

ISOMERIZATION OF THE AZO-GROUP IN A TETRAHYDRO-THIADIAZEPINE

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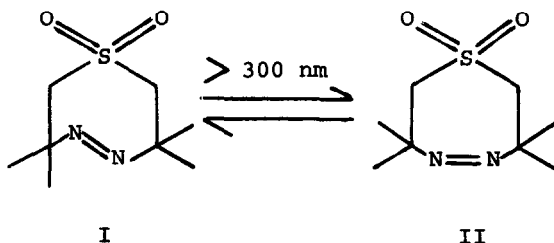
Summary: The preparation, isomerization and decomposition of the cis and trans isomer of a heterocyclic azo-compound is described.

Cis-trans isomerization in cyclic azo-compounds is well documented in the eight to ten-membered ring size<sup>1,2)</sup>. To date, however, only one seven-membered ring system has been isolated and characterized<sup>3)</sup>. We now wish to report an example(I, II) of the isomerization of a seven-membered azo-ring system containing an additional heteroatom.

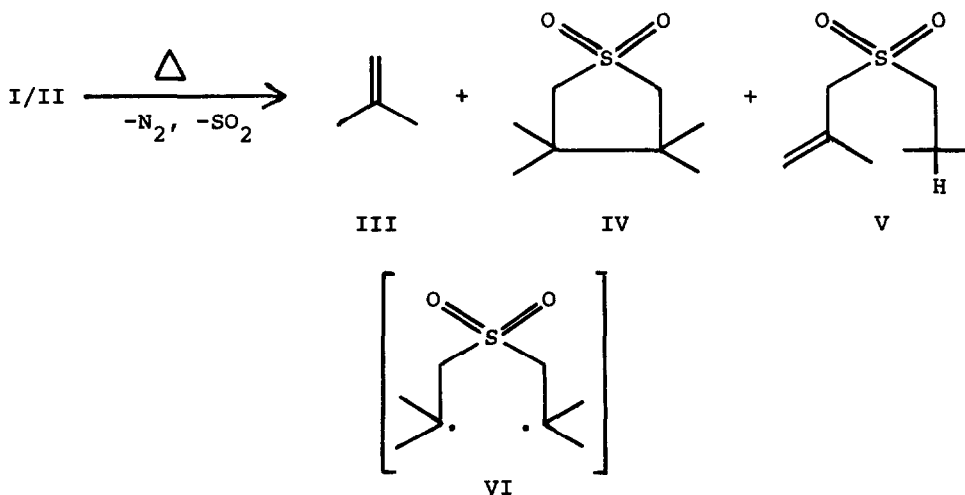
The oxidation of 3,3,6,6-tetramethyl-2,3,4,5,6,7-hexahydro-1,4,5-thia-diazepin-1,1-dioxide<sup>4)</sup> with iodine in diethylether<sup>5)</sup> gave  $\Delta^4$ -trans-3,3,6,6-tetramethyl-2,3,6,7-tetrahydro-1,4,5-thia-diazepin-1,1-dioxide(I) in 60% yield, after column chromatography over silica gel, using benzene/hexane as eluent (mp.: 138-140°C(dec.) from i-propanol/heptane. <sup>1</sup>Hnmr(CDCl<sub>3</sub>): 2.70 (AB, J=13, CH<sub>2</sub>), 2.21 & 1.50 (s, CH<sub>3</sub>). <sup>13</sup>Cnmr(CDCl<sub>3</sub>): 75.7 (s, C-quat.), 68.8 (t, CH<sub>2</sub>), 20.3 & 26.4 (q, CH<sub>3</sub>). UV(ethanol):  $\lambda_{\max.}$  = 418,  $\epsilon$  = 33).

In the low-temperature irradiation<sup>6)</sup> of I under nitrogen ( $5 \times 10^{-5}$  M in toluene at -60°C) we obtained  $\Delta^4$ -cis-3,3,6,6-tetramethyl-2,3,6,7-tetrahydro-1,4,5-thia-diazepin-1,1-dioxide(II). By following the ratio of the integrated areas of the signals of I to those of II with irradiation time, it could be shown that an equilibrium was established (ratio 30:70 after 3 hours). The formation of II could also be observed at room temperature, although equilibrium could not be attained because of concomitant decomposition. By irradiation of the individual isomers it was shown that whereas I isomerized to II without decomposition, II reverted only in traces (5%) to the trans-isomer, yielding principally isobutylene

(III) under elimination of nitrogen and sulfur dioxide. A preparative scale irradiation of a 2% benzene solution of I at room temperature gave II in 79% yield; II is in benzene virtually insoluble and precipitates during irradiation (mp.: 108°C(dec.) from ethanol.  $^1\text{Hnmr}(\text{CDCl}_3)$ : 3.46 (s, CH<sub>2</sub>), 1.72 (s, CH<sub>3</sub>).  $^{13}\text{Cnmr}(\text{CDCl}_3)$ : 67.0 (s, C-quat.), 62.0 (t, CH<sub>2</sub>), 28.9 (q, CH<sub>3</sub>). UV(ethanol):  $\lambda_{\text{max.}}$  = 404 nm,  $\epsilon$  = 95).



