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Chromate Oxidation of Alkylpyrazines

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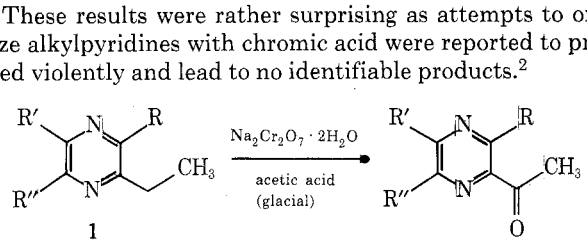
The most convenient preparation of acetylpyrazines previously reported in the literature is a two-step synthesis consisting of a treatment of alkylpyrazines with *N*-bromosuccinimide (NBS), followed by oxidation to the corresponding ketones using either sodium 2-propanenitronate or pyridine 1-oxide.[1] We have now found that 2,3-dialkylpyrazines can be oxidized in one step by sodium dichromate in acetic acid, in good yields, to the corresponding 2-acyl-3-alkylpyrazines. When the 3 position is not substituted, the acylpyrazines are obtained only in very low yields.

These results were rather surprising as attempts to oxidize alkylpyridines with chromic acid were reported to proceed violently and lead to no identifiable products.[2]



1 2

As is shown in Table I, oxidation of 2-ethyl-3-methylpyrazine (**1a**), 2,3-diethylpyrazine (**1b**), and a mixture of 2-ethyl-3,5-dimethylpyrazine (**1c**) and 2-ethyl-3,6-dimethylpyrazine (**1d**) with sodium dichromate in acetic acid gave the corresponding 2-acetylpyrazines **2a, 2b** and a mixture of **2c** and **2d.** When 2-ethyl-5-methylpyrazine (**1e**) and ethylpyrazine (**1f**) were oxidized by the same procedure, the ketones **2e** and **2f** were obtained in only very low yield.

As the alkylpyrazines are expensive and are partially destroyed during the oxidation, it was found more economical to halt the oxidation when approximately one-half of the substrate was oxidized. The alkylpyrazines were easily separated from the ketones by distillation. Increasing the amount of oxidizing agent increased the amount of the ketone but also increased the destruction of the substrate.

Table I

		Yield, %[a]
1a, R = CH_3; R′ = H; R″ = H	**2a**	53
1b, R = Et; R′ = H; R″ = H	**2b**	67
1c (d), R = CH_3 (CH_3); R′ = CH_3 (H); R″ = H (CH_3)	**2c** (d)	57
1e, R = H; R′ = CH_3; R″ = H	**2e**	9
1f, R = H; R′ = H; R″ = H	**2f**	1

Application of this procedure to alkylpyridines led to almost total destruction. Oxidation of 4-ethyl-3-methylpyridine and 4-ethylpyridine gave the corresponding ketones in 5 and 4% yield, respectively. When 3-ethyl-4-methylpyridine and 2-ethylpyridine were oxidized, no identifiable products were obtained.

Experimental Section

All the NMR spectra were run on a Varian HA-100 spectrometer. All chemical shifts are reported in parts per million (δ) relative to Me_4Si. The mass spectra were run on CEC Model 21-103C and AEI MS9 mass spectrometers. Mass spectral major fragmentation peaks are listed in decreasing order of intensity.

2-Acetyl-3-ethylpyrazine (2b). 2,3-Diethylpyrazine (**1b,** 1088 g, 8 mol) was heated to 118°, and a solution of sodium dichromate dihydrate (1500 g) in glacial acetic acid (3000 g) was added in 3 hr with agitation at 118°. Agitation was continued for another 1 hr at 118°, when GLC analysis (20 ft × 0.25 in., 20% Carbowax 20M column) indicated that the reaction mass contained 50% ketone **2b** and 50% starting material **1b.** The reaction mass was then cooled and quenched in 12 l. of water. The solution was extracted four times with toluene (1000 g), and the combined extracts were washed once with water (5 l.) and with 5% sodium carbonate solution (1500 g). The solvent was removed in vacuo, and the residue was fractionated to give starting material **2a** (481.4 g, 3.54 mol) and ketone **2b** (447.0 g, 2.98 mol): yield 67%; bp 77° (6 mm); NMR 1.28 (3 H, t, $-CH_2CH_3$), 2.68 [3 H, s, $-(C{=}O)CH_3$], 6.15 (2 H, q, $-CH_2CH_3$), 8.46 (1 H, d, ArH), 8.60 ppm (1 H, d, ArH); mass spectrum *m/e* 150 (molecular ion), 107, 43, 52, 108.

