ALKYLATION OF π-DONATING COMPOUNDS BY METHOXYALLENE—ARYLSULPHENYL CHLORIDE ADDUCTS

I. P. Smolyakova, V. A. Smit, A. I. Lutsenko, and E. D. Daeva

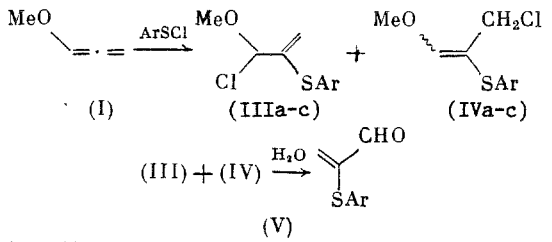
UDC 66.095.253:542.955:547.541.5:547.315.1-31:547.1'128

Reaction of methoxyallene with arylsulphenyl chlorides proceeds nonselectively with formation of mixtures of 1,2- and 2,3-arylthiochloro adducts, the composition of which depends on the nature of the reagent and solvent. π-Donating compounds of various types in the presence of Lewis acids are alkylated by adducts of methoxyallene with arylsulphenyl chlorides and primarily products are formed by attack at the C^3 atom of the reagent.

It is known that simple vinyl ethers easily attach to arylsulphenyl chlorides to give with quantitative yield α-methoxy-β-arylthioalkyl chlorides [1]. It was found recently that these adducts can be used as electrophiles for alkylation of a series of π-donors, such as trimethylsilyl ethers of enols (TMSEEs) [2], allylsilanes [3, 4], or vinyl ethers (VEs) [5].

In this work the regioselectivity of addition of arylsulphenyl chlorides to methoxyallene (I) and the possibility of using the adducts formed as alkylation agents (preliminary report [6]) has been studied.

Data on the Ad_E reaction of (I) with arylsulphenyl chlorides are absent from the literature. It was found that reaction of (I) with p-MeC_6H_4SCl (IIa), p-ClC_6H_4SCl (IIb), or 2,4,6-$Me_3C_6H_2SCl$ (IIc) proceeds easily at −78°C and leads to formation of a mixture of 1,2-(III) and 2,3-addition products (IV) [addends (IV) are a mixture of Z and E isomers]



Ar = *n*-MeC_6H_4 (a), *n*-ClC_6H_4 (b), 2,4,6-$Me_3C_6H_2$ (c); (Va), 63%; (Vc), 92%.

Adducts (III) and (IV) are unstable and upon hydrolysis give 2-arylthioprop-2-en-1-al (V). Data on the structures and isomeric composition of mixtures of (III) + (IV) were obtained from the PMR spectra of the reaction mixtures.

Study of the regioselectivity of addition has shown that the ratio of regioisomers depends mainly on the nature of the reagent and solvent used (Table 1). Thus, mostly formation of 2,3-adduct (IVa) is observed in the reaction of (I) + (IIa) in CD_2Cl_2 at −78°C, while under the same conditions Ad_E-reaction of (IIb) leads mainly to (IIIb). Upon carrying out these reactions in pentane the fraction of 1,2-adduct increases. In all cases preferential or exclusive formation of Z-isomer (IV) was observed. Temperature has no influence on the course of the Ad_E reaction.

In pentane conversion of (III) to (IV) and/or of Z-(IV) to E-(IV) are not observed (over 48 h) even at 20°C. In $CDCl_3$ or CD_2Cl_2 partial conversion of (III) to (IV) and of Z-(IV) to E-(IV) occurs; however, products of self-condensation are also formed (PMR spectral data). In the presence of Lewis acids (for example $TfOSiMe_3$) both isomerization and formation of by-products increase markedly.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 114-121, January, 1990. Original article submitted April 22, 1988.

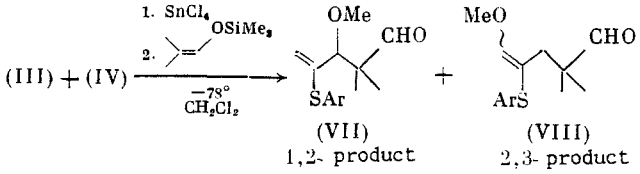
0568-5230/90/3901-0101$12.50

TABLE 1. Composition of Products from Reaction of ArSCl with Methoxyallene*

Solvent	T, °C	p-MeC$_6$H$_4$SCl		p-ClC$_6$H$_4$SCl	
		(IIIa):(IV a)	Z : E	(IIIb):(IV b)	Z : E
CD_2Cl_2	−78	3 : 10	4 : 5	5 : 2	6 : 1
CD_2Cl_2	0	1 : 10	4 : 5	–	–
Pentane	−78	5 : 4	Only Z	4 : 1	Only Z
Pentane	0	3 : 2	Only Z	4 : 1	Only Z

*According to PMR 10 min after mixing of the reagents.

