ALKYLATION OF SILYL ETHERS OF ENOLS BY EPISULFONIUM SALTS AND β-HALOALKYL ARYL SULFIDES AS A METHOD FOR THE INTRODUCTION OF THE β-ARYLTHIOALKYL GROUP INTO CARBONYL COMPOUNDS

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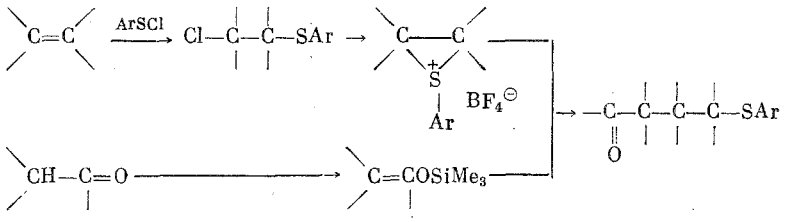
The reaction of the silyl ethers of enols with various electrophiles has been the subject of intensive recent study. Special interest is found in reagents which provide for the introduction of an alkyl residue with functional groups. Such electrophiles as acetals, ketals, carbonyl compounds, α-chlorothioethers, and α-chloroethers are commonly used for this purpose [1]. Among the possible electrophiles, β-haloalkyl aryl sulfides have attracted our attention because 1) they may be readily obtained from any alkene or arylsulfenyl halide [2], 2) they are converted by the action of Lewis acids into episulfonium (ES) salts or ES-like intermediates which are capable of alkylating active π-donor aromatic compounds [3], and, 3) the alkylation of silyl ethers of enols by these reagents holds interest for the synthesis of complex polyfunctional molecules from simple carbonyl compound and alkene precursors [4] (Scheme 1). The transformation shown in Scheme 1 implies that the opening of the ES ring by the action of the nucleophile, namely the trimethylsilyl ether of an enol (TMSE), occurs as an attack of a π-donor at the ES carbon atoms. However, the feasibility of such a reaction is not self-evident, since the literature also indicates the process of an alternative process involving the attack of the nucleophile at the ES sulfur atom. Thus, while the major process in the reactions of ES with ArH π-donors is β-arylthioalkylation (C-attack), the formation of significant amounts of diaryl sulfides (as the result of S-attack) is also found (Scheme 2) [3].

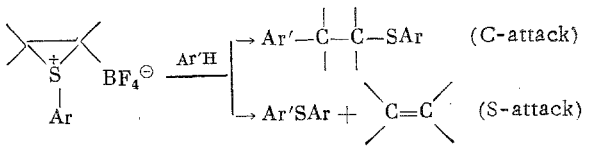
The transfer of the SAr group in the reaction of β-chloroalkyl aryl sulfides with a number of alkenes apparently also takes place by S-attack [5]. Hence, the first goal of the present study was clarification of the possibility of carrying out the alkylation of TMSE by ES salts.

As a model, the reaction of the TSME of cyclohexanone (I) with a number of β-haloalkyl aryl sulfides (IIa-c) which are readily obtained by the Ad_E reaction of alkenes with ArSCl [2] was studied as a model. The reaction of (I) and (II) proceeds readily under ordinary conditions for electrophilic addition to TMSE, i.e., in CH_2Cl_2 in the presence of $TiCl_4$

Scheme 1



Scheme 2



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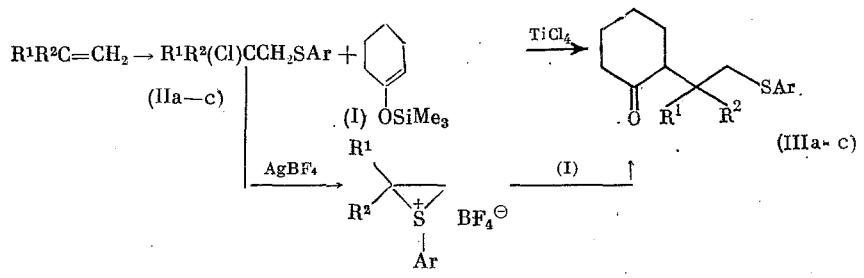
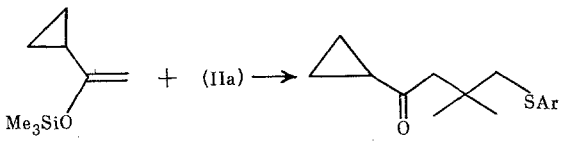
Scheme 3



