Ion Radicals. 39. Reactions of 10-Methyl- and 10-Phenylphenothiazine Cation Radical Perchlorates with Ketones[1,2]

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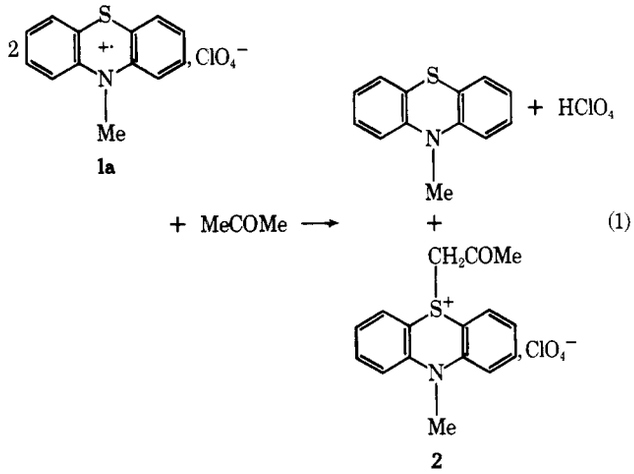
Reactions of 10-methyl- (**1a**) and 10-phenylphenothiazine cation radical perchlorate (**1b**) with butanone, cyclopentanone, cyclohexanone, and tetralone-1 led to ketoalkyl sulfonium perchlorates in which substitution at the α position of the ketones had occurred. Similar reactions were carried out between **1a** and methyl isopropyl ketone, acetophenone, and indanone-1. Several of the sulfonium salts were converted into the corresponding ylides by treatment with base. Reaction of 5-(2-indan-1-onyl)-5,5-dihydro-10-methylphenothiazine perchlorate (obtained from **1a** and indanone-1) with nucleophiles gave good yields of 2-substituted indanones.

We have earlier reported that the cation radicals of thianthrene and phenoxathiin react with dialkyl and alkylaryl ketones to give β-ketoalkylsulfonium salts.[5] Analogous reactions of 10-methyl- (**1a**) and 10-phenylphenothiazine cation radical (**1b**) have been carried out and are reported here. Although they gave for the most part reasonably good yields of sulfonium salts the reactions were rather slow. In our earlier work with the cation radicals of thianthrene (**1c**) and phenoxathiin (**1d**) the reactions were sufficiently facile to occur in acetonitrile solution. In the present work it was necessary in all but one case to use the ketone as the solvent, and even in that way reactions sometimes took several days. The stoichiometry of the reactions is illustrated in eq 1. Reactions of **1a** and **1b** with



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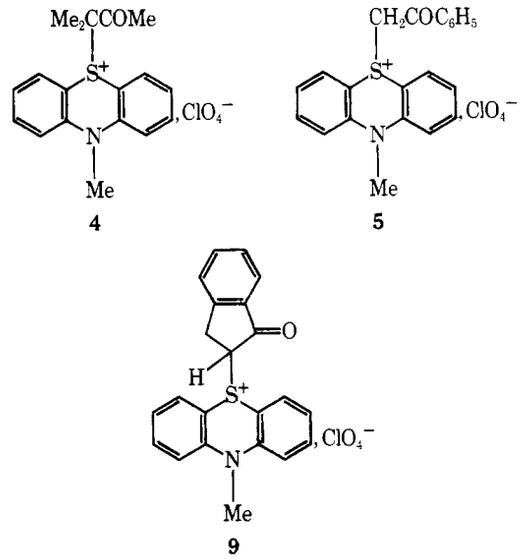
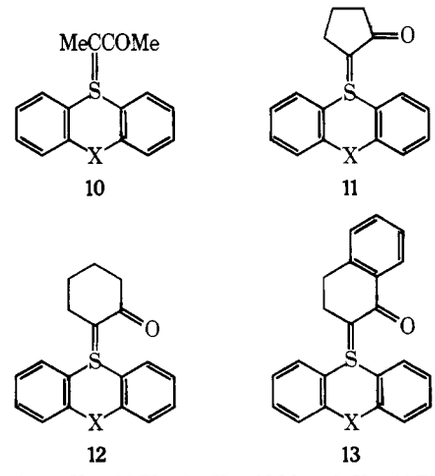
butanone, cyclopentanone, cyclohexanone, and tetralone-1 gave the products **3, 6, 7,** and **8,** while reactions of **1a** with methyl isopropyl ketone, acetophenone, and indanone-1 gave **4, 5** and **9,** respectively. Each product was characterized by elemental analysis[6] (except **9**) and NMR spectroscopy. Product **9** was further characterized by its reactions with nucleophiles, described below.



