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PROTON AND CARBON MAGNETIC RESONANCE STUDIES ON THE MECHANISM OF THE 2,2-(1,2-ETHYLENEDITHIO)BORNANE REARRANGEMENT INTO 2,3-(1,2-ETHYLENEDITHIO)-2-BORNENE

Brunon Pruski, Róża Antkowiak and Wiesław Z.Antkowiak*

Faculty of Chemistry, A.Mickiewicz University
Grunwaldzka 6, 60-780 Poznań, Poland

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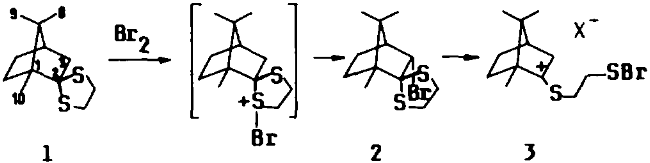
Abstract: The transformation of camphor ethylenedithioacetal (1) caused by bromine was followed by proton and carbon NMR. It was found that a rapid bromination to 3-bromoderivative (2) occurred in the first stage. Next, this product was slowly converted into the 2-(2-bromothioethylthio)-2-bornyl cation, (3) stable for up to one hour at room temperature. When quenched with water it yielded the rearranged product (4) containing a dihydro-1,4-dithiine ring.

On the basis of literature reports concerning the rearrangement of 1,3-dithiolanes into dihydro-1,4-dithiins under the influence of bromine, it can be assumed that in the first stage of the reaction a bromosulfonium[1-5/] ion is formed. However, further stages of bromosulfonium ion transformation have not yet been unambiguously determined. Palumbo[1/] and Salazar[6/] suggested that the reaction involves the opening of the dithiolane ring with formation of an unsaturated sulfide; their proposal differs from the one put forward by Majerski[7/] which assumes that the alfa bromo-derivative of dithioacetal is first formed and then transfomed into the final product.

The latter suggestion has been corroborated by the results of our investigations performed on camphor ethylene-dithioacetal (1) described in this report. This compound under the influence of bromine in tetrachloromethane or acetic acid is transformed into a mixture of 2,3-(1,2-ethylenedithio)-2-bornene (4) and 3-endo-bromo-2,2-(1,2-ethylenedithio)bornane (2) in the ratio 3:1 and 7:1 respectively[8/]. To determine the precise course of the reaction of 1 with bromine we decided to follow the transformations by means of proton and carbon magnetic resonance.

According to our observations the addition of bromine to a TFA/ CD_2Cl_2 (1:5) solution of 1 present in the NMR tube caused a quick bromination of the vicinal position leading to formation of 2 for which the characteristic absorption of the H-3-exo at 4.98 ppm was observed. The rate of the reaction was so high that immediately after mixing of the reagents, no starting material could be detected in the PMR spectrum of the dark-cherry reaction mixture which consisted of the brominated dithioacetal 2 and the carbocationic intermediate 3 (scheme 1).



1 2 3

$X = Br^-$ or CF_3COO^-

Scheme 1.

Forty minutes after the beginning of the reaction the carbocationic product appears at a maximum concentration of 80% and during the subsequent 40 minutes this decreases to about 50%. Hence, both to slow down the processes and to create conditions enabling the CMR spectrum to be recorded, the temperature was decreased to -30° after the carbocation had been generated during the first 40 minutes. As a result, it was possible to keep the solution unchanged for several hours, whereas a further decrease in temperature led to a solidification of the solution. The PMR spectrum obtained in such conditions showed three characteristic singlets coming from three methyl groups at 0.89, 1.11 and 1.39 ppm, and in addition one-proton signal at 2.53 ppm, four-proton multiplet centered at 3.40 ppm and two-proton pseudotriplet at 4.27 ppm.

