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

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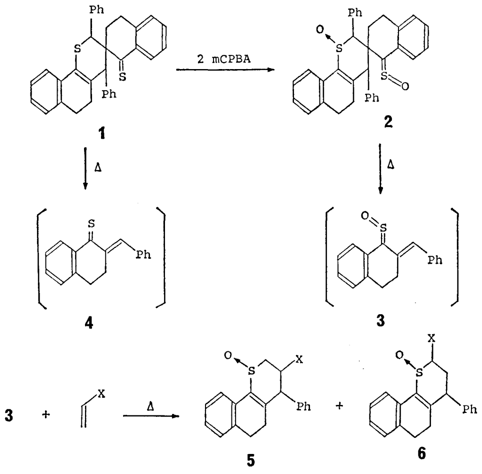
Synopsis. The cycloaddition reaction of 2-benzylidenetetralin-1-thione *S*-oxide with acrylonitrile (or styrene) gave a mixture of 2- and 3-cyano(or phenyl)-4-phenyl-3,4,5,6-tetrahydro-2*H*-naphtho[1,2-*b*]thiopyran *S*-oxide. Pummerer reaction of these *S*-oxides resulted to afford the corresponding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

α,β-Unsaturated sulfines[1)] 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.

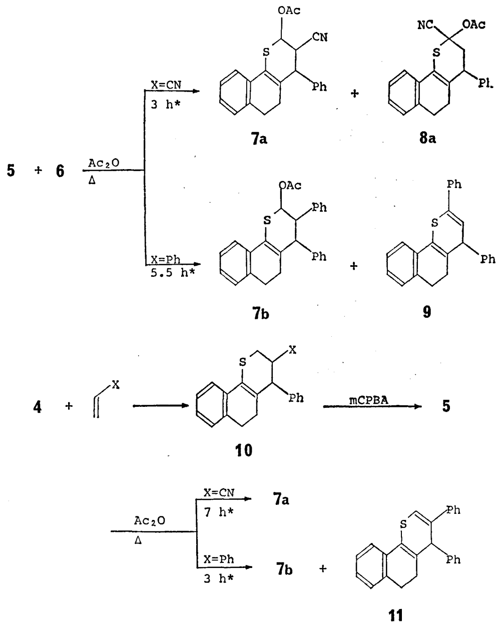
When a mixture of **2** and acrylonitrile in xylene was heated to reflux, a mixture of the adducts **5a** and **6a** were obtained. They were separated and identified by the conversion into their sulfides by Pummerer reaction. Refluxing of the mixture (**5a** and **6a**) in acetic anhydride afforded 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 $\mathrm{OCOCH_3}$ in their IR spectra. The ^{1}H-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 ^{13}C-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 ^{1}H-NMR spectrum of **8a** showed signals at δ 3.96 (m, 1H) and 2.83 (m, 2H) and the ^{13}C-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 $\mathrm{OCOCH_3}$. The ^{1}H-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 ^{13}C-NMR spectrum showed the three methine carbon signals at δ 50.8, 51.4, and 75.7. Also, **7b** was identical 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 $\mathrm{OCOCH_3}$ and the mass spectrum showed a molecular ion peak at 352. The ^{1}H-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 ^{13}C-NMR spectrum showed a signal at δ 50.1 for the C-4 carbon. These data and elementary analysis



a: X=CN, b: X=Ph

Scheme 1.



a: X=CN, b: X=Ph * Reaction time

Scheme 2.

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 ketone[3)] 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. ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25 MHz) spectra were recorded on a JEOL JNM-FX 100 spectrometer with Me_4Si 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**[2b)] (0.65 g) and acrylonitrile (1.2 g) in dry xylene (6 cm^3) 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 $C_{20}H_{17}NOS$: 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 $C_{25}H_{22}OS$: 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 cm^3) 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); ^{1}H-NMR ($CDCl_3$) 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); ^{13}C-NMR ($CDCl_3$) 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 $C_{22}H_{19}O_2NS$: 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); ^{1}H-NMR ($CDCl_3$) 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); ^{13}C-NMR ($CDCl_3$) 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 $C_{22}H_{19}O_2NS$: 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); ^{1}H-NMR ($CDCl_3$) 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); ^{13}C-NMR ($CDCl_3$) δ 28.1 (t), 28.7 (t), 50.1 (d). Found: C, 84.99; H, 5.62; S, 8.96%. Calcd for $C_{25}H_{20}S$: 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); ^{1}H-NMR ($CDCl_3$) 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); ^{13}C-NMR ($CDCl_3$) 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 $C_{27}H_{24}O_2S$: 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 cm^3 of dichloromethane a solution of mCPBA (0.57 g in 25 cm^3 dichloromethane) was added at 0 °C under a nitrogen atmosphere in 30 min. After the addition of 30 cm^3 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 $C_{20}H_{17}NOS$: 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}; ^{1}H-NMR ($CDCl_3$) 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 $C_{25}H_{22}OS$: 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); ^{1}H-NMR ($CDCl_3$) δ 2.08—2.88 (m, 4H), 4.51 (s, 1H), 6.70 (s, 1H), 6.82—7.44 (m, 14H); ^{13}C-NMR ($CDCl_3$) δ 28.2 (t), 29.8 (t), 51.4 (d). Found: C, 85.41; H, 5.92; S, 9.12%. Calcd for $C_{25}H_{20}S$: C, 85.19; H, 5.72; S, 9.09%.

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