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OXIDATION OF N-ALKYL-N′-TOSYLHYDRAZINES WITH $Hg(OAc)_2$. A NEW SYNTHESIS OF ETHERS

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Abstract—N-Alkyl-N′-tosylhydrazines with $Hg(OAc)_2$ in the presence of alcohols or phenol give high yields of corresponding ethers. Reactions in the presence of acetic acid are also examined.

Oxidation of N-alkyl-N′-tosylhydrazines with SeO_2[1] and Na_2O_2/H_2O_2[2], leading to sulphinic esters and hydroperoxides respectively, in high yield and under selective and mild conditions, has been reported in previous papers.

RESULTS AND DISCUSSION

In the presence of several nucleophilic agents, N-alkyl-N′-tosylhydrazines can easily be oxidized with $Hg(OAc)_2$, according to the following reaction scheme:

$$Ts{-}\underset{H}{N}{-}\underset{H}{N}{-}R + HOY \xrightarrow[\text{room temp}]{Hg(OAc)_2} R{-}O{-}Y + N_2$$

$Y = CH_3, CH_3CH_2, (CH_3)_2CH, C_6H_5, CH_3CO$

The starting materials are obtained by reducing the corresponding tosylhydrazones or tosylhydrazides, as described in detail in previous papers.[3]

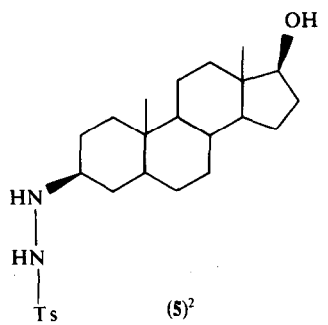
The reaction allows transformation of a carboxylic or carbonylic group into the corresponding $\rangle C{-}O{-}Y$ (dialkylethers, alkylphenylethers, alkylacetates) moiety. The results obtained from different substrates are reported in Table 1.

Pure samples of the above-mentioned compounds were obtained by column chromatography of the reaction mixtures. The products were identified by comparison with authentic samples and/or by physico-chemical analyses.

As can clearly be seen from Table 1, the yields decrease when passing from methanol to isopropanol. Moreover, yields decrease in the case of phenol and acetic acid, probably on account of minor nucleophilicity of the corresponding reagents.

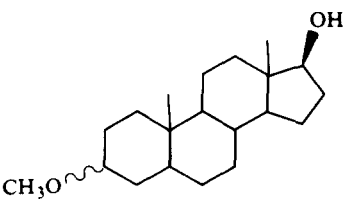
It may be interesting to note that this synthetic method enables good-yield conversion of carbonyl to alkoxy groups even in polyfunctional compounds containing an unprotected alcoholic group.

The reaction has already been successfully applied to tosylhydrazine **5** which had been obtained by reducing the tosylhydrazone of 17β-androstanol-3-one, according to the following scheme:

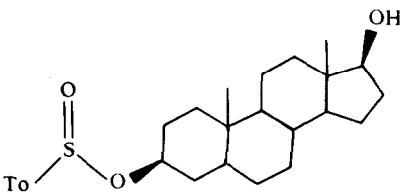


(5)[2]

MeOH
$Hg(OAc)_2$



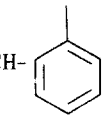
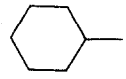
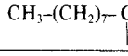
(5a) $3\alpha^{19}$ (10%) — (5a′) $3\beta^{19}$ (40%)



(5f), (25%)

