

THERMOLYSIS AND PHOTOLYSIS OF N-THIOSULFINYL-2,4-DI-t-BUTYL-6-METHYLANILINE. FORMATION AND NOVEL DISPROPORTIONATION OF SULFUR DIIMIDE

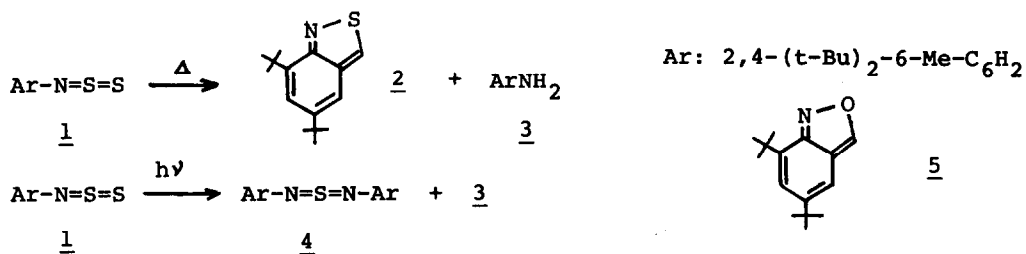
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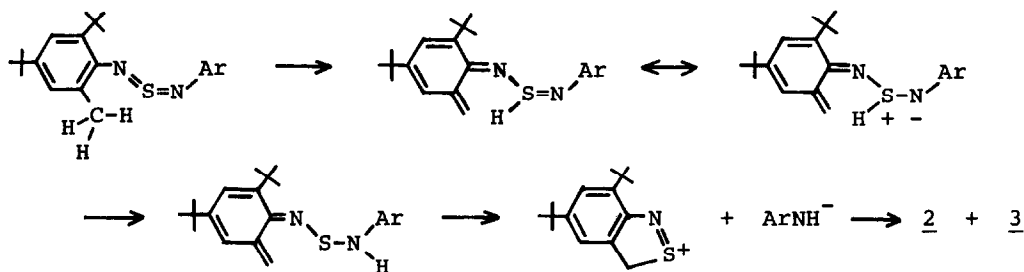
Considerable attention has been focused in recent years on preparation and reactions of heterocumulenes containing sulfur.¹⁾ Barton et al.²⁾ and we³⁾ have recently described preparation and some properties of N-thiosulfinylanilines. We now wish to report thermolysis and photolysis of this new class of compound. We chose N-thiosulfinyl-2,4-di-t-butyl-6-methylaniline (1)³⁾ as a suitable N-thiosulfinylaniline because it is stable and readily prepared from the corresponding aniline in high yield.

Thermolysis of 1 in benzene (reflux, 21 hr) led to the formation of benzisothiazole 2 (32 %) and aniline 3 (26 %),⁴⁾ while irradiation (medium pressure mercury lamp, Pyrex-filter) in pentane at room temperature for 33 hr gave rise to sulfur diimide 4 (71 %) and 3 (27 %). In both reactions some sulfur was also formed. The photolysis in benzene and 2-propanol gave similar results, the yields of 4 and 3 being 44 and 32 % in the former and 42 and 35 % in the latter, respectively.⁵⁾



Sulfur diimide 4 obtained in the photolysis was found to undergo clear thermal disproportionation (refluxing benzene, 3 hr) to yield 2 (94 %) and 3 (91 %). This new mode of reaction of sulfur diimide presumably proceeds via

1,5-hydrogen shift from methyl group to sulfur atom followed by prototropy and cyclization depicted in the following scheme.⁶⁾



The fact that 4 gives 2 under milder conditions than 1 is suggestive of intermediacy of 4 in the thermolysis of 1 leading to 2. However, since the formation of 2 and 3 from 1 is analogous to our previous finding⁷⁾ that 2,4-di-*t*-butyl-6-methylnitrosobenzene affords benzisoxazole 5 and 3 when heated in benzene, involvement of thionitrosobenzene (Ar-N=S) seems also probable. Further study to clarify this point and to establish the mechanism of formation of 4 is now in progress.

References and Notes

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- 2) D.H.R. Barton and M.J. Robson, *J. Chem. Soc. Perkin I*, 1254 (1974).
- 3) Y. Inagaki, R. Okazaki, and N. Inamoto, *Tetrahedron Lett.*, 4575 (1975).
- 4) *p*-Dimethylamino-*N*-thiosulfinylaniline has been reported to give the corresponding azo compound and sulfur upon heating.²⁾
- 5) Satisfactory elemental analyses and reasonable spectral data were obtained for new compounds 2 and 4.
- 6) It should be noted that the first step bears a close resemblance to the reaction of sulfur diimide with olefins recently reported by Sharpless et al. [K.B. Sharpless and T. Hori, *J. Org. Chem.*, 41, 176 (1976)].
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