

Adducts of Bromo- and Dibromocarbenes with Dicyclo[6.1.0]non-2-ene and Tricyclo[8.1.0.0^{1,9}.0^{4,6}]deca-2,6-diene in Reaction with Potassium *tert*-Butylate

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Abstract—Adducts of bromo- and dibromocarbenes with bicyclo[6.1.0]non-2-ene and tricyclo[8.1.0.0^{1,9}.0^{4,6}]deca-2,6-diene were studied in reaction with potassium *tert*-butylate in DMSO. The main process was formation of polycyclic cyclopropanes.

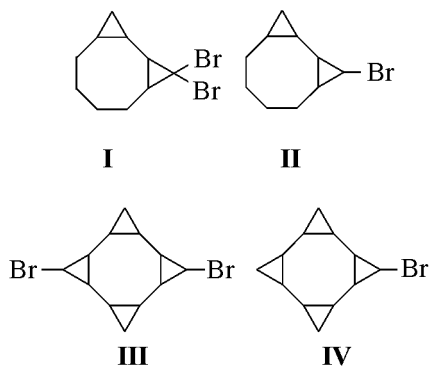
Cyclic cyclopropane polyenes are of interest as synthetic precursors of triangulanes with cyclic substituents [1–4]. Developing approaches to synthesis of the latter we studied the dehydrohalogenation in the series of isomeric dichlorocarbene adducts to bicyclo [6.1.0]non-1-, -2-, and -4-enes. Although in general these reactions occur with conservation of small rings and with migration of multiple bonds, from the reaction of potassium *tert*-butylate and the adduct with reciprocal 1,3-position of 1,1-dichlorocyclopropane ring and unsubstituted three-membered fragment in an eight-membered ring was separated a single product, 3-chlorotricyclo[7.1.0.0^{2,4}]dec-2-ene [5].

We report here on the extension of these investigations to the study of dehydrohalogenation effected with potassium *tert*-butylate on a series of promising bromosubstituted polycyclic compounds **I–IV**. The specific structural feature of the initial **I–IV** compounds is the presence of reciprocally 1,3-located

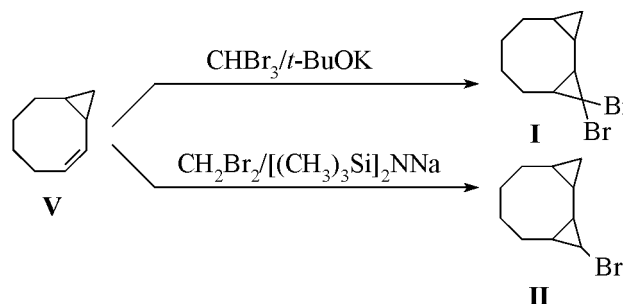
unsubstituted and bromosubstituted cyclopropane fragments.

Bromides **I**, **II** were prepared from bicyclo[6.1.0]non-2-ene (**V**) that in its turn was obtained by two-stage cyclopropanation of 1,3-cyclooctadiene including dichlorocarbene addition followed by reduction of the monoadduct with lithium in *tert*-butanol [6]; the direct cyclopropanation of 1,3-cyclooctadiene with diazomethane was inefficient [7]. Reaction of cycloolefin **V** with dibromocarbene generated by von Doering method [8] afforded adduct **I** in 60% yield (Scheme 1), and the bromocarbene obtained from dibromomethane in the presence of sodium bis(trimethylsilyl)amide by procedure [9] adds to cycloolefin **V** providing compound **II** in 40% yield. The structure of the latter was determined by NMR spectroscopy (see EXPERIMENTAL).

