isfactorily by using rapid stirring of the suspension, α-methylnaphthalene proved to be inert.

Experimental Section

All hydrogenations were performed in a divided H-type cell with two glass frits of medium porosity as the dividing membrane. The catholyte volume was approximately 100 mL. The electrolyte was 0.2 M H_2SO_4, and the working electrode consisted of six carbon rods (6 mm diameter, 100 mm long), onto which the catalyst metal had been electroplated. The geometric area of the catalyst electrode was approximately 69 cm^2. A piece of Pt sheet was used as the counter electrode. This assured that the anodic reaction was the production of O_2. All experiments were performed at constant current using a H.P. 6266B DC power supply.

The plating solutions used for cathode preparation were either a 2% aqueous H_2PtCl_6 solution, a 2% $RhCl_3$ solution in 0.1 M H_2SO_4, or a 2% $PdCl_2$ solution in 0.1 M H_2SO_4. In one case the H_2PtCl_6 supplied by Alfa Ventron failed to give the expected platinum black plating. Each carbon rod was plated separately centered in a cylindrical Pt-sheet anode using 1 A for 5 min. The Ni|C electrodes were plated from a solution of 10 g of $NiSO_4$ in 50 mL of H_2O + 50 mL of concentrated NH_4OH with a current of 1 A for 5 min.

Most hydrogenations were performed using 2 g of substrate. After the electrolysis was stopped the catholyte was extracted either directly or in the case of hydrogenation of aniline, after basification with $NaHCO_3$, with 5 × 100 mL of CH_2Cl_2, dried over $MgSO_4$, and evaporated.

The products were identified by NMR of the reaction mixture and comparison of the gas liquid chromatography (GC) retention times with these of authentic samples, or after isolation by preparative GC or high-pressure liquid chromatography by their NMR and MS data. Quantitation was performed by GC using internal standards. Current yields were calculated using an assumed stoichiometry of 6 e^-/molecule.

The most abundant isomer of 2,6-dimethylcyclohexanol, produced in 82%, gave a NMR spectrum with a sharp doublet at 1.0 ppm demonstrating equivalency of the two methyls. The methine proton next to the hydroxyl group gave an unresolved singlet at 3.55 ppm with no observable splitting indicating an axial–equatorial or equatorial–equatorial coupling. On this basis the isomer was identified as the *cis,cis*-2,6-dimethylcyclohexanol.

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Registry No.—*cis*-3 (R = 2-Me), 7443-70-1; *trans*-3 (R = 2-Me), 7443-52-9.

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Chemistry of Sulfenamides. 1. Study of the Rearrangements of Sulfenanilides

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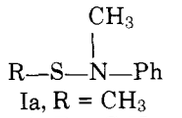
The thermal rearrangement of *N*-arylsulfenamides was first reported by Zincke and Eismayer.[1] Later the rearrangement of various sulfenanilides was studied by Moore and Johnson,[2] and the rearrangement of *N*-thiazolylsulfenamides was reported by Hoggarth.[3] More recently, the rearrangement has been studied by Davis and co-workers.[4] We would like to report here the results of our studies on the rearrangements of *N*-methylalkanesulfenamides Ia–d.



Ia, R = CH_3
b, R = C_2H_5
c, R = i-C_3H_7
d, R = t-C_4H_9

The sulfenamides were prepared by reaction of the appropriate sulfenylchloride with *N*-methylaniline and purified by vacuum distillation. Unless care was taken the methanesulfenanilide (Ia) rearranged to a mixture of *o*- and *p*-methylthio-*N*-methylanilines during distillation; however, the ethane, 1-methylethane- and 1,1-dimethylethanesulfenanilides could be vacuum distilled without decomposition. The structures of the sulfenanilides were confirmed by examination of their spectra and the observation that under acidic conditions in the presence of iodide ion iodine was liberated.[5,6] The NMR spectra of Ia–Id exhibited resonances for the *N*-methyl groups, the *S*-alkyl groups, and 5-aromatic protons and established that the sulfur atom was attached to the nitrogen atom and not to the aromatic ring.