A mixture of adducts (IIIa) + (IVa) in the presence of $SnCl_4$ even at −78°C reacts with the TMSEE of isobutyric aldehyde (VI) giving a mixture of 1,2-(VIIa) and 2,3-products (VIIIa) of alkylation of 2,2-dimethyl-3-methoxy-4-p-tolylthiopenten-4-al (VIIa) and 2,2-dimethyl-5-methoxy-4-p-tolylthiopenten-4-al (VIIIa) with total yield of 80%

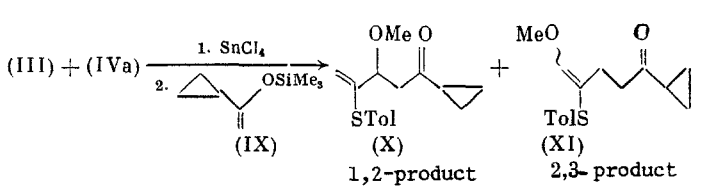


The ratio of (VII) to (VIII) depends on the ratio of the (III) and (IV) isomers. Thus, upon using a mixture of (IIIa) and (IVa) in CH_2Cl_2, mainly 2,3-adduct (VIIIa) [(VIIa):(VIIIa) = 1:9] was formed, and when the reagent was formed in pentane [(IIIa):(IVa) = 3:2], 1,2- and 2,3-isomers were isolated in equal amounts [(VIIa):(VIIIa) = 1:1] (compare with the data of Table 1). The experiments indicated that temperature, duration of exposure of (IIIa) + (IVa) adducts to Lewis acid, and the order of addition of the reagents do not have a substantial effect on the ratio of the obtained alkylation products. Thus, the ratio of (VIIa) to (VIIIa) for the system p-TolSCl, methoxyallene, and $SnCl_4$ is determined mainly by the ratio of 1,2- and 2,3-isomers in the starting adducts.

We were unable to explain the nature of the influence of Lewis acids on the regioselectivity of alkylation of (VI) since with other catalyts ($TiCl_4$, $ZnCl_2$, $TfOSiMe_3$) side reactions proceed to a significant degree.

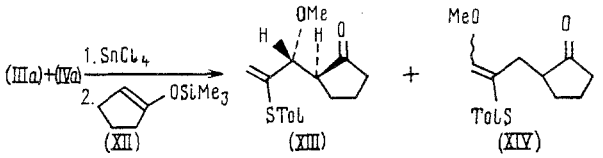
Attempts to use adducts (IIIb) and (IVb) obtained in pentane in order to increase the yield of 1,2-product of alkylation did not give the desired result. In this case the fraction of 2,3-alkylation product in the final mixture was greater than the fraction of the starting 1,2-adduct of (IIb) with (I) [(IIIb):(IVb) = 4:1, (VIIb):(VIIIb) = 3:5].

Investigation of the influence of nucleophiles (TMSEEs) on the regioselectivity of alkylation was of definite interest. It was found that upon using the TMSEE of methylcyclopropyl ketone (IX) also a mixture of 1,2- and 2,3-alkylation products is formed, i.e., 1-cyclopropyl-3-methoxy-4-p-tolylthiopent-4-en-1-one (X) and 1-cyclopropyl-5-methoxy-4-p-tolylthiopent-4-en-1-one (XI), respectively, in a ratio of ~7:9 with total yield of 49%*

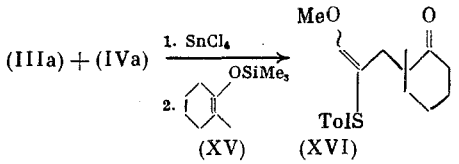


Analogously adducts (IIIa) and (IVa) alkylate the TMSEE of cyclopentanone (XII) with formation of a mixture of 2-(1'-methoxy-2'-p-tolylthioprop-2'-enyl)cyclopentanone (XIII) and 1-(3'-methoxy-2'-p-tolylthiopropen-2'-yl)cyclopentanone (XIV) in a ratio of 1:1 with total yield of 34%

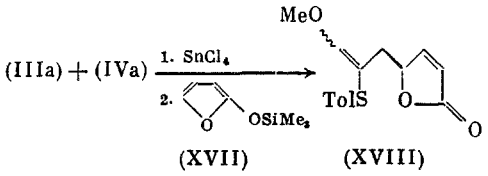
*In this and in all the following cases a mixture of (IIIa) and (IVa) (3:10), obtained in CH_2Cl_2 at −78°C, was used.



