

THE STRUCTURE OF (4+2) π TYPE TROPONE PHOTODIMER*¹

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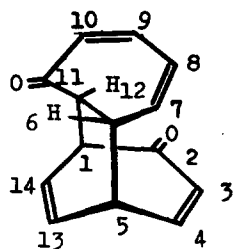
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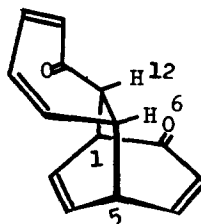
Recently it has been shown that tropone undergoes photodimerization giving several dimers (1,2,3) rather than the valence isomerization which frequently occurred in substituted tropone derivatives when they were exposed to mercury light (4).

Kende has reported the formation of three cyclic dimers of (6+4) π (I), (4+2) π (II) and (6+2) π (III) type, by irradiation of tropone in acetonitrile (3). Independently we have obtained the two dimers, (I) and (II), by irradiation of tropone in ethereal solution (1). Comparison of the physical constants of our dimers with those of Kende showed that they were the same (5) and a structure for dimer I proposed by Kende agreed with that assigned by us (1,3). However we assigned a structure to dimer II, differing in stereochemistry from that proposed by Kende. In this communication we wish to describe our studies which establish the structure of dimer II.

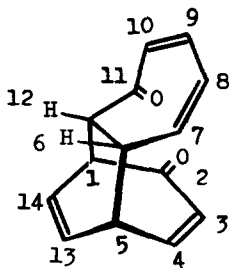
Tropone, on external irradiation of an ethereal solution in a Pyrex vessel with mercury lamp (Toshiba H-400p) for 48 hours, afforded two crystalline dimers: m.p. 137° (I)(5 %) and m.p. 117-118° (II)(9 %) (6) accompanied by a large amount of oily and polymeric material. The structure of dimer I has already been reported (1) and that of dimer II was established as IIa from the following physical and chemical evidence. Ultraviolet spectrum: $\lambda_{\text{max}}^{\text{MeOH}}$ in m μ (log ϵ) 224 (4.04), 290 (3.74) (7); infrared spectrum (KBr): 1667 (s), 1653 (sh), 1631 (w) cm^{-1} ; mass spectrum: m/e 212 (M), 128 (base peak). By catalytic hydrogenation of II over Pd-C, 4 mole equivalents of hydrogen were taken up to give an octahydro derivative (IV) m.p. 97-98°; infrared spectrum (KBr): 1690 cm^{-1} ; mass spectrum: m/e 220 (M). The evidence cited above indicates the presence of both α,β unsaturated ketone and cycloheptadienone groups in II (1,3,7,8), suggesting a (4+2) π type cycloaddition



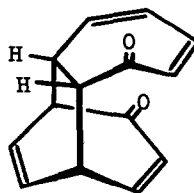
IIa



IIb



IIc



IIId

structure for dimer II. Of the 8 possible stereoisomeric structures of this mode of cycloaddition, the dipole moment 5.70 D, measured in benzene at 25°, eliminated the head-to-tail structures (such as IIId), leaving the head-to-head structures (such as IIa-IIc) for further structural examination since the estimated dipole moments, using unit moment 3.07 D for a carbonyl group, for a head-to-tail dimer and a head-to-head dimer are roughly 3.5 and 5 D respectively (9).

