LITERATURE CITED

1. V. M. Karpov, T. V. Mezhenkova, V. E. Platonov, and G. G. Yakobson, Bull. Soc. Chim. Fr., 980 (1986).
2. V. V. Bardin, G. G. Furin, and G. G. Yakobson, J. Fluorine Chem., 14, No. 6, 455 (1979).
3. Yu. V. Pozdnyakovich and V. D. Shteingarts, J. Fluorine Chem., 4, 283, 297 (1974).
4. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, No. 15, 4899, 4907 (1977).
5. A. A. Voityuk, Zh. Strukt. Khim., 29, No. 1, 138 (1988).
6. L. M. Yagupol'skii, Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents [in Russian], Naukova Dumka, Kiev (1968), p. 229.
7. J. Emsley, J. Finney, and L. Sutcliffe, High-Resolution Nuclear Magnetic Resonance Spectroscopy [Russian translation], Vol. 2, Mir, Moscow (1969), p. 215.

S-TOSYLSULFENAMIDES, NEW ELECTROPHILIC SULFOSULFENYLATING AGENTS

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A method has been developed for the synthesis of thiosulfonates by the electrophilic addition of S-tosylsulfenamides to olefins or their electrophilic substitution in aromatic systems. SO_3, $Py \cdot SO_3$, and $BF_3 \cdot Et_2O$ were used as activators. The addition of S-tosylsulfenamides to olefins proceeds through electrophilic trans addition.

Thiosulfonates (RSO_2R') form an important class of organic compounds, which often have biological activity [1, 2] and find use as insecticides [3]. Two major approaches have been described for the synthesis of thiosulfonates: 1) through the oxidation of the corresponding diaryl and dialkyl disulfides [4] and 2) by the direct introduction of the thiosulfonate group as a nucleophile [2, 5]. Both these approaches have considerable disadvantages. Thus, despite the availability of the starting reagents, the oxidative method provides only thiosulfonates with identical substituents at the S(II) and S(VI) atoms. Nucleophilic introduction of the thiosulfate group yields a broad range of products but requires the use of electron-deficient molecules as substrates.

In recent years, we have developed a method for the activation of weak electrophiles, including sulfenamides, using SO_3 and its complexes [6, 7]. Such activation permits the generation of electrophilic species from molecules virtually lacking electrophilic properties.

S-Tosylsulfenamides were first synthesized only in 1972 [8] and have not been studied extensively. The application of sulfonate activation permits us to convert the ordinary electronic characteristics of the RSO_2S group from nucleophilic to electrophilic. Thus, in the present work, we searched for new sulfosulfenylating agents due to repolarization (umpolung) of the sulfonylthio group and studied the reactions of these compounds with a number of model unsaturated substrates. This method of functionalization of olefins provides a pathway for reactions different fundamentally in chemo- and regiospecificity from the addition of the RSO_2S group with its ordinary polarity.

We have discovered that, upon activation by Lewis acids such as $BF_3 \cdot Et_2O$, SO_3, or complexed SO_3, S-tosylsulfenamides (Ia) and (Ib) are active synthetic equivalents of $R{-}SO_2S^+$ capable of electrophilically adding to various olefins:

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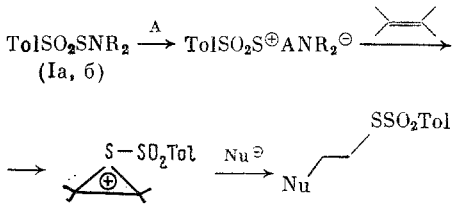
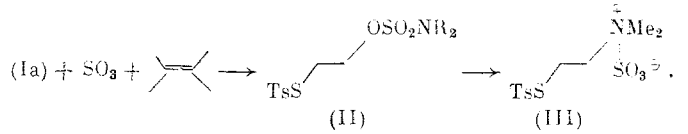


R = Me (a), $(CH_2CH_2)_2O$ (b); A—Lewis acid.

The reactivities of the starting compounds with different substituents at the sulfur atom differ considerably. This is obvious in the case of the synthetically most convenient activation by pyridine–SO_3. N,N-Dimethyl-S-tosylsulfenamide (Ia) readily undergoes electrophilic addition upon activation by Py·SO_3, while N-morpholino-, N-piperidino-, and N,N-diethyl-S-tosylsulfenamides do not even begin to react upon heating at reflux in methylene chloride for 24 h.

