Unexpected condensation of 3-chloro-1,2,3-trimethyl-4-methylidenecyclobutene with 1,2-dimethyl-3,4-dimethylidenecyclobutene

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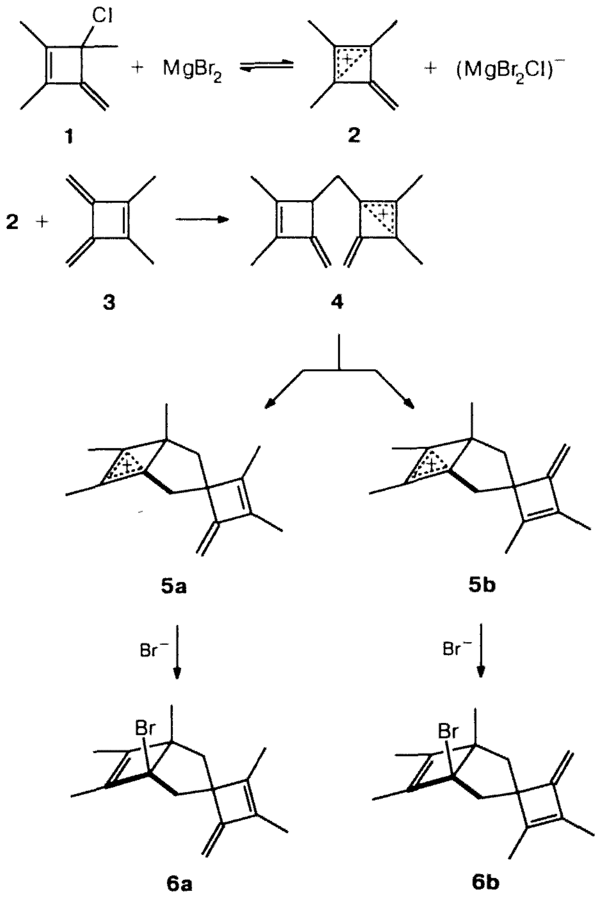
Condensation of 3-chloro-1,2,3-trimethyl-4-methylidenecyclobutene with 1,2-dimethyl-3,4-dimethylidenecyclobutene under the action of $MgBr_2$ leading to spiro compounds was observed. The scheme of the process is discussed.

Key words: cyclobutene; spiro{bicyclo[3.2.0]heptane-3,1'-cyclobutane}; magnesium bromide; cyclobutenyl cation; cyclization; X-ray analysis.

The reaction of 3-chloro-1,2,3-trimethyl-4-methylidenecyclobutene (**1**) containing 1,2-dimethyl-3,4-dimethylidenecyclobutene (**3**) impurity with allylmagnesium bromide to prepare 3-allyl-1,2,3-trimethyl-4-methylenecyclobutene according to the procedure described earlier[1] unexpectedly led to a mixture of diastereomeric 1*S*,3*R*,5*R*- and 1*S*,3*S*,5*R*-1-bromo-5,6,7,2',3'-pentamethyl-4'-methylidenespiro{bicyclo[3.2.0]hept-6-ene-3,1'-cyclobut-2'-enes} (**6a** and **6b**) in the ratio of 6 : 1 (Scheme 1). The structure of the main crystalline compound **6a**, which could be separated from a minor impurity of **6b**, was established using X-ray analysis. From the empirical formula of compounds **6a** and **6b** ($C_{16}H_{21}Br$) it was natural to assume that they were synthesized on condensation of two molecules having a cyclobutane skeleton and four one-carbon substituents without participation of the propene fragment of allylmagnesium bromide. Such condensation could follow the pattern of the Friedel—Crafts reaction between chloride (**1**) and triene (**3**) under the action of magnesium bromide as a Lewis acid, which is formed under the reaction conditions (*cf.* Ref. 2). The goal of this work was to verify the above assumption.

Magnesium bromide was obtained *in situ* by the reaction of magnesium with an excess of allyl bromide. When allylmagnesium bromide was not detected any longer in aliquots of the reaction mixture, a mixture of chloride **1** and triene **3** was added. Subsequent conventional workup actually led to a mixture of compounds **6a** and **6b**.