Several of the sulfonium salts were converted into the corresponding ylides by treatment with an alkylamine in solution. Each ylide (**10, 11, 12, 13**) was characterized by NMR and parent-peak mass spectrum or analysis.



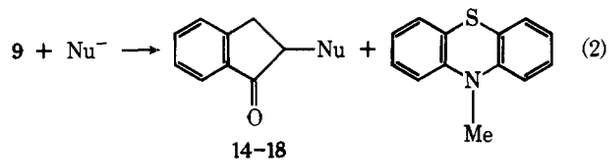
10–12, X = *N*-Ph; **13a**, X = N-Me; **13b**, X = N-Ph

Compound **9** was used for displacement reactions with nucleophiles (eq 2), and gave a series of substituted indanones (**14–18**) whose NMR spectra showed well-defined couplings

Table I. Chemical Shifts and Coupling Constants of Keto-Ring Protons in Substituted Indanones[a]

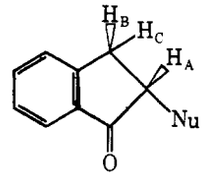
Registry no.	Compd	δ_A	δ_B	δ_C	J_{BA}[b]	J_{CA}[b]	J_{BC}[b]	Solvent
61723-05-5	14[c]	4.14	3.84	3.30	8.0	4.0	18.0	$CDCl_3$
61723-06-6	15[d]	4.29	3.51	3.83	8.0	3.5	18.0	$CDCl_3$
61723-07-7	16[e]	4.39	3.88	3.32	8.0	5.0	18.0	$CDCl_3$
1775-27-5	17[f]	4.74	3.85	3.32	7.0	3.5	18.0	CD_3CN
61723-09-9	18[g]	5.78	4.16	3.65	8.0	6.0	17.5	CD_3CN
61723-11-3	9	4.64	*h*	*h*	7.0	4.5	*h*	CD_3CN

[a] A Varian XL-100 NMR instrument was used. [b] In hertz. Each proton, H_A, H_B, H_C, appeared as two well-defined doublets. [c] Aromatic protons, m, 4 H, δ 7.84–7.38. [d] Aromatic protons, m, 8 H, δ 7.87–7.33; Me, s, δ 2.45. [e] Aromatic protons, m, 4 H, δ 7.90–7.30; CH_2, q, δ 4.58, J = 7.0 Hz; Me, t, δ 1.20, J = 7.0 Hz. [f] Aromatic protons, m, 4 H, δ 7.78–7.36; lit.[7] values: δ H_A, H_B, H_C 4.65, 3.84, 3.42; J_{BA}, J_{CA}, J_{BC} 7.3, 3.5, and 18.5 Hz in $CDCl_3$. [g] (As the ClO_4^- salt) aromatic protons, m, 4 H, δ 7.96–7.52; pyridine protons, *o*-, d, δ, 8.78, J_{om} 6 Hz; *m*-, t, δ 8.12, $J_{m(o,p)}$ = 7 Hz; *p*-, t, δ 8.64, $J_{p,m}$ = 7 Hz. [h] Multiplets obscured by overlap with *N*-Me signal, s, δ 3.56; aromatic protons, m, 12 H, δ 8.02–7.28.



14–18

among the keto-ring protons. These couplings are given in Table I. In all cases, except **15**, the chemical shift of H_B is larger than that of H_C. A curious inversion of positions occurs in **15** in which H_B (characterized by the larger coupling J_{BA} = 8 Hz) appears at higher field than H_C, indicating the probable shielding effect of the tolyl ring on protons H_B and H_C in **15**. The assignments of coupling constants are made on the basis of the larger couplings being expected for cis protons (H_A and H_B) and are in accord with data reported by Jackson et al. for **17**.[7]



14–18

14, Nu = SCN; 15, Nu = O_2S—⟨⟩—Me;