We used two types of olefins, which differ relative to the products of the addition of (Ia) with activation by SO_3 and Py·SO_3. The initial product of this addition is always a β-sulfonylthiosulfamate (II). However, the possibility of a sulfamate–betaine rearrangement [9], significantly facilitated in the case of vicinally located RS substituent by the nucleophilic action of the sulfur unshared electron pair, may lead to betaine (III) as the reaction product instead of sulfamate (II).



Thus, olefins may be divided into two groups relative to their addition products: 1) conformationally rigid olefins (IV)-(VII), for which antiperiplanar conformation of the toslylthio and sulfamate groups is impossible and the sulfur unshared electron pair cannot facilitate leaving of the sulfamate group (the corresponding β-sulfonylthiosulfamates are stable) and 2) conformationally mobile olefins (VIII) and (IX), for which antiperiplanar conformation of the RS–C–C–OY fragment is readily achieved and betaine addition products (III) are expected.

The reaction of S-tosylsulfenamide (Ia) with norbornadiene (IV) leads to a mixture of three sulfamates: 1,2-addition product (X) (see Table 1) and products of the homoallylic participation of the second double bond (XI) and (XII). The stereochemistry of the 1,2-addition product determined by PMR spectroscopy indicates the electrophilic nature of the RSO_2S^+ species taking part in this reaction. The exo-endo configurational arrangement of the substituents of product (XI) is in good accord with steric control in an ion pair mechanism for Ad_E reactions [9]. On the other hand, the almost complete lack of exo-exo epimer (XII) indicates the extremely low effective electrophilicity of the reagent, which is much lower than for arylsulfenamides, in which exo-endo and exo-exo epimers are formed in comparable amounts [9].

The reaction with norbornene proceeds much more slowly. We attribute the drop in the yield of the desired product (XIII) to 13% to this low rate. In all cases, a competing reaction gives p-tolyl-p-toluenethiosulfonate (XIV), which is a product of transformation of the Ts· radical [10], which is generated in our case upon the radical dissociation of the S-sulfonylsulfenamide. The yield of (XIV) increases with temperature. This product is completely absent when the reaction is carried out at -60°C but its yield rises to 5% when the reaction is carried out at -20°C. The yield of (XIV) is 20-26% for all reactions carried out at about 20°C. Thus, reactions with sufficiently active olefins are best carried out at reduced temperature.

The lack of skeletal rearrangement products indicates, in our opinion, low effective electrophilicity of the reagent formed.

The result of the reaction of S-tosylsulfenamide (Ib) with norbornene upon SO_3 activation proved somewhat unexpected. Only the addition–elimination product, namely, nortricyclene thiosulfonate (XV) is formed with the complete absence of sulfamate (XIII).

TABLE 1. Electrophilic Addition of S-Sulfonylsulfenamides to Olefins

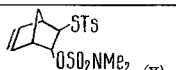
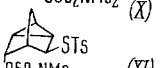
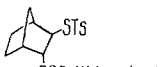
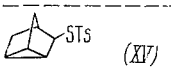
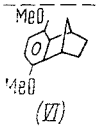
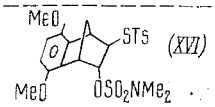
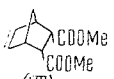
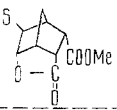
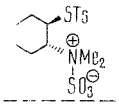
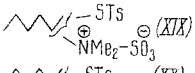
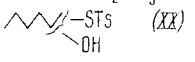
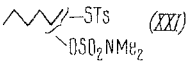
Olefin	S-Sulfonyl-sulfenamides	Means of activation	Products	Yield, %	Reaction temperature, °C (time, h)
 (IV)	(Ia)	Py. SO_3	 (X)  (XI)  (XII)	38 20 Traces	-20(3)
 (V)	(Ia)	Py. SO_3	 (XIII)	13	20(72)
(V)	(Ib)	SO_3	 (XIV)	42	-60(1)
 (VI)	(Ia)	Py. SO_3	 (XVI)	11	20(3)
 (VII)	(Ia)	$BF_3 \cdot Et_2O$	 (XVII)	25	20(24)
(VII)	(Ib)	$BF_3 \cdot Et_2O$	(XVII)	23	20(24)
 (VIII)	(Ia)	Py. SO_3	 (XVIII)	20	20(24)
(VIII)	(Ia)	SO_3	(XVIII)	12	-60(1)
 (IX)	(Ia)	Py. SO_3	 (XIX)  (XX)  (XXI)	15 24 (95:55) 8 (45:55)	20(72)

