Iodosulfenylation of olefins with sulfenamides in the presence of metal iodides

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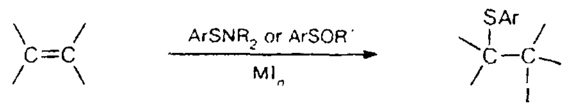
Reactions of arylsulfenamides, arylsulfenates, thiobisamines, and dithiobisamines with olefins in the presence of zinc, tin(II), tin(IV), antimony(III), or magnesium iodides were investigated. In the case of cage olefins, the reactions afford mixtures of 1,2-iodosulfides and diiodides, the ratio between which depends on the type of iodine-containing Lewis acid. Iodosulfides were obtained in the highest yields in the reactions of cage olefins upon activation with zinc or tin(II) iodides. In the case of olefins prone to the Wagner—Meerwein rearrangement (bicyclo[2.2.1]heptanes) or to the addition—elimination reaction (camphene), the corresponding products formed. A reaction mechanism is proposed.

Key words: iodosulfenylation, iodosulfides, metal iodides, sulfenamides, sulfenates, thiobisamines, dithiobisamines, electrophilic addition.

In this work, we report the results of studies of iodosulfenylation of olefins with sulfenamides and sulfenates in the presence of zinc, magnesium, tin(II), tin(IV), or antimony(III) iodides (Scheme 1).

Scheme 1



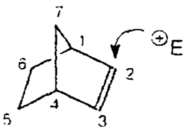
MI$_n$ = ZnI$_2$, MgI$_2$, SnI$_2$, SnI$_4$, SbI$_3$

The reactions performed by us demonstrated that arylsulfenamides and arylsulfenates act as electrophilic iodosulfenylating reagents in the reactions with alkenes in the presence of metal iodides. The reactions proceed at room temperature in chloroform or dichloromethane to form mixtures of products whose structures depend essentially on the choice of the initial olefin. It was found that twice the molar amount of zinc iodide was required. Apparently, this is due to the fact that one mole of the activating agent is trapped by the amide that formed in the course of the reaction. The remaining salts were used in equimolar amounts. The reactions in the presence of tin(IV) iodide were carried out upon cooling with ice.

Results and Discussion

Reactions with norbornene. Norbornene is a convenient model olefin for studying various electrophilic addition reactions because it provides information on the iodosulfenylating reagent in regard to several aspects. First, the rigidity of the norbornane skeleton prevents the substituents at positions 2 and 3 from being located in antiperiplanar positions. In the case of iodosulfides, this implies that the anchimeric assistance to the elimination of the iodine atom provided by sulfur is hindered. Therefore, the number of possible side processes decreases.

Second, the stereochemistry of the addition product unambiguously testifies to a species that acts as the electrophile. The abundant published data provide evidence that the attack of the electrophile occurs predominantly (in most cases, exclusively) from the sterically less hindered *exo* side[1]:



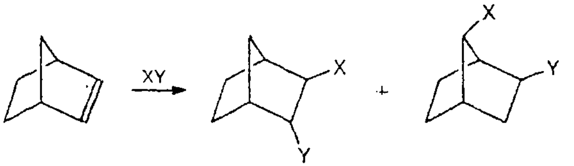
Third, the fact that the cation generated in the first stage of electrophilic addition can undergo the Wagner—Meerwein rearrangement makes it possible to estimate the effective electrophilicity of the reagent,[2] which, in turn, allows one to judge its structure and the structure of the intermediate.

The reactions of arylsulfenamides and arylsulfenates with norbornene in the presence of metal iodides afforded mixtures of 2,3- and 2,7-iodosulfides **1a—c** and **2a—c**, respectively (Scheme 2), in 50—70% total yields (Table 1).

Based on the ratio of the isomers, *viz.*, unrearranged (**1**) and rearranged (**2**) products, new sulfenylating systems can be regarded as reagents with moderate (zinc and tin iodides as activating agents) and low (magnesium and antimony iodides) effective electrophilicities.

Published in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1569—1582, September, 2000.

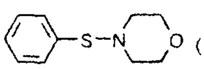
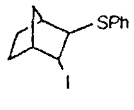
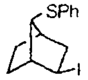
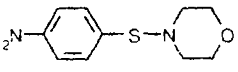
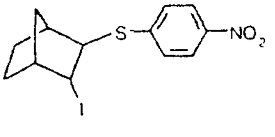
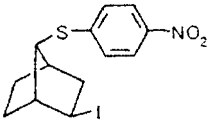
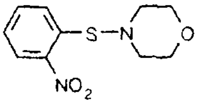
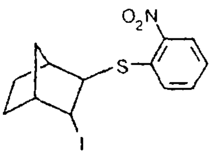
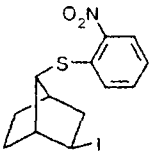
Scheme 2



1a—c **2a—c**

All the reagents under study are inferior in the amount of the rearranged product to sulfenylating reagents prepared using activation of sulfenamides and sulfenates with sulfuric anhydride. Previously,[3] when studying electrophilic sulfenylation, it has been concluded that the difference in the ratio between the unrearranged and rearranged products (**1** and **2**, respectively) is attributable to the difference in the structure of the intermediates. This signifies that the intermediates in sulfamato- and sulfonatosulfenylation reactions (**7a**) are more polar than those in the reactions under study (**8**). In regard to the electrophilicity, the reagents of the first group correspond to a reagent based on the Py · SO_3 complex.[3] When activation was carried out with the use of the Py · SO_3 complex, the rearrangement product was obtained in lower yield than that obtained with the use

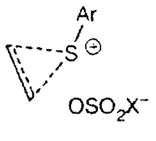
Table 1. Products of the reactions of sulfenic acid derivatives with norbornene in the presence of metal iodides

Activated compound	Product		Yields of products (%) with the use of different activating agents				
			ZnI_2	SnI_2	SnI_4	SbI_3	MgI_2
 (**3**)		(**1a**)	48	—	—	—	36*
		(**2a**)	8	—	—	—	—
 (**4**)		(**1b**)	37	59	35	62	80
		(**2b**)	25	0	15	8	0
 (**5**)		(**1c**)	51	65	40**	—	—
		(**2c**)	14	11	—	—	—
PhSOEt	**1a**		55	61	77**	18	0
	2a		18	0	—	7	0

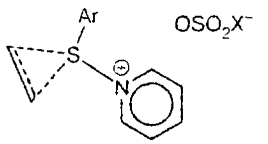
* Diphenyl disulfide was isolated as a by-product in 35% yield.

** 2,3-*exo*-*endo*-Diiodobicyclo[2.2.1]heptane (**6**) was isolated as a by-product in ~15% yield.

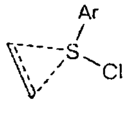
of sulfuric anhydride.[3] Based on this fact, it was concluded that the pyridine molecule is involved in the intermediate complex (**7b**). Analogously, it can be proposed that the reactions involving activation with zinc or tin iodide proceed through a structurally similar intermediate (**8**). The intermediate of chlorosulfenylation with sulfenyl chlorides (**7c**) is the least polar compound of all the compounds under study. As a consequence, the addition of sulfenyl chlorides is not accompanied by rearrangements. Activation with magnesium iodide gave the same result. This suggests that the polarity of intermediate complex **8** based on this Lewis acid is similar to the polarity of complex **7c**. The complex with antimony iodide is intermediate in polarity between complexes **7b** and **7c**.



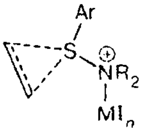
7a



7b



7c



8

X = OAlk, $NAlk_2$

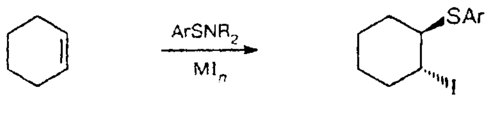
As expected, the effective electrophilicities of the reagents based on sulfenates are higher than those of the reagents based on sulfenamides, and the effective electrophilicities of the reagents based on sulfenamides containing an acceptor substituent in the ring are higher than those without such substituents.

With the aim of extending the scope of the new reagents, we performed iodosulfenylation of norbornene with sulfenamide **5** in acetonitrile in the presence of zinc iodide and lithium perchlorate. In this process, unlike bromosulfenylation in the presence of phosphorus(v) oxobromide,[4] the doping effect was observed. Thus, the ratio between the 2,3-isomer (unrearranged) and the 2,7-isomer (rearranged) changed from 3 : 1 to 1 : 1. It can be suggested that in the case of activation with phosphorus compounds, an intermediate complex of the reagent with alkene dissociates completely to give the bromide anion and an organic cation, due to which the addition of $LiClO_4$ has no polarizing effect on the intermediate. At the same time, in the case of activation with zinc iodide, the iodine atom in the intermediate complex is either covalently bound to the metal atom or involved in a compact ionic pair. Hence, the transformation into a more polar form can occur under conditions of doping addition.

It should also be noted that the use of magnesium iodide as the activating agent led to radically different results. Thus, activation of sulfenamides gave rise only to unrearranged products, whereas sulfenates oxidized iodide to free iodine.

Reactions with cyclohexene. To verify the suggestion that sulfenylation in the presence of metal iodides proceeds through a bridging intermediate, we studied the reaction with cyclohexene (Scheme 3).