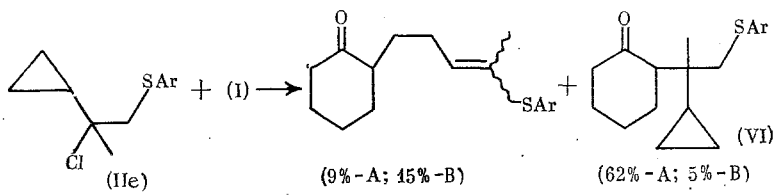
$R^1 = R^2 = Me$; $Ar = 4\text{-}ClC_6H_4$ (IIa); (IIIa) 73%—A, 54%—B; $R^1 = Me$; $R^2 = H$; $Ar = 2,4,6\text{-}Me_3C_6H_2$ (IIb; (IIIb); 40%—B; $R^1 = Ph$; $R^2 = H$; $Ar = 4\text{-}MeC_6H_4$ (IIc) (IIIc) 90%—A, B.

Scheme 4



(IV) - 65%

Scheme 5



(9% - A; 15% - B) (62% - A; 5% - B)

(method A). The reaction may also be carried out by the prior generation of ES by a previously described method [6] with subsequent reaction with TMSE (method B). In both variants, the reaction proceeds unequivocally and the major product is the corresponding β-arylthioalkyl derivative of cyclohexanone (IIIa-c). We should also stress the high regioselectivity giving exclusive formation of the Markovnikov adducts (ArS electrophile) (the 2H signal of the CH_2SAr fragment at 3 ppm is found in the PMR spectrum of all the adducts).

Analogously, the result of the reaction of (IIa) with the TMSE of methyl cyclopropyl ketone is the formation of [2,2-dimethyl-3-(4-chlorophenylthio)]propyl cyclopropyl ketone (IV).

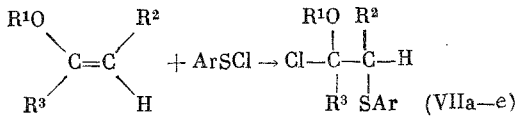
Comparison of alkylation methods A and B shows that method A is more suitable for preparative work but its applicability is limited to substrates containing a sufficiently labile halogen atom such as (IIa) and (IIc). In principle, method B is more general and suitable in all cases when the corresponding ES salt is obtained from β-haloalkyl aryl sulfides or directly from alkenes. In particular, method B was used to alkylate α-trimethylsiloxystyrene employing the ES derivative of ethylene (IId).

$$\underset{\text{(IId)}}{BrCH_2CH_2SAr} + PhC(OSiMe_3)=CH_2 \xrightarrow{AgBF_4} \underset{\text{(IIId)}}{ArSCH_2CH_2CH_2COPh} \quad (20\%)$$

Some specific advantages of method A were found in the reaction of (2-chloro-2-cyclopropyl)propyl 4-chlorophenyl sulfide (IIe) with (I). Thus, carrying out the reaction with previously generated ES (method B) gave products (V) and (VI) in low yields.* On the other hand, the use of method A markedly increased the total yield and the major product is 2-[1-methyl-1-cyclopropyl-2-(4-chlorophenylthio)]ethylcyclohexanone (VI) (see Scheme 5).

