An Unusual Nucleophilic Substitution on an Aromatic Substrate. Reaction of 2,5-Dimethyl-3,4-dinitrothiophen with Sodium Arenethiolates in Methanol

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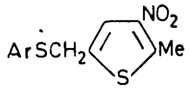
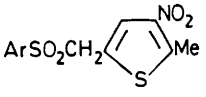
Summary The reaction between 2,5-dimethyl-3,4-dinitrothiophen and sodium arenethiolates gives aryl 2-(5-methyl-4-nitro)thenyl sulphides *via* an unusual nucleophilic substitution, as shown by the ^{1}H n.m.r. spectra of the isolated sulphides and the corresponding sulphones.

In relation to our studies in the thiophen series,[1] we report on the reaction of 2,5-dimethyl-3,4-dinitrothiophen[2] (**1**) with sodium benzenethiolate and sodium 2,4,6-trimethylbenzenethiolate.



(2) Ar = Ph
(3) Ar = 2,4,6-$Me_3C_6H_2$



(4) Ar = Ph
(5) Ar = 2,4,6-$Me_3C_6H_2$

Reaction of equimolar amounts of (**1**), sodium benzenethiolate, and benzenethiol in methanol (17 h reflux), followed by column chromatography gave a colourless solid product (**2**) (70% yield, m.p. 36° from light petroleum b.p. 30—50°). Analytical data (C,H,N,O,S, and molecular weight) corresponded to the formula $C_{12}H_{11}NO_2S_2$. An analogous reaction with sodium 2,4,6-trimethylbenzenethiolate afforded a colourless solid product (**3**), m.p. 86—87°, (from light petroleum b.p. 30—50°) corresponding to the formula $C_{15}H_{17}NO_2S_2$. Oxidation of (**2**) and (**3**) by peracetic acid furnished (**4**) and (**5**) respectively [(**4**), m.p. 166° (from EtOH), analytical data corresponding to the formula $C_{12}H_{11}NO_4S_2$; (**5**), m.p. 153° (from EtOH), analytical data corresponding to the formula $C_{15}H_{17}NO_4S_2$].

The ^{1}H n.m.r. spectra of $(CD_3)_2SO$ solutions of compounds (**2**)—(**5**) were examined. Compound (**2**) showed signals at τ 2·56 (1H), 2·71 (5H), 5·54 (2H), and 7·34 (3H), and compound (**3**) at τ 2·87 (1H), 3·07 (2H), 5·98 (2H), 7·33 (3H), 7·65 (6H), and 7·79 (3H). The lowest-field signal of both these spectra exhibits the primary structure of a triplet (*J* 0·84 Hz). Compound (**4**) showed signals at τ 2·27 (5H), 2·66 (1H), 4·98 (2H), and 7·29 (3H) and compound (**5**) at τ 2·63 (1H), 2·94 (2H), 5·15 (2H), 7·29 (3H), 7·49 (6H), and 7·72 (3H).

On the basis of these spectral data the aryl 2-(5-methyl-4-nitro)thenyl sulphide structure was assigned to compounds (**2**) and (**3**) and the aryl 2-(5-methyl-4-nitro)thenyl sulphone structure was assigned to compounds (**4**) and (**5**).

The reaction studied thus seems to be an unusual nucleophilic substitution which involves attack of the nucleophile on a side-chain carbon atom of an aromatic substrate and departure of the leaving group from the ring.

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[1] F. Sancassan, M. Novi, G. Guanti, and C. Dell'Erba, *J. Heterocyclic Chem.*, 1975, **12**, 1083 and references therein.
[2] W. Steinkopf, I. Poulsson, and O. Herdey, *Annalen*, 1938, **536**, 128.

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