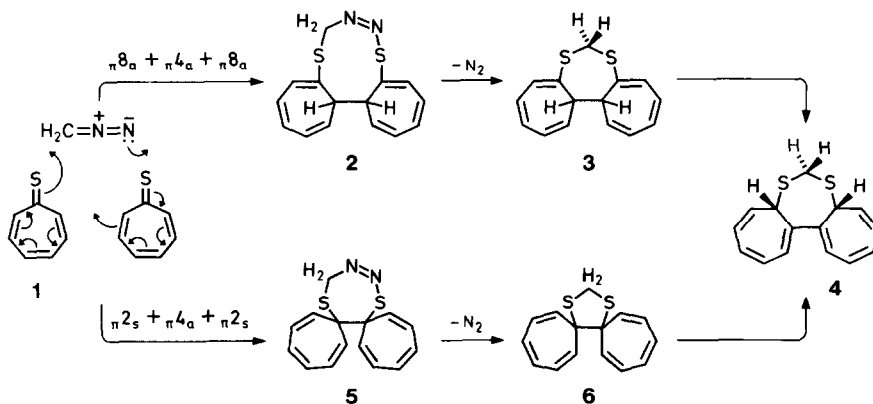


TROPOTHIONE AND DIAZOMETHANE; REVISION AND NEW APPROACH

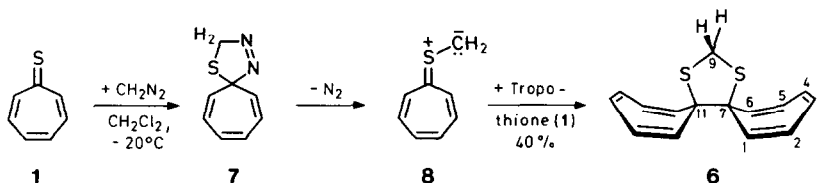
Rolf Huisgen* and Joaquin Rodriguez Moran

Institut für Organische Chemie der Universität München
 Karlstr. 23, D-8000 München 2, BRD

Summary A re-examination of the title reaction suggests a 1,3-dipolar cycloaddition of the intermediate tropothione *S*-methylide to tropothione furnishing the dispiro-dithiolane 6 which was isolated and underwent a [7.7]-sigmatropic shift on warming to give the tricyclic dithiepane derivative 3.



In 1973 T. Machiguchi *et al.*¹ obtained 68% of $C_{15}H_{14}S_2$, mp 120-121°C, from tropothione (1) and diazomethane at 0-10°C; the structure 4 was based on a careful ¹H NMR study with double resonance. The authors quoted Schönberg's studies² and tentatively proposed the two mechanistic pathways shown above, both beginning with a daring *termolecular* symmetry-allowed cycloaddition.



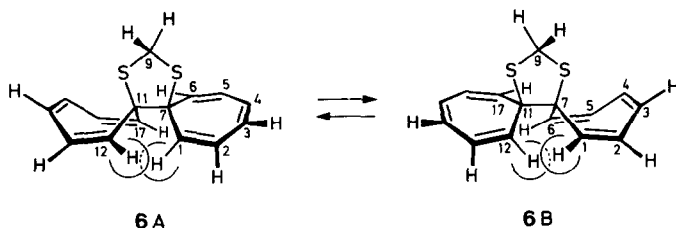
In the meantime the mechanism of the Schönberg reaction was clarified,³ its essence being the 1,3-dipolar cycloaddition of a thiocarbonyl ylide to a second molecule of the thione. Accordingly, a new reaction sequence involving the intermediates 7 and 8 was foreseen. We expected to halt the reaction of 1 and diazomethane at low temperature at the stage of the 1,3,4-thiadiazoline 7 and to intercept the tropothione *S*-methylide (8) by another dipolarophile.

However, in contrast to the system thiobenzophenone + diazomethane,³ the initiating cycloaddition was not faster than the N₂ extrusion and the thiocarbonyl ylide 8 combined *in situ* with a second molecule of trophothione (1).

We added 1.5 equiv of diazomethane to trophothione ⁴ in dichloromethane at -78°C; in 4 h at -20°C the red color of 1 vanished. After chromatography on silica gel at -40°C (CHCl₃/hexane), 36% of the crystalline dispiro-dithiolane 6, mp 98-100°C, was isolated.