Analysis of the nmr spectrum of dimer II with the aid of double resonance experiment (10) provided definite assignment of protons (Fig. 1) and the following coupling constants: $J_{7,8}=10.5$, $J_{6,7}=4.0$, $J_{6,12}=11.0$, $J_{1,12}\approx 0$, $J_{1,14}=7.5$, $J_{1,3}=2.3$, $J_{13,14}=8.5$, $J_{5,13}=6.5$, $J_{5,6}=3.2$, $J_{4,5}=8.4$, $J_{3,4}=11.0$ cps. Consideration of the relation between coupling constants and dihedral angles of the methine protons eliminated the possible structure IIb, since the dihedral angles of the methine protons of IIb, measured on a Dreiding model, are $\angle H_{6,12}=0^\circ$, $\angle H_{5,6}=80-85^\circ$ and $\angle H_{1,12}=80^\circ$ while estimated angles based on the observed coupling constants are $\angle H_{6,12}=0^\circ$ or $140-145^\circ$, $\angle H_{1,12}=90^\circ$ and $\angle H_{5,6}=55^\circ$. The structure IIb was also eliminated by chemical evidence. The octahydro derivative (IV) (vide supra) underwent intramolecular aldol condensation to afford a ketol (V) when treated with hot base, although the condensation occurred very slowly on treatment of IV with cold base (11). Thus, heating IV in alcoholic hydroxide solution under reflux

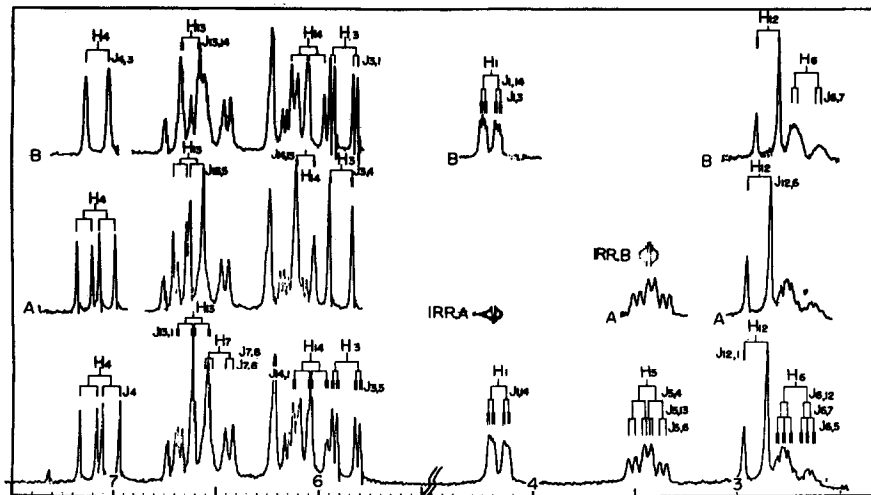
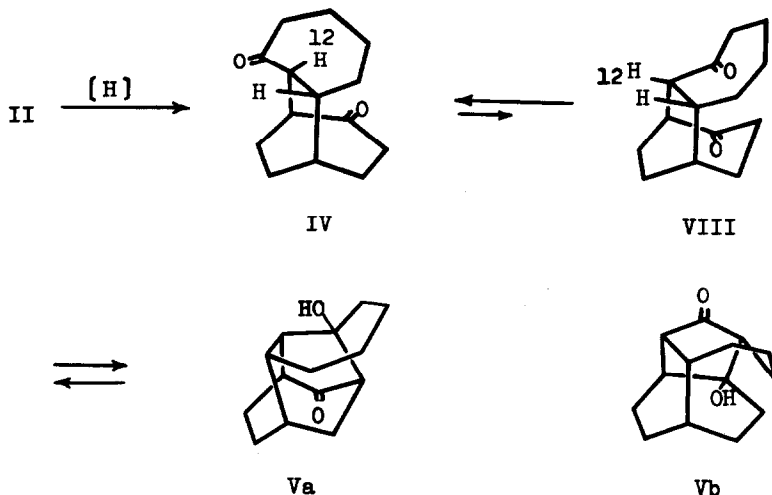


Fig. 1 NMR Spectra of Dimer II at 100 Mc.

afforded a 8:1 mixture of IV and V, m.p. 152-153°, in 90 % yield. The structure of Va could be assigned on the basis of spectra: $\nu_{\text{max}}^{\text{CHCl}_3}$ 3663, 3448, 1742 cm^{-1} ; mass: m/e 220 (M), and from consideration of a molecular model showing that the ketol Va is less sterically hindered than Vb. The transformation of IV to V is reversible. When V was treated with hot base, a 3:2 mixture of V and IV was obtained in 80 % yield (12). The formation of ketol V from IV can not be explained on the basis of structure IIb, which was proposed by Kende (3).