Upon heating Ia neat at 150 °C in an oil bath, it was observed that it was transformed into a mixture of *o*- and *p*-methylthio-*N*-methylanilines. Vacuum distillation of the crude rearrangement products followed by column chromatography of the sulfide-containing fraction over Florisil in hexane gave 2-methylthio-*N*-methylaniline (IIa) and 4-methylthio-*N*-methylaniline (IIIa) as pure liquids. These compounds were identified by their spectroscopic properties. The NMR spectrum of the ortho isomer showed a complex coupling pattern between δ 7.5 and 6.3 that gave an integrated area of four protons, a broad peak for the amino hydrogen at δ 4.75, a three-proton singlet at δ 2.76 for the *N*-methyl group, and a three-proton singlet at δ 2.18 for the *S*-methyl group. The IR spectrum indicated the presence of the N–H group and an absorption band at 750 cm^{-1} which indicated that this was the ortho isomer. The para isomer gave an NMR spectrum that was composed of an aromatic region, δ 7.48 to 6.15, characteristic of the AA'BB' system of a para-disubsitituted benzene, a broad N–H singlet at δ 4.68, a three-proton singlet for the *N*-methyl group at δ 2.6, and a three-proton singlet for the *S*-methyl group at δ 2.25. The IR spectrum indicated the presence of the N–H group and an absorption band at 820 cm^{-1} which further substantiated the assignment of the para structure. The same products were obtained upon heating Ia at 60 °C in CCl_4, acetonitrile, or CCl_4 with HBr in acetic acid added.

The ethanesulfenanilide (Ib) rearranged as did Ia upon heating in CCl_4 at 60 °C, and the products were separated and identified by the same general procedure just described, the only difference being the presence of an *S*-ethyl group in place of an *S*-methyl group. Under the same conditions, the rearrangement of the *S*-isopropyl, Ic, and *S*-*tert*-butyl, Id, derivatives was not observed, the only products of these attempted rearrangements being *N*-methylaniline and mixtures of dialkyl di- and trisulfides. Heating Ic neat at 150 °C gave a mixture of *N*-methylaniline, isopropyl sulfide, and isopropyl trisulfide. Refluxing Ic in acetonitrile with a trace of *p*-toluenesulfonic acid added gave *N*-methylaniline and isopropyl disulfide as the only identifiable products and heating Ic in benzene with aluminum chloride gave *N*-methylaniline, isopropyl disulfide, and isopropyl trisulfides. Refluxing Ic in

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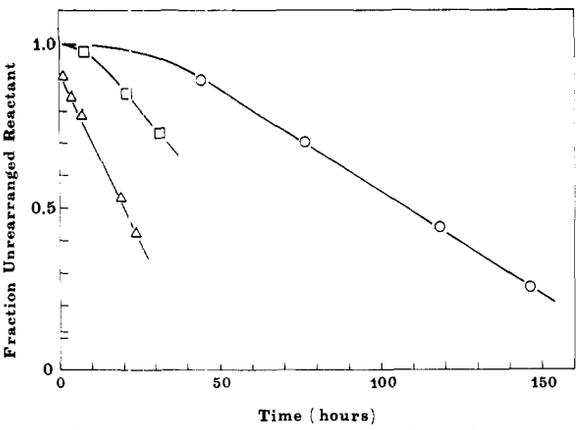

Figure 1. Plot of the fraction of unrearranged Ia vs. time in various solvents (open circles, CD_3CN; squares, CCl_4; triangles, CCl_4 with HBr/HOAc).

ethanol with a molar equivalent of aniline hydrochloride gave *N*-methylaniline, aniline, and isopropyl disulfide as the products. In each of the cases just mentioned, there also were obtained colored materials that were not identified. Similar attempts with Id gave as products disulfides and trisulfides and *N*-methylaniline.

