ADDUCTS OF VINYL ETHERS WITH ARYLSULFENYL CHLORIDES AS REAGENTS FOR ELECTROPHILIC ALKYLATION OF VINYL ETHERS

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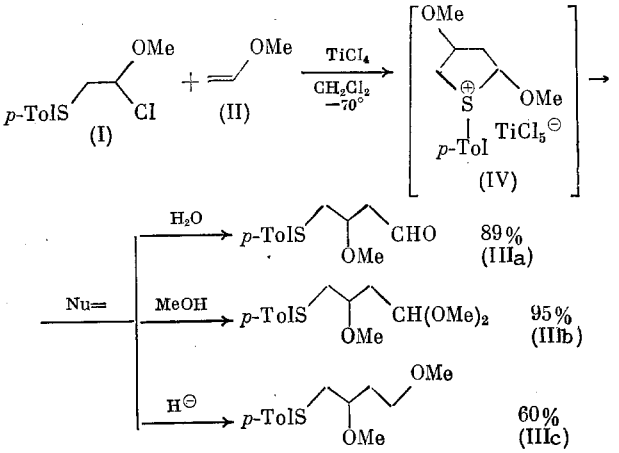
Addition of arylsulfenyl chlorides to vinyl ethers gives the corresponding β-arylthio-α-chloro-α-alkoxyethers in quantitative yield [1]. The use of these adducts as electrophilic alkylation agents has been reported in examples of reactions with π-donors such as trimethylsilyl enol ethers [2-5] or trimethylallylsilane [6, 7].

The aim of the present work is to examine the possibility of using vinyl ethers (VE)* as π-donors in this reaction.

It is found that β-p-tolylthio-α-chloroethyl methyl ether (I), which is the product of addition of p-tolylsulfenyl chloride (p-TolSCl) to methyl vinyl ether (II), in the presence of catalysts such as $TiCl_4$ and $SnCl_4$ reacts readily with (II) even at −70°C to form adducts of composition 1:1, the nature of which is determined by the type of nucleophile introduced at the stage when the reaction mixture is further treated. Thus 4-p-tolylthio-3-methoxybutan-1-al (IIIa) is formed if water is that nucleophile; treatment of the reaction complex with MeOH gives the corresponding acetal, 4-p-tolylthio-1,1,3-trimethoxybutane (IIIb), while with a hydride ion ($n\text{-}Bu_4NBH_4$) as donor, the reduction product, 4-p-tolylthio-1,3-dimethoxybutane (IIIc), is given. These findings made it possible to conclude that the initial product of the interaction of (I) with (II) is the five-membered 1-p-tolyl-2,4-dimethoxythiophanium salt (IV)



The formation of analogous salts with aryl substitutents instead of methoxy groups (for example, 1-p-tolyl-2,4-diarylthiophanium salts) has previously been observed for reactions of styrene + TolSCl adducts with styrenes [9]. These salts were isolated in the form of perchlorates. In our case salt (IV) turned out to be much less stable; we succeeded in obtaining it in a free state by precipitation with absolute ether from the reaction complex solution in CH_2Cl_2 at −60 to −70°C. Treatment with methanol of salt (IV) isolated in this way gave acetal (IIIb) in high yield. Salt (IV) decomposes completely at −20°C to form a colored tarry residue.

(I) reacts in a similar manner with other vinyl ethers — 2-methoxypropene (V), 2-methyl-1-methoxypropene (VI), and dihydropyran (VII) — to give 5-p-tolylthio-4-methoxypentan-2-one

*For previous communication, see [8].

