Tetrahedron Letters No. 41, pp 3961 - 3962.   0040-4039/79/1008-3961\$02.00/0

2-BENZYLIDENE-1-THIOTETRALONE S-OXIDE : A NOVEL METHOD OF GENERATING TRANSIENT α,β-UNSATURATED SULFINE

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Abstract : 2-Benzylidene-1-thiotetralone dimer S-oxide and S,S'-dioxide have been prepared by the oxidation of the dimer with m-chloroperbenzoic acid. The α,β-unsaturated sulfine generated by the thermolysis of these oxides was trapped by norbornene.

Although a wide variety of aryl sulfines are known as stable substances,1) no convenient method for the generation of α,β-unsaturated sulfines has been reported.

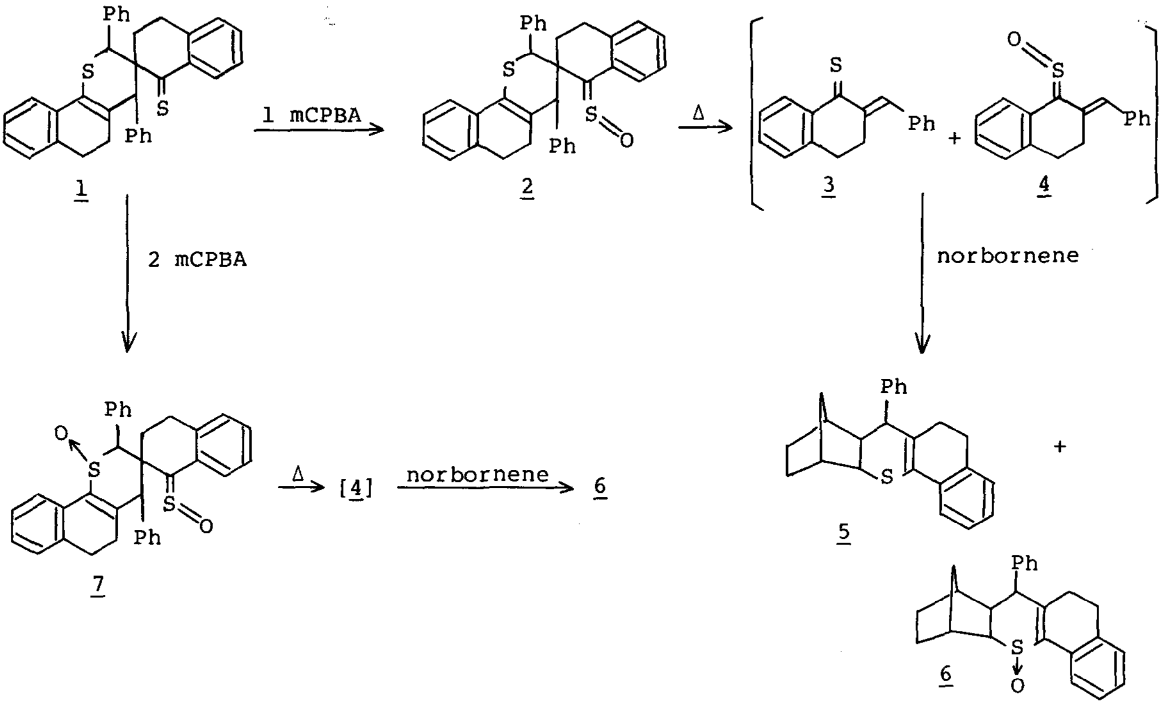
In view of the generation of the α,β-unsaturated thiones by the thermolysis of the corresponding dimers,2) 3,4-dihydro-2H-thiapyrans, their S-oxide 2 and S,S'-dioxide 7 have been considered to be likely α,β-unsaturated sulfine precursors. Therefore, we attempted the oxidation of 2-benzylidene-1-thiotetralone dimer 12) by m-chloroperbenzoic acid (mCPBA). To 1 (2 mmol) dissolved in 30 ml of dichloromethane a solution of mCPBA (2 mmol in 20 ml dichloromethane) was added at room temperature under nitrogen atmosphere in 30 minutes. The color of solution turned from deep-blue to sky-blue. After stirring for 45 minutes the solution was washed with aqueous sodium bicarbonate and dried over anhydrous sodium sulfates. The solvent was evaporated and the residue was recrystallized from benzene-ligroin to give sulfine 2** : yield 63% ; mp 166-169 °C ; IR (KBr) 1105 (C=S=O)3) cm^{-1} ; NMR (CDCl$_3$) δ 2.00-3.00 (m, 8H), 3.50 (s, 1H), 5.07 (s, 1H), 7.00-7.53 (m, 17H), and 9.07 (m, 1H)4) ; MS (15 eV) m/e 516 (M$^+$), 468 (1), 435 (5), 266 (21), 250 (80), 249 (100), 218 (81).

The α,β-unsaturated sulfine 4 generated by the thermolysis of 2 was trapped by norbornene. A suspension of 2 (0.82g) and norbornene (0.3g) in dry xylene 5 ml was refluxed for 3 hr under nitrogen atmosphere. The solvent was evaporated and the residue was chromatographed on Wakogel C-200 to give 5 (yield 46%, mp 96.5-98.5 °C (98.5-99.5 °C)5)) and 6** : colorless needles ; yield 75% ; mp 201-203 °C ; IR (KBr) 1040-1060 (S=O) cm^{-1} ; NMR (CDCl$_3$) δ 1.20-2.00 (m, 8H), 2.08-2.68 (m, 4H), 3.02-3.36 (m, 3H), 7.04-7.48 (m, 8H), and 8.28 (m, 1H) ; MS (70 eV) m/e 360 (M$^+$, 5), 344 (38), 343 (100), 250 (12), 249 (23).

Similarly, we have also prepared the α,β-unsaturated sulfine dimer 7** by the reaction of 1 (4 mmol) [dissolved in 100 ml of dichloromethane] with 8 mmol of mCPBA [30 ml of dichloromethane] : greenish yellow needles ; yield 82% ; mp 121-123 °C ; IR (KBr) 1100 (C=S=O) and 1040-1050 (S=O) cm^{-1} ; NMR ($CDCl_3$) δ 1.93-3.10 (m, 8H), 3.77 (s, 1H), 4.70 (s, 1H), 7.00-7.53 (m, 16H), 7.77 (m, 1H),[4] and 9.10 (m, 1H)[4] ; MS (15 eV) m/e 531 (M^+-1), 530, 436 (40), 266 (100), 250 (44), 249 (38), 234 (38), 233 (34), 218 (92).

The thermolysis of 7 with norbornene gave 6 in 78% yield.

At present we are investigating the oxidation of other α,β-unsaturated thione dimers to explore the scope of the preparation of α,β-unsaturated sulfine dimers.



References and Notes

** These new compounds (2, 6, and 7) gave satisfactory values in elementary analyses.

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(Received in Japan 21 June 1979)