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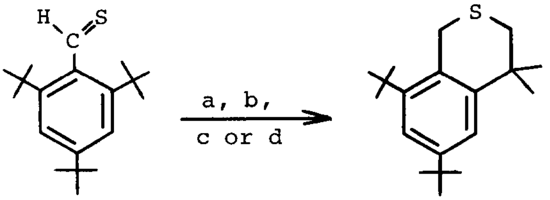
THERMAL AND PHOTOCHEMICAL REACTIONS OF A STABLE THIOBENZALDEHYDE, 2,4,6-TRI-t-BUTYLTHIOBENZALDEHYDE

Renji Okazaki,* Akihiko Ishii, Nobuo Fukuda, Hiroyuki Oyama,
and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University
of Tokyo, Hongo, Tokyo 113, Japan

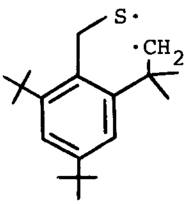
Summary: Thermal and photochemical reactions of the title compound gave benzothiolane 2 in high yield; the reaction with free radicals also afforded 2 along with some other products.

We have recently reported the synthesis of the first stable thiobenzaldehyde, 2,4,6-tri-t-butylthiobenzaldehyde (1).[1] The ready availability and thermal stability of 1 enable us to study the chemical reactivities of the thioaldehyde about which only little has been known so far.[2] Recent papers[3] on some reactions of thioaldehydes prompted us to report our preliminary results on the reactivities of 1.

The thioaldehyde 1 is stable even upon prolonged heating in refluxing benzene in the absence of oxygen,[1] but when a degassed benzene solution of 1 was heated at 200 °C in a sealed tube for 14 h a benzothiolane derivative 2 was obtained in almost quantitative yield (97%) [eq. (1)].[4,5]



1 2 (1)



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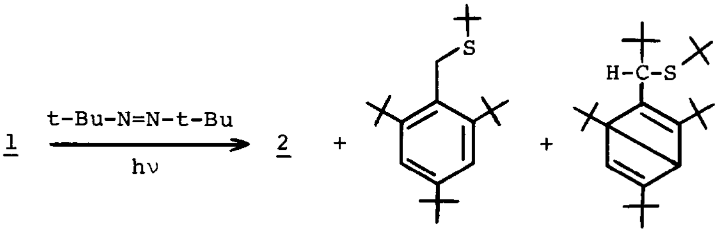
a: Heated at 200 °C in benzene (sealed tube), 97%
b: hν (medium pressure Hg lamp) in benzene, 91%
c: hν (Na lamp) in benzene, 96%
d: Heated at 80 °C with AIBN in benzene, 78%

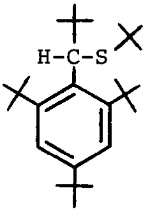
Photoreactions of 1 also gave 2 in high yields: irradiation of a degassed benzene solution of 1 using a medium pressure mercury lamp (probably $\pi \rightarrow \pi^*$ excitation) (8 h) or a sodium lamp ($n \rightarrow \pi^*$ excitation) (24 h) led to 2 in 91% or 96% yield respectively. The photochemical formation of the 6-membered thiolane derivative 2 is unusual since the photoreactions of aromatic thioketones having δ-hydrogens are known to give cyclopentanethiol derivatives, not 6-membered thiolanes.[6] That the present reaction readily proceeds via $n \rightarrow \pi^*$ excitation is of particular interest in view of the fact that the δ-cyclization of aromatic thioketones takes place only via a higher excited state S_2 ($\pi \rightarrow \pi^*$).[6] Although we have at present no evidence to distinguish between a concerted $[2_\pi + 2_\sigma]$ reaction and a radical cyclization via diradical 3, the difference in regioselectivity between the present reaction and that of aromatic thioketones is interesting.

Surprisingly, the formation of 2 was observed also in the reactions of 1 with 1-cyano-1-methylethyl (78%) and t-butyl (20%) radicals (generated by thermolysis of α,α'-azobisisobutyronitrile (AIBN) in refluxing benzene and by photolysis[7] of 2,2'-dimethyl-2,2'-azopropane in benzene respectively). In the reaction with t-butyl radicals, 4 (17%) and 5 (30%) were also formed [eq.(2)].[5]



(2)

