

STEREOSELECTIVE BEHAVIOUR OF *s*-TRITHIANE DERIVATIVES  
IN THE PRESENCE OF METHOXIDE IONS IN VARIOUS SOLVENTS

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*s*-Trithiane and 1,3-dithiane as well as their alkyl derivatives have been found to show remarkable stereoselectivity in base catalysed reactions<sup>1,2</sup>. This stereoselectivity is caused by a high equatorial preference of the resulting carbanions. Stereitwieser recently suggested that the principal mechanism of stabilisation of such carbanions by adjacent sulphur was by polarization<sup>3,4</sup>.

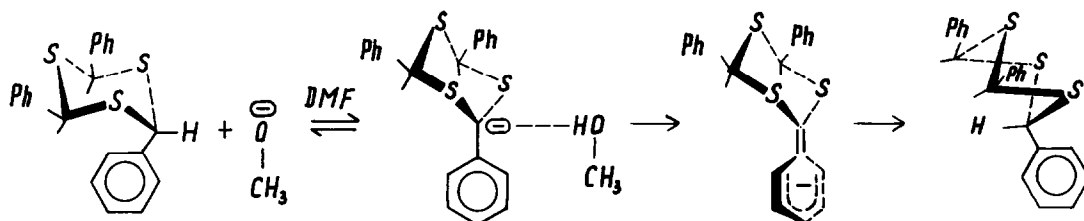
2,4,6-Trisubstituted *s*-trithiane derivatives exist in two isomeric forms as lower melting  $\alpha$ -isomers (cis-trans form) and  $\beta$ -isomers (cis-cis form)<sup>5</sup>. We were studying the stereochemical behaviour of  $\alpha$ -2,4,6-triphenyl-*s*-trithiane ( $\alpha$ -TPT) and  $\alpha$ -2,4,6-trimethyl-*s*-trithiane ( $\alpha$ -TMT) in the presence of sodium methoxide in various solvents: *N,N*-dimethylformamide (DMF), ethylene glycol and methanol-chloroform mixture. The progress of the reaction was followed by PMR spectroscopy. The results are listed in Table 1.

Table 1. Solvent influence on the stereochemical results of the reaction of *s*-trithiane derivatives with sodium methoxide

Compound	Solvent	Reaction conditions and results	Steric course
$\alpha$ -TPT	DMF	Heating up to 80°C during 2 min, the solution turned reddish, PMR spectrum taken after cooling	Complete inversion
$\alpha$ -TPT	DMF	PMR spectrum measured immediately after reagents addition at room temp.	80% inversion
$\alpha$ -TPT	CH <sub>3</sub> OD+CDCl <sub>3</sub> 1:4	Reflux for 2 hrs, H <sub>e</sub> - D exchange observed	Complete retention
$\alpha$ -TPT	HOCH <sub>2</sub> CH <sub>2</sub> OH	Warmed to achieve the substrate solubility	Complete inversion
$\alpha$ -TMT	DMF+small amount of CH <sub>3</sub> OD	Reflux for 2 hrs, H <sub>e</sub> - D exchange observed	Complete retention

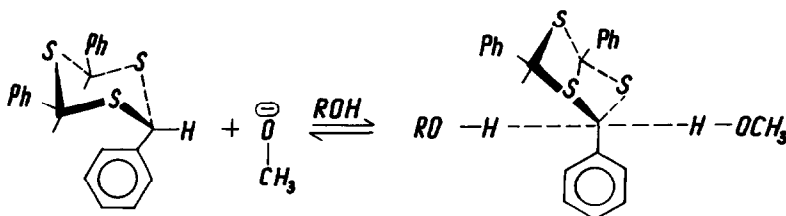
Under the experimental conditions used, the reaction proceeded with retention or inversion of configuration. Our suggestions on the mechanisms of the performed reactions are consistent with Cram's <sup>6</sup> results and are as follows:

#### Inversion of configuration of $\alpha$ -TPT in DMF



In DMF solution the  $\text{CH}_3\text{O}^-$  ion extracts the equatorial proton from  $\alpha$ -TPT and it is possible that the carbanion produced is slightly symmetrically solvated by the solvent. This carbanion is relatively long lived due to the low concentration of proton donors in the solvent of high dielectric constant, and can attain the coplanarity with the phenyl group necessary for resonance stabilization of the transition state. The reddish colour of the reaction mixture indicates that negative charge is highly delocalized in the anion derived from  $\alpha$ -TPT <sup>7</sup>. The solvated carbanion recaptures proton giving the thermodynamically more stable  $\beta$ -isomer <sup>5</sup>.

