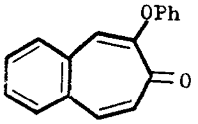
Tetrahedron Letters No.18, pp. 2175-2180, 1968. Pergamon Press. Printed in Great Britain.

PHOTODIMERIZATION OF 2-METHYL-4,5-BENZOTROPONE (1)

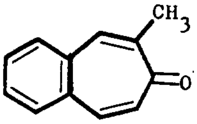
T. Mukai, T. Miyashi and Y. Tanaka*
Department of Chemistry, Faculty of Science
Tohoku University, Sendai, Japan

(Received in Japan 30 December 1967).

Recently, several interesting examples of the photodimerization of the tropone derivatives have been reported (1,2,3,4,5). Of these examples, the photodimerization of 2-phenoxy-4,5-benzotropone (I) reported by Chapman et al (2) is noteworthy in that migration of the phenyl group during dimerization was observed. In order to investigate the effect of the condensed benzene ring on the photo-behavior of the troponoid systems and to compare the results with the photodimerization of I, the photochemistry of 2-methyl-4,5-benzotropone (II) was studied. It was discovered that II, on irradiation, did not afford any of the valence tautomers obtained in the case of the monocyclic troponoids (6), but gave two kinds of photoproducts including a dimer. The result will be reported here.



(I)



(II)

When a solution of I in acetonitrile was irradiated externally in Pyrex vessel, under nitrogen atmosphere using high pressure mercury lamp (Toshiba H400-p), two products, III, m.p. 267°, and IV, m.p. 304-6°, were obtained in 2～3 and 9～10 % yield accompanied with a large amount of polymer. The yields of III and IV were practically unchanged, if benzene, acetone and isopropyl alcohol were used as the solvent. Elemental analysis and molecular weight determination by mass spectroscopy (Table I) show that IV is a dimer, $C_{24}H_{20}O_2$ and III is a dehydrogenated

---

* Present Address: Research Laboratory, Taisho Pharmaceutical Co., Ltd.

product, $C_{24}H_{18}O_2$. The similarity of IR and UV spectra of III to those of the starting material (II) suggests that III has the skelton of the 4,5-benzotropone. On the other hand, it is likely from its spectral data (Table I) that IV has an endo cyclic styryl ketone chromophor (7).

TABLE I. Spectral data of II and its Photo-products (III and IV)

	m/e	IR (cm^{-1}) in KBr	UV mμ (log ε) in MeOH(a) or $CHCl_3$(b)
II		1614, 1590	a 354 (3.71), 337 (3.89) 271 (4.63) and 233 (4.60)
III	338	1618, 1582	a 358 (4.20), 340 (4.26) 279 (4.63) and 230 (4.62)
IV	340	1691	b 301 (4.22)

The nmr spectrum of III at 60 Mc, in $CDCl_3$ exhibits all signals in aromatic proton field (multiplets at δ 7.80-7.40, 12 H), except for a doublet of the methyl protons (δ 2.35, J=1.0 cps, 6 H). Splitting of the methyl signal is ascribed to the long range coupling with H_A at the C-3 position. This means that the bond

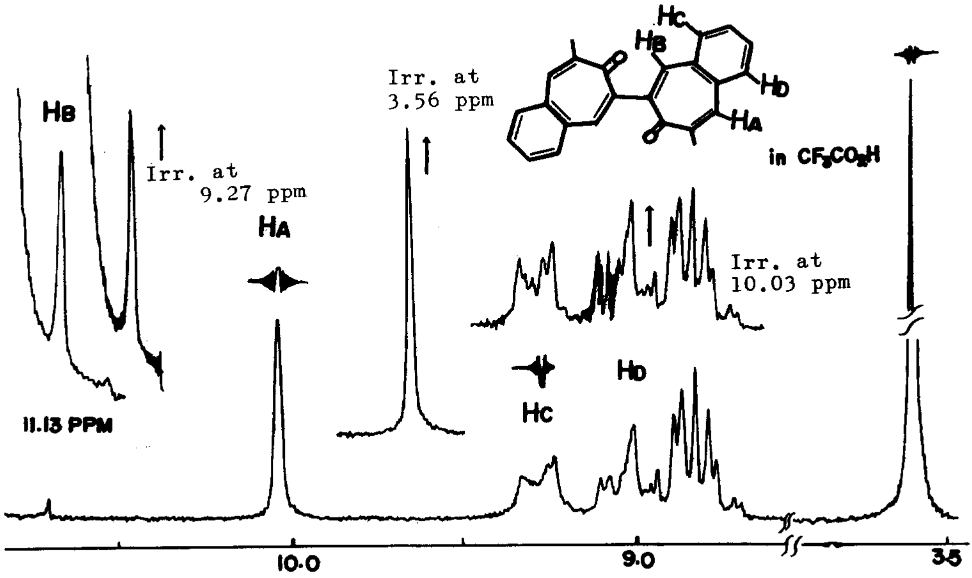
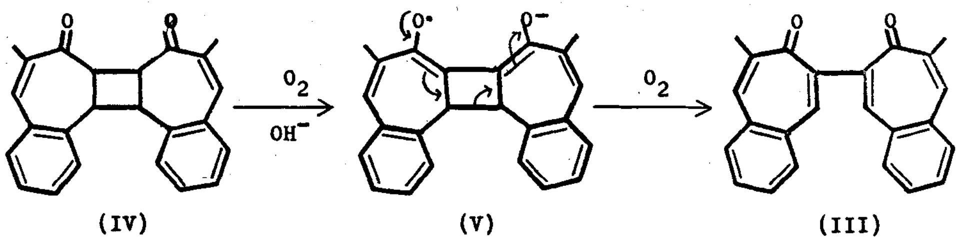


