drol so separated were positively identified by melting points and infrared spectra. Similar behavior was observed on heating compound 1 for 24 hr with dilute sulfuric acid, trifluoroacetic, trichloroacetic, formic, and oxalic acids, and water–methanol (50:50, v/v).

**In Concentrated Sulfuric Acid.** When 0.5 g of 1 was mixed with 10 ml of concentrated sulfuric acid, the white powder appeared to be completely insoluble. The heterogeneous mixture became light orange in color after a few days of vigorous mixing at room temperature. The mixture was then slowly added into a large amount of cracked ice. A white solid separated immediately. About 0.4 g of material was isolated and identified as starting material by mixture melting point and comparison of infrared spectra. In fuming sulfuric acid (30%), only a water-soluble white solid was obtained.

**Attempted Preparation of Perfluorobenzopinacol (2). Photochemical.** Photochemical reactions were carried out in a manner similar to that described previously. Only intractable tar was obtained when decafluorobenzophenone (5) was irradiated in isopropyl alcohol, *n*-hexane, isopropyl alcohol–*n*-hexane, or cyclohexane, with ultraviolet light at 350 nm. Tar formation appeared to be even more extensive when 253.7-nm light was used. A mixture of decafluorobenzophenone and decafluorobenzhydrol in *n*-hexane was also irradiated, but the resulting material neither solidified nor could it be distilled in vacuo. The reaction of decafluorobenzophenone with tributyltin hydride in benzene or acetonitrile was carried out according to the procedure described by Hammond.[12] No solid could be isolated, even after column chromatography.

**Reaction with Zinc.** To a glacial acetic acid solution (5 ml) containing 1 g of decafluorobenzophenone was added 2 g of zinc powder and the mixture was stirred vigorously for 24 hr at room temperature. The reaction mixture was poured into a large volume of cold water. The resulting solid, together with zinc, was collected by filtration, dried, and extracted with ether. From the ether layer was isolated 0.9 g of white solid. This compound was identified as decafluorobenzhydrol (6) by mixture melting point and by its infrared spectrum.

**Reaction with Sodium Amalgam.** Decafluorobenzophenone (2.7 g) and sodium amalgam (2%, 54 g) were mixed vigorously in 54 ml of tetrahydrofuran under a nitrogen atmosphere. The reaction mixture turned to a red-wine color in a few minutes, then blue after 2 hr, and was deep red after 24 hr. The blue mixture exhibited ESR signals. Only a dark-brown, oily residue was obtained after the reaction mixture was decomposed with dilute acetic acid.

**Reaction with "Magnesium Subiodide".** This procedure was based on the method described by Gomberg and Bachmann.[14] Decafluorobenzophenone (3.64 g, 0.01 mol), dissolved in 5 ml of benzene, was added into "magnesium subiodide", prepared from magnesium powder (0.486 g suspended in 12.5 ml of ether or THF) and 1.4 g of iodine. This mixture was gently refluxed for 1 day, but all of the starting ketone was recovered.

**Registry No.**—**1**, 54293-20-8; **3**, 1536-23-8; **4**, 1944-05-4; **5**, 853-39-4; **6**, 1766-76-3; sodium hydroxide, 1310-73-2; iodine, 7553-56-2; zinc, 7440-66-6.

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# Carbon-13 Nuclear Magnetic Resonance Spectra of 2*H*-1-Benzopyran-2-ones (Coumarins) in Chloroform and Sulfuric Acid


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Coumarins appear extensively in nature as photosensitizing agents[1] and have recently been employed as blue-green laser dyes.[2] Our interest in the photobleaching of laser dyes has prompted us to examine the carbon-13 NMR spectra of coumarins in neutral and acidic solvents. Ultimately, it is the structure, electronic distribution, and environment of the dye which determine its photostability. The lifetime of laser dyes could be improved if these factors could be understood and controlled. The carbon-13 chemical shift can be a reliable indicator of the ground-state electronic environments of carbon atoms in molecules[3] and should provide valuable insight into the nature of the coumarin structure.

