

THE CHEMICAL STUDY OF PSEUDOAROMATIC COMPOUNDS. III<sup>1)</sup>

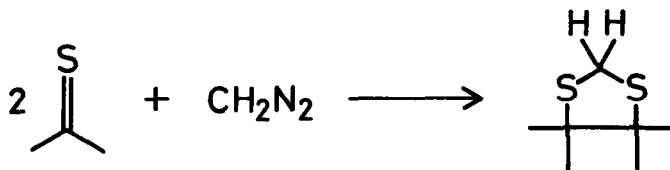
NOVEL TYPE OF CYCLOADDUCT FROM THE REACTION OF TROPOTHIONE WITH DIAZOMETHANE

Takahisa Machiguchi\*, Yasuhiro Yamamoto, Masamatsu Hoshino, and Yoshio Kitaharat

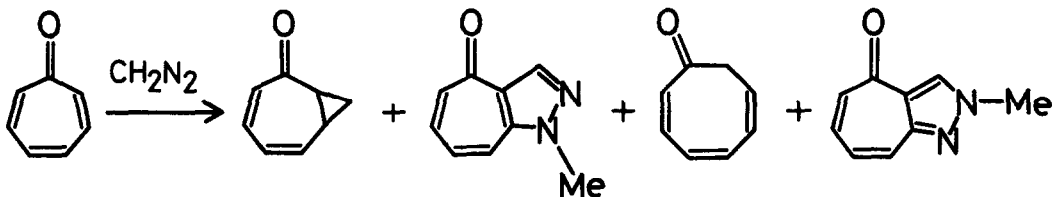
Department of Chemistry, Faculty of Science and Engineering,  
Saitama University, Urawa, Saitama 338, and †Department of Chemistry,  
Faculty of Science, Tohoku University, Sendai 980, Japan

(Received in Japan 4 May 1973; received in UK for publication 4 June 1973)

The reaction of various thiocarbonyl compounds with diazomethane have been investigated in detail by Schönberg *et al.*,<sup>2)</sup> and they reported the reaction of two reactants mentioned above to give 2:1 adducts of cyclopenta-1,3-dithiolane derivatives without exception.<sup>3)</sup>



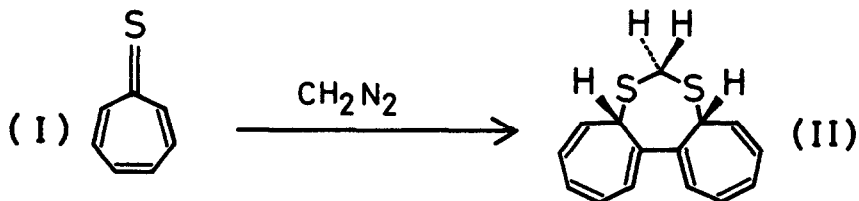
As a part of the program of studies on the chemistry of tropothione (cycloheptatrienethione) (I), the S-analogue of tropone, we carried out the reaction of (I) with diazomethane. Many such adducts as shown below have been reported for the reaction of parent tropone with diazomethane.<sup>4),5)</sup>



Conversely with parent tropone, we have found that (I) reacts smoothly and rapidly along with immediate disappearance of the deep red color, to form stereospecifically the sole product (II) in a good yield.

---

\* Author to whom correspondence and enquires should be addressed.



To a freshly prepared dichloromethane or benzene solution of (I) (8.2 mM), there was added dropwise, at 0° or 10°C, an ethereal solution containing a large excess of  $\text{CH}_2\text{N}_2$  (from 100 mM of N-nitrosomethylurea). The reaction mixture was

