

REACTIONS OF A STABLE THIOBENZALDEHYDE WITH ORGANOMETALLICS

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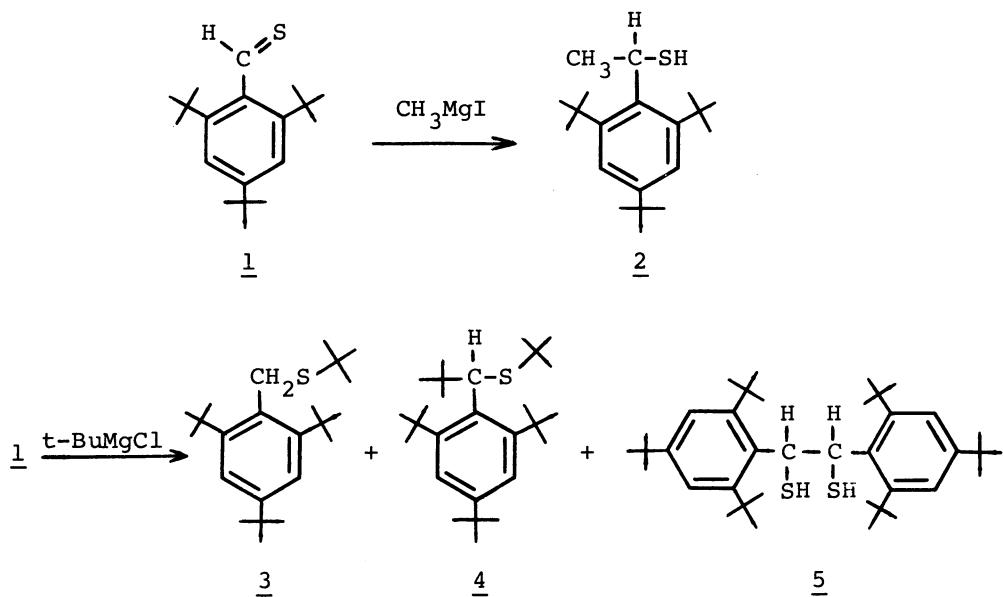
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Reactions of 2,4,6-tri-*t*-butylthiobenzaldehyde with Grignard and organolithium reagents gave products via the anion radical of the thioaldehyde. The first example of dimerization of thioketyl radicals was also presented.

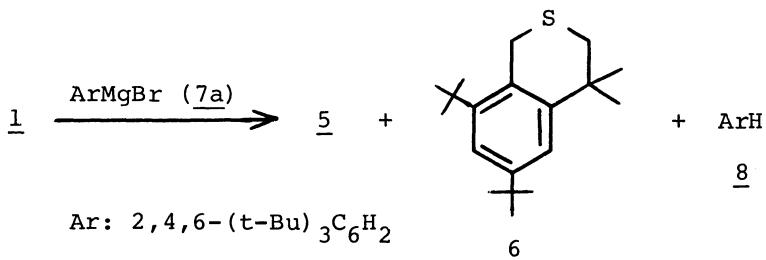
Although the chemistry of thioketones is relatively well established,¹⁾ only little has been known for the chemistry of thioaldehydes because of limited availability of compounds suitable for studies on their reactivities. Very recently, however, a couple of preparative methods of thioaldehydes have been reported by us and other groups which enable one to study chemical behaviors of thioaldehydes. We synthesized a very stable thiobenzaldehyde, 2,4,6-tri-*t*-butylthiobenzaldehyde (1)²⁾ and Vedejs prepared an aliphatic thioaldehyde, 2,2-dimethylpropanethial stable in solution.³⁾ Baldwin found an efficient preparative method of some thioaldehydes in solution.⁴⁾

We wish to report here the first example of reactions of a thiobenzaldehyde with organometallics leading to the formation of some interesting products.⁵⁾

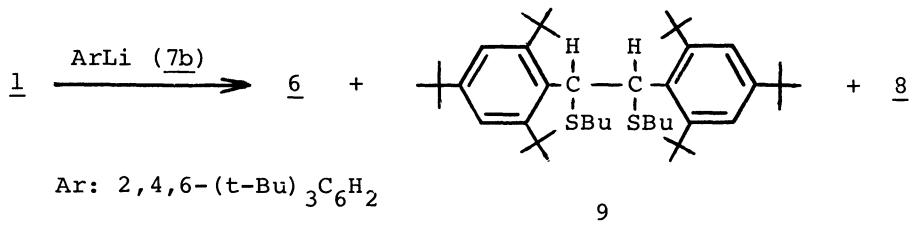
The reaction of 1 with methylmagnesium iodide (ether, 0 °C) resulted in the formation of thiol 2 (81%).⁶⁾ The reaction with *t*-butylmagnesium chloride (ether, 0 °C) gave three products, 3 (27%), 4 (13%), and 5 (31%).⁶⁾



