**Bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (3).** (a) To a solution of the diazo compound **5d** (0.60 g, 4 mmol) in dry tetrahydrofuran at room temperature was added dropwise with stirring under argon a solution of selone **5e** (~4 mmol) in dry tetrahydrofuran (5 mL) until the red color disappeared and a pale-green color persisted. Removal of solvent under reduced pressure and recrystallization from ether (- 20 °C) yielded the light-sensitive selenadiazoline **9**: 1.1 g, 77% yield; mp 115–120 °C dec; IR ($CCl_4$) 1585, 1580 $cm^{-1}$; UV (cyclohexane) $\lambda_{max}$ 301 nm ($\epsilon$ 2000); $^1H$ NMR ($CDCl_3$) $\delta$ 5.70 (4 H, s), 1.26 (12 H, s), 0.90 (12 H, s).

The crude selenadiazoline **9** (1.0 g, 3 mmol) was pyrolyzed at 185 °C for 8 h. Flash chromatography[15] (hexanes) followed by solvent removal and sublimation yielded the olefin **3**: 0.30 g, 40% yield; mp 108–109 °C; IR (KBr) 3058, 1475, 1360 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 5.13 (4 H, s), 1.42 (12 H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 151.2, 138.1, 52.0, 31.0; MS, *m/e* 244 ($M^+$), 229 ($M^+ - CH_3$). Anal. Calcd for $C_{18}H_{28}$: C, 88.3; H, 11.6. Found: C, 88.4; H, 11.5.

(b) The phosphoranylidenehydrazone **5c** (3.64 g, 8.8 mmol) and selenium (2.0 g, 25 mmol) were heated at 185 °C with stirring under argon for 24 h. The cooled mixture was extracted with ether (2 × 20 mL) and filtered through Celite. Concentration, followed by flash chromatography (hexanes), yielded olefin **3** (1.41 g, 65%), identical with that described in part a.

(c) The selone **5e** (1.40 g, 7.0 mmol) and the phosphoranylidenehydrazone **5c** (2.20 g, 55 mmol) were heated to 200 °C under nitrogen overnight. Removal of volatiles, followed by flash chromatography and recrystallization from ethanol, afforded the olefin **3** (0.87 g, 65% yield), identical with that described in part a.

**Reactions of 3.** (a) Bromine (40 mg, 0.25 mmol) in $CDCl_3$ (0.5 mL) was added dropwise at room temperature to a solution of olefin **3** (30 mg, 0.13 mmol) in $CDCl_3$. An exothermic reaction immediately occurred with liberation of an acidic gas. $^1H$ NMR showed a complex spectrum and TLC (silica gel, hexanes) showed a minimum of four components in the mixture.

(b) A solution of potassium permanganate (153 mg, 1 mmol) and sodium hydroxide (200 mg, 10 mmol) in 40% aqueous *tert*-butyl alcohol (15 mL) was added to a solution of olefin **3** (367 mg, 1.5 mmol) in *tert*-butyl alcohol (10 mL). The mixture was heated, with stirring, to 75 °C for 2 days. Filtration through Celite and extraction with ether yielded starting olefin **3** (327 mg, 89% recovery). Similar results were obtained with methylcyclohexane as solvent.

(c) A solution of potassium permanganate (10 mg), potassium periodate (460 mg, 2 mmol), anhydrous magnesium sulfate (120 mg, 2 mmol), and olefin **3** (240 mg, 1 mmol) in 40% aqueous *tert*-butyl alcohol (10 mL) was stirred at room temperature for 3 days. Filtration through Celite, followed by extraction with ether, afforded unreacted olefin **3** (180 mg, 70% recovery) as well as 50 mg of a mixture of more polar compounds.

(d) A solution of olefin **3** (198 mg, 0.8 mmol), potassium permanganate (830 mg, 5.3 mmol), and dicyclohexyl-18-crown-6 (5 mg) in benzene[17] (10 mL) was stirred at room temperature for 2 weeks. Filtration through Celite followed by extraction with ether afforded the unreacted olefin **3** (174 mg, 88% recovery). Similar negative results were obtained with benzyltriethylammonium chloride in benzene with aqueous alkaline permanganate[18] and also with benzyltriethylammonium permanganate[19] in benzene.