Scheme 3



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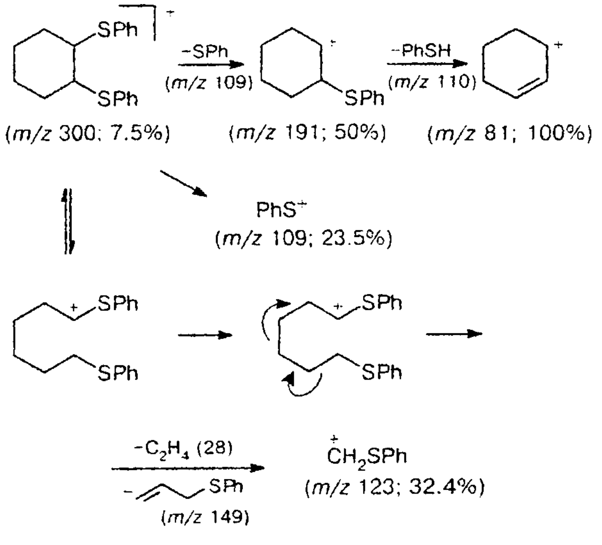
The reaction proceeding through a three-membered intermediate complex of type **8** would be expected to afford exclusively the *trans* isomer of iodosulfide **9**. The stereochemistry of the latter formed in the reaction was established based on the data of the previous study.[5] In the cited work, it was demonstrated that the structure of the compound under investigation can be judged from the change in the width of the signals for the protons of the substituents in the ^1H NMR spectra recorded in solvents with different polarity (the ω effect). It was found that the widths of both signals decrease on going from a more polar solvent ($CDCl_3$) to a less polar solvent (C_6H_6), which is indicative of the formation of *trans*-iodosulfide.

Unexpectedly, the reaction of sulfenamide **3** with cyclohexene in the presence of zinc iodide gave rise to 1,2-bis(phenylthio)cyclohexane (**10**). The structure of the reaction product was established by mass spectrom-

Scheme 4

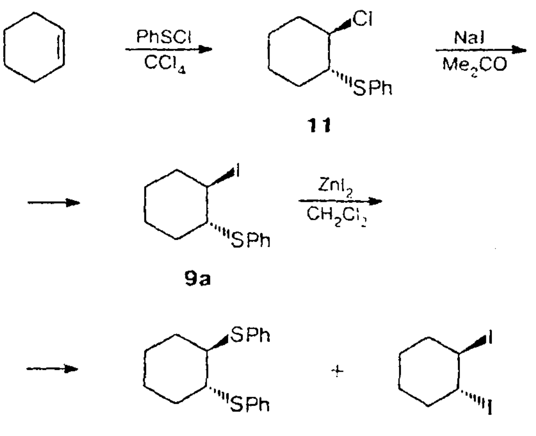


etry. The mass of the molecular ion (*m*/*z* 300) corresponds to the molecular formula $C_{18}H_{20}S_2$. The [M + 1]/M ratio (21.9%) implies the presence of about eighteen carbon atoms in the molecule. The [M + 2]/M ratio (10.7%) suggests the presence of two sulfur atoms. The scheme of degradation confirms the proposed structure of the resulting product (Scheme 4).

Elimination of the SPh radical (*m*/*z* 109) followed by liberation of the PhSH molecule (*m*/*z* 110), giving rise to the cyclohexenyl carbocation (*m*/*z* 81, 100%), confirms the presence of two phenylthio groups in the molecule. The formation of a peak with *m*/*z* 123 in the course of degradation suggests the 1,2-arrangement of these substituents.

To elucidate the mechanism of formation of bis(sulfide) **10**, we performed an independent synthesis of this compound involving the preparation of chlorosulfide **11**, the replacement of the chlorine atom by the iodine atom according to the Finkelstein reaction, and the reaction of the resulting iodosulfide **9a** with zinc iodide (Scheme 5).

Scheme 5



As a result, we isolated a compound which, according to the data of NMR and IR spectroscopy, was identical to that prepared previously. This fact along with the fact that we obtained a small amount of iodosulfide **9a** expected in the reaction with ZnI_2 proved that bis(sulfide) **10** can be generated from the initially formed β-iodosulfide under the reaction conditions.

In both reactions, 1,2-diiodocyclohexane (**12**) was obtained as a by-product. These data suggest the existence of a number of equilibria with the intermediate formation of iodonium and episulfonium ions or the corresponding ionic pairs. Under the reaction conditions, these equilibria are shifted to the right toward symmetrical products (Scheme 6).

On the whole, the reactions with cyclohexene afforded 1,2-addition products in moderate yields (Table 2), which is attributable to the occurrence of the above-mentioned processes of formation of diiodides and disulfides. Tin(II) iodide as the activating agent proved to be best suited for performing these reactions. However, even in this case, the yields were no higher than 48%, whereas the above-described two-step synthesis involving the Finkelstein reaction afforded the major product in a total yield of >70%. Hence, the reagent proposed by us has a synthetic significance primarily for the preparation of iodosulfides based on cage olefins in which the replacement is hindered (particularly, for the preparation of rearranged products).

Reactions with camphene. Electrophilic addition to camphene (Scheme 7) can give rise to products of the Wagner—Meerwein rearrangement (**A**) and addition—elimination reactions (**B**).

It is known that the rearrangement of the carbon skeleton of camphene requires a higher effective electrophilicity than that required for the rearrangement of the norbornane skeleton. For example, sulfenylation under conditions of activation of sulfenates[6] or sulfenamides[3] with the Py·SO_3 complex did not afford rearranged products. When zinc iodide was used as Lewis acid, exclusively addition—elimination products were obtained (**13**, Table 3).

For comparison, we carried out sulfenylation of camphene with *N*-(phenylthio)morpholine under conditions of activation with sulfur trioxide and also obtained exclusively an addition—elimination product (**13a**). This casts doubt upon the correctness of the use of the term

Scheme 6

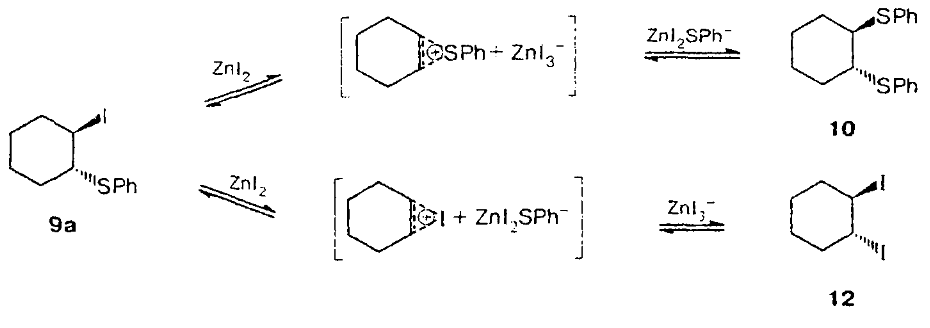
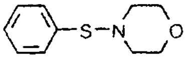
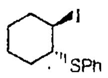
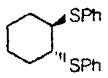
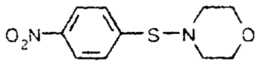
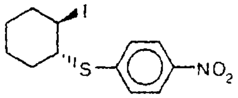
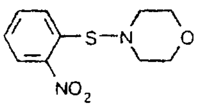
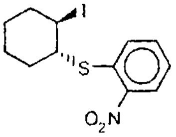


Table 2. Products of the reactions of sulfenic acid derivatives with cyclohexene in the presence of metal iodides

Activated compound	Product		Yields of products (%) with the use of different activating agents				
			ZnI_2	SnI_2	SnI_4	SbI_3	MgI_2
 (3)		(9a)	6	41	0	0	12
		(10)	48	0	0	0	0
 (4)		(9b)	32	0*	0	0	55
 (5)		(9c)	20	—	—	—	—

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* Diaryl disulfide, which is a product of degradation of the starting sulfenamide, was isolated as a by-product.

"effective electrophilicity" for the description of the ratio of the products obtained in the reactions with camphene.

This fact can be explained taking into account the peculiarity of the reactions with camphene. In the latter case, in contrast to the reactions of norbornene in which two addition products are compared, one of the products is formed upon *abstraction* of the proton from the initially formed carbocation. Consequently, the result of the reaction should be affected by the basicity of the medium.

