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2-Methyl- and 5-Methyl-9-hydroxyphenalenone

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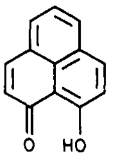
9-Hydroxyphenalenone (**1**) possesses a strong intramolecular hydrogen bond[1] which is of the symmetric double minimum type.[2-4] Low-temperature electronic spectroscopy[5] has recently allowed the characterization of the ground- and excited-state potential surfaces of **1** with respect to classical and tunneling motion of the hydrogen-bonded nucleus (hydrogen or deuterium). In order to extend these studies we have synthesized the title compounds. In 2-methyl-9-hydroxyphenalenone (**2**) the substituent breaks the symmetry of the potential surface (the minima are split by 100-200 cm^{-1}),[6] whereas more complicated behavior is expected[7] for the symmetrically substituted 5-methyl-9-hydroxyphenalenone (**3**).



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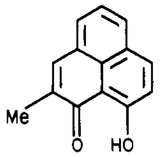

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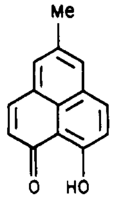

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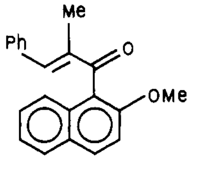

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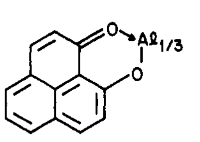

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Our synthetic approach to these compounds relies on the methodology employed by Koelsch and Anthes[8] in their original preparation of **1**. Thus our work toward **2** began with the synthesis of α-methyl-1-cinnamoyl-2-methoxynaphthalene (**4**) which was obtained by standard methods.

The final step in the Koelsch procedure—cyclization and dephenylation—proved to be unexpectedly difficult, and could only be achieved under particularly forcing conditions (Scholl condensation). As a result the overall yield for the preparation of **2** was low (10%) in comparison to the yields routinely obtained in the improved synthesis of **1** (85%). The preparation of **3** was accomplished in the usual manner by treatment of the condensation product of 6-methyl-2-methoxynaphthalene and cinnamoyl chloride with an additional mole of aluminum chloride, although the yield (40%) was again lower than that obtained in the case of the parent compound. The yield of all of these compounds has been considerably improved by the realization that the primary problem in this synthetic scheme lies with the decomposition of the very stable aluminum complexes (e.g., **5**) which are present at the conclusion of these reactions. These complexes are quite resistant to hydrolysis and this normally leads to a considerable loss in insolable product. By focusing on the decomposition of the aluminum complexes we were able to substantially improve the yields of **1**,[8-12] and it seems likely that the compound is formed quantitatively.

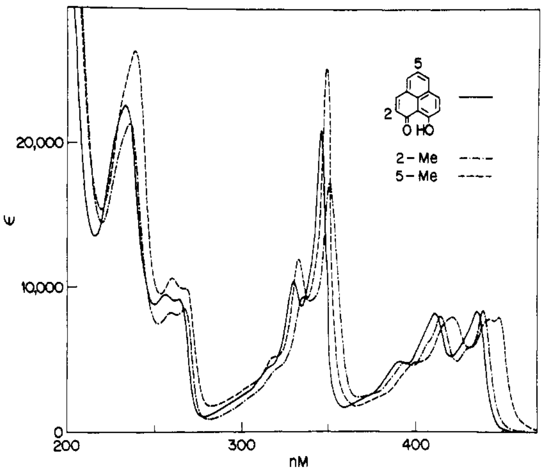

Figure 1. Electronic spectra of **1**, **2**, and **3** (3.57×10^{-5} M in hexane).

As may be seen from Figure 1, the electronic excitation properties of **1**, **2**, and **3** are quite similar. An interesting difference occurs in the chemical shift of the hydroxylic protons which absorb at **1** (δ 16.02), **2** (δ 16.27), and **3** (δ 15.83). It has recently been shown that such chemical shifts provide a sensitive index of the strength of a hydrogen bond with large δ values being associated with the strongest hydrogen bonds.[13,14] The series given above, therefore, reinforce the idea that the *potentiality* of symmetry does not guarantee the strongest hydrogen bond. The strength of the hydrogen bond in this case apparently depends on a subtle blend of steric and electronic[3] effects, for if one accepts the foregoing index of hydrogen bond strength,[13,14] then the asymmetric **2** possesses the most well developed hydrogen bond. The order of hydrogen bond strength in the symmetrical **1** and **3** may be accounted for with the second-order Jahn-Teller (SOJT) theory of hydrogen bond strength.[3]

The coefficients of the highest occupied and lowest unoccupied Hückel molecular orbitals of (symmetrical) **1** are $c_{\mathrm{HOMO},2} = 0.182$, $c_{\mathrm{LUMO},2} = 0.145$, $c_{\mathrm{HOMO},5} = 0.385$, and $c_{\mathrm{LUMO},5} = 0.0$, at positions 2 and 5, respectively. The first-order perturbation of the energy gap ($\Delta E = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}$) is given by $\delta\Delta E = (c_{\mathrm{LUMO},X}{}^2 - c_{\mathrm{HOMO},X}{}^2)\delta\alpha_X$, where $\delta\alpha_X$ is the change in Coulomb integral at position X as a result of substitution ($\delta\alpha = -0.3\beta$ for methyl, β negative).[3,15] Thus in the case of 5-substitution (**3**) we obtain $\delta\Delta E = 0.044\beta$ and as the energy gap is calculated to be decreased by substitution (a view supported by the electronic spectra,

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(15) Cf. ref 3. Note that $\delta\alpha$ is negative for an increase in electronegativity at the site of substitution.