16, Nu = —S—C(=S)—OEt; 17, Nu = Br; 18, Nu = —N⁺⟨⟩

The reactions of **1a** and **1b** with butanone and of **1a** with methyl isopropyl ketone gave sulfonium salts (**3** and **4**) in which substitution had occurred at the branched α-carbon atom rather than at the α-methyl group. Analogous reactions were reported with thianthrene and phenoxathiin cation radicals (**1c** and **1d**).[5] These modes of substitution are consistent with the view[8] that the reaction involves electrophilic addition to the enol. Substitutions at the α-carbon atoms of unsymmetrical ketones, e.g., halogenations, which have been shown to involve the enol, also occur at the more substituted carbon atom, the controlling factor being addition to the more stable enol when a choice is available.[9,10]

The reactions of **1a** and **1b** with ketones are slower than the corresponding reactions of thianthrene and phenoxathiin cation radicals (**1c** and **1d**). Rates of reaction were not measured but it was found that whereas solutions of ketones and **1c** or **1d** in acetonitrile reacted readily, the reactions of similar solutions of **1a** and **1b** were very slow, so much so that ketones were themselves used as solvents for reactions of **1a** and **1b**. Quantitative rate comparisons are to be made. Differences in rates may be attributed at this stage to differences in positive charge density at the sulfur atom in the several cation radicals.

There is a statistical advantage of two sulfur atoms in **1c**, while in the other cation radicals positive charge density is also localized at atoms (nitrogen and oxygen) where reaction with the ketones cannot be fruitful. In accordance with this idea, HMO calculations of comparative charge densities in the cation radicals **1a–d** have shown that these decrease at the sulfur atom in the order **1c, 1d, 1a** $\simeq$ **1b**.[11]

Experimental Section

10-Methyl- (**1a**) and 10-phenylphenothiazine cation radical perchlorates (**1b**) were prepared and assayed as described earlier.[12]

Reaction of 1a with Acetone. Formation of 2. A solution of 644 mg (2.06 mmol) of **1a** in 40 mL of acetone was stirred for 48 h. The dark green solution was concentrated on the aspirator, and the residue taken up in CH_2Cl_2. Ether was added to precipitate 100 mg (0.27 mmol, 26%) of crude **2**. Decolorization with charcoal and crystallization from CH_2Cl_2–ether gave a cream-colored solid: mp 161–163 °C dec; λ_{max} (CH_3CN) (10^{-3} ϵ) 320 nm (6.3), 269 (8.9), 253 (8.0), 219 (38.0); ^1H NMR (Me_2SO-d_6) δ 8.00–7.34 (m, 8 H, aromatic), 4.79 (s, 2 H, $-CH_2-$), 3.74 (s, 3 H, 10-CH_3), 2.12 (s, 3 H, CH_3). Addition of D_2O caused the disappearance of the singlet at δ 4.79.

Anal. Calcd for $C_{16}H_{16}NSClO_5$: C, 52.0; H, 4.36; N, 3.79; S, 8.66; Cl, 9.59. Found: C, 52.2; H, 4.65; N, 4.09; S, 8.81; Cl, 9.44.

The ether filtrate from crude **2** was concentrated and chromatographed on a silica gel (Merck 30-70 ASTM mesh) column. Elution with CCl_4 gave 300 mg (1.41 mmol, 137%) of crude 10-methylphenothiazine.

Reaction of 1a with Butanone. Formation of 3a. A solution of 1.02 g (3.26 mmol) of **1a** in 20 mL of butanone was stirred for 6 h, after which 30 mL of water was added. The solution was extracted with pentane and next with CH_2Cl_2. Evaporation of the pentane solution, dissolving in methanol, and precipitation with water gave 320 mg (1.50 mmol, 92%) of crude 10-methylphenothiazine. The CH_2Cl_2 solution was dried ($MgSO_4$), concentrated, and precipitated with ether, giving 375 mg (0.98 mmol, 60%) of crude **3a**. Crystallization from CH_2Cl_2–ether gave **3a**: mp 142–144 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 334 nm (4.6), 268 (5.2), 251 (6.4), 218 (20.0); ^1H NMR ($CDCl_3$) δ 7.94–7.16 (m, 8 H, aromatic), 5.47 (q, 1 H, –CH–, J = 7 Hz), 3.88 (s, 3 H, 10-CH_3), 2.26 (s, 3 H, CH_3CO–), 1.35 (d, 3 H, CH_3, J = 7 Hz).

