max (2-propanol) 234 nm (ε 5930).

Anal. Calcd for $C_4H_7N_3O_3S$: C, 27.12; H, 3.98; N, 23.72. Found: C, 27.25; H, 4.12; N, 23.45.

The filtrate from the crystallization of **6a** was concentrated under reduced pressure to leave a partially crystalline residue. An NMR spectrum of this residue suggested that a mixture of **6a** and 2-cyanopropanamide in a molar ratio of approximately 1:4 was present. The crystalline portion of the residual mixture was sublimed (0.01 kPa) to obtain 2-cyanopropanamide: mp 90–94 °C (lit.[10] mp 96–98 °C); NMR (Me_2SO-d_6) δ 1.37 (d, J = 7 Hz, 3 H), 3.62 (q, J = 7 Hz, 1 H), 7.26 (br s, 1 H), 7.58 (br s, 1 H); IR (KBr) 3360, 3195, 2255, 1720, 1670, 1638 cm^{-1}.

4-Methyl-2*H*-1,2,6-thiadiazin-3(6*H*)-one 1,1-Dioxide (7a). A solution of 8.90 g (0.05 mol) of **6a** in 225 mL of DMF was hydrogenated over Raney nickel. After filtration, the solution was concentrated under reduced pressure on the steam bath; heating was continued for 1 h after the solvent had evaporated. The residue was partitioned between 100 mL of water and 110 mL of ethyl acetate and the mixture made strongly alkaline with 10% aqueous NaOH. The aqueous phase was washed with ethyl acetate, acidified with 6 N hydrochloric acid, and extracted with three 150-mL portions of ethyl acetate. After drying (Na_2SO_4) and evaporation of the ethyl acetate under reduced pressure, the residue was triturated with methylene chloride to obtain **7a**: 3.80 g (47%), mp 156–158 °C. The analytical sample was recrystallized from ethanol–methylene chloride: mp 156–158 °C; NMR (Me_2SO-d_6) δ 1.77 (s, 3 H), 7.24 (s, 1 H), 11–12 (br s, 2 H); IR (KBr) 3215, 1660, 1645, 1345, 1160 cm^{-1}; UV max (2-propanol) 210 nm (ε 5280), 280 (4020); pK_a 2.55 and 8.23 (±0.05);[5] mass spectrum, m/e 162 (M^+).

Anal. Calcd for $C_4H_6N_2O_3S$: C, 29.63; H, 3.73; N, 17.28. Found: C, 29.57; H, 3.63; N, 17.23.

***N*-Ethyl-*N'*-(3-methyl-5-isoxazolyl)sulfamide (6b).** Ethylsulfamoyl chloride (43.2 g, 0.30 mol) was added dropwise to a solution of 29.4 g (0.30 mol) of **5b** in 200 mL of pyridine at 5–10 °C. The mixture was stirred overnight at room temperature and concentrated under reduced pressure. The residue was stirred with 600 mL of water, and the solution was cleared by filtration and acidified with 6 N hydrochloric acid; **6b** crystallized rapidly: 46.2 g (75%), mp 133–136 °C. The analytical sample was recrystallized from aqueous ethanol: mp 133–135 °C; NMR (Me_2SO-d_6) δ 1.03 (t, J = 7.5 Hz, 3 H), 2.12 (s, 3 H), 2.90 (m, 2 H), 5.63 (s, 1 H), 7.71 (t, J = 6 Hz, 1 H), 11.13 (br s, 1 H); IR (KBr) 3290, 2705, 1618 cm^{-1}; UV max (2-propanol) 232 nm (ε 10 100).

Anal. Calcd for $C_6H_{11}N_3O_3S$: C, 35.11; H, 5.40; N, 20.48. Found: C, 35.24; H, 5.14; N, 20.68.

6-Ethyl-5-methyl-2*H*-1,2,6-thiadiazin-3(6*H*)-one 1,1-Dioxide (7b). A solution of 20.5 g (0.10 mol) of **6b** in 225 mL of DMF was hydrogenated over Raney nickel. After filtration, the solution was concentrated under reduced pressure on the steam bath. The residue was first washed with petroleum ether (bp 30–60 °C) and then triturated with 100 mL of tetrahydrofuran. The resultant solid was dissolved in water and the solution acidified with 6 N hydrochloric acid to precipitate **7b**: 4.10 g (20%), mp 147.5 °C; NMR (Me_2SO-d_6) δ 1.27 (t, J = 7 Hz, 3 H), 2.28 (s, 3 H), 3.83 (q, J = 7 Hz, 2 H), 5.52 (s, 1 H), 12.7 (br s, 1 H); IR (KBr) 3090, 1648, 1600 cm^{-1}; UV max (2-propanol) 218 nm (ε 4800), 293 (7810).

