The Scope of the Pummerer Reaction[1]

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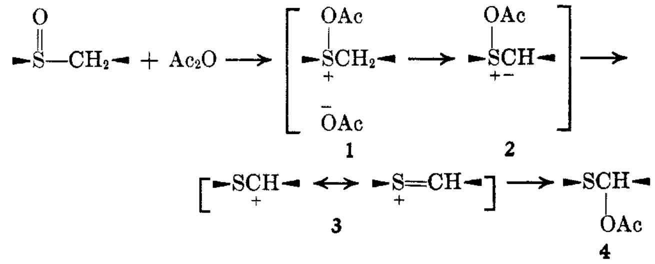
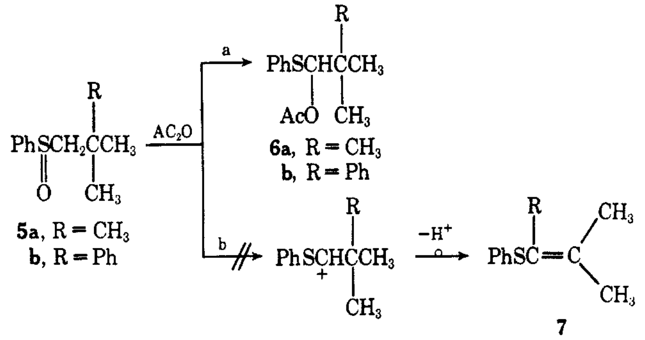
The reactions of acetic anhydride with certain hindered sulfoxides, β-oxy sulfoxides, vinyl sulfoxides, and unsymmetrical sulfoxides are described.

The decomposition of sulfoxides in hot acetic anhydride,[3] a reaction analogous to that reported by Pummerer,[4] has been shown to be an attractive preparative route to α-acetoxy sulfides[3] and certain α,β-unsaturated sulfides.[5,6] The acyloxysulfonium salt **1**, the ylide **2**, and the carbonium ion[7] **3** have been suggested as intermediates; however, the mechanism of the reaction has not been vigorously defined and has been the subject of much speculation.[8]

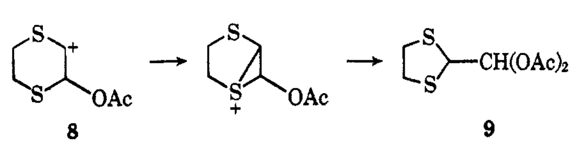


We would like to report at this time additional examples which relate to the scope of this reaction.

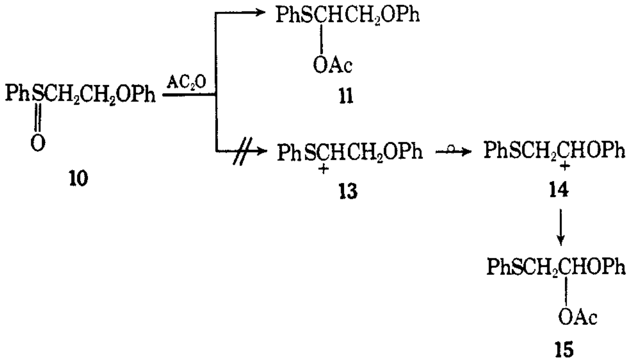
Hindered Sulfoxide.—The reaction of acetic anhydride with the hindered sulfoxides **5a** and **5b** were examined at 100° in an atmosphere of nitrogen. In both cases very selective reactions occurred to give the α-acetoxy sulfides **6**. In neither case were there any products found of type **7**, which could logically result by reaction as shown in path b. The acetates **6a** and **6b** were isolated pure, and their structures were established by their conversion into the 2,4-dinitrophenylhydrazones of the corresponding aldehydes. The reactions of **5a** and **5b** were slow in comparison with similar reactions with unhindered sulfoxides. The conversion of **5a** into **6a** at 100° was 55% after 21 hr and 87% after 42 hr; after 66 hr no starting sulfoxides could be detected (vpc). *n*-Butyl methyl sulfoxide, by comparison, was found to be reacted completely in 4.5 hr at 100°.



β-Oxy Sulfoxides.—The formation of the rearranged acetate **9** from **8** (formed *in situ*) has been cited[7b] as evidence for the carbonium-ion intermediate of type **3** in the Pummerer reaction. We have examined the reaction of acetic anhydride with **10** and **16**, both of which could give more stable rearranged carbonium ion as intermediates, to determine whether rearrangement products might be generally formed from reaction of acetic anhydride with β-oxy sulfoxides.



The reaction of β-(phenylsulfinyl)phenetole (**10**) with acetic anhydride was carried out for 23.5 hr at 100°. The products were recovered **10** (~19.6%), β-(phenylsulfonyl)phenetole (~5.4%), and β-acetoxy-β-(phenylthio)phenetole (**11**, mp 70–71°, 76%). The acetate **11** was obtained pure, and its structure was confirmed by its conversion into β-phenoxyacetaldehyde semicarbazone. There was no evidence for the formation of **15**, which could result by rearrangement of the carbonium ion **13** to the more stable carbonium ion **14**.[9]



Simarily, reaction of the sulfoxide **16**[10] with acetic anhydride for 24 hr at 100° gave recovered sulfoxide **16** (23%) and the acetate **17** (55%). Desulfurization of the product with Raney nickel gave only tetrahydrofurfuryl acetate, derived from **17**. There was no

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[2] From the Ph.D. Thesis of L. D. Edwards, The University of Minnesota, 1967.

