Notes

Synthesis and Spectral Properties of Ethylmethylsulfonium 3,4-Dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide

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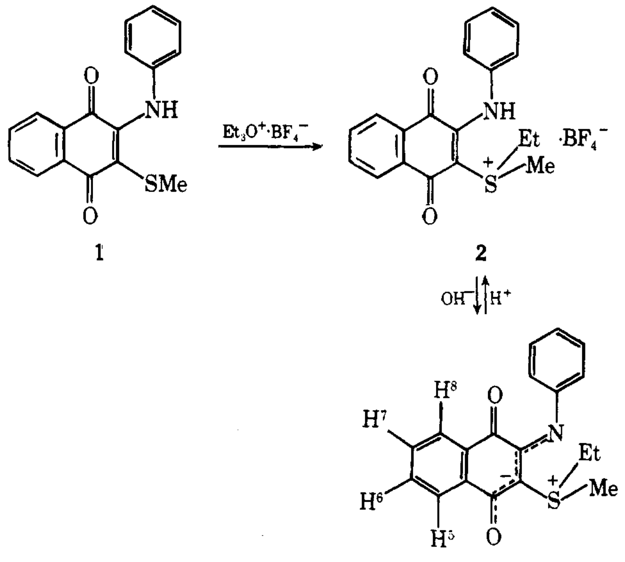
Sulfonium ylides are stabilized when the negative charge is delocalized by electron-withdrawing groups such as carbonyl,[1] cyano,[2,3] sulfonyl,[4] or an aromatic system.[5] It was of interest to determine the ability of the phenylimino ($C_6H_5N{=}$) group to delocalize the negative charge. The 3-ethylmethylsulfonium ylide **3** of 2-anilino-1,4-naphthoquinone was synthesized as a representative compound for this study.[6]

2-Anilino-3-(methylthio)-1,4-naphthoquinone[7] (**1**) was allowed to react with triethyloxonium tetrafluoroborate in anhydrous dichloromethane to give 85% of (3-anilino-1,4-dioxo-2-naphthyl)ethylmethylsulfonium tetrafluoroborate (**2**) as red crystals: λ_{max} (MeOH) 228, 268, 428 nm (ϵ 25 100, 23 800, 4100); λ_{max} (0.1 N HCl) 221, 260, 268 sh, 293 sh, 340, 420 nm (ϵ 19 300, 20 500, 18 900, 10 700, 3800, 3300); λ_{max} (0.1 N NaOH) 271, 438 nm (ϵ 23 800, 3300).

When a solution of the sulfonium tetrafluoroborate **2** in tetrahydrofuran was stirred with an aqueous solution of sodium bicarbonate, the initial red color changed to black. Dilution with water gave 77% of the stable ylide ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2-(1*H*)-naphthylenylide (**3**) as purple-black, monoclinic crystals:[8] λ_{max} (MeOH) 229, 269, 428 nm (ϵ 26 000, 24 900, 4530); λ_{max} (0.1 N HCl) 222, 260, 267 sh, 290 sh, 340, 415 nm (ϵ 20 200, 21 600, 20 200, 12 400, 4690, 4360); λ_{max} (0.1 N NaOH) 270, 437 nm (ϵ 23 900, 3270).

It is seen from the above that the electronic spectra of **2** and **3** are virtually identical, indicating that they produce the same chromophoric system in the same solvent. The spectra in methanol and in dilute alkali are superimposable if one corrects for solvent effect and absorption by carbonate in the alkali.

As was observed with diethylsulfonium 1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylide[1] (**4**), the ^1H NMR spectrum (Figure 1) of sulfonium ylide **3** (in Me_2SO-d_6) exhibits magnetic nonequivalence of methylene protons. The ambient (32 °C) spectrum (Figures 1 and 2) displays the methyl protons of the ethylmethylsulfonium moiety as a somewhat broadened singlet at δ 3.15 and the methyl protons of the ethyl moiety appear as a rather broad triplet at δ 1.26 (J = 7.4 Hz). The methylene group of the ethyl moiety appears as two nonequivalent protons at δ 3.45 and 3.98. These protons form the AB portion of an ABX_3 spectrum (J_{AB} = 12 Hz, J_{AX} = J_{BX} = 7.4 Hz). The double quartet at δ 3.98 shows noticeable broadening due to what is presumed to be steric hindrance from the adjacent *N*-phenyl group. When the solution of **3** is heated to 60 °C [Figure 2 (b)] all peaks from the ethylmethylsulfonium moiety sharpen and the signals from the methylene protons, which now appear as a pair of double quartets similar to that reported for the methylene protons of **4**,[1] approach each other in chemical shift. Upon further heating to 80 °C the methylene resonance lines sharpen further and come closer together in chemical shift. The progressive shift towards each other ($\Delta\delta$ 0.52 at 32 °C to $\Delta\delta$ 0.45 at 100 °C) suggests that an extremely high temperature would be needed for coalescence. Decomposition was noted when the temperature was elevated to 190 °C (boiling solution) and no further information could be obtained.



