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Application of Copper(I) Halides to Modifying Reactivity of Polyhalomethanes and Arenesulfonyl Chlorides in Free-Radical Addition. "Cross-Halogenation" Reaction

A.S. Dneprovskii†, A.N. Kasatochkin, V.P. Boyarskii, A.A. Ermoshkin, and A.A. Yakovlev

St. Petersburg State University, St. Petersburg, 198504 Russia
e-mail: vadimpb@newmail.ru

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Abstract—In the free-radical addition of a number of organohalogen reagents to cyclic alkenes and dienes in the presence of copper(I) halides the composition of the reaction products is governed by the stage of a fast halogen transfer from the copper derivative to the alkyl radical. Under these conditions in contrast to the free-radical addition reactions initiated by UV light or peroxide initiators the intramolecular rearrangements are suppressed, the stereoselectivity of the reaction changes, and also some adducts contain halogen atoms different from those present in the organohalogen reagent employed.

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The free-radical addition of organohalogen reagents to multiple bonds in the presence of transition metals compounds is a promising method for the synthesis of various halogen derivatives [1]. The sequence of elementary stages of this process advanced in [2] may be considered nowadays as general by accepted (Scheme 1, addition of CCl_4, M = Cu).

It was established [2] that the reaction proceeded via the formation of free radical **A**. Stage (1) is a one-electron transfer from the metal atom to the polyhalomethane molecule. Stage (3) consisting in the ligand transfer from the metal atom to the radical-adduct **A** occurs efficiently even with the low reactive benzyl and allyl radicals. This results in significantly longer kinetic chains as compared to the typical free-radical conditions (Scheme 2), namely, at UV irradiation or in the presence of peroxide initiators, e.g., benzoyl peroxide.

Scheme 1.

$$M^+ + CCl_4 \longrightarrow [M]^{2+} + [CCl_4]^{\bullet-} \longrightarrow MCl^+ + {}^\bullet CCl_3 \quad (1)$$

$${}^\bullet CCl_3 + RCH{=}CH_2 \longrightarrow \underset{\mathbf{A}}{R\dot{C}HCH_2CCl_3} \quad (2)$$

$$\mathbf{A} + MCl^+ \longrightarrow RCHClCH_2CCl_3 + M^+ \quad (3)$$

Scheme 2.

$$CCl_4 \xrightarrow{h\nu} Cl^\bullet + {}^\bullet CCl_3 \quad (1)$$

$${}^\bullet CCl_3 + RCH{=}CH_2 \longrightarrow \mathbf{A} \quad (2)$$

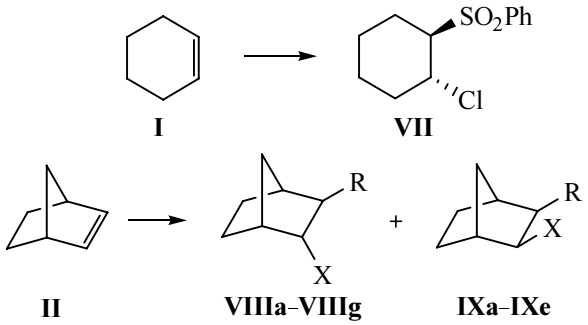
$$\mathbf{A} + CCl_4 \longrightarrow RCHClCH_2CCl_3 + {}^\bullet CCl_3 \quad (3)$$

We formerly [3] demonstrated that in the free-radical addition of polyhalomethanes to double bonds of cycloalkenes in the presence of palladium(II) halogen complexes the transfer of a halogen atom to the primarily arising radical-adduct occurred not only from the molecule of the oganohalogen reagent [Scheme 2, stage (3)], but also from the metal complex [Scheme 1, stage (3)]. In the presence of different halogens in the palladium complex and the polyorganomethane the resulting product contained a mixture of organohalogen compounds. In the presence of palladium compounds we also observed the changes in the stereochemical composition of the reaction products and in the relative amounts of the rearranged and nonrearranged compounds.

In this study we used for modification of the reactivity of the organohalogen reagents and also for preparation of halides containing a halogen atom foreign to the composition of the employed addend more accessible copper(I) derivatives. We investigated in the presence of copper(I) chloride or bromide the reactions of tetrachloromethane, bromotrichloromethane, chloroform,

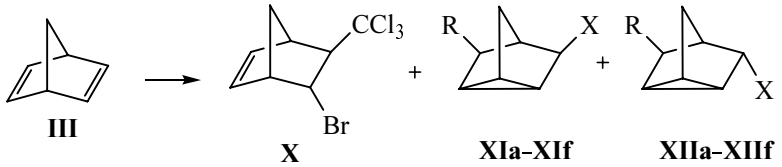
† Deceased.

Scheme 3.



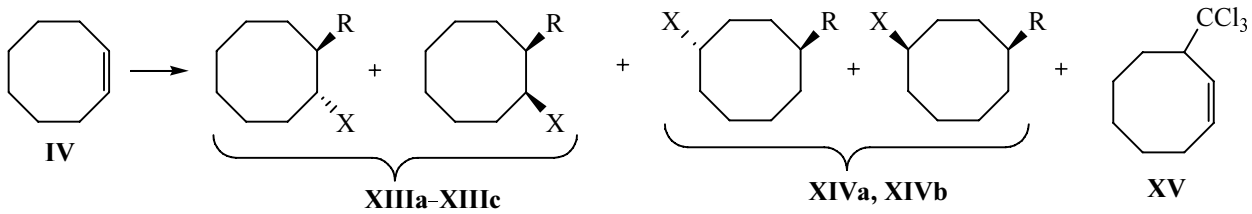
I **VII** **II** **VIIIa–VIIIg** **IXa–IXe**

VIII, X = H, R = CCl_3 (**a**); X = Cl, R = $CHCl_2$ (**b**), CCl_3 (**c**), CCl_2CN (**d**), Ts (**e**); X = Br, R = $CHCl_2$ (**f**), CCl_3 (**g**); **IX, X** = Cl, R = $CHCl_2$ (**a**), CCl_3 (**b**), CCl_2CN (**c**); X = Br, R = $CHCl_2$ (**d**), CCl_3 (**e**).



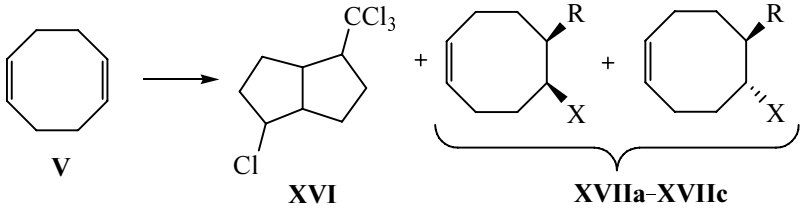
III **X** **XIa–XIf** **XIIa–XIIf**

X = Cl, R = Ts (**a**), CCl_3 (**b**); X = Br, R = CCl_3 (**c**), Ts (**d**); R = *p*-$FC_6H_4SO_2$, X = Cl (**e**), Br (**f**).



