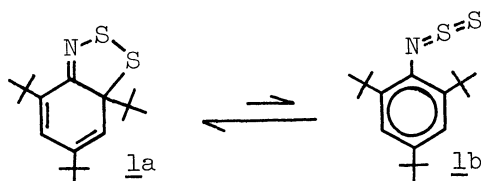


OXIDATION OF 5H-1,2,3-DITHIAZOLE DERIVATIVE.
FORMATION OF A NEW TYPE OF THIOLSULFINATE AND
ITS DECOMPOSITION INVOLVING OXYGEN MIGRATION

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Oxidation of 5H-1,2,3-dithiazole derivative equilibrated with 2,4,6-tri-*t*-butyl-N-thiosulfinylaniline by *m*-chloroperbenzoic acid gives two kinds of thiolsulfinate type compounds. One of them undergoes thermal decomposition involving oxygen migration, and the other undergoes unusually facile retro-ene reaction.

Compound 1a is the only entity of 5H-1,2,3-dithiazole ring system, and, in solution, exists as a tautomeric mixture with 1b as the minor component.¹⁾ We wish to report here interesting observations found in the oxidation of this novel heterocyclic compound: i.e., 1) the isolation of a new type of thiolsulfinate which undergoes thermal oxygen migration and 2) unusually facile retro-ene reaction of another oxidation product.



Treatment of dithiazole 1 with slightly deficient amount of *m*-chloroperbenzoic acid (MCPBA) in dichloromethane gave 2, 3, and 4.²⁾ Yields and reaction conditions are shown in Table. Increase of the product ratio 3/2 on lowering the reaction temperature indicates that the attack of MCPBA on S² is a less energy-demanding process.

The structure of a new type of thiolsulfinate 2 was determined by X-ray

crystallographic analysis³⁾ since conclusive evidence for that could not be obtained by spectroscopic⁴⁾ and chemical behavior. The identity of 3 was established by spectral data⁴⁾ and by alkaline hydrolysis affording 5.⁵⁾

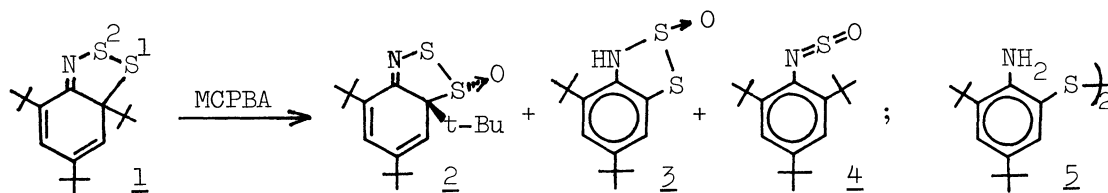


Table. Yields of the products

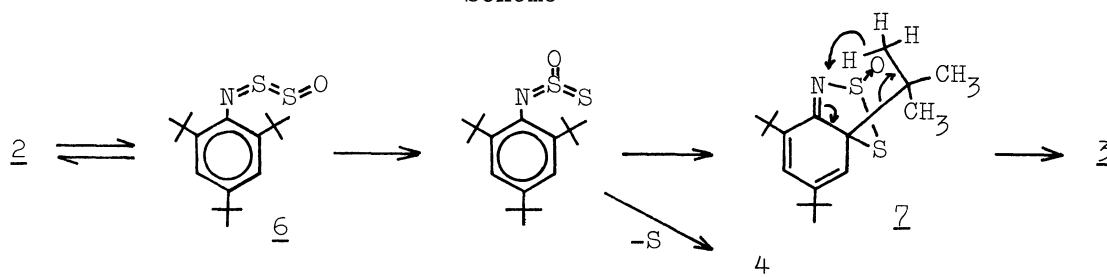
Temp. (°C)	Time (min)	Conversion (%)	Yield (%)			
			<u>2</u>	<u>3</u>	<u>4</u>	<u>3/2</u>
39	3	92	44.8	43.9	1.3	0.98
22	30	91	36.3	44.0	5.8	1.21
0	20	98.5	34.3	42.9	6.2	1.25
-23	20	99.5	36.7	50.6	5.8	1.38
-78	40	94.3	20.6	62.2	2.9	3.02

Although 2 is quite stable at room temperature, it undergoes thermal decomposition in refluxing benzene (3.5 h) to give 3 (13.5%), 4 (24.4%), and 2,4,6-tri-*t*-butylaniline (28.7%) along with recovered 2 (14.7%). Formation of 3 and 4 is noteworthy, because it indicates the occurrence of oxygen migration from S¹ to S² during the thermolysis. Thermal behavior of a thiolsulfinate has recently attracted considerable attention because of its intriguing decomposition mode and the conclusion has been drawn from Block's extensive studies that alkyl thiolsulfonates do not undergo oxygen migration like $RS(O)SR' \rightleftharpoons RSS(O)R'$.⁶⁾

In view of this conclusion and the reversible cyclization between 1a and 1b,¹⁾ the most attracting route to 3 and 4 is that involving cycloreversion of 2 to 6 as shown in the following scheme,⁷⁾ the driving force of which is aromatization. There still remain, however, other possibilities, because 2 is not a simple alkyl thiolsulfinate for which the above conclusion by Block was obtained.⁸⁾ Whatever mechanism it may follow, the thermal decomposition of 2 is unambiguous demonstration of oxygen migration in thiolsulfinate type compounds.