TABLE 2. Electrophilic Aromatic Ring Substitution by S-Sulfonylsulfenamides

Substrate	S-Sulfonyl-sulfenamide	Means of activation	Products	Yield, %	Reaction temperature, °C (time, h)
MeO— (XXII)	(Ia)	$BF_3 \cdot Et_2O$	MeO— —STS (XXIV)	23	40(2) or 20(24)
(XXII)	(Ib)	$BF_3 \cdot Et_2O$	" (XXIV)	20	40(2) or 20(24)
EtO— (XXIII)	(Ia)	$BF_3 \cdot Et_2O$	EtO— —STS (XV)	36	20(24)

Dimethoxybenzonorbornene (VI) reacts with (Ia) upon activation with $Py \cdot SO_3$ to give expected sulfamate (XVI) but this reaction is complicated by extensive substitution in the aromatic ring, which has two electron-donating methoxy groups. On interaction of (Ia) with the diester of norbornenedicarboxylic acid (VII), the second carbomethoxy group of the substrate acts as an external nucleophile. Lactone (XVII) may hold interest from the viewpoint of its biological activity.

Cyclohexene (VIII) is a convenient model substrate for elucidating the stereochemistry of the addition. The reaction of (VIII) with (Ia) upon activation by both free SO_3 and $Py \cdot SO_3$ leads to the same product, namely, betaine (XVIII), which may be readily converted to the corresponding amine by treatment with 10% hydrochloric acid at reflux, followed by making the solution basic and extraction of the amine obtained with ether [11]. The formation of the trans-1,2-adduct corresponds to a scheme entailing the electrophilic addition of an RSO_2R^+ species with formation of an episulfonium ion.

The reaction with 1-hexene was carried out to determine the regioselectivity. This reaction proceeds virtually without regioselectivity to give a slight predominance for the anti-Markovnikov addition product (55:45).

Another important result emerged in the reaction with 1-hexene, namely, the extraordinary stability of sulfamate (XXI) from a conformationally mobile olefin. This is the first case described for stability of a β-thiosulfamate. We attribute this finding to the significant π-electron-withdrawing capacity of the tosyl group, such that the sulfur unshared electron pair conjugated with this group offers reduced nucleophilic facilitation for loss of the sulfamate group.

S-Tosylsulfenamides (Ia) and (Ib) may also undergo substitution reactions in activated aromatic systems containing strong electron donor substituents (Table 2). Thus, the corresponding para-alkoxyphenylthiosulfonates (XXIV) and (XXV) are formed in the reaction with anisole (XXII) and phenetole (XXIII) upon activation with $BF_3 \cdot Et_2O$. On the other hand, the selection of the substrates for this reaction is limited since the reaction does not proceed even with tert-butyl- and ethylbenzenes.

p-Tolyl-p-toluenethiosulfonate (XIV) is also isolated as a side-product in 23-26% yield.

Hence, a new method is proposed for the synthesis of thiosulfonates containing a second functional group.

EXPERIMENTAL

The reaction was monitored by thin-layer chromatography on Silufol silica gel plates. The purity of the products was monitored by thin-layer chromatography. All the solvents were dried by distillation over P_2O_5. The preparative separation of the reaction products was carried by chromatography on a column packed with Silpearl silica gel using 1:3 ethyl acetate–hexane as the eluent. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz and Varian 400 spectrometer at 400 MHz. The ^{13}C NMR spectra were taken on a Varian FT-80A spectrometer at 20 MHz. The IR spectra were taken for chloroform solutions on a UR-20 spectrometer. The mass spectra were taken on a Varian MAT-212 mass spectrometer with direct sample inlet at 70 eV.

N-Morpholino-S-tosylsulfenamide (Ib) was synthesized according to the procedure of Markley and Dunbar [8].

