

The Reaction of 2-Benzylidenetetralin-1-thione *S*-oxide with Acrylonitrile or Styrene

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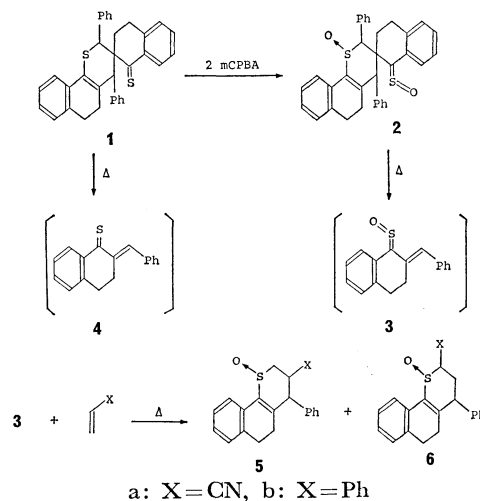
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Synopsis. The cycloaddition reaction of 2-benzylidenetetralin-1-thione *S*-oxide with acrylonitrile (or styrene) gave a mixture of 2- and 3-cyano(or phenyl)-4-phenyl-3,4,5,6-tetrahydro-2*H*-naphtho[1,2-*b*]thiopyran *S*-oxide. Pummerer reaction of these *S*-oxides resulted to afford the corresponding acetates.

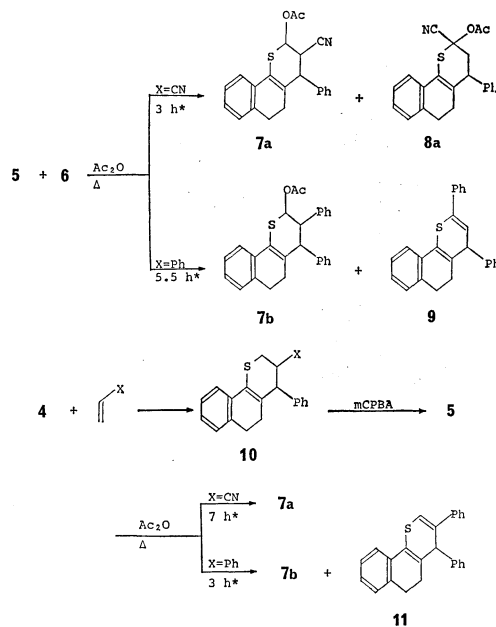
α,β -Unsaturated sulfines¹⁾ have been inaccessible compounds and their chemical properties have not been investigated. Previously, we reported the generation of α,β -unsaturated sulfine [2-benzylidenetetralin-1-thione *S*-oxide (**3**)] by the thermolysis of its dimer (**2**), and the cycloaddition reaction of **3** with norbornene.^{1b)} α,β -Unsaturated thiones such as the compound (**4**) are known to react with various kinds of olefins giving Diels-Alder type 1,4-cycloaddition products,²⁾ and we are interested in the reaction of **3** with some olefinic compounds.

When a mixture of **2** and acrylonitrile in xylene was heated to reflux, a mixture of the adducts **5a** and **6a** were obtained. They were separated and identified by the conversion into their sulfides (**5a** and **6a**) in acetic anhydride afforded two acetates **7a** and **8a**. Both **7a** and **8a** showed absorptions at 2250 cm⁻¹ for cyano group and at 1760 and 1210 cm⁻¹ for OCOCH₃ in their IR spectra. The ¹H-NMR spectrum of **7a** showed signals at δ 3.68 (dd, $J=4$ and 6 Hz), 3.93 (d, $J=6$ Hz), and 6.34 (d, $J=4$ Hz). These signals were readily assigned to those of the C-3, the C-4 and the C-2 protons, respectively. The proton-noise-decoupled ¹³C-NMR spectrum of **7a** also showed three methine carbon signals at δ 37.1, 45.4, and 69.5. The structure of **7a** was further confirmed by an independent synthesis. Namely, oxidation of **10a** with *m*-chloroperbenzoic acid (mCPBA) followed by the treatment with acetic anhydride produced the acetate, which was completely identical with that obtained from **5a**. The ¹H-NMR spectrum of **8a** showed signals at δ 3.96 (m, 1H) and 2.83 (m, 2H) and the ¹³C-NMR spectrum showed signals at δ 41.7 for the C-3, 44.4 for the C-4, and 71.9 for the C-2 carbons.

