Dehydrohalogenation of adducts of dichlorocarbene with cyclooctene and its peripherally cyclopropanated analogs

T. S. Kuznetsova, O. V. Kokoreva, E. B. Averina, A. N. Zefirov, Yu. K. Grishin, and N. S. Zefirov*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 0290. E-mail: kuzn@org.chem.msu.su

Dehydrohalogenation of three isomeric adducts of dichlorocarbene with bicyclo[6.1.0]non-1-, -2-, and -4-enes under the action of potassium *tert*-butoxide in DMSO was studied. In the course of dehydrohalogenation of the substrates under study, different isomerization processes, which were accompanied by repeated migrations of multiple bonds that formed, occurred depending on the structure of dichlorides, while no skeletal rearrangements were observed.

Key words: cyclopropanation, dichlorocyclopropanation, polyspirocyclopropanes, dehydrohalogenation.

The problem of the synthesis of triangulanes[1] is still unresolved. One possible approach to the synthesis of [8]-cyclotriangulane involves peripheral cyclopropanation of cyclooctene derivatives.[1–5]

This approach involves the following stages: (a) addition of monobromocarbene to the cyclooctene double bond; (b) dehydrobromination accompanied by migration of the cyclopropene double bond to the *endo* position with respect to the eight-membered ring; and finally, either repetition of these two stages or (c) cyclopropanation at the double bond.[1–3]

It is readily seen that the migration of the double bond to the methylenecyclopropane position is the key idea of the overall process. In this case, elimination of hydrohalide accompanied by the transfer of the reaction center allows one to avoid the synthesis of difficultly accessible precursors, such as 1-halobicyclo[6.1.0]nonane, whose eight-membered ring contains the functional group that is capable of being eliminated.

When developing synthetic approaches to ring-substituted and cyclic triangulanes,[1–5] we came to the conclusion that dehydrohalogenation should be studied experimentally for a series of adducts of dichlorocarbene with cyclooctene and related cycloolefins containing an eight-membered ring. Actually, the addition of dichlorocarbene has been studied in substantially more detail than that of other halocarbenes. This reaction is preparatively convenient, and detailed universal procedures were developed for performing it. However, dehydrohalogenation of dichlorocyclopropanes is poorly studied. It is known that under conditions of dehydrohalogenation (a strong base in a polar solvent) the latter compounds initially form highly reactive cyclopropenes, which often add nucleophiles under the reaction conditions[6–8] or appear to be unstable and undergo further conversions, namely, *exo* isomerization of the cyclopropene double bond[9,10] or rearrangements.[10–13]

It is known[10,14] that dehydrochlorination of 9,9-dichlorobicyclo[6.1.0]nonane under the action of potassium *tert*-butoxide in dimethyl sulfoxide affords bicyclo[6.1.0]nona-1,6-diene. We considered the results of this reaction, which seem to be very interesting. First, the reaction proceeds with retention of the small ring. Second, the reaction is accompanied by long-distance migrations of multiple bonds rather than simple β-elimination. To put it differently, this reaction is accompanied by the pronounced transfer of the reaction centers. Finally, this reaction affords the diene structure, which is promising in synthesis; in particular, it is suitable for the synthesis of ring-substituted triangulanes.[4,5]

The aforesaid gave impetus to an investigation of dehydrohalogenation of three isomeric tricyclic dichlorocyclopropanes, *viz.*, 5,5-dichlorotricyclo[7.1.0.0^{4,6}]decane (**1**), 3,3-dichlorotricyclo[7.1.0.0^{2,4}]decane (**2**), and 2,2-dichlorotricyclo[7.1.0.0^{1,3}]decane (**3**), which are cyclopropanated analogs of 9,9-dichlorobicyclo-[6.1.0]nonane. Our objective was to elucidate whether dehydrochlorination of dichlorides **1**—**3** can afford endocylcic olefins or dienes, which can serve as starting compounds for preparing ring-substituted triangulanes.