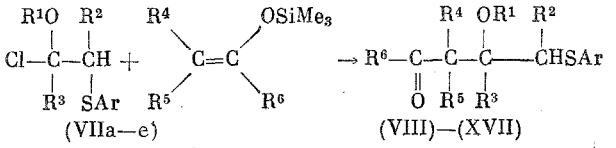
*Apparently, the major cause of the complications in this case is the capacity of the generated ES to undergo carbonium ion rearrangements (see work on the rearrangements of substrates such as (IIe) [7]).

Scheme 6



$R^1 = Bu$; $R^2 = R^3 = H$ (VIIa); $R^1 = Et$; $R^2 = H$; $R^3 = Me$ (VIIb); $R^1 = R^2 = Me$; $R^3 = H$ (VIIc); $R^1 = R^2 = -(CH_2)_3-$; $R^3 = H$ (VIId); $R^1 = R^2 = -(CH_2)_2-$; $R^3 = Me$ (VIIe)

Scheme 7

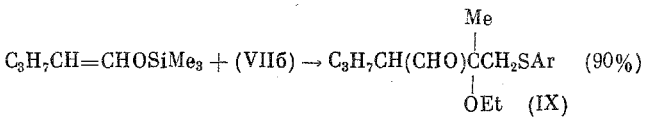


Scheme 8

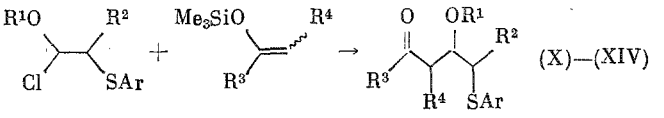
aldehyde – aldehyde

$$C_3H_7CH{=}CHOSiMe_3 + (VIIa) \rightarrow \underset{(VIII)}{C_3H_7CH(CHO)CH(OBu)CH_2SAr} \quad (95\%)$$

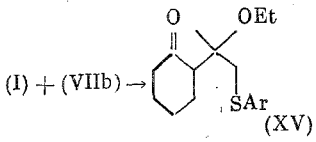
aldehyde – ketone

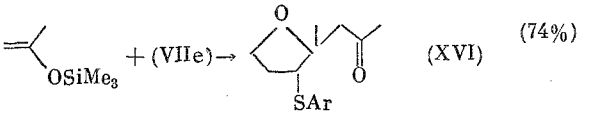


ketone – aldehyde (Table 1)



ketone – ketone





The use of method A for the reaction of β-chloro-β-alkoxyalkyl aryl sulfides (VIIa-e) which are the unstable adducts of vinyl ethers with ArSCl is especially successful [8]. The result of the reaction of (VIIa-e) with various TMSE is the formation of aldol products, in accord with general scheme 7.

The nature of the reagents in this reaction may be varied in a rather broad range, which permits carrying out all possible variants of selective cross-aldol condensation with TMSE as the methylene component and adduct (VII) as the carbonyl component.

The TMSE of α,β-unsaturated carbonyl compounds also react. Thus, the TMSE of crotonaldehyde with (VIIa) yields the product of the 1,4-addition, 5-butoxy-6-(4-chlorophenylthio)-hex-2-en-1-al (XVII)

$$(VIIa) + CH_2{=}CHCH{=}CHOSiMe_3 \rightarrow (XVII) \quad (60\%)$$

The stereochemistry of the opening of the ES derivatives in the alkylation of TMSE was studied for salts (IIf) and (IIg) [9] obtained, respectively, from cis- and trans-butene with 2-trimethylsiloxypropene. In both cases, the major reaction product is 4-methyl-5-(chlorophenylthio)hexan-2-one (XVIII). The adduct (XVIIIa) obtained from (IIf) is different from (XVIIIb) obtained from (IIg) as indicated by gas–liquid chromatography and PMR spectroscopy. The 250-MHz PMR spectra confirm the existence of two separate adducts and permit the assign-