Scheme 7

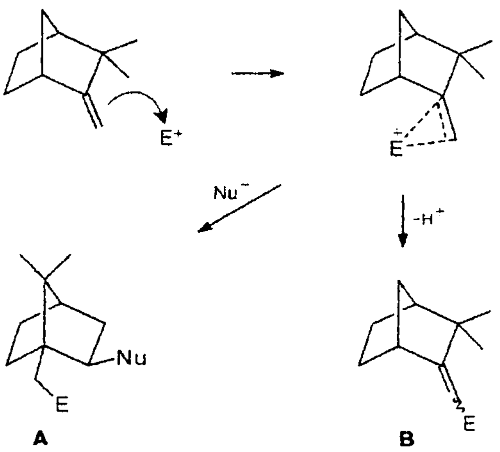
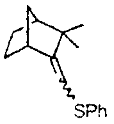
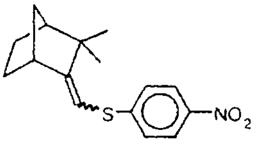
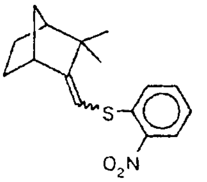


Table 3. Products of the reactions of sulfenic acid derivatives with camphene in the presence of ZnI_2 as the activating agent

Activated compound	Product		Yield (%) (ratio between *E* and *Z* isomers)
3		(13a)	76 (15 : 1)
4		(13b)	48 (6 : 1)
5		(13c)	33 (7 : 1)
PhSOEt	**13a**		54 (7 : 1)

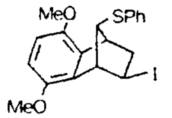
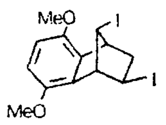
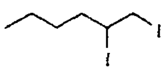
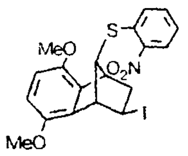
Analogously, the term "effective electrophilicity" is apparently inapplicable for the description of other processes involving addition—elimination as a competitive process, for example, the formation of nortricyclanes upon addition to norbornene.

The isomers of the resulting vinyl sulfides were identified based on the results published previously.[6] In the cited work, ^{1}H NMR spectral studies were performed with the use of the nuclear Overhauser effect (NOE) and it was demonstrated that the proton at the double bond, which gives a signal at higher field, corresponds to the *E* isomer.

Noteworthy are the unusual ratios between the *E* and *Z* isomers of the reaction products (from 6 : 1 to 12 : 1). In most of the known reactions of electrophilic reagents with camphene, this ratio varies from 1 : 1 to 3 : 1. This fact is indicative of the high selectivity of the reagent, which may be due to large steric hindrances in the transition state. An even higher selectivity of the reaction with sulfuric anhydride results apparently from the fact that the high activity of the complex of sulfenamide with sulfuric anhydride makes it possible to perform the reaction upon substantial cooling.

Reactions with 3,6-dimethoxybenzonorbornadiene and hex-1-ene. In some cases, the reactions with 3,6-dimethoxybenzonorbornadiene and hex-1-ene afforded diiodides (**15** and **16**) rather than the expected iodosulfides **14** (Table 4). However, taking into account the reactions with cyclohexene (see above), these results can be attributed to the rearrangement of the initially formed iodosulfenylation products.

Table 4. Products of the reactions* of arylsulfenamides ($ArSNR_2$) with 3,6-dimethoxybenzonorbornadiene and hex-1-ene

$ArSNR_2$	*t***/h	Product		Yield (%)
3	24		(**14a**)	35
			(**15**)	36
4	24		(**16**)	86
5	36		(**14b**)	51
			15	13

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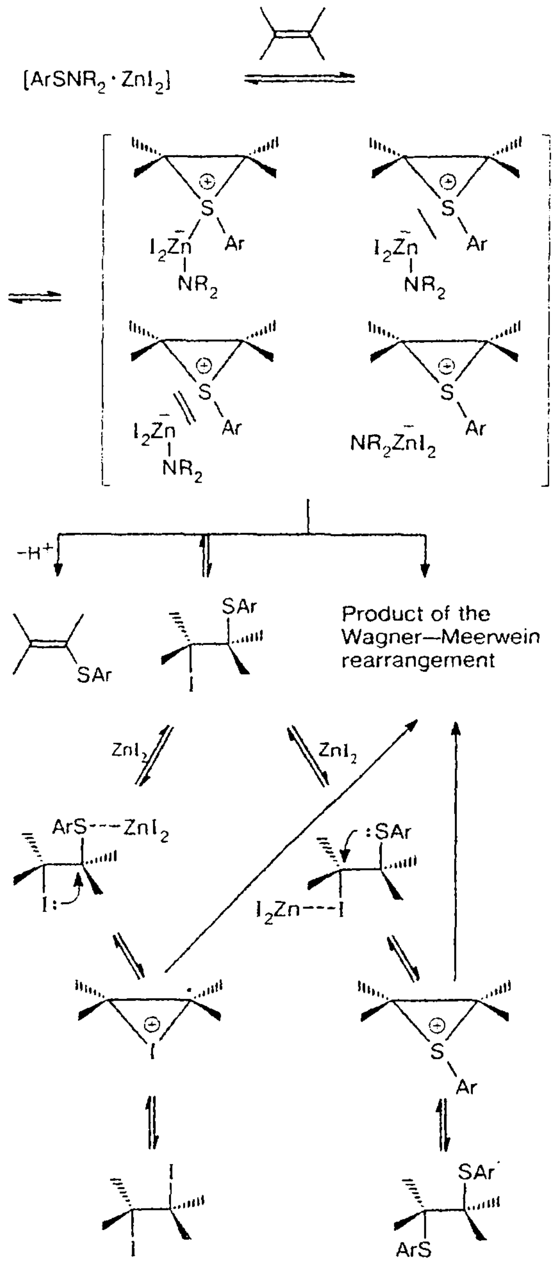
* CH_2Cl_2 was used as the solvent.

** The reaction time.

Iodosulfenylation in the presence of zinc iodide can proceed through a series of equilibria which involve the formation of episulfonium and iodonium cations and give rise to β-iodosulfides along with β-disulfides and β-diiodides, respectively (Scheme 8). In addition, the reactions can afford products of the Wagner—Meerwein

Scheme 8

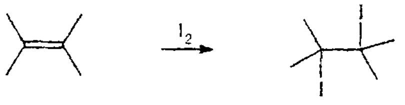


rearrangement as well as addition—elimination products. Probably, 3,6-dimethoxybenzonorbornadiene and hex-1-ene are systems in which the above-considered equilibria are shifted toward the predominant formation of diiodides.

To account for the formation of diiodides in the reactions with 3,6-dimethoxybenzonorbornadiene, we proposed three versions.

1. Unstable sulfenyl iodide ArSI is initially formed. This compound rapidly decomposes to give disulfide and iodine and the latter adds to alkene to form diiodide:

$$2\,\mathrm{ArSI} \longrightarrow \mathrm{ArSSAr} + \mathrm{I_2},$$



However, additional studies demonstrated that the reaction of 3,6-dimethoxybenzonorbornadiene with iodine gave rise to a mixture of at least three isomeric diiodides, whereas exclusively one isomer was obtained under the conditions of the reaction of sulfenamide with zinc iodide. Against this mechanism is the fact that the reaction mixture did not contain diaryl disulfide.

2. If the attack of the electrophile in the case of 3,6-dimethoxybenzonorbornadiene occurs exclusively from one side (only from *endo* or only from *exo*), the opposite configurations of the reaction products can serve as proof of our suggestion. Thus, the rearrangement should afford *syn*-sulfide and *anti*-iodide (in the case of the "*exo*-attack") and conversely (in the case of the "*endo*-attack") (Scheme 9).

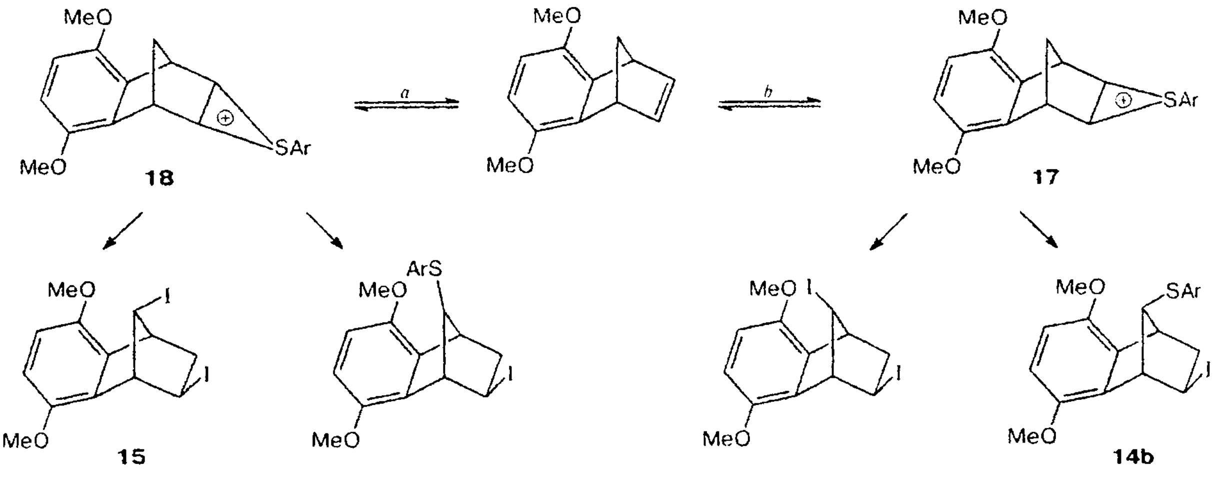
To verify this suggestion, we carried out special NMR studies of products **14b** and **15** that formed in the reaction of 3,6-dimethoxybenzonorbornadiene with *N*-(nitrophenylthio)morpholine in the presence of zinc iodide.

