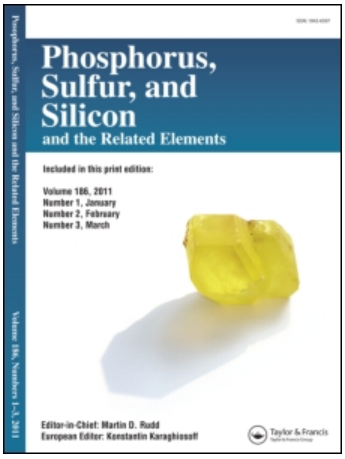

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P. K. Claus[a]; H. A. Schwarz[a]; W. Rieder[a]; W. Vycudilik[a]
[a] Lehrkanzel für Allgemeine und Organische Chemie, University of Vienna, Vienna, Austria

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ON THE REARRANGEMENT OF *N*-ARYL SULFIMIDES[1]

by

P. K. Claus*, H. A. Schwarz, W. Rieder, and W. Vycudilik**

Lehrkanzel für Allgemeine und Organische Chemie, University of Vienna, A 1090 Vienna, Austria

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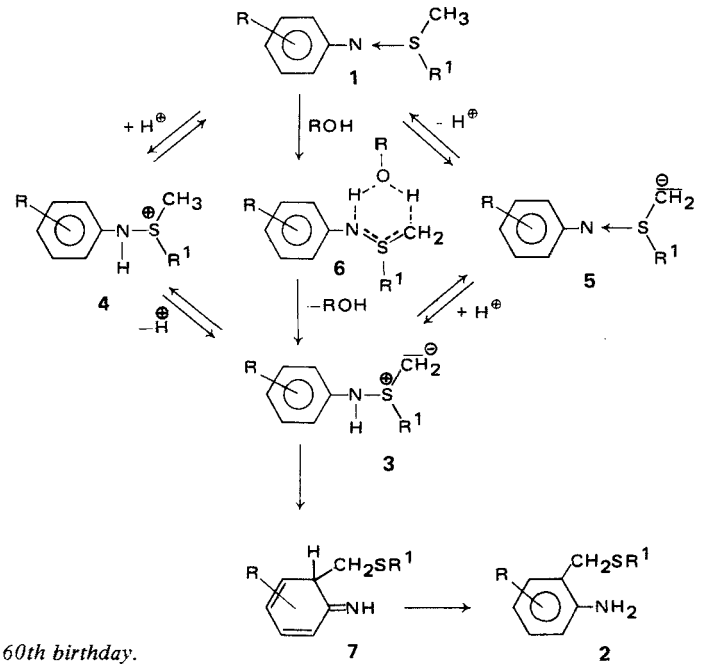
ABSTRACT

N-Aryl-*S,S*-dialkylsulfimides, **1**, with R^1 = alkyl other than CH_3, have been rearranged by heating in ethanol yielding *o*-alkylthiomethyl-anilines, **2**, as main products. Isomeric *o*-methylthioalkyl-anilines, **14**, are formed in minor amounts only. Reactions of sulfimides, **1**, with $R^1 = CH_3$, with certain alkylating or acylating agents yielded *o*-methylthiomethylated, *N*-alkylated or -acylated products **9**. Mechanistic considerations are discussed. The rearrangement of sulfimides **1** has been assumed to occur via [2,3]-sigmatropic reactions of intermediate azasulfonium ylids **3**. Attempts to resolve (+)-camphor-10-sulfonates of *N*-aryl sulfimides failed, but optically active *N*-aryl sulfimides could be obtained by reaction of anilines with optically active sulfoxides and P_4O_{10}. Optically active 2,6-disubstituted sulfimides, **1**, could be rearranged in ethanolic KOH to yield optically active cyclohexadienimines **12**, indicating a transfer of asymmetry from sulfur to carbon and supporting the assumption of a sigmatropic rearrangement.

N-Aryl sulfimides, **1**, with a wide variety of substituents R at the aromatic ring and R^1 at the sulfur atom are easily available now.[2,3] *N*-Aryl sulfimides with $R^1 = CH_3$ have been rearranged to *o*-methylthiomethyl-anilines **2** ($R^1 = CH_3$) either by heating in aprotic solvents in presence of triethylamine or by heating in ethanol without additional base present[4] or by refluxing in *tert.*-butanol in presence of KO^tBu.[5] This rearrangement has been assumed to occur *via* [2,3]-sigmatropic reaction of intermediate azasulfonium ylid **3**,[4,6] and is obviously related to the rearrangement of phenoxysulfonium ylids assumed to be intermediates in reactions of phenols with sulfoxides in presence of certain electrophilic



