The crude product was sublimed under a vacuum (0.1 mm) onto a cold finger that was chilled with a dry ice - acetone slurry. Sublimation took place at room temperature; a warm water bath (50-55 °C) was employed in some experiments. The first sublimation yielded 70-75% of the fluffy crystalline anhydride, whereas resublimation transferred 92-95% of the product to the cold finger. The residue in each sublimation was identified as 2,3-epoxysuccinic acid. The twice-purified sublimate melted sharply at 63-64 °C, but the melt crystallized as thin needles around 110-125 °C, with the second product melting at 146-147 °C. The melting behavior was repeated on a rock-salt wafer, and the infrared spectrum of the second crystallization product was identical with that of 2,3-epoxysuccinic acid (m.p. 148-149 °C).

The mass spectrum of the sublimate (m.p. 63-64 °C) gave the following major m/e peaks, with the most intense peak assigned a value of 100 (in parentheses) (all other peak heights were normalized to this peak height): 17 (6), 18 (25), 25 (4), 26 (9), 28 (9), 29 (33), 41 (6), 42 (100) (ketene ion), 44 (6), 69 (48), 114 (molecular ion).

Anal. Calcd. for C4H2O4: C, 42.1; H, 1.8. Found: C, 42.0; H, 1.8.

2,3-Epoxysuccinanilic Acid

A solution of ethereal aniline (0.093 g, 0.001 mole) was refluxed with purified 2,3-epoxysuccinic anhydride (0.112 g, 0.001 mole). The solution was concentrated to a crystalline mass that was recrystallized several times from acetone - light petroleum, m.p. 179-180 °C.

Anal. Calcd. for C10H9NO4: C, 58.0; H, 4.4; N,

6.8; acid equivalent 207. Found: C, 57.9; H, 4.6; N, 6.9; acid equivalent 207.

Derivatives of 2,3-Epoxysuccinic Acid

Ethereal solutions of purified 2,3-epoxysuccinic anhydride (0.001 mole) were heated under reflux with 0.001 mole of the aromatic amines and aromatic hydrazines described in Table I. All derivatives were recrystallized several times from acetone light petroleum.

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Reaction of phenols with acetic anhydride - dimethyl sulfoxide¹

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Various reactions of dimethyl sulfoxide resulting in mild oxidation of alcohols have been recognized for over seven years.² Recently, the valuable Moffatt technique (2), employing dimethyl sulfoxide – dicyclohexylcarbodiimide with, for example, pyridinium trifluoroacetate, has also been found (1, 4) to cause alkylation of certain phenols. By this means naphthols Ia and IVa have been converted into ketones III and V, and

the product of monoalkylation has been isolated by using certain phenols with free ortho or para positions (1, 4).

Recently, we became concerned with the use of a mild technique for the oxidation of an alcohol in the presence of a phenol substituent. Consequently, an attempt was made to utilize the acetic anhydridedimethyl sulfoxide method (3). Shortly afterwards, it became evident that phenols will also react with this reagent. Support for this view was provided by allowing β naphthol to react in an acetic anhydride – dimethyl sulfoxide solution for 20 h at room temperature. A thin-layer chromatogram of the crude product indicated the presence

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²A succinct review of such reactions, apparently proceeding through oxysulfonium intermediates, has been prepared (1); see also refs. 2 and 3.

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of three components. After chromatography on silica gel, β -naphthol acetate (16%), thio ether II (18%), and ketone III (11%) were isolated. The structures of acetate I*a* and ketone III were readily established by comparison with authentic samples. The structure of thio ether II was proposed on the basis of its elemental composition and infrared spectrum. Confirmation was provided by the results of a proton magnetic resonance and mass spectral study.