**Bi-2,2,5,5-tetramethylcyclopentylidene (10).** Bi-3,3,5,5-tetramethylcyclopenten-4-ylidene (**3**; 35.7 mg) in ethanol (2 mL) was hydrogenated over platinum black (5 mg) until no further hydrogen was taken up (6.73 mL, ~1.5 h). The mixture was filtered through Celite and concentrated. Chromatography on silica gel (1 g; pentane) and recrystallization from ethanol afforded 31.3 mg of **10**: 88% yield; mp 103–104 °C (lit.[9] mp 104–105 °C); $^1H$ NMR ($CDCl_3$) $\delta$ 1.51 (8 H, s), 1.34 (24 H, s); and other spectra identical with those reported for **10**.

**2-(3,3,5,5-Tetramethylcyclopenten-4-ylidene)fenchane (4).** (-)-Selenofenchone (0.97 g, 4.51 mmol) was slowly added at room temperature to a stirred solution of crude diazo compound **5d** (0.68 g, 4.51 mmol). The progress of the reaction can be monitored by the disappearance of the orange color of **5d**, the solution becoming lemon yellow with light-yellow crystals precipitating. The mixture was concentrated with a stream of nitrogen and the crude selenadiazoline dried at room temperature under vacuum (1 torr) affording lemon-yellow crystals: 1.64 g, 99% yield. Recrystallization from ether at -20 °C afforded the crystalline light-sensitive selenadiazoline **12**: mp 131–132 °C; IR ($CCl_4$) 1630, 1595, 1470, 1455, 900 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.63 (2 H, s), 2.76 (1 H, brd), 2.00–0.54 (27 H, complex).

Crude selenadiazoline **12** (1.40 g, 3.84 mmol) was heated at 135 °C under positive nitrogen pressure for 2 days, and the temperature then was raised to 170 °C for 4 h. After being cooled, the reaction mixture was dissolved in dichloromethane, filtered, and concentrated. Flash chromatography,[15] followed by Kugelrohr distillation [65 °C (0.1 torr)], afforded olefin **4** as colorless crystals: 417 mg, 42% yield; mp 70–73 °C; IR ($CHCl_3$) 3040, 3015, 1390, 1365 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 5.15 (2 H, AB q), 2.05–0.9 (28 H, complex); MS, *m/e* 258 ($M^+$), 243 ($M^+ - CH_3$). Anal. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.17; H, 11.61.

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**Registry No. 3**, 78305-12-1; **4**, 82338-35-0; **5a**, 81396-36-3; **5b**, 81396-37-4; **5c**, 82338-36-1; **5d**, 81396-38-5; **5e**, 79958-61-5; **6**, 933-52-8; **7**, 31934-42-6; **8**, 81396-35-2; **8** mesylate, 82338-37-2; **9**, 82338-38-3; **10**, 71691-01-5; **11**, 61849-83-0; **12**, 82338-39-4; diazomethane, 334-88-3; phenylvinyl sulfide, 1822-73-7; 2,4-dibromo-2,4-dimethylpentanone, 17346-16-6.

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## Synthesis of 6-Thiaellipticine and Related Compounds via Heterocyclic *o*-Quinodimethane Intermediates

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Indole-2,3-quinodimethane intermediates derived from 2-ethyl-3-[$\alpha$-(3-pyridyl)vinyl]indole (**1**)[1] and 3-ethyl-2-[$\alpha$-(4-pyridyl)vinyl]indole (**2**)[2] by way of thermal suprafacial [1,5] sigmatropic hydrogen shift have been applied to the synthesis of the antitumor carbazole alkaloid ellipticine (**3**)[1,2] (Scheme I). We have now used this approach for the synthesis of 6-thiaellipticine[3,4] and congeners. It is known that olefins are provided on pyrolysis of tertiary alcohols by direct elimination of water.[5] In conjunction with a synthesis of 6-thiaellipticine and related compounds, we examined the thermal decomposition of a series of alcohols in the expectation that dehydration followed by