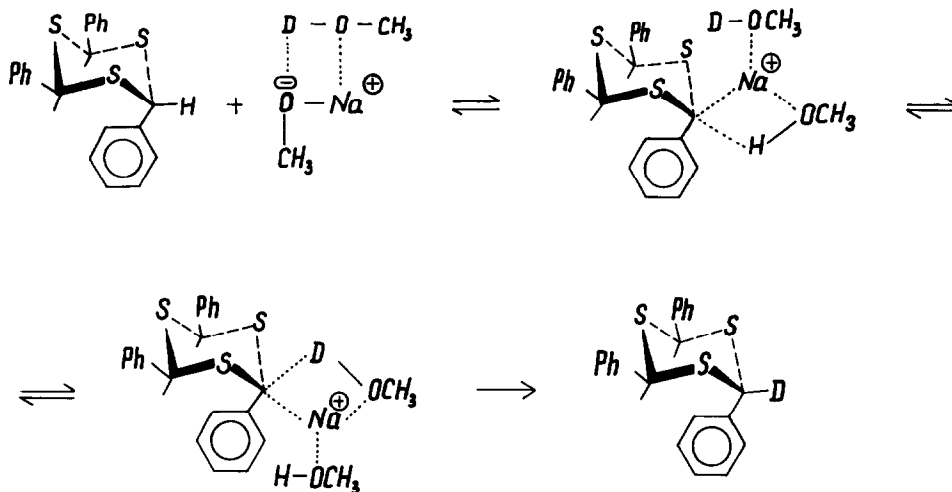
#### Inversion of configuration of $\alpha$ -TPT in ethylene glycol



In a highly polar, protic solvent the resulting carbanion is solvated at the front by a leaving group and at the back by a proton donor. Due to the action of strongly proton-donating reaction medium, proton transfer from the solvent to the anion with simultaneous isomerization to the  $\beta$ -form occurs immediately. The reaction conditions inhibit the conjugation between the carbanion centre and phenyl group. This conclusion is confirmed by the lack of the reddish colour of the reaction mixture.

#### Retention of configuration of $\alpha$ -TPT in the $\text{CH}_3\text{OD}-\text{CDCl}_3$ solvent mixture

The decrease of dielectric constant of the reaction mixture by the introduction of chloroform changed the reaction course. We can suppose that in the presence of  $\text{CDCl}_3$  tight ion-pairs are formed instead of free  $\text{CH}_3\text{O}^-$  ions.



Under these conditions asymmetric solvation<sup>6</sup> probably occurs, which makes isomerization more difficult. Asymmetric solvation may induce some asymmetry in the coplanarity of the carbanion favouring retention in this way. In the reaction products no  $\beta$ -isomer was found and we conclude that the reaction proceeds with retention of configuration.

#### Retention of configuration of $\alpha$ -TMT in DMF

$\alpha$ -TMT did not change its configuration in the presence of  $\text{CH}_3\text{O}^-$  ions in the solvent of high dielectric constant. Similar behaviour of  $\alpha$ -TMT in the presence of alkali *t*-butoxide in *t*-butyl alcohol-*d* (solvent of low dielectric constant) was observed by Fukunaga et al.<sup>2</sup>.

PMR spectrum in  $(\text{CD}_3)_2\text{CO}$  of  $\beta$ -triphenyl-*s*-trithiane ( $\beta$ -TPT) prepared in our laboratory showed a multiplet for the aromatic protons between  $\delta$  7.4–7.18 and a sharp singlet at  $\delta$  5.6 which can be assigned to the trithiane ring hydrogen resonance (position analogous to the  $\alpha$ -isomer). Campaigne<sup>8</sup> observed for the  $\beta$ -TPT crystallized from benzene two signals at  $\delta$  7.4 and  $\delta$  7.2 in  $(\text{CD}_3)_2\text{CO}$ . He assigned the former one to the trithiane ring hydrogen resonance and the latter to the phenyl hydrogen resonance but did not observe the peak at  $\delta$  5.6. We found that  $\beta$ -TPT additionally shows the sharp singlet at  $\delta$  7.18 when the compound was crystallized from benzene. After recrystallization from other solvents this signal disappears. On the basis of the above-mentioned results and integration of PMR spectrum, our conclusion was that each molecule of  $\beta$ -TPT crystallizes with a molecule of benzene and the peak at  $\delta$  7.18 corresponds to the benzene protons. This conclusion was supported by elemental analysis as well as by the literature data<sup>9</sup>.

The fact of obtaining of  $\beta$ -TPT of high purity (m.p. 236–236.3°C), whereas the melting points quoted in the literature varied from 221°C<sup>10</sup> and 225–226°C<sup>11</sup> to 229–230°C<sup>8</sup>, should be emphasized. The above described isomerization reaction of  $\alpha$ -TPT can be applied to prepare  $\beta$ -TPT in quantitative yield from its  $\alpha$ -isomer or from the mixture of the two isomers.

#### References and Notes

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