ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 3, pp. 340–354. © Pleiades Publishing, Ltd., 2011.
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Reactions of Cyclopropanes with Potassium Dihaloiodates

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Received May 17, 2010

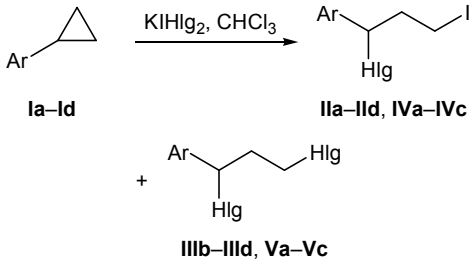
Abstract—Reactions of potassium dihaloiodates with arylcyclopropanes and polycyclic compounds containing a cyclopropane fragment characterized by different degrees of strain lead to formation of mixed 1,3-halogenation products. If iodohalogenation should give rise to products having a iodine atom in the benzylic position, 1,3-dichloro or 1,3-dibromo derivatives are formed. Iodohalogenation of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane is stereoselective and is accompanied by Wagner–Meerwein rearrangement.

DOI: 10.1134/S1070428011030031

Development of convenient methods for building up three-membered carbon ring favored studies on new modes of functionalization of cyclopropanes. Electrophilic addition at the σ-C–C bond in cyclopropane ring leads to formation of 1,3-disubstituted derivatives. Of specific interest are reactions ensuring introduction of two different substituents that are capable of being successively modified. Examples of such transformations are reactions of cyclopropanes with $AgOAc–I_2$, $TlOCOCX_3–I_2$ (X = H, F) [1], and $PhI(OCOCX_3)_2$ (X = Cl, F) [2–4], which gives rise to products containing a iodine atom and acetoxy group. In this connection, mixed halogenation of cyclopropanes is also interesting. Up to now, the only publication on mixed halogenation of cyclopropanes described mainly bromochlorination of the small ring and contained only one example of addition of iodine chloride to phenylcyclopropane [5].

The present work was aimed at studying reactions of cyclopropanes with potassium dihaloiodates. As shown previously [6, 7], the latter smoothly react with equimolar amounts of alkenes in chloroform at –20 to 0°C with formation of mixed halogenation products. We examined iodohalogenation of mono- and diarylsubstituted cyclopropanes, as well as of polycyclic compounds containing a cyclopropane fragment. We found that $KIHlg_2$ (Hlg = Cl, Br) reacts with an equimolar amount of cyclopropanes to give iodohalogenation and dihalogenation (chlorination and bromination) products (Scheme 1). The yields did not exceed 50% (Tables 1, 3–6), and they did not change upon raising the temperature, regardless of whether the reaction was carried out on exposure to light or in the dark. The latter fact suggests electrophilic mechanism of the process. The use of 2 equiv of the reagent is a crucial factor responsible for increase of the conversion of initial cyclopropanes. Tables 1 and 2 contain the yields of mixed halogenation products **II**–**V** from monoarylcyclopropanes substituted in the aryl fragment.

Scheme 1.



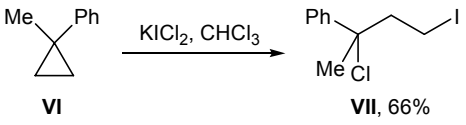
Ar = 4-$MeOC_6H_4$ (**a**), 4-MeC_6H_4 (**b**), Ph (**c**), 4-BrC_6H_4 (**d**); **II**, **III**, Hlg = Cl; **IV**, **V**, Hlg = Br.

Haloiodides **IIa** and **IVa** formed by reaction of $KIHlg_2$ with 4-methoxyphenylcyclopropane are unstable. The ^1H and ^{13}C NMR spectra of the reaction mixtures, recorded in 1 h after the reaction started, contained signals typical of compounds **IIa** and **IVa**; however, tarring was observed visually. In fact, after 48 h the ^1H NMR spectra lacked signals of haloiodides, but signals typical of dibromide **Va** remained unchanged. Introduction of an electron-withdrawing substituent into the aromatic ring deactivates the small

ring. In the reaction of 4-bromophenylcyclopropane with $KIHlg_2$ under standard conditions, 14% of the initial cyclopropane was recovered from the reaction mixture, whereas nitrophenylcyclopropane (a mixture of 4- and 2-nitrophenylcyclopropanes at a ratio of 1:6) failed to react at all.

The reaction of 1-methyl-1-phenylcyclopropane (**VI**) with $KICl_2$ in chloroform gave only mixed halogenation product **VII** (Scheme 2), but the ^{1}H NMR spectrum of the reaction mixture contained signals of other compounds which were not identified. Taking into account that these compounds were not formed in the reaction with an equimolar amount of $KICl_2$ (in this case, the initial cyclopropane was partly recovered from the reaction mixture), we presumed that they result from the reaction of **VII** with excess $KICl_2$. Compound **VII** is unstable, and it undergoes partial decomposition upon attempted isolation by column chromatography.

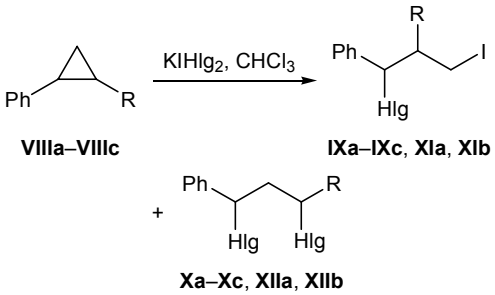
Scheme 2.



VI **VII**, 66%

The reaction of potassium dihaloiodates with 1-alkyl-2-phenylcyclopropanes **VIIIa–VIIIc** involves cleavage of both C^2–C^3 and C^1–C^2 bonds. In the first case, iodohalogenation products are mainly formed, whereas in the second case, the corresponding dichlorides and dibromides are obtained exclusively (as mixtures of *erythro* and *threo* isomers (Scheme 3; Tables 3, 4). Increase in the size of the alkyl substituent reduces the reactivity of 1-alkyl-2-arylcyclopropanes.

Scheme 3.



VIIIa–VIIIc **IXa–IXc**, **XIa**, **XIb**

Xa–Xc, **XIIa**, **XIIb**

R = Me (**a**), *i*-Pr (**b**), cyclohexyl (**c**); **IX**, **X**, Hlg = Cl; **XI**, **XII**, Hlg = Br.

The formation of dichlorides and dibromides in the reactions of $KIHlg_2$ with monoaryl-substituted cyclopropanes could be rationalized assuming that the initial cyclopropane reacts with chlorine or bromine generated as a result of decomposition of IHlg (Scheme 4). However, the degree of dissociation of IBr is quite significant (8%), whereas the degree of dissociation of ICl under analogous conditions is as low as 0.3% [8].

Table 1. Reaction of monoaryl-substituted cyclopropanes **Ia–Id** with $KICl_2$

Comp. no.	Ratio **I**–$KICl_2$	Temperature, °C	Yield, %		
			I	**II**	**III**
Ia	1:2	0–20	–	90[a]	–
Ib	1:2	0–20	–	41	3
Ic	1:1	0–5	43	47	9
	1:2	0–5	–	67	24
Id	1:2	0–20	14	46	17

[a] According to the ^{1}H NMR data in 1 h after the reaction started; after 48 h, polymerization occurred, and signals of compound **IIa** disappeared.

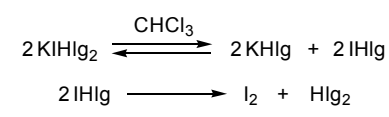
Table 2. Reaction of monoaryl-substituted cyclopropanes **Ia–Ic** with $KIBr_2$ at 0–20°C

Compound no.	Ratio **I**–$KIBr_2$	Yield, %	
		IV	**V**
Ia[a]	1:2	15	17
Ib	1:2	43	36
Ic[b]	1:2	79	16

[a] According to the ^{1}H NMR data, in 1 h after the reaction started a mixture of products was formed, the main components being compounds **IVa** and **Va**, as well as polymerization products; after 48 h, only signals from compound **Va** and polymerization products were present in the ^{1}H NMR spectrum.

[b] At 0–5°C.

Scheme 4.



To estimate the contribution of cyclopropane bromination process to the formation of compounds **XIIa** and **XIIb** we examined the reaction of 1-alkyl-2-phenylcyclopropanes **VIIIa** and **VIIIb** with bromine in chloroform at 0–20°C (i.e., where the yield of dibromides was especially high). We found that the reaction mixtures contained both diastereoisomeric compounds **XIIa** and **XIIb** resulting from cleavage of the C^1–C^2 bond in the initial cyclopropanes and dibromides **XIIIa** and **XIIIb** formed by opening of the

Table 3. Reaction of 1-alkyl-2-arylcyclopropanes **VIIIa**–**VIIIc** with $KICl_2$

Compound no.	*cis–trans* Isomer ratio	Ratio **VIII**–$KICl_2$	Yield, %		
			VIII	**IX** (*erythro/threo*)	**X** (*erythro/threo*)
VIIIa	42:58	1:1	18, *cis*	64 (53:47)	10 (66:34)
		1:2	0	74 (53:47)	25 (57:43)
VIIIb	27:73	1:1	41, *cis*	42 (27:73)	9 (63:37)
		1:2	0	25 (29:71)	70 (67:33)
VIIIc	20:80	1:2	54	27 (29:71)	13 (63:37)
		1:2[a]	0	55 (43:57)	35 (64:36)

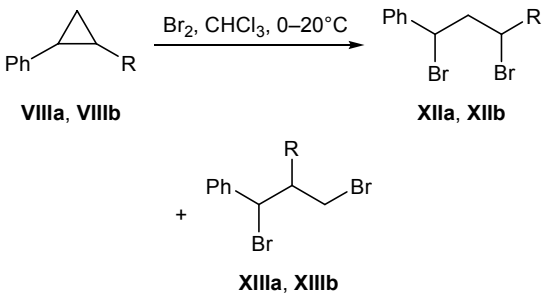
[a] The reaction was carried out at 25°C (reaction time 3 h).

Table 4. Reactions of 1-alkyl-2-arylcyclopropanes **VIIIa** and **VIIIb** with $KIBr_2$ and Br_2

Reagent	Compound no.	*cis–trans* Isomer ratio	Ratio **VIII**–reagent	Yield, %			
				VIII (*cis/trans*)	**XI** (*erythro/threo*)	**XII** (*erythro/threo*)	**XIII** (*erythro/threo*)
$KIBr_2$	**VIIIa**	42:58	1:1	19, *cis*	22 (56:44)	23 (57:43)	–
			1:2	–	27 (53:47)	48 (52:48)	–
	VIIIb	27:73	1:1	47 (45:55)	12 (37:63)	20 (59:41)	3 (43:57)
			1:2	13, *cis*	20 (42:58)	46 (57:43)	5 (50:50)
Br_2	**VIIIa**	42:58	1:1	–		64 (57:43)	27 (59:42)
	VIIIb	27:73	1:1	19, *cis*		49 (50:50)	32 (23:77)
			1:2	–		77 (48:52)	11 (33:67)

three-membered ring at the C^1–C^3 bond (Scheme 5); the yield of the latter was quite appreciable (Table 4).

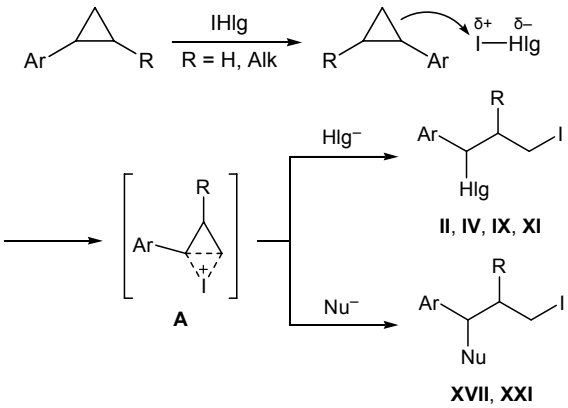
Scheme 5.



R = Me (**a**), *i*-Pr (**b**).

These findings are not consistent with the facts that only traces of **XIIIb** were detected in the iodobromination of compound **VIIIb** and that no dibromide **XIIIa** was formed in the iodobromination of **VIIIa**. Although some contribution of the halogenation process to the formation of dichlorides and dibromides cannot be ruled out completely, we presumed that the reaction of arylcyclopropanes with potassium dihaloiodates follows a pattern analogous to the mechanism proposed previously for the iodination of phenylcyclopropane with MOAc–I_2 (M = Ag, Tl) [1] and iodoso carboxylates [4] (Scheme 6).

