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PHOTODIMERIZATION REACTION OF TROPONE[1]

T. Tezuka, Y. Akasaki and T. Mukai
Department of Chemistry, Faculty of Science
Tohoku University, Sendai, Japan

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Photocycloaddition reactions are of special interest from the point of molecular orbital symmetry considerations.[2,3] Recently we have found that irradiation of tropone in acidic media provided a trans $(6+6)\pi$ type cycloaddition product, dimer I,[4] whereas in neutral media such as in ether it afforded two different dimers, one of which was confirmed to be a $(6+4)\pi$ type cycloaddition product, dimer II. The recent publication of Kende,[5,6] describing the formation of dimer II in addition to two other dimers on irradiation of tropone in acetonitrile, prompted us to report an outline of our study on dimer II.

Tropone, on external irradiation of an ethereal solution in a Pyrex vessel with mercury lamp (Toshiba H-400p), afforded dimer II, m.p. 137° (decomp),[7] (5% yield) and colorless needles, m.p. 117-118° (9 %)[8] accompanied by a large amount of oily and polymeric materials. The structure of II was elucidated from the following physical and chemical evidence. The mass spectrum included peaks with m/e 212 (molecular ion), 149, 106 (corresponding to tropone) and 78 (base peak, benzene).[9] Upon heating at melting point for 10 min II decomposed to tropone, which was identified by IR spectrum and by formation of picrate, m.p. 99°. The UV and IR spectra of II supported the presence of cis diene and saturated and α,β-unsaturated keto groups: λ_{max}^{MeOH} in mμ (log ε), 228 (sh, 4.00), 257 (3.67), 268 (3.69) and 285 (sh); ν_{max}^{KBr} in cm^{-1} 3030, 2899, 1695, 1670, 1653, 835 and 702. The nmr spectrum of II showed absorptions ascribed to eight olefinic and four aliphatic protons (Fig. 1_a). Assignment of these protons was provided by decoupling technique. When methine protons H_1, H_2 and H_7 appearing at around τ 6.50 in $CDCl_3$-C_6D_6 (1:1) were saturated, an AA' BB' type coupling pattern for H_8-H_{11} was observed centered at τ 4.80 (Fig. 1_b). This coupling pattern

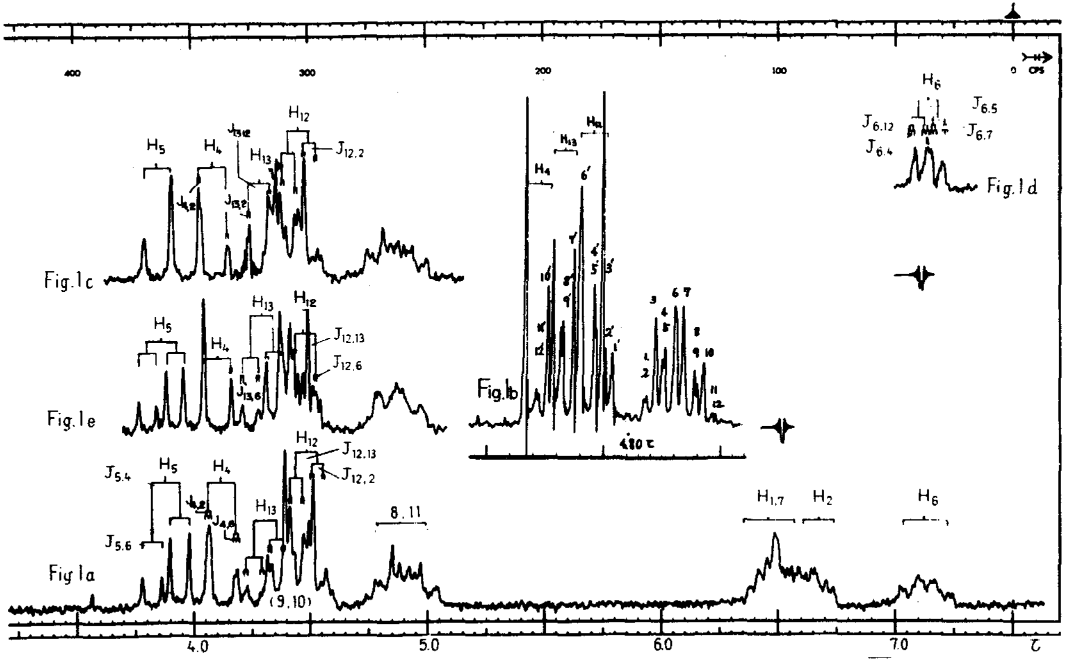
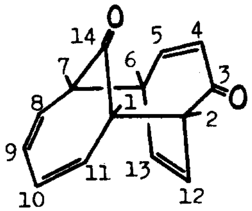