** *To Prof. K. Kratzl on his 60th birthday.*

reagents yielding *o*-alkylthioalkyl-phenols.[7-12] A strong indication for a concerted mechanism *via* a cyclic transition state is the exclusive formation of *o*-methylthiomethyl-anilines **2**.[4] Kinetic studies[6] showed electron-donating substituents at the aromatic ring to increase the rate of rearrangement. Obviously the rate of rearrangement is mainly influenced by the basicity of the nitrogen atom of **1**, which determines the positions of protonation-deprotonation equilibria between **1**, **3**, **4**, and **5**. Rearrangements in ethanol (without additional base present) are much faster than rearrangements in aprotic solvents in presence of triethylamine. In the latter case protonated amine arising in low concentrations *via* deprotonation steps **1** → **5** or **4** → **3** represents the sole protonating agent in the reaction mixture. Reactions of sulfimides **1** with protic solvents (H_2O, alcohols) also might be considered to occur *via* cyclic six-membered transition states, **6**, without formation of intermediates **4** or **5**. The rate of rearrangement of formed azasulfonium ylid **3** to cyclohexadienimine **7** should be high compared with the rate of the total reaction, **1** → **2**: rearrangements of deuterated sulfimides (with S,S-di-CD_3) in ethanol as solvent, respectively, of sulfimides, **1**, with $R^1 = CH_3$ in D_2O as solvent, indicated only little exchange of deuterons, respectively, protons with the solvent.[6]

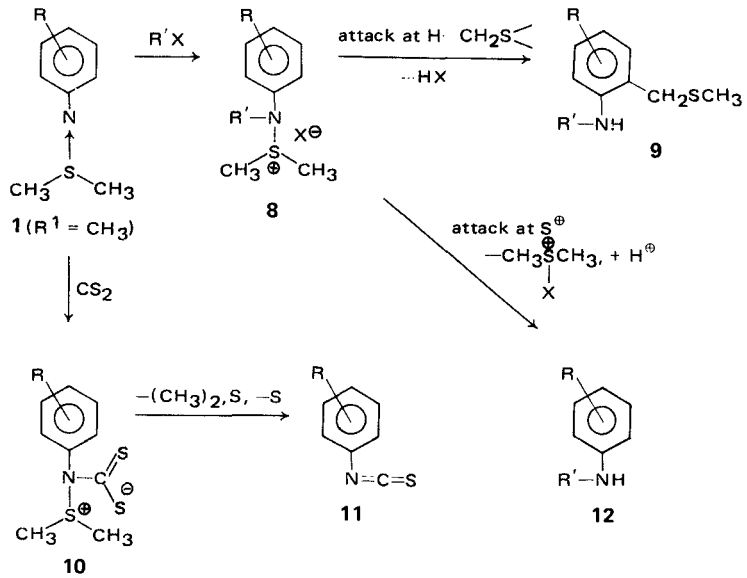
Discussion of Results

The reaction of sulfimides, **1**, with protic solvents is related to reactions observed with alkylating or acylating agents; instead of protonation alkylation (acylation) at the nitrogen atom occurs to give an azasulfonium intermediate **8**, which is deprotonated at the S–CH_3 group by attack of base X^- (or of a negatively charged centre arising within the R′ group) and subsequently rearranged to yield finally *o*-methylthiomethylated, *N*-alkylated or -acylated anilines **9**.[13]

This type of reaction could be observed with CH_3J, acetic anhydride, ethyl chloroformate, and phenyl isothiocyanate, yielding *N*-methyl-*o*-methylthiomethyl-aniline (**9**, R′ = CH_3), *N*-acetyl-*o*-methylthiomethyl-aniline (**9**, R′ = CH_3CO), ethyl *N*-(*o*-methylthiomethyl-phenyl-)carbamate (**9**, R′ = $COOC_2H_5$), and 2-methylthiomethyl-diphenyl urea (**9**, R′ = $CONHC_6H_5$), respectively. The reaction of sulfimides **1** with CH_3J obviously involves analogous intermediates **8** as have been assumed recently by Gassman[14] in reactions of *N-tert*.butyl-*N*-chloro-anilines with dimethyl sulfide.

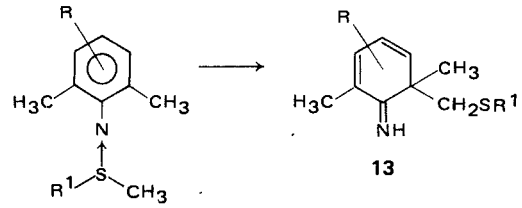
On the contrary, reaction of *N*-4-chlorophenyl-*S,S*-dimethyl sulfimide (**1**, R = 4-Cl, $R^1 = CH_3$) with CS_2 yielded 4-chlorophenyl isothiocyanate **11** as main product; instead of proton abstraction from *S*-methyl groups of the zwitterion, **10**, dimethyl sulfide and sulfur are split off (possibly *via* an unstable thiosulfoxide).

A second pathway in all these reactions (rearrangements in protic solvents, alkylations or acylations of sulfimides **1**) results in the formation of aniline derivatives **12** (R′ = H, alkyl or acyl). This pathway sometimes becomes dominating, depending on the basicity, respectively, nucleophilicity (thiophilicity) of the anionic centre X^- and on the nature of substituents R at the aromatic ring. Deprotonation at S–CH_3 results in rearrangement, attack at the positive sulfur in displacement of the aniline group of **3**, respectively, **8**. The displacement of the aniline group becomes dominating in case of powerful



electron-withdrawing groups at the aromatic ring; thus, the yields of rearranged products **2** or **9** are low in case of R = NO_2 because of preferred scission of the S–N bond.

