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A NEW SYNTHESIS OF THIOKETONES FROM HYDRAZONES AND DISULFUR DICHLORIDE

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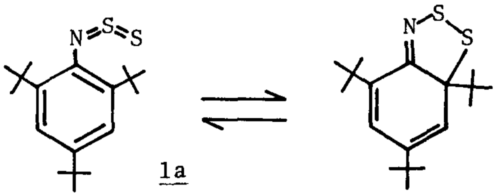
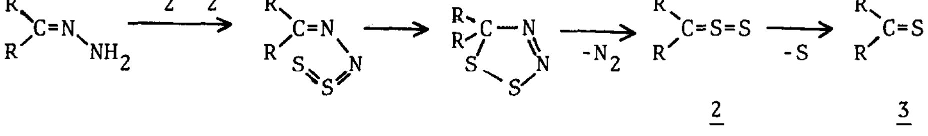
Summary Reaction of ketone hydrazones with disulfur dichloride in the presence of triethylamine in benzene at 0 °C - room temperature afforded the corresponding thiones in a moderate to high yield, probably via thioxothioketone ($R_2C{=}S{=}S$) intermediate.

We previously reported the synthesis of some N-thiosulfinylanilines (Ar-N=S=S) by the reaction of anilines with disulfur dichloride and the reversible ring-chain tautomerism for 1 (i.e., 1a ⇌ 1b).[1]



In view of this tautomerism, we reasoned that the reaction of hydrazones with disulfur dichloride would give thioxothioketone (2), a novel type of S(IV)-thiocumulene, as in the following scheme.[2]



The reaction of ketone hydrazones with disulfur dichloride indeed proceeded very smoothly under mild conditions, but, contrary to the expectation, thioketones (3) were obtained in moderate to high yields instead. A recent communication on the synthesis of hindered thioketones by de Mayo et al.[3] with hydrazones as the starting materials prompted us to report our preliminary results on the above reactions, since we thought our procedure is simpler and the conditions are milder.

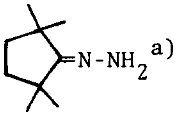
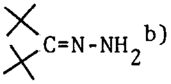
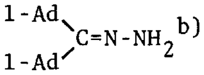
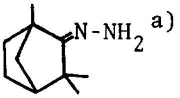
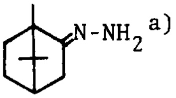
The representative example is as follows. To a benzene solution (20 ml) of triethylamine (11 mmol), was added simultaneously benzene solutions (10 ml each) of 2,2,5,5-tetramethylcyclopentanone hydrazone (5 mmol) and disulfur dichloride (5 mmol) at about the same rate using two dropping funnels during 15 min at 0 °C. After stirring for 30 min at room temperature, precipitated triethylamine hydrochloride was filtered off and the yield of 2,2,5,5-tetramethylcyclopentanethione in the filtrate was estimated by means of the visible spectrum. The benzene solution was washed with water, dried, and evaporated in vacuo and the residue was subjected to bulb to bulb distillation[4] to give the pure thione (500 mg, 58%).[5]

The results for other hydrazones are summarized in Table. Of these thiones, bis(1-adamantyl) thioketone is a new compound[6] and probably the most hindered thione ever known. Our method is of synthetic value in view of the experimental simplicity and ready availability of hydrazones from ketones. Furthermore, there is no problem in a large scale preparation.

Unlike the method of de Mayo,[3] the present method was also applicable to the preparation of thiocamphor and thiobenzophenone; they are formed in moderate yields as revealed by the electronic spectra (see Table), but the thin layer chromatography suggested the presence of some by-products, thus the synthetic value of our method being somewhat diminished for the synthesis of these less hindered thioketones. Since our conditions are basic, thiones with an acid sensitive skeleton would be prepared without any rearrangement as in the procedure by de Mayo. Finally it should be noted that the present results indicate that intramolecular cycloaddition of the N=S=S group to a multiple bond is a general phenomenon while thioxothioketone (2) is so unstable[7] that protection by very bulky groups such as t-butyl or 1-adamantyl is not enough to stabilize it; even when the reaction of the hydrazone of di-t-butyl ketone or bis(1-adamantyl) ketone was carried out in toluene at -85 °C, the pink color characteristic of the corresponding thioketones gradually appeared, suggesting the decomposition of 2 into the thioketone.[8]

Table

Synthesis of thioketones from hydrazones

Hydrazones	Yield(%) of thioketones c)	
	Quant.	(58)
	Quant.	(66)
 $\begin{matrix}\text{1-Ad}\diagdown\\ \text{1-Ad}\diagup\end{matrix}\text{C=N-NH}_2$ b)	71	(59) d)
	Quant.	(54)
	63	
$\text{Ph}_2\text{C=N-NH}_2$	54	

a) Prepared by the method of Barton.[9]
b) Prepared by the method of Wynberg.[10]
c) The yields were estimated by the electronic spctra. Values in parentheses indicate an isolated yield.
d) Purified by recrystallization from ethanol.

References and Notes

1. Y. Inagaki, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1975, 4575; idem., Bull. Chem. Soc. Jpn., 52, 1988 (1979).
2. Intramolecular cyclization of the N=S=S group has been postulated to explain the reaction products of thioamides with dialkoxy disulfides. H. Kagami and S. Motoki, J. Org. Chem., 42, 4139 (1975).
3. P. de Mayo, G.L.R. Petrašiūnas, and A.C. Weeden, Tetrahedron Lett., 1978, 4621.
4. In the case of di-t-butyl thioketone and 2,2,5,5-tetramethylcyclopentanethione, a considerable loss of the thiones were observed during rotary evaporation and bulb to bulb distillation because of their high volatility In the case of thiofenchone, some decomposition occurred during bulb to bulb distillation.
5. Benzene is the best among the solvents tried so far. For example, use of dichloromethane or ether as solvent decreased the yield to 30-40% (estimated by UV spectra) in the preparation of di-t-butyl thioketone.
6. Satisfactory elemental analysis was obtained for this compound. Pink crystals, mp 184.5-185.0 °C; λ_{max} (benzene) 548 nm (ε 16.6); λ_{max} (hexane) 548 nm (ε 13.9).
7. For the lability of $>$S=S type compound, see R.D. Baechler and S.K. Daley, Tetrahedron Lett., 1978, 101; R.D. Baechler, S.K. Daley, B. Daly, and K. MaGlynn, ibid., 1978, 105 and references cited therein.
8. At present, the possibility that the thiones are directly formed from concomitant elimination of both sulfur and nitrogen molecules without an intermediacy of **2** cannot be eliminated.
9. D.H.R. Barton, F.S. Guziec, Jr., and I. Shhak, J. Chem. Soc., Perkin Trans. 1, 1974, 1974.
10. J.H. Wieringa, H. Wynberg, and J. Strating, Tetrahedron, 30, 3053 (1974).

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