## Results

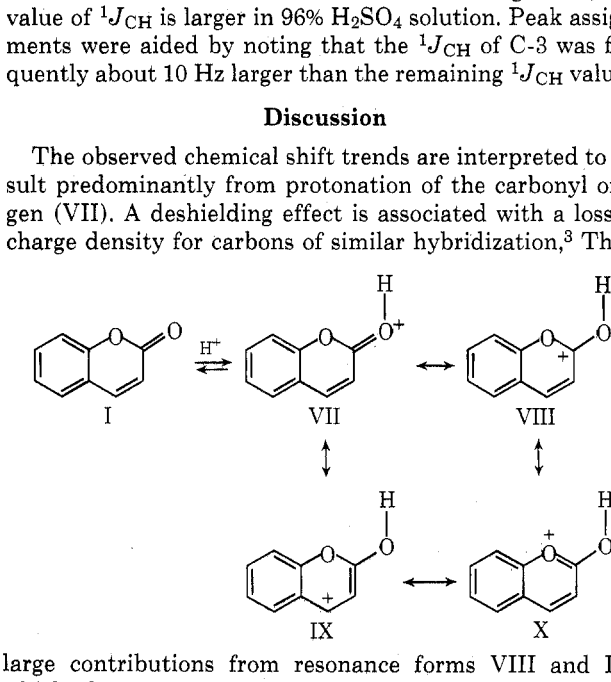
Table I gives the carbon-13 chemical shifts obtained in $CHCl_3$ and 96% $H_2SO_4$, as well as the chemical shift difference, $\Delta$, between these two solvents. Assignments of resonance positions to individual carbon atoms were based on known substituent effects,[4] splitting patterns in proton-coupled spectra, and internal consistency. A positive $\Delta$ indicates that the resonance is deshielded in $H_2SO_4$ relative to $CHCl_3$.

There is a general deshielding pattern ($+\Delta$) for all carbons except C-3, which is shielded for coumarins I–III and V. With few exceptions, most notably coumarin VI, the aromatic carbon resonances are deshielded 0–9 ppm. Larger deshielding trends of between 10 and 20 ppm are observed for C-2 and C-4 with the shift of C-4 always larger than that of C-2. A shielding of 2–6 ppm for C-3 is observed for I–III and V while C-3 is deshielded in IV and VI.

The one-bond carbon–hydrogen coupling constants, $^1J_{CH}$, are included in parentheses in Table I as well as their difference in neutral and acidic solvent. In general, the value of $^1J_{CH}$ is larger in 96% $H_2SO_4$ solution. Peak assignments were aided by noting that the $^1J_{CH}$ of C-3 was frequently about 10 Hz larger than the remaining $^1J_{CH}$ values.

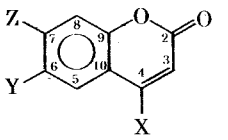
## Discussion

The observed chemical shift trends are interpreted to result predominantly from protonation of the carbonyl oxygen (VII). A deshielding effect is associated with a loss of charge density for carbons of similar hybridization,[3] Thus,




large contributions from resonance forms VIII and IX, which place positive charge at C-2 and C-4, can be used to