Fig. 1. Nmr spectrum of III at 100 Mc, in CF_3COOH

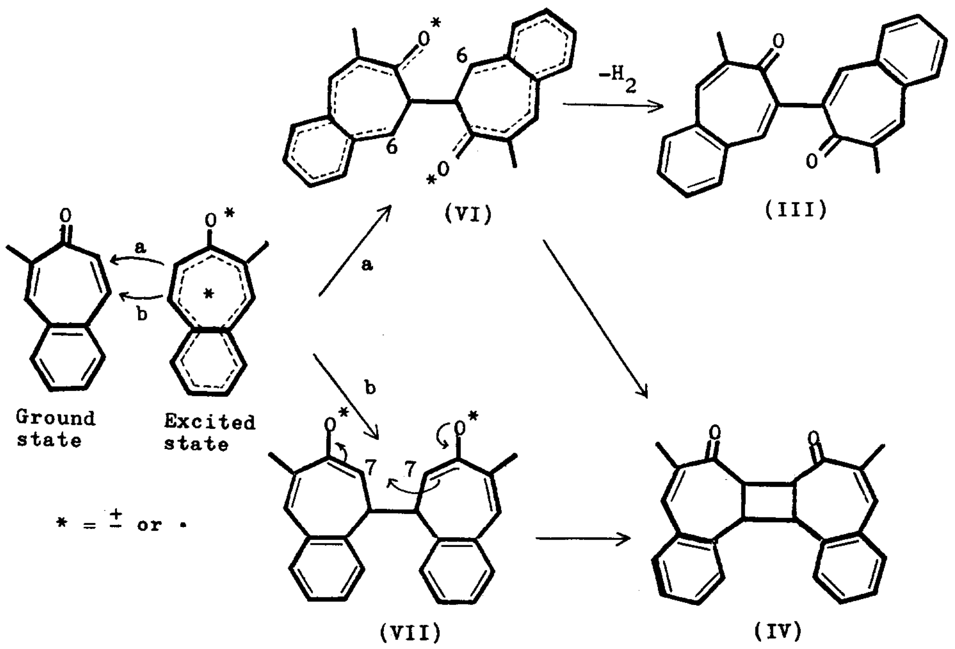
formation does not occur at the C-3 position. When the nmr spectrum of III is measured at 100 Mc. in CF_3COOH, the signals shown in Fig. 1 could be observed. There is no AB type pattern ascribed to two protons situated at the C-6 and 7 positions, which appears in the nmr spectrum of the starting material (II) in the same solvent. Assignment of the protons designated by H_A, H_B, H_C and H_D could be provided by application of the decoupling technique. For instance, the long range coupling between H_B at the C-6 position and H_C at the benzene ring was observed in Fig. 1. This fact indicates that the bond formation should occur at the C-7 positions, thus establishing the structure of product III.

On the other hand, dimer IV is so sparingly soluble in usual organic solvents that it is impossible to measure the nmr spectrum or dipole moment in the usual way. However, when the nmr spectrum is measured at 150° in dimethylsulfoxide-D_6, IV exhibits an obscure AB type pattern ascribed to the methine protons (δ 3.66, 3.72, J=12 cps.). Attempted thermal decompsition and treatment with acid of IV failed to give II. However, upon oxidation by bubbling oxygen into a dioxane solution containing sodium hydroxide at 80~90°, IV afforded III in almost quantitative yield. This transformation can be explained reasonably by the oxidation of a dienolate anion of 1,4-diketone (IV) (8) followed by the oxidative ring opening of an anion radical (V) formed transiently. On the basis of this fact and the physical data described above, the structure of dimer IV was established. Although four stereoisomers are possible for dimer of II, the relationship between III and IV excludes the head-to-tail type structure for IV. However, it is not



enable in this stage to determine whether IV is of the syn or anti type.