Similarly, the reaction of **3** with styrene gave a mixture of the adducts **5b** and **6b**. The Pummerer reaction of the mixture afforded two products **7b** and **9**. The IR spectrum of **7b** showed absorptions at 1760 and 1210 cm⁻¹ for OCOCH₃. The ¹H-NMR spectrum showed signals at δ 3.69 (dd, $J=4$ and 6 Hz) for the C-3, 3.90 (d, $J=6$ Hz) for the C-4, and 6.19 (d, $J=4$ Hz) for the C-2 protons. The ¹³C-NMR spectrum showed the three methine carbon signals at δ 50.8, 51.4, and 75.7. Also, **7b** was iden-



Scheme 1.



Scheme 2.

tical with the spectrum prepared by an independent synthetic route from **10b** (Scheme 2). The IR spectrum of **9** had no band in the near region of 1720 cm⁻¹ for OCOCH₃ and the mass spectrum showed a molecular ion peak at 352. The ¹H-NMR spectrum showed signals at δ 4.31 (d, $J=6$ Hz) for the C-4 and 6.01 (d, $J=6$ Hz) for the C-3 protons. The ¹³C-NMR spectrum showed a signal at δ 50.1 for the C-4 carbon. These data and elementary analysis

were in agreement with the proposed structure (9).

The reaction of **3** with maleic anhydride gave tarry unidentified products. Butyl vinyl ether or 1-morpholinocyclohexene did not react with **3** but the thermal rearrangement of **3** to β -thioxo ketone³⁾ was observed in this case.

As a result, it has been found that the α,β -unsaturated sulfine **3** does not react with electron rich dienophiles and that the cycloaddition reaction of **3** is less regioselective than that of the corresponding α,β -unsaturated thione **4**.

Experimental

All the melting points are uncorrected. ¹H-NMR (100 MHz) and ¹³C-NMR (25 MHz) spectra were recorded on a JEOL JNM-FX 100 spectrometer with Me₄Si as an internal standard. IR spectra were obtained on a Hitachi Model 260-10 infrared spectrometer. Mass spectral data were obtained with a Hitachi RMU-7M double-focusing mass spectrometer.

A Typical Procedure for the Reaction of 3 with Olefins. A suspension of **2^b** (0.65 g) and acrylonitrile (1.2 g) in dry xylene (6 cm³) was refluxed for 2.5 h under a nitrogen atmosphere. The solvent was evaporated to give a mixture of **5a** and **6a** which could not be separated by crystallization or chromatography: yield 32%; colorless powder. Found: C, 75.43; H, 5.29%. Calcd for C₂₀H₁₇NOS: C, 75.21; H, 5.29%. A mixture of **5b** and **6b** (reaction time 1 h): yield 67%; colorless powder. Found: C, 80.84; H, 5.96%. Calcd for C₂₅H₂₂OS: C, 81.04; H, 5.99%.

A Typical Procedure for the Reaction of the Sulfoxide (5 and 6) with Acetic Anhydride. A suspension of a mixture of **5a** and **6a** (2.62 g) in acetic anhydride (15 cm³) was refluxed for 3 h under a nitrogen atmosphere. The excess acetic anhydride was evaporated and the residue was chromatographed on Wakogel C-200 [eluting with benzene-hexane (1:1)]. **7a**: yield 10%; mp 190–191 °C; MS (70 eV) *m/e* 361 (43), 250 (60), 249 (100); ¹H-NMR (CDCl₃) δ 1.76 (s, 3H), 2.12–2.85 (m, 4H), 3.68 (dd, *J*=4 and 6 Hz, 1H), 3.93 (d, *J*=6 Hz, 1H), 6.34 (d, *J*=4 Hz, 1H), 7.04–7.60 (m, 9H); ¹³C-NMR (CDCl₃) δ 20.4 (q), 28.0 (t), 29.9 (t), 37.1 (d), 45.4 (d). Found: C, 73.08; H, 5.21; N, 3.81; S, 8.76%. Calcd for C₂₂H₁₉O₂NS: C, 73.10; H, 5.30; N, 3.88; S, 8.87%.

8a: yield 12%; mp 160–161 °C; MS (70 eV) *m/e* 361 (100), 319 (68), 249 (54); ¹H-NMR (CDCl₃) δ 1.80 (s, 3H), 2.04–2.76 (m, 4H), 2.83 (m, 2H), 3.96 (m, 1H), 7.00–7.36 (m, 9H); ¹³C-NMR (CDCl₃) δ 20.4 (q), 27.9 (t), 29.0 (t), 41.6 (t), 44.4 (d), 71.9 (s). Found: C, 72.75; H, 5.26; N, 3.64; S, 8.90%. Calcd for C₂₂H₁₉O₂NS: C, 73.10; H, 5.30; N, 3.88; S, 8.87%.