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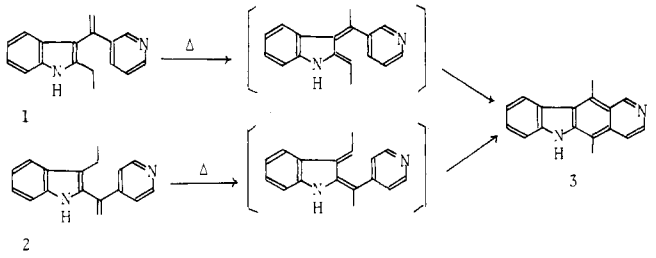
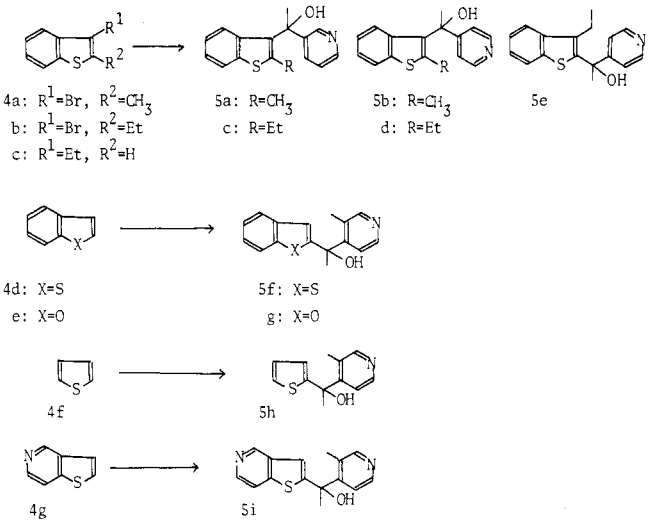
0022-3263/82/1947-3566$01.25/0 

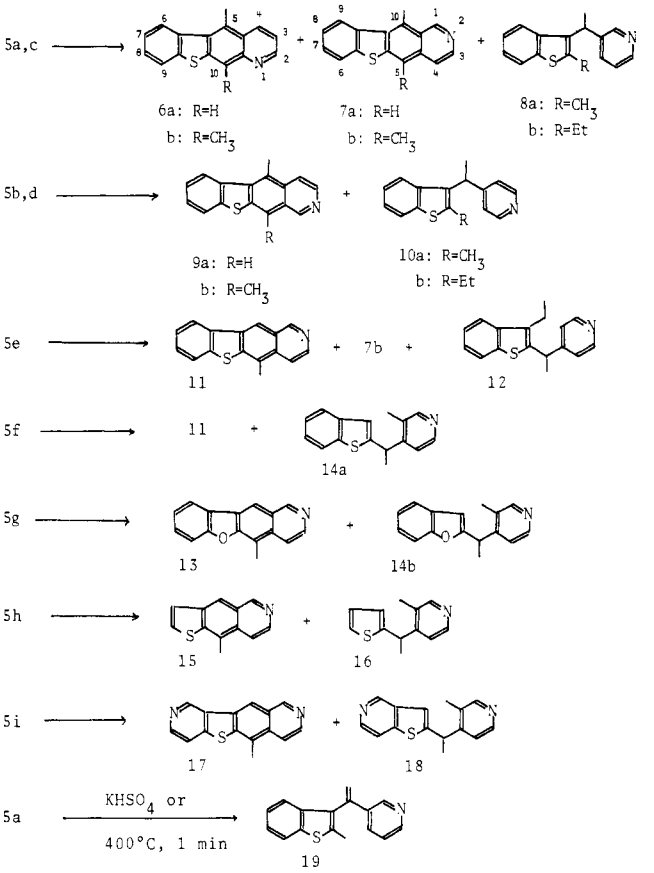
Scheme I



Scheme II



Scheme III



a [1,5] sigmatropic hydrogen shift would occur to yield the cyclization products. This would provide a short synthesis of some polynuclear heterocyclic compounds. Herein we report the results of our studies.

The tertiary alcohols used for the thermal decomposition were prepared as follows. Lithiation of 3-bromo-2-methylbenzo[*b*]thiophene (**4a**;[6] *n*-BuLi, THF, −78 °C), followed by quenching with 3- and 4-acetylpyridine afforded the corresponding tertiary alcohols **5a** and **5b**, respectively (Scheme II). Similarly 2-ethyl-3-lithiobenzo[*b*]thiophene obtained from 3-bromo-2-ethylbenzo[*b*]thiophene (**4b**)[7] was treated with the above acetylpyridines to give the corresponding alcohols **5c** and **5d**. Lithiation of 3-ethylbenzo[*b*]thiophene (**4c**)[8] [lithium diisopropylamide (LDA), THF, 0 °C to room temperature] followed by quenching with 4-acetylpyridine yielded the alcohol **5e**. Lithiation of benzo[*b*]thiophene (**4d**), benzofuran (**4e**), and thiophene (**4f**) (LDA, −78 °C, 0.5 h) followed by quenching with 4-acetyl-3-methylpyridine gave the corresponding alcohols **5f–h**, respectively. Furthermore, the alcohol **5i** was obtained by condensation of thieno[3,2-*c*]pyridine (**4g**)[9] with 4-acetyl-3-methylpyridine through the method above. Yields and physical properties are summarized in the Table I.