Anal. Calcd for $C_6H_{10}N_2O_3S$: C, 37.89; H, 5.30; N, 14.73. Found: C, 37.92; H, 5.46; N, 14.77.

***N*-(3-Methyl-5-isoxazolyl)-*N'*-(4-methoxyphenyl)sulfamide (6c).** This compound was prepared in 33% yield from **5b** by a procedure similar to that used to prepare **2c**. The analytical sample of **6c** was recrystallized from benzene: mp 120.5–122 °C; NMR (Me_2SO-d_6) δ 2.15 (s, 3 H), 3.70 (s, 3 H), 5.71 (s, 1 H), 6.86 (d, J = 9 Hz, 2 H), 7.06 (d, J = 9 Hz, 2 H), 10.07 (s, 1 H), 11.54 (br s, 1 H); IR (KBr) 3265, 1353, 1174, 1155 cm^{-1}; UV max (2-propanol) 231 nm (ε 20 300), 281 (1480).

Anal. Calcd for $C_{11}H_{13}N_3O_4S$: C, 46.64; H, 4.63; N, 14.83. Found: C, 46.84; H, 4.49; N, 14.63.

6-(4-Methoxyphenyl)-5-methyl-2*H*-1,2,6-thiadiazin-3(6*H*)-one 1,1-Dioxide (7c). A solution of 2.83 g (0.01 mol) of **6c** in 100 mL of DMF was hydrogenated over Raney nickel. After filtration, the solution was concentrated under reduced pressure on the steam bath, and heating was continued for 1 h after the solvent had evaporated. The residue was dissolved in dilute aqueous sodium hydroxide, the solution cleared by filtration, and the product precipitated by addition of hydrochloric acid. A second reprecipitation from aqueous solution yielded **7c**: 1.00 g (37%), mp 182–185 °C; NMR (Me_2SO-d_6) δ 1.85 (s, 3 H), 3.79 (s, 3 H), 5.61 (s, 1 H), 7.01 (d, J = 9 Hz, 2 H), 7.76 (d, J = 9 Hz, 2 H); IR (KBr) 3000 (br), 1660, 1614, 1353, 1343, 1180 cm^{-1}; UV max (2-propanol) 228 nm (ε 16 200), 293 (9750).

Anal. Calcd for $C_{11}H_{12}N_2O_4S$: C, 49.25; H, 4.51; N, 10.44. Found: C, 49.32; H, 4.80; N, 10.80.

Registry No. **1a**, 1750-42-1; **1b**, 1072-67-9; **2a**, 71565-64-5; **2b**, 71565-65-6; **2c**, 71565-66-7; **3a**, 71565-67-8; **3b**, 71565-68-9; **3c**, 71565-69-0; **4**, 71565-70-3; **5a**, 35143-75-0; **5b**, 14678-02-5; **6a**, 71565-71-4; **6b**, 71565-72-5; **6c**, 71565-73-6; **7a**, 71565-74-7; **7b**, 71565-75-8; **7c**, 71565-76-9; sulfamoyl chloride, 7778-42-9; ethylsulfamoyl chloride, 16548-07-5; *p*-methoxyphenylsulfamoyl azide, 71565-77-0; 2-cyanopropanamide, 71565-78-1; 4-methylisoxazole, 6454-84-8; hydroxylamine hydrochloride, 5470-11-1.

Supplementary Material Available: Tables of the final atomic parameters, bond lengths, bond angles, and ring torsion angles for **3a** (5 tables, 2 pages). Ordering information is given on any current masthead page.

(10) Fink, R. M.; McGaughey, C.; Cline, R. E.; Fink, K. *J. Biol. Chem.* **1956**, *218*, 1.

Acetoxyl Group Migration in 2-Acetoxy-4-(methylthio)-3,5-xylenol. A Novel Catechol to Phenol Transformation

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While pursuing synthetic studies aimed at preparation of a ring-hydroxylated methyl [4-(methylthio)-3,5-xylyl]carbamate analogue,[1] we observed an unusual catechol to phenol transformation. 2-Acetoxy-4-(methylthio)-3,5-xylenol (**3**) [prepared from rearrangement of 4-(methylsulfinyl)-3,5-xylenol (**1**)[2]] when treated with *N*-methyl isothiocyanate in the presence of triethylamine yielded a quantitative amount of a new compound that still contained acetoxyl and phenolic moieties but was devoid of any carbamate substituents.