We tried several approaches to the synthesis of dibromopentacyclododecene **III**. To our regret, the reactions of diazomethane and bromocarbene with diene **VIII** failed due to the low reactivity of the double bonds in the latter. The most efficient was the method involving reduction of tetrabromide **VI** into

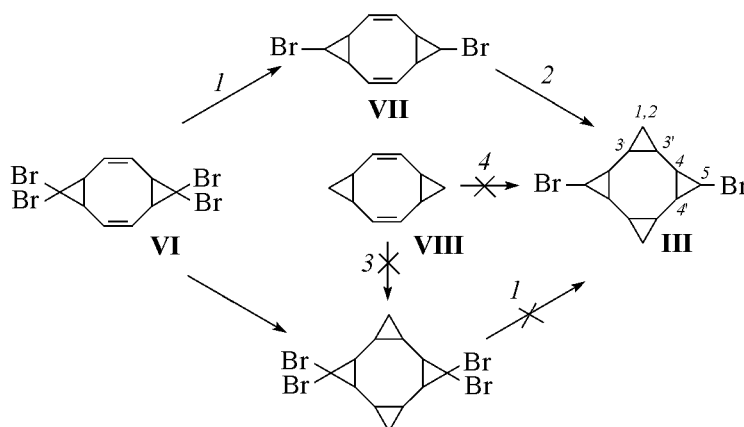


Scheme 1.



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Scheme 2.



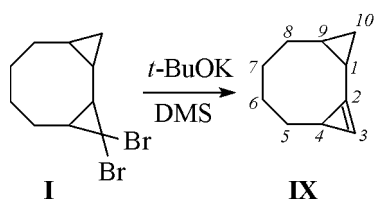
(1) Bu_3SnH , (2) $\text{CH}_2\text{N}_2/\text{Pd}(\text{OAc})_2$, (3) $\text{CHBr}_3/t\text{-BuOK}$, (4) $\text{CH}_2\text{Br}_2/[(\text{CH}_3)_3\text{Si}]_2\text{NNa}$.

dibromide **VII** followed by cyclopropanation (Scheme 2).

The reduction of tetrabromide **VI** with tributyltin hydride [10] occurs under mild conditions (45°C , 2 h) and furnishes dibromide **VII** in 97% yield. The target dibromide **III** was obtained in 92% yield by cyclopropanation of dibromide **VII** with diazomethane in the presence of palladium diacetate along procedure [11, 12]. The structure of dibromide **III** was proved by NMR spectroscopy. In particular, the proton-proton Overhauser effect showed endo,endo position of bromine atoms in the molecule of dibromide **III**. The signals of ^1H and ^{13}C NMR spectra were assigned with the use of two-dimensional correlation spectra. The data are presented in EXPERIMENTAL.

The obtained polycyclic bromides **I-III** were reacted with potassium *tert*-butylate in DMSO solution. We found unexpectedly that the reaction of dibromide **I** with potassium *tert*-butylate resulted in 62% yield of compound **IX** containing a cyclopropene fragment (Scheme 3). The latter apparently arises from combination of dehydrobromination and reduction.

Scheme 3.

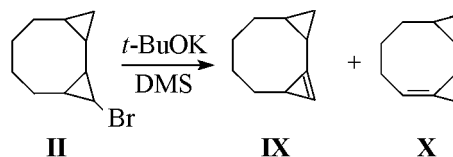


Compound **IX** is sufficiently stable and can be stored for a long time (several weeks at -20°C and several hours a room temperature). Its structure was

reliably proved by mass-spectral data and by ^1H and ^{13}C NMR spectra registered with the use of two-dimensional $^1\text{H}\text{-}^1\text{H}$ and $^1\text{H}\text{-}^{13}\text{C}$ COZY procedure. For instance, the presence of the cyclopropene fragment in the molecule of compound **IX** is evidenced by ^{13}C NMR spectrum: the signals belonging to the tertiary (C^3) and quaternary (C^2) carbon atoms are located in a weak field at δ_{C} 99.89 and 125.29 ppm, and for C^3 carbon is observed a large coupling constant J_{CH} equal to 221 Hz typical for cyclopropene [13] (see EXPERIMENTAL).

Reaction of monobromide **II** with potassium *tert*-butylate in DMSO afforded a mixture of two isomeric cycloolefins **IX** and **X** in overall yield 70% and in 1:1 ratio according to NMR data (Scheme 4).

Scheme 4.