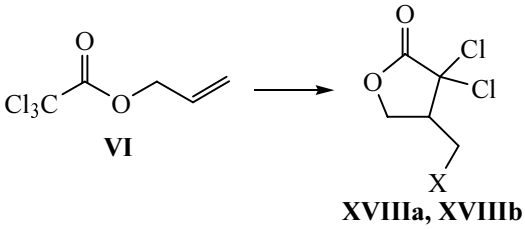
IV **XIIIa–XIIIc** **XIVa, XIVb** **XV**

R = CCl_3, X = Cl (**a**); R = CCl_2CN, X = Cl (**b**), Br (**c**).



V **XVI** **XVIIa–XVIIc**

X = Cl, R = CCl_3 (**a**), Ts (**b**); X = Br, R = Ts (**c**).



VI **XVIIIa, XVIIIb**

X = Cl (**a**), Br (**b**).

and trichloroacetonitrile with cyclohexene (**I**), norbornene (**II**), norbornadiene (**III**), *cis*-cyclooctene (**IV**), and *cis,cis*-cycloocta-1,5-diene (**V**), the intramolecular cyclization of the allyl trichloroacetate (**VI**), and also the reactions of arenesulfonyl chlorides with hydrocarbons **I–III**, and **V** (Scheme 3). These reactions were compared with the typical free-radical processes carried out under UV irradiation or by thermolysis of the benzoyl peroxide.

Table 1. Products of organochlorine reagents addition to cycloalkenes **I–V** in the presence of CuCl[a]

Run no.	Reagent	Substrate	CuCl:substrate, mol/mol	Temperature, °C (time, h)	Reaction products (yield, %)
1	$PhSO_2Cl$	**I**	0.12	80 (50)	**VII** (22)
2[c]	$CHCl_3$	**II**	–[b]	62 (15)	**VIIIa** (78), **VIIIb** (2)
3[c]			0.05[d]	140 (9)	**VIIIb** (62**), IXa** (19)
4[c]	CCl_4		–[b]	77 (15)	**VIIIc** (80)
5			0.05	140 (16)	**VIIIc** (75**), IXb** (12)
6	CCl_3CN		0.05	140 (16)	**VIIId** (81), **IXc** (5)
7	TsCl		0.26	97 (19)	**VIIIe** (70)
8	TsCl	**III**	0.063	80 (10)	**XIa** (26), **XIIa** (22)
9[c]	CCl_4	**IV**	–[b]	97 (4)	**XIIIa** (0.6**), XIVa** (79)
10			1.0	95 (61)	**XIIIa** (30), **XV** (37)
11	CCl_3CN		0.1[b]	80 (9.3)	**XIVb** (13)
12			0.056	95 (19)	**XIIIb** (58)
13[c]	CCl_4	**V**	–[b]	77 (15)	**XVIa** (80)
14			0.05	120 (30)	**XVIa** (25), **XVIIa** (27)
15	TsCl		0.08	120 (24)	**XVIIb** (22)

[a] Solvent acetonitrile.
[b] Reaction under typical free-radical conditions [No CuCl , $(PhCOO)_2$ initiator].
[c] Solvent excess reagent.
[d] Added 80 mol% of 1,10-phenanthroline with respect to CuCl.

The cyclic substrates were chosen in order to follow not only the regioselectivity but also the stereoselectivity of the reaction.

The known main restriction to the addition of low reactive agents like organochlorine reagents under the typical conditions of the free-radical reactions is the competition between the chlorine atom transfer to radical-adduct **A** and this radical addition to the double bond of the substrate leading to the formation of a telomers mixture and decreased yield of the 1:1 adducts [4]. Yet the addition of the organohalogen reagents in the presence of copper(I) halides involves the halogen atom transfer to radical-adduct **A** from the copper(II) derivatives (Scheme1). The rate of this process is close to that of the diffusion-controlled reaction: the rate of a chlorine atom transfer from $CuCl_2$ to an alkyl radical is equal to 1.1×10^9 l mol^{-1} s^{-1} [5], and this value is 10^5 times larger that the transfer rate of a chlorine atom from carbon (for instance, from CCl_4 [6]). Consequently in the presence of copper(I) halides the addition even of the low reactive chlorides occurs at the multiple carbon-carbon bond avoiding the telomerization of alkenes and giving rise mainly to 1:1 adducts.

Thus by the addition of polyhalomethanes and arene-sulfonyl chlorides in the presence of copper(I) chloride we prepared the corresponding adducts (Table 1). The structure of the reaction products was proved using NMR and mass spectra and elemental analyses. The reaction mixtures arising at the addition of polyhalomethanes and trichloroacetonitrile were analyzed by GLC and NMR spectroscopy, the products formed were identified by retention times on two columns of different polarity in comparison with the parameters of authentic samples, and by the presence of characteristic signals in the NMR spectra. The reference compounds were synthesized by independent methods, and their structure was confirmed by ^{1}H NMR spectra.

As seen from the findings in Table 1, the addition of $CHCl_3$ to norbornene in the presence of CuCl used as the reaction initiator proceeded at the C–Cl and not C–H bond leading to the formation accordingly of adduct **VIIIb** (Table 1, run no. *3*) and not **VIIIa** as occurred under the typical conditions of the free-radical reactions (Table 1, run no. *2*) [7].

In going from the reaction initiated with the UV light or peroxides to the reaction in the presence of CuCl the rate of a halogen transfer to the intermediately formed alkyl radical **A** (Scheme 1) increases resulting in predominance of the addition to the double bond in the alkene or alkadiene over the other competing process, intramolecular rearrangement. For instance, it is known that the addition of CCl_4 initiated photochemically or at heating provides with the *cis*-cyclooctene a product of 1,4-addition **XIVa** [8], and with the *cis,cis*-cycloocta-1,5-diene

Table 2. Products of organochlorine reagents addition to substrates **II–V** in the presence of CuBr[a]

Run no.	Reagent	Substrate	CuBr:substrate, mol/mol	Teperature, °C (time, h)	Reaction products (yield, %)
1	$CHCl_3$[b]	**II**	1.6[c]	90 (9)	**VIIIb** (25)[d], **VIIIf** (30)[d], **IXd**(8)[d]
2	CCl_4		1.6	90 (20)	**VIIIc** (14)[d], **VIIIg** (40)[d], **IXe**(6)[d]
3	CCl_3Br[b]		0.05	90 (20)	**VIIIg** (79)[d], **IXe** (11)[d]
4	CCl_4	**III**	1.15	95 (0.5)	**XIb** (4.5)[e], **XIIb** (5.0)[e], **X** (1.7)[e], **XIc** (28)[e], **XIIc** (22)[e]
5			2.5	95 (0.5)	**XIb** (3.7)[e], **XIIb** (4.1)[e], **X** (1.9)[e], **XIc** (34)[e], **XIIc** (26)[e]
6	TsCl		3.2	80 (14)	**XIa** + **XIIa** (8)[f], **XId** (25)[f], **XIId** (22)[f]
7	*p*-$FC_6H_4SO_2Cl$		3.2	80 (14)	**XIe** + **XIIe** (12)[f], **XIf** (21)[f], **XIIf** (18)[f]
8	CCl_3CN	**IV**	2.0	95 (4.5)	**XIIIb** (11)[e], X**IIIc** (24)[e]
9	TsCl	**V**	1.6	90 (24)	**XVIIc** (20)[f]