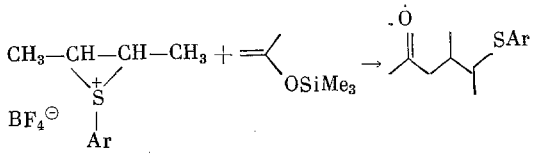
TABLE 1. Products of the Ketone–Aldehyde Cross-Aldol Condensation

Compound	R^1	R^2	R^3	R^4	Yield, %
(X)	Bu	H	$-(CH_2)_3-$		89
(XI)	Bu	H	Ph	H	64
(XII)	Me	Me	Ph	H	98
(XIII)	$-(CH_2)_3-$		Ph	H	63
(XIV)	$-(CH_2)_3-$		Me	H	58

TABLE 2. PMR Spectral Data for (VIIa-e) with the General Formula $(R^1O)CR^3ClCHR^2SAr$

Compound	R^1O	R^2	R^3	CH_nS	CH_nO	ArS
(VIIa)	0,87m(3H) 1,47m(4H) 3,76m(2H)	–	–	3,4t(2H)	5,5m(1H)	7,6s(4H)
(VIIb)	1,3t (3H) 3,5q (2H)	–	1,8s (3H)	3,53m(2H)		7,2s(4H)
(VIIc)	3,43ds (3H)	1,4ds (3H)	–	3.31m (1H)	5,24m(1H)	7,26s (4H)
(VIId)	1,57; 3,7m(6H)	–	–	3,45m(1H)	6,02m(1H)	7,26m(4H)
(VIIe)	4,1m; 2,5m(4H)	–	1,9s (3H)	4,1m(1H)		7,27m(4H)

ment of the threo configuration to (XVIIIa) and the erythro configuration to (XVIIIb) (J_{AB} = = 4.75 and 3 Hz, respectively)



cis-(IIf), trans-(IIg) threo-(XVIIIa), erythro-(XVIIIb)

The opening of (IIf) and (IIg) by the action of n-donors such as F^-, OH^-, and AcO^- proceeds stereospecifically [9]. The present results unequivocally indicate that the same stereospecificity is found for the opening of ES species by the action of significantly less weak nucleophiles, namely, π-donors. Hence, the opening of ES derivatives in the present reaction, in which they act as carbonium electrophiles, proceeds by an S_N2 mechanism without the formation of an open cationoid intermediate.

The stereospecificity noted for the formation of adducts (XVIIIa) and (XVIIIb) is a unique feature of the present reaction and we are unaware of other examples of the stereoselective introduction of a 3-substituted 2-butyl residue by the Ad_E process. Another interesting example of the stereospecificity of the β-arylthioalkylation of TMSE is the formation of (XIV) (see Table 1). ^1H and ^{13}C NMR spectroscopy indicates trans configuration of the ring substituents.

These results indicate that the reaction of TMSE with ES or β-haloalkyl aryl sulfides permits for variation in the nature of both reagents in a rather broad range and, thus, may be considered a general method for the β-arylthioalkylation of carbonyl compounds (see Scheme 1). This reaction considerably expands the scope of the preparative applicability of Ad_E reactions of TMSE and may serve as the basis for the synthesis of various complex structures.

EXPERIMENTAL

The gas–liquid chromatographic analysis was carried out on a 1 m × 4 mm column packed with 5% XE-60 on an LKhM-8MD chromatograph with a flame ionization detector. The mass

TABLE 3. Mass Spectral Data and Elemental Analyses of (III)-(XXII)