Anal. Calcd for $C_8H_{10}ON_2$: *m/e* 150.0793. Found: *m/e* 150.0787.

2-Acetyl-3-methylpyrazine (2a). By the above procedure, except that the reaction was run at 80°, oxidation of 2-ethyl-3-methylpyrazine (**1a,** 165 g, 1.35 mol) with a solution of sodium dichromate dihydrate (780 g) in glacial acetic acid (1560 g) gave starting material **1a** (47.6 g, 0.39 mol) and ketone **2a** (69.4 g, 0.51 mol): yield 53%; bp 71° (6 mm); NMR 8.60 (1 H, d, ArH), 8.46 (1 H, d, ArH), 2.71 [3 H, s, $-(C{=}O)CH_3$], 2.82 ppm (3 H, s, $-CH_3$); mass spectrum *m/e* 136 (molecular ion), 43, 94, 93, 42, 67.

Anal. Calcd for $C_7H_8ON_2$: *m/e* 136.0637. Found: *m/e* 136.0642.

2-Acetyl-3,5-dimethylpyrazine (2c) and 2-Acetyl-3,6-dimethylpyrazine (2d). By the same procedure, treatment of a mixture of 2-ethyl-3,5-dimethylpyrazine (**1c**) and 2-ethyl-3,6-dimethylpyrazine (**1d**) (1142 g, 8.4 mol) with a solution of sodium dichromate dihydrate (1575 g) in glacial acetic acid (3150 g) at 80° gave a mixture of starting material **1c** and **1d** (649.0 g, 4.77 mol) and a mixture of ketones **2c** and **2d** (312.6 g, 2.08 mol): yield 57%; bp 70° (7 mm); NMR (mixture) 8.32 (1 H, s, ArH), 2.73 [3 H, s, $-(C{=}O)CH_3$], 8.52 (1 H, s, ArH), 2.74 [3 H, s, $-(C{=}O)CH_3$], 2.46 or 2.66 ppm (3 H each, 2 s, $-CH_3$); mass spectrum *m/e* 150 (molecular ion), 108, 107, 66, 122, 81.

Anal. Calcd for $C_8H_{10}ON_2$: *m/e* 150.0793. Found: *m/e* 150.0790.

2-Acetyl-5-methylpyrazine (2e). By the previous procedure, oxidation of 2-ethyl-5-methylpyrazine (**1e,** 19.5 g, 0.16 mol) with a solution of sodium dichromate dihydrate (30 g) in glacial acetic acid (60 g) gave starting material **1e** (8.2 g, 0.07 mol) and ketone **2e** (1.1 g, 0.008 mol): yield 9%; bp 80° (8 mm); mp 55–56°; NMR 2.60 (3 H, s, $-CH_3$), 2.64 [3 H, s, $-(C{=}O)CH_3$], 8.46 (1 H, s, ArH), 9.08 ppm (1 H, s, ArH); mass spectrum *m/e* 136 (molecular ion), 43, 94, 93, 39, 67.

Anal. Calcd for $C_7H_8ON_2$: *m/e* 136.0637. Found: *m/e* 136.0631.

Acetylpyrazine (2f). By the same procedure except that the reaction was run at 116°, treatment of ethylpyrazine (**1f,** 17.3 g,

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.

Acknowledgment. I wish to express my appreciation to Dr. W. I. Taylor for his interest in this work. I also wish to thank Mr. M. Jacobs for the NMR analyses, Ms. A. Sanderson for the mass spectral analyses, and Mr. H. Bondarovich for the high-resolution mass spectral analyses.

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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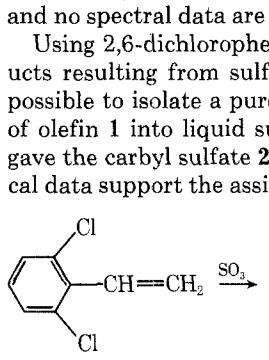
Cyclic sulfonate–sulfate anhydrides **2** (carbyl sulfates) have been proposed as intermediates in some sulfonations of olefins[1] with sulfur trioxide. Evidence for these intermediates comes from the identification of isolated products, usually after alkaline hydrolysis of the sulfonation mixture. In 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.**



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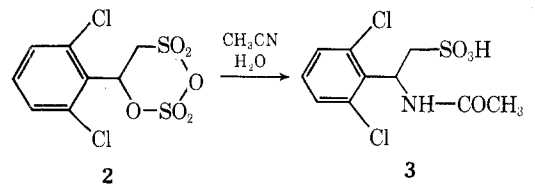

2 **3**

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 (tritration 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-