(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 $P^0_{H_2O}$.[3] By the vapor pressure equality principle[2] adduced above, P_{H_2O} in any phase in equilibrium with saturated brine must therefore be $\sim 0.75\ P^0_{H_2O}$. 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

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[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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distillation alone at pressures near 1 atm and below since the vapor is richer in *ether* than is the solution.[7] However, the composition of the homogeneous ether–water azeotrope is so close to that of water-saturated ether[8] that even saturated brine alone can remove enough water for the composition of the ether solution to move to the ether-rich side of azeotrope. Distillation of a brine-treated ether solution is not very efficient for drying since the azeotrope boils only slightly lower than pure ether,[8] but at worst the water concentration in the distalland will not increase.

Registry No. NaCl, 7647-14-5.

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(7) Othmer, D. F.; Wentworth, T. O. *Ind. Eng. Chem.* **1940**, *32*, 1590. This is easily confirmed by distilling a two-phase ether–water mixture and noting that the distillate is homogeneous (ref 4b, p 1366, verified by author). The author has also observed that even ether just saturated with water at 20 °C upon distillation at normal pressure (bp 34 °C) gives separation of an aqueous phase in the *pot*.

(8) Horsley, L. H. In "Azeotropic Data-III"; American Chemical Society: Washington, DC, 1973; *Adv. Chem. Ser.* No. 116, p 23. The data in note 7 also shows that the azeotrope must be homogeneous, contrary to the statement in Lurie, A. P., ref 3b, 1965; Vol. 8, p 478.

Bromination of Some *c*-Fused Thiophenes. Thioanhydrides from Thiophenes

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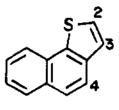
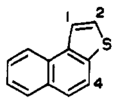
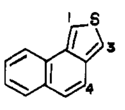
Fusion of a thiophene ring to the 1,2-positions of naphthalene can give three isomeric naphthothiophenes **1**–**3**, each of which is a phenanthrene analogue. Electrophilic substitution has been studied with **1**[1,2] and **2**[3] but not with the *c*-fused thiophene **3**.[4] We report here the first studies on electrophilic substitution in **3** and the novel conversion of the thiophene ring in **3** to a thioanhydride.



1



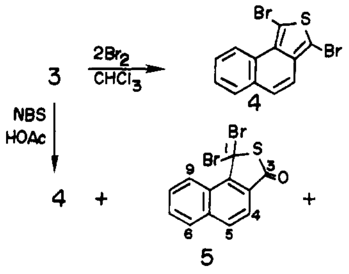
2



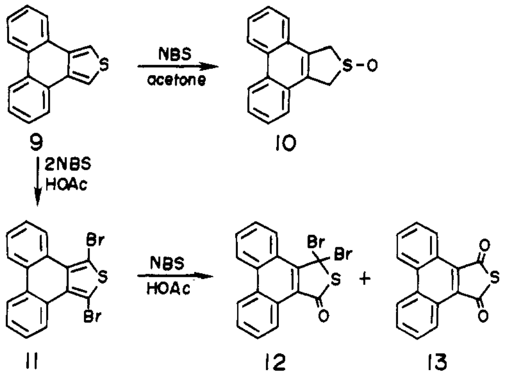
3

Molecular orbital calculations[1,5] on the preferred sites of electrophilic substitution in **1** and **2** are not in agreement with experiment. For example, the preferred positions of attack in **1** are predicted[4] to be 3 > 2 > 5, whereas bromination, formylation, and acetylation occurred predominantly in the 2-position, and nitration gave a mixture of 2- and 5-nitro products. Only if the 2-position was blocked with a methyl substituent did substitution occur in the supposedly preferred 3-position.[2] With **2**, the predicted[5] preferences were for positions 1 > 2 > 5; experimentally,[3] nitration, bromination, formylation, and acetylation occurred in the 2-position, and *not* in the 1-position. There are no MO predictions for substitution in **3**, nor is there any experimental information.

Scheme I



Scheme II

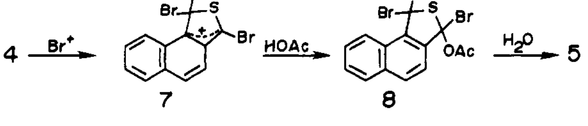


Bromination of **3**[4,6] in chloroform with 1 equiv of bromine gave a mixture of mono- and dibromo products which could not be readily resolved into its components. With 2 equiv of bromine, the 1,3-dibromo derivative **4** was obtained (Scheme I). The ^{1}H NMR spectrum of **4** showed that the two vinyl protons at C4 and C5 were still present (δ 7.27, 7.28, J = 10 Hz). As with **1** and **2**, substitution occurred in the thiophene ring and not at the "vinyl" positions, as in phenanthrene.

Bromination of **3** with *N*-bromosuccinimide (NBS) in acetic acid gave, in addition to **4**, the thiolactone **5** and the thioanhydride **6**. Similar bromination of **4** also gave **5** and **6**, and long exposure of **5** to laboratory air gave **6**. The structure of **6** was proved not only by its spectral properties but also by hydrolysis to the known[7] naphthalene-1,2-dicarboxylic acid.

The relative positions of the bromines and carbonyl group in **5** are based on an analysis of the NMR spectrum in the presence of shift reagent. Lactone **5** showed peaks at δ 8.97 and 7.81 assigned to the C9 and C4 protons, respectively. It was the latter peak (a doublet, coupled with the C5 proton at δ 8.09, J = 8 Hz) which was most shifted downfield with europium shift reagent.

We conclude that while there is not a large difference in the bromination rates of **3** at C1 or at C3, the former position probably has a slight advantage. The formation of **5** can be rationalized via the intermediates **7** and **8**. One possible driving force for electrophilic attack at C1 is to convert that carbon from sp^2 to sp^3 hybridization, thus reducing the "peri" interaction with the C9 proton.



To examine the possible generality of the conversion of a thiophene to a thioanhydride via bromination/hydrolysis,

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(1) Clarke, K.; Gregory, D. N.; Scrowston, R. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2956.

(2) Clarke, K.; Gregory, D. N.; Scrowston, R. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 63.

(3) Clarke, K.; Rawson, G.; Scrowston, R. M. *J. Chem. Soc. C* **1969**, 537. For studies on the closely related benzodithiophenes, see: Gronowitz, S.; Dahlgren, T. *Chem. Scr.* **1977**, *12*, 97.

(4) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932.

(5) Zahradnik, R.; Pārkānyi, C. *Collect. Czech. Chem. Commun.* **1965**, *30*, 195.

(6) Horner, C. J.; Saris, L. E.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron Lett.* **1976**, 2581.

(7) Fieser, L. F. *J. Am. Chem. Soc.* **1929**, *51*, 951.

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