[a] Solvent acetonitrile.
[b] Solvent excess reagent.
[c] Added 80 mol% of 1,10-phenanthroline with respect to CuBr.
[d] Content in the reaction mixture (by the ^{1}H NMR data).
[e] Content in the reaction mixture (according to GLC) .
[f] Preparative yield.

bicyclo[3.3.0]octane derivative **XVI** [9]. We demonstrated that the addition of CCl_4 to *cis*-cyclooctene (**IV**) and *cis,cis*-cycloocta-1,5-diene (**V**) in the presence of CuCl (both in the stoichiometric and catalytic quantities) gave rise mainly to the nonrearranged adducts **XIIIa** and **XVIIa** respectively (Table 1, runs nos. *10*, *14*). Under the typical conditions of the free-radical reactions only traces of compound **XIIIa** were obtained (Table 1, run no. *9*), and no formation of compound **XVIIa** was observed (Table 1, run no. *13*). The formation of unsaturated compound **XV** in a considerable amount (Table 1, run no. *10*) in the course of polyhalomethanes addition to the *cis*-cyclooctene in the presence of copper(I) halides may be satisfactorily rationalized as due to the oxidation of the intermediate 2-(trichloromethyl)-cyclooctyl radical with the copper(II) derivatives [10] arising in the initiation stage.

The other characteristic feature of the reaction in the presence of copper derivatives is the change in the reaction stereoselectivity. For instance, the addition of polyhalomethanes and related compounds to the norbornene under typical conditions of the free-radical reactions (Table 1, runs nos. *2*, *4*) led exclusively to the formation of *exo,endo*-disubstituted norbornanes **VIII**, whereas the reaction in the presence of CuCl yielded notable amounts of *exo,exo*-disubstituted isomer **IX** (Table 1, runs nos. *3*, *5*, *6*). Likewise in the reaction of CCl_4 with *cis*-cyclooctene in going from the typical free-radical process to that in the presence of CuCl the ratio of *cis*- and *trans*-isomers of 1-chloro-2-trichloromethyl-cyclooctane **XIIIa** altered from 50:50 [8] to 43:57.

The variations in the stereoselectivity observed are caused by the fact that in the presence of the copper(I) chloride the reaction products form mainly as a result of a chlorine atom transfer to radical **A** from the copper(II) chloride. The contribution of the chlorine transfer from the organochlorine reagent is here negligibly small.

An important feature of the reactions carried out in the presence of copper(I) halides is the formation of the so-called "cross-halogenation" products containing a halogen atom lacking in the composition of the initial organohalogen addend. Thus by the addition of polychloromethanes and arenesulfonyl chlorides to the double bond of cycloalkenes in the presence of stoichiometric and superstoichiometric amounts of CuBr we prepared the corresponding bromo derivatives (Table 2).

It was found that CCl_4 addition to norbornadiene in acetonitrile in the presence of a double excess CuBr led to the formation prevailingly of diastereomers of 3-trichloromethyl-5-bromotricyclo[2.2.1.$0^{2,6}$]heptane (**XIc** + **XIIc**) in an overall yield 60% (Table 2, runs nos. *4*, *5*), the addition of trichloroacetonitrile to the *cis*-cyclooctene under these conditions gave rise to a mixture containing 24% of (2-bromocyclooctyl)dichloroacetonitrile (**XIIIc**) and 11% of (2-chlorocyclooctyl)dichloroacetonitrile (**XIIIb**) (Table 2, run no. *8*), the addition of arenesulfonyl chlorides $ArSO_2Cl$ (Ar = *p*-$CH_3C_6H_4$, *p*-FC_6H_4) to the norbornadiene in the presence of over three-fold excess

Table 3. Dependence on the reaction conditions of the yield and products ratio in the intramolecular cyclization of ester **VI**[a]

Run no.	Amount of reagent **VI**, mol	CuHlg/(VI), mol/mol	Reaction temperature, °C	Yield, %		(**XVIIIb**)/(**XVIIa**), mol/mol
				XVIIIa	**XVIIIb**	
1	0.2	CuCl, 0.05	120	43	–	0
2	0.2	CuCl, 1.0	120	35	–	0
3	0.05	CuBr, 1.0	120	24	31	1.3
4	0.2	CuBr, 1.0	120	11	29	2.7
5	0.2	CuBr, 3.0	120	2.5	9.5	3.8
6	0.6	CuBr, 1.0	120	3	8	2.7
7	0.2	CuBr, 1.0	95	2	7.3	3.7

[a] Solvent acetonitrile, reaction time 20 h.

of CuBr provided a mixture of 5-halotricyclo[2.2.1.0^{2,6}]-hept-3-yl aryl sulfones **XI** and **XII** in an overall yield up to 55% and bromides content up to 80–85% (Table 2, runs nos. *6*, *7*).

Similar relationships were observed also in the reaction of intramolecular cyclization suffered by allyl trichloroacetate (**VI**) (Scheme 3). In the reaction carried out in the presence of equimolar or superequimolar quantities of CuBr alongside lactone **XVIIIa** was also obtained bromine-containing lactone **XVIIIb**.

The analysis of data in Table 3 shows that the yield of compounds **XVIIIa** and **XVIIIb** grows with the rising temperature and with decreasing compound **VI** concentration in the reaction mixture. The superstoichiometric content of CuBr resulted in an increased relative yield of bromine-containing lactone **XVIIIb** in the mixture of the reaction products and in a considerably reduced overall yield of the products. This effect is due to the capability of alkyl radicals to react with the cations of bivalent copper [11] arising in the initiation stage of the process under study [Scheme 1, equation (1)]. The copper(II) cations oxidize radical-adducts **A** [Scheme 1, equation (2)] into the corresponding carbocations which react with the initial unsaturated substrates initiating their telomerization and thus decreasing the yield of the target 1:1 adducts.

Based on Scheme 1 describing the addition mechanism of organohalogen compounds to the multiple bonds in the presence of transition metal compounds we suggest as the most probable the mechanism of the cross-halogenation reaction involving CuBr represented on Scheme 4 by an example of arenesulfonyl chloride addition.