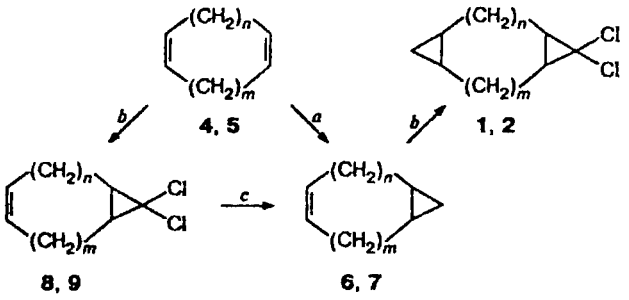
The initial dichlorocyclopropanes **1** and **2** were prepared according to two procedures based on [1+2]-cycloaddition of carbenes to cyclooctadienes **4** and **5** (Scheme 1).

According to the first procedure, the starting dienes were initially cyclopropanated with diazomethane in the presence of $Pd(OAc)_2$ [15,16] (stage *a*) and then olefins **6** and **7** were introduced into the reaction (stage *b*) with dichlorocarbene (phase-transfer synthesis with the use

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 938—942, May, 1999.

1066-5285/99/4805-0929 $22.00

Scheme 1

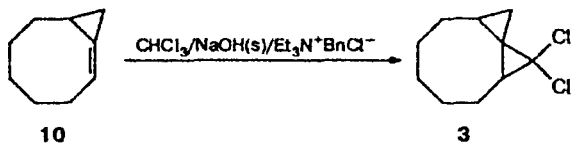


1, **4**, **6**, **8**: $n = m = 2$
2, **5**, **7**, **9**: $n = 0$, $m = 4$

Reagents: *a*, $CH_2N_2/Pd(OAc)_2$;
b, $CHCl_3/NaOH(s)/Et_3N^+BnCl^-$; *c*, Li/Bu^{t}OH.

of solid NaOH) to obtain target dichlorides **1** and **2** as mixtures of *cis* and *trans* isomers in yields higher than 60%. However, although direct cyclopropanation of dienes **4** and **5** afforded olefins **6** and **7**, their actual yields at this stage were low (40%) due to formation of mixtures of the initial diene and mono- and bisadducts, which were difficult to separate. We demonstrated that reduction of dichlorides **8** and **9**, which were formed as a result of addition of dichlorocarbene (stage *b*) to the initial dienes,[17] with lithium in Bu^{t}OH [18] readily yielded olefins **6** and **7**, owing to which the three-stage procedure for the preparation of dichlorides **1** and **2** ($b \rightarrow c \rightarrow b$) appeared to be preferable to the two-stage procedure ($a \rightarrow b$, see Scheme 1).

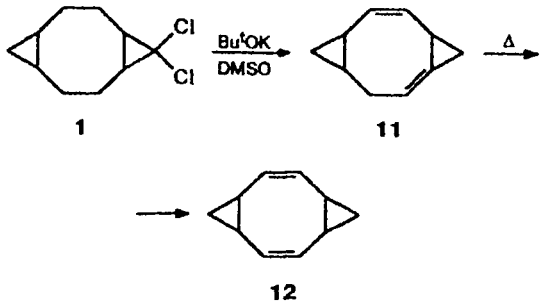
The initial 2,2-dichlorotricyclo[7.1.0.0^{1,3}]decane (**3**) was prepared in 82% yield by dichlorocyclopropanation of bicyclo[6.1.0]non-1-ene (**10**).[19]



The structures of polycyclic dichlorides **2** and **3** were established by NMR spectroscopy and GLC-mass spectrometry (see Experimental). The values of the spin-spin coupling constants of the methine protons ($J_{H(1)H(2)}$ = 4.9 Hz) are indicative of the *anti* arrangement of two small rings in molecule **2**.

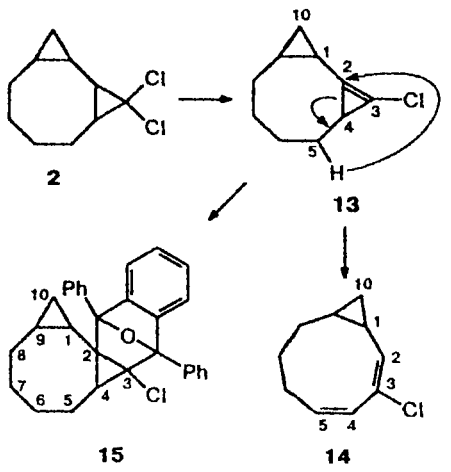
Dehydrohalogenation of dichlorocyclopropanes **1**—**3** was carried out under the action of potassium *tert*-butoxide in DMSO under the standard conditions at 20 °C.