When the rearrangement of Ia in acetonitrile-d_3 was carried out with added *N,N*-dimethylaniline, two new products were observed. Analysis of the product mixture by GC/MS indicated that the new products were methylthio-*N,N*-dimethylanilines based upon the observed molecular ions at *m/e* 167. The *o*- and *p*-methythio-*N,N*-dimethylanilines were prepared by the reaction of methanesulfenyl chloride with dimethylaniline in chloroform. After purification of the products by distillation, they were identified by their NMR spectra and by comparison with the published sepectra.[7] These compounds were shown to be identical with those obtained in the trapping experiment by comparison of the chemical shifts of the sulfur and nitrogen methyl groups, and by comparison, by coinjection onto a gas chromatograph with the material obtained from the rearrangement reaction. The yield of the trapped product was approximately four times the yield of the normal rearrangement products.

The above described experiment suggests two interpretations. Either the rearrangement is in part intermolecular or the rearrangement is exclusively intramolecular with rearrangement occurring following sulfenanilide–amine exchange. The latter is known to occur between primary amines and sulfenanilides and has been used to account for the presence of crossover products when arenesulfenanilides are rearranged in the presence of aniline derivatives.[4] Davis has reported that no crossover products were found when arensulfenanilides were rearranged in *N,N*-diethylaniline[4] since tertiary amines cannot undergo sulfenanilide–amine exchange. Since the sulfenanilide–amine exchange reaction can be ruled out as a reaction pathway for the tertiary amines, the transfer of alkylthio groups from the alkanesulfenanilide to *N,N*-dimethylaniline must have been the result of an intramolecular reaction. This is the first unambiguous demonstration of such an intermolecular rearrangement of sulfenanilides.

We have also made a brief study of the kinetics of the rearrangement by monitoring the NMR spectrum of the reaction mixture as a function of time, Figure 1. Fortunately, the *N*-methyl resonance of the reactant (Ia), δ 3.33, is different from that of IIa, δ 2.75, and IIIa, δ 2.65, so that the relative concentrations of reactants and products can be determined by measuring peak heights in the spectrum. Evaluation of concentrations determined this way shows that in CCl_4 and CCl_4 with a trace to HBr/HOAc, the reaction appears to be zero order, that is a plot of concentration vs. time is linear. The rate is enhanced by the addition of acid so that the reaction also appears to be acid catalyzed.[4] When the kinetics of the rearrangement of Ia in acetonitrile-d_3 was followed by NMR, the plot of concentration vs. time is linear after an initial induction period. This evidence also suggests that the reaction is catalyzed by some species generated in the reaction.

The evidence given above suggests that the rearrangement is at least in part intermolecular. If the slow step in the reaction is the displacement of a protonated amine from the conjugate acid of the sulfenamide by either *N*-methylaniline or *N,N*-dimethylaniline giving the sulfide as one product and an aniline, *N*-methylaniline, as the other, then it is also possible to rationalize the linear plot of concentration vs. time since the reactant is regenerated (eq 1).

$$\mathrm{PhNMeR' + RSN(H^+)\text{—}Me \rightarrow NMe_2\text{–}Ph\text{–}SR + PhN^+H_2Me} \quad (1)$$

R′ = H or Me

It is also possible to rationalize the failure of the *S*-isopropyl and *S*-*tert*-butyl derivatives to react because that reaction corresponds to a nucleophilic displacement in the isobutyl- and neopentylhydrocarbon systems which are known to be slower than displacements in ethyl- and *n*-propylhydrocarbon systems.[8]

The conclusions of the present study are that (1) the rearrangements of sulfenanilides probably provide a convenient route to ortho and para alkythioanilines and (2) the rearrangement is at least in part intermolecular based upon the trapping experiment with *N,N*-dimethylaniline.