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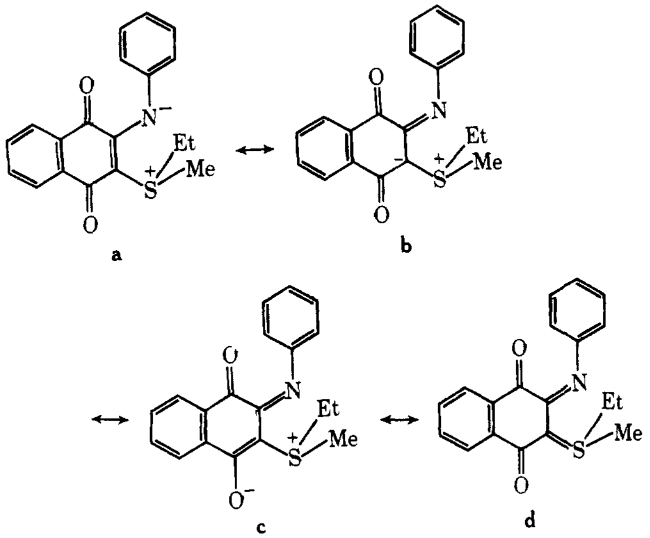

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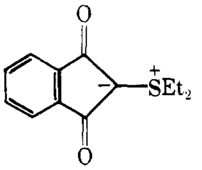

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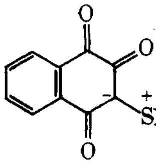

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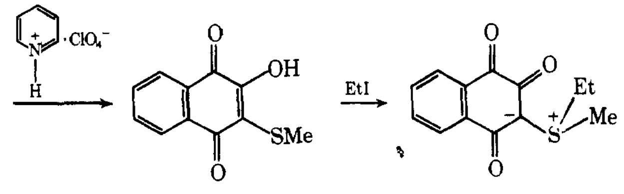

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The low-field region of the ^1H NMR spectrum of ylide **3**

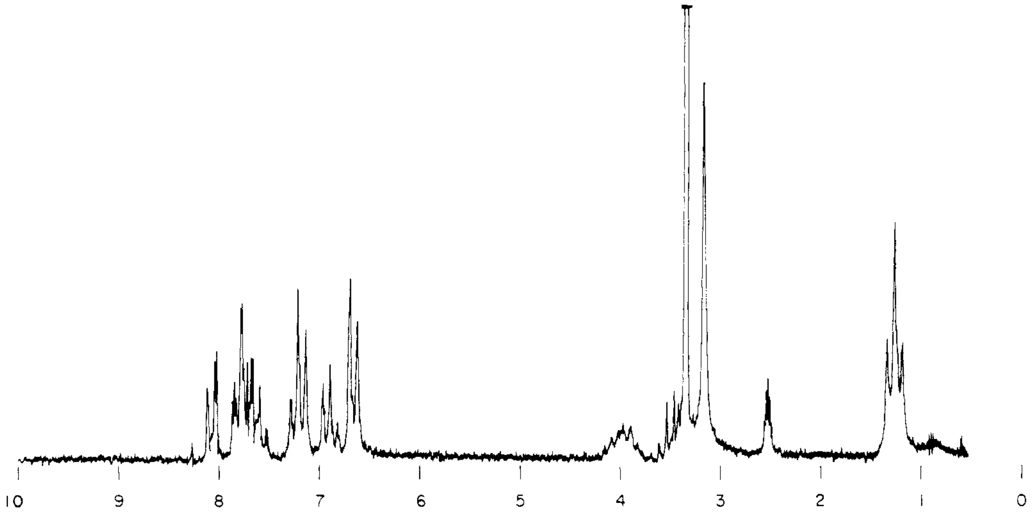

Figure 1. ^{1}H NMR spectrum (100 MHz) of ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (3) in Me_2SO-d_6.

