

Synthesis of 2,4,6-Tri-*t*-butylthiobenzaldehyde, the First Stable Thiobenzaldehyde

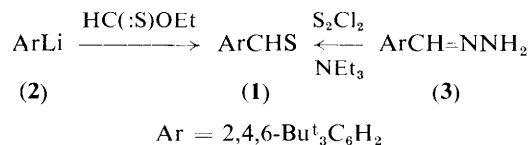
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The title compound, an extremely stable thiobenzaldehyde, was prepared by the reaction of 2,4,6-tri-*t*-butylphenyl-lithium with *O*-ethyl thioformate or the reaction of 2,4,6-tri-*t*-butylbenzaldehyde hydrazone with disulphur dichloride.

In numerous attempts to prepare monomeric thioaldehydes, it has been revealed that the thioaldehyde can be isolated only when it is stabilised by the mesomeric effect due to heteroatoms such as nitrogen and sulphur.¹ Simple thioaldehydes (*e.g.*, thioformaldehyde,^{2,5} thioacrylaldehyde,^{3,4} thiobenzaldehyde^{3,5}) are so unstable that they can only be detected spectroscopically²⁻⁵ or by chemical trapping.⁶

We report the first example of a stable thioaldehyde (**1**) isolated without resort to stabilisation by heteroatoms. The treatment of 2,4,6-tri-*t*-butylphenyl-lithium (**2**), prepared from 2,4,6-tri-*t*-butylbromobenzene and *n*-butyl-lithium in tetrahydrofuran, with *O*-ethyl thioformate followed by chromatographic purification (SiO₂), afforded 2,4,6-tri-*t*-butylthiobenzaldehyde (**1**) in 56% yield. The thioaldehyde (**1**) was also synthesized by oxidative sulphurisation⁷ of the hydrazone (**3**) with disulphur dichloride in the presence of triethylamine in 40% yield. The thioaldehyde (**1**) is a purple crystalline compound† (m.p. 146–147 °C), ¹H n.m.r. (CCl₄) δ 1.30 (9H, s), 1.32 (18H, s), 7.22 (2H, s), and 13.02 (1H, s); ¹³C n.m.r.



(CDCl₃) δ 31.3, 32.9, 34.8, 37.0, 121.8, 145.1, 145.6, 149.5, and 250.4 p.p.m.; λ_{max} (hexane) 338 (ε 1850) and 564 nm (19); λ_{max} (EtOH) 340 (ε 1690) and 552 nm (19); *m/z* 290(*M*⁺), 257, 233, and 57. It is extremely stable. No appreciable change can be observed when stored in the solid state at room temperature over a year or refluxed in benzene in the absence of oxygen for 2 weeks; in the presence of oxygen it is quantitatively oxidised to the corresponding aldehyde. This stability is surprising considering that the parent thiobenzaldehyde has been reported to polymerise above –160 °C.³

The monomeric nature of (**1**) is obvious from the above spectral data. The thioformyl proton resonates at δ 13.02, the lowest field ever reported,¹ suggesting that (**1**) has an almost pure thioformyl group. The thioformyl carbon resonance occurs at δ 250.4 p.p.m., which is reasonable judging from the relationship between δ_{C=O} and δ_{C=S}⁸ (δ_{C_HS} calculated for

† Satisfactory elemental analyses (C, H, S) were obtained.

(1) is 247.4 p.p.m.; cf. 2,4,6-tri-*t*-butylbenzaldehyde $\delta_{\text{CHO}} = 202.7$ p.p.m.). The electronic absorption in the visible region (550–560 nm) is fairly close to that reported for thiobenzaldehyde (575 nm)³ and shows a hypsochromic shift with increase in solvent polarity, suggesting its $n \rightarrow \pi^*$ nature.

The thioaldehyde (1) is considered to have 'the purest thioformyl group' among those so far isolated and hence would be useful for studying the physical and chemical properties of the thioformyl group.

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