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ORGANIC PHOTOCHEMISTRY. IV.[1] A NOVEL PHOTODIMERIZATION IN THE TROPONOID SYSTEM. A DIMER OF 2-METHOXY-6-PHENYLTROPONE

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During a study of the photochemistry of the methyl ethers of 3-, 4- and 5-phenyltropolones, 2-methoxy-6-phenyltropone (I) was found to undergo a new type of dimerization[1,2] which is the first example of a 1,8-dipolar addition, in the photochemistry of conjugated ketones, to afford a hydrofuran derivative.

External irradiation of a methanol solution of I, in a Pyrex vessel under nitrogen atmosphere using a high pressure mercury lamp (Toshiba H400-p), affords the following four photo-products; the dimer II (4 % yield), $C_{28}H_{24}O_4$,[3] mol. wt. 432 (osmometry), m.p. 172°; 1-methoxy-4-phenyl- $\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (III) (15 %), m.p. 63°; 3-methoxy-7-phenyl- $\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (IV) (13 %), m.p. 128°; and methyl 4-oxo-2-phenylcyclopentenylacetate (V) (8 %), m.p. 77°.

The dimer II exhibits absorption at 320 mμ (log ε 4.20, in MeOH) and at 1681 cm^{-1} (KBr), indicating the absence of a tropone nucleus but the presence of extended conjugation and a conjugated carbonyl group. It does not possess any photochemical relationship with other photo-products III, IV and V, since irradiation of these compounds gives products which do not include the dimer II.[4] Pyrolysis of II at 430° reconverts it to the starting material (I), while treatment with hot dilute acid gives 4-phenyltropolone, m.p. 95°.

The nmr spectrum of II is relatively straightforward and can be unambiguously assigned (see Table) with the aid of double resonance experiments and solvent-induced shifts, in $C_6D_6/CDCl_3$ mixtures, to separate overlaping signals.

Consideration of the coupling constants[5] and chemical shifts[6] given in the

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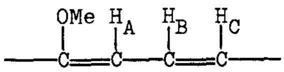
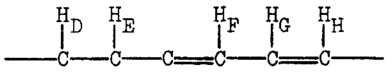
* Varian Associates.

Table leads immediately to the following arrangement of protons.[7]



$$-\overset{OMe}{C}=\overset{H_A}{C}-\overset{H_B}{C}=\overset{H_C}{C}-$$



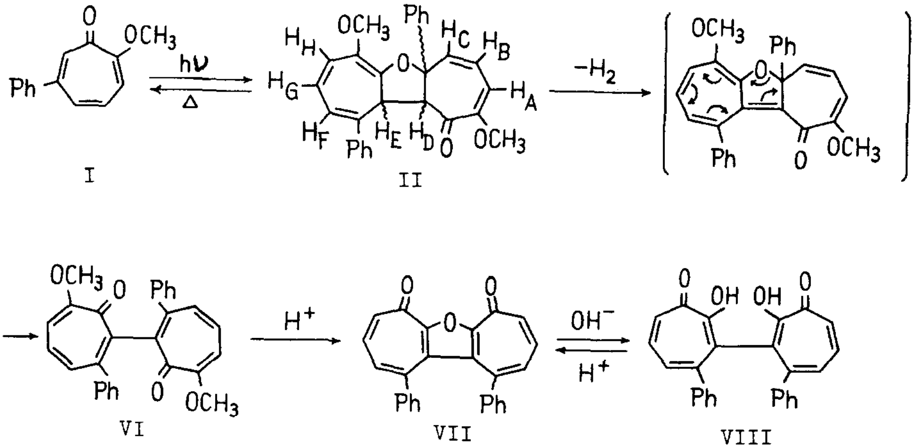
$$-\overset{H_D}{C}-\overset{H_E}{C}-C=\overset{H_F}{C}-\overset{H_G}{C}=\overset{H_H}{C}-$$

TABLE. Assignment of 100 Mc Spectrum ($CDCl_3$)*

Proton(s)	ppm	multiplicity	J(cps)
phenyl (10 H)	ca. 7.2	complex multiplet	
methoxyl (3 H)	3.39	sharp singlet	
methoxyl (3 H)	3.45	d	(0.4)
H_A (1 H)	5.56	d of q	(8.5, 0.4)
H_B (1 H)	5.94	d of d	(8.5, 11.3)
H_C (1 H)	6.67	d	(11.3)
H_D (1 H)	4.04	d	(9.0)
H_E (1 H)	3.75	d of d of d	(9.0, 1.5, 0.5)
H_F (1 H)	6.02	d of d of d	(4.6, 1.5, 1.5)
H_G (1 H)	6.29	d of d	(12.0, 4.6)
H_H (1 H)	6.39	d of d of d	(12.0, 1.5, 0.5)

* Measured on a Varian HA. 100. Coupling constants are assumed to be approximately equal to the splittings; d=doublet, q=quartet.