(Figure 1) shows distinct patterns for the two aromatic moieties. The *N*-phenyl protons appear as an A_2B_2C pattern which is typical for monosubstituted phenyl compounds substituted by a strong electron-donating group. A first-order analysis of the spectrum gives ortho protons at δ 6.66 (dd, J = 2 Hz, 8.5 Hz), meta protons at δ 7.19 (dd, J = 8.5, 8.5 Hz), and para proton at δ 6.90 (dt, J = 2, 8.5 Hz). The aromatic protons of the naphthoquinone moiety appear as a complex ABCD system. Here again a first-order analysis indicates protons at δ 7.61 (m, C_6 H), 7.70 (m, C_7 H), 7.80 (dd, J = 2, 8.5 Hz, C_5 H), and 8.07 (dd, J = 2, 8.5 Hz, C_8 H). The upfield shift of C_5 H(Δδ 0.27) vs. C_8 H suggests that in solution there is less double bond character to the C_4 carbonyl than the C_1 carbonyl, in agreement with the negative charge of the ylide being partially delocalized by the C_4 carbonyl.

The ^{1}H NMR signal (δ 3.15) of the SCH_3 of ylide **3** is downfield from that (δ 3.05) of the SCH_3 of sulfonium salt **2**, and has the same chemical shift as the SCH_3 in ethylmethylsulfonium 3,4-dihydro-1,3,4-trioxo-2(1*H*)-naphthylenylide (**7**). It is evident that the negative charge of **3** is delocalized in degree similar to that of **7**. The phenylimino group, therefore, appears to behave like the carbonyl group in delocalizing the negative charge of a sulfonium ylide.

Ylide **7** was prepared by alkylating 2-hydroxy-3-(methylthio)-1,4-naphthoquinone (**6**) with ethyl iodide. Methylthio derivative **6** was obtained by pyridinium perchlorate demethylation[9] of dimethylsulfonium 3,4-dihydro-1,3,4-trioxo-2(1*H*)-naphthylenylide[10] (**5**).

The x-ray crystal structure of ylide **3** has been determined by Lovell and Cosulich.[11] The observed bond lengths and angles suggest that the four resonance forms depicted by a, b, c, and d are important and that the negative charge is delocalized through the bonds C(2)–N, C(2)–(3), C(3)–C(4), C(4)–O(4), and C(3)–S (Figure 3).

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Samples for analysis were dried in vacuo over P_2O_5 at 100 °C for 18–24 h. Ultraviolet absorption spectra were measured on a Cary recording spectrophotometer. Infrared spectra were determined on a Perkin-Elmer spectrophotometer (Model 21). NMR spectra were determined on Varian A-60 and HA-100 spectrometers with tetramethylsilane as internal standard.

(3-Anilino-1,4-dihydro-1,4-dioxo-2-naphthyl)ethylmethylsulfonium Tetrafluoroborate (2). To a stirred solution of 5.90 g (0.02 mol) of 2-anilino-3-(methylthio)-1,4-naphthoquinone[7] (**1**) in 150 mL of dichloromethane was added a solution of 17.9 g (0.094 mol) of triethyloxonium tetrafluoroborate in 100 mL of dichloromethane. The solution was stirred at room temperature for 22 h and then evaporated in vacuo to give a red, crystalline residue. Recrystallization from methanol afforded 7.01 g (85%) of **2** as red crystals: mp 210–212 °C; ν_{max} (KBr) 1672, 3310 cm^{-1}.

Anal. Calcd for $C_{19}H_{18}NO_2SBF_4$: C, 55.5; H, 4.41; N, 3.41; S, 7.80; F, 18.5. Found: C, 55.4; H, 4.35; N, 3.33; S, 8.15; F, 18.3.