Of two possible stereoisomeric structures (IIa and IIc), detailed nmr analysis provided evidence that IIa is favoured over IIc. Consideration of dihedral angles of the methine protons on a Dreiding molecular model of IIa gave $\angle \text{H}_{1,12} = 90^\circ$, $\angle \text{H}_{6,12} = 145^\circ$ and $\angle \text{H}_{5,6} = 60^\circ$ while that of IIc gave $\angle \text{H}_{1,12} = 60-70^\circ$, $\angle \text{H}_{6,12} = 0^\circ$ and $\angle \text{H}_{5,6} = 45^\circ$. Since the observed coupling constants deduced the dihedral angles $\angle \text{H}_{1,12}$, $\angle \text{H}_{6,12}$ and $\angle \text{H}_{5,6}$ to be 90° , 0° or 145° and 55° respectively, the relation of angles and coupling constants is satisfied in IIa better than in IIc.

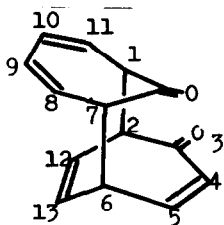
In addition, comparison of the chemical shifts of the olefinic protons of the dimer also supported the structure IIa. Olefinic proton of C_{13} (H_{13}) appeared at 3.38 τ while that of C_{14} (H_{14}) at 3.95 τ , the difference in their chemical shift being 0.57 τ (13, 14). This is an usually large difference in chemical shift for olefinic protons of this kind when they are compared to those of H_6 , H_7 in VI and VII, which are equally shielded by carbonyl groups at C_{10} and C_{11} (15) and/or H_{12} , H_{13} in I. Chemical shifts of H_6 and H_7 in VI were 3.35 and 3.73 τ and/or those



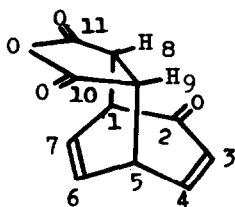
in VII were 3.43 and 3.78 τ respectively (13); the differences of chemical shifts between H_6 and H_7 in VI and VII are 0.38 and 0.35 τ respectively. In dimer I, olefinic protons H_{12} and H_{13} which are shielded by a diene part equivalently appeared at 4.47 and 4.29 τ , the difference in chemical shift being only 0.18 τ (13). The extremely large difference in chemical shift between H_{13} and H_{14} as well as high field position of H_{14} in dimer II could be explained by assuming that H_{14} is specially shielded by the carbonyl group at C_{11} , which is located above H_{14} in IIa. If the structure of dimer II is IIc, the difference in chemical shift between H_{13} and H_{14} may be of the magnitude seen in the olefinic protons (H_6 and H_7) in VI and VII.

The olefinic protons H_3 and H_4 of the unsaturated ketone in II showed respective chemical shifts 4.13 and 2.93 τ in $CDCl_3$. The field position and difference in chemical shift of these protons are in good correspondence with those of H_3 and H_4 in VII, which showed chemical shifts 4.20 τ (for H_3) and 2.90 τ (for H_4) in the same solvent. This evidence indicates that there is no anisotropically influential group, such as carbonyl group, located spatially close to H_3 and H_4 in II (3). Therefore, it may be concluded on the basis of all evidence cited that IIa is more favourable than IIc for the structure of dimer II.