Compound	Chemical formula	m/z	Found, %		Calculated, %	
			C	H	C	H
(IIIa)	$C_{16}H_{21}ClOS$	296	64,59	7,04	64,74	7,13
(IIIb)	$C_{18}H_{26}OS$	290				
(IIIc)	$C_{21}H_{24}OS$	324	77,74	7,47	77,73	7,45
(IIId)	$C_{17}H_{18}OS$	270				
(IV)	$C_{15}H_{19}ClOS$	282	63,53	6,75	63,70	6,77
(V)	$C_{18}H_{23}ClOS$	322	66,77	7,26	66,96	7,18
(VI)	$C_{18}H_{23}ClOS$	322	67,52	7,55	66,96	7,18
(VIII)	$C_{17}H_{25}ClO_2S$	328	62,74	8,28	62,08	7,66
(XIX)	$C_{17}H_{27}ClO_2S$	330	62,68	8,24	61,87	8,22
(IX)	$C_{16}H_{23}ClO_2S$	314				
(XX)	$C_{18}H_{25}ClO_2S$	316	60,47	7,86	60,64	7,95
(X)	$C_{18}H_{25}ClO_2S$	340				
(XXI)	$C_{14}H_{15}ClOS$	266				
(XI)	$C_{20}H_{23}ClO_2S$	362	65,93	6,96	66,19	6,39
(XII)	$C_{18}H_{19}ClO_2S$	334				
(XIII)	$C_{19}H_{19}ClO_2S$	346	65,48	5,72	65,79	5,52
(XIV)	$C_{14}H_{17}ClO_2S$	284	58,43	6,12	59,04	6,02
(XV)	$C_{17}H_{23}ClO_2S$	326				
(XXII)	$C_{17}H_{25}ClO_2S$	328				
(XVI)	$C_{14}H_{17}ClO_2S$	284	58,43	6,12	59,04	6,02
(XVII)	$C_{16}H_{21}ClO_2S$	312				
(XXIII)	$C_{16}H_{25}ClO_2S$	316	59,91	7,93	60,64	7,95
(XVIIIa)	$C_{13}H_{17}ClOS$	256	60,65	6,49	60,80	6,67
(XVIIIb)		256	60,84	6,48		

spectra were taken on a Varian CH-6 mass spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz and a Bruker WM-250 spectrometer at 250 MHz. The chemical shifts are given on the δ scale relative to TMS as internal standard. The coupling constants are given in Hz. In all cases except for those indicated, the solvent was CCl_4 and the frequency was 60 MHz.

Products (IIIb), (IIIc), (VI), (VIII), (IX), (X), and (XV) are a mixture of erythro and threo isomers. The PMR data are given for the mixtures. The starting β-haloalkyl aryl sulfides were prepared from ethylene, propylene, isobutylene, styrene [6], and 1-methyl-1-cyclopropylethylene [7] according to published methods. The ES salts were prepared according to our previous method [6] using a solution of $AgBF_4$ in dichloroethane.

The adducts of ArSCl with the vinyl ethers were prepared in CH_2Cl_2 at −60°C by analogy with the procedure of Toyoshima et al. [8]. The adducts of p-ClC_6H_4SCl butyl vinyl ether (VIIa), ethyl isopropenyl ether (VIIb), methyl propenyl ether (VIIc), 2,3-dihydro-4H-pyran (VIId), and 4,5-dihydrosylvan (VIIe) were characterized by their PMR spectra and used without separation (Table 2).

The enol trimethylsilyl ethers were obtained from cyclohexanone, methyl cyclopropyl ketone, acetophenone, pentanal, acetone, and crotonaldehyde according to House et al. [10] and their physical constants were in accord with literature values.

Reactions of β-Haloalkyl Aryl Sulfides and ES Salts with TMSE. Method A. A solution of $TiCl_4$ in CH_2Cl_2 was added to a mixture of 2 mmoles (Ia) and 4 mmoles (I) at −30°C. After 1 h, the reaction mixture was warmed to 20°C and aq. $NaHCO_3$ was added. The reaction mixture was extracted with $CHCl_3$, dried over Na_2SO_4, and separated by thin-layer chromatography to yield 0.43 g (73%) (IIIa).

2-[1,1-Dimethyl-2-(4-chlorophenylthio)]ethylcyclohexanene (IIIa) was obtained as a yellow oil. PMR spectrum: 0.98 s (3H), 1.08 s (3H), 1.3-2.3 m (9H), 3.1 q (2H, J_{AB} = 12), 7.18 s (4H). The mass spectral and elemental analysis data for this compound are given in Table 3.