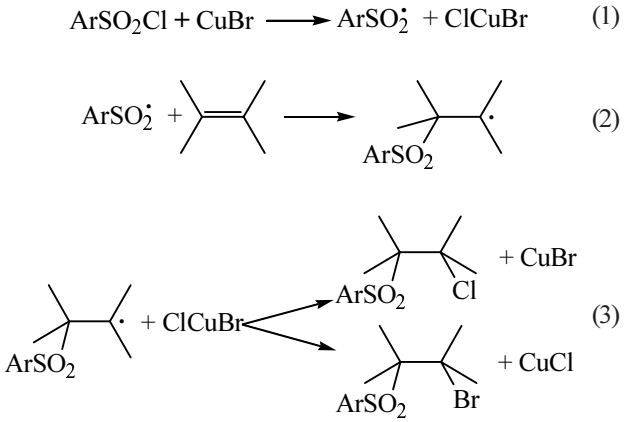
The addition product is produced at the stage (3) by a transfer of a halogen atom to the radical-adduct from the mixed salt ClCuBr formed in the initiation stage. Thus under our conditions it is impossible to avoid the formation of chloroalkyl aryl sulfones. Actually, the ratios of chloroalkyl aryl sulfones to bromoalkyl aryl sulfones obtained are well consistent with the published values of the halogen transfer rate to alkyl radical from $CuCl_2$ and $CuBr_2$ (1.1×10^9 and 4.3×10^9 l mol^{-1} s^{-1}, respectively) [12].

This cross-halogenation reaction is obviously of synthetic interest for it provides a possibility to prepare difficultly accessible bromine-containing organic compounds starting with organochlorine reagents. We plan further to optimize the process for preparative application of the reaction.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker AMX-300 (300 MHz) in $CDCl_3$. The structure of the reaction products was confirmed by ^{1}H, ^{13}C, ^{1}H-2D-COSY, and ^{1}H-2D-NOESY NMR spectra. Mass spectra were measured on an MKh-1321 instrument. The composition of the reaction products was determined by means of GLC and NMR spectroscopy. The GLC analysis was performed on a chromatograph Chrom-5

Scheme 4.



equipped with packed glass columns 2500×3mm, stationary phases 10% SE-30 on Chromaton N-Super and 5% OV-225 on the same carrier, carrier gas helium, a flame-ionization detector.

Norbornene (99%), norbornadiene (99%), *cis*-cyclooctene (99%), *cis,cis*-cycloocta-1,5-diene (99%), bromotrichloromethane (99%), *p*-toluenesulfonyl chloride (99%), *p*-fluorobenzenesulfonyl chloride (99%), benzenesulfonyl chloride (99%) were commercial products. Benzoyl peroxide, acetonitrile, chloroform, and tetrachloromethane were purified by standard procedures [13, 14]. Cyclohexene (99.5% by GLC data) [14], trichloroacetonitrile (99% by GLC data) [15], allyl trichloroacetate (99% by GLC data) [14], copper(I) chloride [16], and copper(I) bromide [17] were prepared by known methods.

***exo*-2-(Trichloromethyl)bicyclo[2.2.1]heptane (VIIIa)**. A mixture of 1.1 g of norbornene, 16 ml of chloroform, and 0.1 g of benzoyl peroxide were boiled at reflux for 15 h in a weak flow of argon. On completion of the reaction (GLC monitoring)the unreacted chloroform was distilled off, the residue was passed through a column 4 cm high packed with silica gel (eluent petroleum ether–tetrachloromethane, 1:2). The solvent mixture was evaporated to obtain 80% of compound **VIIIa** in a mixture with ***exo*-2-(dichloromethyl)-*endo*-3-chlorobicyclo-[2.2.1]heptane (VIIIb)** in a ratio 1:0.02. ^{1}H NMR spectrum of the mixture of compounds **VIIIa** and **VIIIb**, δ, ppm: 5.7 m (0.02H, $HCCl_2$), 4.14 m (0.02H, HCCl), 2.65 m (2H, $HCCl_3$ + H^1), 2.38 s (1H, H^4), 1.92 d (1H, H^3), 1.72–1.16 (7H). The spectral data are identical to those published in [18].

***exo*-2-(Trichloromethyl)-*endo*-3-chlorobicyclo-[2.2.1]heptane (VIIIc)** was prepared by the addition of tetrachloromethane to the norbornene in a similar way. Yield 80%. ^{1}H NMR spectrum, δ, ppm: 4.23 m (1H, HCCl), 2.64 m (2H, $HCCl_3$ + H^4), 2.55 s (1H, H^1), 2.1 m (2H), 1.78–1.38 (4H). The ^{1}H NMR spectrum was similar to that published in [19].

***exo*-2-(Dichloromethyl)-*endo*-3-chlorobicyclo-[2.2.1]heptane (VIIIb) and *exo*-2-(dichlormethyl)-*exo*-3-chlorobicyclo[2.2.1]heptane (IXa)**. In an ampule of 20 ml capacity was charged 1.3 g of norbornene, 10 ml of chloroform, 0.07 g of copper(I) chloride, and 0.1 g of 1,10-phenanthroline. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated for 9 h at 140°C. Then the ampule was opened, the solvent was evaporated, and the residue was passed through a column 4 cm high packed with silica gel (eluent tetrachloromethane). The solvent was evaporated to obtain 81% of a mixture of compounds **VIIIb** and **IXa** in a ratio 1:0.3. ^{1}H NMR spectrum, δ, ppm: 5.7 m (0.7H, $HCCl_2$), 5.57 m (0.3H, $HCCl_2$), 4.14 m (0.7H, HCCl), 4.0 m (0.3H, HCCl), 2.64 s (1H, H^4), 2.54 m (2H, $HCHCl_2$ + H^1), 2.1 m (2H), 1.75–1.36 (4H). These data are well consistent with the spectra of compounds **VIIIb** and **IXa** described in [18]. Mass spectrum, *m/z* (I_{rel}, %): 179 (0.1), 177 (0.18), 175 (0.23), 143 (0.25), 141 (0.67), 131 (0.32), 129 (1), 115 (0.23), 113 (0.32), 109 (0.23), 105 (0.85).

***exo*-2-(Trichloromethyl)-*endo*-3-chlorobicyclo-[2.2.1]heptane (VIIIc) and *exo*-2-(trichloromethyl)-*exo*-3-chlorobicyclo[2.2.1]heptane (IXb)**. In an ampule of 40 ml capacity was charged 0.8 g of norbornene, 12 ml of tetrachloromethane, 0.02 g (5 mol%) CuCl, and 20 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated for 16 h at 140°C. On completion of the reaction the ampule was opened, the solvent was evaporated, and the residue was passed through a column packed with silica gel (eluent tetrachloromethane). The solvent was evaporated to obtain 87% of a mixture of compounds **VIIIc** and **IXb** in a ratio 1:16. ^{1}H NMR spectrum, δ, ppm: 4.23 m (0.84H, HCCl), 4.18 m (0.16H, HCCl), 4.18 m (0.16H, HCCl), 2.95 d (0.16H, $HCCl_3$), 2.76 s (0.16H, H^1), 2.64 m (1.84H, $HCCCl_3$ + H^4), 2.55 c (0.84H, H^1), 2.1 m (2H), 1.78–1.38 (4H). The signals from the minor set correspond to *exo,exo*-adduct **IXb** [19]. Mass spectrum, *m/z* (I_{rel}, %): 249 (0.1), 247 (0.3), 245 (0.2), 215 (0.1), 213 (0.28), 211 (0.32), 177 (0.6), 175 (1), 149 (0.2), 147 (0.28), 139 (0.24), 135 (0.24), 111 (0.64), 109 (0.8).