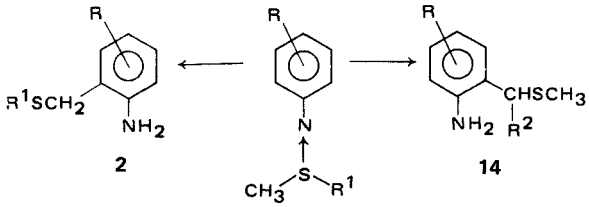
Sigmatropic rearrangements are known to proceed with high stereospecifity.[15] In order to resolve the question of stereospecifity in rearrangements of *N*-aryl sulfimides **1** we attempted to prepare optically active *N*-aryl sulfimides with CH_3-groups in 2- and 6-position of the aromatic ring, which might be rearranged to yield optically active cyclohexadienimines, **13**. It had been shown earlier[4] that cyclohexadienimines, **13**, may be isolated in spite of their extreme sensitivity towards protic agents.



13

The following results led to to investigate the preparation and rearrangement of optically active *S*-methyl-*S*-ethyl sulfimides, **1** ($R^1 = C_2H_5$). Rather little had been known about rearrangements of sulfimides **1** with R^1 = alkyl other than CH_3. Rearrangements of *S,S*-diethyl and *S,S*-tetramethylene sulfimides have been reported.[4] Gassman[16] very recently reported on some reactions which are assumed to include rearrangements of *N*-aryl azasulfonium intermediates with *S*-β-ketoalkyl groups.

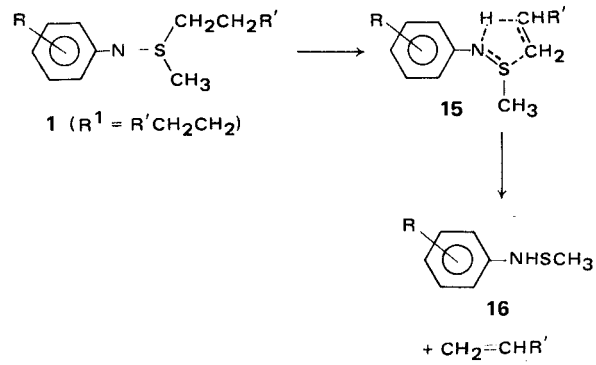
Rearrangement of *N*-aryl sulfimides **1**, with $R^1 = CH_3CH_2$ or $CH_3CH_2CH_2$, by refluxing in ethanol or toluene–ethanol yielded mainly alkylthiomethyl-anilines, **2** ($R^1 = CH_3CH_2$ or $CH_3CH_2CH_2$). In case of rearrangement of *N*-4-chlorophenyl-*S*-methyl-*S*-ethyl sulfimide (**1**, R = 4-Cl, $R^1 = CH_3CH_2$) the nmr spectrum of the isolated rearranged product **2** (R = 4-Cl, $R^1 = CH_3CH_2$) indicated also the presence of a second product in minor amounts (~5%): a doublet at 1.64 ppm (CH_3CH) and a singlet at 1.92 ppm (CH_3S) are assumed to be due to the presence of isomer, **14** ($R^2 = CH_3$; a quartet to be expected as CH_3CH-signal could not be detected obviously because of the small amounts of **14** besides **2**). The results indicate that proton abstraction occurs nearly exclusively from *S*-methyl groups and not from α-positions of *S*-ethyl or *S*-*n*-propyl groups, and are in accordance with earlier findings on Pummerer Rearrangements of unsymmetrical dialkyl sulfoxides[17] which had been explained by the higher acidity of S–CH_3 compared to S–CH_2R protons.



1 ($R^1 = R^2CH_2$)

Similarly, according to the higher acidity of benzylic protons, the rearrangement of *N*-4-chlorophenyl-*S*-benzyl-*S*-methyl sulfimide (**1**, $R^1 = C_6H_5CH_2$) yielded exclusively a product **14** with $R^2 = C_6H_5$. No traces of an isomeric compound, **2** ($R^1 = C_6H_5CH_2$) could be detected.

Rearrangements of *N*-aryl sulfimides, **1**, with R^1 = ethyl or *n*-propyl could not be achieved by heating in aprotic solvents in presence of triethylamine. Instead of rearrangement formation of unstable products was observed which have not been isolated in a pure state as yet but are assumed on basis of tentative nmr data to be *N*-aryl methanesulfenamides **16**. (Similar observations have been made by Vilsmaier[18].) Sulfenamides, **16**, are assumed to be formed by β-elimination *via* a cyclic, five-membered transition state, **15**, similarly as it has been proposed for β-eliminations of sulfenic acids from alkyl sulfoxides.[19] Oae[20] found analogously a β-elimination of *N*-tosyl sulfenamides on pyrolysis of *N*-tosyl-*S*-alkyl sulfimides. The higher basicity of the nitrogen center in *N*-aryl sulfimides **1** as compared to that in *N*-tosyl sulfimides causes β-elimination to occur at low temperatures already. *N*-4-Chlorophenyl-*S*-methyl-*S*-isopropyl sulfimide (**1**, R = 4-Cl, R^1 = isopropyl)[2] proved to be rather unstable even at room temperature. On rearrangements in ethanol elimination is strongly supressed in favour of rearrangement as the faster reaction, which is initiated by protonation at the nitrogen atom of **1**.