To = Tolyl

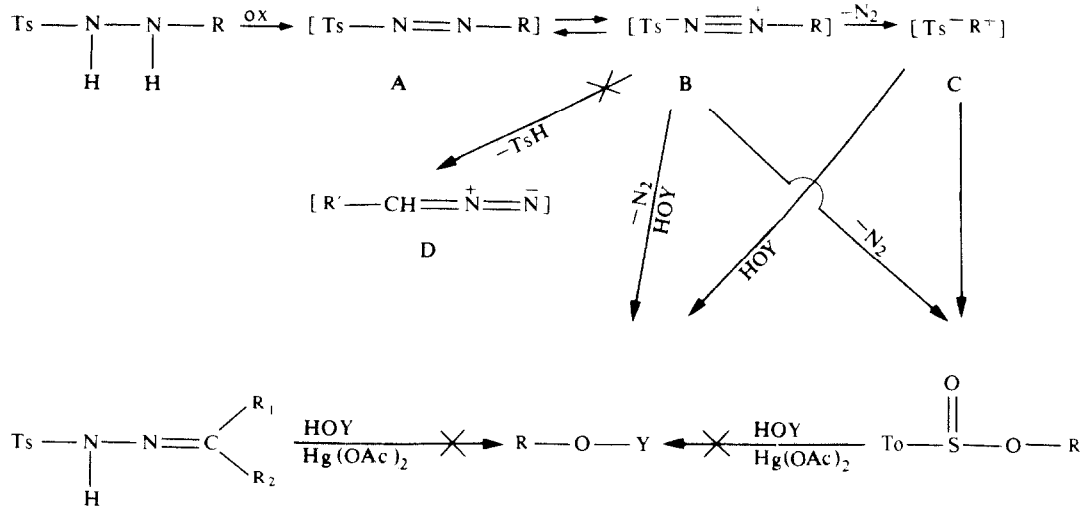
Table 1. Yields (%) obtained for ethers R–O–Y

R– \ Y–	CH_3–	C_2H_5–	$(CH_3)_2CH$–		CH_3–CO–
(1) CH_3–$(CH_2)_6$–	**(1a)**$^{4a,b}_{(71)}$	**(1b)**$^{5}_{(65)}$	**(1c)**$^{4b}_{(52)}$	**(1d)**$^{6}_{(22)}$	**(1e)**$^{7}_{(37)}$
(2) CH_3–$(CH_2)_{15}$–	**(2a)**$^{8}_{(74)}$	**(2b)**$^{9}_{(53)}$	**(2c)**$^{10}_{(51)}$	**(2d)**$^{11}_{(41)}$	**(2e)**$^{12}_{(37)}$
(3) 	**(3a)**$^{13}_{(53)}$	**(3b)**$^{14}_{(33)}$	**(3c)**$^{15}_{(29)}$	**(3d)**$^{16}_{(16)}$	**(3e)**$^{14}_{(31)}$
(4) CH_3–$(CH_2)_7$–$CH(CH_3)$– 	**(4a)**$_{(67)}$	**(4b)**$^{17}_{(51)}$	**(4c)**$_{(32)}$	**(4d)**$_{(25)}$	**(4e)**$^{18}_{(36)}$

[a]Yields of compounds **1a–e**, **2a–e** and **3a–e** are determined by GLC (external standard method). Yields of compounds **4a–e** are given for pure, isolated products.

Epimeric 3α-methoxyandrostan-17β-ol and 3β-methoxy-androstan-17β-ol,[19] were separated by preparative HPLC (see Experimental Section), and characterized by physico-chemical analyses (microanalysis, IR, ^{1}H-NMR). The configurational isomers were further characterized on the grounds of "chemical shift" and coupling constant (J) of the proton on carbon atom linked to the methoxy group (>CH–OCH$_3$), as similarly observed earlier for the corresponding N-alkyl, N'-tosylhydrazines.[2] ines.[2]

In all reactions described, variable yields of the corresponding sulphinic ester are obtainable as a side reaction product together with small amounts of transposition products. The hypothesized mechanism is analogous to the one previously proposed for oxidation with Na_2O_2/H_2O_2,[2] according to the following scheme:



The intermediate tosylazoalkane **A**, in equilibrium with ion pair **B**, rapidly decomposes releasing nitrogen and forming the corresponding ion pair **C**, which can then either interact with HO–Y to give the final product, or rearrange to the corresponding sulphinic ester. The Hg^{2+} ions, present in high excess in the reaction mixture, probably give rise to interaction with the Ts^- ion of solvated ion pair **B** or **C**, causing the ion pairs to loosen, thereby enabling alcohol or, more generally, the nucleophile to be incorporated. This mechanism explains partial retention of configuration in the oxidation of the tosylhydrazine of 17β-androstanol-3-one. It also accounts for the small quantities of transposition products, in the cases examined.