[3] L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959).

[4] R. Pummerer, *Ber.*, **42**, 2282 (1909); **43**, 1401 (1910).

[5] W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961).

[6] W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

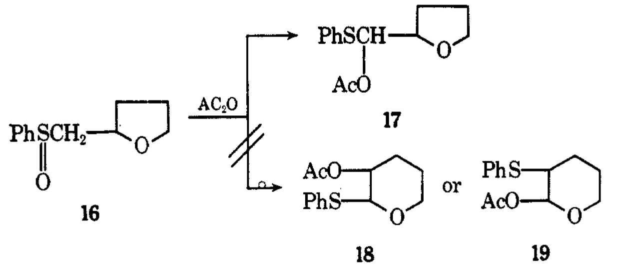
[7] (a) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955); (b) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963); (c) C. R. Johnson, J. C. Sharp, and W. G. Phillips, *Tetrahedron Lett.* 5299 (1967); (d) W. E. Parham and S. H. Goren, *J. Org. Chem.*, **30**, 728 (1965).

[8] For discussion and leading references, see T. L. Moore, *ibid.*, **32**, 2786 (1967), and ref 7.

[9] For leading references, see ref 7b.

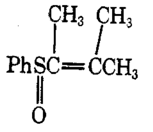
[10] This sulfoxide was chosen since it is known that tetrahydrofurfuryl tosylate undergoes rearrangement upon solvolysis to 3-acetoxytetrahydrofuran, and the rearranged carbonium ion would be more stable since the vacant p orbital would be adjacent to oxygen rather than sulfur. *Cf.* D. Gagnaire and A. Butt, *Bull. Soc. Chim. Fr.*, 309 (1961), and S. Moon and J. M. Lodge, *J. Org. Chem.*, **29**, 3453 (1964).

evidence (vpc) for 3-acetoxytetrahydropyran or 2-acetoxytetrahydropyran, which would have been formed had the product contained the rearrangement products **18** or **19**. Authentic 3-acetoxytetrahydropyran and 2-acetoxytetrahydropyran were prepared for the analysis.



Since no rearrangement products accompanied the reaction of sulfoxides **5**, **10**, and **16**, in their reaction with acetic anhydride, it was concluded that carbonium ions, if formed as intermediates, undergo solvolysis quite rapidly; rearrangement products are to be expected only in cases, such as **8**, where structural features for rearrangement are exceptionally favorable.

We have observed that vinyl sulfoxides, such as 2-methyl-3-phenylsulfinyl-2-butene (**20**) and cyclohexenyl phenyl sulfoxide (**21**), are stable to hot acetic anhydride (100° for 24 hr). Similarily, phenyl *p*-tolyl sulfoxide and phenyl *o*-tolyl sulfoxide were recovered, essentially quantitatively, even when benzoic anhydride at 187° was used in place of hot acetic anhydride. Failure of vinyl sulfoxides to undergo the Pummerer reaction with acetic anhydride is consistent with the conclusion that elimination of acetic acid from **1** occurs by a cyclic elimination mechanism[7a] as shown in **22**. The possibility cannot, however, be excluded that the ylide **2** is an intermediate and that hydrogen atoms in vinyl sulfoxides are not acidic enough to undergo E1 or E2 elimination reactions under the conditions of reaction.



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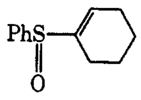

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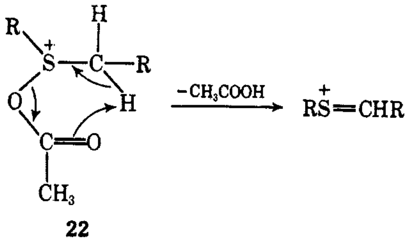

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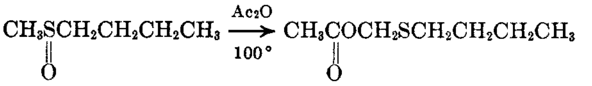
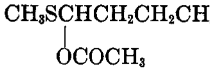
In a recent study of the selectivity of the Pummerer reaction, Johnson, Sharp, and Phillips[7c] concluded that removal of the proton from **1** is the product-determining (and possibly rate-determining) step of the reaction and that carbonium ions of type **3** are formed as intermediates. These workers observed that the only products formed from a series of unsymmetrical methyl alkyl sulfoxides were those derived by migration of acetate to the least substituted α carbon. Our results with two unsymmetric sulfoxides were less definitive than those reported, but were in agreement and consistent with the conclusion that the most acidic hydrogen of the sulfoxide is preferentially lost.