The reaction of dichloride **1** with Bu^{t}OK under these conditions afforded diene **11**,[5] which was unstable at room temperature. The latter was isolated by flash distillation in 45% yield. Compound **11** remained unchanged for some time at −30 °C as a solution in pentane. Thermolysis of diene **11** at ~100 °C led to migration of the methylenecyclopropane multiple bond to form thermodynamically more stable diene **12** containing the *exo*-oriented cyclopropane fragments.[20]



Dehydrohalogenation of dichloride **2** proceeded differently. Under the action of potassium *tert*-butoxide in DMSO at 15 °C, compound **2** gave only one reaction product, *viz.*, chlorocyclopropene **13** (Scheme 2). Compound **13** was rather stable and remained unchanged upon storage at least for 3 days. However, when heated (above 100 °C), chlorocyclopropene **13** underwent complete isomerization accompanied by opening of the cyclopropene ring to form chlorodiene **14**.

Scheme 2



The structures of cyclopropene **13** and chlorodiene **14** were completely confirmed by ^{1}H NMR spectra obtained with the use of the double resonance and 2D ^{1}H—^{1}H COSY correlation techniques as well as by ^{13}C NMR spectra. The mass spectra of chlorides **13** and **14** have signals at *m/z* 170 and 168 ([M]$^+$) and at *m/z* 133 ([M − Cl]$^+$), which confirm the molecular formulas of these compounds.

The ^{1}H and ^{13}C NMR spectra of compound **13** have characteristic high-field signals corresponding to the cyclopropane fragment. The values of the constants J_{HH} and $^1J_{CH}$ for these signals are typical of these systems.[21]

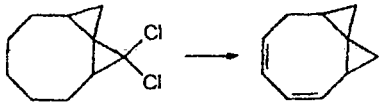
The ^{13}C NMR spectrum of molecule **13** is indicative of the presence of an unsaturated three-membered ring. The tertiary carbon atoms of the multiple bond of this ring have chemical shifts typical of cyclopropenes.[22] The methine C atom of the cyclopropene fragment is characterized by the high value of $^1J_{CH}$ (172 Hz). The noticeable downfield shift of this signal (δ 27.9) compared to that of cyclopropene is caused by the effect of the substituent (Cl). The absence of spin-spin coupling of the H(1) proton with other protons, except for those which also belong to the cyclopropane ring, and the presence of spin-spin coupling between the H(4) proton and the protons of the methylene group $C(5)H_2$ unambiguously reveal the position of the multiple bond.

The structure of chloride **13** is additionally confirmed by diene synthesis with diphenylisobenzofuran to form adduct **15** in quantitative yield (see Scheme 2).

The structure of this adduct was unambiguously established by NMR spectroscopy. In the NMR spectrum of adduct **15** in $CDCl_3$, it was difficult to assign signals for the protons of the eight-membered ring due to their substantial overlapping, while these signals appeared to be rather well resolved when C_6D_6 was used. The ^1H and ^{13}C NMR spectra are indicative of the retention of the eight-membered and saturated three-membered rings in the product of the diene synthesis. It should be noted that the signals for the protons of the small ring of product **15** are observed at higher field (at δ 0.1—0.7 in $CDCl_3$ and at δ 0.2—0.4 in C_6D_6) compared to those of compound **13** and the methine proton of the chlorine-substituted cyclopropane fragment is subjected to substantial (0.95 ppm in C_6D_6) deshielding.

The structure of compound **14**, which is a product of opening of the cyclopropene fragment of chloride **13** to form a conjugated diene system, was also established based on the ^1H and ^{13}C NMR spectra. The values of the constants J_{HH} allow one to judge the position of the Cl atom in the molecule (see Experimental).

Finally, we studied dehydrohalogenation of 2,2-dichlorotricyclo[7.1.0.0^{1,3}]decane (**3**). This substrate is of particular interest because it has the structure of ring-substituted triangulane. Treatment of dichloride **3** with potassium *tert*-butoxide in DMSO at 15 °C afforded tricyclo[7.1.0.0^{1,3}]deca-4,6-diene (**16**) as the major reaction product.