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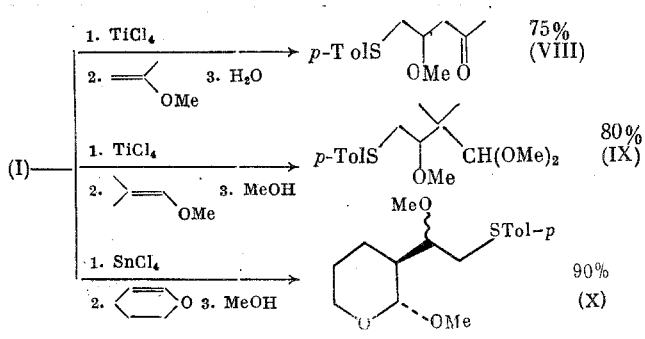
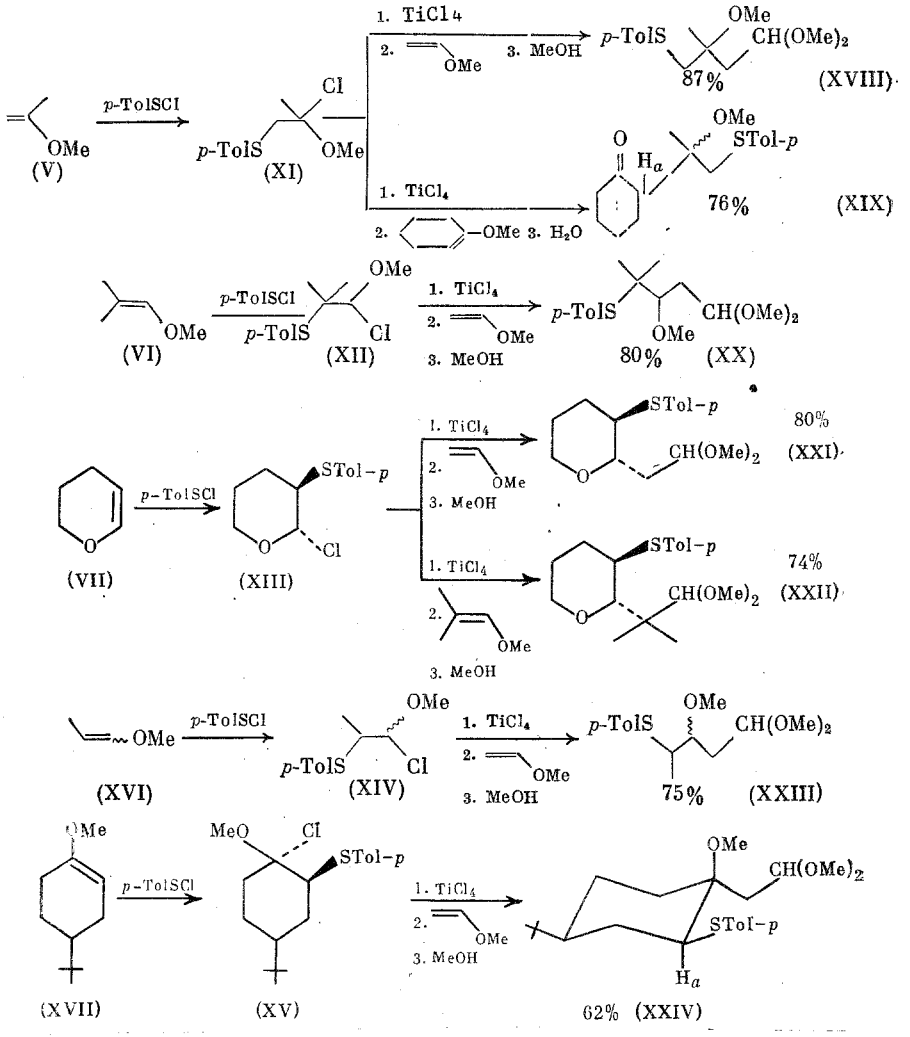
(VIII), 2,2-dimethyl-4-p-tolylthio-1,1,3-trimethoxybutane (IX), and 2-(1'-methoxy-2'-p-tolylthioethyl)-1-methoxyoxane (X) respectively:



It has been shown also that not only (I) but also other p-tolylthiochloro adducts (XI)-(XV),* obtained by addition of p-TolSCl to vinyl ethers (V), (VI), (VII), 1-methoxypropene (XVI), or 4-tert-butyl-1-methoxy-1-cyclohexene (XVII), respectively, under the same conditions are capable of alkylating vinyl ethers of different structure, giving adducts (XVIII)-(XXIII) in high yield:

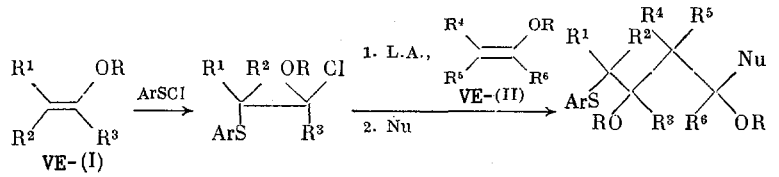


All reactions shown in the schemes were carried out with a stoichiometric ratio of reagents; the formation of oligomeric products was not observed. This is evidently due to the fact that in all cases the initial alkylation products are thiophanium salts (similar to

*In all cases the adducts were obtained directly in the reaction mixture and were used without further purification.