Experimental Section

Melting points are corrected. Infrared spectra were run on a Perkin-Elmer 137 spectrophotometer and absorbances are reported in cm^{-1}. Thin-layer chromatograms were run on glass plates coated with a 0.01 in. layer of silica gel PR-254 (Brinkman). GPC analyses were done using a 5 ft by ⅛ in. copper column packed with 5% SE-30 on 60/80 Chromosorb W. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer with tetramethylsilane as the internal standard and carbon tetrachloride as the solvent, unless otherwise indicated. Mass spectra were obtained with a DuPont-492 double-focusing high-resolution spectrometer at an ionizing electron energy of 75 eV, an inlet temperature of 200 °C, and using either the direct or gas chromatograph inlet system. The following materials were obtained commercially and used without purification: *N*-methylaniline, *N,N*-dimethylaniline, and methyl, ethyl, and isopropyl disulfide. *tert*-Butyl disulfide was purified from a crude mixture of disulfide and trisulfide by fractional distillation at 0.1 mmHg through a 6 in. column packed with glass helices.

***N*-Methylmethanesulfenanilide.** In a 100-mL round-botton flask, 4.7 g (0.05 mol) of dimethyl disulfide was dissolved in 50 mL of chloroform, and while the solution was stirred, it was cooled to −40 °C. Then 2.26 mL of liquid chlorine, previously condensed into a graduated centrifuge tube and cooled in a dry ice–acetone bath, was allowed to evaporate into the solution of disulfide while the bath temperature was kept between −35 and −40 °C. The contents of the flask were transferred to an addition funnel and added slowly with stirring to a solution of 10.7 g of *N*-methylaniline (0.1 mol), 50 mL of ether, 5 g of NaOH, and 20 mL of water contained in a 200-mL flask which had been placed in an ice bath. After the addition of sulfenyl chloride was complete, the reaction mixture was stirred for 10 min and transferred to a separatory funnel. The organic layer was separated and washed with tap water until the pH of the aqueous phase was about 6. The organic layer was then separated and dried over sodium sulfate and filtered; the filtrate was concentrated under reduced pressure. The resulting oil was then distilled at 0.1 mmHg, and the fraction boiling at 70–80 °C was collected and analyzed as follows: NMR δ 7.3–6.38 (m, 5, aromatic), 3.33 (s, 3, NCH_3), 2.12 (s, 3, SCH_3); MS *m/e* (rel intensity) 155 (3.5), 154 (3.5), 153 (35), 138 (21), 123 (14), 109 (11), 107 (16), 106 (57), 105 (14), 104 (21), 97 (21), 94 (2), 91 (1.4), 79 (29), 78 (23), 77 (100), 76 (3.5), 74 (3.5), 66 (7), 65 (14), 64 (9.3), 63

(14); $n^{25}D$ 1.5760. The yield based on methanesulfenyl chloride was 70%. Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.19. Found: C, 62.92; H, 7.17.

***N*-Methylethane- and 1-Methylethanesulfenanilide.** The same procedure was followed as outlined for *N*-methylmethanesulfenanilide beginning with the appropriate disulfide. The yields were similar and analytical data are as follows respectively: $n^{25}D$ 1.5653; bp 70 °C (0.1 mm); NMR δ 7.18–6.5 (m, 5, aromatic), 3.2 (s, 3, NCH_3), 2.6 (q, 2, J = 8 Hz, $\mathbf{SCH_2}CH_3$), 1.1 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); MS *m/e* (rel intensity) 169 (3.9), 168 (9), 167 (54), 152 (5.4), 140 (3.9), 139 (18), 138 (45), 123 (11.8), 122 (11.8), 109 (27), 108 (4.5), 107 (45), 106 (100), 105 (18), 104 (30), 98 (57), 80 (34), 79 (34), 78 (100), 66 (16), 65 (18), 64 (9), 51 (50). Anal. Calcd for $C_9H_{13}NS$: C, 64.67; H, 7.78; N, 8.35. Found: C, 64.37; H, 7.64; N, 8.37.

***N*-Methyl-1-methylethanesulfenanilide:** $n^{25}D$ 1.5575; NMR δ 7.2–6.5 (m, 5, aromatic), 3.32 (s, 3, NCH_3), 3.28 (septuplet, 1, $\mathbf{SCH}(Me)_2$), 8.82 (d, 6, J = 8 Hz, $SCH(\mathbf{CH_3})_2$); MS *m/e* (rel intensity) 181 (100), 139 (15), 117 (5), 116 (5), 106 (10), 105 (11), 99 (13), 97 (90), 76 (15), 75 (20), 74 (80), 64 (33), 60 (20), 59 (15), 58 (55). Anal. Calcd for $C_{10}H_{15}NS$: C, 66.29; H, 8.28; N, 7.73. Found: C, 66.11; H, 8.14; N, 7.56.

