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The Generation and Trapping of Thiobenzaldehyde and Thioacetaldehyde

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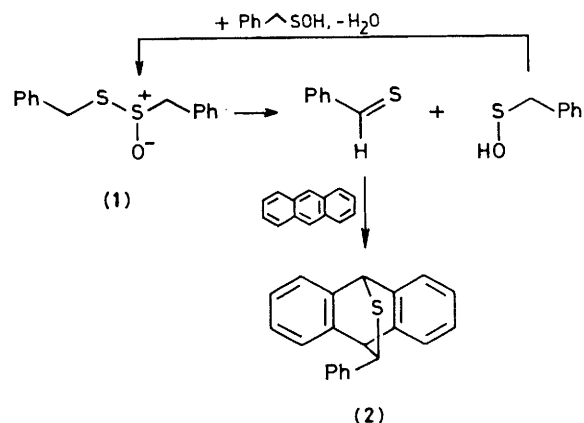
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Thiobenzaldehyde and thioacetaldehyde have been generated by thermolysis of alkyl thiosulphinates under preparatively useful conditions and trapped with aromatic and aliphatic 1,3-dienes, the adducts with anthracene being convenient and high yielding sources of such thioaldehydes; thiobenzaldehyde has been shown to undergo the 'ene' reaction.

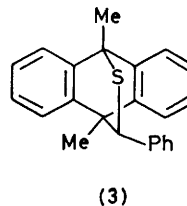
In work related to the chemistry of 4-mercaptoazetidin-2-ones we observed that isomerisation of these species provided thioaldehydes which could be trapped by nucleophiles¹ and also by intramolecular 'ene' reactions.² As a result, we became interested in the chemistry of these poorly known compounds which have received little attention because of their tendency to polymerise. Recently however, it was reported that electron-deficient thioaldehydes could be generated photochemically and trapped with electron-rich 1,3-dienes.³ We report here the efficient thermal generation of thiobenzaldehyde and thioacetaldehyde, and their trapping with aliphatic and aromatic dienes.

S-Alkyl thiosulphinates are known to decompose to thio-carbonyl compounds and sulphenic acids at elevated temperatures and the sulphenic acids have been trapped.⁴ Thus, we heated *S*-benzyl phenylmethanethiosulphinate (1)⁵ (1.00 mmol) in toluene at 100 °C for 1 h in the presence of an excess of anthracene, and isolated after chromatography 1.93 mmol of adduct (2)[†] (97%, m.p. 160–163 °C (decomp.); λ_{max} (MeCN) 212 (36 000) and 279 (3 000) nm; δ [(CD₃)₂SO, 300 MHz] 4.57 and 4.69 [2 × d, 2 × 1H, *J* 2.5 Hz, Ar₂CHCH and Ar₂CHCH(Ph)S], 5.59 (s, 1H, Ar₂CHS), 6.77–6.88 (m, 3H, ArH), 7.05 (m, 1H, ArH), 7.10–7.29 (m, 6H, ArH), 7.42 (m, 1H, ArH), and 7.48–7.55 (m, 2H, ArH)}. The stoichiometry of the reaction shows that, under these conditions, the sulphenic acid formed regenerates more alkyl thiosulphinates (1), Scheme 1. When this thermolysis was repeated in the absence of anthracene, a blue colour was observed, λ_{max} 580–590 and 610 nm (shoulder) which disappeared after 15 min. This is the same as the reported spectrum of thiobenzaldehyde at 77 K on NaCl generated by flash vacuum pyrolysis of allyl benzyl sulphide.⁶

Under similar conditions, 9,10-dimethylantracene produced adduct (3) [87% based on alkyl thiosulphinate, m.p. 140–150 °C (decomp.); λ_{max} (MeCN) 280 (2 900) nm; δ