The signal at 4.27 ppm was assigned to appropriate protons on the basis of the PMR spectrum of the intermediate generated from 2,2-(1,2-tetradeuteroethylenedithio)bornane under identical conditions. Specific deuteration of the substrate led to the complete disappearance of absorption at 4.27 ppm and partial loss of that at 3.40 ppm. The PMR spectrum revealed signals which arise only from the resonance of the bicyclic protons. In this case the most deshielded protons were the two located at C-3. Their signals at 3.66 ppm (H-exo) and 3.24 ppm (H-endo) were shifted over about 1 ppm towards lower field in comparison with the chemical shift of the same protons of the starting dithioacetal 1. The absorption pattern of these two protons presents a typical AB system[9] with a very high value of the geminal coupling constant J=23.0 Hz which is almost 10 Hz higher than that of the substrate. This increase in the coupling constant may result from a decrease in the value of the angle between geminal protons at the C-3 position as a result of the hybridization change of the neighboring carbon atom or it could be due to a parallel arrangement of both protons against a vicinal π orbital[10].

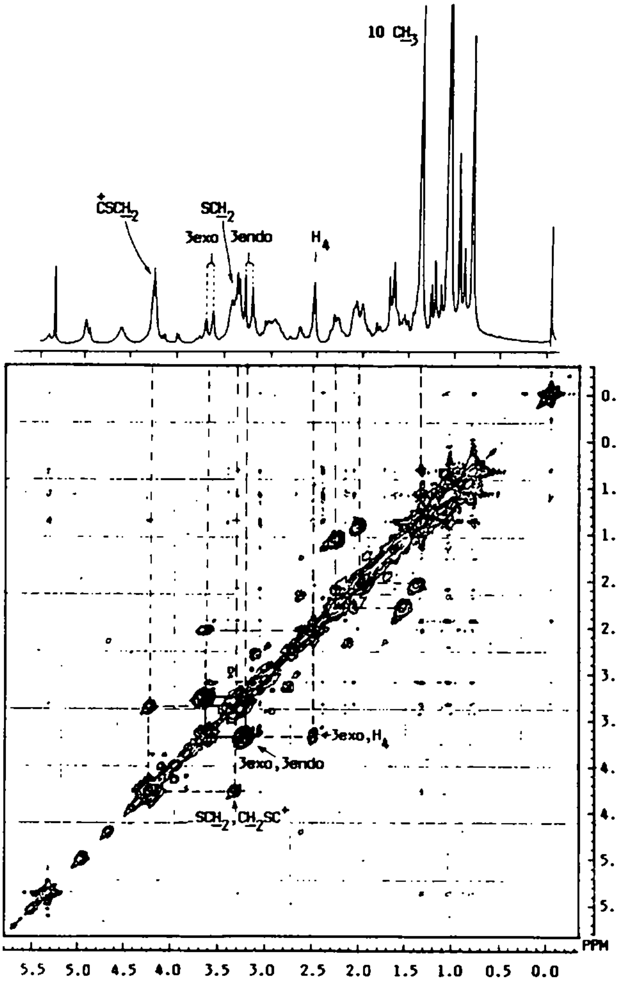


Figure 1. ^{1}H-^{1}H COSY spectrum of 2-(2-bromothioethylthio)-2-bornyl cation 3. Approx. 54 mg in 0.5 ml TFA/CD$_2$Cl$_2$ (1:5) at 242 K.

Irrespective of the reason, however, the increase in the value of the geminal coupling constant supports a nearby carbocationic center.

The coupling between the protons of the dithioethylene system, absorbing at 4.27 ppm and 3.36 ppm, was observed on a two-dimensional ^1H-^1H NMR spectrum (fig.1), confirming the identity of these signals. An increased deshielding of two of these ethylene protons (α CH_2) points out to the presence of a carbocationic center (stabilized by a resonance induced by the sulphur atom) in close vicinity.

This interpretation indicates that the carbenium ion 3 formed contains a sulfide fragment attached to the carbocationic center, resulting from 1,3-dithiolane ring opening.

It was also found that the 3-bromodithioacetal 2 in a solution of CD_2Cl_2/TFA (5:1, v/v) undergoes a transformation (though more slowly than 1) into a product revealing the carbocation 3 properties and a similar pattern of PMR absorption. This observation, demonstrates the structural identity of both carbocations (yielded from 1 and 2), and supports the proposal that the reaction of 1 with bromine proceeds via intermediate 2.