Scheme 1



Magnesium bromide causes ionization of chloride **1** with formation of 1,2,3-trimethyl-4-methylidenecyclobutenyl cation **2** (which is short-lived or exists in the form of an ion pair).* Electrophilic addition of cation **2** to the terminal carbon atom of the methylene group of triene **3** leads to cation **4**, which undergoes intramolecular cyclization.[3] The two diastereomeric cyclobutenyl cations **5a** and **5b** formed as a result of this

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* As far as we know, cation **2** was not generated before under «long life» conditions.

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process react with bromide anions to give compounds **6a** and **6b**, respectively.

The structure of compounds **6a** and **6b** was determined based on the data of ^{1}H and ^{13}C NMR spectra and confirmed by X-ray analysis (for **6a**).

The signals in the ^{1}H NMR spectra of compound **6a** were assigned with consideration of their multiplicity, relative intensity, and chemical shifts, as well as the results of double resonance. Thus, when the protons of the methyl group with δ 1.64 were irradiated, the signals of δ 4.01 and 4.11 (=CH_2) and 1.54 (CH_3) became narrower, whereas the width of signals of the methyl groups with δ 1.56 and 1.52 remained unchanged. Irradiation of the protons with δ 1.56 resulted in narrowing of only the signal δ 1.52. Therefore, the methylene group and the methyl groups with δ 1.64 and 1.54 are linked with the same cyclobutene ring, and the other two methyl groups (δ 1.56 and 1.52) are in the other ring. The signals in the ^{13}C NMR spectrum of compound **6a** were assigned with consideration of their multiplicity and chemical shifts, and the assignment of signals in the ^{1}H and ^{13}C NMR spectra of compound **6b** was carried out by analogy with compound **6a**.

The spatial structure of the molecule of triene **6a** is shown in Fig. 1. The bond lengths of the molecule of **6a** are close to the usual ones.[4] The most significant deviation from the expected value of 1.966(29) Å[4] was found for the C—Br bond, whose length is 1.909(3) Å. However, the value of 1.91 Å is normal for a covalent C—Br bond.[5] The length of the C(1)—C(5) bond (1.592(6) Å) almost coincides with the average length (1.588(25) Å) for a $(C)_3C—C(C)_3$ fragment.[4] The decrease in the C(2′)—C(2″) bond length to 1.463(7) Å compared to the value of 1.489(15) Å in the C_{exo}—C=C fragment[4] could be assigned to the contribution of isomeric structure **6b**, but such an interpretation does not correlate with the standard[4] bond lengths C(2′)—C(3′) 1.355(7), C(3′)—C(4′) 1.459(6), and C(4′)—C(4″) 1.334(7) Å.

According to the calculations performed by the molecular mechanics method using the MMX program, the boat-like conformation of the molecule found in crystals is more stable than the chair-like conformation by 2.3 kcal mol^{-1}, while according to quantum-chemical calculations using the PM3 method (the MNDO program[6]), the chair-like form is more stable (Scheme 2). The bending angle in the envelope conformation of the five-membered ring is equal for the boat-like form to 32.8(4)° (experimental), 27.8° (MMX), and 17.0° (PM3). It is interesting to note that the five-membered ring of the molecule must be planar according to the data from the quantum-chemical calculations using the MNDO program.

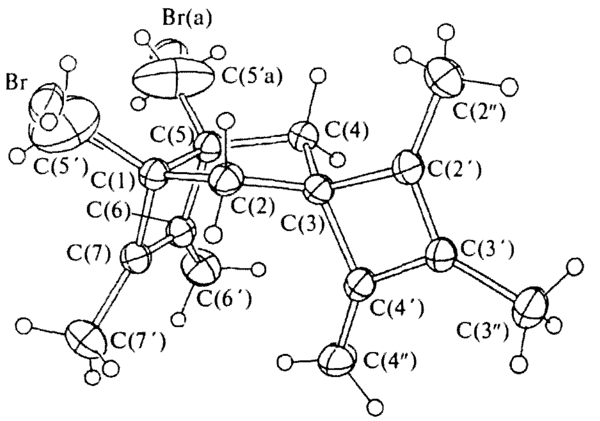
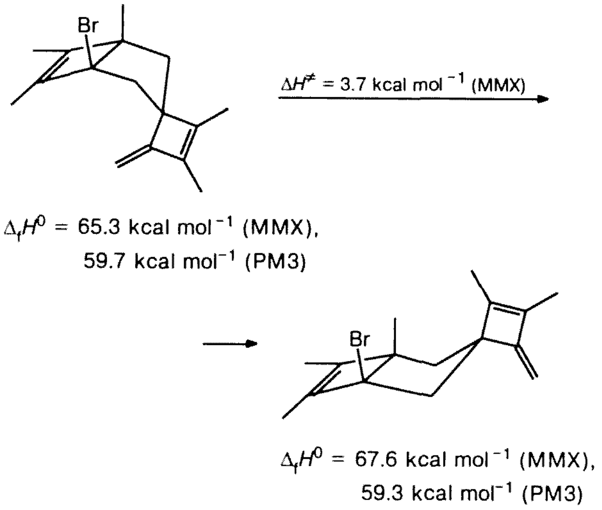


Fig. 1. Spatial structure of the molecule of compound **6a**.