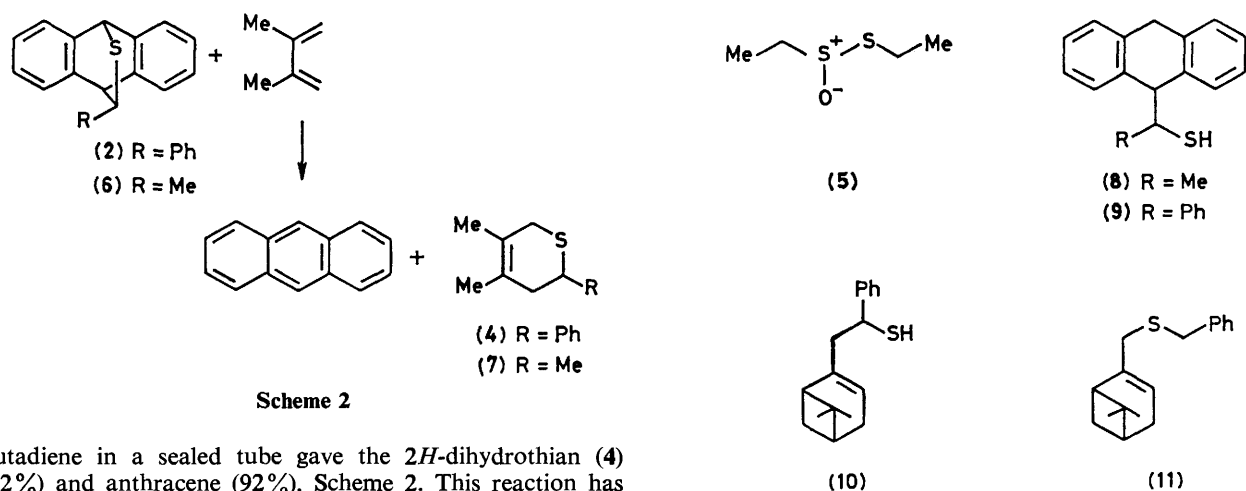
Scheme 1



(CD₂Cl₂, 300 MHz) 1.74 and 2.33 (2 × s, 2 × 3H, 2 × CH₃), 4.24 (s, 1H, PhCHS), 6.55 (br. s, 2H, ArH), and 7.02–7.50 (m, 11H, ArH)], while 2,3-dimethylbutadiene gave the 2*H*-dihydrothian (4) [95%, b.p. 130–135 °C at 0.4 mmHg; δ (CDCl₃, 300 MHz) 1.73 and 1.78 (2 × br. s, 2 × 3H, CH₃C=CCH₃), 2.40–2.49 and 2.53–2.65 (2 × m, 2 × 1H, PhCH-CH₂), 2.93 and 3.48 (2 × m, 2 × 1H, SCH₂C=), 3.98 (dd, 1H, *J* 6, 9 Hz, PhCHS), and 7.25–7.38 (m, 5H, ArH)].

The adduct (2) serves as a source of thiobenzaldehyde itself. Thus, heating (2) in the presence of 2,3-dimethyl-

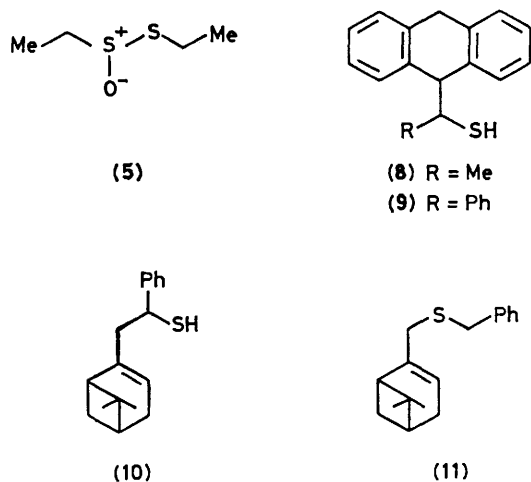
[†] All new compounds have been fully characterised by spectroscopy.



butadiene in a sealed tube gave the 2*H*-dihydrothian (4) (92%) and anthracene (92%), Scheme 2. This reaction has the advantage over alkyl thiosulphinate thermolysis that no sulphenic acid is produced, so it could have synthetic applications where a thioaldehyde is required free from other reactive species.