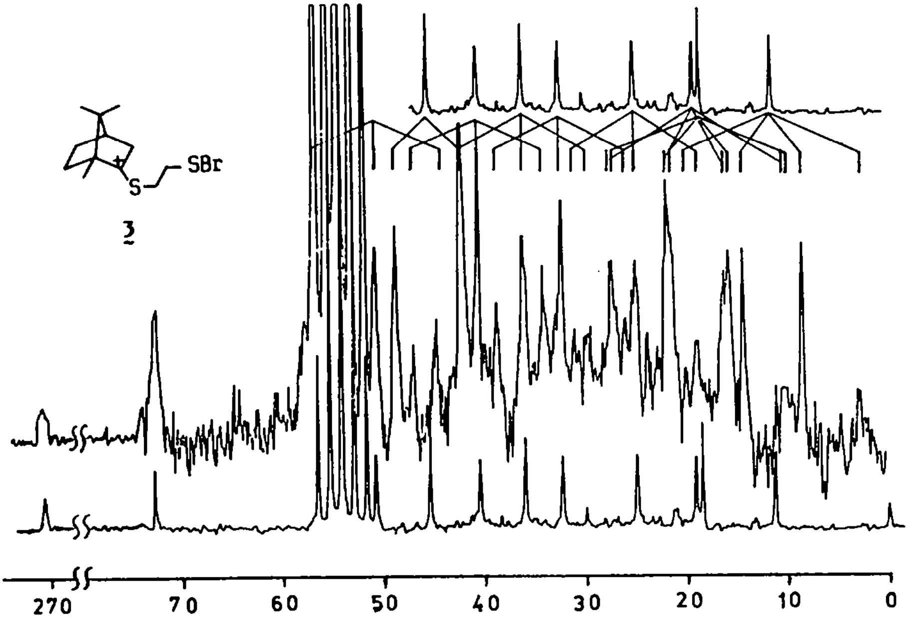
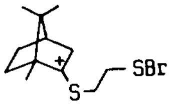
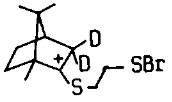
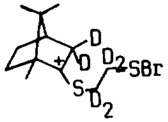


Figure 2. ^{13}C NMR spectra (^1H-decoupled and ^1H-coupled) of cation 3 at 243 K.

Further conclusions concerning the structure of carbocation 3 were based on the analysis of the carbon magnetic resonans spectra (fig.2). The cationic intermediate was generated in conditions considered favorable for slowing down intramolecular processes.

First of all it was found that the spectrum shows a singlet absorption at 271.97 ppm, which gives unquestionable evidence of the presence of a carbocationic center in a molecule. Similar values were reported by Servis[11/] and Okuyama[12/] for 2-methyl-2-norbornyl and 1,3-dithiolan-2-yl cations, respectively. It was also found that both the singlet absorption of the positive carbon and the observation that the spectrum reveals the same number of signals of a given multiplicity (3x1°, 5x2°, 1x3° and 3x4°) as the spectrum of starting material **1**, tes-

Table 1. The carbon chemical shift (ppm) and signal multiplicity for **3** and related carbocations.

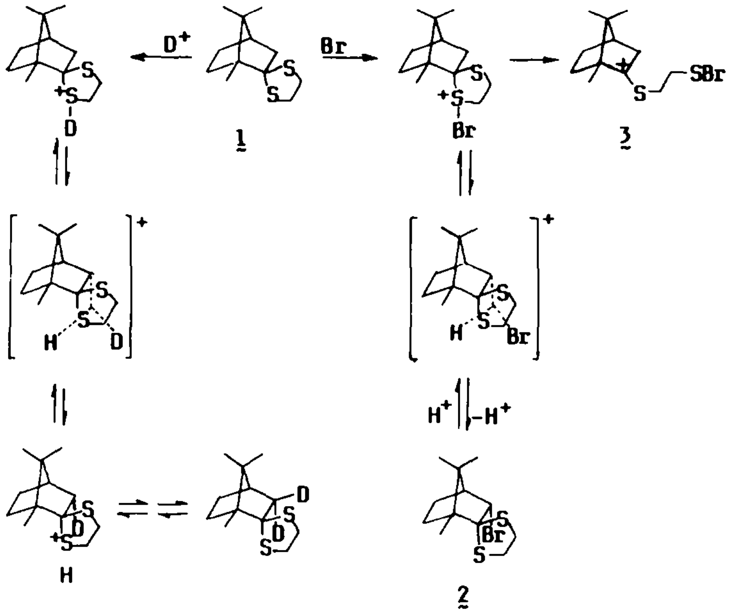
Position C				
	$CDCl_3/TFA/Br_2$	$CD_2Cl_2/TFA/Br_2$	$CD_2Cl_2/TFA\text{-}d/Br_2$	$CD_2Cl_2/TFA\text{-}d/Br_2$
C_1	72.79 s	73.44 s	73.44 s	73.55 s
C_2	271.11 s	271.97 s	272.09 s	272.30 s
C_3	50.69 t	51.23 t	-	-
C_4	45.38 d	45.82 d	45.71 d	45.71 d
C_5	24.91 t	25.35 t	25.24 t	25.24 t
C_6	35.96 t	36.39 t	36.50 t	36.50 t
C_7	54.27 s	the signal is covered by the midle line of CD_2Cl_2 quintet		
C_8	19.17 q	19.39 q	19.39 q	19.50 q
C_9	18.63 q	18.85 q	18.85 q	18.85 q
C_{10}	11.48 q	11.81 q	11.81 q	11.91 q
* C-S-C^+	32.49 t	32.71 t	32.82 t	-
* C-S-Br	40.62 t	40.94 t	40.94 t	-