N,N-Dimethyl-S-tosylsulfenamide (Ia). A solution of 4.46 g (0.04 mole) N,N-dimethylaminosulfenyl chloride in methylene chloride was added dropwise with rapid stirring to an aqueous solution of 10.46 g (0.049 mole) tosylsodium dihydrate with cooling to 0-10°C. The mixture was stirred for an additional 15 min. The organic layer was separated and dried over Na_2SO_4. The solvent was distilled off to give 9.25 g (62%) of an oily product consisting of pure (Ia) as indicated by PMR spectroscopy. This product was used in subsequent reactions without further purification. When necessary, this product may be purified by chromatography although the yield is thereby significantly reduced.

Addition Reactions of S-Sulfonylsulfenamides to Olefins Activated by $Py \cdot SO_3$ (general procedure). A mixture of 1 mole S-tosylsulfenamide, 1 mole $Py \cdot SO_3$, and 2 moles olefin in absolute CH_2Cl_2 was stirred until the sulfenamide disappeared. The insoluble precipitate was filtered off and the solution was evaporated. In case of sulfamate formation, the residue was purified by chromatography. In the case of betaine formation, 2-3 ml methanol was added to the residue and the precipitate formed was filtered off.

Reaction of (Ia) with Norbornadiene (IV). A mixture of 1.5 g (6.5 mmoles) (Ia), 1 g (6.5 mmoles) $Py \cdot SO_3$, and 1.2 g (13 mmoles) norbornadiene gave 2.1 g of an oily product, 1.4 g of which was separated by column chromatography: a) 0.06 g (5%) p-tolyl-p-toluenethiosulfonate (XIV) [R_f 0.56, mp 76-77°C (78°C [12]). PMR spectrum in CCl_4 at 60 MHz: 7.3-6.9 m (8H, arom), 2.3 s (6H, CH_3). Found: C, 60.65; H, 5.03%. Calculated for $C_{14}H_{14}O_2S_2$: C, 60.40; H. 5.07%], b) 0.66 g (38%) N,N-dimethyl-trans-exo-3-(p-tosylthio)bicyclo[2.2.1]-hept-5-en-2-ylsulfamate (X) [R_f 0.28. PMR spectrum in CCl_4 at 60 MHz: 8.0 d and 7.5 d (4H, arom), 6.2 m (2H, HC=), 4.2 t (1H, CHO), 3.55 t (1H, HCS), 3.2 m (1H, HC^1), 2.8 s (7H, CH_3N

and HC^4), 2.4 s (3H, CH_3), 1.9 m (2H, HC^7). ^{13}C NMR spectrum in $CDCl_3$: 139.31 and 134.54 (2C, C=), 129.96 and 127.10 (4H, arom), 86.95 (C–O), 56.01 (C–S), 48.39, 45.89, 45.70, 38.42 (2C, CH_3N), 21.67 (CH_3). IR spectrum (ν, cm^{-1}): 1610, 1330, 1150. Mass spectrum, m/z (I, %): 279 (50) [M – OSO_2NMe_2], 248 (30) [M – Ts], 124 (65) [OSO_2NMe_2], 91 (100) [Tol]. Found: C, 47.74; H, 5.51%. Calculated for $C_{16}H_{21}NO_5S_3$: C, 47.62; H, 5.24%], and c) 0.34 g (20%) N,N-dimethyl-exo-5-(p-tosylthio)tricyclo[2.2.1.$0^{2,6}$]heptane-endo-3-ylsulfamate (XI) with a slight impurity of exo-3-epimer (XII). For (XI): R_f 0.23. PMR spectrum in CCl_4 at 60 MHz: 7.9 and 7.15 d (4H, arom), 4.5 br.s (1H, HCO), 3.8 br.s (1H, HCS), 2.9 s (6H, CH_3N), 2.4 s (4H, CH_3 and HC^4), 1.9-1.5 m (5H). Mass spectrum, m/z (I, %): 248 (35), 155 (65) [Ts], 124 (40%), 91 (100%).