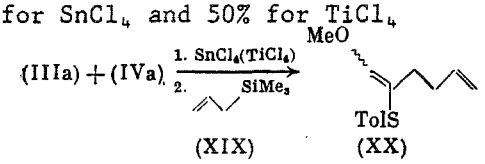
An exception among the silyl ethers used is the thermodynamic TMSEE isomer of 2-methylcyclohexanone (XV), which easily reacts with a mixture of (IIIa) and (IVa) giving only the 2,3-regioisomer 2-methyl-2-(3'-methoxy-2'-p-tolylthiopropen-2'-)cyclohexan-1-one (XVI) in 80% yield



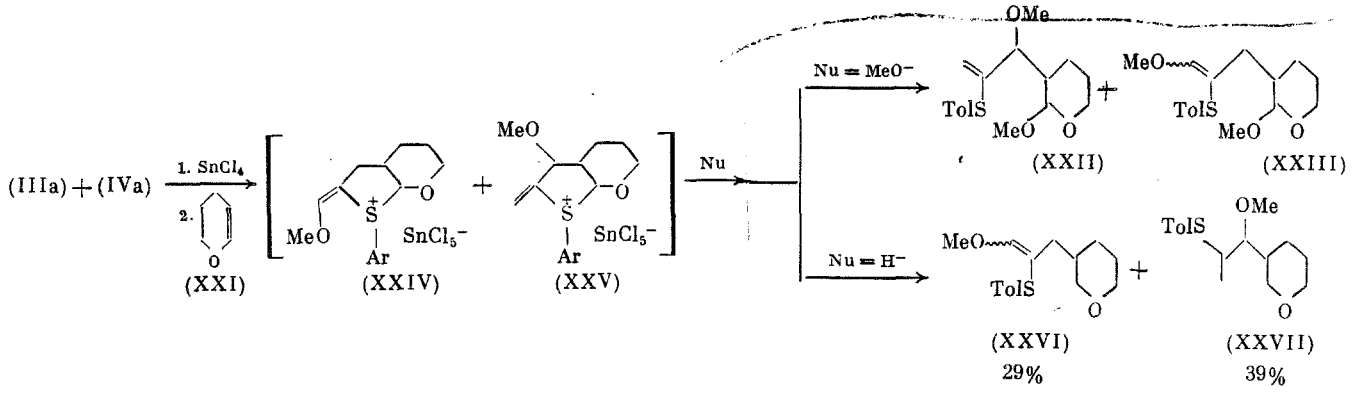
Upon using silyl ketene acetals as nucleophiles in reaction with a mixture of (IIIa) and (IVa), as in the case of (XIV), 2,3-regiospecificity is observed. Thus, upon reaction of a mixture of adducts (IIIa) and (IVa) with the silyl ether of crotonolactone (XVII) in the presence of Lewis acid only the 2,3-product 7-methoxy-2-p-tolylthiohepta-2,6-dien-4-olide (XVIII) is formed with 36% yield



It was found that the mixture of adducts (IIIa) and (IVa) in the presence of Lewis acid easily alkylates trimethylallylsilane (XIX) forming only 1-methoxy-2-p-tolylthiohexa-1,5-diene (XX) with yield of 90% for $SnCl_4$ and 50% for $TiCl_4$



Adducts (IIIa) and (IVa) easily alkylate dihydropyran (XXI) at −78°C in the presence of Lewis acids giving, after treatment of the reaction mixture with MeOH, the 1,2- and 2,3-regioisomers 2-methoxy-3-(3'-methoxy-2'-p-tolylthiopropen-2'-yl)oxane (XXII) and 2-methoxy-3-(1'-methoxy-2'-p-tolylthiopropen-2'-yl)oxane (XXIII) in a 4:3 ratio with total yield of 95% upon using $SnCl_4$ and 70% with $TiCl_4$ (see [4])



By analogy with reactions of VEs with VE–ArSCl adducts one can assume that reaction of the mixture of (IIIa) and (IVa) with (XXI) gives mostly cyclic thiophenium salts (XXIV) and (XXV), which are then opened by external nucleophiles (in this case MeO^-). Upon treatment of the reaction mixture with n-Bu_4NBH_4, together with the expected product 3-(3'-methoxy-

TABLE 2. Chemical Shifts (δ, ppm) of the Proton at the Double Bond and R_f's for Z,E-Isomers of 2,3-Alkylation Products

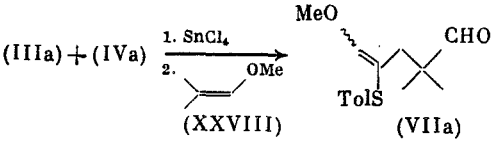
Product	Z-isomer		E-isomer		Product	Z-isomer		E-isomer	
	δ *	R_f *	δ *	R_f †		δ *	R_f *	δ *	R_f †
(VIIIa)	6,43	0,41	6,62	0,57	(XVIII)	6,54	0,31	6,69	‡
(VIIIb)	6,44	0,23	6,64	0,38	(XX)	6,40	0,56	6,51	0,66
(XI)	6,50	0,45	6,56	0,58	(XXIII)	6,39	0,54	6,61	0,71
(XVI)	6,45	0,39	6,61	‡					

*In $CDCl_3$.
†Ethane–hexane, 1:1, Silufol.
‡E-Isomers of compounds (XVI) and (XVIII) were not isolated separately. Chemical shifts were determined from spectra of mixtures of geometrical isomers.