*Assignments may be interchanged between the two carbons.

tify that a positive charge was formed as a result of the heterolytic cleavage of the C-S bond and was localized at C-2. Analysis of the values of the chemical shifts of the remaining carbon atoms (table 1) confirms the conclusion that the intermediate under investigation has the carbocationic structure **3**.

At this stage of the reaction the possibility of observing the product of a further intramolecular rearrangement (e.g.Wagner-Meerwein type) was discounted on the grounds of our observations concerning isotopic exchange[13/]. Thus reaction of **1** with bromine in deuterated trifluoroacetic acid leads to an immediate exchange of protium at C-3 for deuterium, as revealed by the disappearance of signals at 3.66, 3.24 ppm and 51.23 ppm in the PMR and CMR spectrum, respectively, of the carbocation formed. Exchange occurred so quickly, that in the spectrum of the carbocation being formed, no protonated system at C-3 position was observed. It can then be assumed that the reason for such a considerable increase in the acidity of these protons in comparison with the starting dithioacetal is the presence of a carbocationic center at the vicinal position (C-2). It should be added that the dithioacetal **1** does not undergo any change in a solution of $NaOD-D_2O$-dioxane, whereas in the solution of CD_2Cl_2-TFA-d only 48 hours after the reaction at room temperature 75% of the protium was observed to be exchanged for deuterium at C-3 (in both exo and endo positions) as shown by a decrease in the intensities of appropriate signals at 2.61, 2.22 (PMR) and 55.26 ppm (CMR). In view of the large difference in the rate of the isotopic exchange in carbocation **3** and dithioacetal **1**, it is assumed that in both cases different reasons account for the proton acidity at the C-3 position, which probably results from structural differences and the appearance of the positive charge in close vicinity.

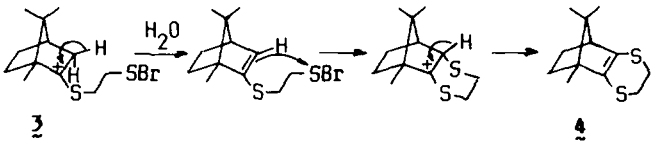
Our studies therefore demonstrate that when dithioacetal **1** is treated with bromine, the 3-bromoderivative **2** is quickly formed (probably through the bromosulfonium ion intermediate). The bromine atom in compound **2** then undergoes a reverse exchange for hydrogen in the transformation process of **2** into carbocation **3**. Such an easily reversible exchange of a hydrogen atom for bromine, as well as a slower exchange of protium for deuterium in the dithioacetal molecule before the dithiolane ring opening occurs, may result from steric intramolecular interactions and may also be characteristic of the systems with a rigid eclipsed conformation. It is highly likely that the crowding of substituents localized around C(2)-C(3) in the endo and exo positions, which we observed[14/] in the X-ray structural analysis of compound **2**, provides a situation favorable for the formation of a two electron three center bond proposed for other systems by Olah[15]. This would explain the mechanism (scheme 2) of the easily reversible isotopic and element exchange observed.



Scheme 2.