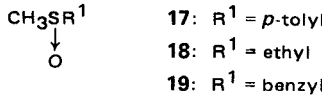


Optically active *N*-tosyl sulfimides with high configurational stability are known since the work of Clarke, Kenyon, and Phillips.[21] The configurational

relationships between optically active sulfoxides, *N*-tosyl sulfimides, and sulfoximides have been elaborated recently by Cram *et al.*[22] by applying a series of sophisticated stereochemical reaction cycles. The question of configurational stability of other sulfimides has been little investigated as yet. We investigated briefly some possibilities for preparation of optically active *N*-aryl sulfimides, **1**.[23]

Optically pure methyl-*p*-tolyl sulfoxide (**17**) would have been rather easily available, but the reaction of **17** with anilines and P_4O_{10} in presence of triethylamine did not yield isolable amounts of sulfimide **1**. Thus, we prepared sulfimides, **1**, with $R^1 = CH_3CH_2$ by reactions of anilines with methyl ethyl sulfoxide **18** of limited optical purity. Applying the Andersen method,[24] we prepared (–)(R)-methyl ethyl sulfoxide (**18**) ($[\alpha]_D = -33.3°$). Using the same (–)-menthyl ester of (–)(S)-methanesulfinic acid for preparation of sulfoxides **17** and **18**, we got (+)(R)-**17** with $[\alpha]_D = +49.2°$ (optical pure (+)(R)-**17**: $[\alpha]_D = +156°$ [25]). Thus, the optical purity of prepared sulfoxides (+)(R)-**17** and (–)(R)-**18** was 31.5%.

Reactions of various anilines with (–)(R)-**18** ($[\alpha]_D = -33.3°$) in presence of P_4O_{10} and triethylamine yielded corresponding sulfimides **1** which showed rather small positive values of optical rotation ($[\alpha]_D = +0.5$ to $+10.7°$), reactions with (–)(R)-**19**



17: R^1 = *p*-tolyl
18: R^1 = ethyl
19: R^1 = benzyl

($[\alpha]_D = -25.8°$, optical purity 26.3%) yielded corresponding sulfimides, **1**, which showed small negative values of optical rotation ($[\alpha]_D = -1.0°$ to $-2.1°$). In analogy to the formation of optically active *N*-tosyl sulfimides with (S)-configuration by reaction of *p*-toluenesulfonamides with (R)-sulfoxides (inversion of configuration at the S-atom),[26] the configuration of prepared *N*-aryl sulfimides, **1**, is assumed to be (S). The optical purity of these sulfimides is unknown as yet, and several attempts to elucidate configuration and optical purity have been unsuccessful as yet. Mild hydrolysis in diluted aqueous H_2SO_4 (at conditions which caused loss of about one third of optical purity of (–)(R)-**17**) of (+)-*N*-aryl-*S*-methyl-*S*-ethyl sulfimides, **1** ($R^1 = CH_3CH_2$) yielded racemic sulfoxide **17** only.

N-Aryl sulfimides, **1**, form crystalline (+)-camphor-10-sulfonates, but repeated recrystallizations resulted in partial resolution only. Recrystallization of the (+)-camphor-10-sulfonate of *N*-2,6-dimethyl-4-chlorophenyl-*S*-methyl-*S*-ethyl sulfimide, **1** (R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$), for instance, until constant value of optical rotation (which was equally $[\alpha]_D \sim +22°$, whether the starting material was racemic sulfimide or (+)-sulfimide with a value $[\alpha]_D = +10.7°$), and regeneration of the sulfimide by treatment of the camphorsulfonate with base yielded (–)-sulfimide with $[\alpha]_D = -5.5°$. The reason for this behavior is not quite clear; we assumed a fast racemization of *N*-aryl azasulfonium salts, **4**, in polar solutions, though it has been found recently[27] that *N*-acyl azasulfonium salts are reasonably stable towards racemization.

The rearrangement of *N*-2,6-dimethyl-4-chlorophenyl-*S*-methyl-*S*-ethyl sulfimide (**1**, R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$) could not be achieved in aprotic solvents in presence of triethylamine (as had been observed similarly on rearrangements of other S-methyl-S-alkyl sulfimides), but proceeded without formation of major amounts of byproducts in refluxing ethanol, preferably in presence of added KOH. Isolated cyclohexadienimines, **13**, proved to be thermally stable in absence of acids and could be purified by distillation at diminished pressure. Nmr spectra of compounds **13** with $R^1 = CH_3CH_2$ did not indicate the presence of significant amounts of isomeric rearranged products **13** (carrying in analogy to compounds **14** an *o*-α-methylthioethyl group). The structure of cyclohexadienimine (**13**) with R = 4-Cl and $R^1 = CH_3CH_2$, for instance, has been derived unambiguously from nmr data; the signals of the ethylthiomethyl group occur at 1.18 ppm (triplet, $J = 7$ Hz, 3 protons), 2.49 ppm (quartet, $J = 7$ Hz, 2 protons), 2.70 ppm (doublet, $J = 13$ Hz, 1 proton) and 2.91 ppm (doublet, $J = 13$ Hz, 1 proton), the signal of the 2-CH_3 group as singlet at 1.28 ppm, the signal of the 6-CH_3 group at 1.97 ppm (weakly resolved triplet due to allylic coupling with 5-H), the signals of the two ring protons as weakly resolved multiplets at 6.05 ppm and 6.25 ppm and the signal of the imino proton as a broad peak at 9.5 ppm.