3 **16**

It is worthy of note that this diene was formed as a result of repeated (no less than eight times!) migrations of double bonds. However, in spite of the presence of the spirocyclopropane fragment, the reaction was not accompanied by skeletal rearrangements.

Diene **16** was isolated by preparative gas chromatography. Its structure was established by NMR spectroscopy with the use of the double heteronuclear resonance and 2D correlation $^1H—^1H$ COSY techniques. Two multiple bonds in the molecule form the conjugated 1,3-diene system. The observed spin-spin coupling constants of the terminal protons of the diene fragment are indicative of its conjugation with one cyclopropane ring. The ^1H and ^{13}C NMR spectra of the spiropentane fragment, which gives signals at the highest field, can be rather readily interpreted. In this case, the signal for the tertiary carbon atom (δ 17.56) confirms the presence of a *spiro*-atom in the molecule. The mass spectrum has the major peak at *m/z* 132 ($[M]^+$), which corresponds to the molecular formula $C_{10}H_{12}$.

In conclusion, note that dehydrohalogenation of eight-membered *gem*-dichlorocyclopropanes **1**—**3** under the action of potassium *tert*-butoxide in DMSO was not accompanied by skeletal rearrangements and, depending on the structure of the dichlorides, led to rather long-distance migrations of the multiple bonds that formed. This makes it possible to prepare interesting synthetically promising diene structures, which are difficultly accessible with the use of other synthetic procedures.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument (400 and 100 MHz, respectively). The mass spectra were obtained on Varian MAT-311A and MX-1321A instruments. The GLC analysis was carried out on a Chrom-5 chromatograph (flame ionization detector, 3000×3-mm column, 15% SE-30 on Chromaton N-AW, nitrogen as the carrier gas, 60 mL min^{-1}). Preparative gas chromatography was performed on a PAKhV-08 instrument (katharometer as the detector, 5600×5-mm column, 10% SE-30 on Chromaton N-AW, helium as the carrier gas, 180 mL min^{-1}). The initial olefins, *viz.*, bicyclo[6.1.0]non-4-ene (**6**),[15] bicyclo[6.1.0]non-2-ene (**7**),[16] and bicyclo[6.1.0]non-1-ene (**10**),[19] were prepared according to procedures reported previously. Dimethyl sulfoxide was dried according to a known procedure.[23]

Dichlorocyclopropanation (general procedure). Finely dispersed NaOH (11.8 g, 0.3 mol) was added portionwise with intense stirring to a mixture of cycloalkene (**4**—**7** or **10**) (0.01 mol), $CHCl_3$ (7.8 mL, 0.01 mol), and $Et_3N^+BnCl^-$ (0.3 g) in hexane (60 mL) at 5—10 °C. The reaction mixture was stirred at 10 °C for 1 h and then at 20 °C for 1 h. Ice water (100 mL) was added and the mixture was extracted with hexane or chloroform. The organic solutions were dried with $MgSO_4$, the solvent was distilled off, and the residue was distilled *in vacuo*. The physicochemical constants of dichlorides **8** [17] and **9** [17] and also dichloride **1** [24] (a 3 : 1 mixture of isomers) correspond to the published data.

3,3-Dichlorotricyclo[7.1.0.0^{2,4}]decane (2) was prepared from olefin **7** in 63.4% yield, b.p. 104—106 °C (2 Torr). ^1H NMR ($CDCl_3$), δ: 0.10 (ddd, 1 H, *anti*-$H(10)_a$, ^2J = 4.5 Hz, ^3J = 4.3 and 4.6 Hz); 0.62 (m, 1 H, $H(7)_a$); 0.65 (m, 1 H, 1 H(9)); 0.84 (m, 1 H, H(1)); 0.97 (ddd, 1 H, *syn*-$H(10)_b$, ^2J = 4.5 Hz, ^3J = 8.3 and 8.5 Hz); 1.11 (m, 1 H,