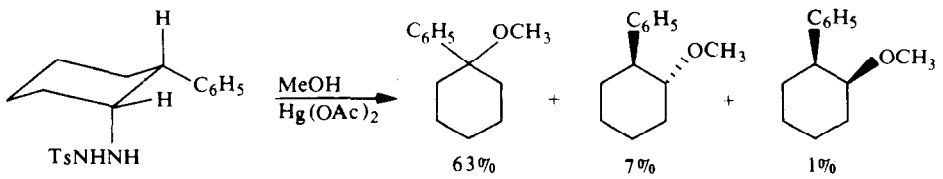
Further evidence that transposition occurs was shown by the following examples. In the particular case of N-heptyl-N'-tosylhydrazine oxidation, the transposition product, 2-methoxyheptane, was isolated from the reaction mixture, analyzed by GLC and compared with a specimen sample[20] (about 5% external standard method). A similar result was obtained for the oxidation of N-hexadecyl-N'-tosylhydrazine (isolation of about 6% of 2-methoxyhexadecane).

To reveal any transposition possibilities better, a substrate capable of forming a particularly stable carbocation during oxidation was chosen. More specifically, cis-N-(2-phenylcyclohexyl)-N'-tosylhydrazine **6**, obtained as the major product from the reduction of a mixture of E,Z-2-phenylcyclohexanone tosylhydrazone, was utilized. Cis-N-(2-phenylcyclohexyl)-N'-tosylhydrazine **6** was assigned its structure on the basis of ^{1}H-NMR spectra. More precisely, the assignment of the signals related to the proton >CHNHNHTs (3.35δ) and

that of the group $C_6H_5CH\langle$ (2.82δ, double triplet, J' = 12 Hz, J'' = J''' = 4 Hz) was confirmed by the ^{1}H-NMR spectrum of cis-N-(2-phenyl-1-deuterocyclohexyl), N'-tosylhydrazine **6'**. The signal is not, in fact, present in the lower fields of the latter's spectrum, whereas the double triplet at 2.82δ becomes a double doublet with the subsequent disappearance of one of the two small coupling constants (J''' = 4 Hz).

Tosylhydrazine **6** configuration and conformation were established on the basis of the coupling constant values: the signal at 3.35δ ($W_{1/2}$ = 7.5 Hz) shows no ax–ax couplings. It follows then that the tosylhydrazine group is in the axial position. The signal at 2.82δ shows a J = 12 Hz, typical of ax–ax coupling, together with small ax–eq coupling constants. It follows then that the C_6H_5 group is in the equatorial position.

Oxidation of tosylhydrazine **6** with $Hg(OAc)_2$/MeOH leads mainly to the formation of 1-phenyl-1-methoxycyclohexane (**6a''**)[21] as a result of transposition according to the following scheme:



6 **6a''**[21] **6a**[22] **6a'**[22]

Product identification and yields were ascertained by GLC-MS (capillary column, see Experimental) and matched with specimen samples.

In order to exclude diazocompound **D** as an intermediate, the reaction was studied using trans-N-(4-phenyl-1-deuterocyclohexyl)-N'-tosylhydrazine **7'** as the substrate. The latter's structure was clarified on the basis of the ^{1}H-NMR spectrum of the corresponding non-deuterated compound **7**. In this case, the reaction mixture was purified by silica gel filtration and analyzed by GLC-MS. The two ethers **7'a'** and **7'a''** could then be isolated and identified as the main products, corresponding alcohols as by-products (trans isomer[24] about 6% cis-isomer[24] about 0.5%). Corresponding acetates[25] appeared in trace quantities (about 1%).