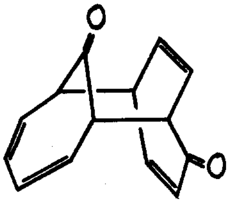
Fig. 1. NMR Spectra of Dimer II measured on a Varian HA 100 in C_6D_6 except for Fig. 1b.

is similar to the AA' BB' type pattern observed for dimer I, suggesting that II also has a symmetrical cis diene system as in I. Each line of this pattern is marked by numbering in Fig. 1b. On saturation of H_6, the signals of H_5 and H_{13} appearing at τ 3.87 and 4.29 respectively showed doublets with small splittings (Fig. 1c). On the other hand, on saturation of H_{13} the signal of H_6 appeared as a quartet with small splittings (Fig. 1d). When H_1, H_2 and H_7 at around τ 6.50 were saturated, the signal of H_{13} appeared as quartet while H_4 and H_{12} showed broad doublets (Fig. 1e). From the above decoupling experiments, the following coupling constants were obtained: $J_{2,4}$=0.8, $J_{2,12}$=5.8, $J_{2,13}$=1.0, $J_{4,5}$=12.0, $J_{4,6}$=0.2, $J_{5,6}$=8.1, $J_{6,7}$=5.5, $J_{6,12}$=1.2, $J_{6,13}$=7.0 and $J_{12,13}$=10.0 cps.

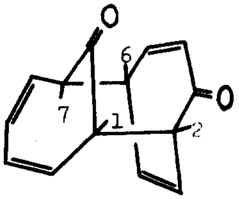
Summarizing the evidence cited above, two possible structures IIa or IIb are deduced for dimer II. Catalytic hydrogenation of II over 10 % Pd-C in ethanol afforded an octahydro derivative (III), b.p.$_{0.07}$ 150-155° (bath temperature), $\nu_{max}^{CHCl_3}$ in cm^{-1} 1690 (seven-membered C=0), and a hydroxyketone (IV),[10] m.p. 79°, $\nu_{max}^{CHCl_3}$ in cm^{-1} 3597, 3448 (OH) and 1736 (five-membered C=0).



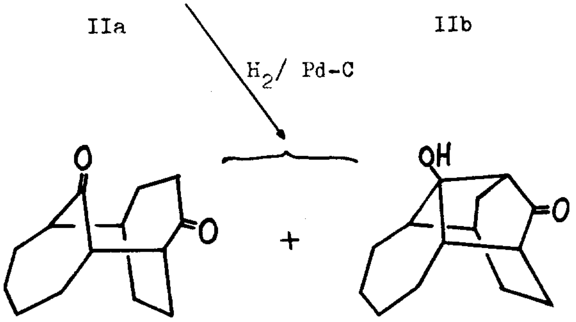
IIa



IIb

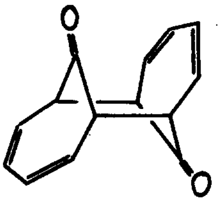


IIc



III

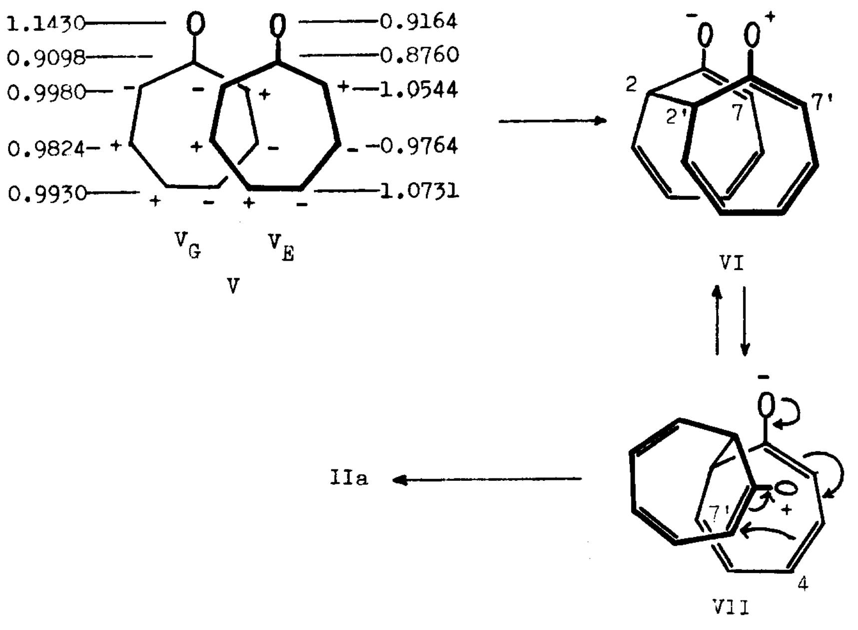
IV



I

The hydroxyketone (IV) was also obtained from III by treatment with base as reported by Kende.[5] The formation of IV from II or III indicates that the two carbonyl groups at C_3 and C_{14} in II must be spatially close, strongly supporting IIa for the structure of II. Inspection of a Dreiding model still offered slight possibility that the strained structure such as IIc in which H_1 and H_7 are trans would fit the above description. However, the observed coupling constant between H_6 and H_7 (5.5 cps, v.s.) suggested the dihedral angle between H_6 and H_7 to be about 50°, eliminating structure such as IIc. Thus, it is concluded that IIa is the only possible structure for dimer II.