Anal. Calcd for $C_{17}H_{18}NSClO_5$: C, 53.2; H, 4.73; N, 3.65; S, 8.34; Cl, 9.26. Found: C, 53.4; H, 4.88; N, 3.59; S, 8.21; Cl, 9.04.

Reaction of 1a with Methyl Isopropyl Ketone. Formation of 4. After stirring a solution of 978 mg (3.13 mmol) of **1a** in 20 mL of ketone for 90 min ether was added to precipitate 453 mg (1.14 mmol, 73%) of crude red-brown **4**. Decolorization and crystallization from CH_3CN gave colorless **4**: mp 116–119 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 340 nm (5.5), 320 (5.5), 272 (8.9), 219 (34.0); ^1H NMR (CD_3CN) δ 7.98–7.26 (m, 8 H, aromatic), 3.63 (s, 3 H, 10-CH_3), 2.14 (s, 3 H, CH_3CO–), 1.44 (s, 6 H, CH_3).

Anal. Calcd for $C_{18}H_{20}NSClO_5$: C, 54.4; H, 5.06; N, 3.52; S, 8.05; Cl, 8.93. Found: C, 54.3; H, 5.16; N, 3.58; S, 7.80; Cl, 8.80.

Workup of the filtrate from crude **4** gave 320 mg (1.50 mmol, 96%) of crude 10-methylphenothiazine.

Reaction of 1a with Acetophenone. Formation of 5. Use of 642 mg (2.05 mmol) of **1a** in 30 mL of ketone for 72 h and workup as with

4 gave 245 mg (0.57 mmol, 56%) of crude **5**. Crystallization from CH_3CN–ether gave **5**: mp 143–146 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 320 nm (6.8), 250 (23.4); ^1H NMR (Me_2SO-d_6) δ 8.18–7.34 (m, 13 H, aromatic), 5.42 (s, 2 H, $-CH_2-$), 3.73 (s, 3 H, 10-CH_3).

Anal. Calcd for $C_{21}H_{18}NSClO_5$: C, 58.4; H, 4.20; N, 3.24; S, 7.42; Cl, 8.23. Found: C, 58.5; H, 4.40; N, 3.50; S, 7.44; Cl, 8.45.

The mother liquor from crude **5** was worked up by TLC to give, with pentane, 228 mg (1.07 mmol, 104%) of crude 10-methylphenothiazine.

Reaction of 1a with Cyclopentanone. Formation of 6a. A solution of 967 mg (3.10 mmol) of **1a** and 1.5 mL of cyclopentanone in CH_3CN was stirred for 48 h, concentrated to small volume, and placed on a silica gel column. Elution with ether gave 10-methylphenothiazine which was purified by TLC to give 371 mg (1.71 mmol, 112%). Elution with acetone gave crude **6a**, which was decolorized and crystallized from CH_2Cl_2–ether, to give 250 mg (0.63 mmol, 20%) of **6a**: mp 112–113 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 324 nm (5.7), 271 (7.0), 253 (8.9), 222 (34); ^1H NMR (CD_3CN) δ 8.18–7.34 (m, 8 H, aromatic), 4.73 (t, 1 H, –CH–, J = 10 Hz), 3.74 (s, 3 H, 10-CH_3), 2.31 (m, 2 H, $-COCH_2$), 1.85 (m, 4 H, $-CH_2CH_2-$). Addition of D_2O caused the disappearance of the triplet at δ 4.73.

Anal. Calcd for $C_{18}H_{18}NSClO_5$: C, 54.6; H, 4.58; N, 3.53; S, 8.09; Cl, 8.95. Found: C, 54.8; H, 4.67; N, 3.71; S, 8.02; Cl, 8.71.

Reaction of 1a with Cyclohexanone. Formation of 7a. After reaction of 664 mg (2.13 mmol) of **1a** with 30 mL of cyclohexanone the ketone was pumped off and the residue worked up as for **6a**, giving 184 mg (0.864 mmol, 82%) of 10-methylphenothiazine and 230 mg (0.56 mmol, 52%) of **7a**: mp 117–118 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 328 nm (7.9), 271 (10.1), 253 sh, 220 (46.0); ^1H NMR ($CDCl_3$) δ 8.12–7.24 (m, 8 H, aromatic), 5.36 (d of d, J = 13 and 7 Hz), 3.90 (s, 3 H, 10-CH_3), 2.82–1.12 (m, 8 H, $-CH_2CH_2CH_2CH_2-$). The doublets at δ 5.36 disappeared on adding D_2O.