When the reaction was repeated with α -naphthol, only the corresponding acetate IVb (30%) and ketone V (21%) were detected in the reaction product. Again, the structures of both components were confirmed by comparison with known specimens. These preliminary experiments suggest that the acetic anhydride – dimethyl sulfoxide reagent may present a useful approach to certain phenol alkylation problems. The reaction observed here with β -naphthol is reminiscent of an earlier observation involving a Mannich-type reaction between phenol IVa, formaldehyde, and a thiol (5). However, we assume that the acetic anhydride – dimethyl sulfoxide reaction involves intermediates such as VI and VII.³

⁸The reaction between sulfoxides and acid anhydrides (the Pummerer reaction) appears to proceed via an intermediate such as VI (7). The formation of sulfonium ion VII followed by intramolecular alkylation to yield thio ether II or by further alkylation to give ketone III is consistent with a view expressed by Burdon and Moffatt (4) for similar reactions involving dicyclohexylcarbodiimide – dimethyl sulfoxide. In summary, the oxidation of an alcohol in the presence of a phenol substituent with acetic anhydride – dimethyl sulfoxide may be expected to result in extensive alkylation of the phenol ring system. Studies now in progress in other laboratories (1, 4) on the dicyclohexylcarbodiimide – dimethyl sulfoxide technique will doubtlessly help to define the further scope and mechanism of this reaction.⁴

EXPERIMENTAL⁵

Reaction between β-Naphthol and Acetic Anhydride – Dimethyl Sulfoxide

A solution of β -naphthol (2.9 g) in dimethyl sulfoxide (60 ml) – acetic anhydride (40 ml) was allowed to stand at room temperature for 20 h. After dilution with ethyl acetate (150 ml), the yellow-green solution was extracted with water. Removal of the solvent from the ethyl acetate phase

⁴For a recent review of reactions involving dimethyl sulfoxide, refer to ref. 6.

Melting points were determined on a Kofler melting point apparatus. The reaction products were confirmed by comparison with authentic samples (mixture melting point and infrared spectra (in potassium bromide)). Further support for the structures was provided by the proton magnetic resonance spectra (Varian A-60, with deuteriochloroform as solvent and tetramethylsilane as internal standard), the mass spectra (by J. L. Očcolowitz, Defence Standard Laboratories, Maribyrnong, Victoria, Australia), and the elemental analyses (by Dr. A. Bernhardt, Max-Planck Institut, Mülheim, Germany).



⁵All solvents, acetic anhydride, and dimethyl sulfoxide (from calcium oxide) were distilled. Silica gel (0.05–0.20 mm) supplied by E. Merck AG (Darmstadt) was used for column chromatography. Thin-layer chromatograms were performed with silica gel G (E. Merck) and developed by immersion in iodine vapor.

gave a yellow, oily residue. Thin-layer chromatography (CHCl₃ as the mobile phase) indicated a three-component mixture. A solution of the residue in 4:1 petroleum ether (b.p. 66°) - benzene was chromatographed on silica gel. Elution with the same solvent gave a fraction which crystallized from petroleum ether to yield 0.60 g of β -naphthol acetate melting at 68° and identical⁵ with an authentic sample. Fractions eluted with 2:1 to 1:2 petroleum ether-benzene were combined and crystallized from petroleum ether to provide 0.80 g of 1-(methylthiamethylene)-2-acetoxynaphthalene (II), m.p. 89°; $\nu_{\rm max} \ 1 \ 760 \ {\rm cm^{-1}}$; proton magnetic resonance peaks at 2.0 (three methyl protons), 2.32 (three methyl protons), 4.02 (two methylene protons), and 7.0-8.05 (six aromatic protons) δ ; mass spectral peaks at m/e246 (M⁺), 204, 157, and 128.6

Anal. Calcd. for C14H14O2S: C, 68.25; H, 5.74; O, 12.99. Found: C, 68.11; H, 5.58; O, 12.82.

Continued elution with benzene gave ketone III. Crystallization from benzene-petroleum ether yielded 0.60 g melting at 69–70°. Ketone III was identical⁵ with a specimen $(m.p. 70^\circ)$ prepared by the reaction of β -naphthol and the dimethyl sulfoxide – dicyclohexylcarbodiimide - phosphoric acid reagent (1, 4).

Reaction between *a*-Naphthol and Acetic Anhydride -Dimethyl Sulfoxide

The preceding experiment was repeated as de-_scribed, except that 1.3 g of α -naphthol was substi-

6Only the major fragmentation values are recorded.

tuted for β -naphthol. In this case, a thin-layer chromatogram indicated that two components comprised the crude reaction product. After column chromatography on silica gel, both α -naphthol acetate IVb (0.50 g, m.p. 43°, petroleum ether as solvent) and ketone V (0.50 g, m.p. 50°, benzene petroleum ether as solvent) were isolated. Authentic specimens of both products were prepared (1, 4) and used to confirm⁵ the assigned structures.

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