The ^{1}H NMR spectrum of diiodide **15** has two signals for the protons at the C(10) atom. One of these signals is observed as a doublet of doublets (δ 2.10, J = 14 and 8 Hz) and the second signal is observed as a doublet of doublets of doublets (δ 2.86, J = 14, 3.8, and 3.8 Hz). The value J = 8 Hz for the signal for the proton at δ 2.10 demonstrates that this proton is in the *trans* position with respect to the iodine atom, and the absence of the third spin-spin coupling constant (with the proton at the C(1) atom) is indicative of its *endo*-arrangement. Consequently, the iodine atom at the C(9) atom has an *exo*-configuration. Analogously, it can be concluded that the iodine atom in compound **14b** adopts an *exo*-configuration.

The configuration of the iodine atom at position 11 was established by studying NOE in the ^{1}H NMR spectrum of compound **15**. This spectrum has three multiplets at δ 4.08, 3.88, and 3.60 along with the above-mentioned signals at δ 2.10 and 2.86 and the signals for the methoxy groups and aromatic protons, the signals for two protons coalescing into a multiplet at δ 3.60. For the protons giving signals at δ 2.10 and 2.86, NOE is observed only for the signal at δ 3.60 (~9%). From this it follows that the signals for the HC(9)I and HC(4) protons coalesce into this multiplet. At the same time, the absence of NOE for the remaining two signals (at δ 4.08 and 3.88) indicates that the proton and the iodine atom at C(11) are in the *anti* and *syn* orientations, respectively, without regard to a particular signal belonging to the proton at the C(11) atom.

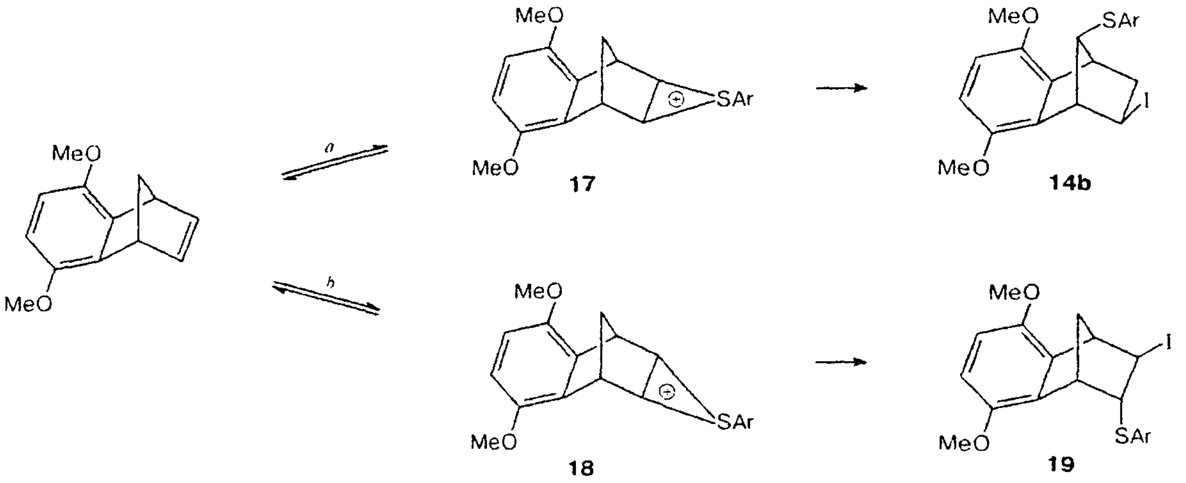
The signals in the NMR spectrum of compound **14b** were identified by the ^{1}H—^{1}H double resonance method. We managed to perform additional irradiation at the frequency of the proton at δ 3.68 (HC(1)) only with simultaneous irradiation of the signal at δ 3.71 (HCS or

Scheme 9



Note. a, endo-Attack; *b, exo*-attack.

Scheme 10



Note. a, endo-Attack; *b, exo*-attack.

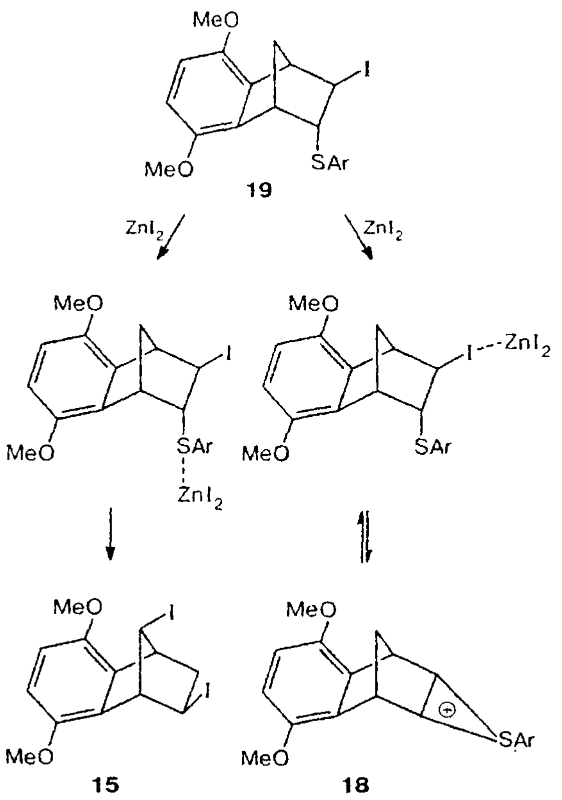
HC(8)). In this case, the spin-spin coupling constant J = 1.5 Hz for the signal for the proton at δ 3.59 (HCI), the spin-spin coupling constant J = 3.5 Hz for the signal at δ 2.75 (*exo*-HC(10)), and both spin-spin coupling constants J = 1.5 Hz for the signal at δ 4.05 (HCS or HC(8)) disappear. Additional irradiation at the frequency of the proton at δ 2.75 (*exo*-HC(10)) led to the disappearance of the spin-spin coupling constants J = 15, 4.7, and 3.5 Hz in the signals for the protons at δ 2.05 (*endo*-HC(10)), 3.59 (HCI), and 3.68 (HC(1)), respectively. These facts allow us to make the assignment of all the signals except for two signals at δ 4.05 and 3.71. In the spectrum recorded with the use of NOE at the frequency of the proton at δ 4.05, only a response in the region of the signals at δ 3.71 and 3.68 was observed. Hence, two conclusions can be made. First, the absence of the Overhauser effect at the HCI proton makes it possible to unambiguously assign the signal at δ 4.05 to the HCS proton (and, correspondingly, the signal at δ 3.71 to the HC(8) proton). Second, the absence of response for the proton at δ 2.75 (*exo*-HC(10)) provides evidence for the *anti* orientation of the HCS proton and, consequently, for the *syn* orientation of the arylthio group.

Therefore, it was established that the substituent at position 11 in both products is in the *syn* orientation. Based on this fact, the mechanism assuming attack of the electrophile exclusively from one side of the double bond was rejected, and a third mode of formation of diiodide was suggested to account for the configurations of the resulting compounds.

3. According to this mechanism, the attack of the electrophile (ArS^+) can occur both from the *endo*- and *exo*-sides of the double bond (Scheme 10). The *exo*-attack results in the formation of episulfonium ion **17**, which undergoes immediate rearrangement to form iodosulfenylation product **14b**. The attack of the electrophile from the *endo*-side affords episulfonium ion **18**. In the latter case, the attack of the nucleophile giving rise to 1,2-addition product **19** proceeds more rapidly than the rearrangement.

Then, compound **19**, which is unstable under the reaction conditions, reacts with zinc iodide to give diiodide **15** (Scheme 11).

Scheme 11

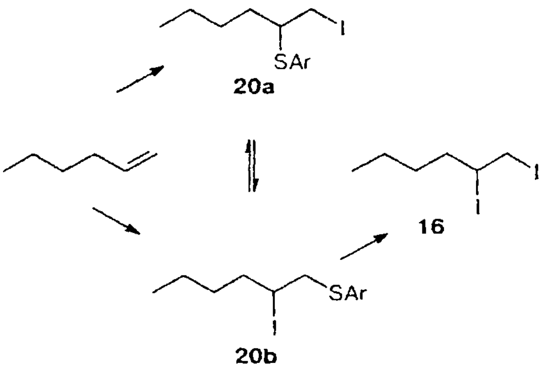


In this case, the competitive attack of Lewis acid at the iodine atom results in the reversible formation of ion **18** rather than giving rise to stable rearranged products.

Therefore, the ratio between products **14** and **15** in the reactions of 3,6-dimethoxybenzonorbornadiene with sulfenamides in the presence of zinc iodide allows one to judge the ratio between the rates of the *endo*- and *exo*-attacks of the electrophile.

In the case of the reaction with hex-1-ene, the resulting iodosulfide undergoes rapid rearrangement to form the most stable Markovnikoff isomer (**20b**), in which the formation of the complex at the sulfur atom is sterically less hindered, resulting in the predominant formation of diiodide (Scheme 12).

Scheme 12



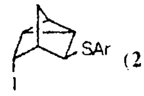
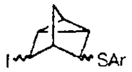
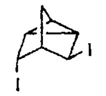
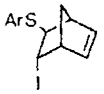
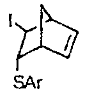
Reaction with norbornadiene. We chose norbornadiene as the model diene for iodosulfenylation. As expected, stereoisomeric nortricyclanes **21** and **22** were obtained as the major reaction products (Table 5).