$H(5)_a$); 1.19 (m, 1 H, $H(8)_a$); 1.21 (m, 1 H, $H(6)_a$); 1.35 (dd, 1 H, H(2), ^3J = 10.2 and 4.9 Hz); 1.48 (ddd, 1 H, H(4), ^3J = 2.7, 10.2, and 10.9 Hz); 1.84 (m, 1 H, $H(8)_b$); 1.89 (m, 1 H, $H(6)_b$); 2.14 (ddd, 1 H, $H(5)_b$, ^2J = 13.9 Hz, ^3J = 2.7 and 8.5 Hz); 2.20 (dd, 1 H, $H(7)_b$, ^2J = 12.5 Hz, ^3J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 10.90 (C(9), J = 164 Hz); 14.19 (C(10), J = 160 Hz); 18.20 (C(1), J = 160 Hz); 25.08 (C(5), J = 130 Hz); 27.93 (C(6), J = 128 Hz); 29.37 (C(7), J = 126 Hz); 29.53 (C(8), J = 126 Hz); 32.16 (C(2), J = 166 Hz); 35.54 (C(4), J = 166 Hz); 67.06 (C(3)). MS, m/z (I_{rel} (%)): 204* $[M]^+$ (0.5), 169 $[M - Cl]^+$ (0.5), 134 $[M - 2\ Cl]^+$ (1), 113 (15), 97 (100), 83 (14), 67 (21), 57 (68), 41 (80).

2,2-Dichlorobicyclo[7.1.0.0^{1,3}]decane (3) was prepared from olefin **10** in 82% yield, b.p. 84—89 °C (2 Torr). ^{1}H NMR ($CDCl_3$), δ: 0.90—1.10 (m, 2 H, $H(10)_a$, $H(10)_b$); 1.11—1.25 (m, 3 H); 1.30—2.00 (m, 8 H); 2.02—2.10 (m, 1 H, $H(10)_b$). ^{13}C NMR ($CDCl_3$), δ: 8.32 (C(10)); 16.24 (CH_2); 20.44 (C(9)); 25.40 (CH_2); 26.22 (CH_2); 28.60 (C(3)); 29.06 (CH_2); 29.37 (CH_2); 32.93 (C(1)); 62.33 (C(2)). Found (%): C, 58.88; H, 6.80; Cl, 33.86. $C_{10}H_{16}Cl_2$. Calculated (%): C, 58.82; H, 6.68; Cl, 34.31.

Dehydrochlorination of dichlorides 1—3. A solution of dichlorocyclopropane (8 mmol) in anhydrous DMSO (7 mL) was added dropwise to an intensively stirred solution of potassium *tert*-butoxide (24 mmol) in anhydrous DMSO (20 mL) under an argon atmosphere upon cooling (bath, 10 °C). The reaction mixture was stirred for 5 h and then hexane (50 mL) and ice water (20 mL) were added. The organic layer was washed three times with water and dried with $MgSO_4$. Then the solvent was removed.

Tricyclo[7.1.0.0^{4,6}]deca-1,7-diene (11) was prepared from compound **1** and isolated by flash distillation *in vacuo* (10^{-2}—10^{-3} Torr) in 40% yield. The ^{1}H and ^{13}C NMR spectra correspond to the published data.[5]