***exo*-2-(Dichlorocyanomethyl)-*endo*-3-chlorobicyclo[2.2.1]heptane (VIIId) and *exo*-2-(dichlorocyanomethyl)-*exo*-3-chlorbicyclo[2.2.1]heptane (IXc)** were obtained by adding trichloroacetonitrile to norbornene along a similar procedure. The yield of compounds **VIIId** and **IXc** was 86%, the ratio of the adducts 1:0.06. The spectrum of the mixture contained characteristic signals identical in position and multiplicity to the peaks in the published spectrum of compound **VIIId** [20]. At the same time the spectrum of the reaction mixture contained less strong resonances which by analogy to the spectrum of the mixture of compounds **VIIIc** and **IXb** might be assigned to *exo,exo*-isomer **IXc**. ^{1}H NMR spectrum, δ, ppm: 4.19 m (0.94H, HCCl),

4.07 m (0.06H, HCCl), 2.72 m (0.12H, $HCCCl_2CN$ + H^1), 2.62 m (1.88H, $HCCCl_2CN$ + H^1), 2.50 m (0.06H, H^4), 2,47 m (0.94H, H^4), 2.2–1.33 m (6H). Mass spectrum, *m/z* (I_{rel}, %): 204 (0.17), 202 (0.22), 168 (0.2), 166 (0.48), 121 (0.38), 119 (0.97), 117 (1).

***endo*-2-Bromo-*exo*-3-(trichloromethyl)bicyclo-[2.2.1]heptane (VIIIg) and *exo*-2-bromo-*exo*-3-(trichloromethyl)bicyclo[2.2.1]heptane (IXe)** were obtained by adding bromo-trichloromethane to norbornene in the presence of CuBr at 90°C within 20 h by the procedure similar to that used in preparation of the mixture of isomers **VIIIc** and **IXb**. Yield of compounds **VIIIg** and **IXe** 90%, isomers ratio 1:0.14. ^{1}H NMR spectrum, δ, ppm: 4.28 m (0.86H, HCBr), 4.21 m (0.14H, HCBr), 2.96 d (0.14H, $HCCCl_3$), 2.63 s (1H, H^1), 2.56 s (1H, H^4), 2.15 m (2H), 1.7–1.65 m (2H), 1.63–1.4 (2H). The assignment of char-acteristic signals in the spectrum was performed using the data on the spectrum of compound **VIIIg** [21].

Chloroform and tetrachloromethane addition to nor-bornene in the presence of CuBr. In an ampule of 30 ml capacity was charged 0.4 g of norbornene, 6 ml of a chlorine-containing reagent, excess of CuBr (with respect to norbornene, 0.66 g), and 10 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated at 90°C. On completion of the reaction the ampule was opened, the solvent was evaporated, and the residue was passed through a column packed with silica gel (eluent tetrachloromethane). The solvent was evaporated, and the residue was analyzed with the use of ^{1}H NMR and mass spectra. The chloroform addition (reaction time 9 h) led to the formation of 63.5% of chlorine-containing adduct **VIIIb** and a mixture of bromine-containing adducts *endo*-2-bromo-*exo*-3-(dichloromethyl)bicyclo-[2.2.1]heptane (**VIIIf**) and *exo*-2-bromo-*exo*-3-(di-chloromethyl)bicyclo[2.2.1]heptane (**IXd**) in a ratio 1:1.5. The ratio of isomers **VIIIf** and **IXd** was 1:0.25. ^{1}H NMR spectrum, δ, ppm: 5.74 m (0.4H, $CHCl_2$), 5.58 m (0.6H, $CHCl_2$), 4.20 m (0.47H, HCBr), 4.17 m (0.4H HCCl), 4.01 m (0.13H, HCBr), 2.58–1.3 m (9H). Mass spectrum, *m/z* (I_{rel}, %): 260 (0.45), 258 (0.81), 256 (0.54), 225 (0.27), 223 (0.9), 221 (0.72), 187 (1), 185 (1).

In the reaction with tetrachloromethane the overall yield of chlorine-containing compound **VIIIc** and the mixture of bromide derivatives **VIIIg** and **IXe** was 60%, the ratio of chlorine to bromine derivatives was 1:3.4; the ratio of isomers **VIIIg** to **IXe** was 1:0.15.

***endo*-5-Bromo-*exo*-6-(trichloromethyl)bicyclo-[2.2.1]hept-2-ene (X), *exo*-3-bromo-*exo*-5-(trichloromethyl)tricyclo[2.2.1.0$^{2.6}$]heptane (XIc), and *endo*-3-bromo-*exo*-5-(trichloromethyl)tricyclo-[2.2.1.0$^{2.6}$]heptane (XIIc)** were obtained by a modified method [22]. Into a test tube of 50 ml capacity was charged a solution of 3 ml (29.5 mmol) of diene **III** in 29.5 ml (300 mmol) of bromotrichloromethane; a weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, then the reaction mixture was for 20 min placed under UV irradiation (of a mercury lamp of medium pressure) at 30°C while stirring in a weak flow of argon. On completion of the reaction the unreacted bromotrichloromethane was distilled off, and the residue was distilled in a vacuum. The fraction boiling within 100–150°C (2 mm Hg) was subjected to column chromatography on silica gel (eluent petrolrum ether) and separated in two fractions. The first fraction contained compound **X** as the main component [^{1}H NMR spectrum, δ, ppm: 6.59 d.d (1H, H^2), 6.30 d.d (1H, H^3), 4.35 t (1H, H^5), 3.30 s (1H, H^4), 3.15 m (1H, H^1), 2.89 d.d (1H, H^6), 2.29 d (1H, H^7), 1.66 m (1H, $H^{7'}$)] and a small amount of *exo*-5-bromo-*exo*-6-(trichloromethyl)bicyclo[2.2.1]-hept-2-ene (12% according to GLC and ^{1}H NMR data: in the ^{1}H NMR spectrum characteristic signals of protons at a double bond appeared at 6.27 and 6.19 ppm). The second fraction contained the diastereomers **XIc** and **XIIc** mixture in a ratio 69:31 (according to GLC and ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm (**XIc**): 3.96 s (1H, H^5), 2.83 s (1H, H^3), 2.57 s (1H, H^4), 2.37 d (1H, H^7), 2.06 d (1H, $H^{7'}$), 1.84–1.55 m (3H, H^1 + H^2 + H^6); (**XIIc**): 4.03 s (1H, H^5), 3.65 s (1H, H^3), 2.51 s (1H, H^4), 2.37 d (1H, H^7), 1.84–1.55 m (3H, H^1 + H^2 + H^6), 1.46 s (1H, $H^{7'}$).