This type of photodimerization is usual in the case of α,β-unsaturated ketones (9), but our observation, together with the dimerization of dibenzocycloheptatrienenone reported recently (10) are the first examples in the photoreaction of the troponoid systems. In addition, the formation of III is also an interesting photoreaction of troponoids. Therefore, the possible pathways for the formation of III and IV shall be discussed. The dimer IV may be formed by one-step cycloaddition of II to a second molecule of II (10) or by the stepwise cycloaddition described later. Although III was obtained in the base-catalysed autooxidation of IV as mentioned before, IV did not give III under the irradiation conditions used. For instance, the irradiation of a benzene solution of IV in the presence of oxygen, iodine or benzophenone did not provide even a trace of III. In addition, when a solution of II in isopropyl alcohol was irradiated under completely degassed condition, III and IV were obtained in the exactly same yield as in the usual conditions. These facts suggest that IV cannot be considered as an intermediate in the formation of III from II. Consequently, there exists the possibility that $n-\pi^*$ excited state of II attacks a ground state molecule of II to give



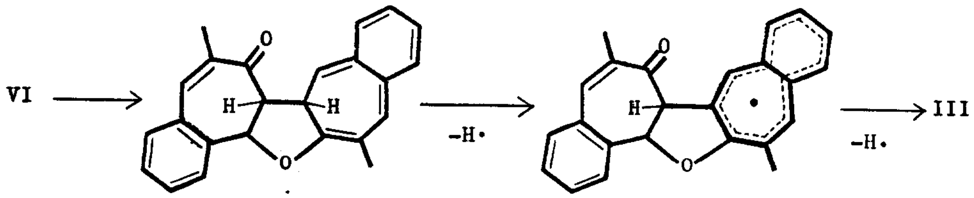
an intermediate (VI), which affords not only III by some dehydrogenation process[+], but gives also the dimer IV by the bond formation at the C-6 positions. The dehydrogenation does not take place by the oxygen present, but is assumed to arise from hydrogen abstraction by excited ketones such as II or IV. Although another intermediate (VII) is possible for the formation of dimer IV (12), it cannot afford III. The intermediate (VI) has a quinonoid structure as a partial structure, but it is favored over VII in the degree of steric hindrance to formation of the corresponding intermediates. The fact that the irradiation of II affords only a head-to-head type dimer such as IV may be ascribed to the steric interference of the methyl group at C-2 position during the course of the photodimerization.

Aknowledgement. The authors thank Professor K. Suzuki of Yuwate University for his cooperation in early stage of this work. Financial support from Sankyo Co. is also acknowledged.

REFERENCES

1. Organic Photochemistry VII. Preceding paper, T. Tezuka, Y. Akasaki and T. Mukai, *Tetrahedron Letters*, **1967**, No. 49.
2. O. L. Chapman, H.G. Smith, R. W. King, D. J. Pasto, M. R. Stoner, *J. Am. Chem. Soc*., **85**, 2031 (1963).
3. (a) T. Mukai, T. Tezuka, Y. Akasaki, *ibid*., **88**, 5025 (1966) (b) T. Tezuka, Y. Akasaki and T. Mukai, *Tetrahedron Letters*, **1967**, 1397.

[+] One of the possible pathways for the formation of III from VI is via an intermediate having hydrofuran ring depicted here (see ref. 5 and 11).



4. (a) A. S. Kende, *J. Am. Chem. Soc.*, **88**, 5026 (1966) (b) A. S. Kende, J. E. Lancaster, *ibid.*, **89**, 5283 (1967).
5. T. Mukai, T. Miyashi and M. C. Woods, *Tetrahedron Letters*, **1967**, 433.
6. (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963). (b) D. J. Pasto, *Org. Photochem.* **1**, 155 (1967).
7. R. D. Campbell and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 3456 (1957).
8. W. G. Dauben, G. A. Boswell and W. Templeton *J. Org. Chem.*, **25**, 1853 (1960).
9. (a) P. E. Eaton, W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966) (b) J. L. Ruhlen, P. A. Leermakers, *ibid.*, **88**, 5672 (1966) (c) E. Y. Y. Lam, D. Valentine and G. S. Hammond, *ibid.*, **89**, 3482 (1967).
10. W. Tochtermann, G. Schnabel und A. Mannschreck, *Ann.*, **705**, 169 (1967).
11. The carbonyl oxygen atom of tropones is liable to form tetrahydrofuran ring. A. S. Kende, *Tetrahedron Letters*, **1967**, 2661 and Ref. 5.
12. T. Mukai, T. Tezuka, T. Miyashi and Y. Akasaki, *Sci. Repts. Tohoku Univ.*, *I*, **50**, 186 (1967).