversibility. The debromination product **1** can be detected provided that Br_2 is prevented from readding to it by efficient scavenging. In the reactions of **3** with gaseous HBr this task is accomplished by the gas stream, which is able to remove the released molecular halogen from the reaction mixture. In the debromination of **4** in dimethylformamide the released Br_2 is consumed in an oxidation–reduction involving the solvent and producing Br_3^- and H^+.[28] The latter, scarcely investigated redox step is probably influenced by the concomitant pH changes and may affect the rate profile of the entire process. In the debrominations occurring in the presence of *cis*-stilbene, Br_2 is scavenged by addition to this olefin, which is present in a large excess and is about 10^4 times more reactive than **1**.[29]

Also in the last case an alternative, concerted elimination of E2 type, which would be geometrically allowed and could involve the scavenger olefin as the nucleophilic species promoting the abstraction of Br^+ from the dibromide, can be excluded. In fact, this mechanism would imply a dependence of the debromination rate on the concentration of the scavenger, which is not found in the data of Table III.

Debrominations occurring in dimethylformamide in the absence of added specific nucleophiles have been alternatively interpreted as involving a bromonium ion mechanism[20] and a nucleophilic role for dimethylformamide.[30] The occurrence of debromination of **4** in acetonitrile also, but not in the less polar 1,2-dichloroethane, allows us to exclude, at least for compound **4**, the need of any external nucleophile and is again consistent with the mechanism of Scheme II, where the nucleophile effecting the Br^+ abstraction is produced by the heterolytic cleavage of a C–Br bond in the substrate itself, a process that is expected to be accelerated by polar solvents.

The amounts of olefin **1** formed in the presently investigated reactions of bromohydrin **3** with HBr are much higher than those of *trans*-stilbene detected in the analogous reactions of the *erythro*- and *threo*-2-bromo-1,2-diphenylethanol, where ratios of this olefin to the *meso*-dibromide ranging between 9:91 and 22:78 were observed.[12] This can be due to several factors. First, in contrast to stilbenes, which underwent fast HBr addition and/or oligo- and polymerization, olefin **1** does not react with HBr. Second, this olefin adds Br_2 at a rate that is slower by about 3 orders of magnitude relative to that of *trans*-stilbene,[12] thus making removal of the released Br_2 by the HBr stream much more efficient. Related to the latter factor is probably the increase in the olefin to dibromide ratio found with decreasing solvent polarity (Table I). The rate of olefin bromination is known to fall dramatically on passing from the moderately polar 1,2-dichloroethane to the nonpolar carbon tetrachloride solvent,[4] so that Br_2 should be most easily removed before readding to the olefin in the latter solvent.

All these effects make difficult an evaluation of the relative tendencies of the bromonium–bromide ion pairs respectively arising from the acyclic stilbene and the tricyclic 5*H*-dibenz[*b*,*f*]azepine system to release molecular Br_2 in the reaction of bromohydrins with HBr. However, the unprecedented easy debromination of dibromide **4** indicates a particularly high propensity of the corresponding bromonium–bromide ion pair **5** to revert back to olefin and Br_2.

This feature can be rationalized on the basis of the structural parameters obtained by X-ray diffraction. These show strongly inequivalent bromine atoms, with a rather longer Br(2)–C(11) bond, and an internal C(10)–C(11)–C(11a) angle considerably larger than the tetrahedral value. The C(11) carbon, having both the larger 121° internal angle and the longer 2.04-Å C–Br bond, appears thus to be particularly inclined to C–Br bond breaking to give a Br^- anion and a bromonium ion. We want to stress that the latter species should be essentially free from angle strain, since the recently reported structure of an alkene bromonium ion[6] shows for the interatomic angles corresponding to C(9a)–C(10)–C(11) and C(10)–C(11)–C(11a) in **5** values nearing 120°, which seem to be more easily borne in the presently investigated tricyclic system. Because nucleophilic attack by counteranion at the bromonium carbons reintroduces angle strain in the product, this transient species, generated in whatever way, is therefore attacked at the bromonium–bromine to give olefin **1**, again endowed with a less strained structure.

It has been previously pointed out[12] that, in general, the reversible or irreversible nature of the electrophilic step in olefin bromination cannot be revealed by simple kinetic measurements, unless particular features make the reverse reaction detectable. No direct information concerning the importance of the k_{-3} process of Scheme I has been accordingly obtained from the presently carried out kinetic measurements of the bromination of **1**. However, the fact that this process is very important for the bromonium–bromide ion pair **5a** generated from bromohydrin **3** and from dibromide **4** suggests an extensive involvement of the k_{-3} reaction also in the case of the corresponding bromonium–tribromide ion pair **5b** formed as the intermediate of the bromination of **1**. This, besides an important electronic effect of the electron-withdrawing N(5)-substituent, can contribute to the low reactivity of the 10,11-double bond of compound **1** toward electrophilic bromination.