***exo*-3-(Trichloromethyl)-*exo*-5-chlorotricyclo-[2.2.1.0$^{2.6}$]heptane (XIb) and *exo*-3-(trichloromethyl)-*endo*-5-chlorotricyclo[2.2.1.0$^{2.6}$]heptane (XIIb)** were obtained by a modified method [22]. Into an ampule of 20 ml capacity was charged a solution of 3.2 ml (31.5 mmol) of diene **III** and 0.5 g (2 mmol) of benzoyl peroxide in 10 ml (104 mmol) of tetrachloromethane; a weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, then the ampule was sealed and heated for 15 h at 66°C. The ampule was opened, the unreacted tetrachloromethane was distilled off, and the residue was distilled in a vacuum collecting the fraction boiling at 133°C (10 mm Hg). The fraction consisted of a mixture of diastereomers **XIb** and **XIIb** in a ratio 65:35 (according to GLC and ^{1}H NMR

data). Yield 6.4 g (83%). ^{1}H NMR spectrum, δ, ppm: (**XIb**), 3.91 s (1H, H^5), 2.82 s (1H, H^3), 2.55 s (1H, H^4), 2.37 d (1H, $H^{7'}$), 2.02 d (1H, $H^{7''}$), 1.80–1.65 m (3H, $H^1 + H^2 + H^6$); (**XIIb**): 4.0 s (1H, H^5), 3.61 s (1H, H^3), 2.49 s (1H, H^4), 2.37 d (1H, $H^{7'}$), 1.80–1.65 m (3H, $H^1 + H^2 + H^6$), 1.45 s (1H, $H^{7''}$).

2-(Trichloromethyl)-1-chlorocyclooctane (XIIIa). In an ampule of 60 ml capacity was charged 2.28 g of copper(I) chloride, 14 ml of tetrachloromethane, 3 ml of *cis*-cyclooctene (**I**), and 26.5 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, then the ampule was sealed and heated for 8.5 h at 95°C. The ampule was opened, the acetonitrile was distilled off, the residue was treated with tetrachloromethane, the solution obtained was passed through a bed of silica gel 2 cm thick, the tetrachloromethane was distilled off, the residue was distilled in a vacuum collecting the fraction boiling within 135–140°C (12 mm Hg). The reaction product obtained was a mixture of *cis*- and *trans*-isomers in a ratio 43:57 (according to ^{1}H NMR data; the ^{1}H NMR spectrum was in a full agreement with the published data [8]). ^{1}H NMR spectrum, δ, ppm: 4.94 m [0.428H, HCCl (*cis*-**XIIIa**)], 4.61 m [0.572H, HCCl (*trans*-**XIIIa**)], 2.95 m [0.428H, $HCCCl_3$ (*cis*-**XIIIa**)], 2.83 m [0.572H, $HCCCl_3$ (*trans*-**XIIIa**)], 2.3–1.2 m [12H, CH_2 (*cis*-**XIIIa** + *trans*-**XIIIa**)].

(2-Chlorocyclooctyl)dichloroacetonitrile (XIIIb) was obtained by adding trichloroacetonitrile to *cis*-cyclooctene (**I**) in the presence of 5 mol% of copper(I) chloride at 95°C by the procedure described for the synthesis of compound **XIIIa**. Reaction time 19 h. Yield 57.6%, bp 115°C (2.5 mm Hg). Yield 57.6%. ^{1}H NMR spectrum, δ, ppm: 4.71 br.t (0.32H, HCCl, *cis*-isomer), 4.41m (0.68H, HCCl, *trans*-isomer), 2.78 m (1H, $HCCCl_2CN$, both isomers), 2.3–1.2m (12H, CH_2, both isomers). Mass spectrum, *m/z* (I_{rel}, %): 258 (0.45), 256 (1.26), 254 (1.26), 222 (2.26), 220 (12.6), 218 (19.5), 184 (8.79), 182 (28.1), 154 (9.44), 146 (21.8), 109 (100). Found, %: C 47.32; H 5.67; N 5.62. $C_{10}H_{14}Cl_3N$. Calculated, %: C 47.18; H 5.54; N 5.50.

4-(Trichlormethyl)-1-chlorocyclooctane (XIVa) was prepared by the procedure described for compounds **XIb** and **XIIb**. mp 63.5–64°C (publ: mp 64–65.5°C [8]). ^{1}H NMR spectrum, δ, ppm: 4.23 br.s (1H, HCCl), 2.7 br.s (1H, $HCCCl_3$), 2.6–1.4 m (12H, CH_2) is well consistent with the data published in [8].

(4-Chlorocyclooctyl)dichloroacetonitrile (XIVb) was obtained by adding trichloroacetonitrile to *cis*-cyclooctene (**I**) by the procedure described for compounds **XIb** and **XIIb**. Yield 13%, bp 95°C (1.5 mm Hg). ^{1}H NMR spectrum, δ, ppm: 4.26 m (1H, HCCl), 2.53 m (1H, $HCCCl_2CN$), 2.3–1.4 m (12H, CH_2). Found, %: C 47.20; H 5.50; N 5.47. $C_{10}H_{14}Cl_3N$. Calculated, %: C 47.17; H 5.54; N 5.50.

2-(Trichloromethyl)-6-chlorobicyclo[3.3.0]octane (XVI) was obtained by the addition of tetrachloromethane to diene **V** initiated by the benzoyl peroxide in the same way as described for the synthesis of compound **VIIIa**. ^{1}H NMR spectrum, δ, ppm: 4.15 s (1H, HCCl), 2.87 m (3H, $HCCCl_3$, H^1,H^5), 2.76–1.8 m (8H). The spectrum is similar to the ^{1}H NMR spectrum of compound **XVI** published in [9].

Tetrachloromethane addition to cycloocta-1,5-diene (V) in the presence of CuCl. In an ampule of 35 ml capacity was charged 1 ml of diene **V**, 10 ml of tetrachloromethane, 0.05 g (5 mol%) of CuCl, and 15 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, then the ampule was sealed and heated for 30 h at 120°C. The ampule was opened, the solution was evaporated, and the residue was subjected to column chromatography on silica gel (eluent tetrachloromethane). On removing the solvent the residue was distilled in a vacuum, bp 112°C (8 mm Hg). The overall yield of compound **XVI** and **5-(trichloromethyl)-6-chlorocyclooct-1-ene (XVIIa)** (diastereomers mixture) was 52.1%. ^{1}H NMR spectrum contained a set of signals corresponding to compound **XVI**, and also to the mixture of isomers **XVIIa**. ^{1}H NMR spectrum, δ, ppm: 5.95–5.90 m (1H, HC=C), 5.71–5.62 m (1H, HC=C), 4.98 m (0.8H, HCCl, main isomer), 4.51 m (0.2H, HCCl, minor isomer), 3.28 m (0.2H, $HCCCl_3$, minor isomer), 2.83 m (0.8H, $HCCCl_3$, main isomer), 2.72–1.82 (8H).

Synthesis of chlorocycloalkyl aryl sulfones by the addition of arenesulfonyl chlorides to alkenes in the presence of copper(I) chloride. General procedure. In an ampule of 60 ml capacity was charged 1.5–3 mmol of copper(I) chloride, 20–30 mmol of arenesulfonyl chloride, 20–30 mmol of cycloalkene, and 30–35 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated at 80°C. Then the ampule was opened, the acetonitrile was distilled off, the residue was treated with chloroform, the solution obtained was passed through a bed of silica gel 0.5 cm thick, the chloroform was distilled off, and the residue was recrystallized from ethanol or a mixture ethanol–chloroform.

