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THE FORMATION OF THIOPHENES BY A BASE-CATALYZED SULFOXIDE DEHYDRATION

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We recently reported the synthesis of benzo[*c*]selenophene by a reaction which represents the first instance of a base-catalyzed selenoxide dehydration.[1] The closest analogous sulfoxide reactions reported consist of the treatment of dibenzyl sulfoxide (1) and the thiapyran sulfoxide 2 with limited amounts of phenyllithium to give moderate yields of the respective episulfides 3 (cis and trans) and 4.[2] We now report the formation of some condensed thiophenes (5, 6 and 7) by base-catalyzed sulfoxide dehydrations, employing even as weak a base as sodium hydroxide.

Sulfoxide 8,[3] which was stable on heating with water alone, gave a milky emulsion when heated to 100° with 30% aqueous sodium hydroxide, the naphthalene-like odor of benzo[*c*]thiophene (5) becoming quickly noticeable. Steam distillation of the unstable 5[3,4] gave mainly polymer, but 5 could be isolated from the distillate in low yield (4%) in the form of its tetracyanoethylene adduct 9.[1] Similar treatment of sulfoxide 10[3] (steam distillation from 30% aqueous sodium hydroxide) gave the far more stable naphtho[1,2-*c*]thiophene (6)[3] in a recrystallized yield of 38%.

Due to their virtual insolubility in water, the cis and trans sulfoxide pair 11 and 12[5] were subjected to base dehydration in benzene solution, oxygen being rigorously excluded. In all experiments (see Table 1) the product was the purple tetraphenylthieno[3,4-*c*]thiophene (7),[5] which was either isolated directly or converted by tetracyanoethylene (TCNE) to the adduct 13, mp 217-219° dec.[6] Grignard reagents and methyllithium gave rather low yields, but high yields were obtained in 30 min using lithium diisopropylamide (LDA) at room temperature.

Table 1

Dehydrations of Sulfoxides 11 and 12 Using Various Bases

Sulfoxide	Base	Reaction time, hrs	Yield (%) 7
11	MeMgBr	3.5	12^a
11	EtMgBr	4.0	9^a, 11^b
12	EtMgBr	4.0	6^b
11	MeLi	4.0	11^b
11	LDA	0.5	77^a, 85^b, 76^c
12	LDA	0.5	80^b
11	NaOH ^{d}	48.0	45^a, 69^b
12	NaOH ^{d}	48.0	43^a, 76^b

a) By isolation of 7.

b) By titration with TCNE.

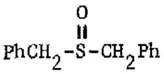
c) By isolation of adduct 13.

d) 50% aqueous NaOH with cetyltrimethylammonium bromide.

Aqueous sodium hydroxide in the presence of a phase-transfer catalyst reacted slowly but cleanly at 80°, good yields of 7 being obtained after 2 days. If oxygen is present, even in the dark, the sulfoxide is consumed within 4 hrs, the product being the diketone 14[5] (48%) rather than the thienothiophene 7. In a control experiment under similar dark conditions, thienothiophene 7 was unchanged to the extent of 87%, indicating that the precursor of diketone 14 was not the thienothiophene but rather an anion of the sulfoxide.

The alkaline dehydration of sulfoxides is a reaction which should allow the direct observation of less stable condensed thiophenes which are highly acid sensitive. The thienofuran 15, for example, has been generated from sulfoxide 16 by acetic anhydride and trapped as an adduct in situ; a transient pale violet color corresponding to a band at 550 nm could be observed in the absence of a trapping agent.[7] We have now found that dehydration of sulfoxide 16 in benzene by hydroxide ion and phase-transfer catalyst affords a deep blue air-sensitive solution (λ_{max} 577 nm), the color of which we attribute to the elusive thienofuran 15.

The sulfoxide dehydrations which occur in the presence of aqueous sodium hydroxide are particularly interesting from a mechanistic point of view. We propose these reactions proceed via a dianion (i.e. 17) which protonates on the sulfoxide oxygen to give a monoanion (i.e. 18) which then eliminates hydroxide ion. Monoanion 18 is an intriguing species in that it is the anion of a "thiaenol" (*i.e.* 19)[8].



$\mathrm{PhCH_2-\overset{\overset{O}{\|}}{S}-CH_2Ph}$

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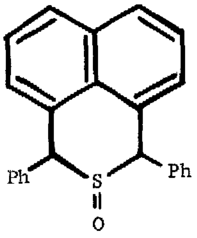

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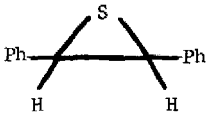
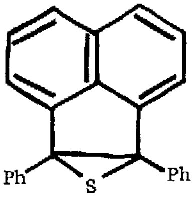


3 cis/trans



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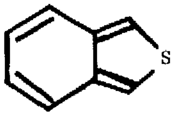

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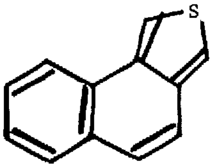

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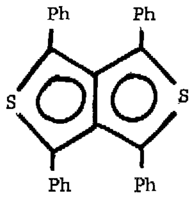

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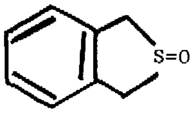

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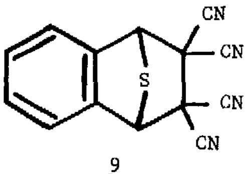

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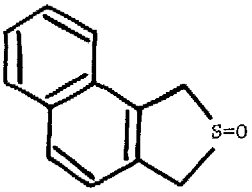

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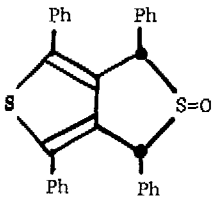

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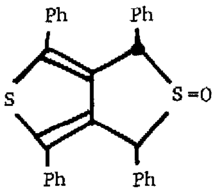

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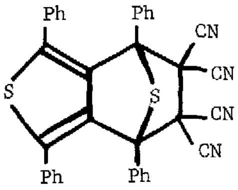

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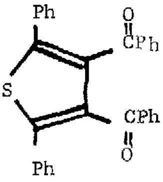

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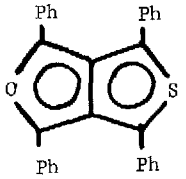

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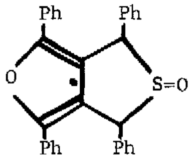

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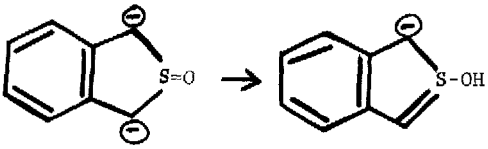
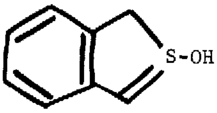


17 **18**



19

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5. M. P. Cava, M. Behforouz, G. E. M. Husbands and M. Srinivasan, J. Am. Chem. Soc., **95**, 2561 (1973).
6. Satisfactory elemental analyses (C, H, N) were obtained for adducts **9** (mp 172° dec.) and **13**.
7. M. P. Cava, M. A. Sprecker and W. R. Hall, J. Am. Chem. Soc., **96**, 1817 (1974).
8. Monoanions of sulfoxides are unlikely intermediates in these reactions, as evidenced by the fact that treatment of 1.0 equiv. of sulfoxide **12** with 1.28 equiv. of the base LDA under standard reaction conditions (i.e. Table 1) afforded product **7** in only 15% yield. It may be pointed out also that dianions have also been proposed in the conversion of sulfoxides **1** and **2** into episulfides **3** and **4**.[2]