(VI)), which are incapable of reacting with a further molecule of vinyl ether under the conditions used. It is appropriate to note that in the majority of the previously known reactions for electrophilic alkylation of vinyl ethers [10], in particular the addition of acetals in the presence of Lewis acids [11], oligomerization is a common complication, and in order to suppress this process it is necessary to take 2-3 equivalents of the alkylation reagent.

The results shown on the schemes above can be reflected in a general form by the following scheme:



The information given shows that it is possible to have a wide variation for both the nature of the substituents R^1-R^3 in VE-(1) used to obtain the electrophilic alkylation agent and R^4-R^6 acting as π-donor on alkylation. It is possible from this to consider the new reaction as a fairly general method for coupling molecules of vinyl ethers according to the scheme $C_2 + C_2$ with introduction of an arylthio group and a nucleophilic residue on the ends of a four-link chain fragment. The chemical selectivity of this codimerization is predetermined by the order of mixing the reagents; all three consecutive reactions occur in the same flask. The polyfunctional compounds obtained as a result of this belong to a class of aldol-type adducts, with this method making it possible to obtain all four types of adducts from cross aldol condensation, corresponding to the combinations aldehyde—aldehyde (IIIa-c), (IX), (X), (XX)-(XXIII), aldehyde—ketone (VIII), ketone—aldehyde (XVIII), (XXIV), ketone—ketone (XIX). The difference in the method outlined from other contemporary varieties of controlled aldol condensation (see, for example, [12, 13]) lies in the fact that it permits the formation of adducts which are protected or modified on the carbonyl and which contain additionally a highly reactive γ-arylthio group [14]. Previous findings indicated the theoretical possibility of using the proposed intermediates of the condensation of vinyl ethers — thiophanium salts of type (IV) — for subsequent alkylation reactions using the most active π-donors (trimethylsilyl enol ethers or allylsilanes).*

The structures of the adducts obtained in the present work have been substantiated by a combination of analytical and spectral data (mass spectra, PMR spectra).

According to the data of ^1H and ^{13}C NMR, adducts (XXI), (XXII), and (XXIV) are stereochemically distinct and their structure corresponds to trans-addition of the electrophile (p-TolSCl) and nucleophile (VE-(II)) to the double bond of VE-(I).† The PMR spectra showed that (XXIII) is a mixture of two diastereomers in the ratio 3:1, which corresponds to the ratio of Z- and E-isomers in the initial (XVI). In the case of adducts (X) and (XIX), the formation of mixtures of two diastereomers in the approximate ratio 1:1 has also been recorded, which indicates the low stereoselectivity for formation of the aldol bond under the conditions used‡. In the PMR spectrum of (X) the presence of two doublets from the acetal group CH with J = 10 and 7.2 Hz leads to the assumption that this proton has the same configuration in both isomers and that (Xa) and (Xb) differ only in the orientation of the MeO group in the side chain.

It was found also that electrophiles such as β-arylthio-α-chloroalkyl ethers can alkylate ethoxyacetylene (XXV). Thus reaction of (I) with (XXV) leads, after treatment of the reaction mixture with methanol, to the formation of (XXVI), which is the product of the elimination of the β-MeO group.

*Isolation in a pure form of the corresponding adducts derived from alkylation of these nucleophiles with salt (IV) was not achieved because of the complexity of the product mixture formed (optimization of conditions was not carried out), but their formation was accurately recorded from the data of PMR and mass spectrometry.

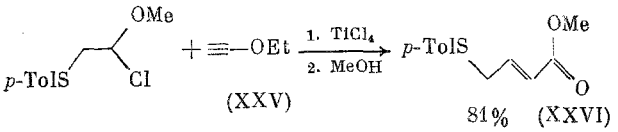
†Compare with the data in [15] on the stereoselectivity for reaction of (XIII) with trimethylsilyl acetone ether.