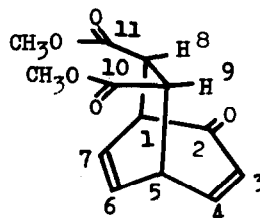
Related evidence which may be consistent with this conclusion was observed on thermal behavior (16) and mass spectral fragmentation of dimer II. Both (6+6) π type and (6+4) π type (I) dimers reverted to tropone when heated at their melting points, while II did not afford tropone on heating at its melting point (16) but instead gave a new compound when heated in benzene under reflux. The mass spectral



I



VI



VII

fragmentation of both (6+6) π dimer and I exhibited peaks at m/e 106 (tropone, 23.8 % for the former and 63.0 % for the latter) and 78 (benzene, base peak for both compounds). The mass spectrum of VI showed peaks at m/e 132 (50 %), 131 (base peak), 104 (55 %), 103 (39 %) and 78 (53 %). However dimer II exhibited peaks at m/e 184 (56.3 %), 156 (23 %), 155 (49.6 %), 141 (99.8 %), 128 (base peak) and 115 (92 %), but no measurable amount of tropone or dehydrotropone peaks in the mass spectrum. The relatively intense peaks of a series m/e 184, 156, 155 and 128 could be explained by comparably rapid decarbonylation at C_{11} giving m/e 184, subsequently another decarbonylation at C_2 giving 156, 155 and deacetylation affording the naphthalene peak (128). The fact that the base peak in mass spectrum of II is naphthalene (m/e 128) instead of tropone may support the assigned configuration of the ring juncture at C_6 and C_{12} of IIa (17, 18).

On the basis of the structure IIa the formation of the ketol V can be explained as follows. The octahydro derivative IV, on treatment with base, epimerized first to VIII, which rapidly afforded the ketol by aldol condensation. The equilibrium between IV and VIII will be directed toward IV so that the epimeric ketone VIII could not be detected by our procedure. Five atoms of hydrogen were exchanged by deuterium on treatment with sodium deuterioxide in *d*-alcohol at room temperature, accompanied with the formation of a small amount of the ketol, indicating that the epimerization at C_{12} of IV is possible.

The mechanistic path way for the formation of dimer II is of interest. It may be explained either by a two step trans cycloaddition mechanism or by one step Diels Alder type cycloaddition of trans or Möbius type tropone, which is formed by excitation, to a second molecule of tropone in the ground state. We are investigating this point as well as the chemistry of dimer II.

Acknowledgement. Financial support from Sankyo Co. is acknowledged.

REFERENCES AND FOOTNOTES

- * Organic Photochemistry VI. For part V, see reference 1.
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 5. We thank Dr. A. S. Kende for comparison of IR spectra of our dimers with his dimers.
 6. Satisfactory elemental analyses for all compounds whose melting point are cited in this paper were obtained.
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 9. We thank Dr. H. Watanabe, Shionogi Co. Ltd., for measurement and discussion of dipole moment.
 10. We thank Dr. M. C. Woods, Varian Associate, and Mr. Miura for double resonance experiments and helpful discussion of nmr spectra.
 11. On standing in cold base for 40 hours IV was converted to V (ca. 9 %).
 12. Reconversion of V to IV (ca. 20 %) also occurred when V was treated with cold base for 36 hours.
 13. Nmr spectra of I, II, VI and VII were taken in CDCl_3 +d-benzene (1:1), CDCl_3 , pyridine and CDCl_3 respectively.
 14. Olefinic protons H_{13} and H_{14} in II measured in pyridine solution appeared at 3.42 and 3.97 τ respectively; the difference in chemical shift between these protons is 0.55 τ . This indicates that both of these protons is slightly shifted to higher field in pyridine solution than in CDCl_3 but the difference of chemical shift between H_{13} and H_{14} is of the same order as that obtained in CDCl_3 .
 15. For the preparation and the structural confirmation, see T. Nozoe, T. Mukai, T. Nagase and H. Toyooka, Bull. Chem. Soc. Japan, 33, 1247 (1960).
 16. We are indebted to Dr. A. S. Kende for his helpful suggestion concerning the unusual thermal behaviour of dimer II and stereochemistry of junction.
 17. However this is not conclusive but only suggestive to the structure of dimer II, because we do not have any evidence that IIc does not give naphthalene as base peak in mass spectral fragmentation.
 18. We thank Mr. T. Sato for measurement of mass spectra.