Scheme 6.



Potassium dihaloiodates in chloroform undergo reversible decomposition into potassium halide and iodine halide [8] (Scheme 7).

Scheme 7.

$$KIHlg_2 \xrightarrow{CHCl_3} KHlg + IHlg$$

Table 5. Reaction of 1,2-diarylcyclopropanes **XIVa**–**XIVc** with $KICl_2$ at 0–20°C

Compound no.	*cis*–*trans* Isomer ratio	Ratio **XIV**–$KICl_2$	Yield, %	
			XIV (*cis*/*trans*)	**XV** (*meso*/*dl*)
XIVa	*trans*	1:2	–	32 (46:54)
XIVb	5:95	1:1	56, *trans*	41 (40:60)
		1:1[a]	50, *trans*	46 (40:60)
		1:2	–	51 (39:61)
		1:2[b]	–	80 (39:61)
		1:3	–	99 (43:57)
XIVc	78:22	1:2	6, *cis*	32 (39:61)

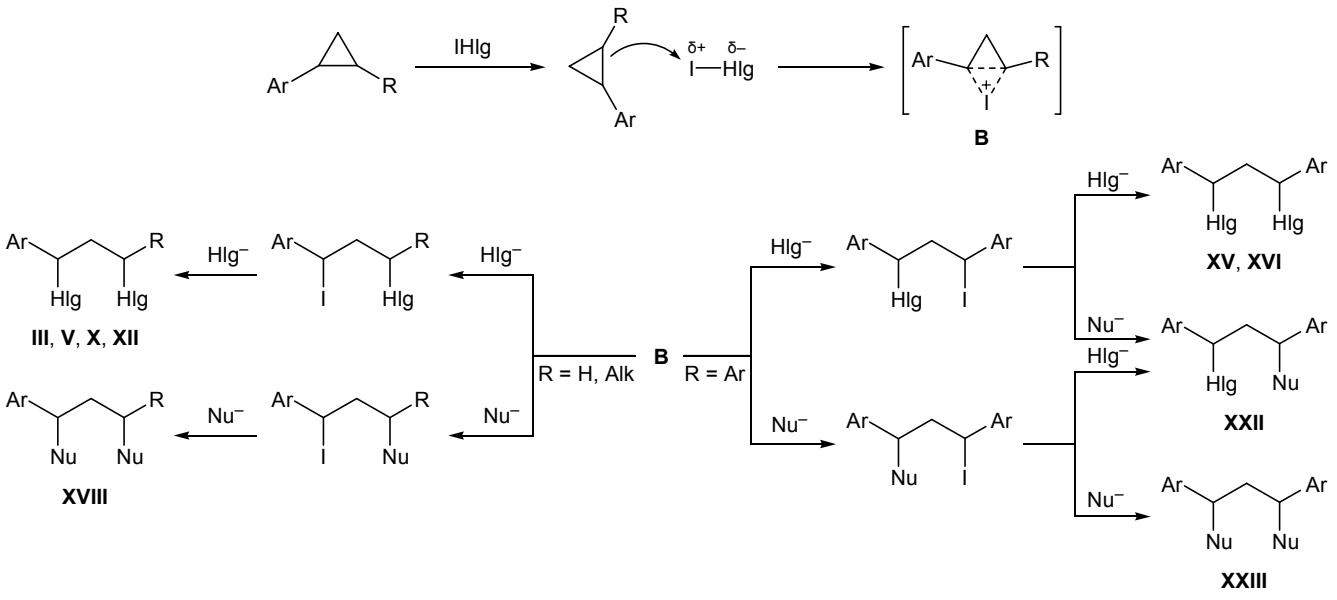
[a] At 0–60°C.
[b] The reaction was carried out in the dark.

Table 6. Reaction of 1,2-diarylcyclopropanes **XIVa**–**XIVc** with $KIBr_2$

Compound no.	*cis*–*trans* Isomer ratio	Ratio **XIV**–$KIBr_2$	Yield, %	
			XIV (*cis*/*trans*)	**XVI** (*meso*/*dl*)
XIVa	*trans*	1:2	8[a]	13 (50:50)
XIVb	5:95	1:1	48, *trans*	44 (41:59)
		1:2	11, *trans*	82 (50:50)
	23:77	1:1	24 (28:72)	25 (40:60)
		1:2	14 (22:78)	36 (43:57)
		1:2[b]	10 (11:89)	45 (46:54)
		1:3	–	39 (44:56)
XIVc	78:22	1:2	20 (74:26)	79 (49:51)

[a] 1,3-Bis(4-methoxyphenyl)prop-1-ene (**XXIV**, 20%), 4-methoxybenzaldehyde (17%), and 4-methoxycinnamaldehyde (3%) were also isolated.
[b] The reaction was carried out in the dark.

Scheme 8.



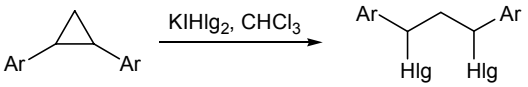
Iodine halides react with cyclopropanes to form iodonium ions like **A** (Scheme 6) and **B** (Scheme 8). Though the formation of four-membered chloronium or bromonium ion is hardly probable [9], the formation of analogous iodonium ion cannot be ruled out. Cations **A** and **B** are stabilized via addition of nucleophile; the latter may be chloride or bromide ion or external nucleophile (provided that it is present in the reaction mixture). If the product contains iodine atom in the benzylic position, it is readily replaced by chlorine or bromine to produce the corresponding dihalide. Liberated iodide ion is oxidized with iodine halide to molecular iodine, and this reaction requires an additional amount of the reagent (Scheme 9).

Scheme 9.

$$I^- + IHlg \longrightarrow I_2 + Hlg^-$$

The mobility of iodine atom in the benzylic position and its facile replacement by chlorine or bromine are indicated by the results of reactions of $KIHlg_2$ (Hlg = Cl, Br) with 1,2-diarylcyclopropanes. Regardless of the substituents in the aromatic rings and *cis*/*trans* isomer ratio, these reactions afforded mixtures of *dl* and *meso* isomers of 1,3-diaryl-1,3-dihalopropanes **XV** and **XVI** (Tables 5, 6). The reactions of 1,2-diarylcyclopropanes with equimolar amounts of potassium dihaloiodates were characterized by only 50% conversion of the substrates (Tables 5, 6), and no iodohalogenation products were detected.* On the other hand, the conversion of 1,2-diphenylcyclopropane in the reaction with 2 equiv of $KICl_2$ was 100% (Scheme 10).

Scheme 10.

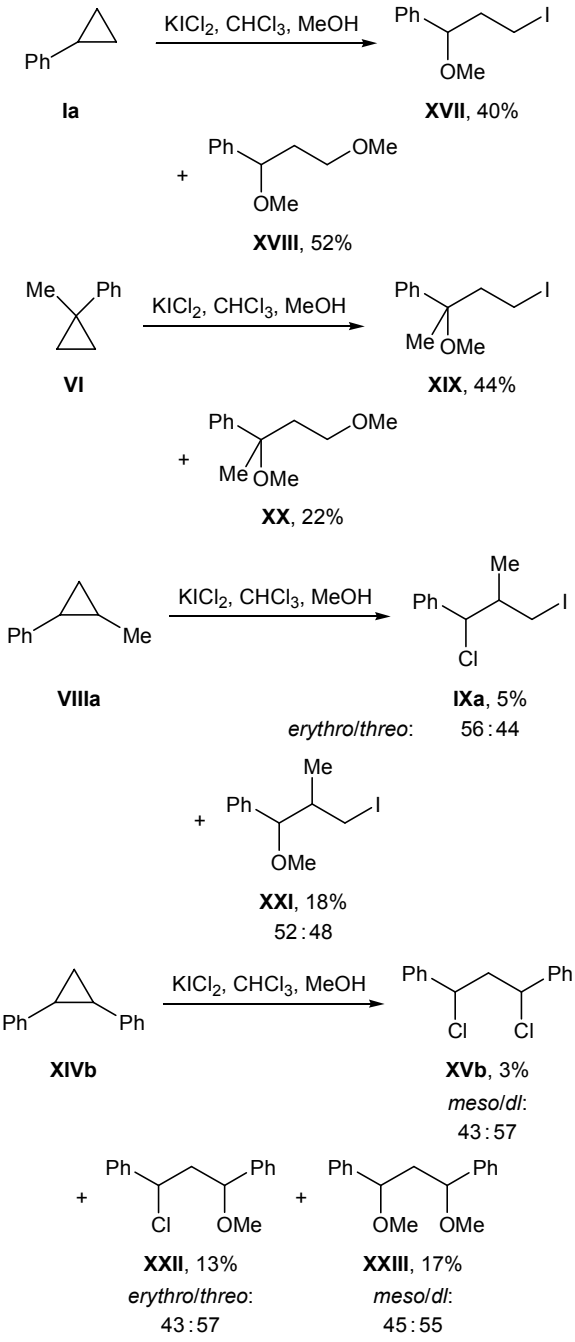


XIVa–XIVc **XVa–XVc**, **XVIa**, **XVIb**

Ar = 4-$MeOC_6H_4$ (**a**), Ph (**b**), 4-FC_6H_4 (**c**);
XV, Hlg = Cl; **XVI**, Hlg = Br.

Arylcyclopropanes reacted with potassium dichloroiodate in chloroform in the presence of methanol as external nucleophile to give dimethoxy derivatives **XVIII**, **XX**, and **XXIII**, as well as 1-chloro-3-methoxy-1,3-diphenylpropane (**XXII**) (Scheme 11), which is very consistent with the mechanism proposed above for iodohalogenation of arylcyclopropanes (Schemes 6, 8).

Scheme 11.

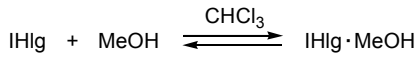


Reduced reactivity of potassium dihaloiodates in a mixture of chloroform with methanol should be noted. In the reaction of cyclopropane **VIIIa** with $KICl_2$ we isolated 38% of the initial compound (*cis*/*trans* ratio 1 : 1), and in the reaction with cyclopropane **XIVb** 36% of the initial compound (*trans*)

* The ^1H NMR spectrum of the reaction mixture contained signals which cannot be assigned to diaryldihalopropanes, but the concentration of these compounds was insignificant, and we failed to isolate them as individual substances.

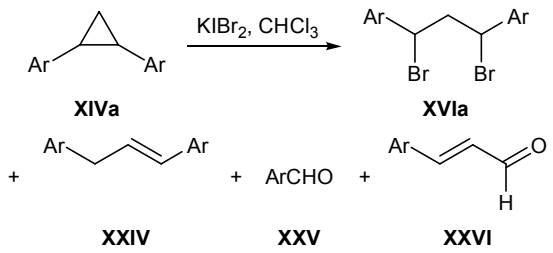
was recovered. This relation was typical of all cyclopropanes examined in the present work. A probable reason is formation of complexes by iodine halides and methanol [8] (Scheme 12).

Scheme 12.



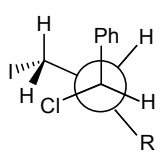
Single-electron transfer (SET) mechanism was proposed previously to rationalize the formation of dichlorides and dimethoxy derivatives in the reactions of propellanes with iodine chloride in methylene chloride and methanol, respectively [10]. Insofar as transformation of a substrate molecule into radical ion is known to facilitate valence isomerization and favor formation of fragmentation products [11], we believe that reactions of potassium dihaloiodates with cyclopropanes having electron-donating groups in the aromatic ring involves intermediate formation of radical cations. This assumption makes it possible to rationalize formation of such compounds as 1,3-bis(4-methoxyphenyl)prop-1-ene (**XXIV**), 4-methoxybenzaldehyde (**XXV**), and 4-methoxycinnamaldehyde (**XXVI**) in the reaction of 1,2-bis(4-methoxyphenyl)cyclopropane (**XIVa**) with potassium dibromoiodate (Scheme 13).

Scheme 13.

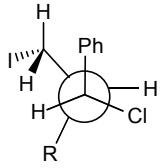


Ar = 4-$MeOC_6H_4$.