Therefore, norbornadiene behaves as a typical homoconjugated diene system to give 1,4-addition products. The formation of diiodides (**22a** and **22b**) agrees with the results obtained previously[7] in the reaction of norbornadiene with the $PI_3—R_2NCl$ system.

Reactions of thio- and dithiobisamines. Thio- and dithiobisamines, like sulfenates and sulfenamides, react with alkenes upon activation with Lewis acids to form addition products, *viz*., β,β′-disubstituted dialkyl sulfides and disulfides. Thus the use of $POCl_3$ and $POBr_3$ as activating agents made it possible to prepare bis(β,β′-haloalkyl) sulfides and disulfides[8] in one step (Scheme 13).

With the aim of extending this method of activation of sulfenamides and sulfenates to a new class of compounds, we carried out reactions of addition of thio- and dithiobis(morpholine) to norbornene in the presence of metal iodides. It should be noted that the yields in these reactions (Table 6) were, on the average, lower (10—50%) than those obtained in the reactions of sulfenic acid derivatives and the formation of rearranged products was not observed. Diiodides were obtained as by-products.

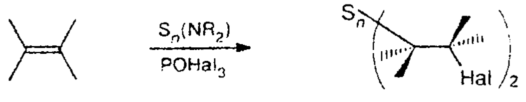
Table 5. Products of the reactions of *N*-(nitrophenylthio)morpholines **4** and **5** (ArSX) with norbornadiene

ArSX	Activating agent	Products	Yield (%)
4	ZnI_2	 (**21a**) + +  (**21b**)	38 (2 : 1)
		 (**22a**) + +  (**22b**)	46 (3 : 2)
5	SnI_2	 (**21c**)	47
		 (**23a**)	15
		 (**23b**)	~2
		Diiodides **22**	~3

The maximum yields were achieved in the reactions with the use of zinc or tin(IV) iodides as activating agents.

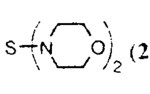
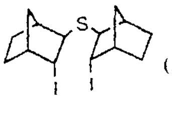
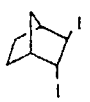
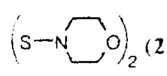
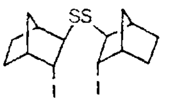
Previously,[9] it has been demonstrated that thio- and dithiobisamines add to alkenes to form bis(β,β′-diaminoalkyl) sulfides and disulfides (Scheme 14), *i.e.*, the replacement of the amine component in thio- and dithiobisamines by the halogen atom does not occur upon activation with chlorine- or fluorine-containing Lewis acids. This may be attributed to the fact that under the reaction conditions, the dialkylamino group is more nucleophilic than chlorine and fluorine but is less nucleophilic than iodine.

Scheme 13



n = 1, 2; Hal = Cl, Br

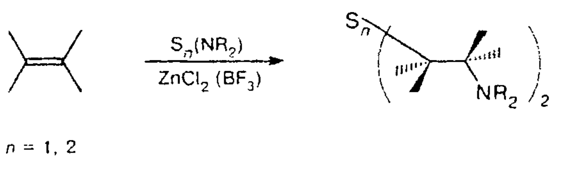
Table 6. Products of the reactions of thio- and dithiobisamines with norbornene in the presence of metal iodides

Activated compound	Product	Yields of products (%) with the use of different activating agents				
		ZnI_2	SnI_2	SnI_4	SbI_3	MgI_2
 (24)	 (26)	60	5	32	20	25
	 (6)	29	—	15	—	18
 (25)	 (27)	16	26	41	24	20
	6	—	—	—	—	9

Therefore, the proposed procedure for the synthesis of β-iodoalkyl sulfides is not versatile. In some cases, the reactions products were obtained in low yields due to side processes giving rise to diiodides (for example, the reaction with hex-1-ene). Sometimes, the reactions afforded products other than addition products (camphene and cyclohexene in the reactions with phenylthiomorpholine). The reaction performed with cyclohexene demonstrated that the two-step procedure for the preparation of β-iodoalkyl sulfides involving the Finkelstein replacement of the chlorine atom in the product of addition of sulfenyl chloride to olefin afforded the target products in higher yields.

In the case of cage olefins in which the nucleophilic replacement is hindered due to weakening of the anchimeric assistance provided by the sulfur atom and in the cases requiring the preparation of a Wagner—Meerwein rearrangement product, the proposed procedure gives satisfactory results, which are quite competitive with those obtained according to other procedures. At the same time, the reactions with β-iodoalkyl sulfides giving rise to unexpected products allow one to draw conclusions regarding the possible mechanism of conversions and to describe the activation process with Lewis acids in more detail.

Scheme 14



Experimental

The ^1H NMR spectra were recorded on a Varian VXR-400 instrument (at 400 MHz for ^1H and at 100 MHz for ^{13}C) with HMDS as the internal standard. Preparative separation of the reaction products was carried out by column chromatography on Silpearl silica gel. The purity of the resulting compounds was checked by TLC on Silufol plates.

Iodosulfenylation of olefins with sulfenic acid derivatives in the presence of metal iodides (*general procedure*). ZnI_2 (5 mmol) or iodide of another metal (2.5 mmol) was added with stirring to a solution of alkene (2.5 mmol) in anhydrous CH_2Cl_2 (4—5 mL) and then a solution of sulfenamide or sulfenate (2.5 mmol) in a minimum amount of anhydrous CH_2Cl_2 was added. The reaction with tin(IV) iodide was performed upon cooling with ice. The reaction mixture was stirred until sulfenamide or sulfenate disappeared (TLC control). Then the reaction mixture was filtered through a short column with silica gel and the solvent was distilled off *in vacuo*. The reaction products were isolated by column chromatography. The yields of the products are given in Tables 1—5. Other physicochemical characteristics are listed in Tables 7—9.

The reaction of norbornene with N-(phenylthio)morpholine (3) afforded **2-*endo*-iodo-3-*exo*-(phenylthio)bicyclo[2.2.1]heptane (1a)** and **2-*exo*-iodo-7-*syn*-(phenylthio)bicyclo[2.2.1]heptane (2a)** as colorless oils.

The reaction of norbornene with ethyl phenylsulfenate afforded compounds **1a** and **2a** and **2-*exo*-3-*endo*-diiodobicyclo[2.2.1]heptane (6)** (colorless oil).

The reaction of norbornene with N-(p-nitrophenylthio)morpholine (4) afforded **2-*endo*-iodo-3-*exo*-(*p*-nitrophenylthio)bicyclo[2.2.1]heptane (1b)** as a yellow oil and **2-*exo*-iodo-7-*syn*-(*p*-nitrophenylthio)bicyclo[2.2.1]heptane (2b).**

The IR spectrum of a mixture of **1b** and **2b** (thin film), ν/cm^{-1}: 1340, 1520 (nitro group).

The reaction of norbornene with N-(o-nitrophenylthio)morpholine (5) afforded **2-*endo*-iodo-3-*exo*-(*o*-nitrophenylthio)bicyclo[2.2.1]heptane (1c)** as a yellow oil and **2-*exo*-iodo-7-*syn*-(*o*-nitrophenylthio)bicyclo[2.2.1]heptane (2c)**, m.p. 60—

62 °C. UV of **1c** (EtOH), λ_{max}/nm (ε_{max}): 369 (29.60). UV of **2c** (EtOH), λ_{max}/nm (ε_{max}): 379 (51.64).

The IR spectrum of a mixture of compounds **1c** and **2c** (thin film), ν/cm⁻¹: 1345, 1525 (nitro group).

The reaction of cyclohexene with N-(phenylthio)morpholine (**3**) afforded ***trans*-1-iodo-2-(phenylthio)cyclohexane (9a)** and ***trans*-1,2-bis(phenylthio)cyclohexane (10)** as colorless oils. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 300 $[M]^+$ (7.5), 191 [M − SPh] (50), 123 $[CH_2SPh]$ (32.4), 109 [PhS] (23.5), 81 [M − SPh − PhSH] (100).

The reaction of cyclohexene with N-(p-nitrophenylthio)morpholine (**4**) afforded ***trans*-1-iodo-2-(*p*-nitrophenylthio)cyclohexane (9b)** as a yellow oil. IR (CCl_4), ν/cm⁻¹: 1345, 1530 (nitro group).

The reaction of cyclohexene with N-(o-nitrophenylthio)morpholine (**5**) yielded ***trans*-1-iodo-2-(*o*-nitrophenylthio)cyclohexane (9c)** as a yellow oil.