Method B. A solution of ES salt generated from 2 mmoles (IIa) and $AgBF_4$ [6] was added to 4 mmoles (I) in 5 ml CH_2Cl_2 at 20°C. After 1 h, the mixture was worked up as in method A to yield 54% (IIIa). The following products were obtained by analogy (the method of preparation and yield are given in parentheses); the analytical data are given in Table 3.

2-[1-Methyl-2(2,4,6-trimethylphenylthio)]ethylcyclohexanone (IIIb) (A 41%, B 9%). PMR spectrum: 1.16 d (3H, J = 7), 1.4-1.9 m (10H), 2.2 s (3H), 2.47 s (3H), 2.8 m (2H), 6.68 s (2H).

2-[1-Phenyl-2-(4-methylphenylthio)]ethylcyclohexanone (IIIc) (A 92%, B 90%). PMR spectrum: 1.4-1.9 m (9H), 2.23 s (3H), 3.3 m (3H), 7.15 m (9H), mp 86-88°C (hexane), the gas-liquid chromatographic analysis indicates that the product consists of a 1:1 mixture of isomers.

3-(4-Methylphenylthio)propyl Phenyl Ketone (IIId) (B 20%). PMR spectrum: 1.9 m (2H), 2.4 s (3H), 2.5-3.5 m (4H), 7.1 m (4H), 7.4 m (3H), 7.9 m (2H).

2,2-Dimethyl-3-(4-chlorophenylthio)propyl Cyclopropyl Ketone (IV). (A 65%). PMR spectrum: 0.78 s (4H), 1.06 s (6H), 1.8 m (1H), 2.58 s (2H, CH_2CO), 3.02 s (2H, CH_2S), 7.2 s (4H).

2-[4-Methyl-5-(4-chlorophenylthio)]pent-3-enylcyclohexanone (V) (A 9%, B 15%). PMR spectrum: 1.4-2.3 m (16H), 3.38 s (2H), 5.1 m (1H), 7.18 s (4H).

2-[1-Methyl-1-cyclopropyl-2-(4-chlorophenylthio)]ethylcyclohexanone (VI) (A 62%, B 5%). PMR spectrum ($CDCl_3$, 250 MHz): 0.25 m (4H, $\overline{CH_2CH_2CH}$), 0.62 and 0.71 s (3H), 0.88 m (1H, $\overline{CH_2CH_2CH}$), 1.5-2.5 m (8H), 2.61 and 2.73 d.d (1H, CHCO), 3.28 and 3.34 q (2H, CH_2S, J = 12), 7.22 q (4H, J_{AB} = 8). The isomer ratio was 1.6:1 as indicated by gas-liquid chromatography.

4-Methyl-5-(4-chlorophenylthio)hexan-2-one (XVIII). Threo-(XVIII), (B 55%). PMR spectrum: ($CDCl_3$, 250 MHz): 1.0 d (3H, J = 2.5), 1.21 d (3H, J = 7.5), 2.13 s (3H), 2.3 m (1H), 2.37 q (1H, J_1 = 8, J_2 = 16.5), 2.64 q (1H, J_1 = 4.5, J_2 = 16.5), 3.2 d.q (1H, J_1 = 7, J_2 = = 4.75), 7.29 q (4H, J_{AB} = 7). Irradiation at δ 1.21 gave a doublet at δ 3.2 with J = 4.75 while irradiation at δ 1.0 gave a multiplet at δ 2.3 with J_1 = 4.75, J_2 = 5, J_3 = 16.5, J_{threo} = 4.75.