Reaction of (Ia) with Norbornene (V). A mixture of 1.5 g (6.5 mmoles) (Ia), 1g (6.5 mmoles) Py·So_3, and 1.2 g (13 mmoles) norbornene gave 0.22 g (25%) (XIV) and 0.34 g (13%) N,N-dimethyl-trans-exo-3-(tosylthio)bicyclo[2.2.1]hept-2-ylsulfamate (XIII), R_f 0.33. PMR spectrum in CCl_4 at 60 MHz: 7.7 d and 7.2 d (4H, arom), 4.45 t (1H, HCO), 3.0 t (1H, HCS), 2.8 s (6H, CH_3N), 2.4 s (3H, CH_3), 2.0-1.2 m (8H). ^{13}C NMR spectrum in $CDCl_3$: 129.71 and 127.99 (2C and $2C_{arom}$), 86.70 (C–O), 58.47 (C–S), 42.47, 38.47, 34.81, 29.61, 21.10, 20.13, 8.16. Mass spectrum, m/z (I, %): 281 (73) [M – OSO_2NMe_2], 250 (24), [M – Ts], 155 (50), 91 (100). IR spectrum (ν, cm^{-1}): 1530, 1435, 1380, 1340, 1185, 1150.

Reaction of (Ia) with 3′,6′-Dimethoxybenzonorbornene (VI). A mixture of 0.75 g (3.25 mmoles) (Ia), 0.5 g (32.5 mmoles) Py·SO_3, and 1.4 g (6.5 mmoles) (VI) gave 0.05 g (14%) (XIV) and 0.17 g (11%) 1,4-methano-5,8-dimethoxy-trans-exo-3-sulfonylthio-2-(N,N-dimethylsulfamoyl)-1,2,3,4-tetrahydronaphthalene (XXVI), R_f 0.40. PMR spectrum in CCl_4 at 60 MHz: 7.5 d and 7.15 d (4H, arom), 6.6 br.s (2H, arom), 4.0 br.s (3H, HC^1, HC^4, and HCO), 3.0 m (1H, HCS), 3.65 s (6H, CH_3O), 2.55 br.s (6H, CH_3N), 2.4 s (3H, CH_3), 2.15 br.s (2H, HC^{11}).

Reaction of (Ia) with Cyclohexene (VIII). A mixture of 1 g (4.3 mmoles) (Ia), 0.68 g (4.3 mmoles) Py·SO_3, and 0.72 g (8.6 mmoles) cyclohexane gave 0.34 g (20%) (N-sulfonato-N,-N-dimethylammonio)-2-(tosylthio)cyclohexane (XVIII), mp 168-170°C (methanol). PMR spectrum in DMSO-d_6 at 60 MHz: 7.9 d and 7.5 d (4H, arom), 3.4 m (2H, HCN and HCS), 2.8 s (3H, CH_3), 2.8-0.5 m (8H). Found: C, 43.95; H, 5.58%. Calculated for $C_{15}H_{23}NS_3O_5$: C, 45.78; H, 5.89%.

The corresponding amine may be obtained from the betaine according to our procedure [11]. A sample of 100 mg betaine (XVIII) gave 50 mg (63%) trans-2-tosylthio-N,N- dimethylaminocyclohexane (XXVI). PMR spectrum in CD_2Cl_2 at 400 MHz (δ, ppm, J, Hz): 7.60 d (2H, arom, J = 9), 7.27 d (2H, arom, J = 9), 3.96 d.d.d (1H, HCN, J_1 = 4.7, J_2 = 7.1, J_3 = 11.8), 3.41 d.d (1H, HCS, J_1 = 4.7, J_2 = 7.1), 2.63 s (6H, CH_3N), 2.38 s (3H, CH_3), 2.3-1.1 m (8H).

Reaction of (Ia) with 1-Hexene (IX). A mixture of 1.5 g (6.5 mmoles) (Ia), 1 g (6.5 mmoles) Py·SO_3, and 1.12 g (13 mmoles) 1-hexene gave 3 g of a yellow-green oil. The reaction mixture was divided in half. One half gave 0.19 g (15%) of a mixture of two betaines: (N-sulfonatodimethylammonio)-2-(tosylthio)hexane (XIXa) and 2-(N-sulfonato- N,N-dimethylammonio)tosylthiohexane (XIXb). Found: C, 44.18; H, 5.60%. Calculated for $C_{15}H_{23}NO_5S_3$: C, 45.54; H, 6.37%.