Scheme 2



$\Delta H^{\neq}$ = 3.7 kcal mol^{-1} (MMX)

$\Delta_f H^0$ = 65.3 kcal mol^{-1} (MMX),
59.7 kcal mol^{-1} (PM3)

$\Delta_f H^0$ = 67.6 kcal mol^{-1} (MMX),
59.3 kcal mol^{-1} (PM3)

Experimental

The X-ray analysis for compound **6a** was performed on a SYNTEX P2$_1$ diffractometer using Cu-Kα radiation with a graphite monochromator. The crystals are rhombic: a = 18.539(2), b = 10.638(1), c = 7.5132(8) Å, V = 1481.7(3) Å^3, space group *Pnma*, Z = 4, $C_{16}H_{21}Br$, μ = 3.58 mm^{-1}, d_{calc} = 1.314 g cm^{-3}. A crystal with dimensions of 0.1×0.4×0.6 mm^3 was covered with a thin layer of Vaseline. The intensities of 1190 independent reflections with 2θ < 155° were measured using the θ/2θ scanning technique. Corrections for absorption and a systematic drop (~26%) in the intensities of reference reflections were made with an empirical technique on the basis of the absorption curve of one reflection (absorption 1.1—3.2) and then with the DIFABS program (transmission 0.81—1.51). The structure was solved by a direct method using the SHELX-86 program and refined by the least squares method in a full-matrix anisotropic-isotropic (for hydrogen atoms) approximation using the SHELX-93 program to wR_2 = 0.1382, S = 1.1 for 1190 reflections (R = 0.0521 for 1107 reflections with I > 2σ). The positions of hydrogen atoms were calculated geometrically, but differential synthesis showed the presence of small electronic density peaks at methyl groups C(7′), C(2″), and C(3″), which corresponds to the second orientation of these groups. It follows from the final refinement that the contribution of the minor orientation of the methyl groups

Table 1. Coordinates ($\times 10^4$) and equivalent isotropic parameters (U_{eq}) of non-hydrogen atoms*

Atom	x	y	z	$U_{eq} \cdot 10^3/$ Å^2
Br	3637(1)	895(1)	4465(2)	60(1)
C(1)	4082(2)	1752(3)	2522(4)	39(1)
C(2)	4866(2)	1361(3)	2234(4)	40(1)
C(3)	5250(2)	2500	1401(6)	39(1)
C(7)	3616(2)	1866(3)	873(4)	43(1)
C(2′)	6077(2)	2500	1490(6)	42(1)
C(3′)	6158(2)	2500	−302(6)	42(1)
C(4′)	5383(2)	2500	−632(6)	42(1)
C(5′)	3675(2)	1041(4)	3990(6)	192(19)
C(7′)	3318(2)	884(4)	−306(6)	65(1)
C(2″)	6568(3)	2500	3013(8)	64(2)
C(3″)	6779(3)	2500	−1566(7)	59(1)
C(4″)	4984(3)	2500	−2110(7)	62(2)

* The coordinates of atoms C(4), C(5), C(6), C(6′), C(5′a), and Br(a) (see Fig. 1) can be obtained from the coordinates of atoms C(2), C(1), C(7), C(7′), C(5′), and Br, respectively, by the transformation (x, $0.5-y$, z).

amounts to ~25%. The coordinates and equivalent isotropic parameters obtained for non-hydrogen atoms are listed in Table 1. Positioning the molecule on a mirror image plane leads to superposition of the bromine atom and the methyl group. The attempt to refine the structure in space group $Pna2_1$ did not lead to any change or improvement in the results.

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 or WP 200 SY instruments (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C). The chemical shifts are given in the ppm scale with respect to Me_4Si for solutions in $CDCl_3$; the internal standard was the signal of a solvent at δ_H 7.24 ($CHCl_3$) and δ_C 76.9 ($CDCl_3$).

