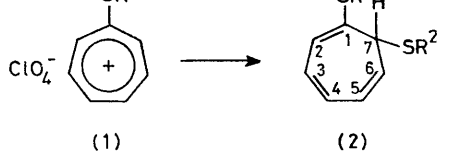
Regiospecific Synthesis of 1,7-Dialkylthiocycloheptatrienes. A Case of Rapid [1,7] Sigmatropic Migration of Unhindered Alkylthio-groups

By Marino Cavazza and Gioia Morganti
(*Istituto di Chimica Generale, Università di Pisa,* 56100 *Pisa, Italy*)
and Francesco Pietra*
(*Facoltà di Scienze, Libera Università di Trento,* 38050 *Povo-Trento, Italy*)

Summary 1-Alkylthiotropenylium ions add alkane- or arene-thiolates at C(2) at low temperatures to give only 1-alkyl-7-alkyl(aryl)cycloheptatrienes which, at room temperature, experience a [1,7] interchange of unhindered alkylthio-groups.

Base additions to monosubstituted tropenylium ions are known to give a mixture of all three possible isomeric, 1,7-, 2,7-, and 3,7-disubstituted cycloheptatrienes,[1] thus lacking synthetic usefulness. We report that, in contrast, alkylthiotropenylium ions add thiolates regiospecifically at C(2) at low temperatures to give only 1,7-dialkylthiocycloheptatrienes. However, at room temperature, an unprecedently rapid [1,7] interchange of unhindered alkylthio-groups occurs.



(1) (2)

Reagents: $NaSR^2$, CH_2Cl_2–abs. EtOH; −50 °C; work-up at −10 °C, and t.l.c. at room temp. for 30 min.

Thus, to methylthiotropenylium perchlorate (**1a**),† (3·8 mmol) in 20 ml of dichloromethane at −50 °C was added, under N_2 with stirring, sodium butanethiolate (5·3 mmol) in 2 ml of abs. ethanol. The mixture was kept overnight at −20 °C, saturated aqueous sodium chloride at −10 °C was added, and the mixture was finally extracted with cold chloroform. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* at −10 °C. An oil (**2a**)‡ was obtained by t.l.c. of the residue (silica gel, n-pentane–benzene, 3:2, R_F 0·5, room temp. for 0·5 h) as the sole product in 38% yield besides much tar. Yields were not optimized but they decreased drastically when less care was taken to maintain low temperatures throughout.

Structure (**2a**) is supported by the ^1H n.m.r. spectrum showing δ (Me_4Si, $CDCl_3$) 0·9 (t, 3H, Me), 1·5 (m, 4H, central CH_2CH_2), 2·4 (s, 3H, SMe), 2·6 (t, 2H, SCH_2), 4·1 (dd, 1H, $J_{7,2}$ 1·1, $J_{7,6}$ 8·0 Hz 7-H), and 5·3–6·6 (m, 5H, 2- to 6-H).

When (**2a**) was kept at 35 °C in $CDCl_3$, the intensity of both the δ 2·4 and 2·6 signals steadily decreased while a singlet at δ 2·0 as well as a triplet at δ 2·7 appeared and increased in intensity. The δ 2·0 singlet and the δ 2·7 triplet can be attributed to SMe and SCH_2, respectively, of (**2b**), the final, equilibrium situation, reached after *ca.* 6 h, corresponding to a mixture of 44% (**2a**) and 56% (**2b**).§

---

† The method of B. Fölisch and E. Haug, *Chem. Ber.*, 1971, **104**, 2324, had to be modified by precipitating the tropenylium perchlorate 3 min after the mixing; in our hands longer times reduced the yields to nil.

‡ Correct elemental analysis and mass spectrum.

§ Correct elemental analysis for $C_{12}H_{18}S_2$ of the oily residue after evaporation of the solution.

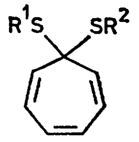
This interpretation is supported by the results of the reaction of (**1b**) with sodium methanethiolate carried out 'in the cold' as above. Thus, a similar ^{1}H n.m.r. spectrum to that above was immediately obtained in $CDCl_3$, the δ 2·4 and 2·0 signals revealing a mixture of 31% (**2b**) and 5·6% (**2a**).[§] The latter mixture, when kept at room temperature, changed composition until, after *ca.* 7 h, it reached equilibrium, ^{1}H n.m.r. analysis showing 44% (**2a**) and 56% (**2b**),[§] *i.e.*, identical with that above.

TABLE. Reaction of (**1a**) (R^1 = Me) and (**1b**) (R^1 = Bu^n) to produce (**2**)

R^1	R^2	Product (% yield)	
Me	Bu^n	(**2a**)	(38)
Bu^n	Me	(**2b**)	(31)[a]
Me	Bu^t	(**2c**)	(52)
Me	*p*-MeC_6H_4	(**2d**)	(43)

[a] Together with (**2a**) (5·6%); (**2a**) and (**2b**) could not be separated by t.l.c.

Similar experiments with (**1a**) and either Bu^tSNa or *p*-MeC_6H_4SNa led, respectively, to (**2c**)[‡] and (**2d**),[‡] as revealed by their ^{1}H n.m.r. spectra in $CDCl_3$ which were nearly identical to that of (**2a**), as far as the 2- to 7-H and Me protons are concerned. In contrast to (**2a**) and (**2b**), the ^{1}H n.m.r. spectra of both (**2c**) and (**2d**) did not change at 35 °C.



(**3**)

We suggest that the interconversion (**2a**) $\rightleftharpoons$ (**2b**) occurs through the tropone dithioacetal (**3**) *via* unusually rapid [1,7] sigmatropic shift of alkylthio groups. Sigmatropic shifts of hydrogen cannot account for the above observations because they are known to require high temperatures with cycloheptatrienes.[2] Within this interpretation, the stability of (**2c**) can be attributed to steric compression between R^1S and R^2S inhibiting the formation of (**3**), whereas electronic factors must also be responsible for the stability of (**2d**).

We thank C.N.R., Roma, for financial support.

(*Received, 26th June* 1978; *Com.* 677.)

---

[1] See, for example, B. Föhlisch, C. Fisher, and W. Rogler, *Chem. Ber.* 1978, **111**, 213.

[2] A. P. Ter Borg, E. Razenberg, and H. Kloosterziel, *Rec. Trav. chim.*, 1965, **84**, 1230; T. Fukunaga, T. Mukai, Y. Akasaki, and R. Suzuki, *Tetrahedron Letters*, 1970, 2975.