The reaction of **23** with acetic anhydride was carried out at 100° for 4.5 hr. Analysis of the crude product (vpc) showed the absence of sulfoxide and the presence of **24** (∼50.3%) and **26** (∼4%, identical retention time to authentic material). The acetate **24** was obtained pure by vpc. No other products were detected in large amounts, and the poor material balance was not explained or improved in a subsequent experiment. These results compare with a 64% yield of **24** obtained by reaction of **23** with acetic anhydride in boiling benzene.[7c]



$$CH_3\underset{\underset{O}{\|}}{S}CH_2CH_2CH_2CH_3 \xrightarrow[100^\circ]{Ac_2O} CH_3\underset{\underset{O}{\|}}{C}OCH_2SCH_2CH_2CH_2CH_3$$

23 **24**

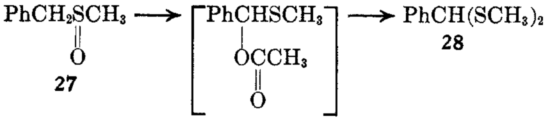


$$CH_3S\underset{\underset{OCOCH_3}{|}}{CH}CH_2CH_2CH_3$$

25

$CH_3SCH{=}CHCH_2CH_3$ **26**

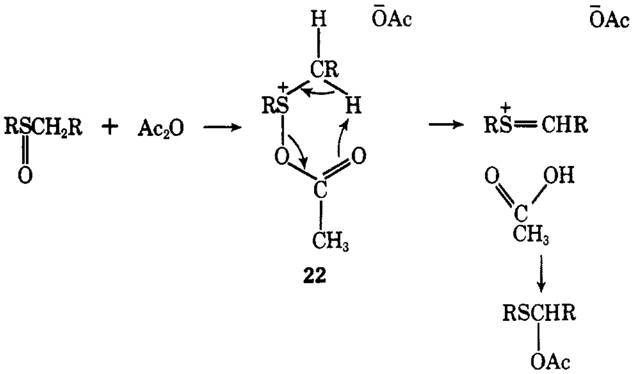
The reaction of benzyl methyl sulfoxide (**27**) with acetic anhydride (100°, 20 hr) gave, subsequent to extraction, water wash, and chromatography, a 57% yield of the dimethyl mercaptal of benzaldehyde (**28**). The product **28** can be rationalized by assuming that the original Pummerer reaction occurred (preferentially) on the more acidic benzyl carbon atom.



$$PhCH_2\underset{\underset{O}{\|}}{S}CH_3 \longrightarrow \left[PhCH\underset{|}{}SCH_3 \atop O\underset{\underset{O}{\|}}{C}CH_3\right] \longrightarrow PhCH(SCH_3)_2$$

27 **28**

While it is recognized that the mechanism of the Pummerer reaction may vary markedly with subtle changes in structure of starting sulfoxide and with changes in reaction conditions, as is characteristic of other elimination and substitution processes, we currently favor the reaction sequence shown in the accompanying equation as the most general one for those reactions involving anhydrides.



This reaction sequence is consistent with (a) the observation that the most acidic hydrogen atom of the sulfoxide is preferentially eliminated; (b) the observation that sulfoxides such as **20** and **21**, which are geometrically unsuited for formation of transition states similar to **22**, are stable to the usual reaction conditions; and (c) the observed rearrangement, characteristic of carbonium-ion intermediates, that has been observed with a sulfoxide where structural features for rearrangement are exceptionally favorable. Alternative mechanisms cannot, however, be eliminated and details of mechansims of this modified Pummerer reaction cannot be considered as settled.

Experimental Section

2,2-Dimethylpropyl Phenyl Sulfide.—Thiophenol (132 g, 1.2 mol) and neopentyl *p*-toluenesulfonate (145 g, 0.6 mol, mp 45–47.5°, 82% yield from *p*-toluenesulfonyl chloride and neopentyl alcohol[11]) were added successively to a solution prepared from sodium (27.7 g, 1.2 g-atom) and 2-ethoxyethanol. The mixture was heated at the reflux temperature under nitrogen for 20 hr and was then cooled and filtered. The precipitate was washed with ether, and water (2000 ml) was added to the combined filtrate and ether wash. The resulting mixture was extracted with four 200-ml portions of ether, and the ether extract was washed with water, dried ($MgSO_4$), and distilled to give 100 g (92.6% yield) of 2,2-dimethylpropyl phenyl sulfide: bp 75–76° (0.85 mm); $n^{25.5}\text{D}$ 1.5339. The nmr spectrum of the sulfide (neat) showed τ 2.50–2.98 (m, aromatic **H**, wt 5), 7.20 (s, $\mathbf{SCH_2}$, wt 2), 9.02 (s, CH_3, wt 9).

Anal. Calcd for $C_{11}H_{16}S$: C, 73.27; H, 8.95; S, 17.78. Found: C, 72.99; H, 9.17; S, 17.68.

2,2-Dimethylpropyl Phenyl Sulfoxide (5a).—Hydrogen peroxide (30%, 11.4 g, 0.10 mol) was added dropwise to a solution of 2,2-dimethylpropyl phenyl sulfide (18.03 g, 0.10 mol), methanol (400 ml), and formic acid (97%, 10 ml), and the mixture was refluxed for 17 hr. Methanol (325 ml) was removed from the mixture by distillation, and the residual liquid was diluted with water (500 ml) and extracted with ether (~300 ml). The dried ($MgSO_4$) extract was distilled to give 14.8 g (75.5% yield) of 2,2-dimethylpropyl phenyl sulfoxide: bp 83–86° (0.1 mm); $n^{23.5}\text{D}$ 1.5358. The nmr spectrum of **5a** (32% CCl_4) showed τ 2.33–2.75 (m, aromatic **H**, wt 5), τ_A 7.38, τ_B 7.52 (AB pattern, $\mathbf{-SOCH_2}$, wt 2, J_{AB} = 13.5 Hz), τ 8.85 (s, CH_3, wt 9).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.58; H, 8.31; S, 16.26.

2,2-Dimethylpropyl phenyl sulfone was prepared [55% yield, mp 38–39° from petroleum ether (bp 60–68°)-benzene] by oxidation of **5a** with hydrogen peroxide in acetic acid (2.5 hr at the reflux temperature).

Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10. Found: C, 62.15; H, 7.40; S, 15.00.

Reaction of 2,2-Dimethylpropyl Phenyl Sulfoxide with Acetic Anhydride. A.—A mixture of **5a** (3.0 g, 0.015 mol) and acetic anhydride (4.6 ml) was heated under an atmosphere of nitrogen for 21 hr at 95°. The mixture was distilled to give 2.9 g of crude 1-acetoxy-2,2-dimethylpropyl phenyl sulfide (**6a**): bp 67–77° (0.8 mm); $n^{20}\text{D}$ 1.520. The product (1.83 g) was chromatographed on alumina (50 g), and the acetate (1.16 g) was eluted with petroleum ether (bp 60–68°)-benzene (4:1, 600 ml). The nearly pure acetate was rechromatographed as described above (on 30 g of alumina) to give pure **6a**: 0.88 g, 30.8% yield; $n^{26}\text{D}$ 1.5221; nmr (~10% CCl_4), τ 2.4–3.0 (m, aromatic **H**, wt 5), 4.05 (s, **-SCH-**, wt 1), 8.1 (s, $\mathbf{CH_3}$CO, wt 1), 8.95 [s, $\mathbf{(CH_3)_3}$C, wt 9].

Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; S, 13.45. Found: C, 65.80; H, 7.62; S, 13.51.

B.—The reaction was repeated as described in A for 24 hr at 100°, and the mixture was analyzed by gas chromatography (liquid phase 20% SE-30, 125°); hexamethylbenzene was used as an internal standard. The mixture contained 1-acetoxy-2,2-dimethylpropyl phenyl sulfide (46.9 ± 0.5%) and 2,2-dimethylpropyl phenyl sulfoxide (53.1 ± 0.5%).

C.—The reaction was repeated, and the mixture was analyzed by vpc (liquid phase 20% Apiezon L, 200°). The per cent conversion of starting sulfoxide was 55, 87, and 100% after 21, 42, and 66 hr, respectively. These analyses showed the presence of only **5a** and **6a**; no 2-methyl-3-phenylthio-2-butene (**7a**) was detected.

Reaction of 1-acetoxy-2,2-dimethylpropyl phenyl sulfide (0.50 g, 0.0021 mol) with 2,4-dinitrophenylhydrazine reagent[12a] gave the **2,4-dinitrophenylhydrazone of trimethylacetaldehyde** (0.32 g, 57% yield, mp 209.5–212°) which was identical with the derivative (mp 210–211°, mmp 209–212°) prepared[13] from trimethylacetaldehyde.

2-Methyl-3-phenylthio-2-butene (7a).—A mixture of methyl isopropyl ketone (43.07 g, 0.5 mol) and thiophenol (40.0 g, 0.36 mol) was stirred at 0°, and dry hydrogen chloride was passed through the stirred mixture while thiophenol (70.17 g, 0.64 mol) was added dropwise; the reaction temperature was maintained below 10°. Hydrogen chloride was passed through the mixture for an additional 40 min. The mixture was then allowed to warm to 30° and was distilled to give 75.8 g of product: bp 113–117° (10 mm); $n^{25}\text{D}$ 1.5725. The distillate was dissolved in ether, and the ether solution was extracted with 2 *M* sodium hydroxide to remove thiophenol. The dried (Na_2SO_4) extract was distilled through a 20-cm spiral wire column. The product (46.5 g) was shown to contain two products by vpc (liquid phase 20% SE-30, 105°) and was purified by fractionation through a Nester-Faust spinning-band column to give 41.26 g (46.3% yield) of pure **7a**: bp 49.5–50.5° (0.03 mm); $n^{26}\text{D}$ 1.5698 [lit.[14] bp 64° (0.7 mm); $n^{25}\text{D}$ 1.5696]; nmr (~10% CCl_4), τ 2.8–3.1 (m, aromatic **H**, wt 5) and 7.9–8.3 (m, CH_3, wt 9).

2-Methyl-3-phenylsulfinyl-2-butene (20).—The oxidation of **7a** (5.35 g, 0.03 mol) with hydrogen peroxide was carried out as described for 2,2-dimethylpropyl phenyl sulfide. The crude product was chromatographed on silica gel, and the column was developed with petroleum ether (bp 60–68°), petroleum ether–benzene (9:1, 150 ml; 7:3, 150 ml; 2:3, 150 ml), benzene (450 ml), benzene–chloroform (9:1, 150 ml, 7:3, 150 ml, 2:3, 150 ml), chloroform (450 ml), and chloroform–ether (9:1, 450 ml). The last fraction gave 4.02 g (71% yield) of pure **20**: mp 75–76.5°; nmr (10% CCl_4), τ 2.50–2.80 (aromatic **H**, wt 5) and 7.8, 8.2, and 8.4 (three singlets, CH_3, wt 9).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.02; H, 7.27; S, 16.48. Found: C, 67.89; H, 7.18; S, 16.35.