Furthermore, no deuterium exchange was noticed in the ^{1}H-NMR spectrum of isolated ethers, hence we may exclude the formation of the diazocompound **D** as a reaction intermediate.

The formation of the ethers from corresponding sulphinic esters may be ruled out because a pure sample of sulphinic ester in the same conditions may be seen to be absolutely stable. Furthermore, the formation of the final product from a corresponding intermediate tosylhydrazone is also to be excluded since oxidation of the latter, by alternative methods, does not give significant amounts of ether.

It should be noted that, at least from a synthesis point of view, the same ethers can be obtained directly from tosylhydrazides or tosylhydrazones without having to isolate intermediate N-alkyl-N'-tosylhydrazines. In this case, tosylhydrazones or tosylhydrazides are reduced to the corresponding N-alkyl-N'-tosylhydrazines by B_2H_6 or $NaBH_4$. The reduction mixture is then treated with methanol and vacuum evaporated. The residue obtained may then be oxidized as previously reported.

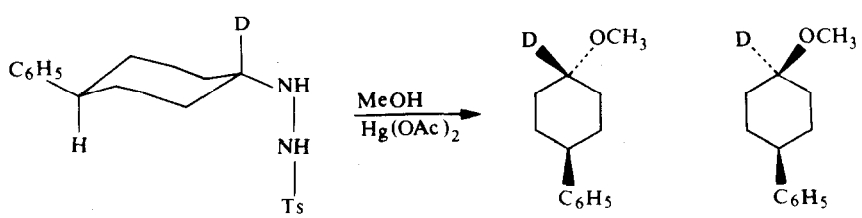
The above is a new method for the high yield synthesis of alkylethers, alkylphenylethers and alkylacetates under mild conditions and starting from aldehydes, ketones or carboxylic acids.

EXPERIMENTAL

Equipment. IR spectra were recorded as films or KBr pellets with a Perkin-Elmer Model 337. ^{1}H-NMR spectra were obtained with a Varian EM-390 spectrometer. Chemical shifts are expressed in values (ppm) relative to a Me_4Si internal standard. All m.p.s reported are uncorrected and were determined with Büchi apparatus. Analytical data (%C, H, N and S) were obtained from Mikroanalytisches Laboratorium, Dr F. Pascher, Bonn (Germany). Analytical liquid chromatography was performed on a Waters Associates ALC/GPG 202/R401 Model equipped with a 60000 M reciprocating pump and UV 440 and RI400 detectors. Preparative separations were performed on a Miniprep LC (2 cm i.d. column) or a Chromatospac Prep 10 chromatograph (4.0 cm i.d. column) both from Jobin-Yvon (Longjumeau, France) equipped with an RI detector. Vapor phase chromatography was performed using a Hewlett-Packard Model 7620A, equipped with a flame ionization detector. Mass spectra were recorded with a Hewlett-Packard HP5980A spectrometer equipped with a Data System 5870A.

N-Alkyl-N'-tosylhydrazines

N-Alkyl-N'-tosylhydrazines were prepared by reduction of the corresponding tosylhydrazones and N-acyl-N'-tosylhydrazides as previously reported.[3]



7' **7'a'**[23] **7'a''**[23]

N-Heptyl-N'-tosylhydrazine **1** was obtained by reduction with B_2H_6 of heptanal tosylhydrazone. A pure sample of **1** was isolated from the reduction mixture by recrystallization from CH_2Cl_2/hexane; m.p. 71–2° (dec); IR (Nujol): 3310–3230 (ν_{NH}); 1320, 1160 (ν_{SO_2}), 1600, 815 (p-C_6H_4) cm^{-1}. ^{1}H-NMR: ($CDCl_3$) δ, 7.60 (q, 4H, AA'BB', J_{AB} = 8 Hz, p-C_6H_4), 2.65 (t, 2H, J = 6 Hz, $-CH_2-N-N-$), 2.42 (s, 3H, CH_3-Ar), 1.28 (m, 10H, $-(CH_2)_5-$), 0.89 (t, 3H, $CH_3(CH_2)_n-$) ppm. Found: C, 58.97; H, 8.64; N, 9.93; S, 11.04. $C_{14}H_{24}N_2O_2S$ requires: C, 59.13; H, 8.51; N, 9.85; S, 11.25%.