3-Chlorocyclo[7.1.0.0^{2,4}]dec-2-ene (13) was prepared from dichloride **2** in 63.5% yield. Compound **13** was isolated by filtration of the reaction mixture through a silica gel layer (40/100 μm) with hexane as the eluent. ^{1}H NMR ($CDCl_3$), δ: 0.38 (ddd, 1 H, *anti*-$H(10)_a$, $^3J_{H(9),H(10)_a}$ = 5.3 Hz, $J_{H(11),H(13)}$ = 5.2 Hz, $^3J_{H(1),H(10)_a}$ = 5.2 Hz, $^2J_{H(10)_aH(10)_b}$ = 4.5 Hz); 1.02 (ddd, 1 H, *syn*-$H(10)_b$, $^3J_{H(9),H(10)_b}$ = 7.5 Hz, $^3J_{H(1),H(10)_b}$ = 8.7 Hz); 1.14 (m, 1 H, H(9)); 1.15—1.20 (m, 2 H, 2 H(8)); 1.18 (m, 1 H, $H(6)_a$); 1.26 (m, 1 H, $H(7)_a$); 1.35 (m, 1 H, $H(5)_a$); 1.47 (m, 1 H, $H(7)_b$); 1.59 (ddd, 1 H, $H(5)_b$, $^3J_{H(4),H(5)_b}$ = 2.0 Hz, $^2J_{H(5)_a,H(5)_b}$ = 13.5 Hz, $^3J_{H(5)_b,H(6)_a}$ = 7.3 Hz); 1.87 (ddd, 1 H, H(1), $^3J_{H(1),H(9)}$ = 7.9 Hz); 2.11 (dddd, 1 H, $H(6)_b$, $^3J_{H(6)_b,H(7)_b}$ = 3.8 Hz, $^2J_{H(6)_a,H(6)_b}$ = 13.6 Hz, $^3J_{H(6)_b,H(7)_a}$ = 3.6 Hz, $^3J_{H(5)_b,H(6)_b}$ = 3.7 Hz); 2.20 (dd, 1 H, H(4), $^3J_{H(4),H(5)_a}$ = 4.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 10.21 (C(1), J = 166 Hz); 12.21 (C(10), J = 163 Hz); 18.34 (C(8), J = 130 Hz); 18.63 (C(9), J = 164 Hz); 26.76 (J = 128 Hz), 28.96 (J = 125 Hz), 29.02 (J = 125 Hz) (C(5)—C(7)); 27.87 (C(4), J = 172 Hz); 107.13 (C(3)); 115.86 (C(2)). MS, m/z: 170 and 168 $[M]^+$, 133 $[M - Cl]^+$.

Tricyclo[7.1.0.0^{1,3}]deca-4,6-diene (16) was prepared from dichloride **3** in 30% yield and isolated by preparative chromatography. ^{1}H NMR ($CDCl_3$), δ: 0.59 (dd, 1 H, *anti*-$H(2)_a$, $^3J_{H(2)_a,H(3)}$ = 5.2 Hz, $^2J_{H(2)_a,H(2)_b}$ = 3.6 Hz); 0.62 (dd, 1 H, *anti*-$H(10)_a$, $^3J_{H(9),H(10)_a}$ = 4.6 Hz, $^2J_{H(10)_a,H(10)_b}$ = 4.0 Hz); 1.05 (dd, 1 H, *syn*-$H(10)_b$, $^3J_{H(9),H(10)_b}$ = 8.0 Hz); 1.21 (m, 1 H, H(9)); 1.28 (dd, 1 H, *syn*-$H(2)_b$, $^3J_{H(2)_b,H(3)}$ = 8.5 Hz); 1.63 (m, 1 H, H(3)); 1.77 (ddd, 1 H, $H(8)_a$, $^3J_{H(7),H(8)_a}$ = 7.9 Hz, $^2J_{H(8)_a,H(8)_b}$ = 12.3 Hz, $^3J_{H(8)_a,H(9)}$ = 7.8 Hz); 2.46 (ddd, 1 H, $H(8)_b$, $^3J_{H(7),H(8)_b}$ = 7.7 Hz, $^3J_{H(8)_b,H(9)}$ = 2.3 Hz); 5.54 (ddd, 1 H, H(7), $^3J_{H(6),H(7)}$ = 11.2 Hz); 5.76 (dd, 1 H, H(5), $^3J_{H(4),H(5)}$ = 11.6 Hz, $^3J_{H(5),H(6)}$ = 4.4 Hz); 5.82 (dd, 1 H, H(4), $^3J_{H(3),H(4)}$ = 4.0 Hz); 5.96 (dd, 1 H, H(6)). ^{13}C NMR (C_6D_6), δ: 13.33 (C(10)); 15.33 (C(2)); 17.56 (C(1)); 17.85 (C(9)); 18.44 (C(3)); 28.90 (C(8)); 125.23 (C(6)); 127.21 (C(5)); 129.64 (C(7)); 131.45 (C(4)).

Tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (12). Heating of diene **11** (0.01 g) in a tube at 100 °C for 1 h afforded a hydrocarbon in quantitative yield (GLC data) which was characterized by a different retention time. The spectral parameters of the resulting compound coincide with the published data.[20] A sample of diene **12** was prepared by independent synthesis, *viz.*, by cyclopropanation of cyclooctatetraene.[20]

3-Chlorobicyclo[7.1.0]deca-1,4-diene (14). Heating of chloride **13** at 100 °C for 1 h afforded diene **14** in quantitative yield. ^{1}H NMR ($CDCl_3$), δ: 0.10 (ddd, 1 H, *anti*-$H(10)_a$, $^3J_{H(1),H(10)_a}$ = 5.0 Hz, $^3J_{H(9),H(10)_a}$ = 5.0 Hz, $^2J_{H(10)_a,H(10)_b}$ = 4.8 Hz); 0.88 (m, 1 H, $H(8)_a$); 0.89 (m, 1 H, H(9)); 1.18 (ddd, 1 H, *anti*-$H(10)_b$, $^3J_{H(1),H(10)_b}$ = 8.2 Hz, $^3J_{H(9),H(10)_b}$ = 8.9 Hz); 1.42 (m, 1 H, $H(7)_a$); 1.51 (m, 1 H, H(1)); 1.67 (m, 1 H, $H(7)_b$); 1.99 (m, 1 H, $H(8)_b$); 2.00 (m, 1 H, $H(6)_a$); 2.93 (m, 1 H, $H(6)_b$, $^2J_{H(6)_a,H(6)_b}$ = 13.8 Hz); 5.43 (ddd, 1 H, H(5), $^3J_{H(4),H(5)}$ = 11.7 Hz, $^3J_{H(5),H(6)_b}$ = 8.9 Hz, $^3J_{H(5),H(6)_a}$ = 9.0 Hz); 6.02 (dd, 1 H, H(4), $^4J_{H(4),H(6)_b}$ = 1.6 Hz); 6.26 (d, 1 H, H(2), $^3J_{H(1),H(2)}$ = 2.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.77 (C(10)); 16.20 (C(1)); 17.06 (C(9)); 24.55, 25.38, 26.51 (C(6)—C(8)); 125.86 (C(4)); 127.67 (C(2)); 130.05 (C(5)); 131.93 (C(3)).

The adduct of chloride 13 with 1,3-diphenylisobenzofuran (15). A mixture of chloride **13** (50 mg, 0.3 mmol) in benzene (2 mL) and 1,3-diphenylisobenzofuran (80 mg, 0.3 mmol) was placed in a sealed tube and kept in the dark at 20 °C for 10 h. Then the solvent was evaporated. Crystalline adduct **15** was obtained in quantitative yield. ^{1}H NMR (C_6D_6), δ*: 0.23 (m, 1 H, *anti*-$H(10)_a$, $^3J_{H(9),H(10)_a}$ = 4.8 Hz, $^3J_{H(1),H(10)_a}$ = 5.0 Hz, $^2J_{H(10)_a,H(10)_b}$ = 5.0 Hz); 0.40 (m, 3 H, H(1), H(9), *syn*-$H(10)_b$); 0.95 (m, 1 H, $H(8)_a$); 1.08 (m, 1 H, $H(7)_a$); 1.29 (m, 1 H, $H(6)_a$); 1.51 (m, 1 H, $H(5)_a$); 1.66 (m, 1 H, $H(7)_b$); 1.78 (m, 1 H, $H(6)_b$, $^2J_{H(6)_a,H(6)_b}$ = 13.8 Hz); 1.96 (dd, 1 H, $H(8)_b$, $^3J_{H(7)_b,H(8)_b}$ = 7.5 Hz, $^2J_{H(8)_a,H(8)_b}$ = 14.5 Hz); 2.10 (ddd, 1 H, $H(5)_b$, $^3J_{H(4),H(5)_b}$ = 3.5 Hz, $^2J_{H(5)_a,H(5)_b}$ = 14.6 Hz, $^3J_{H(5)_b,H(6)_b}$ = 9.3 Hz); 3.12 (dd, 1 H, H(4), $^3J_{H(4),H(5)_a}$ = 11.9 Hz); 7.14—7.35 (m, 9 H, Ar, Ph); 7.73—7.98 (m, 5 H, Ar, Ph). ^{13}C NMR (C_6D_6), δ: 9.11 (C(10)); 12.84 (C(1)); 18.61 (C(9)); 27.00, 28.42, 29.37, 29.61 (C(5)—C(8)); 37.94 (C(2)); 38.88 (C(4)); 66.70 (C(3)); 90.36 (CO); 90.83 (CO); 122.88 (ArCH); 123.34 (ArCH); 126.08 (ArCH); 126.44 (ArCH); 128.80, 128.90 (C_p, Ph); 128.28, 128.47, 128.58, 128.64 (Ph, CH); 134.60, 137.36 (C_{ipso}, Ph).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32876a).