2-Methyl-2-phenylpropyl phenyl sulfide was prepared from neophyl chloride[15] (84.3 g, 0.50 mol), thiophenol (63.5 g, 0.575 mol), and potassium hydroxide (32.3 g, 0.575 mol) in dimethylacetamide (425 ml) essentially as described[16] for other sulfides (20 hr at reflux). There was obtained 119 g (98.6% yield) of sulfide: bp 100–104° (0.01 mm); $n^{25.5}\text{D}$ 1.5950. A redistilled sample, bp 117.5–118.5° (0.02 mm), $n^{25.5}\text{D}$ 1.5969, of product showed an nmr spectrum in 10% CCl_4 of τ 2.5–3.1 (m, aromatic **H**, wt 10), 6.9 (s, $\mathbf{-SCH_2-}$, wt 2), and 8.7 (s, $\mathbf{CH_3-}$, wt 6).

Anal. Calcd for $C_{16}H_{18}S$: C, 79.31; H, 7.49; S, 13.21. Found: C, 79.60; H, 7.25; S, 13.11.

2-Methyl-2-phenylpropyl phenyl sulfoxide (5b) [39.5 g, 77.2% yield, mp 34–37°, bp 149–152° (0.007 mm), $n^{25}\text{D}$ 1.5927] was prepared by oxidation of 2-methyl-2-phenylpropyl phenyl sulfide (48.5 g, 0.2 mol) as described for the oxidation of **5a**. The nmr spectrum of **5b** (10% CCl_4) showed τ 2.5–3.0 (m, aromatic **H**, wt 10), 7.15 (s, $\mathbf{-SOCH_2-}$, wt 2), and 8.35 and 8.55 (two singlets, CH_3, wt 6).

Anal. Calcd for $C_{16}H_{18}OS$: C, 74.39; H, 7.02; S, 12.39. Found: C, 74.62; H, 7.01; S, 12.22.

Reaction of 2-Methyl-2-phenylpropyl Phenyl Sulfoxide with Acetic Anhydride.—The reaction of **5b** (12.95 g, 0.05 mol) with acetic anhydride (15 ml) was carried out as described for **5a**. The crude product (14.4 g, $n^{25}\text{D}$ 1.5650) was chromatographed on silica gel (300 g). Elution of the column with petroleum ether (bp 60–68°)-chloroform (9:1, 1200 ml; 7:3, 1200 ml; 3:2, 1200 ml; 1:1, 1200 ml; 2:3, 600 ml) gave only a trace of material which was discarded. Elution of the column with petroleum ether-chloroform (2:3, 3000 ml) gave 8.2 g (53.9% yield) of 1-acetoxy-2-methyl-2-phenylpropyl phenyl sulfide (**6b**, $n^{25}\text{D}$ 1.5594); elution of the column with additional petroleum ether-chloroform (2:3, 1500 ml) gave 4.35 g (33.6%) of recovered 2-methyl-2-phenylpropyl phenyl sulfoxide, which had $n^{25}\text{D}$ 1.5608. The nmr spectrum of **6b** (10% CCl_4) showed τ 2.5–3.1 (m, aromatic **H**, wt 10), 3.7 (s, SCH, wt 1), 8.3 (s, $\mathbf{CH_3}$CO, wt 3), and *ca.* 8.5 (two singlets, $\mathbf{CH_3}$C, total wt 6).

Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.98; H, 6.71; S, 10.65. Found: C, 71.77; H, 6.89; S, 11.00.

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(11) F. M. Beringer and H. S. Schultz, *J. Amer. Chem. Soc.*, **77**, 5533 (1955).

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(14) T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

(15) W. T. Smith and J. T. Sellas, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 702.

(16) J. R. Campbell, *J. Org. Chem.*, **29**, 1830 (1964).

The acetate **6b** (0.25 g, 0.00083 mol) was treated with 2,4-dinitrophenylhydrazine reagent. The solid, collected after 24 hr, was recrystallized from ethanol to give 0.20 g (74% yield) of the **2,4-dinitrophenylhydrazone of 2-methyl-2-phenylpropanal** [melting point and mixture melting point of a sample (mp 143–144°) prepared from authentic 2-methyl-2-phenylpropanal was 143–144°].

Anal. Calcd for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.07. Found: C, 58.58; H, 5.14; N, 16.79.

β-(Phenylthio)phenetole was prepared from thiophenol (23.2 g, 0.21 mol), β-chlorophenetole[17] (31.4 g, 0.20 mol), and sodium hydroxide (8.4 g, 0.21 mol) in ethanol (100 ml). After 1 hr at the reflux temperature, the mixture was processed to give 42.4 g (92% yield) of product, mp 66–67.5° (from ethanol).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.00; H, 6.13; S, 13.92. Found: C, 73.26; H, 6.14; S, 14.00.

β-(Phenylsulfinyl)phenetole (10), mp 66–68° (from petroleum ether–benzene), was prepared in 85% yield by oxidation of β-(phenylthio)phenetole in acetic acid with hydrogen peroxide at 10°. The nmr spectrum of **10** (~10% $CDCl_3$) showed τ 2.3–3.3 (m, aromatic **H**, wt 10), $SOC\mathbf{H}_2$ centered at 6.85 (t, wt 2), 5.3–6.1 (O–$C\mathbf{H}_2$, AB pattern, further split by two other protons with J_{AB} = 10.6 Hz, calculated chemical shifts τ_A 5.58 and τ_B 5.84, wt 2).

Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; S, 13.02 Found: C, 68.26; H, 5.75; S, 13.28.