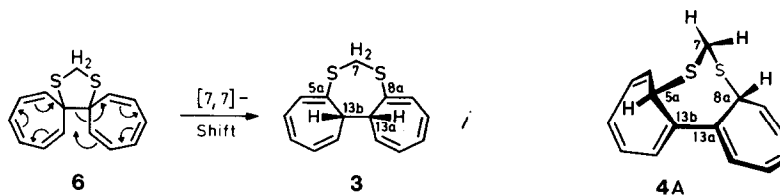
The ¹H NMR spectrum of 6 at 34°C (CDCl₃) was consistent with the presence of two planes of symmetry. The singlet of the 9-H₂ appears at δ 3.57 and the twelve vinylic protons are characterized by only 3 chemical shifts (CDCl₃, 200 MHz, Gaussian multiplication): δ = 5.94 (1-H/6-H), 6.40 (2-H/5-H), and 6.77 (3-H/4-H) with $J_{1,2} = 9.8$ Hz, $J_{1,3} = J_{1,4} = 0.84$ Hz, $J_{2,3} = 4.3$, $J_{2,4} = 2.9$ Hz. The ¹³C NMR spectrum (CD₂Cl₂) shows three doublets at δ 126.8, 128.1, and 132.5 for the twelve vinylic C-atoms, whereas C-7 and C-11 occur as a singlet at 67.6 and C-9 as a triplet at 29.7.

The simplicity of the spectra is due to fast conformational changes at room temperature. The doublet of 1-H/6-H coalesces at -50°C and that of 2-H/5-H around -70°C, whereas the signal of 3-H/4-H shows only loss of fine structure; the 1-H/6-H forms a well-resolved dd at -70°C with $\delta\nu = 18.2$ Hz. This advocates against the inversion of the cycloheptatriene rings which should create the maximum difference in the environment for 3-H/4-H. Furthermore, the ring inversion of cycloheptatriene ⁵ requires only $\Delta G^\ddagger = 6 \pm 0.5$ kcal mol⁻¹, whereas $\Delta G^\ddagger = 11 \pm 1$ kcal mol⁻¹ was determined from $T_c = 221$ K of the 1-H/6-H signal in our case.



The molecular model discloses strong interference of 1-H and 6-H with 12-H and 17-H, illustrated by 6A. A vertical C_2 axis is retained during the interconversion of 6A with its enantiomer 6B. The two cycloheptatriene units remain equal, but the pairwise equivalence of the CH *within each ring* is lost. This harmonizes with ¹³C NMR spectral changes (CD₂Cl₂, 20.15 MHz, H-decoupled): The singlet of C-1/C-6 broadens at 0°C and disappears at -29°C in coalescence; at -29°C the signal of C-2/C-5 follows in broadening and at -46°C the mentioned signals form a hump. At -80°C four singlets show up with $\delta\nu = 222.2$ Hz for C-1 and C-6 and $\delta\nu = 84.8$ Hz for C-2 and C-4; $\Delta G^\ddagger = 10 \pm 1$ kcal mol⁻¹ is calculated from $T_c = 208$ K of C-2 and C-4. Over the whole temperature range the equivalence of the quaternary C-7 and C-11 (s, 67.9) is maintained, and the

singlet of the vinylic C-3/C-4 is virtually unchanged at -80°C . C-7 and C-11 should not remain identical in the inversion of the cycloheptatriene rings.



The dispiro-dithiolane **6** slowly rearranges at room temperature to an isomer (mp $120\text{--}121^{\circ}\text{C}$) which corresponds in all properties to the compound to which Machiguchi *et al.*¹ ascribed structure **4**. Quantitative ^1H NMR analysis recorded a 94% yield and provided the first-order rate constants at 53°C : $k_1 = 3.62 \cdot 10^{-4} \text{ s}^{-1}$ (CCl_4), $3.18 \cdot 10^{-4} \text{ s}^{-1}$ (CDCl_3). We found the spectra of the isomer of mp $120\text{--}121^{\circ}\text{C}$ better consistent with **3** than with **4**; **3** occurred in Machiguchi's mechanism as a precursor of **4** in the framework of a different pathway. Fourteen electrons participate in the symmetry-allowed [7,7]-sigmatropic shift, **6** \rightarrow **3**.