Thermolysis of **5a–e** can be expected to generate benzo[*b*]thiophene-2,3-quinodimethane intermediates, and in the cases of **5f–i**, the reaction would proceed via pyridine-3,4-quinodimethane intermediates.[10] Pyrolysis of **5a** at 400 °C[11] for 7 min resulted in the formation of 5-methylbenzo[*b*]thieno[3,2-*g*]quinoline (**6a**), 11-methylbenzo[*b*]thieno[2,3-*g*]isoquinoline (**7a**), and 2-methyl-3-[$\alpha$-(3-pyridyl)ethyl]benzo[*b*]thiophene (**8a**) (Scheme III). Product **6a** was easily distinguished from **7a** by the singlet at $\delta$ 9.64 attributable to H-1 observed in the $^1$H NMR spectrum of **7a**. The formation of **8a** may occur through a disproportionation reaction of the cyclization intermediate, namely, by hydrogen generated on aromatization of the cyclization intermediates giving **6a** and **7a**. Thermolysis of **5b** was examined under the same conditions as for **5a** to give 5-methylbenzo[*b*]thieno[3,2-*g*]isoquinoline (**9a**) and **10a**. Thermolysis of **5c** gave **6b** and **7b**. In this case, the reduced product **8b** was not obtained as the identical product. 5,10-Dimethylbenzo[*b*]thieno[3,2-*g*]isoquinoline (**9b**) and **10b** were obtained by thermolysis of **5d**.

In the cyclization of **1** and **2** to yield **3**, a higher temperature was required for **2** as compared to **1** as Bergman suggested.[1] Thus, it was of interest to compare the thermolyses of **5a–d** with that of **5e** to determine if the yields of the cyclization products increased relative to **5a–d** or if there were some differences in the reactivity of **5a–d** and **5e**. Thermolysis of **5e** gave 5-methylbenzo[*b*]thieno[2,3-*g*]isoquinoline (**11**), **7b**, and the reduced product **12**. In this reaction, most probably the methyl group would be easily removable as methane by chain reaction on aromatization of the cyclization intermediate.[12] In the cases of **5b** and **5d**, hydrogen is more readily removed than a methyl group on aromatization of the cyclization inter-

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(11) Pyrolysis was examined under a variety of conditions in the range of 220–450 °C; 400 °C was found to give the best results.
(12) The more reasonable mechanistic feature is under investigation. On pyrolysis of 2-methyl-3-($\alpha$-methylvinyl)benzo[*b*]thiophene (400 °C, 30 min), reduction also occurred to yield 2-methyl-3-isopropylbenzo[*b*]thiophene in 30% yield.

Table I. Yields and Physical Data of Alcohols 5a-i[a]

| compd | yield, % | mp, °C | formula | MS, m/e of M+ | $^1$H NMR ($CDCl_3$), δ ($CH_3$ and $CH_2$ signals) |
|---|---|---|---|---|---|
| 5a | 81 | 181-183 | $C_{16}H_{15}NOS$ | 269 | 2.13 (3 H, s), 2.29 (3 H, s) |
| 5b | 82 | 193-195 | $C_{16}H_{15}NOS$ | 269 | 2.03 (3 H, s), 2.64 (3 H, s) |
| 5c | 85 | 129-131 | $C_{17}H_{17}NOS$ | 283 | 1.31 (3 H, t, $J$ = 7.6 Hz), 2.05 (3 H, s), 3.06 (2 H, t, $J$ = 7.6 Hz) |
| 5d | 92 | 175-177 | $C_{17}H_{17}NOS$ | 283 | 1.35 (3 H, t, $J$ = 7.2 Hz), 2.02 (3 H, s), 3.15 (2 H, q, $J$ = 7.2 Hz) |
| 5e | 70 | 151-153 | $C_{17}H_{17}NOS$ | 283 | 0.83 (3 H, t, $J$ = 7.6 Hz), 2.00 (3 H, s), 2.60 (2 H, t, $J$ = 7.6 Hz) |
| 5f | 92 | 203-206 | $C_{16}H_{15}NOS$ | 269 | 2.02 (3 H, s), 2.18 (3 H, s) |
| 5g | 88 | 146-147 | $C_{16}H_{15}NO_2$ | 253 | 1.96 (3 H, s), 2.10 (3 H, s) |
| 5h | 78 | 159-160 | $C_{12}H_{13}NOS$ | 219 | 1.99 (3 H, s), 2.13 (3 H, s) |
| 5i | 36 | 188-189 | $C_{15}H_{14}N_2SO$ | 270 | 2.06 (3 H, s), 2.18 |

[a] Satisfactory analytical data (for C, H, and N) were obtained for all compounds in the table.