***N*-Methyl-1,1-dimethylethanesulfenanilide.** The sulfenyl chloride was prepared by dissolving 10.7 g of *tert*-butyl disulfide in 50 mL of chloroform and chlorinolysis at room temperature with 2.26 mL of liquid chlorine. Titration and NMR indicated an 85% yield of *tert*-butylsulfenyl chloride based on the amount of chlorine. The condensation with 10.7 g of *N*-methylaniline and purification was done as described earlier. The product was distilled at 0.1 mmHg with the head temperature ranging from 80 to 90 °C. The analytical data are as follows: $n^{25}H$ 1.5505; NMR δ 7.18–6.5 (m, 5, aromatic), 3.35 (s, 5, NCH_3), 1.22 (s, 9. $SC(CH_3)_3$); MS *m/e* (rel intensity) 197 (0.7), 196 (1.4), 195 (14), 141 (7), 140 (10), 139 (100), 123 (7), 122 (10), 107 (93), 96 (28), 78 (21), 77 (21), 76 (93), 60 (36), 56 (86), 50 (32). Anal. Calcd for $C_{11}H_{17}NS$: C, 67.69; H, 8.71; N, 7.18. Found: C, 67.45; H, 8.60; N, 7.09.

Rearrangement of *N*-Methylmethanesulfenanilide. Rearrangement was accomplished with either pure or crude sulfenanilide by heating it at 150 °C in an oil bath. The extent of reaction was determined by monitoring the concentration of starting material by GLC. After all of the starting material had vanished, the reaction mixture was distilled under 0.1 mm of pressure and several fractions were collected, ranging from 45 to 90 °C. GLC analysis of the fractions indicated the presence of *N*-methylaniline and two other components. Separation of each component was accomplished by column chromatography. The column was packed with Florisil at a weight ratio of 30/1 and hexane was used as the eluent. Fractions with similar composition as determined by TLC were combined, concentrated under reduced pressure, and then distilled at 0.1 mmHg. The overall yield of rearranged products using *N*-methylaniline as the limiting reagent was 35%.

2-Methylthio-*N*-methylaniline: bp 70 °C (0.1 mm); NMR δ 7.48–6.3 (m, 4, aromatic), 4.7 (s, 1, NH), 7.3 (s, 3, NCH_3), 2.18 (s, 3, SCH_3); IR (neat) 3500 (NH), 750 cm^{-1} (ortho-disubstituted benzene). Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.10. Found: C, 63.00; H, 7.35.

4-Methylthio-*N*-methlaniline: bp 78 °C (0.1 mm); NMR δ 7.38–6.08 (m, 4, ArH), 3.68 (s, 1, NH), 2.6 (s, 3, NCH_3), 2.25 (s, 3, SCH_3); IR (neat) 3500 cm^{-1} (NH), 820 cm^{-1} (para-disubstituted benzene). Anal. Calcd for $C_8H_{11}NS$: C, 62.74; H, 7.19. Found: C, 63.01; H, 7.17.

Rearrangement of *N*-Methylethanesulfenanilide. The same procedure as was described earlier for *N*-methylmethanesulfenanilide was followed and the rearranged products were separated the same way. The combined yield of rearranged products was 30% based on *N*-methylaniline.

2-Ethylthio-*N*-methylaniline: bp 80 °C (0.1 mm); NMR δ 7.32–6.22 (m, 4, ArH), 4.92 (s, 1, NH), 2.78 (s, 3, NCH_3), 2.58 (q, 2, $\mathbf{SCH_2}CH_3$), 1.16 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); IR (neat) 3600 (n-H), 760 cm^{-1} (ortho-disubstituted benzene); MS *m/e* (rel intensity) 169 (5.2), 168 (13), 167 (100), 139 (4.3), 138 (30), 137 (53), 136 (8.6), 135 (22), 134 (13), 110 (6.5), 109 (6.5), 108 (22), 105 (22), 104 (8.6), 103 (8.6), 96 (86), 79 (4.3), 78 (8.6), 77 (22), 65 (17), 58 (17), 43 (22).

