

### Regiospecific Synthesis of 1,2-Dialkylthio-7(alkyl- or aryl)thiocycloheptatrienes and 1,2-Dialkylthio-7-alkoxycycloheptatrienes

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Tropenylidenes, Tropenylum Ions,  
Hydride Abstraction

Hydride abstraction by trityl tetrafluoroborate from a mixture of cycloheptatriene[1,2]- and cycloheptatriene[3,4]-*p*-dithiine gave tropenylum[1,2]-*p*-dithiine tetrafluoroborate. The latter was found to add either methoxide or various thiolates only at the tropenylum C-3, which constitutes the first entry to regiospecifically trifunctionalized cycloheptatrienes. In contrast, cycloheptatriene[1,7]-*p*-dithiine or various other cycloheptatrienes substituted at C-7 with either methylthio or *t*-butylthio groups were found to undergo alkylthiolate abstraction by trityl tetrafluoroborate. This limits the usefulness of the above synthetic methods for polyfunctionalized cycloheptatrienes.

Recently we have reported on the first general regiospecific base additions to monosubstituted tropenylum ions affording 1,7-difunctionalized cycloheptatrienes [1]. Specifically, we have synthesized 1-alkoxy-7(alkyl- or arylthio)cycloheptatrienes [2, 3] and 1-alkylthio-7(alkyl- or arylthio)cycloheptatrienes [4].

To the best of our knowledge general methods for the regiospecific synthesis of trifunctionalized cycloheptatrienes are not available. Therefore we deemed interesting to explore the synthesis of some trifunctionalized cycloheptatrienes. We started with hydride abstraction by trityl tetrafluoroborate from the mixture of difunctionalized cycloheptatrienes **1** and **2** [5] to give the tropenylum ion **3**. We were rewarded by the finding that the latter reacts with either sodium methoxide or a variety of thiolates at low temperatures to give **4** and **5**, respectively, as the sole cycloheptatrienes which could be isolated. The balance of materials was given by untractable tars.

Compounds **5a–c** proved to be extremely labile in acidic media, giving back **3**.

However, there are limitations to the above method. In fact, it could not be extended to cycloheptatrienes **6** [5], **8** [2], **10** and **12** [6]. In all these cases the trityl ion was found to abstract mercaptide rather than hydride from the  $sp^3$  carbon to give the tropenylum ions **7**, **9** [7] and **11** [8]. Such a behaviour finds some analogy in the chemical literature [6, 9]. However, it was somewhat surprising that even with **10** trityl ion prefers to attack the encumbered sulphur atom rather than the hydrogen at the  $sp^3$  carbon. Whether conformational or electronic factor, or both, govern these reactions is open to speculation.

### Experimental

All reactions were run under dry nitrogen. Solvents were dried by standard procedures.  $^1H$  NMR spectra were run in the solvents indicated on Varian T 60 or Jeol PS 100 spectrometers, chemical shifts ( $\delta$ ) being measured from internal tetramethylsilane as reference. IR and UV spectra were run on Perkin Elmer 337 or Unicam SP 800 spectrophotometers, respectively. Melting points were taken with a Kofler apparatus and are uncorrected.

#### Tropenylum[1,2]-*p*-dithiine tetrafluoroborate (**3**)

To a solution of trityl tetrafluoroborate [7] (0.558 g, 1.7 mmol) dissolved in the minimum amount of dry acetonitrile (3 ml) was added at room temperature with stirring under nitrogen the equimolar amount of a *ca.* 1:1 mixture [4] of **1** and **2**. The mixture became warm and darkened. After 5 min dry ether was added to the mixture, which had become less dark, whereby red crystals of **3** precipitated. These were filtered under nitrogen, rinsed with ether and then dried *in vacuo*; yield 0.402 g (88%); m. p. 160 °C (from acetonitrile).

$C_9H_9BF_4S_2$  (268.09)

Calcd	C 40.33	H 3.36	S 23.90,
Found	C 40.10	H 3.30	S 23.70.

UV (acetonitrile):  $\lambda_{max} = 308,442$  nm.

$^1H$  NMR ( $CD_3CN$ ):  $\delta = 8.6$ – $7.8$  (complex m, 5H, tropenylum protons), 3.66 ppm (s; 4H,  $CH_2$ – $CH_2$ ).

#### 7-Methoxycycloheptatriene[1,2]-*p*-dithiine (**4**)

To a suspension of **3** (0.126 g, 0.47 mmol) in dry dichloromethane (15 ml) was added at  $-40$  °C with stirring under nitrogen the equimolar amount of sodium methoxide dissolved in dry methanol (0.2 ml). There was immediate reaction, as indicated by the sudden decolorization of the mixture. A saturated aqueous solution of sodium chloride was then added to the mixture and extracted with ether. Evaporation of the ether extract led to 0.05 g of an oil which was chromatographed on a home-made 2 mm thick layer of neutral alumina (Merck), eluent petroleum ether/ethyl ether (80:20). The  $R_f$  0.4 band (dark under UV) gave **4** as a pale-yellow oil; yield 0.044 g (44%).

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**C<sub>28</sub>H<sub>25</sub>BF<sub>4</sub>S<sub>2</sub> (512.43)**

Calcd C 65.63 H 4.92 S 12.51,  
 Found C 65.40 H 4.91 S 12.30.

<sup>1</sup>H NMR (CD<sub>3</sub>CN): δ = 8.40 (pseudo s, 6H, tropanylium protons), 7.33 (pseudo s, 15H, phenyl-protons), 3.10–2.77 (m, 4H, SCH<sub>2</sub>CH<sub>2</sub>SPh<sub>3</sub>). UV (acetonitrile): λ<sub>max</sub> 387 nm.

**7-*t*-Butylthiocycloheptatriene (10)**

To a suspension of tropanylium tetrafluoroborate (0.933 g, 5.2 mmol) in 0.1 M aq. hydrogen chloride (60 ml) was added sodium *t*-butylthiolate with stirring at room temperature. After further 24 h stirring the mixture was ether extracted, washed with 10% aq. sodium chloride and dried over sodium sulphate. Chromatography over a silica gel layer, eluent petroleum ether/ethyl ether (95:5), gave **10** as a pale-yellow oil (*R<sub>f</sub>* 0.65), yield 0.370 g (39%).

**C<sub>11</sub>H<sub>16</sub>S (180.31)**

Calcd C 73.27 H 8.95,  
 Found C 73.30 H 8.86.

<sup>1</sup>H NMR (CCl<sub>4</sub>): δ = 6.5 (m, 2H, C(3)H–C(4)H), 6.1–5.8 (m, 2H, C(2)H–C(5)H), 5.2 (dd, 2H, C(1)H–C(6)H), 2.8 (t, 1H, *J* = 6 Hz, CHSC(CH<sub>3</sub>)<sub>3</sub>), 1.2 ppm (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>).

**Reactions leading from cycloheptatrienes****8 [1], 10 and 12 [5] to trophenylium ions**

Using the general procedure described above for **7**, **8** gave **9** [6], whereas from either **10** or **12** we obtained **11** [7]. The tropanylium salts **9** and **11** were precipitated by the addition of dried ethyl ether to the mixture.

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