Table II. Yields and Physical Data of Thermal Cyclization Products of Alcohols 5

| alcohol | product[a] | yield, % | mp, °C | formula | MS, m/e of M+ | $^1$H NMR ($CDCl_3$), δ |
|---|---|---|---|---|---|---|
| 5a | 8a | 36 | oil | $C_{16}H_{15}NS$ | | 1.73 (3 H, d, $J$ = 7.2 Hz), 2.28 (3 H, s), 4.55 (1 H, q, $J$ = 7.2 Hz) |
| | 6a[c] | 11 | 168-170 | $C_{16}H_{11}NS$ | 249 | 3.12 (3 H, s) |
| | 7a[c] | 12 | 174-176 | $C_{16}H_{11}NS$ | 249 | 3.24 (3 H, s), 9.64 (1 H, s) |
| 5b | 10a | 38 | oil | $C_{16}H_{15}NS$ | | 1.75 (3 H, d, $J$ = 7.0 Hz), 2.45 (3 H, s), 4.57 (2 H, q, $J$ = 7.0 Hz) |
| | 9a[c] | 24 | 170-172 | $C_{16}H_{11}NS$ | 249 | 3.15 (3 H, s), 8.23 (1 H, s), 9.24 (1 H, s) |
| 5c | 6b[c] | 18 | 179-181 | $C_{17}H_{13}NS$ | 263 | 2.66 (3 H, s), 3.11 (3 H, s) |
| | 7b[c] | 17 | 151-153[b] | $C_{17}H_{13}NS$ | 263 | 2.45 (3 H, s), 2.81 (3 H, s), 9.55 (1 H, s) |
| 5d | 10b | 39 | oil | $C_{17}H_{17}NS$ | | 1.23 (3 H, t, $J$ = 7.2 Hz), 1.74 (3 H, d, $J$ = 7 Hz), 2.88 (2 H, q, $J$ = 7.2 Hz), 4.55 (1 H, q, $J$ = 7.0 Hz) |
| | 9b[c] | 27 | 141-143 | $C_{17}H_{13}NS$ | 263 | 2.63 (3 H, s), 2.79 (3 H, s), 9.31 (1 H, s) |
| 5e | 12 | 12 | oil | $C_{17}H_{17}NS$ | | 1.09 (3 H, t, $J$ = 7.8 Hz), 1.69 (3 H, d, $J$ = 7.0 Hz), 2.77 (2 H, q, $J$ = 7.8 Hz), 4.49 (1 H, q, $J$ = 7.0 Hz) |
| | 11[c] 7b | 38 | 129-130 | $C_{16}H_{11}NS$ | 249 | 2.76 (3 H, s), 8.40 (1 H, s), 9.33 (1 H, s) |
| 5f | 14a | 25 | oil | $C_{17}H_{16}NS$ | | 1.72 (3 H, d, $J$ = 7 Hz), 2.33 (3 H, s), 4.55 (1 H, q, $J$ = 7 Hz) |
| | 11 | 45 | | | | |
| 5g | 14b | 26 | oil | $C_{16}H_{15}NO$ | | 1.64 (3 H, d, $J$ = 6.6 Hz), 2.37 (3 h, s), 5.60 (1 H, q, $J$ = 6.6 Hz), 6.37 (1 H, s) |
| | 13[c] | 45 | 121-123 | $C_{16}H_{11}NO$ | 233 | 2.68 (3 H, s), 9.23 (1 H, s) |
| 5h | 16 | 15 | oil | $C_{12}H_{13}NS$ | | 1.62 (3 H, d, $J$ = 6.4 Hz), 2.28 (3 H, s), 4.44 (1 H, q, $J$ = 6.4 Hz) |
| | 15[c] | 38 | 113-115 | $C_{12}H_9NS$ | 199 | 2.72 (3 H, s), 8.13 (1 H, s), 9.13 (1 H, s) |
| 5i | 18 | 15 | oil | $C_{15}H_{14}N_2S$ | 254 | 1.73 (3 H, d, $J$ = 7 Hz), 2.33 (3 H, s), 4.47 (1 H, q, 4.47 (1 H, q, $J$ = 7 Hz) |
| | 17[c] | 52 | 206-207 | $C_{15}H_{10}N_2S$ | 250 | 2.82 (3 H, s), 7.71 (1 H, d, $J$ = 5.6 Hz), 7.87 (1 H, d, $J$ = 6.2 Hz), 9.52 (2 H, br s) |