When 1 was allowed to react with a very bulky 2,4,6-tri-*t*-butylphenylmagnesium bromide (7a) (THF reflux, 1 h), 5 (14%) and 6 (20%) were formed, no product being found which resulted from an attack of 7a to the carbon and sulfur atoms of the thioformyl group. Refluxing for a longer time (3 h), however, produced only 6 (80%). In both reactions 7a was converted to 1,3,5-tri-*t*-butylbenzene (8) in a high yield.



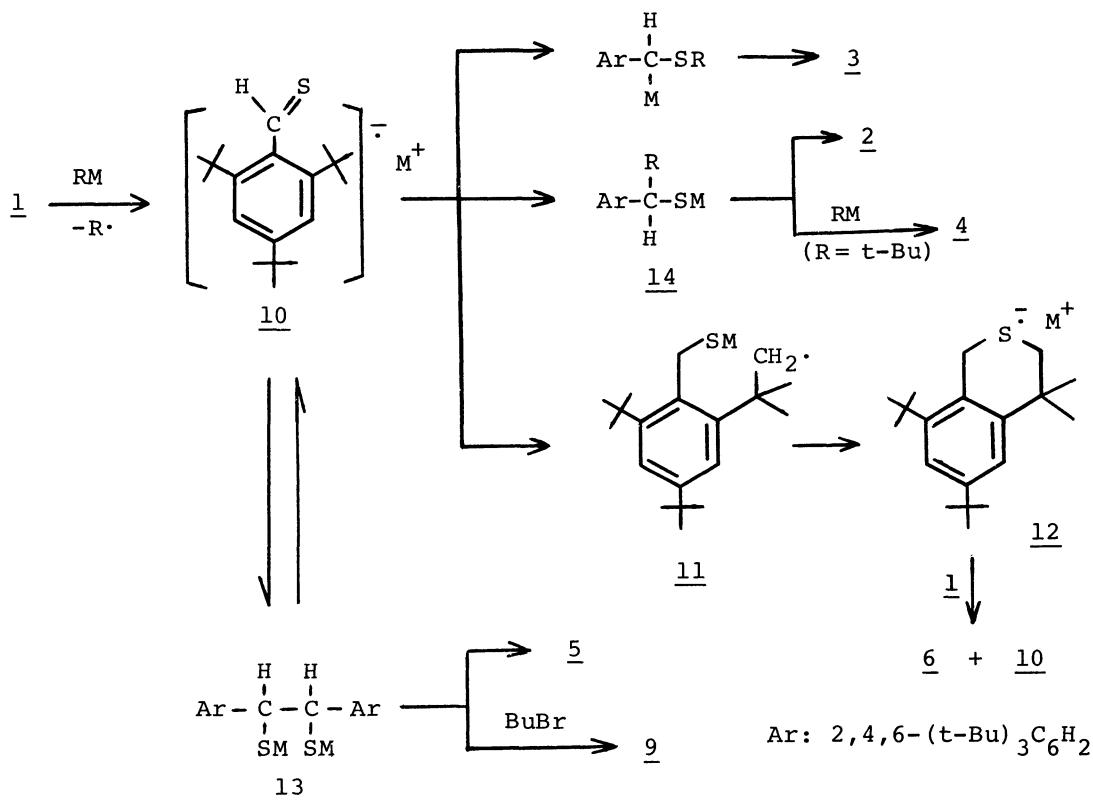
Similar results were obtained in the reaction with 2,4,6-tri-*t*-butylphenyllithium (7b), the products being 6 (13%), 9 (53%), and 8 (94%).⁶⁾



The reactions of thioketones with Grignard and organolithium reagents have been the subject of much interest because of its unique features, e.g., thiophilic addition and double addition to both carbon and sulfur atoms.^{1,7,9)} The mechanism involving single electron transfer (SET) was proposed for these reactions.^{7d,7e,9)} However, any dimerized product of anion radicals (thioketyl radical),⁸⁾ a key intermediate produced via SET, has never been observed so far. The formation of 5 and 9 is the first example of such products and clearly shows the involvement of thioketyl radical 10 in the reaction of 1 with organometallics (Scheme 1). The sulfide 9 results from the reaction of 13 with butyl bromide formed in the preparation of 7b from 2,4,6-tri-*t*-butylbromobenzene and butyllithium.