Oxidation of **10** (2.3 g, 0.01 mol) with 30% hydrogen peroxide [20.5 mol, 0.2 mol in formic acid (30 ml)], and carbon tetrachloride (50 ml) at the reflux temperature gave crude β-(phenylsulfonyl)phenetole which was purified by liquid chromatography on silica gel. The column was eluted with petroleum ether (bp 60–68°) and combinations of petroleum ether and chloroform. Nearly pure **β-(phenylsulfonyl)phenetole** [mp 125–126.5, 127–128° from hexane–benzene (lit.[18] mp 120°)] was obtained by use of petroleum ether–chloroform (7:3); the nmr spectrum of the sulfone (11% $CDCl_3$) showed τ 2.0–3.5 (m, aromatic **H**, wt 10), O–$C\mathbf{H}_2$ centered at 5.65 (t, wt 2), $SO_2C\mathbf{H}_2$ centered at 6.4 (t, wt 2).

Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38; S, 12.23. Found: C, 64.37; H, 5.32; S, 12.26.

Reaction of 10 with Acetic Anhydride.—Acetic anhydride (9 ml, 0.097 mol) and **10** (7.39 g, 0.03 mol) were mixed and heated at 100° under nitrogen. At the end of 23.5 hr the mixture was cooled and diluted with water (1500 ml) and extracted with ether (five 100-ml portions). The ether extract was washed with saturated sodium bicarbonate [three 100-ml portions and water (100 ml)], dried ($MgSO_4$), and concentrated. The semisolid (10.3 g) was chromatographed on silica gel (100 g). Elution of the column with petroleum ether (bp 60–68°) and with petroleum ether–chloroform (9:1, 600 ml) gave 0.129 g of tar which was discarded; elution with petroleum ether–chloroform (4:1, 3900 ml) gave 5.29 g (76% yield based on recovered starting material) of β-(acetoxy)-β-(phenylthio)phenetole (**11**). Elution of the column with petroleum ether–chloroform (4:1, 900 ml) gave, after recrystallization of the product from hexane–benzene, 0.35 g (5.4% yield) of β-(phenylsulfonyl)phenetole (mp and mmp 126.5–128.5). Elution of the column with petroleum ether–chloroform (1:1, 1200 ml) gave 1.47 g (19.6% recovery of **10**, mp 67–68.5° from hexane–benzene).

Acetate **11**, mp 70–71.5°, showed an nmr spectrum (~10% $CDCl_3$) of τ 2.4–3.3 (m, aromatic **H**, wt 10) and 8.0 (s, $C\mathbf{H}_3CO$, wt 3). The three remaining protons formed a typical ABX pattern, with the X proton, SC**H**, centered at τ 3.65, wt 1, and J_{AX} = 6.6 Hz and J_{BX} = 5.2 Hz; the AB protons, $C\mathbf{H}_2O$, gave a pattern such that the outside lines were unobservable, and three observable bands appeared at τ 5.81, 5.89, and 5.92, wt 2.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.59; S, 11.10. Found: C, 66.66; H, 5.54; S, 11.10.

In another run (20.5 hr at 100°) the acid was not neutralized. The entire product was distilled. There was obtained 1.71 g (31% yield) of **phenyl-2(phenylthio)vinyl ether**: bp 132–140° (0.02 mm); $n^{26}D$ 1.6289 [lit.[19] bp 110–113° (0.05 mm); $n^{20}D$ 1.6350].

Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30; S, 14.04. Found: C, 73.70; H, 5.58; S, 14.19.

The **hydrolysis of 11** (0.58 g, 0.002 mol) was achieved using mercuric chloride (1.09 g, 0.004 mol) and sulfuric acid (0.5 ml) in water (20 ml) and methanol (20 ml). The mixture was heated for 0.5 hr at the reflux temperature and was then filtered. The filtrate and wash (methanol) of the precipitate were combined, diluted with water, and extracted with ether. The extract was washed (saturated sodium bicarbonate), dried ($MgSO_4$), and concentrated. The semicarbazone of the residue was prepared in the usual way[12b] and melted at 148.5–150° (from ethanol) (lit.[20] mp 145°). The product was identical (mmp 148.5–150°) with the semicarbazone prepared[12b] from authentic phenoxyacetaldehyde (mp 150–151°).

Anal. Calcd for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 55.79; H, 5.79; N, 21.36.

Phenyl tetrahydrofurfuryl sulfide [84.5% yield, bp 93–95° (0.15 mm), $n^{22}D$ 1.5702] was prepared from thiophenol and tetrahydrofurfuryl tosylate[21] by a procedure similar to that described for 2,2-dimethylpropyl phenyl sulfide. The nmr spectrum of the sulfide (10% CCl_4) showed τ 2.6–3.1 (m, aromatic **H**, wt 5), 5.85–6.6 (m, $\mathbf{CHOCH_2}$, wt 3), and 6.7–7.4 (ABX, SCH_2, and 7.9–8.65 (m, $CC\mathbf{H}_2C\mathbf{H}_2C$, wt 4).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.02; H, 7.27; S, 16.47. Found: C, 68.30; H, 7.54; S, 16.18.