[a] Molecular formulas of all oily poructs were characterized by high-resolution mass spectra except for **18**: **8a**, *m/e* 253.0937 (M+, calcd for $C_{16}H_{15}NS$ 253.0924); **10a**, *m/e* 253.0925 (M+, calcd for $C_{16}H_{15}NS$ 253.0924); **10b**, *m/e* 267.1063 (M+, calcd for $C_{17}H_{17}NS$ 267.1080); **12**, *m/e* 267.1059 (M+, calcd for $C_{17}H_{17}NS$ 267.1080); **14a**, *m/e* 253.0904 (M+, calcd for $C_{16}H_{15}NS$ 253.0923); **14b**, *m/e* 237.1150 (M+, calcd for $C_{16}H_{15}NO$ 237.1152); **16**, *m/e* 203.0759 (M+, calcd for $C_{12}H_{13}NS$ 203.0767). [b] Lit.[3] mp 152.5-153.5 °C. [c] Satisfactory analytical data (for C, H, and N) were obtained.

mediates because of active hydrogen located on the methine at the α-position of benzo[*b*]thiophene. We successively examined the thermal cyclization reaction using pyridine-3,4-quinodimethane intermediates generated by thermolysis of **5f–i**. In these cases, a rather higher temperature was required compared to that for **5a–e**. The alcohols **5f–i** were heated at 450 °C[13] for 7 min to yield the corresponding cyclization products **11**, **13**, **15**, and **17**, respectively. In all cases the corresponding reduced products **14a**, **b**, **16**, and **18** were obtained. Yields and physical data for the thermal cyclization products are given in Table II.

Finally, in order to prove that the reaction proceeded through **19** from **5a**, **5a** was heated at 400 °C for 1 min to give a quantitative yield of 2-methyl-3-[α-(3-pyridyl)-vinyl]benzo[*b*]thiophene (**19**), which was identical with an authentic sample obtained by refluxing **5a** in toluene in the presence of $KHSO_4$. Both **19** and **5a** gave the same product distribution on prolonged pyrolysis at 400 °C.

(13) Below 420 °C, yields of cyclization products extremely decreased.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere except pyrolyses. Tetrahydrofuran (THF) was dried and distilled from $LiAlH_4$ before use. $^1$H NMR spectra were recorded on Varian T-60 and JEOL PS-100 spectrometers with $Me_4Si$ as an internal standard in $CDCl_3$ as a solvent. Mass spectra were determined on a Hitachi RMU-7L instrument.

**General Procedure for the Preparation of 5a–d.** To a stirred −78 °C solution of **4a** and **4b** (50 mmol) in THF (100 mL) was added *n*-BuLi (34 mL of 1.5 M hexane solution, 0.05 mol). After 0.5 h, a solution of acetylpyridine (6.05 g, 50 mmol) in THF (20 mL) at −78 °C was added. After the stirring had been continued at the same temperature for 1 h, the mixture was poured into water and extracted with $CHCl_3$. The extract was washed with water, dried over $Na_2SO_4$, and evaporated to give **5a–d**. Yields and properties are given in Table I.

**3-Ethyl-2-[α-hydroxy-α-(4-pyridyl)ethyl]benzo[*b*]thiophene (5e).** To an ice-cold solution of LDA [prepared from diisopropylamine (5.05 g, 50 mmol) and *n*-BuLi (34 mL of 1.5 M hexane solution, 50 mmol) in THF] was added a solution of **4c**

(8.1 g, 50 mmol) in THF (100 mL). The mixture was stirred at room temperature for 1 h, and then a solution of 4-acetylpyridine (6.05 g, 50 mmol) in THF (20 mL) was added at −78 °C. The mixture was gradually warmed to room temperature. After stirring had been continued at the same temperature for 3 h, the mixture was poured into water and extracted with $CHCl_3$. The extract was washed with water, dried over $Na_2SO_4$, and evaporated to give **5e** (9.9 g, 70%). Properties of this compound are shown in the Table I.