This is not only the first observation of dimerization of a thioketyl type radical in the reactions of thiocarbonyl compounds with organometallics but also the first example of an anion radical derived from a thioaldehyde. The easy dimerization of 10 is noteworthy in view of the reported observation that the anion radical of thiobenzophenone does not dimerize to an appreciable extent.¹⁰⁾

Scheme 1.



The formation of 6 is considered to be another piece of evidence for the SET mechanism since it can be most likely explained by a reaction pathway 10 \rightarrow 11 \rightarrow 12 \rightarrow 6 (Scheme 1). The validity of this pathway is supported by the following facts. 1) A very similar radical-catalyzed cyclization leading to 6 was observed in the reaction of 1 with free radicals such as $\text{Me}_2(\text{CN})\text{C}\cdot$ and $\text{Me}_3\text{C}\cdot$.^{11,12)} 2) The benzothiane 6 was increased at the expense of 5 when the reaction time was prolonged (vide supra), suggesting that 13 is reversibly dissociated to 10 which in turn gives 6.

The formation of the other products 3 and 4 is also explicable in terms of Scheme; the double addition product 4 is probably formed from the reaction of 14 with t-butylmagnesium chloride.¹³⁾

It is concluded that the reaction of the thiobenzaldehyde (1) with organometallics proceeds via a single electron transfer mechanism.

References

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- 2) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1982, 1187.

- 3) E. Vedejs and D. A. Perry, *J. Am. Chem. Soc.*, 105, 1683 (1983).
- 4) J. E. Baldwin and R. C. G. Lopez, *J. Chem. Soc., Chem. Commun.*, 1982, 1029; *Tetrahedron*, 39, 1487 (1983).
- 5) The reaction of 2,2-dimethylpropanethial with phenyllithium has recently been reported (Ref. 3), which prompted us to report our preliminary results.
- 6) The spectral data of the products are as follows. NMR spectra were measured in CCl_4 . 2: NMR δ 1.29 (9H, s), 1.56 (18H, s), 1.80 (3H, d, $J=7.2$ Hz), 2.11 (1H, d, $J=7.2$ Hz, SH), 5.04 (1H, m), and 7.36 (2H, s); MS m/e 306 (M^+) and 57 (base). 3: NMR δ 1.26 (9H, s), 1.34 (9H, s), 1.50 (18H, s), 4.13 (2H, s), and 7.14 (2H, s); MS m/e 348 (M^+) and 57 (base). 4: NMR δ 0.53 (9H, s), 1.27 (9H, s), 1.47 (9H, s), 1.54 (18H, s), 4.59 (1H, s), 7.04 (1H, d, $J=1.2$ Hz, and 7.19 (1H, d, $J=1.2$ Hz); MS m/e 347 (M^+-t-Bu) and 57 (base). 5: NMR δ 1.17 (18H, s), 1.25 (18H, s), 1.76 (18H, s), 2.70 (2H, m, SH), 5.05 (2H, m), 7.01 (2H, d, $J=1.2$ Hz), and 7.45 (2H, d, $J=1.2$ Hz); MS m/e 548 (M^+-H_2S) and 57 (base). 6: NMR δ 1.27 (9H, s), 1.41 (15H, s), 2.61 (2H, s), 3.82 (2H, s), 1.25 (18H, s), 1.2-1.6 (14H, m), 1.76 (18H, s), 5.32 (2H, s), 7.03 (2H, d, $J=6$ Hz), and 7.50 (2H, d, $J=6$ Hz); MS m/e 516 (M^+-2SBu) and 57 (base).
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- 8) The anion radical of thiobenzophenone was detected by ESR in the reaction of thiobenzophenone and organometallics.⁹⁾ This observation, however, does not necessarily lead us to the conclusion that the anion radical is an actual intermediate in the main reaction pathway as pointed out by Beak.⁹⁾
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- 11) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, unpublished results.
- 12) In view of this observation we can not exclude a possibility that 6 is also formed via similar mechanism catalyzed by some radicals produced in the reaction system.
- 13) M. Dagonneau, *C. R. Acad. Sci., Ser. C*, 276, 1683 (1973); 285, (1974).

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