BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2977—2978 (1975)

A Structural Investigation of the 2-Methylthiophene Trimer and Its Related Compounds†

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(Received November 30, 1974)

Synopsis. A structural investigation of the 2-methylthiophene trimer and its crystalline oxidation product has been performed. These compounds have been found to be identical with 2,4-bis(5′-methyl-2′-thienyl)-2-methylthiolane and its sulfone derivative.

Thiophene and alkylthiophen react under the catalytic action of phosphoric acid to give their oligomers. The reaction was investigated by Meisel *et al.* in 1950.[1] Noting the presence of trimers in the reaction products, they proposed a reaction mechanism and elucidated the structure of the thiophene trimer, 2,4-bis-2′-thienylthiolane [**1**]. However, no structural description of the alkylthiophene trimers was undertaken.

In a previous paper,[2] the present authors investigated an oligomerization of 2-methylfuran and elucidated the structure of the 2-methylfuran tetramer. 2-Methylfuran reacts under the catalytic action of phosphoric acid to give its tetramer in a good yield. However, no trimeric compounds are found in the reaction product. Our interest in preparing the 2-methylfuran tetramer led us to reinvestigate the trimerization of thiophene and 2-methylthiophene. In this paper, the authors will try to elucidate the structure of the 2-methylthiophene trimer [**2**] and its related compounds, novel crystalline derivatives of **1** and **2**.

Experimental

*Preparation of **1** and **2**.* Reagent-grade thiophene was used after fractional distillation. The 2-methylthiophene was prepared by the ordinary method[3,4] and was used after fractional distillation; bp 112 °C (750 mmHg). The preparations of **1** and **2** were carried out by the method of Meisel *et al.*

Thiophene trimer [**1**]: bp 181—183 °C (2 mmHg); n_D^{20} 1.6455 (lit,[1] bp 167—170 °C (1 mmHg); n_D^{20} 1.6450).

2-Methylthiophene trimer [**2**]: bp 190 °C (2 mmHg); n_D^{20} 1.6103 (lit,[1] bp 190—193 °C (0.8 mmHg); n_D^{20} 1.6104).

*Preparation of the Crystalline Derivatives of **1** and **2**.* To 20 ml of glacial acetic acid we added 1.5 g (6 mmol) of **1**, followed by 20 ml of an aqueous solution of potassium permanganate (2.6 g, 8 mmol). The solution was stirred at 40—50 °C for 30 min. The resulting solution was treated with sodium hydrogen sulfite to dissolve the precipitated manganese dioxide. The solution was then extracted with two portions of ether. The combined ethereal layers were washed with a saturated sodium hydrogen carbonate solution and then successively twice with water. The ethereal extract was dried over anhydrous magnesium sulfate and concentrated. The residue was crystallized from ethanol to give 0.57 g of a crude product; mp 129.3 °C. The product was treated with active carbon in ethanol and then recrystallized to afford 0.37 g of a colorless crystalline product [**3**]; mp 133.3 °C. Found: C, 50.74; H, 4.27%, mol wt, 285.3 (measured in dioxane by means of a vapor-pressure osmometer). Calcd for $C_{12}H_{12}S_3O_2$: C, 50.67; H, 4.25%; mol wt, 284.4.

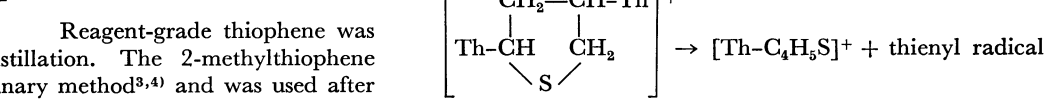
The crystalline derivative of **2** was prepared following the method of the preparation of **3**. From 1.0 g of **2**, 0.1 g of colorless fine crystals [**4**] was obtained; mp 146.5 °C. Found: C, 55.15; H, 5.68%; mol wt, 325.1. Calcd for $C_{15}H_{18}S_3O_2$: C, 55.17; H, 5.55%; mol wt, 326.5.

† Presented in part at the 30th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1974.

Results and Discussion

The NMR spectrum of **1** in CCl_4 reveals a signal at δ 6.7—7.1 (m, 6H). This signal is assigned to the protons of the two thienyl groups. This fact supports the structure of **1** proposed by Meisel *et al.*—2,4-bis-2′-thienylthiolane. Following the structure, the other signals are assigned to the six protons on the thiolane ring; the thiolane ring protons of the 2-position (δ 4.6—5.0, m, 1H), the 3-position (δ 2.0—2.5, m, 2H), the 4-position (δ 3.6—3.9, m, 1H), and the 5-position (δ 2.6—3.5, m, 2H).

The mass spectrum of **1** reveals a metastable ion at *m/e* 112. The presence of the metastable ion at *m/e* 112 (calcd: $(168)^2/252=112.0$) supports the following fragmentation process:



M^+ of **1**, *m/e* 252 *m/e* 168 (rel. intensity 98.8%)

Th; thienyl group

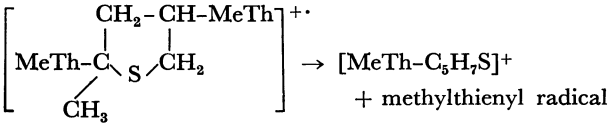
These NMR and mass spectral data are useful for investigating the unknown structure of **2**. If the trimerization of 2-methylthiophene occurs by means of the same reaction mechanism as that proposed by Meisel *et al.*, the following two kinds of structural formulas may be expected: 2,4-bis(5′-methyl-2′-thienyl)-2-methylthiolane or 2,4-bis(5′-methyl-2′-thienyl)-5-methylthiolane.

