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

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Hydride abstraction by trityl tetrafluoborate from a mixture of cycloheptatriene[1,2] and cycloheptatriene[3,4]-p-dithione gave tropenylonium[1,2]-p-dithiin tetrafluoborate. The latter was found to add either methoxide or various thiolates only at the tropenylonium C-3, which constitutes the first entry to regiospecifically trifunctionalized cycloheptatrienes. In contrast, cycloheptatriene[1,7]-p-dithione or various other cycloheptatrienes substituted at C-7 with either methylthio or t-butylthio groups were found to undergo alkylthiolate abstraction by trityl tetrafluoborate. 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 tropenylonium ions affording 1,7-difunctionalized cycloheptatrienes [1]. Specifically, we have synthesized 1-alkoxy-7(alkyl- or arylthio)cycloheptatriens [2, 3] and 1-alkylthio-7(alkyl- or arylthio)cycloheptatriens [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 tetrafluoborate from the mixture of difunctionalized cycloheptatrienes 1 and 2 [5] to give the tropenylonium 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 tropenylonium 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 ecumbered 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 FS 100 spectrometers, chemical shifts (δ) being measured from internal trimethylsilane 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.

Tropenylonium[1,2]-p-dithiin tetrafluoborate (3)

To a solution of trityl tetrafluoborate [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).

\[ \text{C}_9\text{H}_{19}\text{BF}_2\text{S}_2 \] (268.09)

Calcd C 40.33 H 3.36 S 23.90,

Found C 40.10 H 3.30 S 23.70.

UV (acetonitrile): \( \lambda_{\text{max}} = 308.442 \text{ nm} \).

\(^1\text{H NMR} \text{(CD}_3\text{CN): } \delta = 8.6-7.8 \text{ (complex m, 5H, tropenylonium protons), 3.66 ppm (s; 4H, } \text{CH}_2\text{-CH}_2\text{).} \]

7-Methoxycycloheptatriene[1,2]-p-dithiin (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 (Merek), 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%).
C_{10}H_{12}O_{2}S_{2} (212.33)
Caled C 56.57 H 5.69,
Found C 56.20 H 5.70.

{\text{^1}}H \text{ NMR (CDCl}_3\text{): } \delta \text{ 6.2-5.2 (m, 4 H, C}(3)-C(6) \text{ cycloheptatriene protons), 3.74 (d, 1 H, } J = 6 \text{ Hz, CH(OCH}_3\text{), 3.4 (s, 3 H, OCH}_3\text{), 3.2 ppm (s, 4 H, CH}_2\text{-CH}_2\text{).}

7-Methylthiocycloheptatrien[1,2]-p-dithiin (5a)

To a suspension of 3 (0.324 g, 1.21 mmol) in 20 ml of dry dichloromethane at \(-50^\circ\text{C}\) was added with stirring under nitrogen the double molar amount of sodium methanethiolate dissolved in a little dry acetonitrile. The color due to 3 faded within 1 h, after which the mixture was worked up as described above for 4. The \(R_f\) 0.6 chromatographic band, eluent petroleum ether/ethyl ether (75:25), gave 5a as a pale-yellow oil, yield 0.128 g (46%).

C_{10}H_{12}S_{3} (228.39)
Caled C 52.59 H 5.29,
Found C 52.35 H 5.20.

{\text{^1}}H \text{ NMR (CDCl}_3\text{): } \delta \text{ 6.4-5.2 (m, 4 H, C}(3)-C(6) \text{ cycloheptatriene protons), 3.8 (d, 1 H, } J = 8 \text{ Hz, CHSCH}_3\text{), 3.2 (s, 4 H, CH}_2\text{-CH}_2\text{), 2.15 ppm (s, 3 H, S(CH}_3\text{). UV (acetonitrile): } \lambda_{\text{max}} \text{ 345, 280 nm.}

7-t-Butylthiocycloheptatrien[1,2]-p-dithiin (5b)

The reaction and product isolation were carried out as described above for 5a starting from 0.205 g (0.76 mmol) of 3 in 22 ml of dry dichloromethane and 0.091 g (0.8 mmol) of sodium f-butylthiolate. The \(R_f\) 0.7 chromatographic band, eluent petroleum ether/ethyl ether (75:25), gave 5b as a pale-yellow oil; yield 0.062 g (30%).