In conclusion, the results of the present investigation not only confirm in a more impressive way that bromonium ions can be attacked by Br^- at the bromonium Br^+ to give free Br_2 and the corresponding olefins but also show that this reaction can be markedly affected by structural features of the involved products and can therefore play a nonnegligible role in determining the bromination rates of different olefins.

Experimental Section

Materials and Methods. Commercial 5*H*-dibenz[*b*,*f*]azepine (Iminostilbene, Ega, >97%) was used as the starting material. 5*H*-Dibenz[*b*,*f*]azepine-5-carbonyl chloride (**1**) was prepared from 5*H*-dibenz[*b*,*f*]azepine by treatment with gaseous phosgene as reported.[31] 1a,10b-

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Dihydro-6*H*-dibenz[*b,f*]oxireno[*d*]azepine-6-carbonyl chloride (**2**) was obtained from **1** by treatment with *m*-chloroperoxybenzoic acid.[15] *trans*-10-Bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**3**) was prepared by opening of **2** with aqueous HBr in tetrahydrofuran.[14] All products were >99.5% pure by HPLC.

1,2-Dichloroethane and bromine (both C. Erba RPE, >99.5%) were treated as previously reported.[32] Chloroform (C. Erba, >99.5%) and carbon tetrachloride (Riedel-De Haen, 98%) were distilled immediately before use. Gaseous HBr (Matheson) was 99.8% pure.

Evaporation of the reaction mixtures was carried out in vacuo (rotatory evaporator).

NMR spectra were determined with a Varian CFT-20 or a Varian EM-360 spectrometer. IR spectra for comparisons were registered with a Pye-Unicam SP3-300 instrument. UV–vis spectral data were obtained with a Pye-Unicam SP8-400 spectrophotometer. Melting points were obtained by using a Kofler apparatus and were uncorrected.

Reagent purity, product distributions, and yields were determined by HPLC using a Waters 6000 A apparatus equipped with a 25-cm Hypersil 10 ODR column (HPLC) and UV detector (λ 240, 280 nm) with 70:30 methanol/water as the eluent at a flow rate of 1 mL/min. The crude reaction mixtures were dissolved in methanol, and the appropriate amounts of a methanol stock solution of 5*H*-dibenz[*b,f*]azepine-5-carboxamide were added as a standard. The product yields were evaluated by using calibration curves obtained for each product and the standard.

Reactions of Epoxide 2 with HBr. A. Gaseous HBr was bubbled for 1 h into a solution of **2** (0.51 g, 1.89 mmol) in chloroform (50 mL) at 10 °C. The mixture was then washed with water, dried ($MgSO_4$), and evaporated. The crude residue (0.55 g) was crystallized from MeOH to give pure **3** (HPLC), mp 148–150 °C [lit.[14] mp 147–148 °C].

B. Gaseous HBr was bubbled through a solution of **2** (0.65 g, 1.84 mmol) in chloroform (50 mL) for 3 h at 10 °C. After the usual workup, NMR of the crude mixture showed the presence of **1** and **4** in a ratio of about 1:1. These products were separated by TLC (PSC Fertigplatten Kieselgel 60 F254, Merck, 95:5 hexane/ethyl acetate) and identified by comparison (NMR, IR) with authentic samples of **1** and **4**.

Reactions of Bromohydrin 3 with HBr. Gaseous HBr was bubbled into ca. 10^{-2} M solutions of **3** in 1,2-dichloroethane, chloroform, or carbon tetrachloride (10 mL) for 1.5 h at 10 °C. The reaction mixtures, washed with water, dried ($MgSO_4$), and evaporated, were subjected to HPLC analysis. The product yields are reported in Table I.

Olefin **1** and dibromide **4** were also separated by TLC (under the above reported conditions) from experiments carried out on a larger scale.

Treatment of Dibromide 4 with HBr. Gaseous HBr was bubbled for 3 h into a 10^{-2} M solution of **4** in chloroform (8 mL) at 10 °C. After the usual workup, HPLC analysis showed that **4** was recovered in 97% yield.

Treatment of Olefin 1 with HBr. Solutions of **1** (ca. 10^{-2} M) in 1,2-dichloroethane or chloroform were saturated with gaseous HBr and left at room temperature. After 1.5 h, these mixtures were washed with water, dried ($MgSO_4$), and evaporated. Only **1** was detected by HPLC analysis in 85% yield in 1,2-dichloroethane and in 95% yield in chloroform.