**Table I**
**Carbon-13 Chemical Shifts and One-Bond Carbon–Hydrogen Coupling Constants for Substituted Coumarins**




| | | | | | Chemical shift ($^1J_{CH}$)[a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | X | Z | |
| I | H | H | H | A | 172.8 | 110.4 (182) | 159.2 (170) | 131.6 (179) | 130.7 (168) | 138.9 (176) | 119.1 (162) | 153.7 | 121.8 | | | |
| | | | | N[b] | 159.6 | 115.7 (172) | 142.7 (164) | 127.3 (163) | 123.6 (163) | 130.9 (163) | 115.7 (164) | 153.1 | 118.1 | | | |
| | | | | Δ | 13.2 | −5.3 (10) | 16.5 (6) | 4.3 (16) | 7.1 (5) | 8.0 (13) | 3.4 (−2) | 0.6 | 3.7 | | | |
| II | H | Cl | H | A | 173.0 | 112.1 (182) | 157.7 (173) | 130.4 (172) | 136.3 | 138.5 (173) | 120.8 (172) | 152.1 | 122.7 | | | |
| | | | | N | 159.6 | 117.6 (175) | 141.9 (166) | 126.8 (167) | 129.4 | 131.4 (168) | 118.0 (169) | 152.1 | 119.6 | | | |
| | | | | Δ | 13.4 | −5.5 (7) | 15.8 (7) | 3.6 (5) | 6.9 | 7.1 (5) | 2.8 (3) | 0 | 3.1 | | | |
| III | H | H | OH | A | 172.3 | 106.3 (183) | 158.9 (164) | 133.8 (170) | 120.5 (169) | 164.1 | 105.1 (167) | 155.9 | 117.3 | | | |
| | | | | N[c] | 162.0 | 112.0 (173) | 144.8 (164) | 129.7 (163) | 113.8 (163) | 162.4 | 103.0 (162) | 156.4 | 112.3 | | | |
| | | | | Δ | 10.3 | −5.7 (10) | 14.1 (0) | 4.1 (7) | 6.7 (6) | 1.7 | 2.1 (5) | −0.5 | 5.0 | | | |
| IV | OH | H | H | A | 172.6 | 90.4 (175) | 177.6 | 126.0 (175) | 129.8 (170) | 139.2 (172) | 119.1 (164) | 154.5 | 116.2 | | | |
| | | | | N[c] | 160.4 | 89.3 (167) | 163.8 | 121.2 (170) | 121.7 (164) | 130.4 (164) | 114.3 (166) | 151.5 | 114.1 | | | |
| | | | | Δ | 12.2 | 1.1 (8) | 13.8 | 4.8 (5) | 8.1 (6) | 8.8 (8) | 4.8 (−2) | 3.0 | 2.1 | | | |
| V | $CH_3$ | H | OH | A | 171.1 | 106.4 (178) | 173.7 | 130.2 (169) | 120.2 (164) | 163.2 | 105.3 (170) | 155.2 | 117.7 | 21.2 | | |
| | | | | N[c] | 158.6 | 108.4 (170) | 152.9 | 124.3 (163) | 111.1 (164) | 159.3 | 100.4 (163) | 151.3 | 110.1 | 16.4 | | |
| | | | | Δ | 12.5 | −2.0 (8) | 20.8 | 5.9 (6) | 9.1 (0) | 3.9 | 4.9 (7) | 3.9 | 7.6 | 4.8 | $-CH_2-$ | $-CH_3$ |
| VI | $CH_3$ | H | $Et_2N$ | A | 170.4 | 110.5 (169) | 171.1 | 130.0 (172) | 121.8 (169) | 150.9 | 112.7 (172) | 141.9 | 122.5 | 19.5 | 55.6 | 9.6 |
| | | | | N | 161.6 | 108.0 (173) | 152.5 | 125.0 (159) | 108.0 (159) | 150.1 | 97.1 (159) | 155.5 | 108.4 | 18.1 | 43.8 | 12.3 |
| | | | | Δ | 8.8 | 2.5 (−4) | 18.6 | 5.0 (13) | 13.8 (10) | 0.8 | 15.6 (13) | −13.6 | 14.1 | 1.4 | 11.8 | −2.7 |

[a] Chemical shifts are reported in parts per million relative to $Me_4Si$. $^1J_{CH}$ values are contained in parentheses and are given in hertz. A = 96% $H_2SO_4$ solutions; N = $CHCl_3$ solutions; Δ = (A − N) is the chemical shift or coupling constant difference. [b] C-6 has been erroneously assigned in L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley, New York, N.Y., 1972. Spectrum 333. [c] Dimethyl sulfoxide added to enhance solubility.