Analogously, *S*-ethyl ethanethiosulphinate (5)⁷ was thermolysed in the presence of anthracene, giving adduct (6) {74%, m.p. 169–171 °C; λ_{\max} (MeCN) 225 (8 200) and 278 (2 700) nm; $\delta[(\text{CD}_3)_2\text{CO}, 300 \text{ MHz}]$ 1.11 (d, 3H, *J* 6 Hz, CH_3CH), 3.44 (qd, 1H, *J* 6, 3 Hz, CH_3CHS), 4.54 (d, 1H, *J* 3 Hz, Ar_2CHCH), 5.25 (s, 1H, Ar_2CHS), 7.10–7.23 (m, 4H, *ArH*), and 7.32–7.43 (m, 4H, *ArH*)}, and in the presence of 2,3-dimethylbutadiene, giving 2*H*-dihydrothian (7) [83%, b.p. 70–87 °C at 17 mmHg; $\delta(\text{CDCl}_3, 300 \text{ MHz})$ 1.27 (d, 3H, *J* 7 Hz, CH_3CH), 1.63 and 1.69 (2 × br. s, 2 × 3H, $\text{CH}_3\text{C}=\text{CCH}_3$), 1.93–2.06 and 2.17–2.26 (2 × m, 2 × 1H, CH_3CHCH_2), 2.78–2.95 (m, 2H, $=\text{CCHS} + \text{CH}_3\text{CHS}$), and 3.33 (m, 1H, $=\text{CCHS}$)]. The formation and trapping of both aromatic and aliphatic thioaldehydes suggests that this thermolysis procedure is a general method for producing thioaldehydes.

The anthracene adduct (6) was reduced with sodium in liquid ammonia to thiol (8) (84%) which was acetylated with acetyl chloride and pyridine to the corresponding acetyl derivative [ν_{\max} (CHCl_3) 1 690 cm^{-1} ; δ ($\text{CD}_2\text{Cl}_2, 300 \text{ MHz}$) 1.13 (d, 3H, *J* 7 Hz, CH_3CH), 2.21 (s, 3H, CH_3CO), 3.81–3.93 (m, 2H, one of $\text{Ar}_2\text{CH}_2 + \text{CH}_3\text{CHS}$), 4.13 (d, 1H, *J* 6 Hz, Ar_2CHCH), 4.25 (d, 1H, *J* 18 Hz, one of Ar_2CH_2), and 7.19–7.42 (m, 8H, *ArH*)]. However, the adduct of thiobenzaldehyde (2) gave 9,10-dihydroanthracene (72%) under similar conditions, although when the reduction was carried out at –78 °C, the thiol (9) was obtained, which was converted as



before into the acetyl derivative [m.p. 105–108 °C; ν_{\max} (CHCl_3) 1 690 cm^{-1} ; δ ($\text{CD}_2\text{Cl}_2, 300 \text{ MHz}$) 2.37 (s, 3H, CH_3CO), 2.96 and 3.49 (2 × d, 2 × 1H, *J* 19 Hz, Ar_2CH_2), 4.43 and 4.87 (2 × d, 2 × 1H, *J* 6 Hz, $\text{PhCHS} + \text{Ar}_2\text{CHCH}$), 6.55 (m, 2H, *ArH*), 6.99–7.30 (m, 10H, *ArH*), and 7.50 (m, 1H, *ArH*)].

Finally, thiobenzaldehyde generated as above from (1) when allowed to react with β -pinene gave two isomeric adducts (10) (38%) and (11) (19%) showing that thioaldehydes have reactivity for use in ‘ene’ reactions as well as in Diels–Alder additions.

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