N-(2-n-Decyl)-N'-tosylhydrazine **4** obtained by recrystallization of the crude product from the B_2H_6 reduction of 2-decanone tosylhydrazone; m.p. 76–7° (dec) from CH_2Cl_2/hexane; IR (Nujol): 3270, 3230 (ν_{NH}), 1320, 1155 (ν_{SO_2}), 1600, 815 (p-C_6H_4) cm^{-1}. ^{1}H-NMR: ($^2H_6$-DMSO) δ, 8.50 (bs, 1H, D_2O exchange, TsNH–NH–), 7.55 (q, 4H, AA'BB', J_{AB} = 8 Hz, p-C_6H_4), 4.10 (bs, 1H, D_2O exchange, TsNH–NH–), 2.60 (m, 1H, $-CH-N-N-$), 2.40 (s, 3H, CH_3-Ar), 1.40–1.05 (m, 14H, $-(CH_2)_7-$), 0.95–0.70 (d, 3H, J = 6 Hz, $CH_3-CH-N-N-$ and t, 3H, J = 6 Hz, $CH_3-(CH_2)_n-$) ppm. Found: C, 62.73; H, 9.21; N, 8.49; S, 9.57. $C_{17}H_{30}N_2O_2S$ requires C, 62.55; H, 9.26; N, 8.58; S, 9.80%.

Cis-N-(2-phenylcyclohexyl)-N'-tosylhydrazine **6** obtained by reduction of 2-phenylcyclohexanone tosylhydrazone[26,27] with $NaBH_4$ in MeOH/H_2O or with B_2H_6/THF[3] (at 0° for 1 h). The reaction mixture was analyzed by HPLC (Column: Hibar-Si60, 10 μ, 25 cm; eluent: n-hexane/ethyl acetate, 75/25, v/v; flow 2.0 ml/min; detector: UV 440, 254 nm). Capacity factor (K') for main reaction product = 1.7 (cis-N-(2-phenylcyclohexyl)-N'-tosylhydrazine). The product was purified by crystallization from MeOH/H_2O; m.p. 121–3° (dec); IR (Nujol): 3280–3240 (ν_{NH}), 1330, 1165 (ν_{SO_2}), 1600, 815, 750, 690 (p-C_6H_4 and $-C_6H_5$) cm^{-1}. ^{1}H-NMR: ($CDCl_3$)δ, 7.50–7.00 (m, 9H, p-C_6H_4 and $-C_6H_5$), 5.70 (bs, 1H, $-SO_2-NH-NH-$, D_2O exchange), 3.35 (m, 1H, $W_{1/2}$ = 7.5, $-CH-NH-NHTs$), 2.82 (dt, 1H, J' = 12 Hz, J'' = J''' = 4 Hz, $>CH-C_6H_5$), 2.36 (s, 3H, CH_3Ar), 2.30–1.10 (m, 8H, $-(CH_2)_4$) ppm. Found: C, 66.07; H, 7.11; N, 8.18. $C_{19}H_{24}N_2O_2S$ requires: C, 66.25; H, 7.02; N, 8.13%.

Cis-N(-2-phenyl-1-deuterocyclohexyl)-N'-tosylhydrazine **6'**. By reducing with $NaBD_4$ under conditions similar to those already described, the N-alkyl-N'-tosylhydrazine, deuterated at the carbon atom in the α position to the tosylhydrazine group, was obtained. ^{1}H-NMR: ($CDCl_3$), the signal at 3.35δ, showed by the spectrum of the non-deuterated compound **6**, is absent whereas the signal at 2.82δ is transformed into a double doublet (1H, J' = 12 Hz, J'' = 4 Hz). In all other respects the spectrum is similar to that of **6**.

