0.16 mol) with a solution of sodium dichromate dihydrate (30 g) in glacial acetic acid (60 g) gave starting material **1f** (2.03 g, 0.019 mol) and ketone **2f** (0.27 g, 0.002 mol): yield 1%; bp 72° (15 mm); mp 76–77° (lit.[4] mp 76–78°); NMR 2.69 [3 H, s,-(C=O)CH_3], 8.60 and 8.71 (2 H, 2 d, ArH), 9.22 ppm (1 H, s, ArH); mass spectrum *m/e* 43, 122 (molecular ion), 80, 79, 52, 53.

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Registry No.—**1a**, 15707-23-0; **1b**, 15707-24-1; **1c**, 27043-05-6; **1d**, 13360-65-1; **1e**, 13360-64-0; **1f**, 13925-00-3; **2a**, 23787-80-6; **2b**, 32974-92-8; **2c**, 54300-08-2; **2d**, 54300-09-3; **2e**, 22047-27-4; **2f**, 22047-25-2; sodium dichromate dihydrate, 7789-12-0.

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Sulfonation of Unsaturated Compounds. II. Isolation and Characterization of a Carbyl Sulfate

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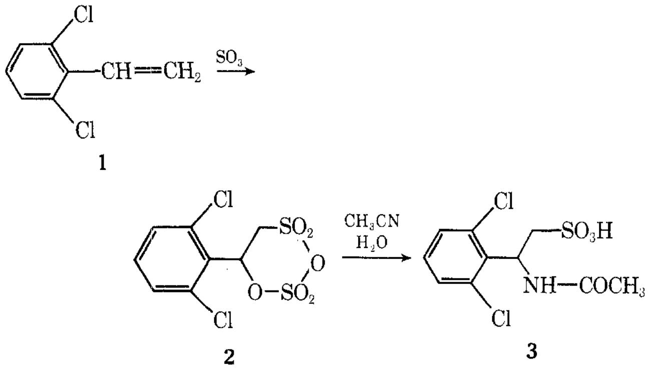
Cyclic sulfonate–sulfate anhydrides **2** (carbyl sulfates) have been proposed as intermediates in some sulfonations of olefins[1] with sulfur trioxide. Evidence for these intermediates comes from the identification of isolated products, usually after alkaline hydrolysis of the sulfonation mixture. In some cases, the carbyl sulfate has been isolated as a crystalline product[2] from a sulfonation mixture. However, these carbyl sulfates have not been characterized directly and no spectral data are available for them.

Using 2,6-dichlorophenylethylene (**1**) to avoid side products resulting from sulfonation into the phenyl ring, it is possible to isolate a pure carbyl sulfate. Dropwise addition of olefin **1** into liquid sulfur dioxide in 1,2-dichloroethane gave the carbyl sulfate **2** in 96% yield. Spectral and analytical data support the assignment of structure **2**.



2 **3**

The carbyl sulfate can also be obtained from the sulfur trioxide–dioxane adduct as sulfonating agent, but in lower yields.

Carbyl sulfate **2** reacted readily with wet acetonitrile to give the β-aminosulfonic acid **3** through a Ritter-type reaction.[3] Treatment of **2** with aqueous alkali, pyridine, and piperidine gave mixtures of sulfate and sulfonate salts.

Experimental Section

1-(2,6-Dichlorophenyl)-1-sulfate-2-sulfonate Anhydride (Carbyl Sulfate, 2). Method A. Freshly distilled sulfur trioxide (Sulfan, Allied Chemicals), 2.6 g (0.032 mol), was added to 25 ml of dry 1,2-dichloroethane at 0°. To this solution 2,6-dichlorostyrene (5.5 g, 0.032 mol) in 12.5 ml of 1,2-dichloroethane was added dropwise over 25 min at 2–6° with stirring. A precipitate of **2** started to appear immediately. After 12 min of stirring 50 ml of pentane was added and the solution was filtered. The product was washed with pentane–1,2-dichloroethane (1:1) and pentane to yield 5.2 g of the thermally unstable carbyl sulfate **2**: 96%; mp 81.5–83.5°; ir (KBr) 3020, 1580, 1447, 1422, 1380, 1250, 1231, 1215, 1190, 957, 913, 749 cm^{-1}; NMR (DMSO-d_6) δ 7.35 (m, 3 H), 6.35 (m, 1 H), 3.55 (m, 2 H); mass spectrum *m/e* 174, 172 (M − $2SO_3$), 139, 137 (M − $2SO_3$ − Cl), 80 (SO_3), 64 (SO_2); neut equiv, calcd 333.17; found (titration with 0.05 *N* NaOH in xylene–isopropyl alcohol, 1:1), 335.

Anal. Calcd for $C_8H_6Cl_2O_6S_2$: C, 28.84; H, 1.82; Cl, 21.29; S, 19.25. Found: C, 29.18; H, 2.12; Cl, 21.62; S, 19.55.

Method B. The dioxane–sulfur trioxide complex[4] was prepared from 2.30 g (0.0288 mol) of sulfur trioxide and 2.53 g (0.0288 mol) of dioxane in dry 1,2-dichloroethane (27.5 ml). A solution of 5.5 g (0.032 mol) of **1** in 12.5 ml of 1,2-dichloroethane was added dropwise over 25 min with stirring at 2–4°. After 15 min of stirring, petane (45 ml) was added and the mixture was allowed to stand in the cold overnight. Filtration and washing as described gave 3.05 g (63.7%) of **2**.

2-(2,6-Dichlorophenyl)-2-(*N*-acetamido)ethanesulfonic Acid (3). A solution of 0.6 g (0.002 mol) of **2** in 15 ml of wet acetonitrile was refluxed for 2 hr. Cooling and filtration gave 0.121 g of **3**: 21.6%; ir (KBr) 3255, 3095, 1670, 1560, 1450, 1250, 1205, 1007, 722 cm^{-1}; NMR (D_2O) δ 7.38 (m, 3 H), 6.27 (m, 1 H), 3.61 (m, 2 H), 2.07 ppm (s, 3 H); mass spectrum *m/e* 174, 172 (M − $CH_3CONHSO_3H$), 139, 137 ($C_6H_3Cl_2CHCH_2$ − Cl), 102 ($C_6H_3Cl_2CHCH_2$ − 2Cl), 101, 64; neut equiv, calcd, 312.18; found (tritration), 308.

Anal. Calcd for $C_{10}H_{11}Cl_2NO_4S$: C, 38.54; H, 3.55; N, 4.51; S, 10.27. Found: C, 38.64; H, 3.44; N, 4.55; S, 10.27.

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Registry No.—**1**, 28469-92-3; **2**, 54276-72-1; **3**, 54276-73-2; SO_3, 7446-11-9; acetonitrile, 75-05-8; 1,2-dichloroethane, 107-06-2.

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Ionization Constants and Volumes of Highly Hindered Pyridines in Methanol[1]

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Although the pK_a's of several 2,6-dialkylpyridinium hydrochlorides have been reported, there is no single com-