Erythro-(XVIII) (B 71%). PMR spectrum ($CDCl_3$, 250 MHz): 0.96 d (3H, J = 7), 1.26 d (3H, J = 7), 2.09 s (3H), 2.32 m (2H), 2.8 q (1H, J_{AB} = 8), 3.29 d.q (1H, J_1 = 3, J_2 = 7), 7.27 q (4H, J_{AB} = 9). Irradiation at δ 0.96 gave 2.32 d.q with J_1 = 3 and J_2 = 8, while irradiation at δ 1.2 gave δ 3.29 d with J = 3, $J_{erythro}$ = 3.

The reaction of adducts (VIIa-e) with TMSE was carried out using method A at from −60° to −75°C for 1 h. The reaction mixture was poured into aq. $NaHCO_3$ at 0°C and then treated as described above.

2-Propyl-3-butoxy-4-(4-chlorophenylthio)butanal (VIII), 95%. PMR spectrum ($CDCl_3$, 250 MHz): 0.87 t (3H), 0.9 t (3H), 1.4 m (8H), 2.63 m (1H, CHCHO), 3.07 m (2H, SCH_2), 3.35 and 3.5 m (2H, CH_2O), 3.65 and 3.75 q (1H, CHO), 7.25 m (4H), 9.65 and 9.73 d (1H, HC=O). The isomer ratio was 1:1.

The reduction of (VIII) by $NaBH_4$ in ethanol gave 2-propyl-3-butoxy-4-(4-chlorophenylthio)butanol (XIX). PMR spectrum: 0.9 t (6H), 1.4-2.0 m (11H), 3.06 m (2HO), 3.5 m (3H), 7.17 s (4H).

2-Propyl-3-methyl-3-ethoxy-4-(4-chlorophenylthio)butanal (IX), 90%. PMR spectrum: 0.19-1.25 m (13H), 2.6 m (1H), 3.07 d (2H), 3.4 q (2H), 7.18 s (4H), 9.68 d.d (1H).

The reduction of (IX) by $NaBH_4$ in ethanol gave 2-propyl-3-ethoxy-3-methyl-4-(4-chlorophenylthio)butanol (XX). PMR spectrum: 0.9-1.5 m (13H), 3.0-3.8 m (8H), 7.22 s (4H).

2-[1-Butoxy-2-(4-chlorophenylthio)]ethylcyclohexanone (X), 89%. PMR spectrum: 0.9 m (3H), 1.3-2.6 m (13H), 3.05 d (2H, J = 6), 3.41 m (2H), 3.8 m (1H), 7.3 m (4H). Warming to 20°C and maintenance of the reaction mixture for 2 h with subsequent workup gave 2-(4-chlorophenylthio)ethylidenecyclohexanone (XXI), 90%. PMR spectrum: 1.67 m (4H), 2.3 m (4H), 3.42 d (2H, J = 8), 6.4 t.t (J_1 = 8, J_2 = 2, signals for the $(ArSCH_2-CH=C\langle$ fragment), 7.2 m (4H). Irradiation of the signal at δ 6.4 gives δ 3.42 s.

2-Butoxy-3-(4-chlorophenylthio)propyl Phenyl Ketone (XI), 64%. PMR spectrum ($CDCl_3$, 250 MHz): 0,85 t (3H), 1.35 m (4H), 3.12 d (2H, J = 6, CH_2O), 3.25 d.d (2H, CH_2S), 3.45 m (2H, CH_2O), 4.11 p (1H, CH-O), 7.22 m (4H), 7.43 m (3H), 7.9 m (2H).

2-Methoxy-3-(4-chlorophenylthio)butyl Phenyl Ketone (XII), 98%. PMR spectrum: 1.26 and 1.33 d (3H, CH_3), 3.25 m (6H), 3.95 m (1H, $CHOCH_3$), 7.2 m (4H), 7.45 m (3H), 7.91 m (2H).