The other half of the reaction mixture was separated by chromatography to give a) 0.1 g (11%) (XIV), b) 0.23 g (24%) of a mixture of 2-tosylthiohexanol (XXa) and tosylthio-2--hexanol (XXb) [R_f 0.66. PMR spectrum in CD_2Cl_2 at 400 MHz (δ, ppm, J, Hz): 7.75 m (2H, arom), 7.32 m (2H, arom), 3.76 m (HCO for (XXb)) and 3.61 m (HCO for (XXa)), 3.5 d.d (J_1 = 1.5, J_2 = 9.5) (HCS for (XXb)) and 3.15 m (HCS for (XXa)), 2.8 s (3H, CH_3), 1.77 br.s (OH), 1.5-0.7 m (9H)], and c) 0.25 g (8%) of a mixture of N,N-dimethyl-2- tosylthio-1-hexylsulfamate (XXIa) and N,N-dimethyltosylthio-2-hexylsulfamate (XXIb) [R_f 0.27. PMR spectrum in CD_2Cl_2 at 400 MHz (δ, ppm, J, Hz): 7.75 m and 7.65 d (2H, arom, J = 9), 7.71 m (2H, arom), 4.61 m (HCO for (XXIb)), 4.53 m (HCO for (XXIa)), 3.22 d.d.d (HCS, J_1 = 5, J_2 = 8, J_3 = 14 for (XXIa)), 3.09 d (HCS, J_1 = 5 for (XXIb)), 2.58 s (6H, CH_3N), 2.4 s (3H, CH_3), 1.8-0.8 m (9H)].

Addition Reactions of S-Tosylsulfenamides to Olefins Activated by SO_3 (general procedure). A solution of the S-tosylsulfenamide in CH_2Cl_2 was added dropwise to a solution of freshly distilled SO_3 in CH_2Cl_2 cooled to –60°C and stirred for 10 min. Then, a solution of the olefin was added at the same temperature. The reaction mixture was brought to –20°C and then treated as in the case of activation with Py·SO_3.

Reaction of (Ib) with Norbornene (V). A mixture of 0.9 g (33 mmoles) (Ib), 0.26 g (3.3 mmoles) SO_3, and 0.6 g (6.6 mmoles) norbornene gave 0.39 g (42%) exo-3-tosylthio-

tricyclo[2.2.1.$0^{2,6}$]heptane (XV), R_f 0.50. PMR spectrum in CCl_4 at 60 MHz (δ, ppm): 7.7 d and 7.2 d (4H, arom), 3.15 br.s (1H, HCS), 2.45 s (3H, CH_3), 2.2 br.s (1H, HC^1), 2.0-1.0 m (7H). Found: C, 59.38; H, 5.97%. Calculated for $C_{14}H_{16}O_2S_2$: C, 59.96; H, 5.75%.

Reaction of (Ia) with Cyclohexene (VIII). A mixture of 1 g (4.3 mmoles) (Ia), 0.34 g (4.3 mmoles) SO_3, and 0.72 g (8.6 mmoles) cyclohexene gave 0.2 g (12%) (XVIII).

Reactions of S-Tosylsulfenamides (Addition to Olefins and Aromatic Substitution) Activated by $BF_3 \cdot Et_2O$ (general procedure). A mixture of 1 mole S-tosylsulfenamide and 1.5 moles boron trichloride etherate was stirred in absolute CH_2Cl_2 for 10 min. Then, 1.5-2 mmoles olefin was added and the mixture was stirred until the S-tosylsulfenamide disappeared. The reaction mixture was washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography.

Reaction of (Ib) with Dimethyl Ester of Bicyclo[2.2.1]hept-5-ene-endo-cis-2,3- dicarboxylic Acid (VII). A mixture of 1.17 g (4.3 mmoles) (Ib), 0.9 g (6.45 mmoles) $BF_3 \cdot Et_2O$, and 1.8 g (8.6 mmoles) (VII) gave: a) 0.2 g (23%) γ-lactone of endo-2-hydroxy-endo-5-methoxycarbonyl-exo-3-tosylthiobicyclo[2.2.1]heptane-6-carboxylic acid (XVII) [R_f 0.05. PMR spectrum in CD_2Cl_2 at 60 MHz: 7.8 d and 7.2 d (4H, arom), 4.6 m (1H, HCO), 3.9 br.s (1H, HCS), 3.6 s (6H, CH_3O), 2.35 s (3H, CH_3), 3.2-2.4 m (3H), 1.7 br.s (2H, HC^7). IR spectrum (ν, cm^{-1}): 1775, 1733, 1600, 1510, 1330, 1130], and b) 0.33 g (25%) (XIV).