‡A similar lack of stereoselectivity was noted previously [3] for the reaction of (XI) with trimethylsilyl cyclohexanone ether. For the possibility of "directing" the stereochemistry of an aldol-type condensation, see review [16].

TABLE 1. Properties of Adducts Obtained

Compound	R_f^*	n_D^{20}	Found/calculated, %†			Empirical Formula	m/z
			C	H	S		
(IIIa)	0.22	1.5404	64.29 / 64.25	7.26 / 7.19	13.95 / 14.29	$C_{12}O_{16}O_2S$	224
(IIIb)	0.42	1.5191	61.63 / 62.19	8.12 / 8.20	11.50 / 11.86	$C_{14}H_{22}O_3S$	270
(IIIc)	0.45	1.5245	64.88 / 64.96	8.63 / 8.39		$C_{13}H_{20}O_2S$	240
(VIII)	0.27	1.5260	65.63 / 65.51	8.38 / 7.61		$C_{13}H_{18}O_2S$	238
(IX)	0.54	1.5228	64.85 / 64.39	8.75 / 8.78	10.54 / 10.74	$C_{16}H_{26}O_3S$	298
(X)	0.50	1.5295	64.92 / 64.83	8.44 / 8.16		$C_{16}H_{24}O_3S$	296
(XVIII)	0.39	1.5350	63.77 / 63.35	8.14 / 8.51		$C_{15}H_{24}O_3S$	284
(XIX)	0.41, 0.51	1.5522	69.18 / 69.82	8.06 / 8.27	10.86 / 10.96	$C_{17}H_{24}O_3S$	292
(XX)	0.60	1.5190	64.15 / 64.39	8.48 / 8.78	10.96 / 10.74	$C_{16}H_{26}O_3S$	298
(XXI)	0.44	1.5310	65.73 / 64.83	8.49 / 8.16		$C_{16}H_{24}O_3S$	296
(XXII)	0.59	1.5399	66.75 / 66.63	8.65 / 8.70	10.33 / 9.88	$C_{18}H_{28}O_3S$	324
(XXIII)	0.41	1.5208	63.61 / 63.35	8.53 / 8.51	11.48 / 11.27	$C_{15}H_{24}O_3S$	284
(XXIV)	0.60	1.5390			8.42 / 8.24	$C_{22}H_{36}O_3S$	380

*Ether–hexane (1:1) as eluant; Silufol.
†The small discrepancies in a number of cases are due to the instability of the adducts.



EXPERIMENTAL

NMR spectra were recorded on Bruker WM-250 (250 MHz for ^1H and 62.9 MHz for ^{13}C), Bruker AM-300 (300 MHz for ^1H), and Tesla BS-467 (60 MHz for ^1H) instruments, with $CDCl_3$ as solvent and TMS as internal standard. Assignment of the signals in the NMR spectra was made on the basis of the values of the chemical shifts and the recording of $\{H^1—H^1\}$ double resonance spectra (for ^1H) and off-resonance (for ^{13}C). Mass spectra were recorded on a Varian MAT CH-6 instrument. Preparative TLC was carried out on 250 × 300 mm plates with a mobile layer of SiO_2 of thickness 2 mm.

p-Tolylsulfenyl chloride was synthesized by chlorination of p-tolylmercaptan with SO_2Cl_2 in CCl_4 at −10°C according to the method in [17]. The data on R_f, n_D, the mass spectrum and elemental analysis for (IIIa) and all other adducts are given in Table 1. The yields of the adducts (given in the schemes) refer to chromatographically pure adducts, which are unique according to the PMR data (250 MHz). The instability of the adducts excluded the possibility of purifying them by distillation.