2'-p-tolylthiopropen-2'-yl)oxane (XXVI), the 1,2-regioisomer with reduced double bond is also formed, i.e., 3-(1'-methoxy-2'-p-tolylthiopropyl)oxane (XXVII).

Results of reaction of (XIX) and (XXI) with (IIIa) and (IVa) indicate that use of different Lewis acids ($SnCl_4$ and $TiCl_4$) does not significantly influence the ratio of 1,2- and 2,3-regioisomers.

Besides dihydropyran, 2-methyl-1-methoxyprop-1-ene (XXVIII) also reacts with adducts (IIIa) and (IVa); however, in this case there is extensive polymerization and the 1:1 product (VII), 2,2-dimethyl-5-methoxy-4-p-tolylthiopenten-4-al was isolated in only 19% yield



Alkylation products corresponding to 2,3-addition to (I) of the ArS group of the C-nucleophile are a mixture of geometric isomers isolated by TLC on SiO_2 (ether–hexane, 1:2) individually. The isomers with the lower R_f value gradually are transformed into another, stable product. As seen from Table 2, the PMR chemical shift (δ) of the proton at the double bond for the isomers with lower R_f value is always lower than that for this proton in the stable isomer. For the geometrical isomer pair of aldehyde (V) it was established by PMR (Overhauser effect) that the adduct with δH of 6.43 ppm has the Z-configuration and the product with δH of 6.62 ppm is the E-isomer. From the relationship of the chemical shifts with the R_f's (see Table 2) one can assume that the unstable isomers with the lower values of δ and R_f have the Z configuration and the stable products are E-adducts.

From PMR data the 1,2-regioisomer (XIII), obtained by reaction of (IIIa) and (IVa) with the TMSEE of cyclopentanone, is one diastereomer, indicating that formation of the new carbon–carbon bond is stereospecific. The coupling constant J_{HJ} = 3 Hz indicates that compound (XIII) has the threo-configuration.

The Z,E-2,3-regioisomers (XXIII), obtained from dihydropyran, are also individual diastereomers. On the basis of the coupling constants for the Z,E alkylation products (XXIII) (respectively, J = 3.5 and 4 Hz) one can assume that trans addition of adduct (IIIa) and MeO^- to the VE double bond occurs.

According to NMR spectroscopy compound (XXVII) also is a single diastereomer, which indicates high selectivity in the formation of the new carbon–carbon bond and reduction of the double bond. Unlike (XXIII) and (XXVII), compound (XXII) is a mixture of two diastereomers in a ratio of ~4:5.

The structure of the obtained compounds were assigned by analytical and spectral methods (NMR, mass spectroscopy).

The obtained data indicate that adducts of methoxyallene with arylsulphenyl chlorides are active electrophiles easily reacting with typical π-donating nucleophiles. The regio-

selectivity of this reaction depends on the nature of the nucleophile but, as a rule, the predominant reaction is nucleophilic attack on the C^3 atom (I). The reaction sequence (I) → (III) + (IV) → adducts with a new carbon–carbon bond is conducted in one pot and can be used to obtain polyfunctional compounds containing the reactive β-methoxy-α-arylthioallyl group.

EXPERIMENTAL

PMR spectra of solutions in $CDCl_3$ were obtained on Bruker WM-250 and Bruker AM-300 instruments. Chemical shifts are given in δ, ppm, and the coupling constants in Hz. Mass spectra were recorded on a Varian MAT CH-6. The R_f values are for Silufol SiO_2 layers in ether–hexane (1:1).

Methoxyallene was obtained by the method of [7].

2-(2',4',6'-Trimethylphenylthio)prop-2-en-1-al (Vc). To a solution of 182 mg (1 mmole) of 2,4,6-trimethylphenylsulphenyl chloride in 10 ml of absolute CH_2Cl_2 at −78°C in an Ar atmosphere a solution of 70 ml (1 mmole) of methoxyallene in 1 ml CH_2Cl_2 was added (until disappearance of the characteristic color of ArSCl). After 10 min the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution cooled to 0°C, extracted with ether, and dried above $CaCl_2$. The residue after solvent removal was chromatographed on a SiO_2 plate (eluent: hexane–ether, 2:1). There was obtained 190 mg (92%) of 2-(2',4',6'-trimethylphenylthio)prop-2-en-1-al with R_f 0.66, mp of 47.5-49.5°C (from hexane), M^+ 206. PMR spectrum (CCl_4): 2.30 s (3H, CH_3), 2.35 s (6H, two CH_3 groups), 5.16 and 5.80 both s (2H, $=CH_2$), 6.92 s (2H, H_{arom}), 9.52 s (1H, CHO).