The remarkable resemblance between the NMR spectra of **1** and **2** indicates the structural resemblance between them. Thus, the signal at δ 6.3—6.8 (m,4H) is assigned to the protons of the two disubstituted thiophene nuclei, while the signal at δ 2.36 (s, 6H) is assigned to the two methyl groups substituted on the thiophene nuclei. The other signals are, then, assigned to the eight protons on the methylthiolane nucleus: the thiolane ring protons of the 3-position (δ 2.1—2.7, m, 2H; overlapped with a broad singlet at δ 2.36),

the 4-position (δ 3.5—4.0 m, 1H) and the 5-position (δ 2.8—3.4, m, 2H), and the methyl protons attached to the 2-position of the thiolane ring (δ 1.8, s, 3H).

The presence of the singlet methyl signal at δ 1.8 shows that one of the two thienyl groups must be attached to the 2-position of the thiolane ring. The other thienyl group must, then, be attached to the 4-position of the thiolane ring. The structure of the two methylthienyl groups probably corresponds to that of the 5′-methyl-2′-thienyl groups, because the α and α' positions of the thiophene nucleus are actually more reactive than the β and β' positions. Therefore, the structure of **2** is identified with 2,4-bis(5′-methyl-2′-thienyl)-2-methylthiolane.

The mass spectrum of **2** reveals a metastable ion at *m/e* 131. This metastable ion supports the following fragmentation process (calcd=(196)²/294=130.6):

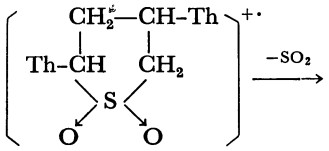


M⁺ of **2**, *m/e* 294 *m/e* 196 (rel. intensity 80.9%)
Meth; methylthienyl group

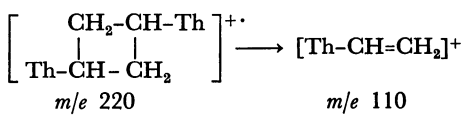
The NMR spectral pattern of **3** closely resembles that of **1**, and the two IR bands of **3** correspond to the characteristic bands due to the sulfone group: NMR ($CDCl_3$) δ 2.5—3.0 (m, 2H), 3.3—3.8 (m, 2H), 3.8—4.2 (m, 1H), 4.6—4.9 (m, 1H) and 6.9—7.4 (m, 4H); IR 1315 ($\nu_{as}SO_2$) and 1135 cm^{-1} ($\nu_{s}SO_2$). These facts support the structure of **3** as a sulfone derivative of **1**: 2,4-bis-2′-thienylthiolane 1,1-dioxide.

The structure of **4** was also identified as 2,4-bis(5′-methyl-2′-thienyl)2-methylthiolane 1,1-dioxide by the NMR and IR spectral data, and by elemental analysis: NMR ($CDCl_3$) δ 1.86 (s, 3H), 2.44 (s, 6H), 2.5—2.9 (m, 2H), 3.1—3.4 (m, 2H), 3.5—4.0 (m, 1H) and 6.5—7.0 (m, 4H); IR 1300 ($\nu_{as}SO_2$) and 1130 cm^{-1} ($\nu_{s}SO_2$).

No metastable ion peaks are found in the mass spectra of **3** and **4**. These spectral data suggest a quite different fragmentation process from those of **1** and **2**. The mass spectrum of **3** reveals the molecular ion peak at *m/e* 284 and some major peaks: *m/e* 110 (rel. intensity 100%), 220 (10%), and others. The presence of these ion peaks suggests the following possible fragmentation process for **3**:

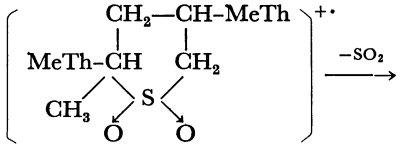


M⁺ of **3**, *m/e* 284

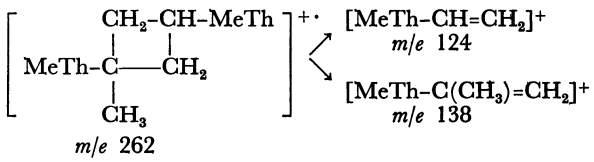


m/e 220 *m/e* 110

The mass spectrum of **4** lacks the molecular ion (*m/e* 326). However, the presence of several ion peaks at *m/e* 262 (rel. intensity 3%), 138 (100%) and 124 (21%) supports the following fragmentation process similar to that discussed in connection with the fragmentation of **3**:



M⁺ of **4**, *m/e* 326



m/e 262

References

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2) A. Ishigaki and T. Shono, This Bulletin, **47**, 1467 (1974).
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4) D. Todd, "Organic Reactions," Vol. 4, p. 378 (1948).