Products obtained in the reactions of potassium dihaloiodates with aryl-substituted cyclopropanes were not separated but were characterized as mixtures. Their structure was determined on the basis of the NMR data. In the ^{1}H NMR spectra of halogenation products of monoaryl-substituted cyclopropanes, signal from the benzylic proton appeared at δ 5.0 ppm as a doublet of doublets with vicinal coupling constants ^3J of ~8 and 6 Hz. Protons in the CH_2X group (X = Cl, Br, I) are diastereotopic, and positions of their signals are considerably different. Each signal appears as a doublet of triplets or double doublet of doublets with a geminal coupling constant ^2J of 10–11 Hz and two vicinal coupling constants ^3J of 5–7 Hz. The position of iodine atom in molecules **II** and **IV** is confirmed by the presence in their ^{13}C NMR spectra of a signal in the region δ_C 2–4 ppm, which is typical of CH_2I group.



threo-**IX**, *threo*-**XI**



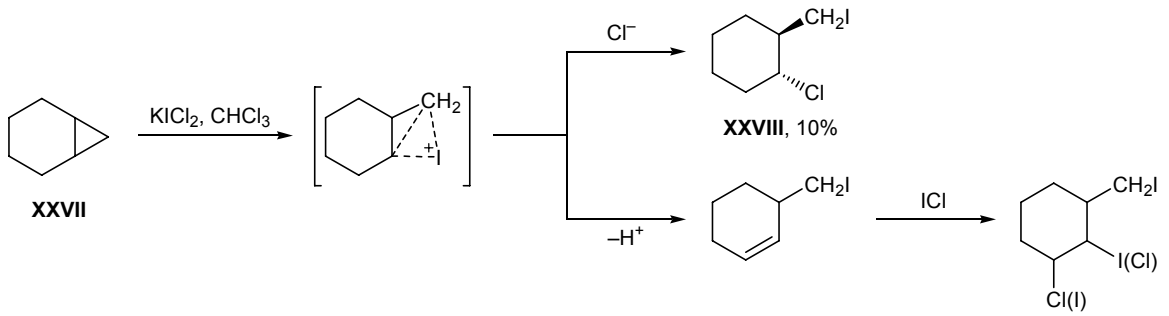
erythro-**IX**, *erythro*-**XI**

Products formed by cleavage of the C^1–C^2 and C^2–C^3 bonds in 1-alkyl-2-phenylcyclopropanes by the action of $KIHlg_2$ displayed in the ^{1}H NMR spectra considerably different signals from protons in the benzylic position. The spectra of compounds **IX** and **XI** contained doublets (J = 6.5–9.0 Hz), while the corresponding signals of compounds **X** and **XII** are doublets of doublets due to coupling with the C^2H_2 protons ($^3J \approx 10$, 2.5–5.5 Hz).

According to PM3 quantum-chemical calculations, the most favorable conformer of *threo* isomers **IX** and **XI** is characterized by *cis* orientation of the chlorine (bromine) atom and CH_2I group. By contrast, *erythro* isomers **IX** and **XI** adopt a conformation with *trans* orientation of the same groups. These findings led us to presume that the chemical shift of the RCH proton (R = Me, *i*-Pr, cyclohexyl) in the *erythro* isomer is larger than the chemical shift of the same proton in the *threo* isomer due to deshielding effect of the halogen atom. The same factor is responsible for the downfield shift of the methylene proton signals of the *threo* isomer as compared to *erythro*. Signal assignment in the ^{1}H NMR spectra of diastereoisomeric compounds **X** and **XII**, as well as of compounds **XV**, **XVI**, **XXII**, and **XXIII** formed in reactions of diarylcyclopropanes with $KIHlg_2$, was made with account taken of the fact that the chemical shifts of diastereotopic methylene protons in *erythro*/*meso* isomers differ to a stronger extent than those for the corresponding *threo*/*dl* isomers [12].

We also tried to perform iodohalogenation of polycyclic compounds containing a cyclopropane fragment. For this purpose, we examined reactions of $KICl_2$ with norcarane (**XXVII**) and *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**XXX**). In the reaction of norcarane with $KICl_2$ in chloroform at 0–20°C, the main products were compounds **XXVIII** and **XXIX** (or **XXIX′**); we failed to unambiguously determine the structure of the trihalo derivative (Scheme 14). Thus electrophilic iodine

Scheme 14.

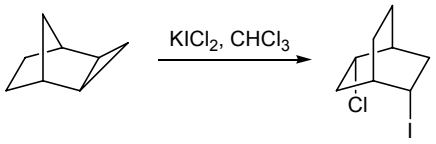


XXVII **XXVIII**, 10% **XXIX**, **XXIX′**, 9%

attacks norcarane molecule at the C^1–C^7 bond. Intermediate carbocation is stabilized via either nucleophilic attack by chloride ion or elimination of proton. In the latter case, addition of iodine chloride to 3-(iodomethyl)cyclohexene yields compound **XXIX** (or **XXIX′**).

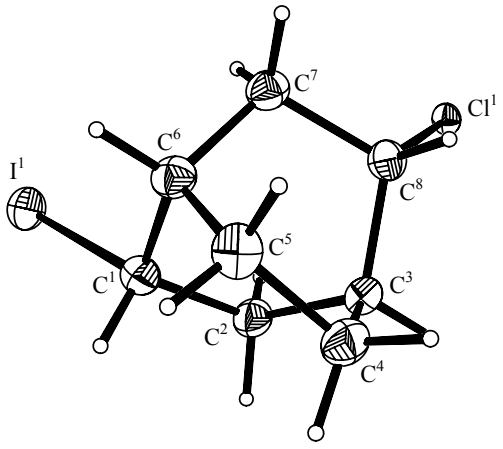
The reaction of potassium dichloroiodate with more strained cyclopropane derivative, *exo*-tricyclo-[3.2.1.$0^{2,4}$]octane (**XXX**) gave chloroiodo derivative **XXXI** as the major product (Scheme 15).

Scheme 15.



XXX **XXXI**, 31%

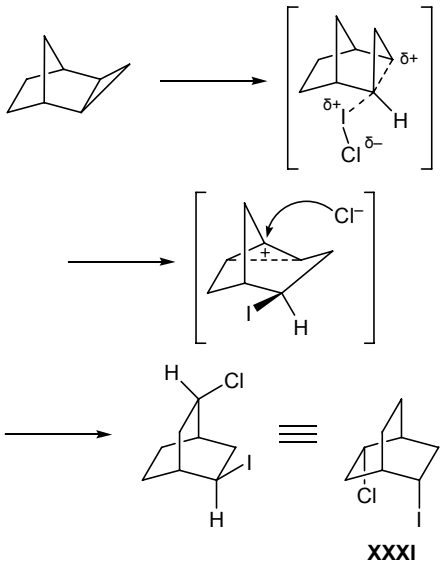
There are no NMR criteria for unambiguous determination of substituent configuration in compounds of the bicyclo[2.2.2]octane series. Therefore, the structure of compound **XXXI** was unambiguously determined by X-ray analysis. It was found that the product is disubstituted bicyclo[2.2.2]octane in which the substituents (iodine and chlorine atoms) are attached to C^2 and C^5, respectively, both being oriented *endo* (see figure). The principal bond lengths and bond angles in molecule **XXXI** are given in Table 7.



Structure of the molecule of *endo*-5-chloro-*endo*-2-iodobicyclo[2.2.2]octane (**XXXI**) according to the X-ray diffraction data.

The structure of compound **XXXI** implies initial attack by electrophilic iodine at the C^2 atom with rupture of the bridging C^2–C^4 bond and subsequent Wagner–Meerwein rearrangement. Nucleophilic attack by counterion (Cl^-) on the carbocationic center is directed from the rear of the "departing" σ-C–C bond to form rearranged chloroiodo derivative (Scheme 16).

Scheme 16.



XXXI

Thus potassium dihaloiodates ($KICl_2$ and $KIBr_2$) are convenient reagents for the halogenation of cyclopropanes. The reactions occur under mild conditions and involve cleavage of C–C bond in the three-membered ring with no halogenation of aromatic ring. If iodohalogenation of aryl-substituted cyclopropanes

should give rise to products containing iodine in the benzylic position, 1,3-dichloro or 1,3-dibromo derivatives are formed.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 and 100.6 MHz, respectively, using tetramethylsilane as internal reference. The ^{13}C chemical shifts were refined using APT pulse sequence. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT TSQ 7000 instrument. The progress of reactions was monitored, and the purity of the isolated compounds was checked, by TLC on Silufol UV-254 plates using petroleum ether.

Quantum-chemical calculations were performed in terms of semiempirical SCF PM3 approximation [13]. Geometric parameters of molecules were optimized by setting a convergence gradient of no larger than 10 cal Å^{-1} mol^{-1}.

Solvents were purified according to standard procedures [14]. Potassium dihaloiodates were synthesized according to the procedure described in [15].

X-Ray analysis of compound XXXI. The X-ray diffraction data were acquired on a Bruker SMART 1000 diffractometer with a CCD (coordinate) detector (MoK_α irradiation, graphite monochromator, λ = 0.71073 Å, ω-scanning). Colorless single crystals of compound **XXXI** were obtained by crystallization from chloroform. $C_8H_{12}ClI$. *M* 270.53. Monoclinic crystals, space group $P2_1/n$; unit cell parameters: a = 9.0698(4), b = 8.8023(4), c = 11.2729(5) Å; β = 99.1480(10)°; V = 888.53(7) Å^3; Z = 4; d_{calc} = 2.022 g× cm^{-3}; μ = 3.830 mm^{-1}; F = 520; T = 100(2) K. Total of 9096 reflections were measured in the θ range from 3.54 to 27.98° from a 0.40×0.30×0.25-mm single crystal; 2017 reflections were independent (R_{int} = 0.0192). The final divergence factors were R_1 = 0.0356, wR_2 = 0.0921 for 1919 reflections with $I > 2\sigma(I)$ and R_1 = 0.0371, wR_2 = 0.0932 for all reflections; number of refined parameters 91; goodness of fit 1.014. The structure was solved by the direct method and was refined by the least-squares procedure with respect to F^2 in anisotropic approximation for all nonhydrogen atoms. The positions of carbon atoms were determined from the Fourier difference syntheses, and the positions of hydrogen atoms were calculated on the basis of geometry considerations and were refined in isotropic approximation. All calculations were performed using SHELXTL software package.

Table 7. Principal bond lengths and bond angles in the molecule of *endo*-5-chloro-*endo*-2-iodobicyclo[2.2.2]-octane (**XXXI**)

Bond	*d*, Å	Angle	ω, deg
I^1–C^1	2.163(4)	$C^6C^1C^2$	109.3(3)
Cl^1–C^8	1.877(5)	$C^2C^1I^1$	110.5(3)
C^1–C^6	1.536(6)	$C^6C^1I^1$	112.0(3)
C^1–C^2	1.543(6)	$I^1C^1H^{1A}$	108.3
C^3–C^8	1.520(6)	$C^3C^8C^7$	110.4(3)
C^7–C^8	1.534(6)	$C^3C^8Cl^1$	110.3(3)
		$C^7C^8Cl^1$	110.6(3)
		$Cl^1C^8H^{8A}$	108.5

General procedure for iodohalogenation of cyclopropanes. A solution of arylcyclopropane in chloroform or a 1 : 1 mixture of chloroform with methanol was cooled to 0°C, potassium dihaloiodate $KIHlg_2$ (Hlg = Cl, Br) was added under stirring, and the mixture was stirred for 1 h. The mixture was then stirred at room temperature for 1–2 h in the reactions with arylcyclopropanes **I**, **VI**, **VIII**, and **XIV** or for 12 h in the reactions with bicyclo[4.1.0]heptane (**XXVII**, norcarane) and *exo*-tricyclo[3.2.1.0^{2,4}]octane (**XXX**). The mixture was washed with a solution of sodium sulfite until iodine color disappeared, the organic layer was separated, the aqueous phase was extracted with three portions of chloroform, the extracts were combined with the organic phase, dried over anhydrous sodium sulfate, filtered through a column, and evaporated under reduced pressure. Preparative chromatographic isolation of iodohalogenation products of arylcyclopropanes **Ib**, **VI**, **VIIIc**, **XIVa**, norcarane (**XXVII**), and *exo*-tricyclo[3.2.1.0^{2,4}]octane was performed using columns charged with silica gel (5–40 μm; eluent petroleum ether). The reactant ratios and yields are given in Tables 1–6.