***trans*-2-Chlorocyclohexyl phenyl sulfone (VII)** was obtained by the reaction of benzenesulfonyl chloride with cyclohexene, reaction time 50 h, mp 81–82°C (publ.: mp 82.0–82.8°C [23]). ^{1}H NMR spectrum, δ, ppm: 7.94 d (2H, $H^{2,6}_{Ph}$), 7.67 d (1H, H^{4}_{Ph}), 7.60 d (2H, $H^{3,5}_{Ph}$), 4.39 br.s (1H, HCCl), 3.34 br.d (1H, $HCSO_2$), 2.4–1.4 m (8H, CH_2).

***endo*-3-Chlorobicyclo[2.2.1]hept-*exo*-2-yl 4-methylphenyl sulfone (VIIIe)** was obtained by the reaction of *p*-toluenesulfonyl chloride with norbornene at 97°C, reaction time 19 h Yield 70%. ^{1}H NMR spectrum, δ, ppm: 7.78 d (2H, $HH^{2,6}_{Ph}$), 7.37 d (2H, H^{3}_{Ar}), 4.42 m (1H, H^3), 2.90–2.85 m (2H, $H^2 + H^4$), 2.53 br.s (1H, H^1), 2.46 s (3H, CH_3), 2.05–1.28 (6H, $H^5 + H^6 + H^7$). Found, %: C 59.20; H 6.10. $C_{14}H_{17}ClO_2S$. Calculated, %: C 59.04; H 6.02.

***exo*-5-Chlorotricyclo[2.2.1.0^{2,6}]hept-*exo*-3-yl 4-methylphenyl sulfone (XIa)** was obtained by the reaction of *p*-toluenesulfonyl chloride with norbornadiene, reaction time 10 h. Compound **XIa** formed alongside compound **XIIa** at the addition of *p*-toluenesulfonyl chloride to norbornadiene; the isomers are easily separated by recrystallization from ethanol Compound **XIa** is less soluble, mp 154–156°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 7.78 d (2H, $H^{2,6}_{Ar}$), 7.39 d (2H, $H^{3,5}_{Ar}$), 3.79 s (1H, H^5), 3.06 s (1H, H^3), 2.47 s (3H, CH_3), 2.45 d (1H, $H^{7'}$), 2.36 s (1H, H^4), 2.04 d (1H, $H^{7''}$), 1.80–1.63 m (3H, $H^1 + H^2 + H^6$). Found, %: C 59.55; H 5.27. $C_{14}H_{15}ClO_2S$. Calculated, %: C 59.46; H 5.35.

***endo*-5-Chlorotricyclo[2.2.1.0^{2,6}]hept-*exo*-3-yl 4-methylphenyl sulfone (XIIa),** mp 146–150°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 7.83 d (2H, $H^{2,6}_{Ar}$), 7.39 d (2H, $H^{3,5}_{Ar}$), 3.99 s (1H, H^5), 3.78 C (1H, H^3), 2.52 d (1H, $H^{7'}$), 2.48 s (3H, CH_3), 2.41 s (1H, H^4), 1.80–1.66 m (3H, $H^1 + H^2 + H^6$), 1.51 d (1H, $H^{7''}$). Found, %: C 59.38; H 5.29. $C_{14}H_{15}ClO_2S$. Calculated, %: C 59.46; H 5.35. Overall yield of compounds **XIa** and **XIIa** 48.8%.

4-Methylphenyl 6-chlorocyclooct-1-en-5-yl sulfone (XVIIb) (a mixture of *cis*- and *trans*-isomers) was obtained by the reaction of *p*-toluenesulfonyl chloride with diene **V**. Reaction time 24 h. The overall yield of diastereomeric reaction products 22%, mp 62–63°C (from ethyl acetate–petroleum ether mixture). ^{1}H NMR spectrum, δ, ppm: 7.78 m (2H, $H^{2,6}_{Ar}$), 7.36 m (2H, $H^{3,5}_{Ar}$), 5.86 (1H, HC=C), 5.58 m (1H, HC=C), 5.12 s (0.9H, HCCl, main isomer), 4.6 m (0.1H, HCCl, minor isomer), 3.79 m (0.1H, $HCSO_2$, minor isomer), 3.43 m (0.9H, $HCSO_2$, main isomer), 2.62–1.59 m (11H). Mass spectrum, *m/z* (I_{rel}, %): 300 (0.13), 289 (0.41), 263 (0.41), 262 (1), 158 (0.06), 157 (0.69), 107 (0.64), 106 (0.38), 91 (0.50). Found, %: C 60.55; H 6.54. $C_{15}H_{19}ClO_2S$. Calculated, %: C 60.29; H 6.41.

Synthesis of bromocycloalkyl aryl sulfones by the addition of arenesulfonyl chlorides to alkenes in the presence of copper(I) bromide. Standard procedure. In an ampule of 60 ml capacity was charged 10.1 g (70.4 mmol) of copper(I) bromide, 20 mmol of arenesulfonyl chloride, 22 mmol of cycloalkene, and 45–50 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated for 14 h at 80°C. Then the ampule was opened, the acetonitrile was distilled off, the residue was treated with chloroform, the solution obtained was passed through a bed of silica gel 0.5 cm thick, the chloroform was distilled off, and the residue was recrystallized from ethanol.

***exo*-3-Bromotricyclo[2.2.1.0^{2,6}]hept-exo-5-yl (4-methylphenyl sulfone (XId)** was obtained together with ***endo*-3-bromotricyclo[2.2.1.0^{2,6}]hept-*exo*-5-yl 4-methylphenyl sulfone (XIId)** by the reaction of *p*-toluenesulfonyl chloride with norbornadiene. Isomers **XId** and **XIId** were separated in the same way as compounds **XIa** and **XIIa**. Compound **XId**: mp 154–156°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 7.78 d (2H, $H^{2,6}_{Ar}$), 7.39 d (2H, $H^{3,5}_{Ar}$), 3.81 s (1H, H^5), 3.07 s (1H, H^3), 2.48 s (3H, CH_3), 2.46 d (1H, $H^{7'}$), 2.39 C (1H, H^4), 2.08 d (1H, $H^{7''}$), 1.81–1.66 m (3H, $H^1 + H^2 + H^6$).

The signal at 3.79 ppm observed in the spectrum corresponds to $ClCH^5$ in compound **XIa**. The intensity ratio of the signals $BrCH^5$ and $ClCH^5$ is 83:17. Mass spectrum, *m/z* (I_{rel}, %): 247 (26.3), 189 (11.6), 187 (11.8), 173 (28.9), 171 (30.3), 145 (2.42), 143 (6.53), 140 (8.94), 139 (12.0), 129 (3.87), 127 (11.0), 108 (6.77), 107 (6.04), 105 (2.90), 92 (44.7), 91 (100). The elemental analysis (found, %: C 52.60; H 4.74) corresponds to the content in the product obtained of 85% $C_{14}H_{15}BrO_2S$ and 15% $C_{14}H_{15}ClO_2S$.

