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THERMAL REARRANGEMENT OF α,β-UNSATURATED SULFINE

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The thermolysis of 2-arylmethylene-1-tetralinthione-S-oxide gave 2-arylcarbonyl-1-tetralinthione: it is considered that the reaction probably proceeded through the intramolecular 1,5-dipolar cycloaddition of the tetralinthione-S-oxide.

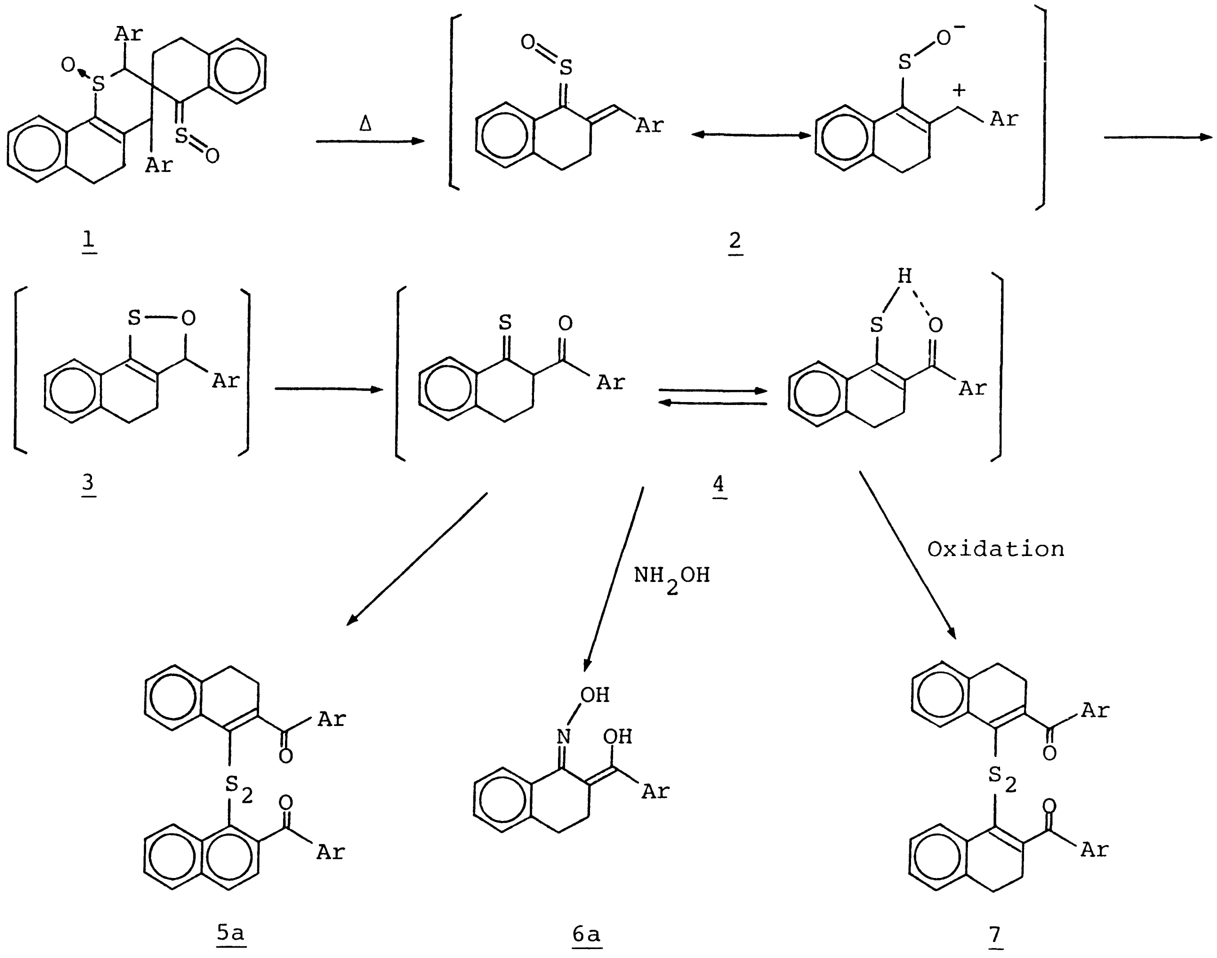
In the preceding communication,$^{1)}$ we reported that 2-benzylidene-1-tetralinthione-S-oxide generated by the thermolysis of the corresponding dimers was trapped by norbornene. In an attempt to trap this α,β-unsaturated sulfine by the other carbon-carbon double bond compounds,$^{2)}$ we found that the disulfide (5a) was formed by the thermolysis of 2-benzylidene-1-tetralinthione dimer S,S'-dioxide (1a) with tetraphenylallene (8). Namely, when a suspension of 1a$^{1)}$ (0.54g) and 8 (0.70g) in dry xylene (5 cm^3) was refluxed for 11h under nitrogen atmosphere, the solution turned from pale yellow to red. The solvent was evaporated and the residue was chromatographed on Wakogel C-200 to give recovered 8 (0.15g) and 5a (pale yellow needles, 0.25g, mp 125-127°C). The IR spectrum of 5a showed band at 1660 cm^{-1} (C=O). The mass spectrum (70 eV) showed ion peaks at m/e 265 (100), 264 (44), 263 (85), 247 (12), 234 (18), 202 (9), 105 (38), and 77 (38). The NMR spectrum ($CDCl_3$, 100MHz) showed signals at δ 2.28-3.04 (m, 4H) and 6.84-7.58 (m, 20H). These data and analytical data (Found: C, 77.38; H, 4.56. Calcd: C, 77.24; H, 4.58) are consistent with the proposed structure (5a).