**General Procedure for the Preparation of 5f–i.** To a −78 °C stirred solution of LDA [prepared from diisopropylamide (1.0 g, 10 mmol) and *n*-BuLi (6.7 mL of 1.5 M hexane solution, 10 mmol) in THF] was added a solution of **4d–g** (10 mmol) in THF (10 mL). After 0.5 h, a solution of 4-acetyl-3-methylpyridine (1.2 g, 10 mmol) in THF (10 mL) was added at −78 °C. After stirring had been continued for 1 h, the mixture was poured into water and extracted with $CHCl_3$. The extract was washed with water, dried over $Na_2SO_4$, and evaporated to give **5f–i**. For the preparation of **5i**, lithiation of thieno[3,2-*c*]pyridine (**4g**) was carried out at 0 °C instead of −78 °C. Yields and physical data are summarized in the table I.

**Pyrolysis of 5.** Alcohol **5** (200–500 mg) was placed in a 10-mL round-bottomed flask equipped with a 30-cm glass tube without a seal and was heated at 400 °C for 7 min. The solid **5** immediately melted and decomposed, accompanied by the formation of water vapor. During the reaction, the reaction mixture mildly refluxed. The dark brownish reaction mixture was chromatographed on silica gel (5–10 g).

**Isolation of 8a, 7a, and 6a.** Hexane–ethyl acetate (3:2) was used as an eluent. The first fraction (30 mL) gave a dark brownish resin. The second (30 mL) afforded **8a**, the third one (15 mL) gave **6a**, and the succesive fraction (20 mL) yielded **7a**.

**Isolation of 6b and 7b.** Hexane–ethyl acetate (3:2) was used as an eluent. Removal of the first fraction (40 mL) gave dark brownish resin, the second one (15 mL) gave **6b**, and the third fraction (20 mL) gave **7b**.

**Isolation of 9 and 10.** Hexane–ethyl acetate (3:2) was used as an eluent. The first fraction (30–35 mL) was discarded. Removal of the second one (30 mL) gave **10**, and the third one (25 mL) gave **9**.

**Isolation of 12, 11, and 7b.** Hexane–ethyl acetate (3:2) was used as an eluent. After the first fraction (35 mL) was discarded, removal of the second one (15 mL) gave **12**. The third one (20 mL) yielded **11**, and removal of the successive fraction (15 mL) afforded **7b**.

**Isolation of 14 and 11 (or 13).** Hexane–ethyl acetate (1:1) was used as an eluent. The first fraction (35 mL) was discarded, and removal of the second one (20 mL) afforded **14**. The third one (30 mL) yield **11** (or **13**).

**Isolation of 15 and 16.** Hexane–ethyl acetate (7:3) was used as an eluent. The first fraction (15 mL) was discarded, and removal of the second one (15 mL) gave **16**. Evaporation of the third one (20 mL) yielded **15**.

**Isolation of 17 and 18.** $CHCl_3$–MeOH (97:3) was used as an eluent. After the first fraction (20 mL) was discarded, the second one (15 mL) was removed and gave, **16**, and removal of the third one (25 mL) yielded **15**. Yields and physical properties of these products are summarized in Table II.

**2-Methyl-3-[α-(3-pyridyl)vinyl]benzo[*b*]thiophene (19).** A mixture of **5a** (2.7 g, 10 mmol) and $KHSO_4$ (1.35 g, 10 mmol) in toluene (100 mL) was stirred under reflux for 14 h. The solution was diluted with benzene, washed with water, dried over $Na_2SO_4$, and evaporated to give **19** (2.4 g, 96%) as an oil: $^1H$ NMR δ 2.37 (3 H, s), 5.36 (1 H, d, $J$ = 1.5 Hz), 5.97 (1 H, d, $J$ = 1.5 Hz); mass spectrum, $m/e$ 251.0772 ($M^+$, calcd for $C_{16}H_{13}NS$ 251.0768).

**Registry No.** **4a**, 10243-15-9; **4b**, 64860-32-8; **4c**, 31283-14-4; **4d**, 95-15-8; **4e**, 271-89-6; **4f**, 110-02-1; **4g**, 272-14-0; **5a**, 82351-75-5; **5b**, 82351-76-6; **5c**, 82351-77-7; **5d**, 82351-78-8; **5e**, 82351-79-9; **5f**, 82351-80-2; **5g**, 82351-81-3; **5h**, 82351-82-4; **5i**, 82351-83-5; **6a**, 82351-84-6; **6b**, 82351-85-7; **7a**, 82351-86-8; **7b**, 21339-68-4; **8a**, 82351-87-9; **9a**, 82351-88-0; **9b**, 23018-34-0; **10a**, 82351-89-1; **10b**, 82351-90-4; **11**, 25121-97-5; **12**, 82351-91-5; **13**, 82351-92-6; **14a**, 82351-93-7; **14b**, 82351-94-8; **15**, 82351-95-9; **16**, 82351-96-0; **17**, 82351-97-1; **18**, 82351-98-2; **19**, 82351-99-3; 2-acetylpyridine, 1122-62-9; 3-acetylpyridine, 350-03-8; 4-acetylpyridine, 1122-54-9; 4-acetyl-3-methylpyridine, 82352-00-9.

