

THERMAL DECOMPOSITION OF TROPONETOSYLHYDRAZONE¹

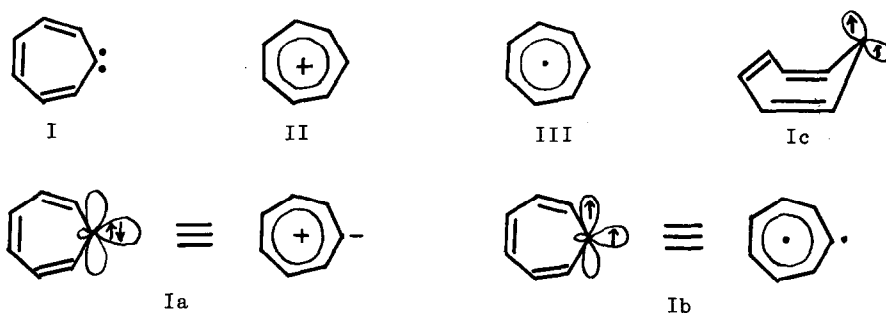
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Cycloheptatriénylidene (I) is of interest from the viewpoint of its structure and chemical behavior as compared with tropylium ion (II)(2) and troyl radical (III)(3). For instance, it is an intriguing problem to know whether the carbene (I) exists as a singlet species (Ia) or triplet species (Ib or Ic)(4). While our investigation of the thermal decomposition of troponetosylhydrazone sodium salt (IV), to examine the formation and the reaction of I, was in progress, Jones and Ennis reported the formation of I by photochemical decomposition of IV and addition reactions of I (5). We now wish to report here an outline of our results obtained so far.



Attempts at photolysis and thermal decomposition at 150° of troponazine (V) (6) have not been successful in the formation of the carbene (I), because of the stability of V. Therefore thermal decomposition of IV, prepared from troponone (7), was carried out. When IV was heated in diglyme at 110°, only tarry product was

obtained after evolution of almost the calculated amount of N_2 gas and isolation of sodium p-toluenesulfinate. However, immediate catalytic hydrogenation of the product using Pd-C or Pt-oxide afforded dicycloheptyl although in poor yield. This fact confirmed the formation of heptafulvalene (VI)(5) and suggested the transient existence of I in this reaction. Refluxing IV in ethanol resulted in decomposition, in which case 7-ethoxytropilidene (VII) was obtained in 60 % yield. Thermal decomposition of IV at about 110° in a mixed solvent system of cyclohexene and diglyme was carried out in an attempt to isolate the spiro compound (VIII), but no such product was obtained (5). On the other hand, the thermal decomposition of IV in diglyme at $105-110^\circ$ in the presence of the olefin dimethyl fumarate afforded in 40 % yield a spirononatriene (IX)(8), m.p. $75.5-76.5^\circ$; m/e 234 (M^+); ν^{KBr} 1718, 746 and 709 cm^{-1} ; λ_{max}^{MeOH} $263\text{ m}\mu$ ($\log \epsilon$ 3.49). The following evidence clarified the stereochemical relation of the two carbomethoxy groups of IX, that is they are situated trans. In the nmr spectra of IX, shown in Fig. 1, saturation of H_B proton changed the doublet peak of the H_A proton to a sharp singlet (9), that is, the shielding effects of the two carbomethoxy groups on the two H_a protons were shown to be equal, as anticipated for the trans form. In addition, the observed value of dipole moment of IX (1.81 D in benzene at 25°) was closer to the calculated value for the trans isomer (2.12 D) than to that of the cis form (2.67 D)(10). Under the same condition as above, IV reacts with dimethyl maleate to give IX in about 25 % yield. This fact suggests that the addition of I to olefins takes place stepwise and leads to the formation of the thermodynamically stable trans isomer (IX). However, the possibility that the cis isomer was formed stereospecifically from I and dimethyl maleate and then isomerized to the trans form under the reaction conditions used, cannot be ruled out (11).