2-p-Tolylthioprop-2-enal (Va) was obtained analogously to (Vc) and characterized in the form of the 2,4-dinitrophenylhydrazone (yield per hydrazone: 63%). R_f 0.36 ($CHCl_3$–hexane, 2:1), mp 148-149°C (from EtOH). PMR spectrum: 2.30 s (1H, NH), 2.40 s (3H, CH_3), 5.15 and 5.66 both s (2H, $=CH_2$), 7.35, 7.95, and 8.35 three m (7H, H_{arom}), 9.13 s [1H (CH)], 11.22 s (1H, =NH).

2,2-Dimethyl-3-methoxy-4-p-tolylthiopent-4-enal (VIIa) and Z,E-2,2-Dimethyl-5-methoxy-4-p-tolylthiopent-4-enal [Z,E-(VIII)]. A) To a solution of 159 mg (1 mmole) of TolSCl in 20 ml absolute CH_2Cl_2 at −78°C in an Ar atmosphere a solution of 70 mg (1 mmole) of methoxyallene in 2 ml CH_2Cl_2 was added. Then a solution of 0.234 ml (2 mmoles) of $SnCl_4$ in 2 ml CH_2Cl_2 previously cooled to −78°C was added followed immediately by a cooled solution of 173 mg (1.2 mmoles) of 2-methyl-1-trimethylsiloxyprop-1-ene (TMSEE of isobutyric aldehyde) in 2 ml CH_2Cl_2. After 5 min the reaction mixture was poured with stirring into a $NaHCO_3$ saturated solution cooled to 0°C, extracted with ether, and dried above $CaCl_2$. The residue after solvent removal was purified by preparative TLC on SiO_2 (eluent:ether–hexane, 1:1). There was isolated 170 mg (64%) of Z-(VIIIa), 15 mg (6%) of E-(VIIIa), and 20 mg (8%) of (VIIa). To a solution of 159 mg (1 mmole) of TolSCl in 5 ml pentane at −78°C in an Ar atmosphere 70 mg (1 mmole) of methoxyallene was added. To the obtained colorless solution 25 ml of absolute CH_2Cl_2 was added, then previously cooled (−78°C) solutions of 0.234 ml (2 mmoles) of $SnCl_4$ in 1 ml CH_2Cl_2 and 173 mg (1.2 mmoles) of the TMSEE of isobutyric aldehyde in 1 ml CH_2Cl_2. After 5 min the reaction mixture was poured with stirring into a saturated solution of $NaHCO_3$ cooled to 0°C, and extracted with Et_2O. The ether extract was passed through a SiO_2 layer. According to NMR data the raw product (~90%) is a mixture of three products: (VIIa), Z-(VIIIa), and E-(VIIIa) in the ratio of 2:1:1. (VIIa): R_f 0.62. n_D^{22} 1.5495, M^+ 264. PMR spectrum: 1.12, 1.18 both s [6H, $C(CH_3)_2$], 2.36 s (3H, CH_3), 3.32 s (3H, OMe), 3.81 s (1H, CHOMe), 4.85, 5.24 both s (2H, CH_2), 7.27 m (4H, H_{arom}), 9.70 s (1H, CHO). Found, %: S 68.30, H 7.72. $C_{15}H_{20}O_2S$. Calculated, %: C 68.14, H 7.62. Z-(VIIIa): R_f 0.41, n_D^{20} 1.5533, M^+ 264. PMR spectrum: 0.99 s [6H, $C(CH_3)_2$], 2.26 s (2H, CH_2), 2.27 s (3H, CH_3), 3.70 s (3H, OCH_3), 6.43 s (1H, =CH), 7.07 m (4H, H_{arom}), 9.45 s (1H, CHO). E-(VIIIa): R_f 0.57, n_D^{20} 1.5580, M^+ 264. PMR spectrum: 1.06 s [6H, $C(CH_3)_2$], 2.32 s (3H, CH_3), 2.33 s (2H, CH_2), 3.72 s (3H, OCH_3), 6.62 s (1H, =CH), 7.10 m (4H, H_{arom}), 9.50 s (1H, CHO). For the E,Z-isomer mixture was found, %: C 67.73, H 7.74, S 11.62. $C_{15}H_{20}O_0S$. Calculated, %: C 68.14, H 7.62, S 12.13.