Ethylmethylsulfonium 3,4-Dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (3). To a stirred solution of 5.00 g (0.012 mol) of **2** in 100 mL of tetrahydrofuran was added 25 mL of saturated aqueous $NaHCO_3$. The resulting mixture was stirred for 3 days at room temperature and then diluted further with water. The resulting suspension was chilled and filtered to give 3.10 g of **3** as purple-black crystals,[8] mp 183–185 °C, ν_{max} (KBr) 1688 cm^{-1}.

Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.6; H, 5.30; N, 4.33; S, 9.92. Found: C, 70.4; H, 5.53; N, 4.24; S, 9.94.

2-Hydroxy-3-(methylthio)-1,4-naphthoquinone (6). A mixture of 2.34 g (0.01 mol) of **5**,[10] 1.43 mL of 70–72% $HClO_4$, and 25 mL of pyridine was heated under reflux for 2 h and allowed to stand at room temperature overnight. The dark reddish-black solution was evaporated in vacuo to a reddish-black crystalline residue. The residue was extracted with four 35-mL portions of boiling ether and the combined ether extracts were evaporated in vacuo to give 1.80 g of red crystals, mp 116–119 °C. Recrystallization from ethyl acetate–petroleum ether (bp 30–60 °C) gave 1.46 g (66%) of **6** as blood-red needles: mp 127–129 °C; λ_{max} (0.1 N HCl) 243, 274, 339, 445 nm (ε 14 400, 20 400, 3520, 1540); λ_{max} (MeOH) 242, 274, 330, 460 nm (ε 15 400, 22 600, 3040, 2220); λ_{max} (0.1 NaOH) 280, 480 nm (ε 24 200, 2200); ν_{max} (KBr) 3320 cm^{-1} (OH); NMR ($CDCl_3$) δ 2.62 (s, 3, SCH_3), 7.59–7.86 (m, 3, C_6 H,C_7 H,OH), 7.95–8.18 (m, 2, C_5 H,C_8 H).

Anal. Calcd for $C_{11}H_8O_3S$: C, 60.0; H, 3.66; S, 14.6. Found: C, 59.9; H, 3.61; S, 14.3.

Ethylmethylsulfonium 3,4-Dihydro-1,3,4-trioxo-2(1*H*)-naphthylenylide (7). A mixture of 6.80 g (0.031 mol) of **6**, 19.3 g (0.124 mol) of ethyl iodide, 4.40 g (0.034 mol) of diisopropylethylamine, and 100 mL of absolute ethanol was heated under reflux for 4.5 h. The dark-colored solution was evaporated in vacuo until crystallization occurred. The mixture was chilled and filtered and the yellow crystals were washed with absolute ethanol and absolute ethanol–ether (1:1) to give 8.11 g of yellow crystals, mp 130–145 °C. Two recrystallizations from absolute ethanol gave 4.72 g (61%) of **7** as yellow crystals: mp 181.5–184 °C; λ_{max} (0.1 N HCl) 225, 268, 326, 390 nm (ε 20 800, 25 300, 2730, 1980); λ_{max} (MeOH) 225, 271, 325, 383 nm (ε 21 100, 25 300, 2480, 1980); λ_{max} (0.1 N NaOH) 268, 287 (sh), 322, 383 nm (ε 23 300, 13 800, 2980, 1980); ν_{max} (KBr) 1695 cm^{-1} (C=O); NMR (Me_2SO-d_6) δ 1.23 (t, 3, CH_2CH_3), 3.15 (s, 3, SCH_3), 3.16–4.17 (4 distinct quartets, 2, CH_2CH_3), 7.65–8.20 (m, 4, Ar).

Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.9; H, 4.87; S, 12.9. Found: C, 62.5; H, 4.82; S, 13.0.

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Registry No.—**1**, 61770-44-3; **2**, 61770-46-5; **3**, 61770-47-6; **5**,