4-Ethylthio-*N*-methylaniline: bp 85 °C (0.1 mm); NMR δ 7.2–6.18 (m, 4, 4 ArH), 3.58 (s, 1, N_1H), 7.34 (s, 3, NCH_3), 2.62 (q, 2, J = 8 Hz, $\mathbf{SCH_2}CH_3$), 1.18 (t, 3, J = 8 Hz, $SCH_2\mathbf{CH_3}$); IR (neat) 3550 (NH), 815 (para-disubstituted benzene); MS *m/e* (rel intensity) 169 (3.8), 168 (7.1), 167 (50), 154 (11), 153 (22), 152 (22), 150 (22), 139 (22), 139 (14), 138 (100), 136 (18), 106 (14), 76 (14), 58 (14), 43 (64.5). Anal. Calcd for $C_9H_{13}NS$: C, 64.67; H, 7.78. Found: C, 65.20; H, 7.82.

Rearrangement of Ia in *N,N*-Dimethylaniline. A solution of 100 μL of *N*-methylmethanesulfenanilide and 200 μL of *N,N*-dimethylaniline in 1 mL of CD_3CN was placed in a small test tube closed with a cork stopper and kept at 60 °C. The reaction was followed by observing the intensity of the *N*-methyl protons of Ia in the NMR spectrum of the mixture. After complete disappearance of the starting sulfenanilide, the reaction mixture was analyzed by GC/MS and NMR. The GC/MS indicated the presence of two components with *m/e* 167 for the parent ions corresponding to the molecular weights of the two isomeric crossover products *o*- and *p*-methylthio-*N,N*-dimethylaniline. Coinjection of samples of *o*- and *p*-methylthio-*N,N*-dimethylaniline prepared by the reaction of methanesulfenyl chloride with *N,N*-dimethylaniline in chloroform onto a gas chromatograph with the product mixture obtained from the rearrangement reaction gave enhancement of the peaks that corresponded to the material with molecular weights of 167.

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Registry No.—Ia, 65605-22-3; Ib, 63533-62-0; IC, 63533-63-1; Id, 65605-23-4; *N*-methylaniline, 100-61-8; dimethyl disulfide, 624-92-0; diethyl disulfide, 110-81-6; diisopropyl disulfide, 4253-89-8; methanesulfenyl chloride, 5813-48-9; ethanesulfenyl chloride, 1496-75-9; isopropanesulfenyl chloride, 19760-04-4; *tert*-butyl disulfide, 110-06-5; *tert*-butanesulfenyl chloride, 52322-55-1; 2-methylthio-*N*-methylanine, 13372-62-8; 4-methylthio-*N*-methylaniline, 58259-33-9; 2-ethylthio-*N*-methylanilene, 65605-24-5; 4-ethylthio-*N*-methylanilene, 65606-25-6.

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A Major Improvement in the Osmium Catalyzed Vicinal Hydroxylation of Olefins by *tert*-Butyl Hydroperoxide

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We recently described a new osmium catalyzed procedure for the cis dihydroxylation of olefins.[2] Although generally superior to the existing[3] methods for this transformation, it involves rather alkaline conditions, and thus is successful only with molecules which are not sensitive to base. This limitation has now been removed with the discovery that Et_4NOH can be replaced by Et_4NOAc[4] if at the same time the solvent is changed from *tert*-butyl alcohol to acetone.[5]

As revealed in Table I, this new procedure works well for base-sensitive molecules. Esters are not hydrolyzed (entries 4–7), and ethyl crotonate gave only the *threo*-glycol (entries 4–6) with no sign of the epoxide which would arise if conjugate addition of *tert*-butyl hydroperoxide were a competing process. Furthermore, even for simple olefins such as 4-octene

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