This interpretation explains the formation of 2 as an intermediate of the transformation under investigation. However, it cannot be excluded that in other conformationally labile systems, the rearrangement of 1,3-dithiolanes into dihydro-1,4-dithiins may proceed without intermediate bromination of the vicinal position.

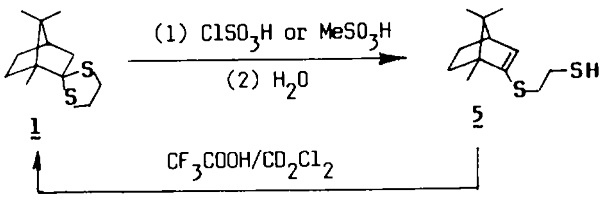
The addition of water to the solution of carbocation 3 at a temperature of -30°C has led to the formation of 2,3-(1,2-ethylenedithio)-2-bornene (4) in 68% yield (scheme 3).



Scheme 3.

The result obtained in this investigation confirms our assumption that carbocation 3 is a real intermediate in the bromine initiated rearrangement process of 1 to 4.

Finally we examined the behaviour of the dithioacetal 1 under the sole influence of a strong acid such as chlorosulfonic or methanesulfonic acid. It appeared that the solution of 1 in this medium when quenched with water yielded a thioenol derivative: 2-(2-thioloethylthio)-2-bornene (5) (scheme 4) with none of the rearrangement product 4. It was also observed that 5, when dissolved in TFA/CD_2Cl_2, or even when chromatographed on silica gel, underwent a recyclization to the starting dithioacetal 1 as shown by NMR.



Scheme 4.

This experiment demonstrated that only the sulfenyl bromide group in 3 is electrophilic enough to react with the adjacent carbon yielding the dihydro-1,4-dithiin 4. It also showed that, although the bromination reaction studied was carried out in acidic solvent and the rate of the reaction seems to depend on the acidity strength, protonation alone cannot account for the observed transformation from 1 to 4.

EXPERIMENTAL

Analytical TLC and preparative column chromatography were performed on silica gel $60F_{254}$ and 60H, respectively. Melting points (uncorrected) were determined using a Boetius PHMK 05 apparatus. The optical rotations were measured at the sodium D line using a polarimeter fitted with a 10 cm cell for 1% solutions. Infrared spectra (cm^{-1}) were monitored on a Perkin Elmer 180 spectrometer. Ultraviolet spectra (nm, ε) were obtained on Schimadzu 160-UV spectrophotometer. Low and high resolution mass spectra were recorded on a Jeol JMS-D-100 mass spectrometer linked to a Texas Instruments 980 B computer (75eV). Combustion analyses were performed using a Perkin-Elmer 240 apparatus. NMR spectra were recorded on a Bruker MSL-300 at 300.13 MHz or a Jeol FX-90 at 89.55 MHz and 22.50 MHz for ^{1}H and ^{13}C,respectively. Chemical shifts (ppm) were referenced to external TMS. The conditions were as follows: temperature 297 K (243 K in the case of ^{1}H-^{1}H correlation and ^{13}C NMR of 3), 5(^{1}H) or 10(^{13}C) mm sample tube, concentration ca 20% in $CDCl_3$, which was used as an internal lock, 90° flip angle/10μs (^{1}H), 11μs (^{13}C), scan repetition time 2s. Typical acquisition parameters were in the case of COSY: spectral width 1.85 KHz, ω_2 domain - size 1K number of data points 1K, ω_1 256 increments zero-filled to 512 W, sine multiplication was used prior to 2D-FT transformation, spectrum was symmetrized about diagonal.

2,2-(1,2-Ethylenedithio)bornane (1)