4-p-Tolylthio-3-methoxybutan-1-al (IIIa) (Method A). To a solution of 0.159 g (0.001 mole) of p-TolSCl in 10 ml of CH_2Cl_2 at −70°C in an atmosphere of Ar was added dropwise to a solution of 0.116 g (0.002 mole) of ether (II) in 1 ml of CH_2Cl_2 until the distinctive color of the sulfenyl chloride had disappeared. A solution of 0.22 ml (0.002 mole) of $TiCl_4$ in 1 ml of CH_2Cl_2 which had previously been cooled to −70°C was then added, and the mixture

was agitated under these conditions for 30 min, treated with an ice-cold solution of $NaHCO_3$, extracted with ether, and dried over Na_2SO_4. After removal of solvent the residue was separated on a SiO_2 plate with hexane-ether (1:1) as eluant. 200 mg (89%) of (IIIa) was obtained. PMR spectrum (250 MHz, δ, ppm): 2.32 s (3H, CH_3), 2.68 and 2.79 two d.d.d, AB part of ABXY spectrum (2H, J_1 = 16.5, J_2 = 8, J_3 = 5.5, J_4 = 2.5 Hz, CH_2CHO), 2.94 and 3.18 two d.d, A'B' part of A'B'X spectrum (2H, J_1 = 14, J_2 = 7.5, J_3 = 5.5 Hz, SCH_2), 3.41 s (3H, OCH_3), 3.84 m (1H, $C\underline{H}OCH_3$), 7.20 m (4H, aromat. H), 9.75 t (1H, J = 2.5 Hz, CHO).

4-p-Tolylthio-1,1,3-trimethoxybutane (IIIb) (Method B). In contrast to method A the reaction mixture was treated with a suspension of CH_3OH–K_2CO_3 cooled to –70°C. After separation on SiO_2 260 mg (95%) of (IIIb) was obtained. PMR spectrum (250 MHz, δ, ppm): 1.80 and 1.99 two d.d.d, AB part of ABXY spectrum (2H, J_1 = 13.5, J_2 = 9, J_3 = 7.5, J_4 = 4 Hz, CH_2), 2.31 s (3H, CH_3), 2.95 and 3.09 two d.d, A'B' part of A'B'X spectrum (2H, J_1 = 13, J_2 = 6.5, J_3 = 5 Hz, SCH_2), 3.30 s, 3.31 s. 3.34 s (9H, three OCH_3 groups), 3.44 m (1H, $C\underline{H}OCH_3$), 4.55 d.d (1H, J_1 = 7.5, J_2 = 4 Hz, $C\underline{H}(OCH_3)_2$, 7.18 m (4H, aromat. H).

4-p-Tolylthio-1,3-dimethoxybutane (IIIc). Compound (IIIc) was obtained according to method A, but the reaction mixture was treated with a solution of 0.51 g (0.002 mole) of $n\text{-}Bu_4NBH_4$ in 3 ml of CH_2Cl_2 (2.5 h at –70°C and 30 min at 0°C). Then the mixture was treated with an ice-cold solution of $NaHCO_3$, extracted with ether, and dried over Na_2SO_4. After removal of solvent the residue was purified by means of TLC, with ether–hexane (1:1) as eluant. 140 mg (60%) of (IIIc) was obtained. PMR spectrum (300 MHz, δ, ppm): 1.87 m (2H, CH_2), 2.30 s (3H, CH_3), 2.99 and 3.07 two d.d (2H, SCH_2), 3.30 s, 3.35 s (6H, two OCH_3 groups), 3.47 m (3H, $C\underline{H}OCH_3$, $C\underline{H}_2OCH_3$), 7.18 m (4H, aromat. H).

5-p-Tolylthio-4-methoxypentan-2-one (VIII). To a solution of 0.159 g (0.001 mole) of p-TolSCl in 10 ml of absolute CH_2Cl_2 at –70°C in an atmosphere of Ar was added a solution of 0.058 g (0.001 mole) of (II) in 1 ml of CH_2Cl_2 until the reaction mixture was decolorized. Solutions of 0.1 ml (0.0011 mole) of 2-methoxypropene in 0.5 ml of CH_2Cl_2 and 0.22 ml (0.002 mole) of $TiCl_4$ in 0.5 ml of CH_2Cl_2, previously cooled to –70°C, were then added successively. After 30 min the mxiture was treated with a mixture of acetone–water–$NaHCO_3$ which had been cooled to –70°C, and was extracted with ether and dried over Na_2SO_4. After removal of solvent the residue was chromatographed on a SiO_2 plate with ether–hexane (1:1) as eluant. 180 mg (75%) of (VIII) was obtained. PMR spectrum (250 MHz, δ, ppm): 2.13 s (3H, $COCH_3$), 2.33 s (3H, CH_3), 2.68 and 2.77 two d.d, AB part of ABX spectrum (2H, J_1 = 16, J_2 = 7.5, J_3 = 6 Hz, CH_2CO), 2.92 and 3.10 two d.d, A'B' part of A'B'X spectrum (2H, J_1 = 13, J_2 = 7.5, J_3 = 5.5 Hz, SCH_2), 3.31 s (3H, OCH_3), 3.81 m (1H, $C\underline{H}OCH_3$), 7.17 m (4H, aromat. H).