Reactions of Bromohydrin 3 with BF_3·Et_2O. BF_3·Et_2O (13–52 μL, 50–200 μmol) was added to ca. 10^{-2} M solutions of **3** in chloroform (5 mL) containing resorcinol (100 μmol) at 25 °C. After times ranging between 1.5 and 7 h the mixtures were washed with water, dried ($MgSO_4$), and evaporated, and the residues were subjected to HPLC analysis. Olefin **1** and 4-bromoresorcinol were the only detected products. The yields are reported in Table I.

Bromination of Resorcinol. A 7.6×10^{-3} M solution of Br_2 in chloroform (60 mL) was added dropwise to 25 mL of a 1.8×10^{-2} M solution of resorcinol in the same solvent at 25 °C. The mixture was allowed to react until it became colorless, then HBr was stripped by a nitrogen stream. The solvent was evaporated, and the residue was crystallized from hexane to give pure (HPLC) 4-bromoresorcinol, mp 98–100 °C [lit.[33] 100–102 °C].

Bromination of Olefin 1. A 0.75 M solution of Br_2 in 1,2-dichloroethane (4 mL) was added to a solution of **1** (0.38 g, 1.5 mmol) in the same solvent (4 mL). After standing at room temperature for 5 days, the solution was washed with saturated aqueous $NaHSO_3$ and water, dried ($MgSO_4$), and evaporated. HPLC analysis of the residue showed the presence of a single product. Crystallization from acetonitrile yielded pure **4**: mp 175–177 °C. Anal. Calcd for $C_{15}H_{10}NOBr_2Cl$: C, 43.35; H, 2.42; N, 3.37; Br, 38.47; Cl, 8.35. Found: C, 43.47; H, 2.37; N, 3.50; Br, 37.95; Cl, 8.60.

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Table VII. Crystal Data

mol formula	$Br_2ClNOC_{15}H_{10}$
MW	415.51
crystal system	tetragonal
space group	$P4_1$
a, Å	12.268 (2)
b, Å	12.268 (2)
c, Å	9.923 (4)
α, β, γ, deg	90.00
V, Å^3	1493.5
Z	4
ρ (calcd), g/cm^3	1.848

Table VIII. Data Collection Details

radiation, λ, Å	Mo Kα, graphite monochromator, 0.710 69
dimension, mm	0.25 × 0.25 × 0.75
μ, cm^{-1}	59.178
F(000)	805.7
2θ range, deg	2.5–65.0
range of indices	h = 0–18; k = 0–18; l = 0–15
scan mode	θ/2θ
scan speed, deg/min	2.0–29.3
scan width, deg	2.0 in 2θ
bkgd counts	for $^1/_2$ the scan time
check reflcns	3 every 100 reflcns; no decay
no. of measd reflcns	3195
no. of unique reflcns	2865
value *R* (int) from merging equiv reflcns	6.23
obsd reflcns, $I > 3\sigma(I)$	1281

Debrominations of Dibromide 4. A. In dimethylformamide. Solutions of **4** in DMF-d_7 were thermostated at 25 °C and the ^{1}H NMR spectrum was registered at time intervals. The relative amounts of **1** and **4** were calculated by integration of the respective vinylic and α-proton signals. The percentages of **1** found at several times are reported in Table III.

B. In 1,2-Dichloroethane and Acetonitrile. Solutions of **4** in 1,2-dichloroethane or acetonitrile were thermostated at 25 °C in the dark in the absence or in the presence of different amounts of *cis*-stilbene. Samples were withdrawn at intervals and analyzed by HPLC. The percentages of **1** found at several times are reported in Table III.

Kinetic Measurements. Bromine solutions were prepared in 1,2-dichloroethane shortly before use and the concentrations adjusted to twice the desired initial concentrations in the kinetic runs (ca. 3×10^{-3} M in the case of *cis*-stilbene and ca. 2×10^{-1} M in the case of **1**). In a few experiments the 1,2-dichloroethane solvent was preventively saturated with oxygen as a free-radical inhibitor. These solutions were prethermostated at 50 °C and mixed with equal volumes of prethermostated olefin solutions of identical concentrations in the same solvent. The reactions were followed at 50 (0.05) °C by monitoring the disappearance of Br_2 at 409 nm for *cis*-stilbene and at 480 nm for **1** and recorded for more than three half-lives. The absorbance/time data were fit to the appropriate third-order rate equation[12] and the rate constants obtained with the usual linear least-squares procedure. Similar values of k_3 were found in runs carried out both in the absence and in the presence of oxygen. The reported values are the average of three independent measurements. Errors are given as standard deviations obtained from the deviations of individual measurements from the average values.