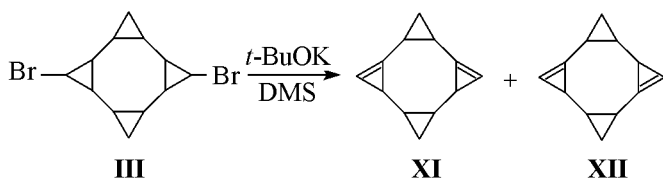
In the ^1H NMR spectrum of the isomer mixture **IX** and **X** the aliphatic protons appear as complicated overlapping multiplets preventing assignment of the signals. Two downfield signals at 6.35 and 5.92 ppm correspond to two olefin protons of isomers **IX** and **X** respectively.

The ^{13}C NMR spectra of **IX** and **X** compounds mixture are more informative. The assignment of the resonance peaks corresponding to olefin **X** was done unambiguously with the use of the data on the respective spectrum of compound **IX**. The difference

in the spectral parameters of compounds **IX** and **X** is consistent with the structural difference. The most characteristic are the signals of the carbon atoms at the multiple bonds. For instance, the carbon in CH= group of compound **X** is considerably deshielded (δ_c 117.16 ppm) as compared to the cyclopropene carbon in olefin **IX** (δ_c 99.85 ppm). The coupling constant found for this atom has a value typical for unstrained multiple bonds, J_{CH} 158 Hz. The coupling constants J_{HH} of CH= groups in these compounds are also different. In olefin **IX** the coupling is rather weak ($^3J_{3,4}$ 2.0 Hz) in agreement with the published data [13]. In the mass spectra of the mixture of compounds **IX** and **X** appears the molecular ion peak at m/z 134 corresponding to the molecular weight of each isomer.

Especially interesting is the reaction between potassium *tert*-butylate in DMSO and polycyclic dibromide **III**. The dehydrohalogenation of dibromide **III** effected by potassium *tert*-butylate provided a mixture of two isomeric olefins **XI** and **XII** in approximately equal amounts (Scheme 5). The 1H and ^{13}C NMR spectra evidence the actual formation of olefins with cyclopropene fragments. Same as with olefin **IX** the double bond does not migrate into the eight-membered ring. In this connection we should mention that in the previously studied dehydrohalogenation of bromide **IV** [14] the corresponding cyclopropene derivative was not isolated and a fast migration of the double bond into the eight-membered ring occurred to result in formation of a cyclic bicyclopropylidene. Compounds **XI** and **XII** were far less stable than compound **IX**, and we failed to isolate them as individual substances.

Scheme 5



The NMR spectra of dehydrohalogenation products **XI** and **XII** are in accordance with the spectra of compound **IX**; moreover, the spectral data of the latter resemble in some aspects those of methylenecyclopropane dimer [15]. The saturated carbons of the cyclopropane fragments in the above hydrocarbons appear as signals in their typical upfield region (10–26 ppm). The carbon atoms in the CH= moieties of the cyclopropene fragments are significantly more shielded (δ 104.4 and 104.8 ppm) as

compared to unstrained cycloolefins. These data are supported by 1H NMR spectra. Alongside a series of strongly overlapped multiplets in the upfield region corresponding to the protons attached to the saturated carbons in the three-membered rings, in the spectrum of the mixture of compounds **XI** and **XII** are observed proton signals in the weak field characteristic of cyclopropene fragments at δ , ppm, 6.71 d.d (3J 1.5, 4J 1.5 Hz) and 6.85 d (3J 2.0 Hz).

Thus the presence in the molecules of polyhalo-derivatives of cycloalkanes of three-membered rings in 1,3 position results in specific behavior in dehydrohalogenation effected by potassium *tert*-butylate: the main result of these reactions becomes formation of polycycloalkenes with cyclopropene fragments.

EXPERIMENTAL

1H and ^{13}C NMR spectra were registered on spectrometer Varian VXR-400 (400 MHz for protons), solvent $CDCl_3$, internal reference TMS. Mass spectra were measured on Varian MAT 311A and 1321A instruments.

The original bicyclo[6.1.0]non-2-ene (**V**) [5], 5,5,10,10-tetrabromotricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**VI**) [10], 5-*endo*-10-*endo*-dibromotricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**VII**) [10], tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (**VIII**) [5, 16], 3,3-dibromotricyclo[7.1.0.0^{2,4}]decane (**I**) [17] were prepared by procedures described before.