The following were obtained according to method B:

2,2-Dimethyl-4-p-tolylthio-1,1,3-trimethoxybutane (IX). PMR spectrum (250 MHz, δ, ppm): 0.86 s, 0.91 s (6H, $C(CH_3)_2$), 2.32 s (3H, CH_3), 2.87 and 3.15 two d.d, AB part of ABX spectrum (2H, J_1 = 2.75, J_2 = 8.75, J_3 = 10.75 Hz, CH_2S), 3.32 d.d (1H, J_1 = 2.75, J_2 = 8.75 Hz, $CHOCH_3$), 3.47 s, 3.49 s, 3.50 s (9H, three OCH_3 groups), 4.07 s (1H, $C\underline{H}(OCH_3)_2$), 7.17 m (4H, aromat. H).

2-(1'-Methoxy-2'-p-tolylthioethyl)-1-methoxyoxane (X). A mixture of two diastereomers in the ratio 1:1 obtained (determined from PMR spectrum). PMR spectrum (250 MHz, δ, ppm): 2.65 m (5H, CH_2CH_2CH in ring), 2.32 s (3H, CH_3), 3.05 m (2H, CH_2), 3.36 s, 3.38 s, 3.40 s, 3.45 s (6H, two OCH_3 groups), 3.56 and 3.66 two m (1H, $CHOCH_3$), 3.93 m (2H, CH_2O), 4.27 d (J = 7.25 Hz) and 4.44 d (J = 10 Hz) (1H, acetal CH), 7.19 m (4H, aromat. H). ^{13}C NMR spectrum (δ, ppm): 20.9 ($\underline{C}H_3$–C_6H_4), 20.7, 22.1, 23.8, 24.9 ($(CH_2)_2$), 36.2, 36.9 (CH_2S), 42.7, 43.7 (CH), 55.2, 55.6 (OCH_3), 58.3, 58.7 (OCH_3), 78.7, 80.1 ($\underline{C}HOCH_3$), 101.8, 103.6 (acetal CH).

3-Methyl-4-p-tolylthio-1,1,3-trimethoxybutane (XVIII). PMR spectrum (250 MHz, δ, ppm): 1.28 s (3H, CH_3), 1.97 m (2H, CH_2), 2.32 s (3H, CH_3), 3.12 s (2H, SCH_2), 3.22 s, 3.30 s, 3.32 s (9H, three OCH_3 groups, 4.57 m (1H, CH), 7.18 m (4H, aromat. H).

4-Methyl-4-p-tolylthio-1,1,3-trimethoxypentane (XX). PMR spectrum (250 MHz, δ, ppm): 1.16 s, 1.23 s (6H, $C(CH_3)_2$), 1.75 and 2.34 two m, AB part of ABXY spectrum (2H, CH_2), 2.35 s (3H, CH_3), 3.22 d.d (1H, J_1 = 13.5, J_2 = 2.75 Hz, $C\underline{H}OCH_3$), 3.37 s, 3.38 s, 3.44 s (9H, three OCH_3 groups), 4.60 d.d (1H, J_1 = 3, J_2 = 9 Hz, $C\underline{H}(OCH_3)_2$), 7.27 m (4H, aromat. H).