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cf. Figure 1), we expect the hydrogen bond strength to be decreased in comparison with 1. The quantitative SOJT theory[3] is also in agreement with the idea of a slightly weakened hydrogen bond in 3 ($\lambda = 0.992$) in comparision to 1 ($\lambda = 0.989$). The above chemical shifts of the hydroxylic protons support this picture.

In the case of 2-substitution (2) the qualitative SOJT theory predicts a very small effect ($\delta\Delta E = 0.004\beta$), and apparently other factors play a dominant role in this compound.

Experimental Section

α-Methyl-1-cinnamoyl-2-methoxynaphthalene (4). A solution of α-methylcinnamic acid (40.6 g, 0.25 mol) and 2-methoxynaphthalene (39.6 g, 0.25 mol) in 1,2-dichloroethane was treated with phosphorus pentachloride (52.0 g, 0.25 mol) and the solution was refluxed with stirring for 5 min. The solution was cooled in an ice bath, and aluminum chloride (33.9 g, 0.25 mol) was slowly added after which the mixture was refluxed for 10 min. The reaction mixture was cooled and quenched with iced hydrochloric acid, and the organic layer was separated. The aqueous layer was extracted with methylene chloride, and then the organic layers were combined and washed with sodium carbonate solution and water. After drying over magnesium sulfate, the solvent was removed to give a viscous green oil (43.7 g, 58% yield). Crystallization from hexane (charcoal) gave yellow needles, 76.2–77.7 °C. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 5.99. Found: C, 83.57; H, 6.13. IR (CsI) 3040 (w, sh), 3010 (w), 2980 (w), 2940 (w), 2840 (w), 1950 (vw), 1617 (vs), 1592 (s, sh), 1574 (m, sh), 1505 (s), 1464 (m, sh), 1444 (s), 1431 (s, sh), 1387 (w), 1337 (w), 1271 (m), 1250 (s), 1230 (s), 1210 (m), 1180 (m), 1163 (w), 1148 (m), 1079 (m), 1059 (s), 1018 (w), 990 (s), 951 (vw), 924 (w), 902 (m), 886 (m), 859 (m), 801 (vs), 763 (m), 748 (m), 727 (vw), 713 (vvw), 690 (m), 633 (m), 610 (m), 580 (m), 546 (m), 517 (s), 448 cm^{-1} (m); UV (hexane) λ_{max} 226 nm (ϵ 69 350), 278 (23 800), 293 (18 300, sh), 320 (4100), 335 (3900); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.83 (d, $J = 1.5$ Hz, 3 H), 3.95 (s, 3 H), 6.8–8.3 (m, 12 H); mass spectrum (relative intensity), *m/e* 145 (20), 185 (100), 302 (62).

2-Methyl-9-hydroxyphenalenone (2). Instead of quenching the above reaction, more aluminum chloride (33.9 g, 0.25 mol) was added and refluxing was continued overnight. The reaction mixture was decomposed with iced hydrochloric acid, and the organic layer was washed with water and dried over magnesium sulfate. Removal of the solvent gave a red oil (ca. 50 g) which was suitable for use in the Scholl reaction. The oil was intimately mixed with aluminum chloride (100 g) and the container immersed in an oil bath which had been preheated to 180 °C. The reaction mixture was held at this temperature for 1 h with stirring and then poured into iced hydrochloric acid. Extraction was carried out with methylene chloride, and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed to give a black oil (30 g), which was distilled (sublimation vessel), recrystallized from ethanol (charcoal), sublimed, and recrystallized from ethanol to give yellow needles (5.9 g, 11% yield), 127.8–129.1 °C. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 80.12; H, 4.90. IR (CsI) 3060 (vvw), 2950 (vvw), 2920 (vvw), 1632 (vs), 1585 (vs), 1480 (w, br), 1363 (m), 1322 (vw), 1260 (m), 1215 (m), 1180 (vw), 1160 (w), 1130 (vw), 1040 (w), 1005 (w), 940 (w), 920 (w, sh), 900 (m), 835 (s), 767 (m), 730 (m), 692 (m), 605 (vw), 563 (w), 536 (w), 464 (m), 428 (w), 402 cm^{-1} (w); UV (hexane) λ_{max} 235 nm (ϵ 21 300), 258 (8200), 267 (8400), 305 (2400, sh), 317 (4200, sh), 335 (9300), 350 (17 600), 374 (2500, sh), 393 (4800, sh), 406 (6000, sh), 414 (8000), 429 (5700, sh), 439 (8400); ^{1}H NMR ($CDCl_3$, Me_4Si) pattern, δ 2.40 (3 H), δ_X 7.86 (1 H, ($J_{AX} = 1.0$ Hz), AB pattern, δ_A 7.16, δ_B 8.04 ($J_{AB} = 9.6$ Hz, 2 H), AB_2 pattern, δ_A 7.51, δ_B 7.9 ($J_{AB} = 8$ Hz, 3 H), 16.27 (s, 1 H); mass spectrum (relative intensity) *m/e* 152 (13), 153 (7), 181 (26), 182 (9), 210 (100).