The spiro compound (IX) was catalytically hydrogenated in the presence of Pd-C or Pt-oxide to give a hexahydro derivative (X), m.p. $56.5-57^\circ$; ν^{KBr} 1724 cm^{-1} ; nmr in CCl_4 at 60 Mc, singlet at τ 7.89 (2H, protons in cyclopropane); dipole moment, 1.80 D (in benzene at 25°). Treatment of IX with dilute acid or passing IX through a column containing silica gel afforded a heptafulvene derivative (XI)(5), oil; m/e 234 (M^+); ν^{KBr} 1733 and 1698 cm^{-1} ; λ_{max}^{MeOH} 252 and $340\text{ m}\mu$; nmr in CCl_4 at 60 Mc, singlet at τ 6.70 (2H, methylene protons), two singlets at τ 6.36 and 6.33 (6H,

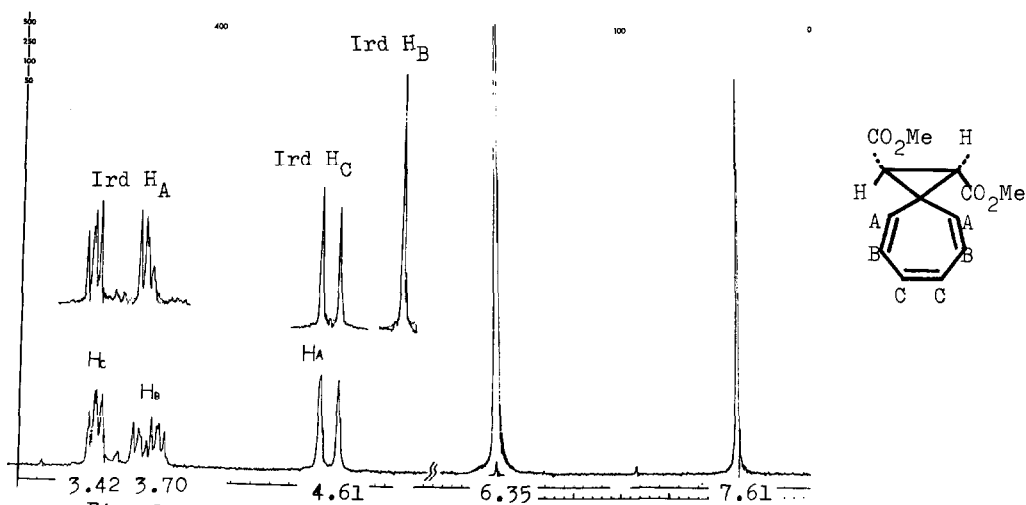
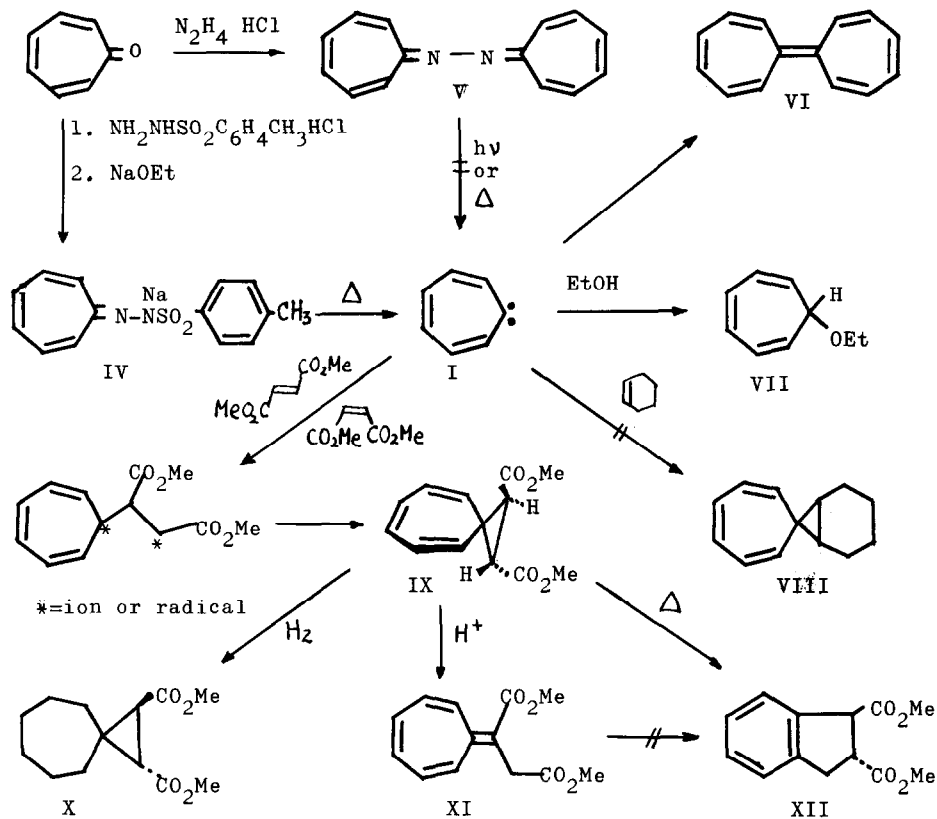
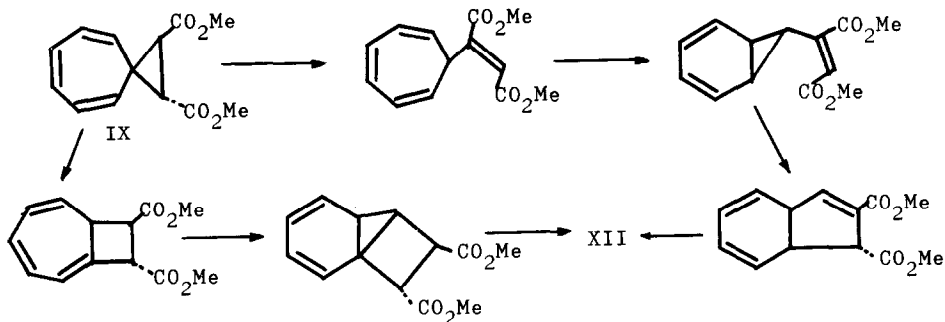