Another point of interest in the oxidation reaction of 1 is the formation of

Scheme



3. The fact that 2 is stable in refluxing dichloromethane even in the presence of *m*-chlorobenzoic acid excludes the possibility that 3 is formed via 2 under the reaction conditions. Since the peracid would attack 1a also at the sulfur S^2 to give 7, the most likely interpretation of the absence of 7 in the reaction products is that 7 is unstable under the reaction conditions to undergo a fast retro-ene type conversion into 3. Direct evidence for intermediacy of 7 was provided by monitoring the reaction spectroscopically: NMR spectrum of a mixture of 1 and MCPBA in CD_2Cl_2 at $-50 \sim -40^\circ C$ showed a set of signals which seemed to be due to 7⁹⁾ (δ 0.87 (s, 9H), 1.20 (s, 9H), 1.42 (s, 9H), 6.11 (d, $J=2$ Hz, 1H), and 6.98 (d, $J=2$ Hz, 1H)) besides two sets of signals due to 2 and 1 (the molar ratio; $\underline{1}:\underline{2}:\underline{7}=1:0.67:0.8$). Upon raising the temperature, decomposition of 7 started at $-30^\circ C$; the intensity of the NMR signals due to 7 gradually decreased with concomitant increase in intensity of the signals due to 3 and 2-methylpropene. Finally, at $34^\circ C$, the signals of 7 were completely replaced by those of 3 and 2-methylpropene.

This unusual instability of 7 with respect to retro-ene reaction is in marked contrast with the stability exhibited by related compounds 1 and 2.¹⁰⁾

References and Notes

- 1) Y. Inagaki, R. Okazaki, and N. Inamoto, *Tetrahedron Lett.*, **1975**, 4575.
Equilibrium constant ($[\underline{1a}]/[\underline{1b}]$) in CD_2Cl_2 at $35^\circ C$ is 14.2.
- 2) 4 was identified by comparison of the spectral data with those of an authentic sample obtained by the reaction of 2,4,6-tri-*t*-butylaniline with thionyl chloride. Formation of 4 is most likely attributable to the oxidation of 1b, because 2,4-di-*t*-butyl-6-methyl-N-thiosulfinylaniline was found to be oxidized by MCPBA under similar conditions to give the corresponding N-sulfinylaniline. All new compounds (2, 3, 4, and 5) gave satisfactory elemental analyses.

- 3) A private communication from Prof. F. Iwasaki, the University of Electro-Communications. We thank Prof. Iwasaki for informing us of the results prior to publication.
- 4) Compound 2: mp 124.7-125.7 °C; IR (KBr): 1080(SO) cm^{-1} ; MS: 339 (M^+); NMR (CCl_4): δ 1.05(s, 9H), 1.18(s, 9H), 1.37(s, 9H), 6.01(d, J=2 Hz, 1H), 6.22(d, J=2 Hz, 1H). Compound 3: mp 160 °C(dec); IR (KBr): 3280(NH) and 1110 cm^{-1} (SO); MS: m/e 283(M^+); NMR(CCl_4): δ 1.34(s, 9H), 1.45(s, 9H), 7.21(ABq, J=1.2 Hz, $\Delta\delta=0.12$, 2H), 7.50(broad s, 1H).
- 5) A similar hydrolysis has been reported. W.K. Warburton, Chem. Rev., 57, 1101 (1957); cf. also L.D. Huestis, M.L. Walsh, and N. Hahn, J. Org. Chem., 30, 2763 (1965).
- 6) E. Block and J. O'Connor, J. Am. Chem. Soc., 96, 3921, 3929 (1974) and references cited therein.
- 7) For examples of sulfur extrusion in S(IV) thiocumulenes and possible existence of such species as $\text{X}=\text{S}(=\text{O})=\text{Y}$ as 1,3-dipole, see R.M. Kellogg, Tetrahedron, 32, 2165 (1976); Y. Inagaki and R. Okazaki, Yuki Gosei Kagaku Kyokaiishi, 36, 1 (1978).
- 8) The occurrence of oxygen migration has been suggested by a tracer study for aryl arenethiolsulfinates. P. Koch, E. Ciuffarin, and A. Fava, J. Am. Chem. Soc., 92, 5971 (1970).
- 9) Of possible two diastereomers, only one seems to be formed as judged from NMR spectroscopy. The orientation of S-O bond is tentatively assumed, on steric ground, to be anti with respect to the t-butyl group attached to carbon adjacent to S^1 . This assignment is also in keeping with the temperature dependence of the product ratio 3/2 (see Table) since the increase of 3 at low temperatures is only compatible with attack from less hindered site leading to an anti sulfoxide.
- 10) Dithiazole 1 is thermally more stable than 2; its complete decomposition requires refluxing in benzene for about 10 h.

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