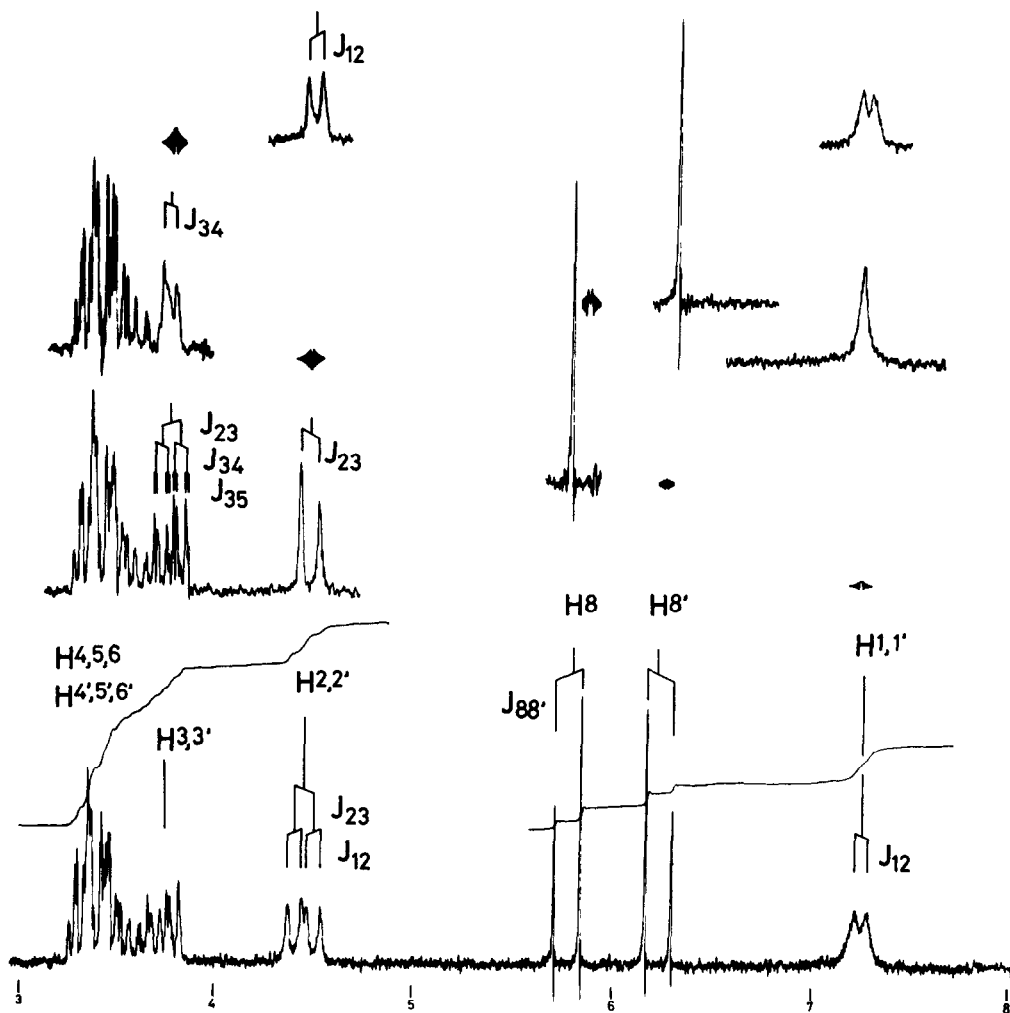
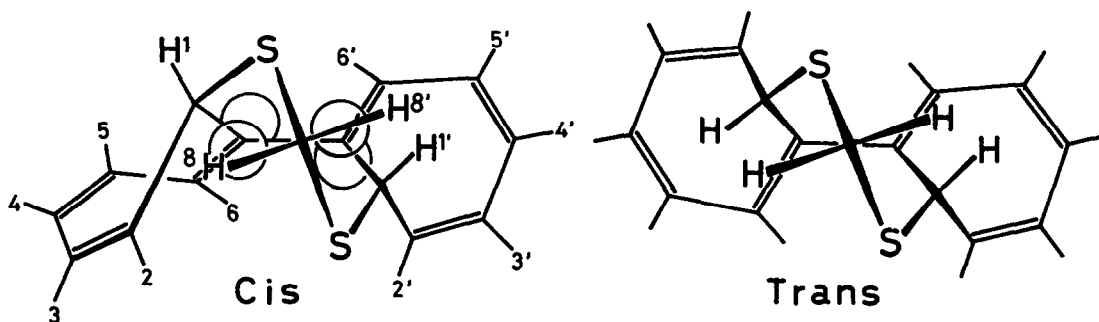


Fig. 1. 100MHz NMR and NMR spectrum of (II).

allowed to stand with stirring for several hours. Then, the remaining residue after solvent removal in reduced pressure below 20°C was purified by silicagel column chromatography and repeated recrystallizations from benzene-MeOH, giving colorless plates (II) of m.p. 120-121°C in 68% yield, (Found: C, 69.97; H, 5.39; S, 24.63: Calcd. for  $C_{15}H_{14}S_2$ : C, 69.72; H, 5.46; S, 24.82%);  $\nu_{\max}$  (KBr): 2973m, 1391s, 1381s, 1195s, 978s, 737vs, and 678vs  $cm^{-1}$ ; nmr ( $CDCl_3$ , TMS):  $\tau$  7.25 (br. d,  $J$  7.0 Hz, 2H,  $H^1$  and  $H^{1'}$ ), 6.24 (d,  $J$  13.0 Hz, 1H,  $H^{8'}$ ), 5.78 (d,  $J$  13.0 Hz, 1H,  $H^8$ ), 4.44 (dd,  $J$  10.0 and 7.0 Hz, 2H,  $H^2$  and  $H^{2'}$ ), 3.75 (ddd,  $J$  10.0, 6.1, and 1.3 Hz, 2H,  $H^3$  and  $H^{3'}$ ), and 3.63-3.25 (complex m, 6H,  $H^{4-6,4'-6'}$ ) shown in Fig. 1. The mass spectrum of (II) included peaks with  $m/e$  258 ( $C_{15}H_{14}S_2^+$ ; molecular ion), 136 ( $C_8H_8S^+$ ; base peak), and 135 ( $C_8H_7S^+$ ).<sup>6)</sup> The microanalytical and molecular weight data are clearly consistent with a 2:1 adduct of (I) and diazomethane minus the elements  $N_2$ . The occurrence of base peak 136 and the strong peak of  $m/e$  135 suggested the typical cleavage of seven membered ring sulfide.<sup>7)</sup>