7b: yield 25%; mp 106–108 °C; MS (70 eV) *m/e* 352 (62), 275 (100); ¹H-NMR (CDCl₃) δ 2.08–2.84 (m, 4H),

4.31 (d, *J*=6 Hz, 1H), 6.01 (d, *J*=6 Hz, 1H), 6.81–7.57 (m, 14H); ¹³C-NMR (CDCl₃) δ 28.1 (t), 28.7 (t), 50.1 (d). Found: C, 84.99; H, 5.62; S, 8.96%. Calcd for C₂₅H₂₀S: C, 85.19; H, 5.72; S, 9.09%.

9: yield 13%; mp 150–151 °C; MS (70 eV) *m/e* 412 (15), 250 (75), 249 (100); ¹H-NMR (CDCl₃) δ 1.60 (s, 3H), 2.20–2.90 (m, 4H), 3.69 (dd, *J*=4 and 6 Hz, 1H), 3.90 (d, *J*=4 Hz, 1H), 6.19 (d, *J*=6 Hz, 1H), 7.12–7.40 (m, 14H); ¹³C-NMR (CDCl₃) δ 20.5 (q), 28.3 (t), 30.1 (t), 50.8 (d), 51.4 (d), 75.7 (d). Found: C, 78.46; H, 5.81; S, 7.75%. Calcd for C₂₇H₂₄O₂S: C, 78.61; H, 5.86; S, 7.77%.

A Typical Procedure for the Oxidation of 10 with mCPBA. To **10^{2b}** (1.0 g) dissolved in 30 cm³ of dichloromethane a solution of mCPBA (0.57 g in 25 cm³ dichloromethane) was added at 0 °C under a nitrogen atmosphere in 30 min. After the addition of 30 cm³ chloroform, the solution was washed with aqueous sodium hydrogencarbonate. The solvent was evaporated and the residue was recrystallized from chloroform–ligroine to give **5a**: yield 67%; mp 240–241 °C; MS (70 eV) *m/e* 319 (M⁺, 3), 249 (37); IR (KBr) 2250 (CN), 1040–1050 (SO) cm⁻¹. Found: C, 75.23; H, 5.30; N, 4.20; S, 10.00%. Calcd for C₂₀H₁₇NOS: C, 75.20; H, 5.36; N, 4.39; S, 10.04%.

5b: yield 64%; mp 223–225 °C; MS (70 eV) *m/e* 370 (M⁺, 4), 218 (77); IR (KBr) 1030 (SO) cm⁻¹; ¹H-NMR (CDCl₃) δ 1.92–2.84 (m, 4H), 3.24 (m, 2H), 3.84 (m, 1H), 4.36 (m, 1H), 7.00–7.32 (m, 13H), 8.03 (m, 1H). Found: C, 81.12; H, 6.01; S, 8.64%. Calcd for C₂₅H₂₂OS: C, 81.04; H, 5.99; S, 8.65%.

Reaction of 5 with Acetic Anhydride. **7a**: yield 24%. **7b**: yield 10%.

11: yield 35%; mp 97–98 °C; MS (70 eV) *m/e* 352 (34), 276 (25), 275 (100); ¹H-NMR (CDCl₃) δ 2.08–2.88 (m, 4H), 4.51 (s, 1H), 6.70 (s, 1H), 6.82–7.44 (m, 14H); ¹³C-NMR (CDCl₃) δ 28.2 (t), 29.8 (t), 51.4 (d). Found: C, 85.41; H, 5.92; S, 9.12%. Calcd for C₂₅H₂₀S: C, 85.19; H, 5.72; S, 9.09%.

References

- 1) a) M. F-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, **1979**, 2397; b) T. Karakasa and S. Motoki, *ibid.*, **1979**, 3961.
- 2) a) J. P. Pradere, G. Bouet, and H. Quiniou, *Tetrahedron Lett.*, **1972**, 3471; K. B. Lipkowitz and B. P. Mundy, *ibid.*, **1977**, 3417; K. B. Lipkowitz, S. Scarpone, B. P. Mundy, and W. G. Bornmann, *J. Org. Chem.*, **44**, 487 (1979); J. P. Guemas, A. Reliquet, F. Reliquet, and H. Quiniou, *C. R. Acad. Sci., Ser. C*, **1979**, 89; b) T. Karakasa and S. Motoki, *J. Org. Chem.*, **43**, 4147 (1978); c) T. Karakasa and S. Motoki, *ibid.*, **44**, 4151 (1979); T. Karakasa, H. Yamaguchi, and S. Motoki, *ibid.*, **45**, 927 (1980); T. Karakasa and S. Motoki, *Chem. Lett.*, **1980**, 879.
- 3) T. Karakasa, H. Ohmura, and S. Motoki, *Chem. Lett.*, **1980**, 825.