Table 7. Data of chromatography and the results of elemental analysis of the reaction products of iodosulfenylation of olefins

Compound	R_f (chromatographic system)	Found/Calculated (%)				Molecular formula
		C	H	N	S	
1a	0.65 (hexane—chloroform, 2 : 1)	47.27[a] 47.73	4.58[a] 4.65	—	—	$C_{13}H_{15}SI$
1b	0.66 (hexane—ethyl acetate, 3 : 1)	41.92[b] 41.61	3.85[b] 3.76	3.79[b] 3.73	—	$C_{13}H_{14}NO_2SI$
1c	0.62 (hexane—ethyl acetate, 3 : 1)	41.52[c] 41.61	3.75[c] 3.76	3.74[c] 3.73	—	$C_{13}H_{14}NO_2SI$
2a	0.48 (hexane—chloroform, 2 : 1)	47.73[a] 47.27	4.65[a] 4.58	—	—	$C_{13}H_{15}SI$
2b	0.54 (hexane—ethyl acetate, 3 : 1)	41.92[b] 41.61	3.85[b] 3.76	3.79[b] 3.73	—	$C_{13}H_{14}NO_2SI$
2c	0.43 (hexane—ethyl acetate, 3 : 1)	41.52[c] 41.61	3.75[c] 3.76	3.74[c] 3.73	—	$C_{13}H_{14}NO_2SI$
6	0.76 (hexane—chloroform, 2 : 1)	24.01 24.16	3.00 2.70	—	—	$C_7H_{10}I_2$
9a	0.63 (hexane—benzene, 2 : 1)	45.52 45.29	4.68 4.75	—	10.00 10.07	$C_{12}H_{15}SI$
9b	0.60 (hexane—ethyl acetate, 6 : 1)	39.09 39.68	3.68 3.89	3.68 3.86	8.37 8.83	$C_{12}H_{14}NO_2SI$
9c	0.62 (hexane—ethyl acetate, 3 : 1)	39.55 39.68	3.71 3.89	3.59 3.86	8.43 8.83	$C_{12}H_{14}NO_2SI$
10	0.53 (hexane—benzene, 2 : 1)	—	—	—	—	—
13a	0.67 (*E* isomer) and 0.73 (*Z* isomer) (hexane—ethyl acetate, 6 : 1)	78.68[d] 78.63	8.36[d] 8.25	—	—	$C_{16}H_{20}S$
13b	0.67 (hexane—ethyl acetate, 6 : 1)	65.98[d] 66.41	6.67[d] 6.62	4.89[d] 4.84	—	$C_{16}H_{19}NO_2S$
13c	0.66 (hexane—ethyl acetate, 10 : 1)	65.93[d] 66.41	6.55[d] 6.62	4.78[d] 4.84	—	$C_{16}H_{19}NO_2S$
14a	0.67 (hexane—chloroform, 3 : 1)	52.00 52.06	4.56 4.37	—	6.98 7.31	$C_{19}H_{19}O_2SI$
14b	0.54 (hexane—chloroform, 3 : 1)	46.96 47.22	3.77 3.75	2.55 2.90	—	$C_{19}H_{18}NO_4SI$
15	0.92 (hexane—chloroform, 3 : 1)	34.14 34.14	3.08 3.08	—	—	—
16	0.64 (hexane)	—	—	—	—	—
21a	0.26 (hexane—benzene, 2 : 1)	41.35 41.84	3.20 3.24	3.57 3.75	8.19 8.59	$C_{13}H_{12}NO_2SI$
21c	0.47 (hexane—ethyl acetate, 4 : 1)	41.35 41.34	3.20 3.14	3.57 3.44	8.19 8.08	$C_{13}H_{12}NO_2SI$
A mixture of **23a** and **23b**	0.47 (hexane—ethyl acetate, 4 : 1)	42.19 41.84	3.29 3.24	3.85 3.75	8.64 8.59	$C_{14}H_{20}NO_2I_2S$
26	0.65 (hexane—chloroform, 2 : 1)	35.95 35.46	4.29 4.25	—	6.84 6.76	$C_{14}H_{20}I_2S$
27	0.65 (hexane—chloroform, 2 : 1)	33.51 33.22	4.01 3.98	—	12.94 12.67	$C_{14}H_{20}I_2S_2$

[a] For a mixture of isomers **1a** and **2a**.

[b] For a mixture of isomers **1b** and **2b**.

[c] For a mixture of isomers **1c** and **2c**.

[d] For a mixture of *Z* and *E* isomers.

Table 8. ^{1}H NMR spectra (CDCl$_3$) of the reaction products of iodosulfenylation of olefins

Compound	δ (*J*/Hz)			
	Alicyclic (aliphatic) protons			Aromatic protons
	HCS	HCI	Other protons	
1a	3.20 (dd, 1 H, J_1 = 2.5, J_2 = 4.3)	3.99 (ddd, 1 H, J_1 = 1.4, J_2 = 4.2, J_3 = 4.4)	1.9—1.2 (m, 6 H); 2.16 (br.s, 1 H, H(4)); 2.42 (br.s, 1 H, H(1))	7.20 (t, 1 H, *p*-H, *J* = 7.3); 7.27 (m, 2 H, *m*-H); 7.37 (d, 2 H, *o*-H, *J* = 7.3)
1b	3.34 (dd, 1 H, J_1 = 2.5, J_2 = 4.3)	4.00 (ddd, 1 H, J_1 = 1.6, J_2 = 4.2, J_3 = 4.4)	1.9—1.2 (m, 6 H); 2.22 (br.s, 1 H, H(4)); 2.50 (br.s, 1 H, H(1))	7.36 (d, 2 H, *J* = 9); 8.13 (d, 2 H, *J* = 9)
1c	3.27 (dd, 1 H, J_1 = 2.5, J_2 = 4.1)	4.06 (ddd, 1 H, J_1 = 1.5, J_2 = 4.0, J_3 = 4.2)	1.9—1.2 (m, 6 H); 2.23 (br.s, 1 H, H(4)); 2.50 (br.s, 1 H, H(1))	7.26 (m, 1 H, *J* = 8.3); 7.39 (d, 1 H, *J* = 8.3); 7.56 (m, 1 H, *J* = 8.3); 8.16 (d, 1 H, *J* = 8.3)
2a	3.37 (br.s, 1 H)	3.89 (dd, 1 H, J_1 = 5.3, J_2 = 8.3)	1.9—1.2 (m, 6 H); 2.14 (dd, 1 H, *endo*-H(3), J_1 = 8.3, J_2 = 14.2); 2.31 (dd, 1 H, H(4), J_1 = 4.1, J_2 = 4.3); 2.75 (d, 1 H, H(1), *J* = 4.1); 2.72 (m, 1 H, *exo*-H(3))	7.19 (t, 1 H, *p*-H, *J* = 7.5); 7.28 (m, 2 H, *m*-H, *J* = 7.5); 7.42 (d, 2 H, *o*-H, *J* = 7.5)
2b	3.51 (br.s, 1 H)	3.91 (dd, 1 H, J_1 = 5.4, J_2 = 8.1)	2.2—1.2 (m, 4 H); 2.23 (d, 1 H, *endo*-H(3), *J* = 8.1); 2.44 (dd, 1 H, H(4), J_1 = 3.9, J_2 = 4.1); 2.63 (m, 1 H, *exo*-H(3)); 2.83 (d, 1 H, H(1), *J* = 3.9)	7.65 (d, 2 H, *J* = 9); 8.13 (d, 2 H, *J* = 9)
2c	3.48 (br.s, 1 H)	3.88 (ddd, 1 H, J_1 = 1, J_2 = 5.3, J_3 = 7.8)	1.8—1.2 (m, 4 H); 2.17 (dd, 1 H, *endo*-H(3), J_1 = 7.8, J_2 = 14.3); 2.45 (dd, 1 H, H(4), J_1 = 4, J_2 = 7.7); 2.67 (ddd, 1 H, *exo*-H(3), J_1 = 5.3, J_2 = 7.7, J_3 = 14.3); 2.83 (d, 1 H, H(1), *J* = 4.3)	7.26 (m, 1 H, *J* = 8.2); 7.50 (d, 1 H, *J* = 8.2); 7.55 (m, 1 H, *J* = 8.2); 8.13 (d, 1 H, *J* = 8.2)
6	—	3.93 (dd, 1 H, *endo*-HCI, J_1 = 2.8, J_2 = 3.9); 4.52 (dd, 1 H, *exo*-HCI, J_1 = 1.6, J_2 = 3.9)	1.68—1.61 (m, 2 H, *exo*-H(5), *exo*-H(6)); 1.40—1.33 (m, 2 H, *endo*-H(5), *endo*-H(6)); 1.48 (m, 1 H, *anti*-H(7)); 2.09 (m, 1 H, *syn*-H(7)); 2.38 (br.s, 1 H, H(1)); 2.49 (br.s, 1 H, H(4))	—
9a	3.56 (dd, 1 H, J_1 = 5.0, J_2 = 9.0)	4.48 (dd, 1 H, J_1 = 5.0, J_2 = 9.2)	2.3—0.9 (m, 8 H)	7.25 (t, 1 H, *p*-H, *J* = 7.0); 7.30 (dd, 2 H, *m*-H, J_1 = 7.0, J_2 = 7.2); 7.41 (d, 2 H, *o*-H, *J* = 7.2)
9b	3.79 (dd, 1 H, J_1 = 4.9, J_2 = 9.7)	4.49 (dd, 1 H, J_1 = 4.9, J_2 = 8.9)	2.0—0.9 (m, 8 H)	7.38 (d, 2 H, *J* = 9.1); 8.15 (d, 2 H, *J* = 9.1)
9c	3.80 (dd, 1 H, J_1 = 4.3, J_2 = 9.2)	4.56 (dd, 1 H, J_1 = 4.3, J_2 = 8.5)	2.4—0.9 (m, 8 H)	7.30 (m, 1 H, *J* = 8.3); 7.41 (d, 1 H, *J* = 8.3); 7.58 (m, 1 H, *J* = 8.3); 8.08 (d, 1 H, *J* = 8.3)
10	3.27 (br.s, 2 H)	—	1.40 (m, 2 H); 1.61 (m, 4 H); 2.24 (m, 2 H, H(3), H(6))	7.18 (t, 2 H, *p*-H, *J* = 7); 7.21 (m, 4 H, *m*-H, *J* = 7); 7.28 (d, 4 H, *o*-H, *J* = 7)
13a	—	—	1.10 (s, 3 H, H$_3$C); 1.11 (s, 3 H, H$_3$C); 1.7—1.2 (m, 6 H); 1.96 (dd, 1 H, H(4), J_1 = 1.4, J_2 = 3.6); 3.19 (d, 1 H, H(1), *J* = 4); 5.67 (s, 1 H, *E* vinylic H); 5.87 (s, 1 H, *Z* vinylic H)	7.12 (t, 1 H, *p*-H, *J* = 7.7); 7.24 (m, 2 H, *m*-H, *J* = 7.7); 7.25 (d, 2 H, *o*-H, *J* = 7.7)
13b	—	—	1.7—0.9 (m, 6 H); 1.16 (s, 3 H, H$_3$C); 1.17 (s, 3 H, H$_3$C); 2.02 (d, 1 H, H(4), *J* = 3.1); 3.19 (d, 1 H, H(1), *J* = 3.7); 5.68 (s, 1 H, *E* vinylic H); 5.88 (s, *Z* vinylic H)	7.25 (d, 2 H, *J* = 9.6); 8.09 (d, 2 H, *J* = 9.6)
13c	—	—	1.7—1.2 (m, 6 H); 1.16 (s, 3 H, H$_3$C); 1.17 (s, 3 H, H$_3$C); 2.02 (d, 1 H, H(4), *J* = 3.4); 3.31 (d, 1 H, H(1), *J* = 3.8); 5.63 (s, 1 H, *E* vinylic H); 5.81 (s, 1 H, *Z* vinylic H)	7.21 (d, 1 H, *J* = 8.4); 7.38 (d, 1 H, *J* = 8.4); 7.50 (m, 1 H, *J* = 8.4); 8.19 (d, 1 H, *J* = 8.4)