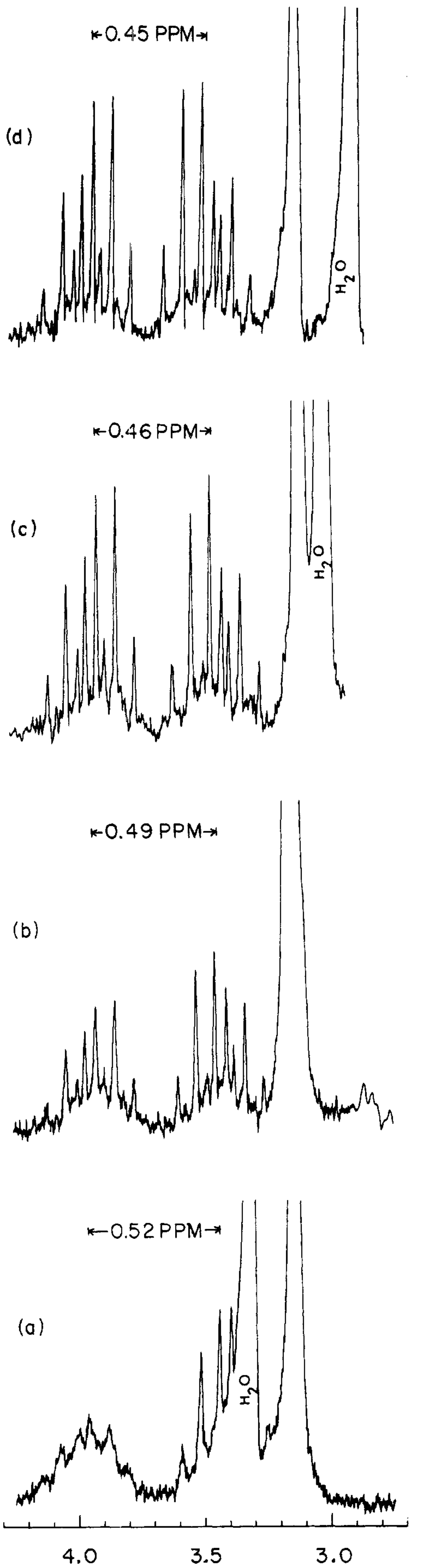

Figure 2. ^{1}H NMR spectra (100 MHz) of ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (**3**) in Me_2SO-d_6 at various temperatures: (a) 32 °C, (b) 60 °C, (c) 80 °C, (d) 100 °C.

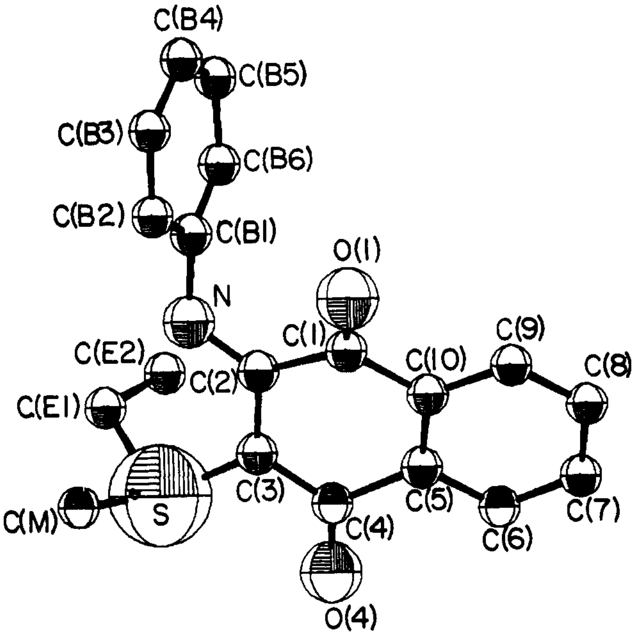

Figure 3. A perspective representation of the structure of ethylmethylsulfonium 3,4-dihydro-1,4-dioxo-3-(phenylimino)-2(1*H*)-naphthylenylide (**3**).

31914-13-3; **6,** 31914-17-7; **7,** 57893-97-7; triethyloxonium tetrafluoroborate, 368-39-8.

References and Notes

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Lithium Triethylborohydride Reduction of Alkyl Methanesulfonate Esters[1,2]

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In the course of preparing some hydrocarbons for another study we required an efficient procedure for the transformation $>C{=}O \rightarrow >CH_2$ for cases in which the carbonyl group is in a sterically hindered neopentyl environment. A number of techniques are available for this reduction,[4] but after trying several of these with uncertain or unsatisfactory results, we decided to test lithium triethylborohydride ($LiEt_3BH$, or Super Hydride) on alkyl methanesulfonate esters (mesylates). This reagent is a powerful hydride donor toward alkyl halides,[9] and we reasoned that it might behave in an analogous fashion toward alkyl mesylates. Further, these esters are usually stable, easily handled compounds, and are ordinarily acces-