Reaction of (Ia) with Dimethyl Ester of Bicyclo[2.2.1]hept-5-ene-endo-cis-2,3- dicarboxylic Acid (VII). A mixture of 1 g (4.3 mmoles) (Ia), 0.9 g (6.45 mmoles) $BF_3 \cdot Et_2O$, and 1.8 g (8.6 mmoles) (VII) gave 0.22 g (25%) (XVIII) and 0.35 g (26%) (XIV).

Reaction of (Ia) with Anisole (XXII). A mixture of 0.7 g (3 mmoles) (Ia), 0.65 g (4.5 mmoles) $BF_3 \cdot Et_2O$, and 0.66 g (6 mmoles) anisole gave: a) 0.2 g (23%) (p-methoxyphenylthio)-tosylate (XXIV) [R_f 0.29. PMR spectrum in CCl_4 at 60 MHz: 7.4-6.8 m (8H, arom), 3.8 s (3H, OCH_3), 2.4 s (3H, OCH_3). IR spectrum (ν, cm^{-1}): 1320, 1150. Mass spectrum, m/z (I, %): 297 (1) [M], 155 (59), 139 (8) [CH_2O–C_6H_4S], 91 (100%)] and b) 0.21 g (25%) (XIV).

Reaction of (Ib) with Anisole (XXII). A mixture of 0.8 g (3 mmoles) (Ib), 0.65 g (4.5 mmoles) $BF_3 \cdot Et_2O$, and 0.66 g (0.6 mmole) anisole gave 0.17 g (20%) (XXIV) and 0.21 g (25%) (XIV).

Reaction of (Ia) with Phenetole (XXIII). A mixture of 0.7 g (3 mmoles) (Ia), 0.65 g (4.5 mmoles) $BF_3 \cdot Et_2O$, and 0.74 g (0.6 mmole) phenetole gave 0.36 g (36%) (p-ethoxyphenylthio)tosylate (XXV), R_f 0.31. PMR spectrum in CCl_4 at 60 MHz: 7.0 d (2H, arom), 6.6 m (4H, arom), 6.05 d (2H, arom), 3.35 q (2H, CH_2O), 1.85 s (3H, CH_3Ph), 0.85 t (3H, CH_3CH_2). Found: C, 58.46; H, 5.32%. Calculated for $C_{15}H_{14}O_3S_3$: C, 58.42; H, 5.23%.

LITERATURE CITED

1. B. G. Boldyrev, S. A. Gorelova, and A. T. Dvorko, Zh. Obshch. Khim., 31, No. 7, 2402 (1961).
2. B. G. Boldyrev and T. A. Trofimova, Zh. Obshch. Khim., 30, No. 12, 4993 (1960).
3. N. N. Mel'nikov, Zh. Vses. Khim. Ova, 33, No. 6, 602 (1988).
4. A. K. Bhattacharya and A. G. Hortmann, J. Org. Chem., 43, No 13, 2728 (1978).
5. D. T. Gibson, J. Chem. Soc., No. 10, 2637 (1931).
6. N. S. Zefirov, N. V. Zyk, Yu. A. Lapin, and A. G. Kutateladze, Zh. Org. Khim., 25, No. 1, 198 (1989).
7. N. S. Zefirov, N. V. Zyk, S. I. Kolbasenko, and A. G. Kutateladze, J. Org. Chem., 50, No. 23, 4539 (1985).
8. L. D. Markley and J. E. Dunbar, J. Org. Chem., 37, No. 15, 2512 (1972).
9. N. S. Zefirov, N. V. Zyk, A. G. Kutateladze, and Yu. A. Lapin, Zh. Org. Khim., 23, No. 2, 392 (1987).
10. C. M. M. da Silva Correa and W. A. Water, J. Chem. Soc. C, No. 15, 1874 (1968).
11. N. S. Zefirov, N. V. Zyk, A. G. Kutateladze, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2868 (1989).
12. G. Palumbo and R. Caputo, Synthesis, 888 (1981).