1-Chloro-3-iodo-1-(4-methoxyphenyl)propane (IIa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.45 m and 2.57 m (1H each, 2-H), 3.18 m and 3.20 m (1H each, 3-H), 3.82 s (3H, OCH_3), 5.05 d.d (1H, 1-H, J = 8.0, 6.1 Hz), 6.91 d (2H, H_{arom}, J = 8.5 Hz), 7.36 d (2H, H_{arom}, J = 8.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 2.8 (CI), 42.9 (CH_2), 55.5 (OCH_3), 63.3 (CCl), 114.3 (C^o), 128.4 (C^m), 132.4 (C^i), 159.9 (C^p). Mass spectrum, *m*/*z* (I_{rel}, %): 312 (7.0) $[M + 2]^+$, 310 (20.0) $[M]^+$, 276 (10.0), 275 (100), 157 (10.0), 155 (27.0), 148 (56.0), 147 (45.0).

1-Chloro-3-iodo-1-(4-methylphenyl)propane (IIb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H,

CH_3), 2.48 m and 2.58 m (1H each, 2-H), 3.20 d.t (1H, 3-H, J = 10.0, 6.5 Hz), 3.30 d.t (1H, 3-H, J = 10.0, 7.4 Hz), 5.00 d.d (1H, 1-H, J = 8.4, 5.9 Hz), 7.20 d (2H, H_{arom}, J = 8.0 Hz), 7.34 d (2H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 2.5 (CI), 21.2 (CH_3), 42.9 (CH_2), 63.2 (CCl), 127.0 (C^m), 129.5 (C^o), 138.0 (C^p), 139.0 (C^i). Mass spectrum, m/z (I_{rel}, %): 296 (13.4) $[M + 2]^+$, 294 (36.5) $[M]^+$, 260 (0.3), 259 (40.1), 139 (29.9), 131 (100), 117 (31.4), 105 (23.3)

1-Chloro-3-iodo-1-phenylpropane (IIc) and 1,3-dichloro-1-phenylpropane (IIIc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **IIc**: 2.49 m and 2.60 m (1H each, 2-H), 3.22 d.t (1H, 3-H, J = 9.4, 6.3 Hz), 3.34 d.t (1H, 3-H, J = 9.4, 7.1 Hz), 5.05 d.d (1H, 1-H, J = 7.4, 6.3 Hz), 7.40 m (5H, H_{arom}); **IIIc**: 3.60 d.t (1H, 3-H, J = 10.6, 5.5 Hz), 3.78 m (1H, 3-H), 5.17 d.d (1H, 1-H, J = 8.5, 5.7 Hz), signals from 2-H and aromatic protons were overlapped by the corresponding signals of **IIc**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IIc**: 2.5 (CI), 43.0 (CH_2), 63.3 (CCl), 127.1 (C^m); **IIIc**: 41.9 (C^3), 42.3 (CH_2), 60.1 (C^1), 127.0 (C^m); common signals: 128.7 (C^p), 128.9 (C^o), 140.4 (C^i). Mass spectrum, m/z (I_{rel}, %): **IIc**: 282 (6.1) $[M + 2]^+$, 280 (20.2) $[M]^+$, 125 (31.1), 117 (100), 115 (28.2), 91 (40.6); **IIIc**: 192 (2.2) $[M + 4]^+$, 190 (15.5) $[M + 2]^+$, 188 (23.2) $[M]^+$, 155 (26.0), 153 (71.8), 127 (21.7), 125 (62.5), 117 (30.7), 115 (21.9), 91 (100), 83 (23.9).

1-(4-Bromophenyl)-1-chloro-3-iodopropane (IId) and 1-(4-bromophenyl)-1,3-dichloropropane (IIId). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **IId**: 2.42 m and 2.54 m (1H each, 2-H), 3.19 d.t (1H, 3-H, J = 9.9, 6.4 Hz), 3.30 d.t (1H, 3-H, J = 9.9, 7.1 Hz), 4.99 d.d (1H, 1-H, J = 8.4, 5.7 Hz), 7.30 d (2H, H_{arom}, J = 8.4 Hz), 7.52 d (2H, H_{arom}, J = 8.4 Hz); **IIId**: 3.56 d.t (1H, 3-H, J = 11.5, 5.4 Hz), 3.77 d.d.d (1H, 2-H, J = 11.5, 8.6, 5.3 Hz), 5.12 d.d (1H, 1-H, J = 8.6, 5.7 Hz), signals from 2-H and aromatic protons were overlapped by the corresponding signals of compound **IId**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IId**: 1.9 (CI), 42.8 (CH_2), 62.3 (CCl); **IIId**: 41.6 (C^3), 42.2 (CH_2), 59.1 (C^1); common signals: 122.7 (C^p), 128.8 (C^m), 132.0 (C^o), 139.4 (C^i). Mass spectrum, m/z (I_{rel}, %), **IId**: 362 (6.6), 361 (2.3), 360 (30.1), 359 (2.1), 358 (23.2) $[M]^+$, 325 (24.8), 323 (26.9), 205 (97.4), 203 (73.4), 197 (86.7), 195 (87.6), 171 (40.1), 117 (65.1), 16 (100), 115 (95.3); **IIId**: 271 (2.1), 270 (8.0), 269 (4.3), 268 (9.4), 266 (12.0) $[M]^+$, 233 (61.6), 231 (53.7). 205 (50.4). 203 (41.9), 183 (47.5), 171 (86.5), 169 (53.2), 116 (66.9), 115 (100), 89 (66.2), 76 (46.9), 75 (58.0), 63 (59.9), 51 (51.7), 50 (68.1).

1-Bromo-3-iodo-1-(4-methoxyphenyl)propane (IVa) and 1,3-dibromo-1-(4-methoxyphenyl)propane (Va). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **IVa**: 2.55 m and 2.73 m (1H each, 2-H), 3.20 d.t (1H, 3-H, J = 10.0, 6.5 Hz), 3.29 d.t (1H, 3-H, J = 10.0, 6.8 Hz), 3.84 s (3H, OCH_3), 5.14 d.d (1H, 1-H, J = 8.2, 6.5 Hz), 6.90 d (2H, H_{arom}, J = 8.7 Hz), 7.38 d (2H, H_{arom}, J = 8.7 Hz); **Va**: 2.55 m (1H, 2-H), 2.81 d.d.t (1H, 2-H, J = 14.7, 8.6, 5.9 Hz), 3.44 d.t (1H, 3-H, J = 10.4, 5.9), 3.57 d.d.d (1H, 3-H, J = 10.4, 7.8, 5.9 Hz), 3.84 s (3H, OCH_3), 5.25 d.d (1H, 1-H, J = 8.6, 6.1 Hz), 6.91 d (2H, H_{arom}, J = 8.6 Hz), 7.39 d (2H, H_{arom}, J = 8.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IVa**: 3.6 (CI), 42.2 (CH_2), 53.0 (CBr); **Va**: 31.3 (C^3), 42.8 (CH_2), 55.1 (C^1); common signals: 55.4 (OCH_3), 114.3 (C^o), 128.7 (C^m), 159.8 (C^p).

1-Bromo-3-iodo-1-(4-methylphenyl)propane (IVb) and 1,3-dibromo-1-(4-methylphenyl)propane (Vb). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **IVb**: 2.38 s (3H, CH_3), 2.59 m (1H), 2.75 d.d.t (1H, 2-H, J = 14.7, 8.3, 6.4 Hz), 3.22 d.t (1H, 3-H, J = 10.0, 6.4 Hz), 3.29 d.t (1H, 3-H, J = 10.0, 6.8 Hz), 5.12 d.d (1H, 1-H, J = 8.3, 6.1 Hz), 7.20 d (2H, H_{arom}, J = 8.0 Hz), 7.34 d (2H, H_{arom}, J = 8.0 Hz); **Vb**: 2.81 d.d.t (1H, 2-H, J = 14.9, 8.6, 5.9 Hz), 3.45 d.t (1H, 3-H, J = 10.3, 5.9 Hz), 3.57 d.d.d (1H, 3-H, J = 10.3, 7.8, 5.9 Hz), 5.22 d.d (1H, 1-H, J = 8.6, 5.9 Hz), signals from 2-H, CH_3, and aromatic protons were overlapped by the corresponding signals of **IVb**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IVb**: 3.5 (CI), 21.3 (CH_3), 42.8 (CH_2), 54.9 (CBr), 127.4 (C^m), 137.7 (C^i); **Vb**: 21.2 (CH_3), 31.1 (C^3), 42.2 (CH_2), 52.8 (C^1), 127.3 (C^m), 137.9 (C^i); common signals: 129.6 (C^o), 139.0 (C^p). Mass spectrum, m/z (I_{rel}, %): **IVb**: 261 (4.5), 260 (45.1), 254 (3.4), 133 (8.6), 105 (100); **Vb**: 214 (15.9), 212 (15.4), 211 (0.4), 105 (100).

1-Bromo-3-iodo-1-phenylpropane (IVc) and 1,3-dibromo-1-phenylpropane (Vc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **IVc**: 2.57 m and 2.75 m (1H each, 2-H), 3.22 d.t (1H, 3-H, J = 10.0, 6.3 Hz), 3.29 d.t (1H, 3-H, J = 10.0, 7.0 Hz), 5.10 d.d (1H, 1-H, J = 8.0, 6.3 Hz), 7.40 m (5H, H_{arom}); **Vc**: 2.81 m (1H, 2-H), 3.45 d.t (1H, 3-H, J = 10.0, 5.7 Hz), 3.57 m (1H, 3-H), 5.22 d.d (1H, 1-H, J = 8.6, 6.1 Hz), signals from 2-H and aromatic protons were overlapped by the corresponding signals of **IVc**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IVc**: 3.3 (CI), 42.7 (CH_2), 54.7 (CBr), 127.4 (C^m); **Vc**: 31.0 (C^3), 42.1 (CH_2), 52.5 (C^1), 127.3 (C^m); common signals: 128.6 (C^p), 128.9 (C^o). Mass spectrum, m/z (I_{rel}, %): **IVc**: 326 (0.3)

$[M + 2]^+$, 324 (0.3) $[M]^+$, 199 (39.1), 197 (39.2), 117 (100), 115 (42.2), 91 (99.2), 83 (28.5); **Vc**: 280 (1.5) $[M + 4]^+$, 278 (1.8) $[M + 2]^+$, 276 (1.1) $[M]^+$, 199 (44.6), 197 (44.9), 117 (81.3), 115 (38.5), 91 (100), 83 (25.5).

3-Chloro-1-iodo-3-phenylbutane (VII). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (3H, CH_3), 2.76 d.d.d and 2.83 d.d.d (1H each, 2-H, ^2J = 14.2, ^3J = 9.6, 5.3 Hz), 3.07 d.d.d and 3.22 d.d.d (1H each, 1-H, ^2J = 11.7, ^3J = 9.6, 5.3 Hz), 7.30–7.60 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –1.5 (CI), 32.3 (CH_3), 51.2 (C^2), 74.4 (CCl), 125.8 (C^m), 127.8 (C^p), 128.6 (C^o), 143.4 (C^i). Mass spectrum, *m*/*z* (I_{rel}, %): 259 (2.7). 258 (26.9) $[M - HCl]^+$, 131 (100), 129 (22.8), 115 (26.7), 103 (62.1), 91 (48.3).