It is predicted from the molecular orbital symmetry consideration that (6+4) π type cycloaddition should not occur photochemically but will occur thermally if the reaction proceeds via a concerted one step process.[2,3] The formation of this unique dimer II may be rationalized on the basis of the two step mechanism described below.



Calculation of the π- electron density of the ground and of π- π^* (or n- π^*) excited state[11a,b] of tropone from LCAO MO coefficients[12] indicated that in the ground state (V_G), the oxygen atom of tropone has negative character compared to the ring, while in the excited state, the oxygen atom has positive character compared to the ring (V_E). An excited molecule of tropone, therefore, tends to approach a second tropone molecule of the ground state in the head-to-head fashion by Coulomb interaction if there is no such strong dipolar interaction in the ground state as in the formation of dimer I in acidic media.[4] Moreover, this type of approach of two molecules of tropone in the transition state, one in the excited and the other in the ground state, is supported by the frontier molecular orbital consideration.[3] If we can safely assume that the overlap between the molecular orbital of the first excited level of tropone in the excited state and the lowest vacant molecular orbital in the ground state plays a significant role in determining the stereochemical course of photocycloaddition, the head-to-head approach shown in V will be one of the lowest energy state. The plus and minus signs of V indicate the symmetry of LCAO MO of the lowest vacant level of tropone.

Oxygen-oxygen intramolecular repulsion in the product may not help simultaneous bond formation between C_2 and $C_{2'}$, and/or C_7 and $C_{7'}$, which leads to the formation of cis (6+6) π type product, but may influence formation of a dipolar intermediate VI. Rotation around the single bond of VI brings the intermediate to a stable conformer such as VII which, in turn, affords the (6+4) π type cycloaddition product (II) by bond formation between C_4 and $C_{7'}$, as shown by the arrows.

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REFERENCE AND FOOTNOTS

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2. R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc., 87, 2046, 4388 (1965).

3. K. Fukui, *Molecular Orbital Theory in Chemistry, Physics and Biology*, P-O. Löwdin, B. Pullman ed., Academic Press Inc., New York, 1964, P 513.
4. T. Mukai, T. Tezuka and Y. Akasaki, *J. Am. Chem. Soc.*, **88**, 5025 (1966).
5. A. S. Kende, *ibid.*, **88**, 5026 (1966).
6. We thank Dr. Kende for identification of our sample with his dimer, m.p. 141-142°, by comparison of IR spectra.
7. Dimer II melted at 141-142° when temperature was raised quickly, but it melted at 137° with decomposition when it was raised slowly. Satisfactory elemental analyses were obtained for all new compounds.
8. Physical data such as nmr and IR spectra of this compound agree with those of the (6+2)π type dimer, m.p. 118-119°, reported by Kende (ref. 5). Studies on the structure of this compound are in progress.
9. H.Budzikiewicz, C.Djerassi and D.H.Williams, *Interpretation of Mass Spectra of Organic Compound*, Holden-Day, Inc., San Francisco, Calif., 1964, P 241.
10. It is likely to suppose that IV was derived from II either by direct reductive transannular bond formation or by subsequent Michael condensation of the primary hydrogenation product (III).
11. a) The values of the π- electron density calculated for n-π* transition are not shown in the text. The calculations clearly indicate that the oxygen atom of tropone has positive character compared to the ring in the excited state regardless of the origin of transitions (π-π* or n-π*).

    b) Although there is no conclusive evidence at present of wether the dimerization of tropone arose from π-π* or n-π* excitation, we suggest on consideration of the solvent effect to the product formation that the trans (6 + 6)π type cycloaddition giving dimer I in acidic media occurs from π-π* transition (ref. 4), while two step cycloaddition giving dimer II may result from n-π* transition state of tropone. Studies on this point are in progress.
12. ASMO calculation of tropone system was carried out by Y. Amako, H. Yamaguchi and H. Azumi, using parameter $\beta_s/\beta_d = 0.5$, $\alpha_{co}=\alpha_{c=c} + 0.2\beta_{c=c}$, for elucidation of UV spectrum of tropone. Detail will be published. We thank them for their permission to use their result before publication.