Anal. Calcd for $C_{19}H_{20}NSClO_5$: C, 55.7; H, 4.92; N, 3.42; S, 7.81; Cl, 8.65. Found: C, 55.9; H, 5.12; N, 3.48; S, 7.60; Cl, 8.57.

Reaction of 1a with Indanone. Formation of 9. A solution of 769 mg (2.46 mmol) of **1a** and 500 mg (3.78 mmol) of indanone-1 in 10 mL of CH_3CN was diluted after 7 h with 30 mL of water and extracted first with petroleum ether and next with CH_2Cl_2. Each extract was worked up as for **6a**, to give 270 mg (1.27 mmol, 103%) of 10-methylphenothiazine and 265 mg (0.60 mmol, 49%) of **9**: mp 110–112 °C; ^1H NMR (CD_3CN) δ 8.02–7.28 (m, 12 H, aromatic), 4.64 (2 d, 1 H, J = 7 and 4.5 Hz, –CH–), 3.72–3.14 (m, 5 H, 10-CH_3 and $-CH_2-$).

Reaction of 1a with Tetralone-1. Formation of 8a. A solution of 639 mg of **1a** in 5 mL of tetralone-1 was stirred for 2 h, during which time a precipitate formed. Ether was added to cause further precipitation, giving 420 mg (0.92 mmol, 90%) of crude, red-brown **8a**. This was decolorized in CH_3CN and recrystallized on adding ether, giving colorless **8a**: mp 141–142 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 335 nm (5.1), 304 (6.0), 252 (25.0); ^1H NMR (CD_3CN) δ 7.95–7.26 (m, 11 H, aromatic), 8.18 (d of d, 1 H, aromatic, J = 8 and 1.7 Hz), 5.01 (d of d, 1 H, α-CH, J = 14 and 5 Hz), 3.74 (s, 3 H, 10-CH_3), 3.00 (d of d, 2 H, γ-CH_2–, J = 7.5 and 3.5 Hz), 2.34–2.08 (m, 1 H, β-CH–), 1.66–1.42 (m, 1 H, β-CH–).

Anal. Calcd for $C_{23}H_{20}NSClO_5$: C, 60.4; H, 4.40; N, 3.06; S, 7.00; Cl, 7.74. Found: C, 60.5; H, 4.70; N, 3.36; S, 7.12; Cl, 7.97.

Reaction of 1b with Butanone. Formation of 3b. After stirring overnight a solution of 1.0 g (2.66 mmol) of **1b** in 20 mL of butanone the ketone was pumped off at room temperature, and the residue washed with 5 × 50 mL of petroleum ether. Decolorization and crystallization from CH_2Cl_2–ether gave 448 mg (1.0 mmol, 75%) of **3b**: mp 119–121 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 324 nm (7.58), 271 (5.91), 252 (10.8), 213 (35.3); ^1H NMR (acetone-d_6) δ 8.45–6.55 (m, 13 H, aromatic), 5.11 (q, 1 H, –CH–, J = 7 Hz), 2.25 (s, 3 H, $-CH_3$), 1.49 (d, 3 H, CH_3, J = 7 Hz).

Anal. Calcd for $C_{22}H_{20}NSClO_5$: C, 59.2; H, 4.52; N, 3.14; S, 7.19; Cl, 7.95. Found: C, 59.2; H, 4.57; N, 3.30; S, 7.39; Cl, 8.20.

The petroleum ether washings were concentrated and purified by TLC on silica gel plates (pentane) giving 375 mg (1.36 mmol, 102%) of 10-phenylphenothiazine.

Reaction of 1b with Cyclopentanone. Formation of 6b. Reaction of 410 mg (1.09 mmol) of **1b** and 10 ml of cyclopentanone for 4 h gave, as above, 160 mg (0.35 mmol, 64%) of **6b**: mp 111–112.5 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 323 nm (11.3), 272 (12.7), 253 (18.5).

Anal. Calcd for $C_{23}H_{20}SNClO_5$: C, 60.3; H, 4.40; N, 3.06; S, 7.00; Cl, 7.74. Found: C, 60.4; H, 4.37; N, 3.28; S, 6.77; Cl, 7.80.

TLC of the concentrated washings gave 165 mg (0.6 mmol, 110%) of 10-phenylphenothiazine.