1-Chloro-3-iodo-2-methyl-1-phenylpropane (IXa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 1.22 d (3H, CH_3, *J* = 6.5 Hz), 3.00 d.d (1H, 3-H, ^2J = 9.8, ^3J = 5.3 Hz), 3.31 d.d (1H, 3-H, ^2J = 9.8, ^3J = 5.9 Hz), 5.04 d (1H, 1-H, ^3J = 6.3 Hz); *threo* isomer: 0.92 d (3H, CH_3, *J* = 6.5 Hz), 3.48 d.d (1H, 3-H, ^2J = 9.6, ^3J = 3.3 Hz), 3.66 d.d (1H, 3-H, ^2J = 9.6, ^3J = 5.4 Hz), 4.75 d (1H, 1-H, ^3J = 8.8 Hz); common signals: 2.04 m and 2.17 m (1H each, 2-H), 7.35 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.0 and 15.1 (CI), 17.0 and 18.7 (CH_3), 41.9 and 42.9 (C^2), 67.7 and 67.8 (CCl); 127.40, 128.42, 128.61, 128.78, 128.81, 128.90, 139.71, 139.86 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 296 (3.9) $[M + 2]^+$, 294 (12.9) $[M]^+$, 131 (17.3), 127 (42.8), 125 (100), 115 (16.7), 91 (29.3). Found, %: C 40.51; H 3.88. $C_{10}H_{12}ClI$. Calculated, %: C 40.75; H 4.07. *M* 294.56

1,3-Dichloro-1-phenylbutane (Xa) was isolated and characterized in a mixture with compound **IXa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 1.84 d (3H, CH_3, *J* = 6.7 Hz), 2.23 d.d.d (1H, 2-H, ^2J = 15.1, ^3J = 10.4, 2.7 Hz), 4.50 d.d.d (1H, 3-H, ^3J = 10.4, 6.5, 2.7 Hz), 5.30 d.d (1H, 1-H, ^3J = 11.0, 2.7 Hz); *threo* isomer: 1.74 d (3H, CH_3, *J* = 6.3 Hz), 2.60 d.d.d (1H, 2-H, ^2J = 14.3, ^3J = 9.9, 6.0 Hz), 3.78 d.d (1H, 3-H, ^3J = 9.9, 5.1 Hz), 5.18 d.d (1H, 1-H, ^3J = 9.4, 6.0 Hz), 2.45 m (2H, 2-H in *erythro* and *threo* isomers), signals from aromatic protons were overlapped by those of compound **IXa**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.2 and 25.5 (CH_3), 50.8 and 52.2 (C^2), 55.2 and 55.8 (C^3), 60.0 and 61.3 (C^1); 127.0, 127.3, 128.0, 128.1, 128.9, 141.0 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 206 (2.6) $[M + 4]^+$, 205 (2.2), 204 (19.2) $[M + 2]^+$, 203 (3.4), 202 (29.1) $[M]^+$, 169 (12.3), 167 (46.3), 131 (96.4), 127 (34.3), 125 (100), 91 (89.0), 32 (63.4), 28 (73.1).

1-Chloro-2-iodomethyl-3-methyl-1-phenylbutane (IXb) and 1,3-dichloro-4-methyl-1-phenylpentane (Xb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **IXb**, *erythro* isomer: 0.99 d and 1.11 d (3H each, CH_3, *J* = 6.8 Hz), 2.05 m (1H, 3-H), 2.25 m (1H, 2-H), 3.20 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 4.3 Hz), 3.32 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 6.8 Hz), 5.28 d (1H, 1-H, ^3J = 6.3 Hz); **IXb**, *threo* isomer: 0.93 d and 1.03 d (3H each, CH_3, *J* = 6.8 Hz), 1.96 m (1H, 3-H), 2.10 m (1H, 2-H), 3.47 d (1H, ICH_2, *J* = 4.1 Hz), 3.48 d (1H, ICH_2, *J* = 5.1 Hz), 5.13 d (1H, 1-H, ^3J = 7.0 Hz); **Xb**, *erythro* isomer: 1.05 d and 1.12 d (3H each, CH_3, *J* = 6.7 Hz), 2.05 m (1H, 4-H), 2.24 d.d.d (1H, 2-H, ^2J = 15.0, ^3J = 11.0, 2.4 Hz), 2.40 d.d.d (1H, 2-H, ^2J = 15.0, ^3J = 11.2, 2.0 Hz), 4.36 d.d.d (1H, 3-H, ^3J = 11.0, 3.9, 2.0 Hz), 5.29 d.d (1H, 1-H, ^3J = 11.2, 2.4 Hz); **Xb**, *threo* isomer: 0.98 d and 1.00 d (3H each, CH_3, *J* = 6.7 Hz), 1.95 m (1H, 4-H), 2.49 d.d.d (1H, 2-H, ^2J = 14.1, ^3J = 10.4, 3.4 Hz), 2.60 d.d.d (1H, 2-H, ^2J = 14.1, ^3J = 10.8, 5.1 Hz), 3.42 d.d.d (1H, 3-H, ^3J = 10.8, 3.5, 3.4 Hz), 5.20 d.d (1H, 1-H, ^2J = 10.4, ^3J = 5.1 Hz); 7.30–7.60 m (H_{arom} in **IXb** and **Xb**). ^{1}H NMR spectrum (C_6D_6), δ, ppm: **IXb**, *erythro* isomer: 0.76 d and 0.99 d (3H each, CH_3, *J* = 7.0 Hz), 1.75 m (1H, 3-H), 2.12 m (1H, 2-H), 2.89 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 4.5 Hz), 3.10 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 6.7 Hz), 5.26 d (1H, 1-H, ^3J = 6.8 Hz); **IXb**, *threo* isomer: 0.72 d and 0.80 d (3H each, CH_3, *J* = 6.9 Hz), 1.85 m (1H, 3-H), 1.94 m (1H, 2-H), 3.27 d.d (1H, ICH_2, ^2J = 10.7, ^3J = 3.9 Hz), 3.31 d.d (1H, ICH_2, ^2J = 10.7, ^3J = 5.1 Hz), 4.99 d (1H, 3-H, ^3J = 7.2 Hz); **Xb**, *erythro* isomer: 0.86 d and 0.94 d (3H each, CH_3, *J* = 6.7 Hz), 1.72 m (1H, 4-H), 2.11 d.d.d (1H, 2-H, ^2J = 14.9, ^3J = 10.8, 2.6 Hz), 2.24 d.d.d (1H, 2-H, ^2J = 14.9, ^3J = 11.2, 2.2 Hz), 4.43 d.d.d (1H, 3-H, ^3J = 10.8, 3.9, 2.2 Hz), 5.42 d.d (1H, 1-H, ^3J = 11.2, 2.6 Hz); **Xb**, *threo* isomer: 0.74 d and 0.78 d (3H each, CH_3, *J* = 6.7 Hz), 1.56 m (1H, 4-H), 2.36 d.d.d (1H, 2-H, ^2J = 14.3, ^3J = 10.4, 3.1 Hz), 2.61 d.d.d (1H, 2-H, ^2J = 14.3, ^3J = 10.8, 5.1 Hz), 3.42 d.t (1H, 3-H, ^3J = 10.8, 3.1 Hz), 5.25 d.d (1H, 1-H, ^3J = 10.4, 5.1 Hz); 7.10–7.35 m (H_{arom} in **IXb** and **Xb**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IXb**, *erythro* isomer: 5.2 (CI), 17.7 and 22.1 (CH_3), 28.4 (C^3), 52.6 (C^2), 66.0 (CCl); **IXb**, *threo* isomer: 4.7 (CI), 17.2 and 19.6 (CH_3), 29.7 (C^3), 52.3 (C^2), 66.3 (CCl); **Xb**, *erythro* isomer: 17.5 and 19.9 (CH_3), 34.6 (C^4), 46.1 (C^2), 61.5 (C^3), 67.1 (C^1); **Xb**, *threo* isomer: 18.6 and 20.9 (CH_3), 34.2 (C^4), 45.7 (C^2), 60.2 (C^3), 66.3 (C^1); 125.9–131.5, 140.0, 140.1, 141.6 (C_{arom} in **IXb** and **Xb**). Mass spectrum, *m*/*z* (I_{rel}, %): **IXb**: 324 (0.1) $[M + 2]^+$, 323 (0.1), 322 (0.3) $[M]^+$, 198 (0.2),

197 (2.8), 196 (0.3), 195 (0.1), 159 (16.6), 127 (29.2), 125 (100); 324 (0.1) $[M + 2]^+$, 323 (0.1), 322 (0.4) $[M]^+$, 198 (0.2), 197 (3.3), 195 (0.2), 159 (16.0), 127 (27.5), 125 (100), 91 (20.0); **Xb**: 234 (0.5) $[M + 4]^+$, 232 (2.4) $[M + 2]^+$, 230 (3.7) $[M]^+$, 195 (2.7), 194 (2.7), 159 (69.7), 138 (80.1), 127 (31.8), 125 (100), 117 (37.0), 115 (37.9), 91 (65.2); 234 (0.4) $[M + 4]^+$, 232 (2.4) $[M + 2]^+$, 230 (3.4) $[M]^+$, 195 (4.2), 159 (71.8), 138 (36.4), 127 (29.5), 125 (100), 117 (31.3), 115 (26.1), 91 (56.6).

1-Chloro-2-cyclohexyl-3-iodo-1-phenylpropane (IXc). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 2.05 m (1H, 2-H), 3.25 d.d (1H, 3-H, ^2J = 10.2, ^3J = 4.5 Hz), 3.35 d.d (1H, 3-H, ^2J = 10.2, ^3J = 7.0 Hz), 5.30 d (1H, 1-H, ^3J = 7.4 Hz); *threo* isomer: 2.17 m (1H, 2-H), 3.45 d.d (1H, 3-H, ^2J = 10.6, ^3J = 4.1 Hz), 3.50 d.d (1H, 3-H, ^2J = 10.6, ^3J = 5.5 Hz), 5.20 d (1H, 1-H, ^3J = 6.3 Hz); common signals: 0.80–2.05 m (CH, CH-$_2$, cyclohexyl), 7.40 m (H_{arom}). ^{1}H NMR spectrum (C_6D_6), δ, ppm: *erythro* isomer: 1.93 m (1H, 2-H), 2.92 d.d (1H, 3-H, ^2J = 10.4, ^3J = 4.5 Hz), 3.12 d.d (1H, 3-H, ^2J = 10.4, ^3J = 6.7 Hz), 5.27 d (1H, 1-H, ^3J = 6.7 Hz); *threo* isomer: 2.02 m (1H, 2-H), 3.25 d.d (1H, 3-H, ^2J = 10.7, ^3J = 4.3 Hz), 3.30 d.d (1H, 2-H, ^2J = 10.7, ^3J = 5.3 Hz), 5.05 d (1H, 1-H, ^3J = 6.7 Hz); common signals: 0.60–1.95 m (CH, CH_2, cyclohexyl), 7.00–7.30 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *erythro* isomer: 6.2 (CI), 38.9 (CH), 52.6 (C^2), 65.8 (CCl); *threo* isomer: 5.1 (CI), 40.0 (CH), 52.3 (C^2), 66.0 (CCl); common signals: 26.3, 26.4, 26.5, 26.69, 26.72, 28.4, 29.4, 31.2, 32.5 (CH_2); 127.4, 127.6, 128.2, 128.3, 128.5, 128.6, 140.0, 140.1 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): *erythro* isomer: 364 (1.5) $[M + 2]^+$, 362 (4.3) $[M]^+$, 237 (3.4), 199 (14.7), 127 (35.9), 125 (100), 117 (48.5), 115 (29.3), 109 (39.0), 91 (35.7), 67 (25.7), 55 (59.6); *threo* isomer: 364 (1.2) $[M + 2]^+$, 362 (3.7) $[M]^+$, 237 (3.5), 199 (15.2), 127 (36.5), 125 (100), 117 (44.6), 115 (26.7), 109 (39.7), 55 (38.6), 41 (30.7).