* For ^{35}Cl isotopes.

* The numbering scheme of hydrogen atoms is identical with that in compound **13**.

References

1. N. S. Zefirov, T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, G. V. Zatonsky, and B. T. Ugrak, *J. Org. Chem.*, 1994, **59**, 4087.
2. N. S. Zefirov, T. S. Kuznetsova, O. V. Eremenko, and O. V. Kokoreva, *Mendeleev Commun.*, 1993, 91.
3. T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, G. V. Zatonsky, and N. S. Zefirov, *Mendeleev Commun.*, 1994, 172.
4. N. S. Zefirov, T. S. Kuznetsova, and A. N. Zefirov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1613 [*Russ. Chem. Bull.*, 1995, **44**, 1543 (Engl. Transl.)].
5. T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, E. B. Averina, A. N. Zefirov, and N. S. Zefirov, *Zh. Org. Khim.*, 1997, **33**, 916 [*Russ. J. Org. Chem.*, 1997, **33** (Engl. Transl.)].
6. T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Am. Chem. Soc.*, 1965, **87**, 3026.
7. J. Arct and B. Migay, *Tetrahedron*, 1981, **37**, 953.
8. R. R. Kostikov and A. P. Molchanov, *Zh. Org. Khim.*, 1996, **32**, 33 [*Russ. J. Org. Chem.*, 1996, **32** (Engl. Transl.)].
9. T. S. Shields and W. E. Billups, *J. Am. Chem. Soc.*, 1968, **90**, 4749.
10. W. E. Billups, B. A. Baker, W. Y. Chow, K. H. Leavell, and E. S. Lewis, *J. Org. Chem.*, 1974, **39**, 274; 1975, **40**, 1702.
11. A. R. Browne and B. Halton, *Tetrahedron*, 1977, **33**, 345.
12. W. E. Billups and L. E. Reed, *Tetrahedron Lett.*, 1997, **26**, 2239.
13. Ch. J. Ransom and C. B. Reese, *Chem. Comm.*, 1975, 970.
14. W. E. Billups, K. H. Leavell, W. Y. Chow, and E. S. Lewis, *J. Am. Chem. Soc.*, 1972, **94**, 1770.
15. Yu. V. Tomilov, V. G. Bordakov, I. E. Dolgii, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 582 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 533 (Engl. Transl.)].
16. K. A. Lukin and N. S. Zefirov, *Zh. Org. Khim.*, 1988, **24**, 1648 [*J. Org. Chem. USSR*, 1988, **24** (Engl. Transl.)].
17. R. R. Kostikov and A. P. Molchanov, *Zh. Org. Khim.*, 1975, **11**, 1861 [*J. Org. Chem. USSR*, 1975, **11** (Engl. Transl.)].
18. A. R. Pinder, *Synthesis*, 1980, **6**, 425.
19. C. L. Osborn, T. S., Shields, B. A. Shoulders, J. F. Crause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, 1965, **87**, 3158.
20. Yu. V. Tomilov, T. L. Mitenina, A. I. Lutsenko, I. E. Dolgii, S. P. Kolesnikov, and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 77 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 65 (Engl. Transl.)].
21. R. W. Crecely, V. S. Watt, and J. H. Goldstein, *J. Mol. Spectr.*, 1969, **30**, 184.
22. H. Hunther and H. Seel, *Org. Magn. Reson.*, 1976, **8**, 299.
23. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966, 146.
24. T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, and N. S. Zefirov, *Zh. Org. Khim.*, 1977, **33**, 929 [*J. Org. Chem. USSR*, 1977, **33** (Engl. Transl.)].

Received October 6, 1998;
in revised form December 1, 1998