5-Methyl-9-hydroxyphenalenone (3). 6-Methyl-2-methoxynaphthalene[16] (9.0 g, 0.052 mol) and cinnamoyl chloride (8.0 mL, 0.052 mol) were dissolved in 100 mL of 1,2-dichloroethane. After the reaction flask was cooled in an ice bath, aluminum chloride (7.0 g, 0.052 mol) was slowly added to the flask, while the solution was mechanically stirred. After about 1 h when the reaction had come to room temperature, a further 7.3 g of aluminum chloride was added to the solution and the reaction mixture taken to reflux. After 3 h the reaction mixture was quenched with iced hydrochloric acid and filtered. The filtrate was extracted with methylene chloride. The solid was repeatedly boiled with hot methylene chloride and filtered until the filtrate became colorless. All the organic extracts were combined, dried over anhydrous sodium sulfate, and taken down on a rotary evaporator to give a yellow solid (10 g). The compound was purified by two sublimations followed by a recrystallization from ethanol (charcoal) to yield yellow needles (4.21 g, 38%) 198.4–198.5 °C. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 80.18; H, 4.85. IR (CsI) 3030 (vw), 2920 (vw), 1631 (vs), 1598 (vs), 1356 (m), 1280 (w), 1238 (m), 1160 (m), 950 (b), 865 (s), 835 (w), 782 (w), 748 (w), 688 (m), 545 (w), 535 (w), 500 cm^{-1} (w); UV (hexane) λ_{max} 239 nm (ϵ 26 400), 259 (10 600) 268 (sh 9900), 318 (sh, 5100), 332 (12 000), 348 (25 200), 378 (2400), 400 (4800), 422 (7900), 442 (7800), 448 (7900); ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.61 (s, 3 H), AB pattern, δ_A 7.13, δ_B 7.99 ($J_{AB} = 9.4$ Hz, 4 H), 7.80 (s, 2 H), 15.83 (s, 1 H); mass spectrum (relative intensity), *m/e* 153 (26), 181 (54), 182 (43), 210 (100).

9-Hydroxyphenalenone (1). When the above procedure (synthesis of 3) was followed for the preparation of 9-hydroxyphenalenone (starting from cinnamoyl chloride and 2-methoxynaphthalene on a 0.5-mol scale), 85 g (86% yield) of crude product was obtained, 193–202 °C (lit. mp 202.4 °C);[8–12,17] IR (CsI) 3050 (br, vvw), 1632 (vs), 1585 (vs), 1483 (m), 1420 (vw), 1360 (m), 1305 (vw), 1239 (vs), 1185 (w), 1143 (w), 961 (vw), 922 (br, w), 845 (s), 807 (vw), 760 (w), 730 (w), 690 (m), 610 (br, w), 552 (vw), 528 (w), 491 (w), 470 (w), 429 cm^{-1} (m); UV (hexane) λ_{max} 234 nm (ϵ 22 600), 256 (9400), 264 (9100), 315 (sh, 4300), 329 (10 400), 344 (21 000), 390 (4800), 411 (8100), 436 (8300); ^{1}H NMR ($CDCl_3$, Me_4Si) AB pattern, δ_A 7.15, δ_B 8.05 ($J_{AB} = 9$ Hz, 4 H); AB_2 pattern δ_A 7.58, δ_B 8.0 ($J_{AB} = 8$ Hz, 3 H), δ 16.02 (s, 1 H); mass spectrum (relative intensity), *m/e* 141 (15), 169 (53), 170 (48), 198 (100).

Registry No. 1, 7465-58-9; 2, 78229-05-7; 3, 78837-89-5; 4, 78837-90-8; α-methylcinnamic acid, 1199-77-5; 2-methoxynaphthalene, 93-04-9; 6-methyl-2-methoxynaphthalene, 26386-94-7; cinnamoyl chloride, 102-92-1.

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On the Formation of 2*H*-Cyclohepta[*b*]furan-2-ones by the Pyrolysis of Aryl Propiolates and Phenyl Tetrolate

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In recent years equilibration of acetylenes with methylenecarbenes ($RC{\equiv}CR' \rightleftharpoons RR'C{=}C{:}$) above 500 °C has been established for aryl- and alkyl-substituted acetylenes[1,2] and for acetylene itself[3] and the methylenecarbenes have been trapped in intramolecular insertion reactions. Acyl acetylenes undergo this rearrangement, and flash

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