1,3-Dichloro-2-cyclohexyl-1-phenylpropane (Xc). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 2.22 d.d.d (1H, 2-H, ^2J = 14.7, ^3J = 10.8, 2.5 Hz), 2.41 d.d.d (1H, 2-H, ^2J = 14.7, ^3J = 11.5, 1.9 Hz), 4.30 d.d.d (1H, 3-H, ^3J = 10.8, 4.2, 1.9 Hz), 5.27 d.d (1H, 1-H, J = 11.5, ^3J = 2.5 Hz); *threo* isomer: 2.50 d.d.d (1H, 2-H, ^2J = 14.3, ^3J = 10.4, 3.5 Hz), 2.57 d.d.d (1H, 2-H, ^2J = 14.3, ^3J = 10.2, 5.2 Hz), 3.33 d.t (1H, 3-H, ^3J = 10.7, 4.2 Hz), 5.19 d.d (1H, 1-H, ^3J = 10.0, 5.0 Hz); common signals: 0.80–2.05 m (CH, CH_2, cyclohexyl), 7.40 m (H_{arom}). ^{1}H NMR spectrum (C_6D_6), δ, ppm: *erythro* isomer: 2.07 d.d.d (1H, 2-H, ^2J = 14.9, ^3J = 11.0, 2.0 Hz), 2.23 d.d.d (1H, 2-H, ^2J = 14.9, ^3J = 11.0, 2.0 Hz), 4.35 d.d.d (1H, 3-H, ^3J = 11.0, 4.1, 2.0 Hz), 5.41 d.d (1H, 1-H, ^3J = 11.0, 2.0 Hz); *threo* isomer: 2.38 d.d.d (1H, 2-H, ^2J = 14.1, ^3J = 11.0, 2.7 Hz), 2.57 d.d.d (1H, 2-H, ^2J = 14.1, ^3J = 11.2, 4.6 Hz), 3.27 m (1H, 3-H), 5.30 d.d (1H, 1-H, ^3J = 11.2, 4.6 Hz); common signals: 0.60–1.95 m (CH, CH_2, cyclohexyl), 7.00–7.30 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *erythro* isomer: 44.5 (CH_{cycl}), 45.9 (C^2), 61.5 (C^3), 66.3 (C^1); *threo* isomer: 44.2 (CH_{cycl}), 45.4 (C^2), 60.3 (C^3), 65.5 (C^1); common signals: 25.97, 26.0, 26.1, 26.2, 26.3, 28.1, 28.4, 29.7, 30.0 (CH_2); 126.9, 127.4, 128.4, 128.8, 128.9 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): *erythro* isomer: 272 (1.5) $[M + 2]^+$, 270 (2.2) $[M]^+$, 199 (6.9), 138 (18.2), 125 (25.8), 117 (42.8), 104 (100), 91 (39.5), 83 (31.6), 67 (19.8), 55 (70.1); *threo* isomer: 272 (1.5) $[M + 2]^+$, 270 (2.6) $[M]^+$, 199 (7.2), 140 (3.4), 138 (9.7), 127 (7.7), 125 (24.4), 117 (43.1), 115 (15.3), 104 (100), 95 (21.2), 91 (48.7), 83 (33.0), 67 (23.9), 55 (67.1), 41 (28.8).

1-Bromo-3-iodo-2-methyl-1-phenylpropane (XIa) was isolated and characterized in a mixture with compound **XIIa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 1.29 d (3H, CH_3, J = 6.5 Hz), 2.13 m (1H, 2-H), 2.96 d.d (1H, 3-H, ^2J = 9.9, ^3J = 5.3 Hz), 3.26 d.d (1H, 3-H, ^2J = 9.9, ^3J = 4.9 Hz), 5.02 d (1H, 1-H, ^3J = 7.6 Hz); *threo* isomer: 0.90 d (3H, CH_3, J = 6.5 Hz), 2.13 m (1H, 2-H), 3.57 d.d (1H, 3-H, ^2J = 9.9, ^3J = 3.3 Hz), 3.72 d.d (1H, 3-H, ^2J = 9.9, ^3J = 5.5 Hz), 4.84 d (1H, 1-H, ^3J = 9.4 Hz); signals from aromatic protons (δ 7.30–7.48 ppm) were overlapped by those of compound **XIIa**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.2 and 16.8 (C^3), 18.7 and 19.1 (CH_3), 41.4 and 42.2 (C^2), 60.6 and 60.8 (C^1); 127.55, 128.00, 128.52, 128.69, 128.77, 128.95, 139.90 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 340 (2.5), 338 (4.1) $[M]^+$, 260 (9.4), 259 (100), 132 (24.2), 131 (67.1), 117 (32.4), 115 (67.1), 91 (61.6); 340 (0.3), 339 (0.5), 338 (0.2) $[M]^+$, 259 (5.7), 254 (4.5), 213 (22.3), 211 (27.2), 131 (100), 91 (79.8).

1-Bromo-2-iodomethyl-3-methyl-1-phenylbutane (XIb) was isolated and characterized in a mixture with compound **XIIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 3.11 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 4.9 Hz), 3.26 d.d (1H, ICH_2, ^2J = 10.4, ^3J = 5.3 Hz), 5.21 d (1H, 1-H, ^3J = 8.2 Hz); *threo* isomer: 3.52 d (2H, ICH_2, J = 4.5 Hz), 5.15 d (1H, 1-H, ^3J = 8.6 Hz); signals from 2-H, 3-H, CH_3, and aromatic protons were overlapped by those of compound **XIIb**. ^{1}H NMR

spectrum (C_6D_6), δ, ppm: *erythro* isomer: 1.82 m (1H, 3-H), 2.17 m (1H, 2-H), 2.81 d.d (1H, ICH_2, ^2J = 10.6, ^3J = 4.9 Hz), 3.03 d.d (1H, ICH_2, ^2J = 10.6, ^3J = 5.1 Hz), 5.16 d (1H, 1-H, ^3J = 8.0 Hz); *threo* isomer: 1.82 m (1H, 3-H), 2.03 m (1H, 2-H), 3.38 d.d (1H, ICH_2, ^2J = 10.8, ^3J = 3.3 Hz), 3.42 d.d (1H, ICH_2, ^2J = 10.8, ^3J = 5.1 Hz), 5.02 d (1H, 1-H, ^3J = 9.0 Hz); signals from CH_3 and aromatic (δ 7.00–7.35 ppm) protons were overlapped by those of compound **XIIb**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *erythro* isomer: 4.1 (CH_2I), 17.1 and 21.8 (CH_3), 29.7 (C^3), 51.5 (C^2), 58.8 (C^1); *threo* isomer: 6.6 (CH_2I), 17.8 and 21.3 (CH_3), 29.8 (C^3), 51.3 (C^2), 60.3 (C^1); 125–132, 140–142 (C_{arom}), overlapped by signals from aromatic carbon atoms in **XIIb**. Mass spectrum, *m*/*z* (I_{rel}, %): 288 (0.3), 287 (1.1) $[M - Br]^+$, 286 (0.3), 160 (11.7), 159 (100), 117 (40.1), 115 (35.1), 91 (47.2), 69 (36.7); 288 (0.2), 287 (1.3) $[M - Br]^+$, 286 (0.3), 160 (10.7), 159 (100), 117 (38.4), 115 (29.0), 91 (43.7), 69 (28.8).

1,3-Dichloro-1,3-bis(4-methoxyphenyl)propane (XVa). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.71 t (2H, 2-H, ^3J = 7.0 Hz), 5.15 t (2H, 1-H, 3-H, ^3J = 7.0 Hz); *meso* isomer: 2.68 (1H, 2-H), 2.99 d.t (1H, 2-H, ^2J = 14.3, ^3J = 7.3 Hz), 4.81 t (2H, 1-H, 3-H, ^3J = 7.3 Hz); common signals: 3.85 m (OCH_3), 6.92 d (H_{arom}, J = 8.4 Hz), 7.32 d (H_{arom}, J = 8.4 Hz). The physical constants of compound **XVa** coincided with those reported previously [16].

1,3-Dichloro-1,3-diphenylpropane (XVb). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.73 t (2H, 2-H, ^3J = 7.8 Hz), 5.27 t (2H, 1-H, 3-H, ^3J = 7.8 Hz); *meso* isomer: 2.75 (1H, 2-H), 3.03 d.t (1H, 2-H, ^2J = 14.3, ^3J = 7.6 Hz), 4.85 t (2H, 1-H, 3-H, ^3J = 7.6 Hz); common signals: 7.20–7.40 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *dl* isomer: 49.7 (CH_2), 60.9 (C^1, C^3), 127.1 (C^m), 128.8 (C^p), 128.95 (C^o), 140.8 (C^i); *meso* isomer: 49.6 (CH_2), 60.2 (C^1, C^3), 127.2 (C^m), 128.9 (C^p), 129.0 (C^o), 140.2 (C^i). Mass spectrum, *m*/*z* (I_{rel}, %): 268 (1.1) $[M + 4]^+$, 266 (6.8) $[M + 2]^+$, 264 (11.1) $[M]^+$, 193 (56.9), 127 (33.2), 126 (24.0), 125 (100), 115 (25.5), 104 (24.6), 103 (21.5), 91 (25.4); 268 (1.2) $[M + 4]^+$, 266 (7.3) $[M + 2]^+$, 264 (12.0) $[M]^+$, 193 (51.7), 127 (33.0), 126 (26.5), 125 (100), 115 (23.5), 104 (21.9), 103 (21.1), 91 (25.2). Found, %: C 66.39; H 5.71. $C_{15}H_{14}Cl_2$. Calculated, %: C 67.92; H 5.28. *M* 265.18. The physical constants of compound **XVb** coincided with those reported previously [17].

1,3-Dichloro-1,3-bis(4-fluorophenyl)propane (XVc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.63 t (2H, 2-H, ^3J = 6.7 Hz), 5.21 t (2H, 1-H, 3-H, ^3J = 6.7 Hz); *meso* isomer: 2.63 (1H, 2-H), 2.96 d.t (1H, 2-H, ^2J = 14.3, ^3J = 7.5 Hz), 4.77 t (2H, 1-H, 3-H, ^3J = 7.5 Hz); common signals: 7.10 m and 7.35 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *dl* isomer: 49.8 (CH_2), 59.9 (C^1, C^3), 115.8 (C^m, J_{CF} = 21.1 Hz), 128.8 (C^o, J_{CF} = 8.0 Hz), 136.6 (C^i); *meso* isomer: 49.7 (CH_2), 59.2 (C^1, C^3), 115.9 (C^m, J_{CF} = 21.8 Hz), 128.9 (C^o, J_{CF} = 8.7 Hz), 135.9 (C^i); 162.7 (C^p in *dl* and *meso* isomers, J_{CF} = 247.3 Hz). Found, %: C 59.26; H 3.87. $C_{15}H_{12}Cl_2F_2$. Calculated, %: C 59.80; H 3.99. *M* 301.16.

1,3-Dibromo-1,3-bis(4-methoxyphenyl)propane (XVIa). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.97 t (2H, 2-H, ^3J = 7.1 Hz), 5.22 t (2H, 1-H, 3-H, ^3J = 7.1 Hz); *meso* isomer: 2.90 d.t and 3.25 d.t (1H each, 2-H, ^2J = 14.4, ^3J = 7.3 Hz), 4.92 t (2H, 1-H, 3-H, ^3J = 7.3 Hz); common signals: 3.80 m (OCH_3), 6.85 d (H_{arom}, J = 8.5 Hz), 7.40 d (H_{arom}, J = 8.5 Hz). The physical constants of compound **XVIa** coincided with those reported previously [18].

1,3-Dibromo-1,3-diphenylpropane (XVIb). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.99 t (2H, 2-H, ^3J = 7.1 Hz), 5.25 t (2H, 1-H, 3-H, ^3J = 7.1 Hz); *meso* isomer: 2.97 (1H,), 3.27 d.t (1H, 2-H, ^2J = 14.7, ^3J = 7.4 Hz), 4.93 t (2H, 1-H, 3-H, ^3J = 7.4 Hz); 7.30–7.40 m (H_{arom} in *dl* and *meso* isomers). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *dl* isomer: 49.3 (CH_2), 53.1 (C^1, C^3), 127.6 (C^m), 128.90 (C^p), 129.03 (C^o), 141.0 (C^i); *meso* isomer: 49.2 (CH_2), 52.0 (C^1, C^3), 127.5 (C^m), 128.95 (C^p), 129.04 (C^o), 140.4 (C^i). The physical constants of compound **XVIb** coincided with those reported previously [19].

1,3-Dibromo-1,3-bis(4-fluorophenyl)propane (XVIc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: *dl* isomer: 2.92 t (2H, 2-H, ^3J = 7.1 Hz), 5.24 t (2H, 1-H, 3-H, ^3J = 7.1 Hz); *meso* isomer: 2.89 (1H, 2-H), 3.24 d.t (1H, 2-H, ^2J = 14.7, ^3J = 7.5 Hz), 4.90 t (2H, 1-H, 3-H, ^3J = 7.5 Hz); common signals: 7.10 m and 7.39 m (H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: *dl* isomer: 49.5 (CH_2), 50.7 (C^1, C^3), 115.9 (C^m, J_{CF} = 21.8 Hz), 136.8 (C^i); *meso* isomer: 49.5 (CH_2), 50.7 (C^1, C^3), 116.0 (C^m, J_{CF} = 21.8 Hz), 136.2 (C^i); common signals: 129.3 (C^o, J_{CF} = 8.0 Hz), 162.7 (C^p, J_{CF} = 250.0 Hz). Found, %: C 45.77; H 2.54. $C_{15}H_{12}Br_2F_2$. Calculated, %: C 46.15; H 3.08. *M* 390.06.