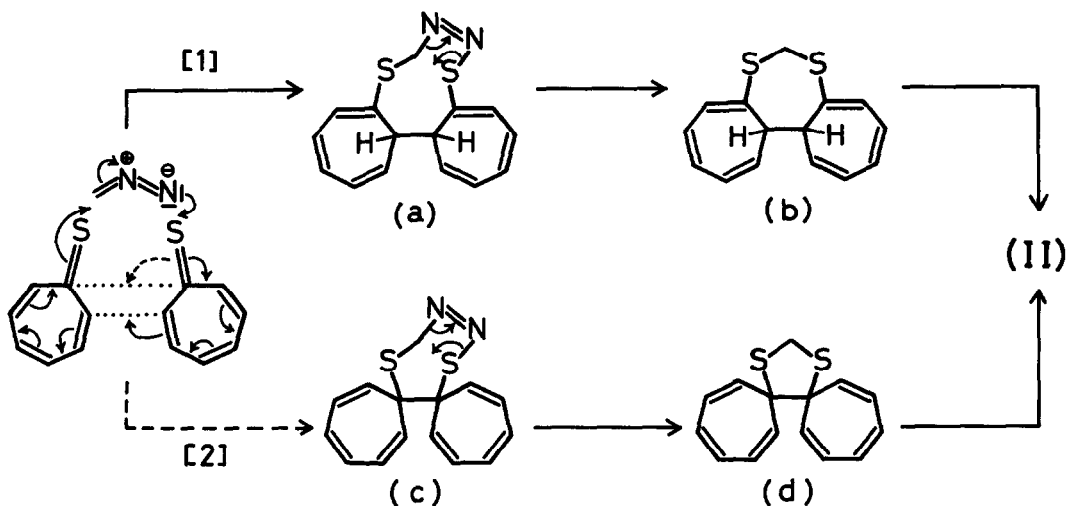
The following evidence clarified the stereochemical relation of two methine protons ( $H^1$  and  $H^{1'}$ ) of (II), that is, they are situated cis.



In the stereo-model, methylene protons ( $H^8$  and  $H^{8'}$ ) of trans-isomer are symmetrically equivalent but those of cis-isomer are chemical shift non-equivalent in agreement with AB type signal in nmr spectrum. Furthermore both of 2p-lobe at C-7 and C-7' positions are orthogonal in accord with ultraviolet spectrum;  $\lambda_{\max}$  (dioxane): 244 ( $\log \epsilon$  3.821) and 294 nm (3.873), which indicates a double chromophore of cycloheptatriene skeleton.

On the basis of the above data, the tricyclic structure (II) was assigned.

We can propose at present tentatively two pathways for this novel formation of (II); [1] by the pericyclic addition<sup>8)</sup> of symmetry-allowed [ $\pi 8_a + \pi 4_a + \pi 8_a$ ] manner



and then the evolution of  $N_2$  and/or a double hydrogen sigmatropic shift, [2] by the cycloaddition of symmetry-allowed  $[\pi_2^s + \pi_4^a + \pi_2^s]$  manner, and doubly sigmatropic rearrangement, as shown in the scheme, respectively.<sup>9)</sup>

Futher investigations on the mechanistic routes are now in progress.

#### REFERENCES AND NOTES

- 1) Part II of this series: T. Machiguchi, K. Okuma, M. Hoshino, and Y. Kitahara, Tetrahedron Letters, in the press; for Part I: T. Machiguchi, M. Hoshino, S. Ebine, and Y. Kitahara, J. Chem. Soc. (Chem. Commun.), 196 (1973).
- 2) A. Schönberg, B. König, and E. Singer, Chem. Ber., 100, 767 (1967).
- 3) M. Fukuyama and A. Ohno, Kagaku no Ryoiki, 22, 1091 (1968).
- 4) M. Franck-Neumann, Tetrahedron Letters, 2143 (1970).
- 5) L. J. Luscus and K. N. Houk, Tetrahedron Letters, 1925 (1972).
- 6) Mass spectra were taken at 75eV by the JEOL JMS-01SG-2 double focusing mass spectrometer which was financed by the Ministry of Education to Saitama Univ.
- 7) Q. N. Porter and J. Baldas, in "Mass Spectrometry of Heterocyclic Compounds," Chapt. 8, Wiley-Interscience, New York, pp. 225 (1971).
- 8) R. B. Woodward and R. Hoffmann, in "Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, p. 169 (1970).
- 9) We cannot preclude the possibility of an initial attack to sulfur atom on the radical derived from  $CH_2N_2$  to give biradical intermediate (ii) which could suffer ring-closure to intermediate (b) or (d).