C_{13}H_{18}S_{3} (270.46)
Caled C 57.73 H 6.71,
Found C 57.40 H 6.50.

{\text{^1}}H \text{ NMR (CDCl}_3\text{): } \delta \text{ 6.2-5.2 (m, 4 H, C}(3)-C(6) \text{ cycloheptatriene protons), 3.65 (d, 1 H, } J = 8 \text{ Hz, CHS(CH}_3\text{), 3.2 (s, 4 H, CH}_2\text{-CH}_2\text{), 2.15 ppm (s, 9 H, C(CH}_3\text{). UV (acetonitrile): } \lambda_{\text{max}} \text{ 345, 280 nm.}

7-p-Tolylthiocycloheptatrien[1,2]-p-dithiin (5c)

The reaction (1 h to go to completion) and product isolation were carried out as described above for 5a starting from 0.230 g (0.86 mmol) of 3 in 25 ml of dried dichloromethane and 0.211 g (1.4 mmol) of sodium p-toluenethiolate. The \(R_f\) 0.65 band, eluent petroleum ether/ethyl ether (80:20) gave 5c as a yellow oil; yield 0.214 g (82%).

C_{16}H_{16}S_{3} (304.49)
Caled C 63.11 H 5.30,
Found C 63.03 H 5.20.

1-H NMR (CDCl}_3\text{): } \delta \text{ 7.0 (AB system, } A \text{ ppm 0.3, } J = 8 \text{ Hz, tolyl aromatic protons), 6.3-5.2 (m, 4 H, C}(3)-C(6) \text{ cycloheptatrienes protons), 4.15 (d, 1 H, } J = 8 \text{ Hz, CH-S-p-tolyl, 3.0 (s, 3 H, CH}_3\text{). IR (neat liquid), } \nu = 3140,3040,2980,1600,1530,1400,1290,1165,1140,908,790,750,700,635 \text{ cm}^{-1}. \text{ UV (acetonitrile): } \lambda_{\text{max}} \text{ 350, 275 nm.}

1-H NMR (CDCl}_3\text{): } \delta \text{ 7.0 (AB system, } A \text{ ppm 0.3, } J = 8 \text{ Hz, tolyl aromatic protons), 6.3-5.2 (m, 4 H, C}(3)-C(6) \text{ cycloheptatrienes protons), 4.15 (d, 1 H, } J = 8 \text{ Hz, CH-S-p-tolyl, 3.0 (s, 3 H, CH}_3\text{). IR (neat liquid), } \nu = 3140,3040,2980,1600,1530,1400,1290,1270,1150,1095,1020,810,750,500. \text{ UV (acetonitrile): } \lambda_{\text{max}} \text{ 350, 275 nm.}

I-Triphenylmethylthio-2-tropenyliumtetrafluoborate (7)

To a solution of trityl tetrafluoborate (0.50 g, 1.51 mmol) in the minimum amount of dry acetonitrile (2.8 ml) was added at room temperature under nitrogen the equimolar amount of 6 [4]. Addition of ether led to the precipitation of 7 as yellow crystals which were filtered under nitrogen; yield 0.742 g (96%); m.p. 182-183 °C (from acetonitrile).
C_{28}H_{25}BF_4S_2 (512.43)
Calcd  C 65.63  H 4.92  S 12.51,
Found  C 65.40  H 4.91  S 12.30.

^1H NMR (CD_3CN): δ = 8.40 (pseudo s, 6H, tropenylum protons), 7.33 (pseudo s, 15H, phenylprotons), 3.10–2.77 (m, 4H, SCH_2CH_2SPh_3). UV (acetonitrile): λ_{max} 387 nm.

7-t-Butylthiocycloheptatriene (10)

To a suspension of tropenylium tetrafluoborate (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_f 0.65), yield 0.370 g (39%).

C_{11}H_{16}S (180.31)
Calcd  C 73.27  H 8.95,
Found  C 73.30  H 8.86.

^1H NMR (CCl_4): 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_3)_3), 1.2 ppm (s, 9H, C(CH_3)_3).

Reactions leading from cycloheptatrienes

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

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