Reaction of 2,6-dimethyl-4-chloro-aniline with (–)(R)-**17** ($[\alpha]_D = -33.3°$) in presence of P_4O_{10} and triethylamine yielded (+)-*N*-2,6-dimethyl-4-chloro-phenyl-*S*-methyl-*S*-ethyl sulfimide (*1*, R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$) with $[\alpha]_D = +10.7°$. Rearrangement of this sulfimide yielded (–)-cyclohexadienimine **13** (R = 4-Cl, $R^1 = CH_3CH_2$) with $[\alpha]_D = -3.3°$. Rearrangement of that (–)-sulfimide with $[\alpha]_D = -5.5°$ which had been obtained by partial resolving via the (+)-camphor-10-sulfonate (see above) yielded (+)-cyclohexadienimine with $[\alpha]_D = +1.0°$. Though the values of isolated cyclohexadienimines **13** were rather low, and neither the optical purity nor the configuration of cyclohexadienimines, **13**, is known, this result shows that the rearrangement of 2,6-

disubstituted sulfimides, **1** to cyclohexadienimines, **13**, proceeds stereospecifically with a transfer of asymmetry from sulfur to carbon. Usually sigmatropic rearrangements proceed with high stereospecifity,[15] and very recently this could be shown to be valid also for [2,3]-sigmatropic rearrangements of sulfonium ylids,[28] resulting in a similar transfer of asymmetry from sulfur to carbon. Thus, also this result of our investigations supports the assumption of a concerted, sigmatropic reaction of intermediate azasulfonium ylids, **3**.

Experimental Section

Reagents (commercially available or prepared according to known procedures) have been purified before use as necessary (distillation or crystallization). Solvents were Merck grades. DMSO was dried by refluxing over CaH_2 at about 100 Torr for 5 hours and fractionation at 12 Torr. CH_2Cl_2 was dried by stirring with P_4O_{10} for several hours and fractionated subsequently. Melting points (uncorrected) were obtained using a Kofler Mikroheiztisch. Tlc was conducted on Merck silica gel HF_{254} or on tlc cards SI F from Riedel-de Haen (solvent: $CHCl_3$ or $CHCl_3/(C_2H_5)_3$ N = 50:1). Column chromatography was performed on Merck silica gel, using $CHCl_3$ as solvent. Frl. H. Martinek obtained the nmr spectra on a Varian Model A-60A (TMS as internal standard). Optical rotations were measured on a Perkin-Elmer photoelectric polarimeter 141.

Preparation of N-Aryl Sulfimides

According to Claus *et al.*[2, 29] Optically active sulfimides, **1**, were prepared by applying the sulfoxide–P_4O_{10} method;[29] 40 mmoles of aniline were dissolved in 50 ml dry $CHCl_3$ (dried over P_4O_{10}) in a two-necked flask with thermometer and addition funnel (with pressure compensation and drying tube). With vigorous stirring 80 mmoles P_4O_{10} and subsequently 80 mmoles sulfoxide (dropwise) were added taking care that the reaction temperature did not exceed 30°. Subsequently 60 mmoles triethylamine were added dropwise while the reaction temperature was kept below 40°. The reaction was monitored by tlc; usually all aniline had disappeared after 3–7 hrs. The mixture was poured into 50 ml 10 *N* NaOH (containing some crushed ice) with stirring. Stirring was continued for 5 min. The $CHCl_3$ layer was separated, and the aqueous layer was extracted once more with 25 ml $CHCl_3$. The combined $CHCl_3$ layers were dried over Na_2SO_4. Evaporation at diminished pressure and room temperature (rotavapor) usually yielded oily residues which were dissolved in ether. The filtered ether solution was poured slowly into a stirred saturated solution of picric acid in ether. The precipitate was filtered and recrystallized from acetone or acetone/ether.

20 Mmoles picrate were suspended in 80 ml ether, and 5 ml 10 *N* aqueous KOH were added with vigorous stirring. After 20 minutes the ether layer was decanted, and the residue was treated analogously with four times 50 ml ether. The combined ether layers were dried over solid KOH and evaporated at room temperature at diminished pressure. Traces of solvents were removed at 10^{-2} Torr. Solid sulfimides, **1** were purified by recrystallization from ether. Yields and further data are given in Table I.