Compound **XIId**: mp 146–150°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 7.83 d (2H, $H^{2,6}_{Ar}$), 7.39 d (2H, $H^{3,5}_{Ar}$), 4.00 s (1H, H^5), 3.83 s (1H, H^3), 2.54–2.39 m (5H, $CH_3 + H^{7'} + H^4$), 1.80–1.68 m (3H, $H^1 + H^2 + H^6$), 1.51 d (1H, $H^{7''}$). The overall yield of compounds **XId** and **XIId** is 47%.

***exo*-3-Bromotricyclo[2.2.1.0^{2,6}]hept-exo-5-yl 4-fluorophenyl sulfone (XIf)** was obtained together with ***endo*-3-bromotricyclo[2.2.1.0^{2,6}]hept-*exo*-5-yl 4-fluorophenyl sulfone (XIIf)** by the addition of *p*-fluorobenzenesulfonyl chloride to norbornadiene.

Compound **XIf**: mp 128°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 7.93 m (2H, $H^{2,6}_{Ar}$), 7.28 m (2H, $H^{3,5}_{Ar}$), 3.83 C (1H, H^5), 3.08 s (1H, H^3), 2.45 m (2H, $H^{7'} + H^4$), 2.10 d (1H, $H^{7''}$), 1.82–1.65 m (3H, $H^1 + H^2 + H^6$). The signal at 3.81 ppm observed in the spectrum corresponds to $ClCH^5$ in compound **XIe**. The intensity ratio of the signals $BrCH^5$ and $ClCH^5$ is 74:26. Mass spectrum, *m/z* (I_{rel}, %): 251 (7.99), 189 (1.74), 187 (1.74), 173 (20.1), 171 (21.5), 145 (1.04), 143 (6.25), 129 (2.64), 127 (7.99), 95 (12.5), 92 (33.3), 91 (100).

The elemental analysis (found, %: C 49.19; H 3.81) corresponds to the content in the product obtained of 72% $C_{13}H_{12}BrFO_2S$ and 28% $C_{13}H_{12}ClFO_2S$. The overall yield of compounds **XIf** and **XIIf** is 38.5%.

6-Bromocyclooct-1-en-5-yl 4-methylphenyl sulfone (XVIIc) (a mixture of *cis*- and *trans*-isomers) was obtained by the reaction of *p*-toluenesulfonyl chloride with diene **V**. Reaction time 24 h. The overall yield of diastereomeric reaction products 19.5%, mp 67–68°C (from ethyl acetate–petroleum ether mixture). ^{1}H NMR spectrum, δ, ppm: 7.78 m (2H, $H^{2,6}_{Ar}$), 7.36 m (2H, $H^{3,5}_{Ar}$), 5.90 m (1H, HC=C), 5.59 m (1H, HC=C), 5.18 m (0.7H, HCBr, main isomer), 5.11 m (0.3H, HCBr, minor isomer), 3.47 m (0.3H, $HCSO_2$, minor isomer), 3.33 m (0.7H, $HCSO_2$, main isomer), 2.62–1.59 m (11H). Mass spectrum, *m/z* (I_{rel}, %): 344 (0.23), 343 (0.34), 341 (0.34), 300 (0.67), 289 (1). Found, %: C 52.57; H 5.60. $C_{15}H_{19}BrO_2S$. Calculated, %: C 52.48; H 5.54.

(2-Bromocyclooctyl)dichloroacetonitrile (XIIIc) was obtained in a mixture with compound **XIIIb** as follows: in an ampule of 60 ml capacity was charged 6.62 g (46.1 mmol) of copper(I) bromide, 3 ml (23.1 mmol) of *cis*-cyclooctene, 5 ml (49.7 mmol) of trichloroacetonitrile, and 40 ml of acetonitrile. A weak argon flow was passed for 15 min through the solution to remove the dissolved oxygen, the ampule was sealed and heated for 4.5 h at 95°C. Then the ampule was opened, the acetonitrile was distilled off, the residue was treated with tetrachloromethane, the solution obtained was passed through a bed of silica gel 0.5 cm thick, the solvent was distilled off, and the residue was distilled in a vacuum collecting the fraction boiling within 95–105°C (1 mm Hg). The ratio of compounds **XIIIb** and **XIIIc** in the reaction product was estimated from the data of GLC and ^{1}H NMR spectrum at 31:68. Mass spectrum, *m/z* (I_{rel}, %): 266 (2.40), 264 (8.54), 262 (7.47), 254 (2.94), 252 (2.67), 220 (64.3), 218 (100), 216 (8.81), 189 (14.7), 187 (14.4), 185 (7.21), 184 (24.3), 183 (17.3), 182 (67.1), 180 (16.5), 155 (19.2), 146 (64.3), 109 (74.3), 107 (84.3).

Compound **XIIIc**. ^{1}H NMR spectrum, δ, ppm: 4.78 m (0.54H, HCBr, *cis*-isomer), 4.56 m (0.46H, HCBr, *trans*-isomer), 2.90 m (0.54H, $HCCCl_2CN$, *cis*-isomer), 2.67 m (0.46H, $HCCCl_2CN$, *trans*-isomer), 2.4–1.4 m (12H, CH_2, both isomers).

Intramolecular cyclization of ester VI. The reaction was carried out in the presence of CuCl and CuBr in acetonitrile in sealed ampules at various temperature. The analysis of the reaction products was performed by GLC and ^{1}H NMR spectroscopy. In the presence of CuCl we obtained in a 43% yield **3,3-dichloro-4-(chloromethyl)-tetrahydrofuran-2-one (XVIIIa)**. ^{1}H NMR spectrum, δ, ppm: 4.68 m (1H, OCH), 4.24 m (1H, OCH), 4.01 m (1H, ClCH), 3.75 m (1H, ClCH), 3.55 m (1H, CH). The ^{1}H NMR spectrum obtained is in agreement with the published data [24]. In the process catalyzed by CuBr according to GLC data a mixture of two components formed whose ratio depended on the reaction conditions. In the ^{1}H NMR spectrum is also observed a signal at 4.20 ppm corresponding to one of the protons in the OCH_2 moiety of **4-(bromomethyl)-3,3-dichlorotetrahydrofuran-2-one (XVIIIb)**. Mass spectrum of the mixture of compounds **XVIIIa** and **XVIIIb**, *m/z* (I_{rel}, %): 252 (0.08), 248 (0.19), 246 (0.12), 171 (0.08), 169 (0.34), 167 (0.26), 157 (0.07), 155 (0.31), 153 (0.24), 125 (0.16), 123 (0.1), 111 (0.06), 109 (0.11), 105 (0.32), 103 (1), 87 (0.95). The presence of the bromine-containing **XVIIIb** is confirmed by the mass spectrum of the mixture: the isotope composition of the molecular ion corresponds to the presence of two chlorine and one bromine atoms. Besides the isotope composition of the fragment ions (*m/z* 167, 169, 171; 153, 155, 157) is consistent with the presence in each of them of one chlorine and one bromine atom [25].

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