2,2-Dimethyl-3-methoxy-4-p-chlorophenylthiopent-4-enal (VIIb) and E,Z-2,2-dimethyl-5-methoxy-4-p-chlorophenylthiopent-4-enal (E, Z) (VIIIb) were obtained by method B with total yield of 83%. (VIIb); yield 30%, R_f 0.48, n_D^{20} 1.5500, M^+ 284, 286. PMR spectrum: 1.09 and 1.13 both s [6H, $C(CH_3)_2$], 3.29 s (3H, OCH_3), 3.79 s (1H, CHOMe), 4.89 and 5.30 both s

(2H, =CH_2), 7.35 m (4H, H_{arom}), 9.67 s (1H, CHO). (Z)-(VIIIb): yield 44%, R_f 0.23, n_D^{20} 1.5618, M^+ 284, 286. PMR spectrum: 0.96 s [6H, $C(CH_3)_2$], 2.22 s (2H, CH_2), 3.62 s (3H, OCH_3), 6.44 s (1H, CH), 7.09 m (4H, H_{arom}), 9.38 s (1H, CHO). E-(VIIIb): yield 9%, R_f 0.38, n_D^{20} 1.5675, M^+ 284, 296. PMR spectrum: 1.06 s [6H, $C(CH_3)_2$], 2.33 s (2H, CH_2), 3.73 s (3H, OCH_3), 6.64 s (1H, CH), 7.29 m (4H, H_{arom}), 9.47 s (1H, CHO).

1-Cyclopropyl-3-methoxy-4-p-tolylthiopent-4-en-1-one (X) and E,Z-1-cyclopropyl-5-methoxy-4-p-tolylthiopent-4-en-1-one E,Z-(XI) were synthesized by method A with total yield of 49%. (X): yield 22%, R_f 0.60, n_D^{22} 1.5482, M^+ 276. PMR spectrum: 0.88 and 1.05 both m (4H, CH_2–CH_2), 1.97 m (1H, CH), 2.37 s (3H, CH_3), 2.97 both d.d (AB-part of ABX-spectrum, 2H, J_{AB} = 17.5, J_{AX} = 9, J_{BX} = 4.5, CH_2), 3.31 s (3H, OCH_3), 4.27 d.d (X-part of ABX-spectrum, 1H, CH), 4.78 s (1H, =CH), 5.35 d (1H, J = 1, =CH), 7.27 m (4H, H_{arom}). Found, %: C 68.76, H 7.16, S 11.55. $C_{16}H_{20}SO_2$. Calculated, %: C 69.53, H 7.29, S 11.60. Z-(XI): yield 11%, R_f 0.45, n_D^{20} 1.5572, M^+ 276. PMR spectrum: 0.83 and 0.97 both m (4H, CH_2–CH_2), 1.84 m (1H, CH), 2.31 s (3H, CH_3), 2.35 and 2.72 both m (4H, CH_2–CH_2), 3.72 s (3H, OCH_3), 6.50 s (1H, =CH), 7.12 m (4H, H_{arom}). E-(XI): yield 16%, R_f 0.58, M^+ 276. PMR spectrum: 0.82 and 0.98 both m (4H, CH_2–CH_2), 1.88 m (1H, CH), 2.32 s (3H, CH_3), 2.51 and 2.72 both m (4H, CH_2–CH_2), 3.74 s (3H, OCH_3), 6.56 s (1H, =CH), 7.12 s (4H, H_{arom}). For the mixture of E,Z-isomers was found, %: C 69.09, H 7.33, S 11.66. $C_{16}H_{20}SO_2$. Calculated, %: C 69.53, H 7.29, S 11.60.

2-(1'-Methoxy-2'-p-tolylthioprop-2'-enyl)cyclopenan-1-one (XIII) and 2-(3'-methoxy-2-p-tolylthioprop-2'-enyl)cyclopentan-1-one (XIV) were obtained by method A with total yield of 34%. (XIII): yield 17%, R_f 0.52, n_D^{23} 1.5580, M^+ 276. PMR spectrum: 1.60-2.40 m [6H, $-(CH_2)_3-$], 2.36 s (3H, CH_3), 2.56 m (1H, CHCO), 3.24 s (3H, OCH_3), 4.13 d (1H, CHOMe, J = 3), 5.07 s (1H, =CH), 5.47 d (1H, =CH, J = 1), 7.25 m (4H, H_{arom}). Found, %: C 68.91, H 7.19, S 12.07. $C_{16}H_{20}O_2S$. Calculated, %: C 69.53, H 7.29, S 11.60. (XIV) was isolated as one geometric isomer with 17% yield, R_f 0.27, n_D^{23} 1.5697, M^+ 276. PMR spectrum: 1.45-2.55 m [9H, $-(CH_2)_3-$ and CH_2–CH], 2.31 s (3H, CH_3), 3.72 s (3H, OCH_3), 6.60 s (1H, =CH), 7.12 m (4H, H_{arom}). Found, %: C 69.36, H 7.37, S 11.73. $C_{16}H_{20}SO_2$. Calculated, %: C 69.53, H 7.29, S 11.60.