3-Iodo-1-methoxy-1-phenylpropane (XVII) and 1,3-dimethoxy-1-phenylpropane (XVIII). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **XVII**: 2.12 m and 2.27 m (1H each, 2-H), 3.17 d.t (1H, 3-H, J = 9.6, 6.7 Hz),

3.26 s (3H, OCH_3), 3.35 m (1H, 3-H), 4.27 d.d (1H, 1-H, J = 8.0, 4.9 Hz); **XVIII**: 1.87 m and 2.08 m (1H each, 2-H), 3.24 s (3H, OCH_3), 3.32 m (1H, 3-H), 3.35 s (3H, OCH_3), 3.52 d.d.d (1H, 3-H, J = 9.6, 6.9, 6.1 Hz), 4.30 d.d (1H, 1-H, J = 8.0, 6.1 Hz); 7.30–7.40 m (H_{arom} in **XVII** and **XVIII**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **XVII**: 2.8 (C^3), 41.8 (CH_2), 56.8 (OCH_3), 83.2 (C^1), 126.6 (C^m), 127.9 (C^p), 128.6 (C^o), 141.1 (C^i); **XVIII**: 38.1 (CH_2), 56.9 (OCH_3), 58.6 (OCH_3), 69.2 (C^3), 80.7 (C^1), 126.7 (C^m), 127.6 (C^p), 128.4 (C^o), 141.0 (C^i). Mass spectrum, m/z (I_{rel}, %): **XVII**: 276 (0.6) $[M]^+$, 148 (2.7), 147 (2.5), 121 (100), 104 (52.8), 91 (12.5), 77 (14.0); **XVIII**: 180 (4.1) $[M]^+$, 165 (5.9). 148 (5.9), 147 (4.8), 121 (100), 77 (15.4).

1-Iodo-3-methoxy-3-phenylbutane (XIX) and 1,3-dimethoxy-3-phenylpropane (XX). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **XIX**: 1.58 s (3H, CH_3), 2.38 d.d.d and 2.43 d.d.d (1H each, 2-H, ^2J = 13.7, ^3J = 11.9, 5.9 Hz), 3.02 d.d.d (1H, 1-H, ^2J = 11.9, ^3J = 9.4, 5.9 Hz), 3.12 (1H, 1-H), 3.15 s (3H, OCH_3); **XX**: 1.60 s (3H, CH_3), 2.11 m (2H, 2-H), 3.12 s (3H, OCH_3), 3.28 (1H, 1-H), 3.29 s (3H, OCH_3), 3.40 d.d.d (1H, 1-H, J = 9.4, 8.2, 6.5 Hz); 7.24–7.40 m (H_{arom} in **XIX** and **XX**). ^1H NMR spectrum (C_6D_6), δ, ppm: **XIX**: 1.15 s (3H, CH_3), 2.31 m (2H, 2-H), 2.85 s (3H, OCH_3), 2.92–3.01 m (2H, 1-H); **XX**: 1.50 s (3H, CH_3), 2.25 t.d (2H, 2-H, J = 8.4, 6.3 Hz), 3.00 s and 3.10 s (3H each, OCH_3), 3.32 d.d.d and 3.46 d.d.d (1H each, 1-H, J = 9.1, 8.4, 6.3 Hz); 7.10–7.50 m (H_{arom} in **XIX** and **XX**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **XIX**: –0.9 (C^1), 23.0 (CH_3), 48.2 (C^2), 50.4 (OCH_3), 80.0 (C^3), 125.9 (C^m), 127.1 (C^p), 128.4 (C^o), 143.7 (C^i); **XX**: 23.8 (CH_3), 41.7 (C^2), 50.2 and 58.5 (OCH_3), 68.9 (C^1), 78.0 (C^3), 126.0 (C^m), 126.9 (C^p), 128.2 (C^o), 144.9 (C^i). Mass spectrum, m/z (I_{rel}, %), **XIX**: 275 (0.5) $[M - 15]^+$, 259 (0.3), 147 (1.4), 136 (8.6), 135 (100), 105 (6.2); **XX**: 179 (0.6) $[M - 15]^+$, 163 (0.1), 147 (2.3), 136 (8.4), 135 (100).

3-Iodo-1-methoxy-2-methyl-1-phenylpropane (XXI) was characterized in a mixture with compound **IXa**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: *erythro* isomer: 1.10 d (3H, CH_3, J = 6.7 Hz), 1.88 sept (1H, 2-H, ^3J = 6.0 Hz), 2.96 d.d (1H, 3-H, ^2J = 9.6, ^3J = 5.7 Hz), 3.29 s (3H, OCH_3), 3.36 d.d (1H, 3-H, ^2J = 9.6, ^3J = 5.9 Hz), 4.21 d (1H, 1-H, ^3J = 5.7 Hz); *threo* isomer: 0.78 d (3H, CH_3, J = 6.7 Hz), 1.70 m (1H, 2-H), 3.24 s (3H, OCH_3), 3.44 d.d (1H, 3-H, ^2J = 9.5, ^3J = 3.5 Hz), 3.64 d.d (1H, 3-H, ^2J = 9.5, ^3J = 5.7 Hz), 3.87 d (1H, 1-H, ^3J = 8.4 Hz); 7.20–7.40 m (H_{arom} in *erythro* and *threo* isomers). ^1H NMR spectrum (C_6D_6), δ, ppm, *erythro* isomer: 1.02 d (3H, CH_3, J = 6.7 Hz), 1.70 m (1H, 2-H), 2.74 d.d (1H, 3-H, ^2J = 9.8, ^3J = 5.9 Hz), 3.07 s (3H, OCH_3), 3.14 d.d (1H, 3-H, ^2J = 9.8, ^3J = 5.9 Hz), 4.12 d (1H, 1-H, ^3J = 5.7 Hz); *threo* isomer: 0.67 d (3H, CH_3, J = 6.8 Hz), 1.49 m (1H, 2-H), 3.06 s (3H, OCH_3), 3.25 d.d (1H, 3-H, ^2J = 9.4, ^3J = 3.3 Hz), 3.54 d.d (1H, 3-H, ^2J = 9.4, ^3J = 5.7 Hz), 3.76 d (1H, 1-H, ^3J = 8.6 Hz); 7.00–7.30 m (H_{arom} in *erythro* and *threo* isomers). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.4 and 15.4 (CI), 16.1 and 17.5 (CH_3), 40.6 and 42.1 (C^2), 56.9 and 57.3 (OCH_3), 86.0 and 87.0 (C^1); 127.1, 127.7, 128.0, 128.2, 128.4, 139.9, 140.0 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 259 (0.1), 122 (7.0), 121 (100), 91 (8.7), 77 (9.8).

3-Chloro-1-methoxy-1,3-diphenylpropane (XXII) and 1,3-dimethoxy-1,3-diphenylpropane (XXIII). ^1H NMR spectrum ($CDCl_3$), δ, ppm: **XXII**, *threo* isomer: 2.27–2.36 m (2H, 2-H), 3.32 s (3H, OCH_3), 4.53 t (1H, 1-H, ^3J = 7.1 Hz), 5.29 t (1H, 3-H, ^3J = 7.1 Hz); **XXII**, *erythro* isomer: 2.27–2.36 m (2H, 2-H), 3.15 s (3H, OCH_3), 3.99 d.d (1H, 1-H, ^3J = 5.9, 8.0 Hz), 4.92 t (1H, 3-H, ^3J = 7.6 Hz); **XXIII**, *dl* isomer: 2.01 t (2H, 2-H, ^3J = 7.1 Hz), 3.29 s (6H, OCH_3), 4.44 t (2H, 1-H, 3-H, ^3J = 7.1 Hz); **XXIII**, *meso* isomer: 1.85 d.t and 2.44 d.t (1H each, 2-H, ^2J = 13.9, ^3J = 7.0 Hz), 3.18 s (6H, OCH_3), 4.07 t (2H, 1-H, 3-H, ^3J = 7.0 Hz); 7.20–7.40 m (H_{arom} in **XXII** and **XXIII**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **XXII**, *threo* isomer: 48.6 (CH_2), 60.6 (C^3), 57.0 (OCH_3), 80.6 (C^1); **XXII**, *erythro* isomer: 48.2 (CH_2), 56.5 (OCH_3), 60.1 (C^3), 81.2 (C^1); **XXIII**, *dl* isomer: 47.6 (CH_2), 56.8 (OCH_3), 80.1 (C^1, C^3); **XXIII**, *meso* isomer: 46.2 (CH_2), 56.4 (OCH_3), 81.0 (C^1, C^3); 126.6–129.0 and 142.0–143.0 (C_{arom} in **XXII** and **XXIII**). Mass spectrum, m/z (I_{rel}, %): **XXII**: 266 (1.1), 264 (1.6) $[M + 4]^+$, 262 (0.1) $[M + 2]^+$, 260 (0.1) $[M]^+$, 230 (3.0), 228 (6.8), 224 (9.8), 193 (11.7), 125 (20.7), 121 (100), 91 (13.1); 262 (0.1) $[M + 2]^+$, 260 (0.1) $[M]^+$, 230 (5.2), 228 (12.0), 193 (5.5), 121 (100); **XXIII**: 228 (1.2), 226 (1.0), 224 (14.0) $[M - HOMe]^+$, 193 (1.9), 192 (1.8), 122 (11.0), 121 (100); 228 (5.5), 226 (0.7), 224 (9.9) $[M - HOMe]^+$, 194 (1.0), 193 (6.9), 125 (11.9), 121 (100), 91 (11.2).

1,3-Bis(4-methoxyphenyl)prop-1-ene (XXIV). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 d (2H, CH_2, ^3J = 6.9 Hz), 3.82 s (6H, OCH_3), 6.22 d.t (1H, 2-H, J_{trans} = 15.7, ^3J = 6.9 Hz), 6.40 d (1H, 1-H, J_{trans} = 15.7 Hz), 6.85 d (2H, H_{arom}, J = 8.7 Hz), 6.88 d (2H, H_{arom}, J = 8.7 Hz), 7.15 d (2H, H_{arom}, J = 8.7 Hz), 7.27 d (2H, H_{arom}, J = 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 38.4 (C^3), 55.3 (OCH_3), 113.9, 127.2 (C_{arom}), 127.5 (C^2), 129.6 (C_{arom}), 130.1 (C^1),

130.4, 132.4, 158.0, 158.8 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 255 (18.7), 254 (100) $[M]^+$, 253 (15.1), 239 (15.0), 223 (40.9), 145 (21.7), 115 (14.9).

1-Chloro-2-iodomethylcyclohexane (XXVIII) and 1-chloro-2-iodo-3-iodomethylcyclohexane (XXIX) [or 2-chloro-1-iodo-3-iodomethylcyclohexane (XXIX′)]. Yield 10% (**XXVIII**), 9.5% (**XXIX** or **XXIX′**), transparent oily substance, R_f 0.40. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **XXVIII**: 2.27 m (1H, 2-H), 3.46 d.d (1H, ICH_2, *J* = 9.9, 1.9 Hz), 3.53 d.d.d (1H, ICH_2, *J* = 9.9, 5.0, 1.7 Hz), 3.71 d.d.d (1H, 1-H, *J* = 11.4, 9.9, 4.2 Hz); **XXIX** or **XXIX′**: 2.56 m (1H, 3-H), 2.95 d.d (1H, CH_2I, *J* = 9.9, 8.8 Hz), 3.18 d.d (1H, CH_2I, *J* = 9.9, 5.9, 5.0 Hz), 4.75 d (1H, 2-H or 1-H, *J* = 2.6 Hz), 4.90 br.s (1H, 1-H or 2-H); 2.00–1.20 m (CH_2 in **XXVIII** and **XXIX**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **XXVIII**: 14.2 (CH_2I), 25.0 and 26.4 (C^4, C^5), 32.8 (C^3) 37.0 (C^6), 45.9 (C^2), 64.1 (C^1); **XXIX** or **XXIX′**: 13.9 (CH_2I); 19.7, 28.1, 28.7 (C^4, C^5, C^6); 37.7 (CHI), 44.3 (CH_2I), 61.79 (CHCl). Mass spectrum, *m*/*z* (I_{rel}, %): **XXVIII**: 261 (0.3), 260 (2.6) $[M + 2]^+$, 259 (1.0), 258 (8.1) $[M]^+$, 257 (16.0), 96 (7.0), 95 (100); **XXIX**: 386 (1.3) $[M + 2]^+$, 384 (4.3) $[M]^+$, 259 (6.4), 257 (22.6), 221 (50.8), 131 (10.4), 129 (36.3), 94 (40.6), 93 (100), 92 (31.0), 9 (44.2), 79 (41.5), 77 (40.4), 67 (19.2).