In view of the result, it has been considered that the reaction proceeded via the rearrangement of α,β-unsaturated sulfine (2a) to the β-thioxo ketone (4a) without trapping of 2a by 8. Therefore, we attempted the thermolysis of 1a alone for a short time. A suspension of 1a (1.55g) in dry xylene (7 cm^3) was refluxed for 15 min. under nitrogen atmosphere. The solution turned deep red. The reaction mixture was chromatographed on Florisil gel to give 4a$^{3)}$ (red powder, 0.13g). The IR spectrum showed four characteristic bands of β-thioxo ketones$^{4)}$ at 1660 [ν(C=O)], 1530 [ν(C=C)], 1230 [ν(C=S)], and 805 cm^{-1}. The mass spectrum (70 eV) showed ion peaks at m/e 266 (M^+, 22), 265 (48), 249 (27), 105 (100), and 77 (65); the monoxime$^{5)}$ (6a): mp 143-145 °C; IR (KBr) 3250 (OH), 1620 (C=C) cm^{-1}; MS (70 eV) m/e 265 (M^+, 6), 249 (6), 248 (20), 105 (100), 77 (36).

Similarly, the thermolysis of 2-(p-chlorobenzylidene)-1-tetralinthione dimer S,S'-dioxide (1b) (1.00g) gave the corresponding β-thioxo ketone (4b) but 4b was identified by its conversion into the disulfide (7b) by an air oxidation$^{3a)}$ (0.17g, mp 180-181 °C). The IR spectrum of 7b showed band at 1660 cm^{-1} (C=O). The ^{1}H-NMR spectrum

($CDCl_3$, 100 MHz) showed signals at δ 2.40-3.00 (m, 8H) and 6.98-7.48 (m, 16H). The ^{13}C-NMR spectrum ($CDCl_3$, 25 MHz) showed the expected fifteen sharp lines at δ 26.9 (t), 27.7 (t), 126.5 (d), 126.7 (d), 127.6 (d), 128.6 (d), 128.8 (d), 130.3 (d), 131.6 (s), 131.9 (s), 134.9 (s), 136.4 (s), 139.5 (s), 145.4 (s), and 195.3 (s, C=O). The mass spectrum (15 eV) showed ion peaks at m/e 300 (67), 299 (100), 298 (37), and 139 (17). These data and analytical data (Found: C, 68.00; H, 4.36. Calcd: C, 68.11; H, 4.03) are consistent with the proposed structure.

It would be probable that these β-thioxo ketones (4) were formed from an unstable intermediate (3), produced by the intramolecular 1,5-dipolar cycloaddition reaction of the α,β-unsaturated sulfines (2).



a: Ar=C_6H_5, b: Ar=p-Cl-C_6H_4

References and Notes

1) T. Karakasa and S. Motoki, Tetrahedron Lett., 1979, 3961.

2) T. Karakasa, H. Ohmura, and S. Motoki, unpublished work.

3) An air oxidation[4a)] of 4a gave the disulfide 7a (oil) instead of 5a but the product could not be purified by distillation or crystallization.

4) a) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyr, V. A. Pickles, and J. S. Shannon, Aust. J. Chem., 18, 673 (1965); b) F. Duus, J. Org. Chem., 42, 3123 (1977).

5) S. Hauptmann, E. Uhlemann, and L. Widmann, J. Prak. Chem., 38, 101 (1968).

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