4 5



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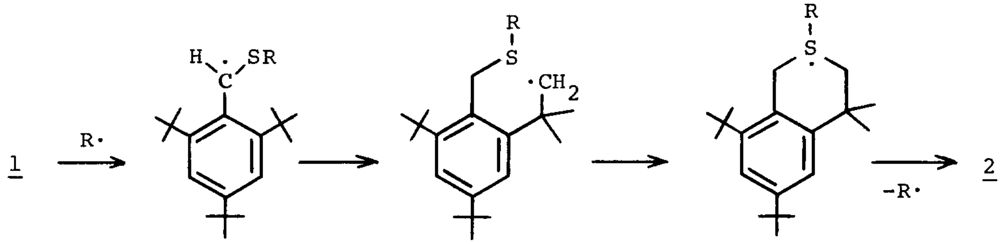
In view of well-established facts that thioketones react with radicals on a sulfur atom,[8] this unusual cyclization to 2 most likely proceeds via a radical-chain mechanism as depicted in Scheme 1. Although many examples are known on radical catalyzed polymerization and isomerization, we are unaware of any precedent of radical-chain cyclization of this type. The Dewar benzene 5 is considered to be formed by the photoreaction of initially formed 6, a double addition product across the thioformyl group, since irradiation of 6 obtained in a separate reaction[9] resulted in the quantitative formation of 5.[10]

The thermal cyclization leading to 2 is very interesting since it is formally an insertion reaction of the thiocarbonyl group to C-H bond and, to our knowledge, no precedent of this type of reaction has been reported in the thermal reactions of thioketones. Although its precise reaction mechanism is not clear at present, the radical-chain mechanism as shown in Scheme 1 catalyzed by adventitious radicals in the reaction solution can be eliminated by the facts that no essential change in the reaction rate and the yield of 2 was observed even when the reaction was carried out in the presence of a radical inhibitor, 2,4-di-t-butyl-4-methylphenol (15 mole% of 1), or with cumene as solvent under otherwise identical conditions. A preliminary result that the reaction does not obey first order kinetics also rules out a mechanism based on a simple unimolecular reaction, e.g., a thermally allowed $[_{\pi}2_{s} + _{\sigma}2_{a}]$ reaction[11] and a reaction via low-lying triplet state of 1. Further mechanistic studies on this unusual cyclization are now underway.



R = $(CH_3)_2(CN)C$ or $(CH_3)_3C$

Scheme 1

References and Notes

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4. This type of cyclization is characteristic of a thiobenzaldehyde. 2,4,6-Tri-t-butylbenzaldehyde did not react at all under identical conditions and was recovered quantitatively.
5. The products had the following spectral data. 2: ^{1}H NMR (δ, CCl_4) 1.27 (s, 9H), 1.41 (s, 15H), 2.61 (s, 2H), 3.82 (s, 2H), and 7.10 (s, 2H); MS m/e 290 (M^+) and 57 (base). 4: ^{1}H NMR (δ, CCl_4) 1.26 (s, 9H), 1.34 (s, 9H), 1.50 (s, 18H), 4.13 (s, 2H), 7.14 (s, 2H); MS m/e 348 (M^+) and 57 (base). 5: ^{1}H NMR (δ, CCl_4) 0.96 (s, 9H), 1.02 (s, 9H), 1.06 (s, 9H), 1.17 (s, 9H), 1.31 (s, 9H), 3.11 (d, 1H, J = 1.5 Hz), 3.57 (s, 1H), 6.03 (d, 1H, J = 1.5 Hz); ^{13}C NMR (δ, $CDCl_3$) 27.3 (q), 29.2 (q), 29.4 (q), 30.5 (q), 32.0 (q), 32.6 (s), 32.8 (s), 34.4 (s), 36.5 (s), 43.5 (s), 45.8 (d), 51.1 (d), 60.9 (s), 133.9 (d), 144.2 (s), 151.5 (s), 160.2 (s); MS m/e 347 (M^+-t-Bu) and 57 (base).
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7. Since the photoreaction of 1 with 2,2'-dimethyl-2,2'-azopropane proceeded much faster than that of 1 alone, 2 formed in this reaction mostly resulted from the reaction of 1 with t-butyl radicals.
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9. The compound 6 was obtained by the reaction of 1 with t-BuMgCl. R. Okazaki, N. Fukuda, H. Oyama, and N. Inamoto, Chem. Lett., in press.
10. Heating of a benzene solution of 5 in a sealed tube (200 °C, 4 h) gave 6 in 62%. A similar interconversion of benzene $\underset{\Delta}{\overset{h\nu}{\rightleftharpoons}}$ Dewar benzene was reported for 1,2,4,5-tetra-t-butylbenzene, suggesting great steric congestion in 6. E. M. Arnett and J. M. Bollinger, Tetrahedron Lett., 3803 (1964).
11. Inspection of the molecular model of 1 suggests that an interesting possibility of $[{}_{\pi}2_{s} + {}_{\sigma}2_{a}]$ cyclization, though usually very unlikely, is conceivable in this very crowded molecule.

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