Phenyl tetrahydrofurfuryl sulfoxide (16) was prepared by oxidation of phenyl tetrahydrofurfuryl sulfide (19.43 g, 0.10 mol) with hydrogen peroxide in acetic acid at 10°. The crude sulfoxide (19.0 g) was chromatographed on silica gel (150 g). Most of the sulfoxide was eluted with benzene, benzene–chloroform, and chloroform, and slightly impure **16** containing trace amounts of sulfide and diphenyl disulfide (vpc, liquid phase 20% SE-30, 150°) was obtained in 80% yield (16.8 g). This product was distilled to give pure **16**: bp 135–137° (0.02 mm); $n^{27}D$ 1.5652; nmr (10% CCl_4), τ 2.2–2.8 (m, aromatic **H**, wt 5), 5.6–6.6 (m, $-\mathbf{CHOCH_2}-$, wt 3), 7.0–7.3 (two doublets, $-SOC\mathbf{H}_2C$, wt 2), and 7.8–8.6 (m, $-CC\mathbf{H}_2C\mathbf{H}_2C$, wt 4).

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.84; H, 6.71; S, 15.22. Found: C, 62.57; H, 6.98; S, 15.33.

Phenyl tetrahydrofurfuryl sulfone was obtained as an oil ($n^{23.5}D$ 1.5440) which was distilled in a Babcock distillation apparatus.

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.40; H, 6.24; S, 14.14. Found: C, 58.21; H, 6.21; S, 14.34.

The reaction of phenyl tetrahydrofurfuryl sulfoxide with acetic anhydride was carried out as described for **5a**. The crude product (3.9 g) was chromatographed on silica gel (80 g), and the column was developed with petroleum ether, benzene, and chloroform, using various logical mixtures of these solvents. There was obtained 2.7 g ($n^{25}D$ 1.5404, 55% yield) of acetoxytetrahydrofurfural phenyl sulfide (**17**, with benzene–chloroform, 3:2, 600 ml) and 0.944 g ($n^{25}D$ 1.5640, 23% recovery) of phenyl tetrahydrofurfuryl sulfoxide.

The nmr spectrum (10% CCl_4) of **17** showed τ 2.4–3.0 (m, aromatic, **H**, wt 5), centered at 3.9 and 4.1 (two doublets, SC**H**, wt 1), 5.8–6.5 (m, $-\mathbf{CHOCH_2}$, wt 3), and 7.9–8.4 ($C\mathbf{H}_3CO$ and $-CC\mathbf{H}_2C\mathbf{H}_2C-$, wt 7).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39; S, 12.68. Found: C, 61.60; H, 6.51; S, 12.48.

Proof of Structure of Acetoxytetrahydrofurfural Phenyl Sulfide.—A mixture of **17** (2.434 g, 0.00965 mol), Raney nickel (*ca.* 45 g), and absolute ethanol (125 ml) was heated at the reflux temperature for 7.5 hr. The mixture was filtered, the nickel was washed with ethanol, and the combined filtrate was dried ($MgSO_4$) and concentrated under a 30-cm spiral wire column. The residue was transferred with ether, and the ether was dried ($MgSO_4$) and concentrated to give 1.1 g (80% yield) of pure (vpc, liquid phase 20% Carbowax 20M, 110°) tetrahydrofurfural acetate ($n^{25}D$ 1.4360). Tetrahydrofurfuryl alcohol (retention time 20.5 min), 2-acetoxytetrahydropyran[22] (retention time 18 min), and 3-acetoxytetrahydropyran (retention time 25.5 min) were shown to be absent (vpc).

3-Acetoxytetrahydropyran.—The procedure of Moon and Lodge[10] gave a mixture of isomeric acetates (20% yield) composed (vpc, liquid phase 20% Carbowax 20M, 100°) of about 87% tetrahydrofurfuryl acetate.

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3-Acetoxytetrahydropyran, bp 70–71° (6 mm), $n^{26}\mathrm{D}$ 1.4383 was prepared by a modification of the procedure of Barker[23] and coworkers who prepared 3-hydroxytetrahydropyran. The crude 3-hydroxypyran (16.8% over-all yield from dihydropyran) was acetylated in pyridine with acetic anhydride to give 3-acetoxytetrahydropyran.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 57.97; H, 8.09.

Cyclohexenyl phenyl sulfoxide was prepared by oxidation of cyclohexenyl phenyl sulfide[24] essentially as described for the preparation of **5a**. The crude sulfoxide (19.9 g) was purified by chromatography on silica gel (200 g) and **21** (11.5 g, 56% yield) was eluted with benzene–chloroform (1:1, 1000 ml; 3:7, 450 ml) and with chloroform (450 ml). The product showed only one peak in vpc (the liquid phase 20% SE-30, 150°) and was distilled, bp 121–122° (0.05 mm), $n^{25}\mathrm{D}$ 1.5881.

Anal. Calcd for $C_{12}H_{14}OS$: C, 69.88; H, 6.84; S, 15.52. Found: C, 69.59; H, 6.89; S, 15.70.

Reaction of *n*-Butyl Phenyl Sulfoxide with Acetic Anhydride.—The reaction of *n*-butyl phenyl sulfoxide[25] (6.0 g, 0.033 mol) with acetic anhydride (9 ml, 0.095 mol) was carried out under nitrogen for 19 hr at 104°. Distillation of the residue gave 4.41 g (82% yield) of **1-butenyl phenyl sulfide**: bp 98–102° (0.15 mm); $n^{25}\mathrm{D}$ 1.5675 [lit.[26] bp 62° (0.22 mm); $n^{20}\mathrm{D}$ 1.5700].

Anal. Calcd for $C_{10}H_{12}S$: C, 73.14; H, 7.37; S, 19.49. Found: C, 72.93; H, 7.51; S, 19.46.