Reactions of Sulfimides, 1, with Alkylating (Acylating) Agents

a) Methyl iodide: 10 mmoles *N*-chlorophenyl-*S,S*-dimethyl sulfimide (**1**, R = 4-Cl, $R^1 = CH_3$)[6, 29] were dissolved in 40 ml ether. After addition of 1 g K_2CO_3 and of 10 mmoles CH_3J (dissolved in 10 ml ether) the mixture was stirred at room temperature for 45 hrs. Evaporation, column chromatography and distillation in a "Kugelrohr" (110°, 0.6 Torr) yielded 55% *N*-methyl-2-methylthiomethyl-4-chloro-aniline (**9**, R = 4-Cl, R' = CH_3; yellowish oil). Nmr ($CDCl_3$): 1.88 (s, 3H), 2.80 (s, 3H), 3.53 (s, 2H), 4.35 (s, broad, 2H), 6.45–7.25 (m, 3H).

b) Acetic anhydride: 10 mmoles **1** (R = 4-Cl, $R^1 = CH_3$) and 11 mmoles $(CH_3CO)_2O$ were refluxed for 1 hr in 50 ml $CHCl_3$. Evaporation, column chromatography and crystallization from benzene/hexane yielded – besides 4-chloro-

TABLE I

New *N*-Aryl Sulfimides 1

Product 1		Picrate	Yield[a]	
R	R^1	mp	(%)	Nmr (δ)[b]
4-Cl	CH_3CH_2	157–159	20	1.29 (t), 2.54 (s), 2.84 (qu), 6.7–7.15 (m)
4-CN	CH_3CH_2	165–168	49	1.33 (t), 2.59 (s), 2.91 (qu), 6.75–7.4 (m)
2,6-di-CH_3	CH_3	187–189	29	2.29 (s), 2.58 (s), 6.65–7.15 (m)
2,6-di-CH_3	CH_3CH_2	149–151	40	1.32 (t), 2.29 (s), 2.52 (s), 2.77 (qu), 6.55–7.05 (m)
2,6-di-CH_3-4-Cl	CH_3CH_2	159–161	63	1.30 (t), 2.24 (s), 2.53 (s), 2.78 (qu), 6.9 (s)
4-Cl	$C_6H_5CH_2$	148–149	39[c]	2.48 (s), 3.89 (d), 4.05 (d), 6.65–7.2 (m), 7.4 (m)

[a] Yield of picrate (for isolation of free **1** from **1**-picrate see also ref. 6). All sulfimides except **1**, R = 4-Cl, $R^1 = C_6H_5CH_2$ (mp 96–100°) have been obtained as oils.

[b] ppm; solvent: $CDCl_3$, 60 MHz; TMS as internal standard; s = singlet, d = doublet, t = triplet, qu = quartet, m = multiplet.

[c] Pure sulfimide **1**, R = 4-Cl, $R^1 = C_6H_5CH_2$, has been obtained in high yields by applying other methods of preparation, see ref. 2.

acetanilide–24% *N*-acetyl-2-methylthiomethyl-4-chloroaniline (**9**, R = 4-Cl, R′ = CH_3CO), mp 144–145° Nmr ($CDCl_3$): 2.01 (s, 3H), 2.20 (s, 3H), 3.70 (s, 2H), 7.2–8.0 (m, 3H), 8.30 (s, broad, 1H).

c) Ethyl chloroformate: 5 mmoles **1** (R = 4-Cl, $R^1 = CH_3$) were dissolved in 20 ml dry benzene. After addition of 6 mmoles of triethylamine in 10 ml benzene, 5.5 mmoles ethyl chloroformate, dissolved in 20 ml benzene, were added dropwise. The mixture was stirred for 2 hrs, extracted with 20 ml H_2O, dried over Na_2SO_4 and evaporated. Column chromatography yielded–besides ethyl *N*-4-chlorophenyl-carbamate–about 60% crude ethyl *N*-2-methylthiomethyl-4-chlorophenyl-carbamate (**9**, R = 4-Cl, R′ = $COOC_2H_5$); mp (after crystallization from benzene/hexane): 98–99°. Nmr ($CDCl_3$): 1.33 (t, J = 7 Hz, 3H), 2.00 (s, 3H), 3.67 (s, 2H), 4.26 (qu, J = 7 Hz, 2H), 7.15–8.0 (m, 3H).

d) Phenyl isocyanate: 10 mmoles **1** (R = 4-Cl, $R^1 = CH_3$) and 10 mmoles phenyl isocyanate were dissolved in 50 ml ether and stirred at room temperature for 15 minutes. Evaporation and crystallization from ethanol yielded 85% 2-methylthiomethyl-4-chlorodiphenyl urea (**9**, R = 4-Cl, R′ = $CONHC_6H_5$), mp 196–199°, identical with the product obtained by reaction of 2-methylthiomethyl-4-chloro-aniline (**2**, R = 4-Cl, $R^1 = CH_3$) with phenyl isocyanate.

e) Carbon Disulfide: 16 mmoles **1** (R = 4-Cl, $R^1 = CH_3$) were dissolved in 50 ml dimethyl formamide, cooled to –70°, and 5 ml CS_2 were added dropwise. After 3 hours the solution was brought to room temperature and filtered (isolation of 57% S). Addition of water, extraction with ligroin and column chromatography with ligroin as solvent yielded 75% 4-chlorophenyl isothiocyanate, mp 45°.