2-Benzoylmethyl-3-(4-chlorophenylthio)oxirane (XIII), 63%. PMR spectrum: 1.5-2.2 m (6H), 2.9-3.9 m (6H), 7.3 m (4H), 7.45 m (3H), 7.85 m (2H).

trans-2-Acetylmethyl-3-(4-chlorophenylthio)oxirane (XIV), 58%. PMR spectrum ($CDCl_3$, 250 MHz): 1.68 m (4H), 2.16 s (3H), 2.57 d.d (1H, J_1 = 8.5, J_2 = 15.5), 2.82 d.q (1H, J_1 = = 4, J_2 = 10, J_3 = 12), 3.02 d.d (1H, J_1 = 5, J_2 = 15.5), 3.32 d.t (1H, J_1 = 5.5, J_2 = 11), 3.71 d.q (1H, J_1 = 5.5, J_2 = 8.5, J_3 = 10), 3.84 m (1H), 7.24 m (4H). Irradiation at the frequency of the signal at δ 3.84 gave δ 3.32 with the disappearance of the constant J = 11, irradiation at δ 3.32 alteration at δ 3.84, irradiation at δ 2.82 gave a change in the multiplet at δ 3.71, while irradiation at δ 2.57 gave δ 3.32 d with J = 5.5 and δ 3.71 m. The double resonance data permit the unequivocal assignment of signals to the following fragments: 1.68 (CH_2CH_2), 2.16 (CH_3CO), 2.57 and 3.02 (CH_2CO), 2.82 (CHS), 3.32 and 3.84 (CH_2-O), 3.71 (CH-O). The coupling constant of 10 Hz corresponds to trans configuration of the ArS and CH_3COCH_2 groups. ^{13}C NMR spectrum ($CDCl_3$, TMS): 26.97, 30.80, 31.62, 47.83, 49.09, 67.88, 78.03, 129.14, 131.73, 132.38, 133.88, 134.41, and 206.52.

2-[1-Methyl-1-ethoxy-2-(4-chlorophenylthio)]ethylcyclohexanone (XV), 75%. PMR spectrum ($CDCl_3$, 250 MHz): 1.11 m (3H), 1.29 and 1.4 s (3H), 1.5-2.5 m (8H), 2.78 and 2.92 m (1H), 3.1-3.5 m (4H), 7.25 m (4H).

The reduction of (XV) by $NaBH_4$ in ethanol yields 2-[1-methyl-1-ethoxy-2-(4-chlorophenylthio)]ethylcyclohexanol (XXII). PMR spectrum: 1.1 s (3H), 1.2 s (3H), 1.5-22 m (9H), 2.83 d (2U), 3.5 (2H), 7.2 s (4H).

2-Methyl-2-acetylmethyl-3-(4-chlorophenylthio)oxalane (XVI), 74%. PMR spectrum: 1.18 s (3H), 1.8-2.5 m (7H), 3.38 q (1H, J_{AB} = 7), 3.75 m (2H), 7.28 m (4H).

E-5-Butoxy-6-(4-chlorophenylthio)hex-2-en-1-al (XVII), 60%. PMR spectrum ($CDCl_3$, 250 MHz): 0.9 t (3H), 1.44 m (4H), 2.65 (2H), 2.88 q (1H), 3.1 q (1H), 3.46 m (3H), 6.13 d.d (1H, J_1 = 8, J_2 = 15), 6.8 d.t (1H, J_1 = 7.5, J_2 = 15), 7.25 m (4H), 9.5 d (1H, J = 8). Irradiation at δ 9.5 gave δ 6.13 d, J = 15 and irradiation at δ 6.13 gave δ 9.5 s and δ 6.8 t.

The reduction of (XVII) by $NaBH_4$ in ethanol gave 5-butoxy-6-(4-chlorophenylthio)hexanol (XXIII).

CONCLUSIONS

1. The reaction of β-haloalkyl aryl sulfides or episulfonium salts with the trimethylsilyl ethers of enols is a general method for the introduction of the β-arylthioalkyl group into carbonyl compounds.

2. The opening of the episulfonium ring in this reaction is regioselective and stereospecific.

3. The reaction permits the synthesis of polyfunctional compounds from simple alkene and carbonyl compound precursors.

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