Reaction of 1b with Cyclohexanone. Formation of 7b. Analogous reaction of 625 mg (1.66 mmol) of **1b** and 5 mL of cyclohexanone gave 250 mg (0.91 mmol, 110%) of 10-phenylphenothiazine and 162 mg (0.34 mmol, 41%) of **7b**: mp 121.5–122.5 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 326 nm (12.0), 273 (9.7), 254 (9.6).

Anal. Calcd for $C_{24}H_{22}SNClO_5$: C, 61.1; H, 4.70; N, 2.97; S, 6.79. Found: C, 60.9; H, 4.85; N, 3.19; S, 6.81.

Reaction of 1b with Tetralone-1. Formation of 8b. After stirring a solution of 375 mg (1.0 mmol) of **1b** in 5 mL of tetralone for 3 h, ether was added to precipitate **8b**. This was decolorized in CH_3CN and crystallized from CH_2Cl_2–ether to give 205 mg (0.39 mmol, 79%) of **8b**: mp 130–131 °C; λ_{max} (CH_3CN) (10^{-3} ϵ) 324 nm (10.1), 253 (27.0); ^1H NMR ($CDCl_3$) δ 8.19 (2 d, 1 H, aromatic), 8.07–7.23 (m, 14 H, aromatic), 6.82 (m, 2 H, aromatic), 4.98 (d of d, 1 H, –CH–, J = 14 and 5 Hz), 3.56–3.1 (m, 2 H, $-CH_2-$), 2.48–2.06 (m, 2 H, $-CH_2-$).

Anal. Calcd for $C_{28}H_{22}NSClO_5$: C, 64.7; H, 4.27; N, 2.69; S, 6.16; Cl, 6.82. Found: C, 64.5; H, 4.09; N, 2.87; S, 6.22; Cl, 7.03.

Filtrates were concentrated and purified by TLC (silica gel, pentane) giving 124 mg (0.45 mmol, 90%) of 10-phenylphenothiazine.

Formation of Ylides 10–13b. A small amount (0.3–1.5 mmol) of the sulfonium salts **3b, 6b–8b** was dissolved in 20 mL of methanol and 1 mL of triethylamine was added. After 1 min 250 mL of water was added and the solution was extracted with 3 × 50 mL of CH_2Cl_2. After drying over K_2CO_3 the solvent was pumped off and the residue crystallized and characterized by mass and NMR spectroscopy. Ylide **10**, 96% yield, had mp 123–125 °C (from CH_2Cl_2–ether–petroleum ether); *m/e* 345.1174 (calcd, 345.1176); ^1H NMR (CD_3CN) δ 8.00–7.03 (m, 11 H, aromatic), 6.53–6.26 (m, 2 H, aromatic), 2.33 (s, 3 H, $-CH_3$), 1.43 (s, 3 H, $-CH_3$). Ylide **11**, 82% yield, had mp 159.5–161 °C (from CH_2Cl_2–ether–petroleum ether); *m/e* 357.1162 (calcd, 357.1176); and ^1H NMR ($CDCl_3$) δ 7.92–6.42 (m, 13 H, aromatic), 2.4–1.4 (m, 6 H, C_5 ring). Ylide **12**, 88% yield, had mp 119–120 °C (from CH_2Cl_2–ether–petroleum ether); *m/e* 371.1290 (calcd, 371.1333); and ^1H NMR ($CDCl_3$) δ 7.85–7.0 (m, 11 H, aromatic), 6.55–6.35 (m, 2 H, aromatic), 2.38–1.4 (m, 8 H, C_6 ring). Ylide **13b**, 93% yield, had mp 115–117.5 °C (from CH_2Cl_2–ether–petroleum ether); *m/e* 419.133 (calcd, 419.133); ^1H NMR ($CDCl_3$) δ 8.36–6.20 (m, 17 H, aromatic), 3.1–2.1 (m, 4 H, $-CH_2CH_2-$).