Rearrangement of Sulfimides, 1, with $R^1 \neq R^2CH_2$

a) *N*-4-Chlorophenyl-*S*-methyl-*S*-ethyl sulfimide (**1**, R = 4-Cl, $R^1 = CH_3CH_2$): 1.5 mmoles sulfimide were dissolved in 5 ml absolute ethanol. After 3 hrs at room temperature the solvent was removed by evaporation, and the residue was distilled in a "Kugelrohr" (110°, 0.5 Torr), yielding 74% **2** (R = 4-Cl, $R^1 = CH_3CH_2$) as an oil, containing, according to nmr, approx. 5% **14** (R = 4-Cl, $R^2 = CH_3$). Nmr ($CDCl_3$): 1.23 (t, J = 7 Hz, 3H), 2.44 (qu, J = 7 Hz, 2H), 3.65 (s, 2H), 4.08 (s, 2H), 6.55–7.15 (m, 3H).

b) *N*-4-Chlorophenyl-*S*-methyl-*S*-*n*-propyl sulfimide (**1**, R = 4-Cl, $R^1 = CH_3CH_2CH_2$)[2]: 16.5 mmoles sulfimide were dissolved in 50 ml ethanol and refluxed for 1 hr. Evaporation and distillation in a "Kugelrohr" (100°, 0.01 Torr) yielded 85% **2** (R = 4-Cl, $R^1 = CH_3CH_2CH_2$) as an oil. Nmr ($CDCl_3$): 0.97 (t, J = 7 Hz, 3H), 1.2–2.0 (m, 2H), 2.44 (t, J = 7 Hz, 2H), 3.67 (s, 2H), 4.03 (s, 2H), 6.55–7.25 (m, 3H).

c) *N*-4-Chlorophenyl-*S*-methyl-*S*-benzyl sulfimide (**1**, R = 4-Cl, $R^1 = C_6H_5CH_2$)[2]: 9 mmoles of sulfimide picrate, mp 148–149°[2], were added to a solution of 20 mmoles KOH in 50 ml ethanol. The mixture was heated to 80° for 20 minutes, filtered and evaporated. The residue was fractionated by distillation in a "Kugelrohr". At 150° and 0.3 Torr 51% **14** (R = 4-Cl, $R^2 = C_6H_5$) were obtained as a viscous oil. Nmr ($CDCl_3$): 2.00 (s, 3H), 3.98 (s, broad, 2H), 5.09 (s, 1H), 6.55–7.55 (m, 8H).

Rearrangement of 2,6-Dimethyl-Substituted Sulfimides

a) *S,S*-Dimethyl sulfimides (**1** R = 2, 6-di-CH_3-4-Cl [or Br], $R^1 = CH_3$): 10 mmoles sulfimide were refluxed in 50 ml toluene and 5 ml triethylamine for 2 hrs. After evaporation the residue was fractionated in a "Kugelrohr" yielding at 100–120° and 0.4 Torr 20–40% cyclohexadienimine (**13**) (R = 4-Cl or -Br, $R^1 = CH_3$) as oils, containing minor amounts of corresponding 2,6-dimethyl-4-halogeno-anilines. Nmr (CCl_4): a) R = 4-Cl: 1.25 (s, 3H), 1.96 (unresolved m, 3H; allylic coupling of 6-CH_3 with 5-H), 2.03 (s, 3H), 5.99 (m, 1H), 6.23 (m, 1H), 9.65 (s, broad, 1H). b) R = 4-Br: 1.28 (s, 3H), 1.95 (unresolved m, 3H), 2.04 (s, 3H), 6.20 (m, 1H), 6.32 (m, 1H), 9.61 (s, broad, 1H).

b) *S*-Methyl-*S*-ethyl sulfimides (**1**, R = 2,6-di-CH_3-4-Cl [or H], $R^1 = CH_3CH_2$): 5 mmoles sulfimide were dissolved in a solution of 10 mmoles KOH in 20 ml of absolute ethanol, and the mixture was refluxed for 20 minutes (alternatively, sulfimide picrate might be refluxed in ethanolic KOH for 1 hr, and subsequently K-picrate be filtered before evaporation). Evaporation, dissolution of the residue in dry benzene, filtration, evaporation and fractionation in a "Kugelrohr" yielded 55–65% cyclohexadienimine **13** (R = 4-Cl or H, $R^1 = CH_3CH_2$), bp approx. 110° at 0.1 Torr, as slightly yellowish oil. Nmr ($CDCl_3$):

a) R = H: 1.20 (t, J = 7 Hz, 3H), 1.27 (s, 3H), 1.95 (unresolved m; allylic coupling of 6-CH_3 with 5-H), 2.50 (qu, J = 7 Hz, 2H), 2.73 (d, J = 13 Hz, 1H), 2.95 (d, J = 13 Hz, 1H), 5.95–6.3 (m, 3H), 9.47 (s, broad, 1H).

b) R = 4-Cl: 1.18 (t, J = 7 Hz, 3H), 1.28 (s, 3H), 2.49 (qu, J = 7 Hz, 2H), 2.70 (d, J = 13 Hz, 1H), 2.91 (d, J = 13 Hz, 1H), 6.05 (m, 1H), 6.25 (m, 1H), 9.46 (s, broad, 1H).