3-Bromotricyclo[7.1.0.0^{2,4}]decane (II). To a mixture of 9.15 g (0.075 mol) of cycloolefin **V** and 9 g (0.05 mol) of sodium bis(trimethylsilyl)amide in 30 ml of anhydrous hexane was added at cooling to $-20^\circ C$ while stirring 8.7 g (0.05 mol) of dibromomethane. Therewith the reaction mixture heated to $45-55^\circ C$. After cooling of the reaction mixture to room temperature it was treated with 50 ml of ice water. The organic layer was washed with water, the solvent was distilled off, and the residue was distilled in a vacuum. We obtained 4.3 g (40%) of bromide **II** as a mixture of *endo*- and *exo*-isomers, bp $81-83^\circ C$ (2 mm Hg) 1H NMR spectrum (δ , ppm, J , Hz): 0.05 m (1H), 0.6–1.3 m (9H), 1.90 m (2H), 2.20 d.d (1H, 3J 7.9, 2J 12.4), 3.43 t (1H, 3J 7.7). ^{13}C NMR spectrum (δ_c , ppm, J_{CH} , Hz): 12.27 (CH, J_{CH} 163), 14.32 (CH₂, J_{CH} 158), 18.39 (CH, J_{CH} 161), 18.81 (CH, J_{CH} 156), 22.49 (CH, J_{CH} 157), 26.31 (CH₂, J_{CH} 123), 28.73 (CH₂, J_{CH} 125), 29.60 (CH₂, J_{CH} 125), 29.77 (CH₂, J_{CH} 124), 33.47 (CH, J_{CH} 191). Found, %: C 56.06, 55.78; H 6.73, 6.77. M 214, 215. $C_{10}H_{15}Br$. Calculated, %: C 55.81; H 6.98. M 215.

3-endo-9-endo-Dibromopentacyclo-[9.1.0.0^{2,4}.0^{5,7}.0^{8,10}] dodecene (III). Cyclopropanation of 0.8 g of dibromide **VII** with ether solution of diazomethane (prepared from 5 g of *N*-nitroso-*N*-methylurea) in the presence Pd(OAc)₂ at 0°C afforded 1 g of a reaction product. By means of column chromatography on SiO₂ (eluent petroleum ether) dibromide **III** was separated from the reaction product as colorless crystals in amount of 0.8 g (92%), mp 122°C. Mass spectrum, *m/z* (*I*_{rel}, %): 316 (1.2), 318 (2.5), 320 (1.2) [*M*]⁺, 239 (29.5), 237 (35.2), 157 (73.8), 141 (46.7), 129 (86.1), 115 (76.2), 91 (63.1), 77 (39.3), 36 (100). ¹H NMR spectrum (δ, ppm, *J*, Hz)*: 0.34 d.t (2H¹), 0.78 m (2H⁴, 2H⁴, *J*_{4,4'} 10), 0.96 m (2H³, 2H³, *J*_{5,1} 5.1, *J*_{3,4} 7.0, *J*_{3,3'} 11.0), 1.09 d.t (2H², *J*_{1,2} 5.0, *J*_{2,3} 8.5), 3.57 t (2H⁵, *J*_{4,5} 8.0). ¹³C NMR spectrum (δ_C, ppm): 12.88 (C²), 15.50 (C¹), 21.25 (C³), 32.16 (C⁴).

Reactions of bromides I–III with potassium *tert*-butylate (general procedure). A solution of 0.01 mol of monobromide **I** or dibromides **II**, **III** in 10 ml of anhydrous DMSO was added under inert atmosphere at cooling to 0–5°C while stirring to a solution of 0.03 mol (0.05 mol in case of dibromides **II**, **III**) of potassium *tert*-butylate in 40 ml of anhydrous DMSO. The reaction mixture was stirred for 12 h at room temperature, then treated with 50 ml of ice water, the reaction products were extracted into pentane (3×15 ml). The extract was washed with water, the solvent was removed on a rotary evaporator without heating. The residue was analyzed by NMR and GC-MS method.