Trans-N-(4-phenylcyclohexyl)-N'-tosylhydrazine **7** was obtained by reduction of 4-phenylcyclohexanone tosylhydrazone (m.p. 137°, MeOH/H_2O) with $NaBH_4$ in MeOH/H_2O or with B_2H_6 in THF at 0° for 2 h. The reaction mixture was analyzed by HPLC (Column: Hibar-Si60, 10 μ, 25 cm; eluent: hexane/ethyl acetate, 75/25, v/v; flow: 2.0 ml/min; detector UV 440, 254 nm). Capacity factor (K') for the main reaction product = 4.3 trans-N-(4-phenylcyclohexyl)-N'-tosylhydrazine; m.p. 127–8° (dec.); IR (Nujol): 3300–3100 (ν_{NH}), 1320–1170 (ν_{SO_2}), 1600, 810, 750, 690 (p-C_6H_4, and C_6H_5) cm^{-1}. ^{1}H-NMR: ($CDCl_3$) δ, 7.90–7.00 (m, 9H, p-C_6H_4, C_6H_5), 2.90–2.40 (m, 1H, $W_{1/2}$ = 21 Hz, $>CHNHNHTs$), 2.40 (s, 3H, CH_3-Ar), 2.50–2.20 (m, 1H, $W_{1/2}$ = 21 Hz, $C_6H_5-CH_{ax}-$), 2.10–1.00 (m, 8H, 2-$(CH_2)_2-$) ppm. Found: C, 66.09; H, 7.13; N, 8.07. $C_{19}H_{24}N_2SO_2$ requires: C, 66.25; H, 7.02; N, 8.13%.

Trans-N-(4-phenyl-1-deuterocyclohexyl)-N'-tosylhydrazine **7'** was obtained by reduction of 4-phenylcyclohexanone tosylhydrazone with $NaBD_4$ in similar conditions to those for compound **7**; deuteration takes place on carbon atom α to the tosylhydrazine group. No signal appears in the ^{1}H-NMR ($CDCl_3$) spectrum at 2.90–2.40δ and simplification occurs in the 2.10–1.60δ zone for methylenic protons; for all other aspects the spectrum is similar to the preceding one.

Oxidation of N-alkyl-N'-tosylhydrazines with $Hg(OAc)_2$ *in alcohols: general procedure*

The following procedure was employed to obtain the ethers **1a–c**, **2a–c**, **3a–c**, **4a–c**, **5a,a'**, **6a,a',a''**, **7a',a''**. N-alkyl-N'-tosylhydrazine **1** (3.00 mmol) was added in portions in about 30 min to a solution of $Hg(OAc)_2$ (3.83 g, 12 mmol) in the appropriate alcohol (methanol, ethanol, isopropanol) (50 ml) at room temperature and under magnetic stirring. After addition, gas (N_2) evolved rapidly, followed by formation of a solid white precipitate. The mixture was stirred for approx 15 h at room temperature, then filtered through silica gel. The filtrate was evaporated under reduced pressure and the oily residue for compounds **1a–c**, **2a–c**, **3a–c**, **4a–c**, analyzed by GLC (Column: 3 m × 2 mm SS, packed with 10% Carbowax 20M on 100–120 mesh Chromosorb G-HP or W-HP; injector temperature: 250°; detector: flame ionization, 250°; carrier: nitrogen at 20 ml/min; column temperature: 60°; programmed 4 min at 60°, then from 60° to 200° at 15°/min and held.

In the oxidation of compound **5**, the oily residue was analyzed by HPLC (Column: Hibar Si-60,10 μ, 25 cm; eluent: n-hexane/ethyl acetate, 60/40, v/v, flow: 2.0 ml/min; detector: RI). Capacity factors (K') for the main reaction products are: $K'_{5a'}$ = 1.20 (3α-methoxy-androstan-17β-ol), **5a'**[18], 10%; K'_{5a} = 1.40 (3β-methoxy-androstan-17β-ol), **5a'**[18], 40%; K'_{5f} = 2.00 (3β-p-toluensulphinyl-androstan-17β-ol), **5f**, 25%.