Crystallography. A crystal of $Br_2ClONC_{15}H_{10}$, obtained from a solution of compound **4** in acetonitrile, was mounted on a Nicolet R3 automatic four-circle diffractometer. The cell parameters were refined by least squares from the angular positions of 21 reflections in the range $16 < 2\theta < 42°$. The crystal data are reported in Table VII. Pertinent details for the data collection at room temperature are given in Table VIII. The data were processed to yield values of I and $\sigma(I)$.[34] In the estimation of $\sigma(I)$ the uncertainty factor p was set equal to 0.017, as calculated from the variance of the standard reflections.[35] The values of I and $\sigma(I)$ were corrected for Lorentz, polarization, and shape anisotropy effects.[36,37] A total of 1281 independent reflections having $I > 3\sigma(I)$ were used in all subsequent calculations.

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Table IX. Refinement Details

method used to solve struct	Patterson method
type of refinement	full matrix least-squares method
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
H atoms	geometrically located
variables refined	180
a,b values in the weight function: $w = 1.0/(a + F_o + bF_o)$	0.068; 0.0108
final R (isotropic), %	10.19
final R_w (isotropic), %	15.56
final R (anisotropic), %	5.01
final R_w (anisotropic), %	7.75
goodness of fit, s	0.40

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. H atoms were idealized (C-H = 1.0 Å); each H atom was assigned the B value of parent C atom and allowed to ride on it. Details of the refinement procedure are given in Table IX. The final difference Fourier map, with a root-mean-square deviation of electron density of 0.14 e Å^{-3}, showed a pair of peaks with values exceeding 3.0 times the estimated standard deviation located near Br atoms, which, however, are not of chemical significance. Atomic scattering factors were taken from ref 38. The program used was SIR CAOS,[39] on the Data General MV8000/II of Istituto di Strutturistica Chimica CNR.

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Supplementary Material Available: Tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Rapid, Multistep Rearrangements of Hydrocarbon Triplet Biradicals at 4 K. A Possible Example of Hot Molecule Effects in Frozen Organic Solvents

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Abstract: Photolysis of 2,3-diazabicyclo[2.2.1]hept-2-enes with spirocyclopropyl groups at the 7-positions (e.g., **1** and **8**) in organic matrices at 4–35 K produces triplet 2-alkylidene-1,3-cyclopentanediyls (e.g., **2** and **9**, respectively). The products were identified by comparing EPR spectra—including both zero-field splitting parameters and interpretable hyperfine coupling patterns in the $\Delta m_s = 2$ region—with those obtained from authentic samples. The proposed mechanism involves several unusual features, including hot molecule effects in a condensed phase and quantum mechanical tunneling. An important component in the analysis is the substantial thermodynamic stability of trimethylenemethane compared with other hydrocarbon triplets.

In the present work we describe a remarkable series of transformations that occur at 4 K in frozen organic solvents upon photolysis of members of a class of polycyclic azoalkanes typified by structure **1** (Scheme I). The final products are triplet trimethylenemethane (TMM) derivatives such as **2**. These products have been identified by EPR spectroscopy, including comparison of zero-field splitting parameters with those of authentic samples. In addition, interpretable hyperfine splittings have been seen in the $\Delta m_s = 2$ transitions of the product EPR spectra, and these lead to an unambiguous structural assignment.

The proposed route to **2** is necessarily complex and somewhat speculative. It involves two, sequential biradical-to-biradical rearrangements. The first step (I in Scheme I) is consistent with the conventional thermal chemistry of such structures but would be expected to have a barrier that cannot be surmounted by normal thermal activation at 4 K. We propose that this is an example of hot molecule effects in a condensed phase at 4 K. The second step (II) represents an unprecedented departure from the chemistry these structures display under conventional conditions, and we believe quantum mechanical tunneling is involved. Our mechanistic analysis emphasizes the substantial thermodynamic driving force for obtaining a TMM-like structure, indicating that for hydrocarbon triplets, TMM is a thermodynamic sink.

Scheme I

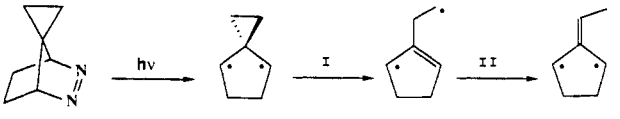

Table I. Zero-Field Splitting Parameters

azoalkane precursor	biradical	$\|D/hc\|$[a]	$\|E/hc\|$[a]
1	**2**	0.0264	0.0035
6[b]	**7**[c]	0.025[b]	0.004[b]
8	**9**	0.0255	0.0030
10	**2**	0.0264	0.0035
11	**9**	0.0255	0.0030
21	**23**[c]	0.0256	0.0045
24	**26**[c]	0.0271	0.009

[a] In cm^{-1}. [b] Reference 4. [c] Tentative assignment.

Identification of TMMs as the Reaction Products

Zero-Field Splitting Parameters and Thermal Stability. Photolysis (304–388 nm or monochromatic 334 ± 2 nm) of 2,3-diazabicyclo[2.2.1]hept-2-ene-7-spirocyclopropane (**1**)[2] in a glassy

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