Results and Discussion

The normal procedure for preparation of *N*-methyl carbamates entails reaction of a hydroxylic moiety with *N*-methyl isothiocyanate in the presence of a suitable catalyst, i.e., boron trifluoride etherate or triethylamine.

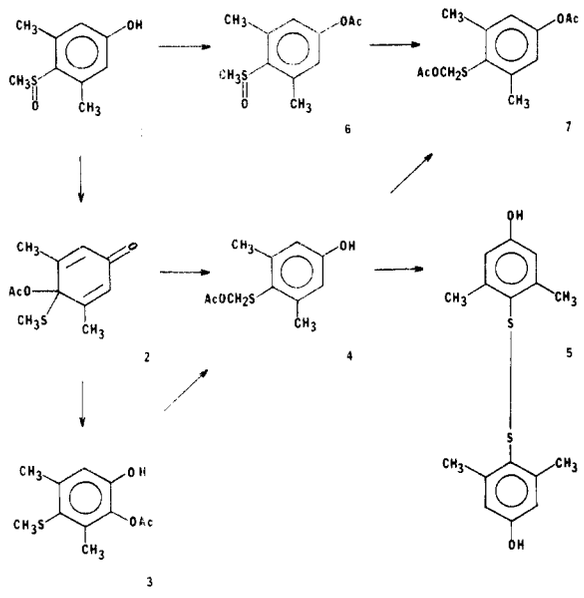
Initial treatment of **3** with *N*-methyl isothiocyanate in the presence of boron trifluoride etherate (at 0 °C) gave a mixture of compounds and obvious polymerization. Upon substituting triethylamine for boron trifluoride etherate and refluxing the mixture overnight, we obtained a quantitative yield of a new compound. (It was later demonstrated that the presence or absence of *N*-methyl isothiocyanate had no bearing on the end result of this reaction.) On the basis of its NMR spectrum which indicated retention of the acetoxyl group, the presence of two aro-

(1) E. S. Oonnithan and J. E. Casida, *J. Agric. Food Chem.*, **16**, 28 (1968).

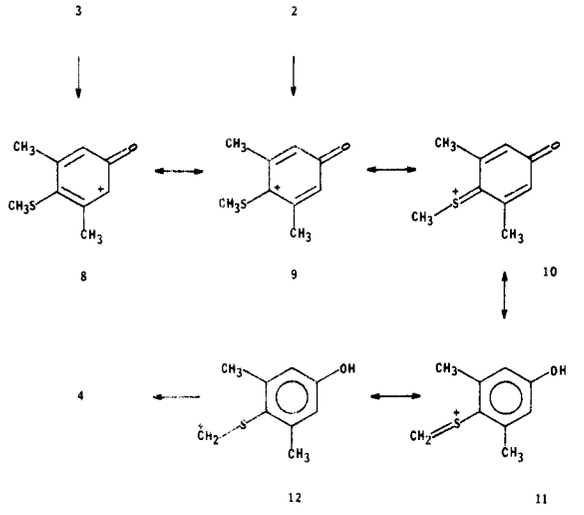
(2) R. R. King, *J. Org. Chem.*, **43**, 3784 (1978).

0022-3263/79/1944-4194$01.00/0

Scheme I



Scheme II



matic protons, and the replacement of the *S*-methyl three-proton singlet in **3** by a two-proton singlet at δ 5.16, the new compound was assigned the structure **4** (see Scheme I). Confirmation of this assignment was indicated by two further chemical transformations. First, mild treatment of **4** with dilute sodium hydroxide produced the disulfide dimer **5**, a reaction indicative of an acyloxymethyl sulfide precursor.[3] Second, acetylation of **4** gave a diacetate derivative **7**, which was identical with the product from a Pummerer rearrangement[4] of the acetylated sulfoxide **6**.

The migration of an acetoxyl group from an aromatic ring to a ring substituent appears to be unprecedented in the literature and constitutes the rather remarkable conversion of a catechol to a phenol structure. A possible mechanistic rationale for this rearrangement is outlined in Scheme II. Thus, base catalysis of **3** could isomerize it to a 2,4-dienone form in which unfavorable compression of the acetoxyl moiety enhances its propensity to eliminate, resulting in formation of the 2,4-dienone cation **8**. Subsequent rearrangement to the 2,5-dienone cation **9** would lead to the resonance forms **10**, **11**, and **12** comparable to the normal Pummerer intermediates expected for this system.[5] Stabilization of resonance form **12** by acetoxylation would lead to the observed product **4**. An analogous conversion of the 2,5-dienone **2**[2] attested to the plausibility of the proposed reaction pathway.