I and II undergo pyrolysis in toluene ( $t_{1/2}(70^\circ\text{C}) > 200$  min. and  $\sim 6$  min. for I and II, respectively) without apparent isomerization to yield isobutylene(III), tetramethylsulfolane<sup>7)</sup>(IV, mp.: 213-214°C) and methyl-sec.-butylsulfone<sup>7)</sup>(V). Quantitative results established by nmr-spectroscopy, which gave no evidence for CIDNP-signals<sup>8)</sup>, showed no difference in product selectivity between the two isomers(essentially the same ratio of III:IV:V = 15:2:5 was found both for I and II). It is not clear at this time whether the formation of III involves the intermediate VI or is concerted in accord with a nonlinear cheletropic elimination of SO<sub>2</sub><sup>9)</sup>.



It is interesting to point out that in water the thermal stability of II is greatly increased ( $t_{1/2}$  (70°C) > 200 minutes). Likewise, in a solution of D<sub>2</sub>O/DCI I (0.2 M) was rapidly (15 min.) and quantitatively isomerized to II at room temperature in the dark. Thus it would seem that the higher dipole moment of the cis-isomer<sup>2)</sup> results in a greater stabilization of the respective transition states by highly polar solvents.

Concerning the stereochemistry of the two isomers, the larger extinction coefficient<sup>10)</sup> suggested the cis-structure for II. Further evidence was the high-field shift of the <sup>13</sup>C resonances of the quaternary carbonatoms in II, relative to I, which is well documented for disubstituted ethylenes and attributed to steric effects in the cis-isomer<sup>11)</sup>. However, since the available data did not seem to lead to an unequivocal stereochemical assignment of I and II the cis-structure II<sup>12)</sup> was finally established by x-ray analysis<sup>13)</sup> (Figure 1).

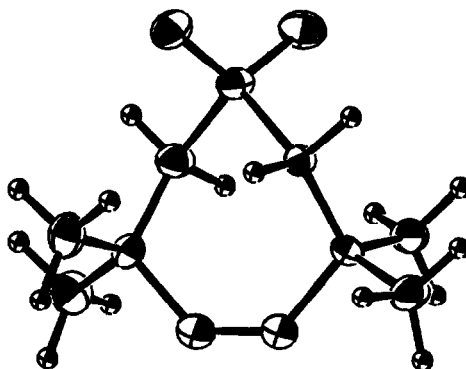


Figure 1: Computer-generated perspective drawing of II.

To summarize, since I and II are isomeric and exist in photochemical equilibrium, we conclude that I possesses the trans-structure. Our results also show that the cis-isomer(II) does not undergo ready isomerization, presumably owing to an energy barrier attributable to ring strain in trans-I.

References and Notes

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- 4) This compound was prepared by the method of H.J. Backer and R. Van der Ley, Rec. trav. chim. 70, 564 (1951), from hydrazine hydrate and dimethyl-allyl-sulfone. It was recrystallized from toluene/hexane to mp. 119-120°C. We thank Dr. J. Rody of Ciba-Geigy Limited for a sample of that material.
- 5) J.R. Roberts and K.U. Ingold, J. Amer. Chem. Soc. 95, 3228 (1973).
- 6) Irradiation conditions: Philipps HPK 125 medium-pressure mercury lamp through Pyrex-glass.
- 7) Isolated by preparative gaschromatography; the products gave mass, ir- and nmr-spectra consistent with the assigned structures.
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- 10) P.S. Engel and C. Steel, Accounts Chem. Res. 6, 275 (1973).
- 11) D.E. Dorman, M. Jautelat and J.D. Roberts, Org. Chem. 36, 2757 (1971).
- 12) The trans-isomer did not form suitable crystals from various solvents or on sublimation at room temperature/ $10^{-4}$  torr.
- 13) The crystal structure was measured in a closed capillary. II crystallizes in a space group Pbcn (Nr. 60);  $a = 19.089$ ,  $b = 10.962$ ,  $c = 10.473 \text{ \AA}$ ;  $V = 2191 \text{ \AA}^3$ ;  $Z = 8$ ;  $D_x = 1.238 \text{ g/cm}^3$ . The crystal structure was determined with an R-factor of 0.074 for 1148 reflections.

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