Formation of Ylide 13a. Treatment of 694 mg (1.51 mmol) of **8a** in 15 mL of CH_3CN with 0.5 mL of *tert*-butylamine for 10 min gave 467 mg of white precipitate. This was suspended in water and extracted with CH_2Cl_2 giving 435 mg (1.22 mmol, 81%) of **13a**: mp 130–131 °C (from CH_2Cl_2–ether); ^1H NMR ($CDCl_3$) δ 8.06 (m, 1 H, aromatic), 7.64–6.98 (m, 11 H, aromatic), 3.46 (s, 3 H, 10-CH_3), 2.72 (t, 2 H, $-CH_2-$, J = 7.5 Hz), 2.09 (t, 2 H, $-CH_2-$, J = 7.5 Hz).

Anal. Calcd for $C_{23}H_{19}NSO$: C, 77.3; H, 5.36; N, 3.92. Found: C, 77.2; H, 5.42; N, 4.01.

Reaction of 9 with Nucleophiles. Formation of α-Substituted Indanones (14–18). Reactions were carried out by stirring a solution of **9** in 10 mL of CH_3CN with the nucleophile for several hours. Workup then varied among the cases. The mixture from ammonium bromide (500 mg, 5.1 mmol) and **9** (294 mg, 0.66 mmol) was diluted with water and extracted with CH_2Cl_2, and the CH_2Cl_2 solution was dried, concentrated, and streaked on silica gel plates. Development with ether–pentane (90:10) gave 88 mg (0.41 mmol, 62%) of 10-methylphenothiazine and 91 mg (0.43 mmol, 65%) of 2-bromo-1-indanone (**17**), mp 33–34 °C (from ethanol) (lit. mp 37–38.5 °C),[13] *m/e* 211.97 (calcd, 211.97). The mixture from 500 mg (6.2 mmol) of sodium thiocyanate and 140 mg (0.32 mmol) of **9** was concentrated and streaked on TLC plates as above, giving 62 mg (0.29 mmol, 92%) of 10-methylphenothiazine and 45 mg (0.24 mmol, 76%) of **14**, mp 92–93 °C (from ether-pentane); λ_{max} (CH_3CN) (10^{-3} ϵ) 290 nm (1.3), 246 (14.0) (lit. mp 91–92 °C[14]).

The mixture from 800 mg (4.04 mmol) of sodium *p*-toluenesulfinate·$2H_2O$ and 312 mg (0.663 mmol) of **9** was concentrated and placed on a silica gel column. Elution with ether–pentane (10:90) gave 104 mg (0.49 mmol, 70%) of 10-methylphenothiazine; elution with CH_2Cl_2 gave 102 mg (0.32 mmol, 46%) of **15**, mp 141–142 °C (from ethanol), λ_{max} (CH_3CN) (10^{-3} ϵ) 290 nm (1.6), 246 (10.1); *m/e* 286.07 (calcd, 286.07). The mixture from 300 mg (1.87 mmol) of potassium ethylxanthate and 607 mg (1.37 mmol) of **9** was worked up similarly to give 255 mg (1.20 mmol, 88%) of 10-methylphenothiazine and 276 mg (1.10 mmol, 80%) of **16**, mp 77–78 °C (from ethanol), λ_{max} (CH_3CN) (10^{-3} ϵ) 280 nm (15.1), 242 nm (16.4).

Anal. Calcd for $C_{12}H_{12}S_2O_2$ (16): C, 57.1; H, 4.79; S, 25.4. Found: C, 57.0; H, 4.75; S, 25.8.

The mixture from 1 mL (12.4 mmol) of pyridine and 631 mg (1.42 mmol) of **9** was concentrated and diluted with ethyl acetate. A light brown precipitate (183 mg) was suspended in water and extracted with CH_2Cl_2. The CH_2Cl_2 solution gave 48 mg (0.155 mmol, 11%) of 2-pyridinium-1-indanone perchlorate (**18**), mp 218–219 °C (from CH_2Cl_2–ether).

Anal. Calcd for $C_{14}H_{12}NClO_5$ (18): C, 54.3; H, 3.90; Cl, 11.5. Found:

C, 54.2; H, 3.88; Cl, 11.6.

Registry No.—**1a,** 54014-67-4; **1b,** 52156-15-7; **2,** 61723-13-5; **3a,** 62723-15-7; **3b,** 61723-17-9; **4,** 61723-19-1; **5,** 61723-21-5; **6a,** 61723-23-7; **6b,** 61723-25-9; **7a,** 61723-27-1; **7b,** 61723-29-3; **8a,** 61723-31-7; **8b,** 61723-33-9; **10,** 61723-34-0; **11,** 61723-35-1; **12,** 61723-36-2; **13a,** 61723-37-3; **13b,** 61723-38-4; acetone, 67-64-1; butanone, 78-93-3; methyl isopropyl ketone, 563-80-4; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; indanone-1, 83-33-0; tetralone-1, 529-34-0; sodium thiocyanate, 540-72-7; sodium *p*-toluenesulfinate, 824-79-3; potassium ethylxanthate, 140-89-6; pyridine, 110-86-1.