(*To be continued*)

Table 8 (*continuation*).

Compound	δ (*J*/Hz)			
	Alicyclic (aliphatic) protons			Aromatic protons
	HCS	HCI	Other protons	
14a	3.57 (br.s, 1 H)	3.60 (m, 1 H)	2.03 (dd, 1 H, *endo*-H(10), J_1 = 7.8, J_2 = 13.4); 2.82 (ddd, 1 H, *exo*-H(10), J_1 = 4, J_2 = 4.2, J_3 = 13.4); 3.68 (br.s, 1 H, H(8)); 3.71 (s, 3 H, H_3CO); 3.73 (s, 3 H, H_3CO); 3.75 (br.s, 1 H, H(1))	6.55 (d, 1 H, *J* = 8.9); 6.60 (d, 1 H, *J* = 8.9); 7.18 (t, 1 H, *p*-H, *J* = 7.3); 7.26 (dd, 2 H, *m*-H, J_1 = 7.3, J_2 = 7.6); 7.43 (d, 2 H, *o*-H, *J* = 7.6)
14b	3.65 (br.s, 1 H)	3.73 (m, 1 H)	2.17 (dd, 1 H, *endo*-H(10), J_1 = 8, J_2 = 14); 2.79 (ddd, 1 H, *exo*-H(10), J_1 = 4.4, J_2 = 4.6, J_3 = 14); 3.75 (br.s, 1 H, H(8)); 3.76 (s, 3 H, H_3CO); 3.78 (s, 3 H, H_3CO); 3.94 (br.s, 1 H, H(1))	6.12 (d, 2 H, *J* = 8.9); 6.18 (d, 1 H, *J* = 8.9); 7.25 (t, 1 H, *p*-H, *J* = 7.3); 7.51 (dd, 2 H, *m*-H, J_1 = 7.3, J_2 = 7.6); 8.09 (d, 2 H, *o*-H, *J* = 7.6)
15	—	3.63 (br.s, 1 H, HC(11)I); 3.75 (m, 1 H, HC(9)I)	2.07 (dd, 1 H, *endo*-H(10), J_1 = 8.1, J_2 = 13.5); 2.84 (ddd, 1 H, *exo*-H(10), J_1 = 3.7, J_2 = 5.1, J_3 = 13.5); 3.74 (s, 3 H, H_3CO); 3.75 (s, 3 H, H_3CO); 3.91 (br.s, 1 H, H(8)); 4.11 (br.s, 1 H, H(1))	6.56 (d, 1 H, *J* = 8.9); 6.61 (d, 1 H, *J* = 8.9)
16	—	3.67 (dd, 1 H, HC(1)I, J_1 = 9.6, J_2 = 11.8); 4.05 (dd, 1 H, HC(1)I, J_1 = 3.8, J_2 = 9.6); 4.32 (dddd, 1 H, HC(2)I, J_1 = 3, J_2 = 3.8, J_3 = 9, J_4 = 11.8)	1.7—0.8 (*m*, 9 H, Bu)	—
21a[a]	4.12 (br.s, 1 H)	3.95 (br.s, 1 H)	2.3—0.9 (m, 6 H)	7.38 (d, 2 H, *J* = 8.9); 8.13 (d, 2 H, *J* = 8.9)
21c[a]	—	3.94 (br.s, 1 H)	1.80 (t, 1 H, *J* = 5); 1.35 (d, 1 H, H(7), *J* = 11.4); 1.42 (t, 1 H, *J* = 5); 1.63 (t, 1 H, *J* = 5); 1.71 (dt, 1 H, H(7), J_1 = 1.5, J_2 = 11.4)	7.21 (m, 1 H); 7.43 (d, 2 H, *J* = 8.9); 8.02 (d, 1 H, *J* = 7.9)
Mixture of **23a**[b] and **23b**[c]	3.26[b] (dd, 1 H, J_1 = 3.0, J_2 = 3.9); 3.51[c] (dd, 1 H, J_1 = 2.9, J_2 = 4.5)	3.97[b] (dd, 1 H, J_1 = 3.2, J_2 = 3.7); 4.03[c] (dd, 1 H, J_1 = 3.3, J_2 = 3.4)	2.0—0.9 (H of the cage of both diastereomers); 2.34 (br.s, 1 H, H(4)); 2.92 (br.s, 1 H, H(1)); 6.19[b] (dd, 1 H, HC=S, J_1 = 2.7, J_2 = 5.7); 6.22[c] (dd, 1 H, HC=S, J_1 = 3.2, J_2 = 6.0); 6.30[c] (dd, 1 H, HC=S, J_1 = 2.8, J_2 = 6.0); 6.41[b] (dd, 1 H, HC=S, J_1 = 3.1, J_2 = 5.7)	7.3—7.2 (m); 7.59[b] (m, 1 H); 7.79[c] (d, 1 H, *J* = 8); 8.15[c] (d, 1 H, *J* = 8); 8.19[b] (dd, 1 H, J_1 = 7, J_2 = 8)
26	3.08[b] (dd, 1 H, J_1 = 2.4, J_2 = 4.4); 3.26[c] (dd, 1 H, J_1 = 2.8, J_2 = 4.8)	4.11[b] (ddd, 1 H, J_1 = 1.3, J_2 = 3.6, J_3 = 5.6); 4.15[c] (ddd, 1 H, J_1 = 1.4, J_2 = 4.2, J_3 = 5.2)	1.9—1.2 (H of the cage of both diastereomers); 2.25[b] (br.s, 1 H, H(4)); 2.36[c] (br.s, 1 H, H(4)); 2.48 (br.s, 1 H, H(1) of both diastereomers)	—
27	2.78[b] (ddd, 1 H, J_1 = 2.4, J_2 = 4.4); 2.97[c] (dd, 1 H, J_2 = 4.6); 3.03[d] (dd, 1 H, J_1 = 2.4, J_2 = 4.5); 3.07[e] (dd, 1 H, J_1 = 2.4, J_2 = 4.5)	3.81[b] (ddd, 1 H, J_1 = 1.4, J_2 = 3.9, J_3 = 4.5); 3.88[d] (ddd, 1 H, J_2 = 4.0, J_3 = 4.3); 4.05[c] (m, 1 H); 4.10[e] (m, 1 H)	1.85—1.00 (H of the cage of all diastereomers); 2.25 (br.s, 1 H, H(4)); 2.36 (br.s, 1 H); 2.44—2.04 (series of br.s, H(1) and H(4) of all diastereomers)	—

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[a] The stereochemistry of the substituents was established by ^1H NMR spectroscopy with the use of NOE.

[b—e] Signals of different diastereomers are marked.