The reaction mixture obtained from compound **6** was analyzed by GLC/MS (Column: OV-101, 25 m, 0.32 mm, i.d., fused Silica; injector (splitter) temperature: 280°; carrier: helium, 2.0 ml/min; column temperature: 100°; programmed 1 min at 100°, then from 100° to 230° at 16°/min and held for 26 min. Yields (Table 1) were calculated by the external standard method using previously prepared authentic specimens as a reference. Pure ethers were obtained by open column chromatography (Silica gel, Si-60, 0.040–0.064 mm) or by high performance liquid preparative chromatography (HPPLC) on LiChroprep 15–25 μ, eluting with n-hexane/ethyl acetate.

2-Methoxydecane **4a**. IR (liquid film): 1095 (ν_{C-O-C}) cm^{-1}. ^{1}H-NMR: ($CDCl_3$)δ, 3.33 (s, 3H, CH_3O-), 3.40–3.20 (m, 1H, $-CH-O-$), 1.50–1.20 (m, 14H, $-(CH_2)_7-$), 1.10 (d, 3H, J = 6 Hz, $CH_3-CH-O-$), 0.87 (t, 3H, J = 6 Hz, $CH_3-(CH_2)$—) ppm. Found: C, 76.42; H, 13.98. $C_{11}H_{24}O$ requires C, 76.67; H, 14.04%.

2-Methoxyhexadecane. The product was prepared starting from 1-hexadecene with $Hg(OAc)_2$ in methanol and then reduced with $NaBH_4$.[28] IR (liquid film): 1095 (ν_{C-O-C}) cm^{-1}. ^{1}H-NMR: ($CDCl_3$)δ, 3.30 (s, 3H, CH_3-O-), 3.45–3.10 (m, 1H, $-CH-O$), 1.60–1.20 (m, 26H, $-(CH_2)_{13}-$), 1.10 (d, 3H, J = 6 Hz, $CH_3-CH-O-$), 0.87 (t, 3H, J = 6 Hz, $CH_3-(CH_2)_{13}-$) ppm. Found: C, 79.42; H, 14.29. $C_{17}H_{36}O$ requires C 79.61; H, 14.15%.

2-Isopropyloxydecane **4c**. IR (liquid film): 1115 (ν_{C-O-C}) cm^{-1}. ^{1}H-NMR: ($CDCl_3$)δ, 3.62 (m, 1H, J = 6 Hz, $(CH_3)_2CH-O-$), 3.60–3.30 (m, 1H, $CH_3-CH-O-$), 1.55–1.20 (m, 14H, $-(CH_2)_7-$), 1.20–1.05 (m, 9H, $(CH_3)_2CH-O-$ and CH_3-CH-), 0.87 (t, 3H, J = 6 Hz, $CH_3-(CH_2)_7-$) ppm. Found: C, 77.78; H, 14.12. $C_{13}H_{28}O$ requires C, 77.93; H, 14.09%.

2-(p-Toluensulphinyl) decane **4f**. This compound was always obtained in the oxidation reactions of compound **4** and was isolated by continuing column elution after separation of the corresponding ethers. IR (liquid film): 1600, 850 (p-C_6H_4), 1140 (ν_{S-O-}) cm^{-1}. ^{1}H-NMR: ($CDCl_3$) δ 7.52 (q, 4H, AA'BB', J_{AB} = 8 Hz, p-C_6H_4), 4.47 (m, 1H, $CH_3-CH-O-S-$), 2.43 (s, 3H, CH_3-Ar), 1.38 (d, 3H, J = 6 Hz, $CH_3-CH-O-S-$), 1.40–1.15 (m, 14H, $-(CH_2)_7-$), 0.90 (t, 3H, J = 6 Hz, $CH_3-(CH_2)_7-$) ppm. Found: C, 68.85; H, 9.50; S, 10.70. $C_{17}H_{28}O_2S$ requires: C, 68.89; H, 9.52; S, 10.80%.