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Reaction of Electrogenerated Nitrobenzene Radical Anion with Alkyl Halides

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Nitrobenzene radical anion formed by the electrochemical reduction of nitrobenzene reacts rapidly with alkyl halides. Electrochemical reduction of nitrobenzene in the presence of alkyl halides leads to a high yield of *N,O*-dialkylphenylhydroxylamines.

The electrochemical reduction of nitrobenzene in aprotic solvents has been studied in detail during the past two decades.[1,2] Nitrobenzene is reduced in two steps, first to a radical anion (eq 1) and then at more negative electrode potentials directly to a dianion (eq 2). Both steps are reversible, but generally the dianion reacts rapidly with solvent, electrolyte, or trace impurities so that the dianion may be observed only under rigorously controlled conditions.[3] The radical anion of nitrobenzene, however, is much less reactive. It has been detected even in strongly basic aqueous solution by ESR spectroscopy.[4,5] The reaction of nitrobenzene radical anion with various proton donors has been studied in detail[1-3] and, generally, if a proton donor is present during nitrobenzene reduction, then phenylhydroxylamine is formed (eq 3). The electrogenerated nitrobenzene radical anion is generally considered to be quite stable and, therefore, reactions other than with proton donors have been studied very little.

$$C_6H_5NO_2 \overset{1e}{\rightleftharpoons} C_6H_5NO_2^{-}\cdot \quad (1)$$

$$C_6H_5NO_2 \overset{2e}{\rightleftharpoons} C_6H_5NO_2^{2-} \quad (2)$$

$$C_6H_5\text{-}NO_2 \xrightarrow[4e^-]{4H^+} C_6H_5\text{-}NHOH + H_2O \quad (3)$$

This paper deals with the reduction of nitrobenzene in dimethylformamide in the presence of simple alkyl halides, which have been found to react rapidly with nitrobenzene radical anion leading in several steps to substituted phenylhydroxylamines. A similar product was obtained when nitrobenzene was reduced in the presence of acetic anhydride, producing *N,O*-diacetylphenylhydroxylamine.[6] Alkyl halides recently have been found to react with many types of electrogenerated anions and radical anions, such as those formed by reduction of ketones and imines,[7] activated olefins,[8-10] Schiff bases,[11] and disulfides.[12]

Results and Discussion

The stability of nitrobenzene radical anion is demonstrated by cyclic voltammetry (Figure 1) carried out at a hanging mercury drop electrode in dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate (TEAP). The presence of an anodic peak, on reversing the direction of voltage sweep just after the initial reduction peak of nitrobenzene, indicates that the nitrobenzene radical anion is not being rapidly consumed in a follow-up chemical reaction. As shown in Figure 1, addition of 1-bromobutane to the solution causes the anodic peak to decrease in size, indicating that the radical anion is reacting with butyl bromide.

Although it is possible to determine the rate of the reaction of nitrobenzene radical anion with 1-bromobutane by cyclic voltammetry or cyclic chronopotentiometry, the theoretical treatment of this set of reactions (eq 12–16) is complex. A sense of the relative rates of reaction of nitrobenzene radical anion with 1-bromobutane and 1-iodobutane may be gained from cyclic chronopotentiometry (Figure 2). In the absence of a follow-up reaction the reverse transition time is one-third of the forward electrolysis time.[13] Reactions consuming the radical anion cause the reverse transition time to be shorter. For a solution of 1.3 mM nitrobenzene, the decrease in the reverse transition time is about the same when 0.5 M 1-bromobutane is present as it is when 0.05 M 1-iodobutane is present. In other words, it requires ten times as much 1-bromobutane as 1-iodobutane to obtain the same apparent rate of disappearance of nitrobenzene radical anion.

The preparative electrochemical reduction of nitrobenzene at −1.3 V vs. SCE (the potential at which nitrobenzene radical anion is formed) in the presence of 1-chlorobutane, 1-bro-