Table 9. ^{13}C NMR spectra ($CDCl_3$) of compounds **1c, 6, 10, 13a**, and **21c**

Compound	δ
1c	34.6, 34.3, 29.0, 28.2 (C(2), C(5), C(6), C(7)); 43.5 (C(4)); 45.6 (C(1)); 59.7 (CS); 134.0, 128.7, 126.5, 125.4 (C(2), C(3), C(4), C(5), arom. C)
6	27.63 and 28.99 (C(5) and C(6)); 34.53 (C(7)); 38.54 (C(3)); 42.00 (C(2)); 46.71 (C(1)); 48.58 (C(4))
10	23.7 (C(4), C(5)); 30.0 (C(3), C(6)); 50.1 (CS); 134.7, 132.7, 129.3, 127.6 (arom. C)
13a	For *E* isomer: 37.8, 29.5, 28.2, 26.4, 24.2, 19.6 (cage); 44.0 (C(4)); 48.8 (C(1)); 106.6 (vinyl. C); 107.7 (C(2)); 129.3, 127.9, 127.6, 125.6 (arom. C); 138.8 (CAr—S); 165.4 (CAr—N)
21c	14.1, 15.1, 21.3, 32.1, 41.7, 50.4 (CS); 124.5, 126.2, 127.0, 125.6, 133.6, 137.6 (arom. C)

The reaction of camphene with N-(phenylthio)morpholine (**3**) afforded a 15 : 1 mixture of **3,3-dimethyl-*E*-** and **3,3-dimethyl-*Z*-2-(phenylthiomethylene)bicyclo[2.2.1]heptanes (13a)**.

The reaction of camphene with ethyl phenylsulfenate yielded a 6 : 1 mixture of *E*- and *Z*-**13a**.

The reaction of camphene with N-(phenylthio)morpholine (**3**) *in the presence of sulfur trioxide.* A solution of *N*-(phenylthio)morpholine (0.49 g, 2.5 mmol) in anhydrous CH_2Cl_2 (5 mL) was slowly added with stirring to a solution of freshly distilled sulfur trioxide (0.2 g, 2.5 mmol) in anhydrous CH_2Cl_2 (5 mL) under a flow of dry argon at −85 °C. Then the reaction mixture was stirred for 10—20 min and a solution of camphene (0.39 g, 2.5 mmol) in anhydrous CH_2Cl_2 (5 mL) was added. The mixture was stirred at this temperature over 1 h and then at −20 °C over 2 h. The products were isolated according to the general procedure. After chromatography on a column, an 18 : 1 mixture of ***E*-** and ***Z*-13a** was obtained in a yield of 0.43 g (71%).

The reaction of camphene with N-(p-nitrophenylthio)morpholine (**4**) was carried out in the presence of ZnI_2 according to the general procedure giving rise to a 6 : 1 mixture of **3,3-dimethyl-*E*-** and **3,3-dimethyl-*Z*-2-(*p*-nitrophenylthiomethylene)bicyclo[2.2.1]heptanes 13b**. The IR spectrum of a mixture of the *Z* and *E* isomers (thin film), ν/cm^{-1}: 1340, 1520 (nitro group).

The reaction of camphene with N-(o-nitrophenylthio)morpholine (**5**) afforded a 7 : 1 mixture of **3,3-dimethyl-*E*-** and **3,3-dimethyl-*Z*-2-(*o*-nitrophenylthiomethylene)bicyclo[2.2.1]heptanes 13c**. The IR spectrum of a mixture of *Z*- and *E*-**13c** (thin film), ν/cm^{-1}: 1345, 1525 (nitro group).

The reaction of 3,6-dimethoxybenzonorbornadiene with N-(phenylthio)morpholine (**3**) afforded **9-*exo*-11-*syn*-diiodo-3,6-dimethoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (15)** as a colorless oil (found (%): C, 34.24; H, 3.09; $C_{13}H_{14}O_2I_2$) and **9-*exo*-iodo-3,6-dimethoxy-11-*syn*-(phenylthio)tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (14a)** as a colorless oil.

The reaction of 3,6-dimethoxybenzonorbornadiene with N-(o-nitrophenylthio)morpholine (**5**) afforded **9-*exo*-11-*syn*-diiodo-3,6-dimethoxytricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (15)** and **9-*exo*-iodo-3,6-dimethoxy-11-*syn*-(*o*-nitrophenylthio)tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene (14b)** as a yellow oil.

The reaction of hex-1-ene with N-(p-nitrophenylthio)morpholine (**4**) yielded **1,2-diiodohexane (16)** as a colorless oil.

The reaction of norbornadiene with N-(p-nitrophenylthio)morpholine (**4**) gave rise to two fractions: a 3 : 2 mixture of **2,6-*endo-exo*-** and **2,6-*endo-endo*-diiodotricyclo[2.2.1.0^{3,5}]heptanes (22a** and **22b)** (R_f 0.76), whose physicochemical constants and spectra are identical to those reported previously,[7] and a 2 : 1 mixture of **2-*endo*-iodo-6-*exo*-(*p*-nitrophenylthio)tricyclo[2.2.1.0^{3,5}]heptane (21a)** and isomeric **2-iodo-6-(*p*-nitrophenylthio)tricyclo[2.2.1.0^{3,5}]heptane (21b)**, whose stereochemistry was not established. The IR spectrum of the mixture (thin film), ν/cm^{-1}: 1340, 1520 (nitro group).

The reaction of norbornadiene with N-(o-nitrophenylthio)morpholine (**5**) afforded three fractions: a mixture of diiodides **22a** and **22b** (R_f = 0.63) and a mixture of **2-*endo*-iodo-6-*exo*-(*o*-nitrophenylthio)tricyclo[2.2.1.0^{3,5}]heptane (21c)**, **5-*endo*-iodo-6-*exo*-(*o*-nitrophenylthio)bicyclo[2.2.1]hept-2-ene (23a)**, and **5-*exo*-iodo-6-*endo*-(*o*-nitrophenylthio)bicyclo[2.2.1]hept-2-ene (23b)**, from which individual compound **21c** (the third fraction, m.p. 126 °C) crystallized out.

Iodosulfenylation of olefins with thio- and dithiobisamines in the presence of metal iodides (*general procedure*). Metal iodide (2 mmol; in the case of ZnI_2, 4 mmol) was added to a solution of alkene (2 mmol) and thiobisamine or dithiobisamine (1 mmol) in anhydrous CH_2Cl_2 (5 mL) upon cooling with ice. The reaction mixture was stirred with cooling until the thiobisamine or dithiobisamine was consumed. Then the reaction mixture was filtered through a column with silica gel and the solvent was evaporated. The reaction products were isolated by column chromatography. The yields of the products are given in Table 6. The physicochemical characteristics are given in Tables 7—9.

The reaction of norbornene with N,N-thiobis(morpholine) (**24**) afforded two fractions: **di(*endo*-2-iodonorborn-*exo*-3-yl) sulfide (26)** (a 2 : 1 mixture of diastereomers) and **2-*exo*-3-*endo*-diiodobicyclo[2.2.1]heptane (6)**.

The reaction of norbornene with N,N-dithiobis(morpholine) (**25**) yielded **di(*endo*-2-iodonorborn-*exo*-3-yl) disulfide (27)** (a mixture of four diastereomers in a ratio of ~2 : 2 : 1 : 1). This reaction in the presence of MgI_2 additionally afforded compound **6**.

Independent synthesis of 1,2-bis(phenylthio)cyclohexane (10). *The synthesis of 1-iodo-2-(phenylthio)cyclohexane.* Chlorosulfenylation of cyclohexene was carried out as follows. A solution of freshly distilled phenylsulfenyl chloride (0.87 g, 6 mmol) in CCl_4 (10 mL) was added to a solution of cyclohexene (0.54 g, 6.6 mmol) in CCl_4 (20 mL). The mixture was refluxed for 1 h. 2-Chloro-1-(phenylthio)cyclohexane **13**, which was obtained without evaporation of the solvent, was dissolved (without additional purification) in anhydrous acetone (30 mL). Then anhydrous NaI (1.80 g, 12 mmol) was added to the solution. The reaction mixture was stirred until the initial compound was consumed, the acetone was evaporated, and the mixture was chromatographed on a short column with silica gel and aluminum oxide (1 : 1). **1-Iodo-2-(phenylthio)cyclohexane (9a)** was obtained in a yield of 1.66 g (87%).

The reaction of 1-iodo-2-(phenylthio)cyclohexane (**9a**) *with zinc iodide.* ZnI_2 (1.60 g, 5 mmol) was added to a solution of 1-iodo-2-(phenylthio)cyclohexane (**9a**) (0.80 g, 2.5 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred in the dark until the initial compound was consumed and then filtered through a column with silica gel. After chromatography on a column (hexane—benzene, 2 : 1), **1,2-bis(phenylthio)cyclohexane (10)** was obtained in a yield of 0.27 g (18%).

Reaction of bicyclo[2.2.1]heptene with *N*-(*o*-nitrophenylthio)morpholine and zinc iodide in the presence of lithium perchlorate. *N*-(*o*-Nitrophenylthio)morpholine (0.24 g, 1 mmol), ZnI_2 (0.64 g, 2 mmol), and $LiClO_4$ (0.01 g, 0.1 mmol) were added to a solution of norbornene (0.10 g, 1.1 mmol) in anhydrous MeCN (5 mL). The products were isolated according to the general procedure. After chromatography on a column,

2-*endo*-iodo-3-*exo*-(*o*-nitrophenylthio)bicyclo[2.2.1]heptane (1c) and **2-*exo*-iodo-7-*syn*-(*o*-nitrophenylthio)bicyclo[2.2.1]-heptane (2c)** were obtained in yields of 0.07 g (18%) and 0.08 g (22%), respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-33093).

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Received February 11, 2000;
in revised form April 11, 2000