Preparation and Rearrangement of Optically Active Sulfimides 1

Optically active sulfoxides (+)(R)-**17** and (–)(R)-**18** were prepared according to [24] and purified by distillation in a "Kugelrohr". (+)(R)-**17**: distillation at 65° and 0.001 Torr, $[\alpha]_D$ = +49.2° (c 2.7, absol. ethanol), (–)(R)-**18**: distillation at 75° and 12 Torr, $[\alpha]_D$ = –33.3° (c 3.46, ethanol). In a similar experiment (–)(R)-**19**, mp 46-55°, $[\alpha]_D$ = –25.8° (c 2.15, ethanol), was obtained by distillation at 100° and 0.001 Torr.

Optically active sulfimides **1** have been prepared by applying the procedure given above and purified via corresponding picrates. Reaction of 4-chloro-aniline with (–)(R)-**18**, $[\alpha]_D$ = –29.0° (c 3.4, ethanol) yielded (+)-sulfimide **1** (R = 4-Cl, $R^1 = CH_3CH_2$), $[\alpha]_D$ = +3.1 (c 4.5, dry acetone). Reaction of 4-cyano-aniline with (–)(R)-**18**, $[\alpha]_D$ = –29.0°, yielded (+)-sulfimide **1** (R = 4-CN, $R^1 = CH_3CH_2$), $[\alpha]_D$ = +0.5°. Reactions of 4-chloro-2,6-dimethyl-aniline with (–)(R)-**18**, $[\alpha]_D$ = –33.3° (c 3.46, ethanol) and $[\alpha]_D$ = –29.0° (c 3.4, ethanol), respectively (parallel experiments), yielded sulfimide **1** (R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$), $[\alpha]_D$ = +10.7° (c 1.4, acetone) and +9.5° (c 3.4, acetone), respectively. Reaction of 2,6-dimethyl-aniline with (–)(R)-**18** ($[\alpha]_D$ = –29.0°) yielded (+)-sulfimide **1** (R = 2,6-di-CH_3, $R^1 = CH_3CH_2$), $[\alpha]_D$ = +7.3° (c 2.4, acetone). Reaction of 4-chloro-aniline with (–)(R)-**19** ($[\alpha]_D$ = –25.8°, c 2.15, ethanol) yielded (–)-sulfimide, **1**, (R = 4-Cl, $R^1 = C_6H_5CH_2$), $[\alpha]_D$ = –2.1° (c 1.0, acetone). Rearrangement of sulfimide, **1**, (R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$), $[\alpha]_D$ = +10.7° (respectively, +8.6°, +8.0°, –5.5° in parallel experiments) by refluxing in ethanolic KOH as described above yielded

cyclohexadienimine, **13**, (R = 4-Cl, $R^1 = CH_3CH_2$), $[\alpha]_D = -3.3°$ (c 1.3, CCl_4), respectively, in parallel experiments, $-4.5°$ (c 1.26), $-3.8°$ (c 1.2) and $+1.0°$ (c = 2.0). Similarly rearrangement of (+)-sulfimide **1** (R = 2,6-di-CH_3, R^1 = 4-Cl), $[\alpha]_D = +7.3°$ (c 2.4, acetone) yielded (−)-cyclohexadienimine **13** (R = H, $R^1 = CH_3CH_2$), $[\alpha]_D = -2.5°$ (c 4.6, CCl_4). Purity of cyclohexadienimines **13** was checked by nmr and glc (in particular, absence of minor amounts of sulfoxide **18** which might arise by hydrolysis of sulfimides **1** with $R^1 = CH_3CH_2$ was established).

Hydrolysis experiments were performed by dissolving sulfimides **1** (*e.g.*, **1**, R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$, with $[\alpha]_D = +10.7°$) in 1% aqueous H_2SO_4. After 4 hrs the solution was saturated with NaCl and extracted with 10 times 10 ml $CHCl_3$. Drying of the combined $CHCl_3$ layers with K_2CO_3, evaporation and distillation of the residue in a "Kugelrohr" at 75° and 11 Torr yielded racemic sulfoxide, **18**. In a control experiment, analogous treatment of (−)(R)-**18**, $[\alpha]_D = -30.3°$ (c 1.55, ethanol) yielded, on re-isolation, (−)(R)-**18** with $[\alpha]_D = -21°$.

(+)-Camphor-10-sulfonates of sulfimides, **1**, were prepared by dissolving approx. 25 mmoles **1** in 10 ml acetone (p.a. Merck) and adding a solution of equimolar amounts of (+)-camphor-10-sulfonic acid(monohydrate) in 35 ml acetone. Thus, *e.g.*, *N*-(2,6-dimethyl-4-chlorophenyl)-*S*-methyl-*S*-ethyl sulfimide (**1**, R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$) yielded on cooling of the acetone solution to −20° 88% (+)-camphorsulfonate, $[\alpha]_D = +24.4°$ (c 2.62, acetone), mp 63–70°. Repeated recrystallizations from acetone yielded a camphersulfonate with $[\alpha]_D = +21.6°$. Treatment of this product with ether and 5 *N* aqueous KOH yielded sulfimide **1** (R = 2,6-di-CH_3-4-Cl, $R^1 = CH_3CH_2$), $[\alpha]_D = -5.5°$. (+)-Camphorsulfonates of this sulfimide with values of optical rotation ~22° have been also obtained with (+)-sulfimides as starting materials.

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