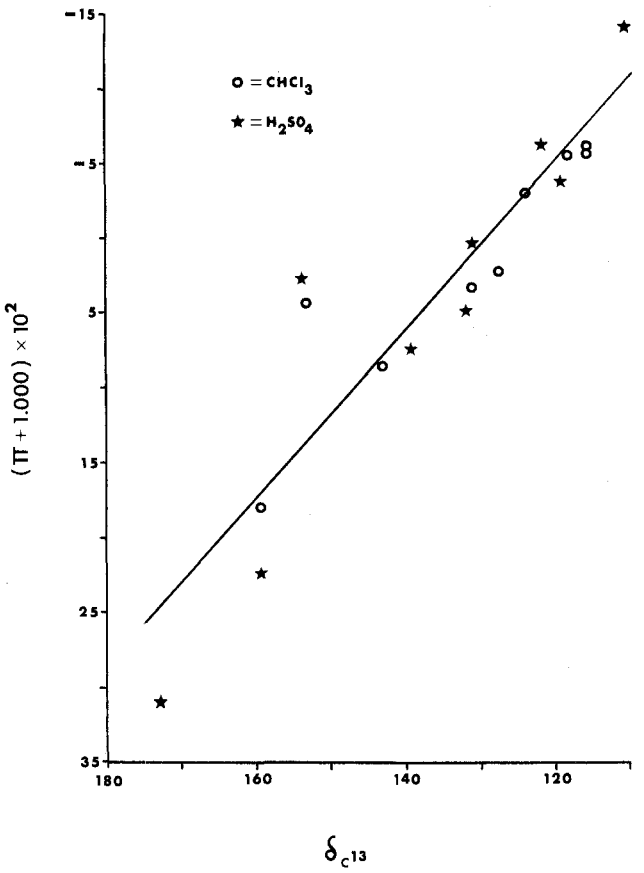



**Figure 1.** Plot of $\pi$ charge density vs. carbon-13 chemical shift for coumarin and protonated coumarin.

rationalize the deshielding noted for these carbons. The chemical shift changes are smaller than those observed for protonated unsaturated aldehydes and ketones.[5]

The effects at C-3 are taken to indicate a substantial contribution from resonance form IX, in which C-3 is now $\beta$ to two vinylic oxygens whose shielding influence[6] opposes the deshielding effect of the adjacent positive charge[7] at C-4. For coumarins I–III and V the shielding effect predominates, whereas for coumarins IV and VI deshielding is observed.

Protonation of the ether oxygen as well as significant contributions from resonance form X appear to be excluded because of the relative constancy of the C-9 chemical shift. Interestingly, resonance forms analogous to X have been shown to contribute significantly in the case of acyclic, saturated esters.[8] Evidently, in the coumarin structure, charge delocalization over the double bond is preferred rather than charge stabilization by the ether oxygen lone pairs.

Chemical shift changes associated with the aromatic ring are taken to be a result of further inductive and positive charge delocalization effects at these carbons. The aromatic carbon chemical shifts for coumarin VI appear to be more grossly affected compared with the rest of the series. This indicates that these carbons experience a stronger perturbation of their electronic environments which may be due to additional protonation at nitrogen. The chemical shift changes for the diethylamino group carbons are consistent with nitrogen protonation. Furthermore, spectroscopic studies of coumarin VI in acidified solution were interpreted in terms of protonation of the diethylamino group.[2]

The increase in $^1J_{CH}$ upon protonation indicates that charge is being lost at the carbon atoms.[9] The changes in $^1J_{CH}$ do not parallel the changes in chemical shift, presumably because the coupling constant is sensitive to other factors such as bond distance, hybridization, and bond polarization.[10] Long-range carbon–hydrogen couplings were observed but are not tabulated because of uncertainties in assignment.