2-Methyl-2-(3'-methoxy-2'-p-tolylthioprop-2'-ene)cyclohexan-1-one (XVI) was obtained by method A with 80% yield. R_f 0.39, n_D^{22} 1.5580, M^+ 304. PMR spectrum: 1.07 s (3H, CH_3), 1.70 m [6H, $-(CH_2)_3-$], 2.29 s (3H, CH_3), 2.30 m (4H, two CH_2 groups), 3.71 s (3H, OCH_3), 6.45 s (1H, =CH), 7.07 (4H, H_{arom}). According to PMR spectroscopy (XVI) contains ≤10% E-isomer: 3.67 s (OCH_3), 6.61 s (=CH).

7-Methoxy-6-p-tolylthiohepta-2,6-dien-4-olide (XVIII) was obtained by method A with 36% yield in the form of one geometric isomer. R_f 0.31 (ether–hexane, 3:1), n_D^{20} 1.5725, M^+ 276. PMR spectrum: 2.30 s (3H, CH_3), 2.44 two d.d (AB-part of ABX-spectrum, 2H, CH_2, J_{AX} = 7, J_{BX} = 6, J_{AB} = 14.5), 5.17 br. t.t (1H, CHO, J_1 = 6, J_2 = 1.75), 6.04 d.d (1H, =CH), J_1 = 5.5, J_2 = 2), 6.54 s (1H, =C<u>H</u>OCH_3), 7.12 m (4H, H_{arom}), 7.48 d.d (1H, =CH, J_1 = 5.5, J_2 = 2).

E,Z-1-Methoxy-2-p-tolylthiohexa-1,5-diene E,Z-(XX) was obtained by method A with 85% yield. E-(XX): R_f 0.66 (ether–hexane, 1:2), n_D^{20} 1.5610, M^+ 234. PMR spectrum: 2.28 m [4H, $-(CH_2)_2-$], 2.33 s (3H, CH_3), 3.73 s (3H, OCH_3), 4.97 m (2H, =CH_2), 5.79 m (1H, =CH), 6.57 s (1H, =C<u>H</u>OCH_3), 7.13 m (4H, H_{arom}). ^{13}C NMR spectrum: 20.83 ($\underline{C}H_3$–C_6H_4), 27.88 and 31.92 (CH_2–CH_2), 59.85 (OCH_3), 108.40 ($\underline{C}$=CH_2), 114.94 (=CH_2), 127.72, 129.45, 131.41, 133.93 (C_{arom}), 137.72 (CS), 153.19 (CO). Z-(XX): R_f 0.56 (ether–hexane, 1:2), n_D^{20} 1.5440, M^+ 234. PMR spectrum: 2.15 m [4H, $-(CH_2)_2-$], 2.31 s (3H, CH_3), 3.71 s (3H, OCH_3), 5.00 m (2H, =CH_2), 5.75 m (1H, =CH), 6.40 s (1H, =C<u>H</u>OCH_3), 7.15 m (4H, H_{arom}). ^{13}C NMR spectrum: 15.17 ($\underline{C}H_3C_6H_4$), 31.82 and 32.70 (CH_2–CH_2), 60.08 (OCH_3), 109.99 ($\underline{C}$=CH_2), 114.41 (=CH_2), 127.72, 129.29, 130.0, 133.50 (C_{arom}), 138.16 (CS), 149.70 (CO). For the mixture of E,Z-isomers was found, %: C 71.42, H 7.48, S 13.35. $C_{14}H_{18}SO$. Calculated, %: C 71.75, H 7.74, S 13.68.

2-Methoxy-3-(1'-methoxy-2'-p-tolylthioprop-2'-enyl)oxane (XXII) and Z,E-2-methoxy-3-(3'-methoxy-2'-p-tolylthioprop-2'-enyl)oxane Z,E-(XXIII) were obtained by method A (treatment of the reaction mixture with MeOH) with total yield of 95% (catalyst $SnCl_4$) and 70% ($TiCl_4$). (XXII): R_f 0.78, n_D^{20} 1.5295, M^+ 308, according to PMR spectroscopy it is a mixture of two diastereomers in the ratio of ~4:5. PMR spectrum: 1.2-2.1 m [5H, CH–$(CH_2)_2$], 2.32 and 2.33 two s (3H, CH_3), 3.28, 3.31, 3.38 and 3.40 four s (6H, 2 OCH_3 groups), 4.77, 4.85, 5.18, and 5.28 four s (2H, =CH_2), 7.24 s (4H, H_{arom}). Z-(XXIII): yield 22% ($SnCl_4$), R_f