3β-p-Toluensulphinyl-androstan-17β-ol **5f**. The title compound was isolated together with compounds **5a** and **5a'** by preparative separation of the reaction mixture performed on an axially compressed column of LiChroprep Si-60, 35 g, 15–25 μ, 25 cm; eluent: n-hexane/ethyl acetate, 75/25, v/v; flow: 30 ml/min; detector: RI; m.p. 174–6° (dec) from methanol/water. IR (Nujol): 3480 (ν_{O-H}), 1110 (ν_{S-O-}), 1050 (ν_{C-OH}) cm^{-1}. ^{1}H-NMR: (CDCl$_3$) δ, 7.52 (q, 4H, AA'BB', J_{AB} = 8 Hz, p-C_6H_4), 4.30 (m, 1H, $W_{1/2}$ = 20 Hz, –CH–O–S(=O)–Ar), 3.66 (t, 1H, HO–CH–), 2.45 (s, 3H, CH_3–Ar), 2.25–0.5 (m, all remaining protons) ppm. Found: C, 72.35; H, 8.96; S, 7.66. $C_{26}H_{38}O_3S$ requires: C, 72.52; H, 8.90; S, 7.43%.

Oxidation of N-alkyl-N'-tosylhydrazines with $Hg(OAc)_2$ *in the presence of phenol or acetic acid: alkylphenylethers* **1d**, **2d**, **3d**, **4d** *and alkylacetates* **1e**, **2e**, **3e**, **4e**

Small portions of N-alkyl-N'-tosylhydrazine **1–4** (3.00 mmol) were added to a solution of $Hg(OAc)_2$ (3.83 g, 12 mmol) and phenol (5.64 g, 60 mmol) in 10 ml of dichloromethane or to a solution of $Hg(OAc)_2$ in acetic acid (50 ml). Mixtures were magnetically stirred at room temperature for 15 h. 2M NaOH (40 ml) was then added and the mixture extracted with dichloromethane. The organic layer was separated and evaporated. The oily residue was GLC analyzed using the same conditions described above.

Products **4d–e** were isolated by preparative LC (eluent: n-hexane/ethyl acetate, 97/3, v/v).

2-Phenoxydecane **4d**. IR (liquid film): 1600, 750, 690 (–C_6H_5), 1245 (ν_{Ar-O-R}) cm^{-1}. ^{1}H-NMR: (CDCl$_3$) δ, 7.40–6.80 (m, 5H, –C_6H_5), 4.30 (m, 1H, J = 6 Hz, –CH–O–Ph), 1.70–1.20 (m, 17H, –$(CH_2)_7$– and CH_3–CH–O–), 0.87 (t, 3H, J = 6 Hz, CH_3–$(CH_2)_7$–) ppm. Found: C, 82.02; H, 11.15. $C_{16}H_{26}O$ requires: C, 81.99; H, 11.18%.

One-step transformation: cyclohexylmethylether **3a** *from cyclohexanone tosylhydrazone*

A solution of cyclohexanone tosylhydrazone (0.80 g, 3 mmol) in anhydrous THF (5 ml) was treated with diborane in THF (12 ml, 1 M) and kept for 30 min under magnetic stirring in argon atmosphere. Methanol (20 ml) was then slowly added and, after approx. 20 min, the mixture was evaporated and a colourless oily residue obtained. The residue dissolved in methanol (approx 10 ml) was added over a period of 10 min to a solution of $Hg(OAc)_2$ (3.83 g, 12 mmol) in methanol (40 ml). Then the mixture was stirred overnight at room temperature and filtered on Si-60 Silica gel (0.200–0.060 mm). The filtrate was evaporated under reduced pressure and the residue analyzed by GLC using the same conditions described above (47% yield).

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