In order to establish a more quantitative relationship between the carbon-13 chemical shifts and charge densities, the electron densities of carbon atoms in coumarin and protonated coumarin were calculated using the CNDO/2 method.[11] A good correlation between chemical shift and total charge or $\pi$ charge densities was obtained. Figure 1 shows the plot of chemical shift vs. $\pi$ charge density ($\rho$ = 0.915).

The reactivity of some coumarins has already been reasonably explained by using various MO indices.[12] The establishment of a chemical shift–charge density relationship enables one to investigate the use of carbon-13 chemical shifts as an aid in the prediction and explanation of phenomena which depend on electron distribution. For example, the reactivity of the coumarins toward nucleophilic attack at C-2 can be assessed by assuming that the $\Delta$'s of Table I represent the difference between ground- and transition-state-like charge distributions. The order of susceptibility to nucleophilic attack would be predicted to be II $\approx$ I > V $\approx$ IV > III > VI. This order is in qualitative agreement with the kinetic results obtained for the ring fission of analogous coumarins.[13]

Although the exact photobleaching mechanism of laser dyes has not been determined, it appears to involve a nonreversible photochemical reaction and depends, in a complex fashion, on such factors as pH, concentration, and solvent.[14] If the mechanism involves the nucleophilic attack by solvent on a photoexcited molecule, the correlation developed here may be applicable, and aid in the design of improved coumarin laser dyes. However, carefully controlled photobleaching studies must be made available which further elucidate the photobleaching mechanism before this can be rigorously pursued. Assuming that the correlation can be applied, it is noteworthy that coumarin VI would be predicted to be the most stable dye in this series. In practice, coumarins substituted in the 7 position with dialkylamino groups are very stable laser dyes.[2]

## Experimental Section

All chemicals were commercially available and used without further purification. Carbon-13 NMR spectra were obtained on a Varian HA-100 spectrometer modified for pulsed operation and equipped with an external fluorine-19 lock.[15] The spectrometer was operated at 25.15 MHz and the probe temperature was 36 ± 2°. Signals were accumulated in a Nicolet 1074 signal averager and Fourier transformed by a PDP-8/L computer. Coupling constants were measured from spectra recorded under gated-decoupling conditions.[16]

Saturated $CHCl_3$ solutions were used and chemical shifts converted to the tetramethylsilane ($Me_4Si$) scale by the relationship $\delta_{Me_4Si} = \delta_{CHCl_3} + 77.1$. In some cases dimethyl sulfoxide was added to enhance solubility. Spectra were also obtained using 3 *M* solutions of the coumarins in 96% $H_2SO_4$. Chemical shifts in 96% $H_2SO_4$ were measured relative to external benzene and converted to the $Me_4Si$ scale using $\delta_{Me_4Si} = \delta_{C_6H_6} + 128.7$.

Standard bond lengths and angles[11] were used in the CNDO/2 calculations.[17]

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**Registry No.**—I, 91-64-5; II, 2051-59-4; III, 93-35-6; IV, 1076-38-6; V, 90-33-5; VI, 91-44-1.

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## Chromate Oxidation of Alkylpyrazines

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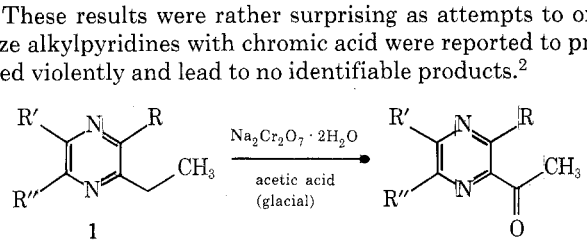
The most convenient preparation of acetylpyrazines previously reported in the literature is a two-step synthesis consisting of a treatment of alkylpyrazines with *N*-bromosuccinimide (NBS), followed by oxidation to the corresponding ketones using either sodium 2-propanenitronate or pyridine 1-oxide.[1] 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,