A solution of camphor ($[\alpha]_D$=+44.0° in EtOH, 20.0 g, 0.13 mole) in 12.5 cm^3 of 1,2-ethanedithiol (14.0 g, 0.15 mole) was saturated with a gaseous HBr at room temperature and the solution obtained was stored for 48 hours in a refrigerator. The reaction mixture was diluted with ethyl ether (200 cm^3), washed with 10% aqueous NaOH, water, dried over $MgSO_4$ and concentrated in vacuum. The residue in the form of a colorles oil (30.0 g) was purified by distillation under reduced pressure to give 1 (29.7 g, 99% yield), b.p. 93-95°C/0.05 mm Hg; m.p. 28°C. $[\alpha]_D$=+24.0° ($CHCl_3$), +27.0° (AcOEt)[16/]; IR (neat): 1480, 1460, 1390, 1370; ^{1}H NMR: 3.33 (m, 1H) and 3.18 (m, 1H, S-C$\underline{H}_2$) 3.05 (m, 2H, SC$\underline{H}_2$), 2.61 (dt, 1H, J= 13.9, $J_{3,4}$=$J_{3,5}$= 3.5, H-3exo), 2.22 (d, 1H, J= 13.9, H-3endo), 1.98 (m, 1H), 1.74 (t, 1H, 2xJ=3.5, H-4), 1.79-1.57 (m, 2H) 1.30 (m, 1H), 1.04 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H); ^{13}C NMR: 12.48 (q, C_{10}), 21.02 (q, C_9), 21.41 (q, C_8), 26.87 (t, C_5), 35.37 (t, C_6), 37.45 (t, $\underline{C}H_2$-S), 41.48 (t, $\underline{C}H_2$S), 46.73 (d, C_4), 49.28 (s, C_7), 54.79 (s, C_1), 55.26 (t, C_3), 77.41 (s, C_2); MS: m/z=228 (M^+), 200, 118(100%), 108. HRMS: calcd for $C_{12}H_{20}S_2$ m/z=228.1007, found m/z=228.1007. Anal. calcd for $C_{12}H_{20}S_2$: C, 63.09; H, 8.83; S, 28.08, found: C, 63.2; H, 8.80; S, 28.18. UV: 0.506 mg of 1 in 2 cm^3 of isooctane, 212 (740), 243 (400).

3-endo-Bromo-2,2-(1,2-ethylenedithio)bornane (2)

A solution of 3-endo-bromocamphor ($[\alpha]_D$=+126.4° in EtOH, 49.3 g, 0.21 mole) in 45 cm^3 of 1,2-ethanedithiol (50.5 g, 0.54 mole) was saturated with a gaseous HBr at room temperature. The reaction mixture was stored for 7 days in a refrigerator. The crystals were filtered off and recrystallized from a dry methanol to give 41.0 g (63%) of 2 mp. 90-91°, $[\alpha]_D$=+100.0° (in $CHCl_3$). ^{1}H NMR: 4.98 (dd, 1H, J=4.0, J=1.7, H-3exo), 3.43-3.31 (m, 1H) and 3.20-3.06 (m, 1H) S-C$\underline{H}_2$, 3.03-2.91 (m, 2H, S-C$\underline{H}_2$), 1.98 (broad t, J=4.0, H-4), 1.97-1.57 (m, 4H), 1.12 (s, 3H), 1.10 (s, 3H), 0.99 (s, 3H). ^{13}C NMR: 16.17 (q, C_{10}), 23.62 (q, C_9), 23.93 (t, C_5), 24.06 (q, C_8), 37.75 (t, C_6), 40.83 (t, S-$\underline{C}H_2$), 43.78 (t, S-$\underline{C}H_2$), 50.84 (s, C_1), 56.79 (d, C_4), 57.86 (s, C_7), 77.07 (d, C_3), 83.78 (s, C_2). IR (KBr): 1420, 1390, 1370, 1270, 830. MS: m/z=308/306 (M^+), 280/278, 227 (100%), 198/196. HRMS: calcd for $C_{12}H_{19}BrS_2$ m/z=308.0092, found m/z=308.0094. Anal. calcd for $C_{12}H_{19}BrS_2$: C, 46.90; H, 6.23; Br, 26.00; S, 20.87, found: C, 47.11; H, 6.35; Br, 25.76; S, 21.12. UV: 0.654 mg of 2 in 2 cm^3 of isooctane 220 (1050).