0.54, n_D^{20} 1.5350, M^+ 308; PMR spectrum: 1.1-2.0 m [5H, $-(CH_2)_2-CH$], 2.30 s (3H, CH_3), 3.33 s (3H, OMe), 3.45 m (1H, CHO), 3.72 s (3H, OMe), 3.83 m (1H, CHO), 4.12 d (1H, CH_{acet}, J = 3.5), 6.39 s (1H, =CH), 7.14 m (4H, H_{arom}). E-(XXIII): yield 18% ($SnCl_4$), R_f 0.71, n_D^{20} 1.5415, M^+ 308. PMR spectrum: 1.2-1.9 m [5H, $-CH-(CH_2)_2-$], 2.32 s (3H, CH_3), 3.36 s (3H, OCH_3), 3.47 m (1H, CHO), 3.71 s (3H, OCH_3), 3.85 m (1H, CHO), 4.14 d (1H, CH_{acet}, J = 4), 6.61 s (1H, =CH), 7.12 m (4H, H_{arom}). For the mixture of E,Z-isomers was found, %: C 66.83, H 8.23. $C_{17}H_{24}SO_3$. Calculated, %: C 66.20, H 7.84.

3-(3'-Methoxy-2'-p-tolylthioprop-2'-enyl)oxane (XXVI) and 3-(1'-methoxy-2'-p-tolylthiopropyl)oxane (XXVII) were obtained by method A (catalyst $SnCl_4$) but the reaction mixture was treated with 375 ml (1.5 mmoles) of n-Bu_4NBH_4 in 2 ml CH_2Cl_2 (10 min at −78°C and 10 min at −20°C). Then the mixture was treated with ice cold $NaHCO_3$ solution, extracted with ether, and dried above Na_2SO_4. The residue after solvent removal was purified by preparative TLC on SiO_2 with eluent ether–hexane (1:1). There was isolated 29% of (XXVI) [predominantly as the Z-isomer which upon standing in solution (CCl_4, $CHCl_3$) was transformed into the E-isomer after several hours] and 39% of (XXVII). Z-(XXVI): R_f 0.32. E-(XXVI): R_f 0.47, n_D^{22} 1.5398, M^+ 278. PMR spectrum: 1.6-1.0 m [5H, $(CH_2)_2CH$], 2.07 m (2H, CH_2), 2.32 s (3H, CH_3), 3.08 d.d (1H, CHO, J_1 = 10, J_2 = 11.5), 3.34 m (1H, CHO), 3.71 s (3H, CH_3), 3.82 m (2H, OCH_2), 6.70 s (2H, =CH), 7.12 m (4H, H_{arom}). (XXVII): R_f 0.41, n_D^{22} 1.5445, M^+ 280. PMR spectrum: 1.28 d (3H, CH_3, J = 7), 1.5-1.95 m [5H, $CH(CH_2)_2$], 2.34 s (3H, CH_3), 3.13 d.d (1H, CHO, J_1 = 8.5, J_2 = 3), 3.33 m (3H, SCH, CHOMe, OCH), 3.52 s (3H, OCH_3), 3.84 br. d.t (1H, CHO, J_1 = 11.5, J_2 = 8.5), 4.04 ddd (1H, CHO, J_1 = 11.5, J_2 = 2, J_3 = 1.75), 7.23 m (4H, H_{arom}). ^{13}C NMR spectrum: 14.97 (CH_3), 21.167 ($CH_3C_6H_4$), 25.372 and 26.860 [$(CH_2)_2$], 39.509 (CH_{cycl}), 46.279 (SCH), 61.898 (OCH_3), 68.299 and 70.496 (two OCH_2 groups), 84.732 (OCH), 129.830, 132.290, 137.109 (C_{arom}).

LITERATURE CITED

1. K. Toyoshima, T. Okuyama, and T. Fueno, J. Org. Chem., 43, 2789 (1978).
2. M. A. Ibragimov, M. I. Lazareva, and W. A. Smit, Synthesis (1985), p. 880.
3. R. P. Alexander and I. Paterson, Tetrahedron Lett., 24, 5911 (1983).
4. V. A. Smit and I. P. Smolyakova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 485 (1985).
5. I. P. Smolyakova, V. A. Smit, and A. I. Lutsenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 119 (1987).
6. I. P. Smolyakova and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 198 (1988).
7. S. Hoff, L. Brandsma, and J. F. Arens, Recl. Trav. Chim. Pays-Bas., 87, 916 (1968).