1-(2',2'-Dimethoxyethyl)-2-p-tolylthiooxane (XXI). PMR spectrum (250 MHz, δ, ppm); 1.6 m (4H, $(CH_2)_2$), 2.12 m and 2.52 d.d.d, AB part of ABXY spectrum (2H, J_1 = 15, J_2 = 9, J_3 = 2.5 Hz, $CH_2CH(OCH_3)_2$), 2.34 s (3H, CH_3), 2.78 d.t (1H, J_1 = 10.5, J_2 = 4 Hz, CHS), 3.33 s, 3.36 s (6H, $CH(OCH_3)_2$), 3.34 m (1H, CHO and 1H from CH_2O), 3.90 m (1H from CH_2O), 4.66 d.d (1H, J_1 = 9, J_2 = 2.5 Hz, $CH(COH_3)_2$), 7.21 m (4H, aromat. H). ^{13}C NMR spectrum (δ, ppm): 20.9 (CH_3–C_6H_4), 27.0, 31.9, 36.8 (three CH_2 groups), 49.8 (CHS), 52.1, 52.8 (two OCH_3 groups, 67.5 (CH_2O), 78.1 (CHO), 101.7 (acetal CH), 129.5, 129.8, 133.4, 137.2 (C_6H_4).

1-(1',1'-Dimethyl-2',2'-dimethoxyethyl)-2-p-tolylthiooxane (XXII). PMR spectrum (250 MHz, δ, ppm): 1.02 s, 1.12 s (6H, $C(CH_3)_2$), 1.59 m, 1.93 m (4H, $(CH_2)_2$), 2.32 s (3H, CH_3), 3.16 m (1H, CHS), 3.28 d (1H, J = 8 Hz, CHO), 3.38 s (1H from CH_2O), 3.50 s, 3.53 s (6H, $CH(OCH_3)_2$), 3.91 m (1H from CH_2O), 4.42 s (1H, $CH(OCH_3)_2$), 7.19 m (4H, aromat. H).

4-p-Tolylthio-1,1,3-trimethoxypentane (XXIII). A mixture of stereoisomers in the approximate ratio 3:1 according to the data from the PMR spectrum. PMR spectrum (250 MHz, δ, ppm): 1.25 d and 1.28 d (3H, J = 9 Hz, CH_3), 1.88 m, AB part of ABXY spectrum (2H, CH_2), 2.33 s and 2.43 s (3H, CH_3), 3.32 m (1H, CHS), 3.33 s, 3.42 s (9H, three OCH_3 groups), 4.54 d.d (1H, $CH(OCH_3)_2$), 7.22 m (4H, aromat. H).

4-tert-Butyl-1-(2',2'-dimethoxyethyl)-2-p-tolylthio-1-methoxycyclohexane (XXIV). PMR spectrum (250 MHz, δ, ppm): 0.82 s (9H, t-C_4H_9), 1.5 m (7H, $CH_2CH_2CHCH_2$), 2.01 and 2.38 two m (2H, $CH_2CH(OCH_3)_2$), 2.32 s (3H, CH_3), 3.07 d.d (1H, J_1 = 12, J_2 = 4.5 Hz, CH_aS), 3.22 s and 3.30 s (9H, three OCH_3 groups), 4.56 d.d (1H, J_1 = 6.5, J_2 = 4.5 Hz, $CH(OCH_3)_2$), 7.20 m (4H, aromat. H).

2-(1'-Methyl-2'-p-tolylthio-1'-methoxyethyl)cyclohexan-1-one (XIX). This was obtained in a similar manner to (VIII). The mixture of diastereomers in the ratio 1:1 was separated by TLC on SiO_2 with ether–hexane (2:3) as eluant. Diastereomer with R_f 0.51 (ether–hexane (1:1), Silufol) – PMR spectrum (250 MHz, δ, ppm): 1.28 s (3H, CH_3), 1.90 m (8H, $(CH_2)_4$), 2.29 s (3H, CH_3), 2.97 d.d (1H, J_1 = 12.5, J_2 = 4.5 Hz, $COCH_a$), 3.15 s (3H, OCH_3), 3.35 and 3.54 two d (2H, J = 12.5 Hz, SCH_2), 7.16 m (4H, aromat. H). Diastereomer with R_f 0.41 (ether–hexane (1:1), Silufol) – PMR spectrum (250 MHz, δ, ppm): 1.42 s (3H, CH_3), 1.85 m (8H, $(CH_2)_4$), 2.32 s (3H, CH_3), 2.85 d.d (1H, J_1 = 11.5, J_2 = 4.5 Hz, $COCH_a$), 3.21 s (3H, OCH_3), 3.12 and 3.49 two d (2H, J = 12.5 Hz, SCH_2), 7.20 m (4H, aromat. H).