Tricyclo[7.1.0.0^{2,4}]dec-2-ene (IX). From 2.94 g of dibromide **I** was obtained 0.8 g (61%) of hydrocarbon **IX**. Mass spectrum, *m/z* (*I*_{rel}, %): 134 (4.3) [*M*]⁺, 119 (18.1), 105 (38.3), 91 (100), 79 (48.9), 65 (31.9), 51 (19.1), 39 (61.7). ¹H NMR spectrum (δ, ppm, *J*, Hz)**: 0.44 d.d.d (1H¹⁰, ³*J*_{1,10} 5.2, ³*J*_{9,10} 5.3; ²*J*_{10,10'} 4.2), 1.03 d.d.d (1H¹⁰, ³*J*_{1,10} 8.6, ³*J*_{9,10} 7.9, ²*J*_{10,10'} 4.2), 1.10 m (1H⁹), 1.08–1.13 m (2H^{8,8'}), 1.41 m (1H⁶), 1.42–1.43 m (2H^{5,5'}), 1.46–1.48 m (2H^{7,7'}), 1.62 m (1H⁴), 1.92 d.d.d (1H, ³*J*_{1,10} 5.2, ³*J*_{1,10'} 8.6, ³*J*_{1,9} 7.8), 2.12 m (1H⁶), 6.42 d (1H³,

³*J*_{3,4} 2.0). ¹³C NMR spectrum (δ_C, ppm): 12.23 (C¹), 12.24 (C¹⁰), 15.93 (C⁴), 18.57 (C⁸), 18.80 (C⁹), 26.83 (C⁶), 29.21 (C⁷), 32.10 (C⁵), 99.89 (C³), 125.29 (C²).

Dehydrobromination of monobromide II. From 1 g (0.005 mol) of monobromide **II** we obtained 0.42 g (70%) of a mixture of olefins **IX**, **X**. Mass spectrum, *m/z* (*I*_{rel}, %): 134 (6.5) [*M*]⁺, 119 (19.6), 105 (28.7), 91 (100), 92 (59.0), 79 (42.6), 66 (17.2), 51 (8.2), 41 (14.7), 39 (18.8), 27 (8.2). ¹H NMR spectrum (δ, ppm, *J*, Hz): 0.13 m (1H), 0.37 m (1H), 0.6–2.2 m (24H), 5.92 m (1H), 6.35 d (1H, ³*J* 1.9). ¹³C NMR spectra (δ_C, ppm, *J*_{CH}, Hz), olefin **IX**: 12.14 (C¹), 12.22 (C¹⁰), 15.86 (C⁴), 18.54 (C⁸), 18.75 (C⁹), 26.76 (C⁶), 29.10 (C⁷), 32.07 (C⁵), 99.85 (C³, 221), 125.58 (C²); olefin **X**: 10.72 (CH₂), 11.66 (CH₂), 14.31 (CH), 17.55 (CH), 18.39 (CH), 24.39 (CH₂), 29.69 (CH₂), 30.84 (CH₂), 117.16 (CH, 158), 134.09 (C).

Dehydrobromination of dibromide III. From 0.8 g (2.7 mmol) of dibromide **III** we obtained 0.23 g (58%) of a mixture of isomer dienes **XI**, **XII**. ¹H NMR spectrum (δ, ppm, *J*, Hz): 0.7–1.7 m (11H), 2.38 m (1H), 6.68 d.d (1H, ³*J* 1.5, ⁴*J* 1.5), 6.82 d (1H, ³*J* 2.0). ¹³C NMR spectra (δ_C, ppm), diene **XI**: 10.85 (CH₂), 14.21 (CH), 14.31 (CH₂), 16.96 (CH), 20.18 (CH), 104.44 (CH), 124.71 (C); diene **XII**: 12.83 (CH₂), 13.24 (CH), 17.19 (CH), 25.88 (CH), 104.88 (CH), 126.60 (C).

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* The numbering of protons in compound **III** is given on Scheme 2. The assignment of proton signals was provided by the data of two-dimensional spectroscopy H–H COZY.

** The numbering of atoms in compound **IX** is given on Scheme 3.

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