The UV shift from 265 nm for **6** to 290 nm for **3** (CH_2Cl_2) suggests a more extended conjugated system in **3**. The ^1H NMR spectrum - identical with that reported¹ - is easily reinterpreted in terms of structure **3**. The AB spectrum of 7-H₂ at δ 3.76 and 4.22 with $J = 13.0 \text{ Hz}$ indicates the *cis* relation of 13a-H and 13b-H. The doublet of 13a-H and 13b-H at δ 2.75 is broad at 27°C and shar-

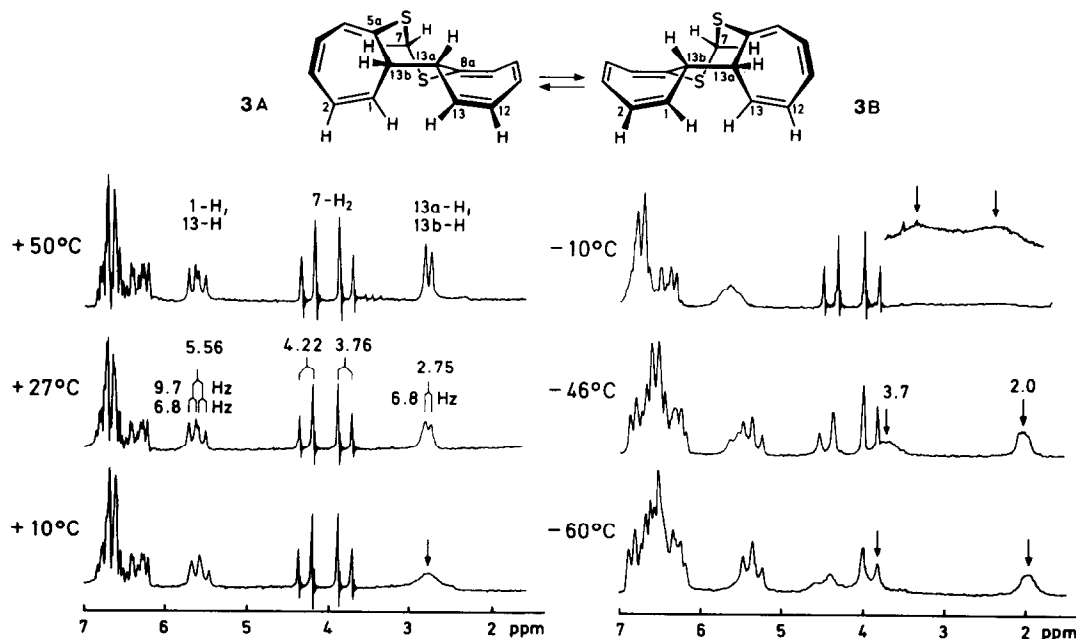


Fig. 1. ^1H NMR spectrum of **3** in CDCl_3 at 80 MHz; temperature dependence

pens at 50°C (Fig. 1); $J_{1,13b} = J_{13,13a} = 6.8$ Hz. The virtual disappearance of this signal at -10°C denotes the slowing of a dynamic process, probably the interconversion of the enantiomeric twist conformations 3A and 3B. The separate broad signals of 13a-H and 13b-H emerge at δ 2.02 and 3.65 at -46°C. $\Delta G^\ddagger = 13 \pm 1$ kcal mol⁻¹ is calculated from T_C 265 K, in accordance with the values observed for 4,6-dithiacycloheptenes.⁶ At -60°C the AB spectrum of 7-H₂ also begins to coalesce due to a different conformational change.

Good evidence for 3 is offered by NMR couplings. On expanding the signal at δ 2.02 (13a-H or 13b-H) at -40°C, a doublet of doublets is recognized. Irradiating the signal of 1-H/13-H at δ 5.5, the dd collapses to a doublet with $J_{13a,13b} = 3.3$ Hz. Models of structures 3 and 4 reveal a twisting of the cycloheptatriene rings by 50-60°C *vs.* each other. $J_{vic} = 3.3$ Hz for 13a-H and 13b-H in 3 accords with a dihedral angle of 50-60°C. On the other hand, the coupling between 5a-H and 8a-H in Machiguchi's formula 4A should be very small in the twisted system.

A strong argument in favor of 3 comes from the two-dimensional Fourier transform (Bruker program HCCORR). The 7-H at δ 3.76 is coupled with ~ 8 Hz to the only vinylic C-atom which bears no H, *i.e.*, C-5a/C-8a (δ 127.7); that size of J is expected for HC-X-C $\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$.

Two *theoretical* reasons make the conversion 3 \rightarrow 4 assumed by Machiguchi seem doubtful. The two suprafacial [1,7]-H shifts are forbidden to be concerted by orbital symmetry and a base-catalyzed process is improbable. Finally, a thermodynamic driving force for an isomerization 3 \rightarrow 4 is not discernible.

The *direct formation* of 3 from tropothione-S-methylide (8) and tropothione (1) by a [$\pi_{10s} + \pi_{8s}$] cycloaddition would be symmetry-allowed. Chromatography of the original reaction product and UV analysis disclosed 2.2-2.5% of 3 besides the main product 6. The amount is too small to warrant the assumption that a minor direct route to 3 participates.

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