The determination of molecular weights was performed with a high-resolution Finnigan MAT 8200 mass-spectrometer. The IR spectrum was recorded on a UR-20 spectrometer, and the UV spectrum was obtained on a Specord UV-VIS spectrometer.

Mixture of 1*S*,3*R*,5*R*- and 1*S*,3*S*,5*R*-1-bromo-5,6,7,2′,3′-pentamethyl-4′-methylidenespiro{bicyclo[3.2.0]hept-6-ene-3,1′-cyclobut-2′-enes} (6a and 6b). Allyl bromide (9.59 g, 79.3 mmol) was added to a mixture of magnesium chips activated with iodine (0.913 g, 37.6 mg-at.) and Et_2O (12.5 mL). Then the mixture containing a crystalline precipitate of magnesium bromide etherate was stirred and refluxed for 0.5 h. After completion of the reaction (allylmagnesium bromide was absent in the reaction mixture), a mixture of 3-chloro-1,2,3-trimethyl-4-methylidenecyclobutene (**1**) (1.41 g, 9.89 mmol) and 1,2-dimethyl-3,4-dimethylidenecyclobutene (**3**) (1.41 g, 13.3 mmol) prepared according to the known procedure[7] was added with stirring and refluxed for 2 h. Then 30 mL of pentane was added to the cooled mixture to precipitate magnesium halide etherates, and the precipitate was filtered off. The solvent was removed from the filtrate, and the residue was held at 60 °C (20 Torr) for complete removal of the solvent and treated with 10 mL of pentane. The crystalline product was filtered off, dried, and sublimed at 120 °C (3 Torr). A mixture of isomers **6a** and **6b** was obtained (1.65 g, 57%). M.p. 123—125 °C (decomp.). Found (%): C, 65.76; H, 7.26; Br, 27.23. $C_{16}H_{21}Br$. Calculated (%): C, 65.72; H, 7.23; Br, 27.24. Found with mass spectrometry: mol. weight 292.0812. $C_{16}H_{21}Br$. Calculated: mol. weight 292.0827. IR (CCl_4), ν/cm^{-1}: 870 s, 1030 s, 1375 s, 1435 s, 1625 s, 1690 m, 2850 m, 2915 m, 2960 s. UV [EtOH, λ_{max}/nm (log ε)]: 233 (4.18). The ratio of **6a** : **6b** is 6 : 1 according to the ^{1}H NMR spectral data.

^{1}H NMR ($CDCl_3$), δ: **6a:** 1.25 (s, 3 H, 5-CH_3); 1.48 and 1.64 (both d, 2 H); 2.15 and 2.28 (both d, 2 H, two AB systems, in each J = 14 Hz, C(2)H_2, C(4)H_2); 1.52 and 1.56 (both m, 6 H, 6,7-CH_3); 1.54 and 1.64 (both m, 6 H, 2′,3′-CH_3); 4.01 and 4.11 (both s, 2 H, C(4′)=CH_2); **6b:** 1.66 and 1.81 (both d, 2 H); 2.30 and 2.49 (both d, 2 H, two AB systems, in each J = 14 Hz, C(2)H_2, C(4)H_2); 4.32 (s, 2 H, C(4′)=CH_2); other signals overlap with the signals of isomer **6a**.

^{13}C NMR, δ: **6a:** 8.2, 8.7, 9.1, and 9.6 (all q, 6,7,2′,3′-CH_3); 20.4 (q, 5-CH_3); 37.5 and 43.7 (both t, C(2), C(4)); 58.9 and 59.6 (both s, C(3), C(5)); 77.6 (s, C(1)); 89.2 (t, C(4′)=$\underline{C}H_2$); 138.2, 138.3, 141.0, 148.5, and 158.7 (all s, C(6), C(7), C(2′), C(3′), C(4′)); **6b:** 8.7, 8.9, 9.4, and 11.6 (all q, 6,7,2′,3′-CH_3); 20.4 (q, 5-CH_3); 38.4 and 44.6 (both t, C(2), C(4)); 58.9 and 59.9 (both s, C(3), C(5)); 77.5 (s, C(1)); 88.3 (t, C(4′)=$\underline{C}H_2$); 138.2, 139.1, 140.8, 153.6, and 156.8 (all s, C(6), C(7), C(2′), C(3′), C(4′)).

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