Reaction of *n*-Butyl Methyl Sulfoxide with Acetic Anhydride.—The product obtained (100°, 20 hr, under nitrogen) from **23**[27] (4.0 g, 0.034 mol) and acetic anhydride (10 ml) was treated with water (150 ml) and then extracted with ether. The extract was washed with aqueous bicarbonate and with water and was then dried and concentrated. The residue (3.91 g) was chromatographed on silica gel (100 g). 1-Acetoxymethyl *n*-butyl sulfide, $n^{25}\mathrm{D}$ 1.4554, bp 86–87° (9 mm) [lit.[28] $n^{25}\mathrm{D}$ 1.4538, bp 53–60° (15 mm)], which showed only one peak when analyzed by vpc (liquid phase 20% diisodecylphthalate, 150°; liquid phase 20% DC-710, 100°), was eluted mostly with petroleum ether (bp 60–68°) and benzene in the ratio of 2:3. The nmr spectrum of **24** (48% CCl_4) showed τ 4.9 (s, $O\mathbf{CH_2}S$, wt 2), $S\mathbf{CH}C_2$ centered at 7.37 (t, J = 7 Hz, wt 2), and 8.0 (s, $\mathbf{CH_3}CO$, wt 3).

Anal. Calcd for $C_7H_{14}O_2S$: C, 51.84; H, 8.70; S, 19.75. Found: C, 52.11; H, 9.00; S, 19.58.

The reaction was repeated, and the crude products were analyzed by vpc (liquid phase 20% DC-710, programmed 40–100°). The yield of **24** was ~50.3%; the yield of 1-butenyl methyl sulfide was 3.9%, and butraldehyde and butyric acid by vpc (Porapak Q, column temperature 130 and 170°, respectively) were shown to be absent.

***cis,trans*-1-Butenyl Methyl Sulfide.**—Hydrogen chloride was bubbled through methyl mercaptan (62.2 g, 1.29 mol) cooled in a Dry Ice–acetone bath, and butraldehyde (46 g, 0.65 mol) was added over a 45-min period. The cold mixture was allowed to stand for 1 hr and was then allowed to warm to 30° and was washed with 2 *N* sodium hydroxide. Phosphoric acid (6 drops) was added, and the dried liquid was distilled rapidly, at atmospheric pressure, through a 12-cm Vigreux column (maximum head temperature 126°). The distillate was washed in ether with 2 *N* sodium hydroxide (two 50-ml portions) and water. The dried solution was distilled to give 20.9 g (31.7% yield) of 1-butenyl methyl sulfide: bp 123–126°; $n^{25}\mathrm{D}$ 1.4809. The nmr spectrum of 26 (75% CCl_4) showed τ 9 (two triplets separated by 1 Hz, $\mathbf{CH_3}$–C, centered at a distance to the outside lines of 8 Hz, wt 3), $\mathbf{CH_3}S$ and $=C-\mathbf{CH_2}-$ (m, τ 7.6–8.2, wt 5), and 3.9–4.9 (AB pattern, $\mathbf{SCH{=}CH}C$, $J_{AB\mathit{cis}}$ = 9.2 and $J_{AB\mathit{trans}}$ = 14.8 Hz, calculated chemical shift τ ($\mathbf{CH}{=}$, *cis*) 4.32, τ ($S\mathbf{CH}{=}C$, *trans*) 4.26, τ (SC=CH, *cis*) 4.46, and τ ($SC{=}\mathbf{CH}$, *trans*) 4.48, total wt 2).

Anal. Calcd for $C_5H_{10}S$: C, 58.80; 9.87; S, 31.33. Found: C, 58.57; H, 9.80; S, 31.25.

Reaction of Benzyl Methyl Sulfoxide with Acetic Anhydride.—A solution of benzyl methyl sulfoxide[7a] (7.7 g, 0.05 mol) in acetic anhydride (15 ml) was heated at 100° under nitrogen for 20 hr. The cooled mixture was treated with water (200 ml) to hydrolyze the anhydride, and the mixture was extracted with ether. The ether was washed with aqueous bicarbonate and was dried ($MgSO_4$). The organic product (9.38 g) was chromatographed on silica gel (100 g), and the column was eluted with petroleum ether to give 2.63 g (57% yield) of the dimethyl mercaptal of benzaldehyde. The product showed only one peak on vpc (liquid phase 20% SE-30, 100°) and gave upon oxidation with hydrogen peroxide bis(methylsulfonyl)benzal: mp 168–169°; mmp 168–169° (lit.[29] mp 162–163°).

Registry No.—2,2-Dimethylpropyl phenyl sulfide, 7210-80-2; **5a**, 10335-98-5; 2,2-dimethylpropyl phenyl sulfone, 10269-15-5; **5b**, 17413-99-9; **6a**, 17414-00-5; **6b**, 17414-01-6; **7a**, 17414-02-7; 2-methyl-2-phenylpropyl phenyl sulfide, 17414-03-8; β-(phenylthio)phenetole, 17414-04-9; **10**, 17414-05-0; β-(phenylsulfonyl)-phenetole, 17414-06-1; **11**, 17414-07-2; phenyl tetrahydrofurfuryl sulfide, 17414-08-3; **16**, 17414-09-4; phenyl tetrahydrofurfuryl sulfone, 17414-10-7; **17**, 17414-11-8; **20**, 17414-14-1; **21**, 17414-12-9; **24**, 17414-13-0; **26** (*cis*), 17414-15-2; **26** (*trans*), 17414-27-6.

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