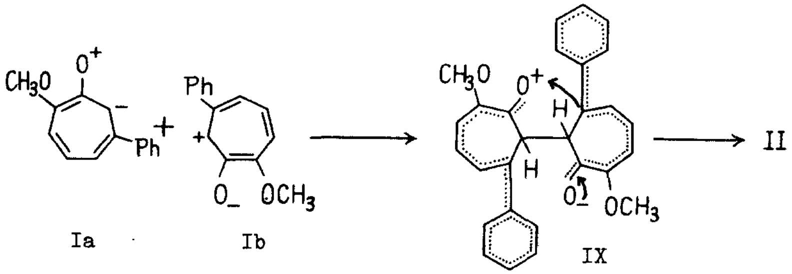
Dehydrogenation of the dimer II with dichloro-dicyano-1,4-benzoquinone in benzene at room temperature furnishes a dimethoxy diphenylditroponyl (VI), m.p. 277°, $\nu\,cm^{-1}$ (KBr) 1613 and 1592 (characteristic of C=O and C=C bonds in tropones). Its nmr spectrum (60 Mc, $CDCl_3$) shows a six-proton methoxyl singlet at 3.90 ppm, suggesting a symmetrical structure. Hydrolysis of compound VI with boiling 1N hydrochloric acid affords a 3,3'-bitroponylene-2,2'-oxide derivative (VII), m.p. 303°, $\nu\,cm^{-1}$ (KBr) 1621 and 1588 (C=O and C=C bonds). Its 100 Mc nmr spectrum ($CDCl_3$) discloses the presence of two phenyl groups [complex broad signals at 6.5 (4H) and 7.1 ppm (6H)] and, more significantly, a six-proton ABX pattern at 6.78 (2H quartet, 7.8 and 1.4 cps splittings), 7.31 (2H quartet, 7.8 and 12.4 cps splittings) and 7.28 ppm (2H quartet, 12.4 and 1.4 cps splittings). Assignment of the ABX pattern was confirmed by measuring the spectrum of VII in a series of mixed solvents ($CDCl_3/C_6D_6$ and $CDCl_3$/acetone). The two large <u>ortho</u> couplings (ca. 12 and 8 cps)[8] and the degree of symmetry unequivocally establish the structure of VII as 4,4'-diphenyl-3,3'-bitroponylene-2,2'-oxide. Because of the large steric interference between the two phenyl groups in compound VII, this molecule is unlikely to be planar.


I II VI VII VIII

Alkaline hydrolysis of VII affords 4,4'-diphenyl-3,3'-ditropolonyl (VIII), m.p. 225°, νcm^{-1} (KBr) 3080 (hydrogen bonded OH), 1620 and 1572 (C=O and C=C bonds); $FeCl_3$ color test characteristic of tropolones. Treatment of VIII with conc. hydrochloric acid reaffords VII. This series of reactions is very similar to that reported for 6,6'-diisopropyl-3,3'-ditropolonyl.[9]

The ease with which VII is formed from the dimer suggests structure II for the latter, and this is the only likely structure compatible with the ultraviolet and infrared spectra and the proton arrangement deduced from the nmr. The stereochemistry of the dimer II is not known, since, although the coupling constant (9 cps; see Table) between H_D and H_E may suggest a <u>cis</u>-configuration of these hydrogen atoms, the <u>trans</u>-arrangement can not be discarded in the case of a strained five-membered ring as in II.

The mechanism for the photodimerization of I is not clear at present, but it is reminiscent of the photocyclization of carbonyl compounds and olefins to form oxetane derivatives. The following 1,8-dipolar addition by a two-step mechanism can be considered as a suggested reaction pathway. The excited molecule (Ia) formed by an n-π^* transition adds to the ground state molecule (Ib) to give an ionic intermediate (IX), which is stabilized by contribution of the phenyl groups to the resonance hydrid. This stabilization of IX by the appropriately located phenyl groups is assumed to be the reason why, of the methyl ethers of 3-, 4- and 5-phenyltropolones, only the compound I could furnish the dimer.



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