***endo*-5-Chloro-*endo*-2-iodobicyclo[2.2.2]octane (XXXI).** Yield 31%, transparent oily substance, R_f 0.32, mp 86–88°C (from chloroform). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.56–1.80 m (5H, 1-H, 7-H, 8-H), 2.00 m (1H, 4-H), 2.30 m (3H, *exo*-6-H, 3-H), 2.70 d.d.t.d (1H, *endo*-6-H, *J* = 14.9, 6.9, 2.0, 0.7 Hz), 4.18 d.d.t (1H, HCI, *J* = 9.0, 7.0, 2.1 Hz), 4.44 d.d.t (1H, HCCl, *J* = 10.0, 6.9, 1.5 Hz). ^{1}H NMR spectrum (C_6D_6), δ, ppm: 0.90–1.10 m (4H, 7-H, 8-H), 1.32 m (1H, 1-H), 1.62 m (1H, 4-H), 1.90 d.d.d.d (1H, *exo*-3-H, *J* = 14.3, 10.2, 3.9, 2.2 Hz), 1.92 d.d.d.d (1H, *exo*-6-H, *J* = 14.3, 10.2, 4.1, 2.4 Hz), 2.44 d.d.t (1H, *endo*-3-H, *J* = 14.5, 5.9, 2.2 Hz), 2.79 d.d.t (1H, *endo*-6-H, *J* = 14.7, 6.9, 1.8 Hz), 3.75 d.d.t (1H, HCI, *J* = 10.0, 6.1, 2.0 Hz), 4.0 d.d.t (1H, HCCl, *J* = 10.2, 6.9, 2.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.6, 23.4 (C^7, C^8), 29.6 (C^2), 34.9 (C^3), 35.3 (C^1), 35.6 (C^6), 36.5 (C^4), 59.0 (C^5). Mass spectrum, *m*/*z* (I_{rel}, %): 270 (0.2) $[M]^+$, 145 (3.0), 143 (10.9), 107 (42.0), 79 (93.3), 44 (100). Found, %: C 35.37; H 4.44. $C_8H_{12}ClI$. Calculated, %: C 35.49; H 4.44. *M* 270.54.

General procedure for the bromination of arylcyclopropanes VIIIa and VIIIb. Molecular bromine was added under vigorous stirring to a solution of arylcyclopropane **VIIIa** or **VIIIb** in chloroform, cooled to 0°C, and the mixture was stirred for 1 h at 0°C and for 1–2 h at room temperature. The mixture was then washed with a solution of sodium sulfite until bromine color disappeared, the organic phase was separated, the aqueous phase was extracted thrice with chloroform, and the extracts were combined with the organic phase, dried over anhydrous sodium sulfate, filtered through a column, and evaporated under reduced pressure. The reactant ratios and yields of the products are given in Table 4.

1,3-Dibromo-1-phenylbutane (XIIa) and 1,3-dibromo-2-methyl-1-phenylpropane (XIIIa). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **XIIa**, *erythro* isomer: 1.84 d (3H, CH_3, *J* = 6.7 Hz), 2.37 d.d.d (1H, 2-H, ^2J = 15.4, ^3J = 10.0, 3.2 Hz), 2.65 m (1H, 2-H), 4.49 d.d.d (1H, 3-H, ^3J = 10.0, 6.5, 3.1 Hz), 5.30 d.d (1H, 1-H, ^3J = 10.8, 3.2 Hz); **XIIa**, *threo* isomer: 1.72 d (3H, CH_3, *J* = 6.7 Hz), 2.65 m (1H, 2-H), 2.80 d.d.d (1H, 2-H, ^2J = 15.1, ^3J = 9.8, 5.5 Hz), 3.72 m (1H, 3-H), 5.21 d.d (1H, 1-H, ^3J = 9.6, 5.5 Hz); **XIIIa**, *erythro* isomer: 1.32 d (3H, CH_3, *J* = 6.5 Hz), 2.60 m (1H, 2-H), 3.20 d.d (1H, 3-H, ^2J = 10.2, ^3J = 5.1 Hz), 3.44 d.d (1H, 3-H, ^2J = 10.2, ^3J = 5.3 Hz), 5.15 d (1H, 1-H, ^3J = 7.45 Hz); **XIIIa**, *threo* isomer: 0.97 d (3H, CH_3, *J* = 6.7 Hz), 2.40 m (1H, 2-H), 3.94 d.d (1H, 3-H, ^2J = 10.0, ^3J = 4.7 Hz), 4.97 d (1H, 1-H, ^3J = 9.4 Hz); the 3-H signal of *threo*-**XIIIa** (δ ~3.70 ppm) was overlapped by the 3-H signal of *threo*-**XIIa**; 7.30–7.50 m (H_{arom} in **XIIa** and **XIIIa**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm; **XIIa**: 26.2 and 26.6 (CH_3), 47.6 and 49.0 (C^3), 50.4 and 50.9 (C^2), 51.3 and 54.1 (C^1); 127.42, 127.63, 128.62, 128.78, 128.87, 128.92, 140.21 (C_{arom}); **XIIIa**, *erythro* isomer: 17.2 (CH_3), 40.3 (C^3), 43.1 (C^2), 59.4 (C^1); **XIIIa**, *threo* isomer: 16.9 (CH_3), 37.9 (C^3), 42.2 (C^2), 58.3 (C^1); 127.95, 128.01, 128.38, 128.51, 128.66, 128.74, 141.55 (C_{arom} in *erythro*-**XIIIa** and *threo*-**XIIIa**). Found for mixture **XIIa**/**XIIIa**, %: C 41.14; H 4.05. $C_{10}H_{12}Br_2$. Calculated, %: C 41.10; H 4.10.

1,3-Dibromo-4-methyl-1-phenylpentane (XIIb) and 1-bromo-2-bromomethyl-3-methyl-1-phenylbutane (XIIIb). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **XIIb**, *erythro* isomer: 1.07 d and 1.14 d (3H each, CH_3, *J* = 6.7 Hz), 1.99 m (1H, 4-H), 2.41 d.d.d (1H, 2-H, ^2J = 15.5, ^3J = 10.9, 2.4 Hz), 2.64 d.d.d (1H, 2-H, ^2J = 15.5, ^3J = 11.0, 2.2 Hz), 4.50 d.d.d (1H, 3-H, ^3J = 10.9, 3.4, 2.2 Hz), 5.40 d.d (1H, 1-H, ^3J = 11.0, 2.4 Hz); **XIIb**, *threo* isomer: 1.00 d and 1.02 d (3H each, CH_3, *J* = 6.8 Hz), 1.86 m (1H, 4-H), 2.74 d.d.d

(1H, 2-H, ^2J = 14.5, ^3J = 10.4, 3.4 Hz), 2.83 d.d.d (1H, 2-H, ^2J = 14.5, ^3J = 10.7, 5.2 Hz), 3.56 d.t (1H, 3-H, ^3J = 10.7, 3.4 Hz), 5.32 d.d (1H, 1-H, ^3J = 10.4, 5.2 Hz); **XIIIb**, *erythro* isomer: 1.15 d (3H, CH_3, J = 6.1 Hz), 2.52 m (1H, 2-H), 3.27 d.d (1H, $BrCH_2$, ^2J = 10.7, ^3J = 4.4 Hz), 3.50 d.d (1H, $BrCH_2$, ^2J = 10.7, ^3J = 4.6 Hz), 5.28 d (1H, 1-H, ^3J = 10.5 Hz); **XIIIb**, *threo* isomer: 0.89 d and 1.03 d (3H each, CH_3, J = 7.0 Hz), 2.45 m (1H, 2-H), 3.83 d.d (1H, $BrCH_2$, ^2J = 10.7, ^3J = 3.0 Hz), 3.89 d.d (1H, $BrCH_2$, ^2J = 10.7, ^3J = 5.0 Hz), 5.25 d (1H, 1-H, ^3J = 9.2 Hz); 1.90 m (1H, 3-H in *erythro*-**XIIIb** and *threo*-**XIIIb**), the CH_3 signal of *erythro*-**XIIIb** (δ 1.07 ppm) was overlapped by signals of compound **XIIb**; 7.15–7.55 m (H_{arom} in **XIIb** and **XIIIb**). ^{1}H NMR spectrum (C_6D_6), δ, ppm: **XIIb**, *erythro* isomer: 1.62 m (1H, 4-H), 2.26 d.d.d (1H, 2-H, ^2J = 15.5, ^3J = 10.8, 2.6 Hz), 2.46 d.d.d (1H, 2-H, ^2J = 15.5, ^3J = 11.2, 2.4 Hz), 4.57 d.d.d (1H, 3-H, ^3J = 10.8, 3.3, 2.4 Hz), 5.51 d.d (1H, 1-H, ^3J = 11.2, 2.6 Hz); **XIIb**, *threo* isomer: 1.45 m (1H, 4-H), 2.58 d.d.d (1H, 2-H, ^2J = 14.5, ^3J = 10.6, 3.2 Hz), 2.83 d.d.d (1H, 2-H, ^2J = 14.5, ^3J = 10.8, 4.9 Hz), 3.53 d.t (1H, 3-H, ^3J = 10.8, 3.2 Hz), 5.39 d.d (1H, 1-H, ^3J = 10.6, 4.9 Hz); 0.74 d, 0.78 d, 0.87 d, and 0.96 d (3H each, CH_3 in *erythro*-**XIIb** and *threo*-**XIIb**, J = 6.8 Hz); **XIIIb**, *erythro* isomer: 3.00 d.d and 3.44 d.d (1H each, $BrCH_2$, ^2J = 11.0, ^3J = 4.5 Hz), 5.21 d (1H, 1-H, ^3J = 10.6 Hz); **XIIIb**, *threo* isomer: 3.63 d.d (1H, $BrCH_2$, ^2J = 11.0, ^3J = 2.7 Hz), 3.76 d.d (1H, $BrCH_2$, ^2J = 11.0, ^3J = 4.9 Hz), 5.17 d (1H, 1-H, ^3J = 9.4 Hz); signals from 2-H, 3-H, and CH_3 protons in **XIIIb** were overlapped by those of compound **XIIb**; 7.00–7.35 m (H_{arom} in **XIIb** and **XIIIb**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **XIIb**: 18.1, 18.5, 20.6, and 21.0 (CH_3); 34.4 and 34.8 (C^4), 46.29 and 46.30 (C^2), 51.7 and 54.8 (C^3), 64.1 and 62.4 (C^1); **XIIIb**, *threo* isomer: 17.1 and 21.6 (CH_3), 29.1 (C^3), 33.5 (CH_2Br), 51.6 (C^2), 58.3 (C^1); 125.0–132.0, 140.0, 140.1, 142.0 (C_{arom} in **XIb** and **XIIb**). Mass spectrum, m/z (I_{rel}, %): **XIIb**: 241 (2.7), 240 (0.9), 239 (3.1) $[M - Br]^+$, 160 (11.1), 159 (100), 117 (40.3), 91 (53.6); 241 (3.0), 240 (0.9), 239 (2.8) $[M - Br]^+$, 160 (10.5), 159 (100), 117 (39.3), 91 (44.8). Found for mixture **XIIb**/**XIIIb**, %: C 44.92; H 5.10. $C_{12}H_{16}Br_2$. Calculated, %: C 45.00; H 5.00. M 320.06.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 08-03-00 707-a) and by the Russian Academy of Sciences (program "Theoretical and Experimental Study on the Nature of Chemical Bond and Chemical Processes").

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