## The Myth of Saturated Aqueous Sodium Chloride Solution (Brine) for Drying Organic Solutions

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Perusal of the experimental sections of this Journal reveals that many workers use saturated brine for preliminary drying of water-saturated organic extracts in the apparent belief that such treatment removes much dissolved water. At least two recent organic laboratory texts assert this to be so.[1] In fact, saturated brine can remove no more than about 25% of dissolved water, as the following analysis shows.

An organic solvent (OS) saturated with water must have the same partial pressure of water, $P_{H_2O}$, as does water saturated with the OS (both phases at the same temperature). This is merely a specific case of the principle that a component distributed between two phases at equilibrium must have the same partial pressure in each phase.[2] For an OS very slightly soluble in water, $P_{H_2O}$ in the OS-rich phase is very slightly less than the vapor pressure of pure water, $P^0_{H_2O}$.

Between 15 and 50 °C, $P_{H_2O}$ of saturated brine is 0.75–0.76 $P^\circ_{H_2O}$.[3] By the vapor pressure equality principle[2] adduced above, $P_{H_2O}$ in any phase in equilibrium with saturated brine must therefore be ~0.75 $P^0_{H_2O}$. Since for the common extracting solvents, water is dilute even when the OS is saturated, the mole fraction of water, $X_{H_2O}$, is proportional to its partial pressure, or nearly so, in its solutions in these solvents (Henry's law).[4] Thus, treating a water-saturated solution with brine can reduce the water concentration only by about a factor of 0.75 $P^0_{H_2O}/P_{H_2O}$, OS satd. Since the denominator must be $<P^0_{H_2O}$, the factor is <0.75. This factor is nearly exactly that by which the *activity* of water in the organic solution is reduced (assuming negligible dilution of the brine).[5]

None of the above militates against the use of NaCl for salting out organics *from* aqueous solutions[6] or of brine for breaking emulsions (especially of dispersed water) or for preventing back-extraction from an organic solution during a water wash. However, brine is not really useful for removing dissolved water *except* for the specific case of ethyl ether extracts *not* further dried before distillation, discussed next.

Ether is unusual among the common extracting solvents in that a water-saturated solution cannot be dried by

(1) (a) Fieser, L. F.; Williamson, K. L. "Organic Experiments", 4th ed; D. C. Heath and Co.: Lexington, MA, 1979; p 51. (b) Durst, H. D.; Gokel, G. W. "Experimental Organic Chemistry"; McGraw-Hill: New York, 1980; p 89 f.

(2) Glasstone S. "Textbook of Phyical Chemistry", 2nd ed.; Van Nostrand: New York, 1946; p 731. The principle is virtually a tautology: if the partial pressure of a component in phase 1 exceeds that in phase 2 (phases in contact), its concentration will fall in phase 1 and rise in phase 2. But then the phases are not in equilibrium.

(3) (a) Mellor, D. W. "Comprehensive Treatise on Inorganic and Theoretical Chemistry"; Wiley: New York, 1961; Vol. 2. Suppl. 2, Part 1, p 787 f. (b) Kuhajek, E. J.; Fiedelman, H. W. In "Kirk-Othmer Encyclopedia of Chemical Technology", 2nd ed.; Vol. 18, Interscience: New York, 1969; p 469. Vapor pressure data for saturated brine were compared with those for pure water given in standard handbooks.

(4) (a) Reference 2, p 701. (b) Marshall, A. *J. Chem. Soc.* **1906**, *89*, 1351.

(5) This assertion requires only the assumption that water vapor behaves as an ideal gas at the temperatures under consideration (ref 2, p 687); $P^0_{H_2O}$ at 30 °C is <0.05 atm.[3a]

(6) The error in the arguments in ref 1a,b for the great drying efficiency of brine lies in incorrectly equating the low solubility of most organics *in* brine with its ability to pull water *out* of organic solutions.

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