(3) L. Horner and P. Kaiser, *Justus Liebigs Ann. Chem.*, **62**, 19 (1959).
(4) R. Pummerer, *Ber. Dtsch. Chem. Ges.*, **43**, 1401 (1910). The rearrangement of sulfoxides to α-substutited derivatives of the corresponding sulfides is well documented and is widely known as the Pummerer reaction.

Experimental Section

Melting points are uncorrected and were determined on a Kofler hot-stage microscope. NMR spectra were recorded on a Varian T-60 NMR spectrometer with Me_4Si as an internal standard. IR spectra were determined by using a Beckman IR-20A spectrophotometer. Mass spectra were determined on a Perkin-Elmer Hitachi mass spectrometer. Thin-layer chromatograms were run on glass plates coated with silica gel GF. Separated components were detected by UV fluorescence and iodine vapor.

4-[(Acetoxymethyl)thio]-3,5-xylenol (4). A solution of 2-acetoxy-4-(methylthio)-3,5-xylenol (**3**; 210 mg) in benzene (10 mL) was treated with an excess of triethylamine (0.1 mL) and refluxed with stirring until thin-layer chromatography (hexane–ethyl acetate, 4:1) studies indicated that the reaction was complete (approximately 18 h). Benzene and triethylamine were removed under vacuum, and the residue crystallized from hexane to yield 4-[(acetoxymethyl)thio]-3,5-xylenol (**4**; 174 mg): mp 107–108 °C; IR (Nujol) 3300, 1710, 1585 cm^{-1}; NMR ($CDCl_3$) δ 6.63 (2 H, s, aromatic H), 5.16 (2 H, s, CH_2O), 2.49 (6 H, s, CH_3), 2.08 (3 H, s, OAc); MS *m/e* 226 (M^+). An identical product was obtained by treatment of the 2,5-dienone **2** under similar conditions for 10 min. A solution of **4** (50 mg) in benzene (5 mL) was shaken with a solution of 1 N sodium hydroxide (2 mL) for 5 min. Separation of the benzene layer and removal of the benzene furnished the disulfide **5**: mp 210 °C dec; IR (Njuol) 3320, 1585 cm^{-1}; NMR ($CDCl_3$) δ 6.52 (4 H, s, aromatic H), 2.21 (12 H, s, CH_3); MS *m/e* 306.

4-(Methylsulfinyl)-3,5-xylyl Acetate (6). A solution of 4-(methylsulfinyl)-3,5-xylenol[2] (**1**; 215 mg) in acetic anhydride (5 mL) and pyridine (3 mL) was stirred for 2 h at room temperature and then neutralized by decantation into a cold saturated solution of sodium bicarbonate (20 mL). After extraction of the neutral solution with chloroform (2 × 50 mL), the chloroform extracts were dried over anhydrous sodium sulfate and then concentrated under vacuum, yielding 4-(methylsulfinyl)-3,5-xylyl acetate (**6**; 227 mg): IR (thin film) 1735, 1565 cm^{-1}; NMR ($CDCl_3$) δ 6.85 (2 H, s, aromatic H), 2.90 (3 H, s, SCH_3), 2.62 (6 H, s, CCH_3), 2.33 (3 H, s, OAc); MS *m/e* 226.

4-[(Acetoxymethyl)thio]-3,5-xylyl Acetate (7). A solution of 4-(methylsulfinyl)-3,5-xylyl acetate (**6**; 112 mg) in a 2:1 mixture of acetic anhydride–acetic acid (5 mL) was stirred on a steam bath until thin-layer chromatographic studies (hexane–ethyl acetate, 3:1) indicated reaction was complete (approximately 4 h). The reaction mixture was then neutralized by decantation into a cold saturated solution of sodium bicarbonate (20 mL) and worked up as described previously. The residue was purified by preparative thin-layer chromatography to give 4-[(acetoxymethyl)thio]-3,5-xylyl acetate (**7**; 85 mg): IR (thin film) 1735, 1730, 1580 cm^{-1}; NMR ($CDCl_3$) δ 6.92 (2 H, s, aromatic H), 5.16 (2 H, s, CH_2O), 2.53 (6 H, s, CCH_3), 2.28 (3 H, s, OAc), 2.04 (3 H, s, OAc); MS *m/e* 268. An identical compound was derived on acetylation of 4-[(acetoxymethyl)thio]-3,5-xylenol (**4**) with acetic anhydride–boron trifluoride etherate.

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Registry No. 1, 22454-92-8; 2, 67031-00-9; 3, 67031-01-0; 4, 71519-00-1; 5, 71519-01-2; 6, 71519-02-3; 7, 71519-03-4.

(5) R. Greenhalgh, W. D. Marshall, and R. R. King, *J. Agric. Food Chem.*, **24**, 266 (1976).