Methyl trans-3-p-Tolylthio-2-propen-1-oate (XXVI). To a solution of 0.159 g (0.001 mole) of p-TolSCl in 10 ml of CH_2Cl_2 at –70°C in an atmosphere of Ar was added a solution of 0.058 g (0.001 mole) of (II) until the reaction mixture was decolorized. Solutions of 0.22 ml (0.002 mole) of $TiCl_4$ in 1 ml of CH_2Cl_2 and 0.08 g (0.001 mole) of ethoxyacetylene (XXV) in 1 ml of CH_2Cl_2, cooled to –70°C, were then added successively. After 1 h a suspension of methanol–K_2CO_3–$NaHCO_3$ cooled to –70°C was added to the reaction mixture, which was then heated over 20 min to –30°C; $NaHCO_3$ with ice was added to the solution with vigorous agitation. The mixture was extracted with ether and dried over $CaCl_2$. After removal of solvent the residue was separated on a SiO_2 plate with ether–hexane (1:1) as eluant. 200 mg (81%) of methyl ester (XXVI) was obtained. R_f 0.67 (ether–hexane (1:1), Silufol), m/z 222. PMR spectrum (60 MHz, δ, ppm): 2.27 s (3H, CH_3), 3.32 m (2H, SCH_2), 3.59 s (3H, $COOCH_3$), 5.63 d.t (1H, J_1 = 16, J_2 = 1.5 Hz, $=CHCOOCH_3$), 6.8 m (1H, CH=C).

CONCLUSIONS

A general preparative method for the chemically selective codimerization of vinyl ethers has been developed, the first stage of which is addition of arylsulfenyl chloride to one vinyl ether and the second is an Ad_E reaction between the adduct obtained and the other vinyl ether in the presence of a Lewis acid followed by treatment of the intermediate with some nucleophile.

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PRODUCTION OF METHOXYNITRONES AND STABLE NITROXYL RADICALS WITH gem-DIMETHOXY GROUPS ATTACHED TO THE α-CARBON ATOM BY THE OXIDATION OF ALDONITRONES IN METHANOL

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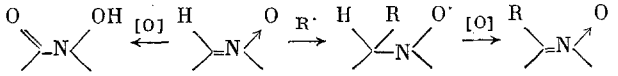
Cyclic and acyclic aldonitrones (AN) are oxidized by a variety of reagents to hydroxamic acids and their derivatives, or more extensively with cleavage of the C—N bond [1]. For example, $Pb(OAc)_4$ and MnO_2 in benzene oxidize 1-pyrroline 1-oxides to 1-acetoxy-2-pyrrolidones and 1-hydroxy-2-pyrrolidones, respectively, and oxidation with aqueous solutions of $NaIO_4$, $KMnO_4$, or NaOBr give the further oxidation products 1-hydroxy-2-pyrrolidones* [1, 2]. On the other hand, cyclic AN give spin adducts with short-lived free radicals, and are used extensively as spin traps [3]. The spin trap of the cyclic AN type most commonly used is 5,5-dimethyl-1-pyrroline 1-oxide (DMPO). Short-lived free radicals are frequently generated by redox reactions, commonly using $Pb(OAc)_4$ as the oxidant [4]. The resulting spin adducts are converted by oxidants to substituted nitrones, but this reaction is complicated by the oxidation of the AN to hydroxamic acids or their derivatives:



We have recently described the preparation of AN of the 3-imidazoline series (Ia-c) [5], which could be of interest as spin traps.

The aim of this investigation was to examine the behavior of imidazoline AN in comparison with DMPO in the presence of oxidants ($Pb(OAc)_4$, PbO_2, and MnO_2) in benzene and methanol.

As in the case of 1-pyrroline 1-oxides [2], reaction of the AN (Ia) with $Pb(OAc)_4$ in benzene gives a 90% yield of 3-acetoxy-1-nitroso-2,2,5,5-tetramethyl-4-oxoimidazolidi

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