Fig. 1. Nmr Spectra of IX in $CDCl_3$ at 100 Mc.

two methyl groups), multiplet at τ 3.72 (5H, ring protons) and broad doublet at τ 2.55 (1H, ring C₁ proton, $J_{1,2}=12$ cps). When IX was heated in diglyme at 150° for 1 hr an interesting rearrangement occurred in 70 % yield affording trans-1,2-dicarbomethoxyindane (XII)(12), m.p. 69-70.5° ; m/e 234 (M⁺) ; ν^{KBr} 1730, 765 and 752 cm⁻¹ ; $\lambda_{\text{max}}^{\text{MeOH}}$ 256, 260, 266 and 273 m μ (log ϵ 3.00, 3.06, 3.13 and 3.12) ; nmr in benzene at 60 Mc, doublet at τ 6.90 (2H, C₃ protons, $J_{2,3}=8.5$ cps), two singlets at τ 6.65 and 6.63 (6H, two methyl groups), three doublets centered at τ 6.10 (1H, C₂ proton, $J_{1,2}=7.5$ cps) and doublet at τ 5.43 (1H, C₁ proton). The compound XII was formed also by passing IX through vpc column (SE-30 or apiezone grease on chromosorb, at 150°) accompanied with the formation of XI. However, when XI was heated under the same condition or passed through the same vpc column, it did not afford XII. This fact proved that XI was not an intermediate in the thermal rearrangement of IX to XII. Thus we can propose at present tentatively two pathways for this rearrangement.



The fact that the carbene (I) does not add to cyclohexene, but reacts easily with electrophilic olefins such as dimethyl fumarate or maleate giving the spiro compound (IX) indicates that I behaves as singlet species like Ia, as suggested by Jones and Ennis (5). However, the triplet species like Ib or Ic cannot completely be discarded, because I reacts stepwise with dimethyl maleate. To elucidate this point, we are making further studies by esr spectroscopy.

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7. C. H. Analyses of all new compounds synthesized here are satisfactory.
8. The melting point of IX was not reported by Jones and Ennis (ref. 5), but our product is no doubt identical with their product from the agreement of physical data.
9. The authors thank Dr. M. C. Woods of Varian Associate for measuring 100 Mc nmr spectrum of IX.
10. Measurement and calculation of dipole moment were carried out by Dr. H. Watanabe, Shionogi Co. Ltd., whom the authors acknowledge. According his opinion, it is difficult to determine strictly the orientation of two carbomethoxy groups of IX from the value of dipole moment.
11. Examination of the possibility of the thermal isomerization of the cis isomer to the trans one are in progress.
12. J. W. Cook and E. F. M. Stephenson, J. Chem. Soc., 1949, 842. From its melting point, the trans isomer (XII) cannot be distinguished from the cis isomer, but treatment of XII with alkali followed by methylation with diazomethane lead to no epimeric isomer.