2,3-(1,2-Ethylenedithio)-2-bornene (4)

Bromine (160 mg, 51.6 µl, 1.0 mmole) in 3 cm^3 of acetic acid was added dropwise to the solution of 228 mg (1.0 mmole) of 1 in 3 cm^3 of acetic acid, then it was stirred for 2 hours at room temperature. Next, the solution was diluted with ethyl ether (50 cm^3), washed with water, 40% aqueous $NaHSO_3$, 10% aqueous Na_2CO_3, water, dried over $MgSO_4$ and concentrated in vacuum. The crude product (230 mg) was purified by distillation under reduced pressure (bp. 80-85°C, 1 mm Hg) to give 200 mg (88%) of 4, $[\alpha]_D$=+38.5° (in $CHCl_3$). ^{1}H NMR: 0.82 (s, 3H), 0.90 (s, 3H), 0.98 (s, 3H), 1.10--2.10 (m, 4H), 2.27 (d, 1H, J=3.5, H-4), 2.79-3.39 (m, 4H). ^{13}C NMR: 10.88 (q, C_{10}), 19.08 (2q, C_9 and C_8), 26.53 (t), 27.09 (t), 27.52 (t), 33.55 (t), 53.53 (s, C_7), 57.39 (s, C_1), 57.48 (d, C_4), 125.92 (s, C_3), 128.52 (s, C_2). IR (neat): 1570. MS: m/z=226 (M^+), 211, 198 (100%), 183, 170, 138. HRMS: calcd for $C_{12}H_{18}S_2$ m/z=226.0851, found 226.0851. Anal. calcd for $C_{12}H_{18}S_2$: C, 63.66; H, 8.01; S, 28.32, found: C, 63.51; H, 8.16; S, 28.28.

2-(2-Bromothioethylthio)-2-bornyl cation (3)

In the NMR tube 50 mg (21.9 mmole) of 1 ($[\alpha]_D$=+23.0° in $CHCl_3$) was dissolved in 400 µl od CD_2Cl_2 and 85 µl of TFA. To the solution 11.3 µl (35 mg, 21.9 mmole) of bromine was added. After 40 minutes the temperature of the dark-cherry solution of 3 was decreased to -30°C and kept while the ^{1}H NMR (300 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded. ^{1}H NMR: 4.27 (m, 2H, -C$\underline{H}_2$SC$^+$), 3.66 (broad d, 1H, J=23.0, H-3exo), 3.36 (m, 2H, -C$\underline{H}_2$-SBr), 3.24 (d, 1H, J=23 Hz, H-3endo), 2.53 (broad s, 1H, H-4), 1.39 (s, 3H, 10-C$\underline{H}_3$), 1.11 (s, 3H), 0.89 (s, 3H); ^{13}C NMR: see table 1.

The solution of 3 was treated with water and the product (48.3 mg, 68%) isolated as described in the previous experiment, shoved identical properties with those of 4.

2-(2-Mercaptoethylthio)-2-bornene (5)

The dithioacetal 1 (456 mg, 2 mmole) was dissolved in 2 ml of chlorosulfonic acid and the resulted dark-cherry solution after 15 min stirring at room temperature was supplied with ice at -30°C. The product was taken up into n-pentane, the solution washed with 10% $NaHCO_3$ aq, water, dried over Na_2SO_4, filtered through an alumina layer and concentrated. The product 5 was isolated from the residue by removing at 100°C/1 mm Hg the starting material (131 mg, $[\alpha]_D$=+24.0°). The remained colorless oil (324 mg. 71%) showed $[\alpha]_D$=-27.5° ($CHCl_3$); IR (neat): 1561, 1387, 1376, 1298, 1290, 1192, 1106, 938 and 820. ^1H NMR: 5.62 (d, 1H, J=3.4, H-3), 2.93 (m, 4H, $-SC\underline{H}_2-C\underline{H}_2S$), 2.37 (t, J=3.4, H-4), 1.93-1.03 (m, 4H), 0.93 (s, 3H), 0.82 (s, 3H), 0.79 (s, 3H); ^{13}C NMR: 11.22 (q, C_{10}), 19.51 (q, C_9), 19.61 (q, C_8), 26.55 (t), 30.34 (t), 31.53 (t), 37.38 (t), 52.18 (d, C_4), 56.13 (s, C_7), 56.46 (s, C_1), 124.83 (d, C_3), 143.09 (s, C_2). MS: m/z=228 (M^+), 227 (100%), 195, 167, 131, 118; HRMS: calcd for $C_{12}H_{20}S_2$ m/z=228.10054, found: 228.10044, calcd for $C_{12}H_{19}S_2$ m/z=227.09272, found 227.09267.

The ^1H NMR spectrum of the product 5 determined immediately after dissolving in TFA-CD_2Cl_2 (1:5) was identical with that of dithioacetal 1.

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