Three Photodimers of 1,1-Dimethyl-2(1*H*)-naphthalenone

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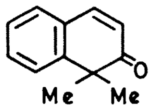
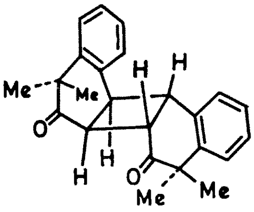
Summary Irradiation of 1,1-dimethyl-2(1*H*)-naphthalenone afforded three photodimers whose structures were elucidated on the basis of dipole-moment and n.m.r. spectral data.

RECENTLY, Carnduff *et al.* reported the isolation of a single photodimer by sunlight-irradiation of 1,1-dimethyl-2(1H)-naphthalenone (I) and elucidated its stereochemistry as (II) by *X*-ray analysis.[1] We have isolated two other dimers (III) and (IV) as well as (II) on irradiation of (I) and determined the stereochemistry of the products by physical data (Table).

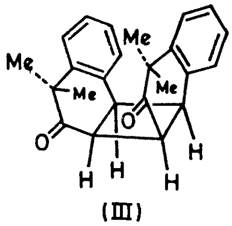
Four stereoisomers are possible for the photodimers of (I). Comparison of the observed dipole-moment values with the calculated values indicates that (II) and (III) are head-to-head isomers and (IV) is a head-to-tail isomer. When the n.m.r. spectrum of (II) is compared with that of (III), signals due to the methyl groups of (III) appear at higher field and signals due to phenyl protons as more complex peaks. This phenomenon may be ascribed to the anisotropic effect of a nearby benzene ring, thus indicating the *syn*-configuration for (III). Since the signals ascribed to the methyl and the phenyl protons of (IV) are more similar to those of (II) than to those of (III), the *anti*-configuration is assigned to (IV). In addition, the fact that among three dimers (IV) exhibits benzyl proton signals at the lowest field and signals due to the proton α



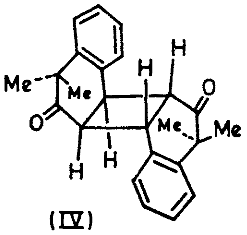
(I)



(II)



(III)



(IV)

to the carbonyl group at the highest field, can be explained on the basis of the anisotropic effect of the carbonyl group and the benzene ring. This suggests (IV) to be an *anti* head-to-tail isomer.

TABLE

		(II)	(III)	(IV)
M.p. and yield[a]		206°, 75%	225°, 7%	261°, 7%
I.r. (CO) (cm^{-1}) in $CHCl_3$		1709	1713	1704
μ(D)	obs. (Benzene, 25°)	3·87	4·23	1·16
	calc.[b]	2·9—4·9	4·7—4·9	0—1·7
N.m.r.[c] (τ) in $CDCl_3$	Methyl protons	8·63 (s) 8·42 (s)	8·86 (s) 8·77 (s)	8·66 (s) 8·40 (s)
	Cyclobutane ring protons (A_2B_2 type)	6·22 (m) 5·88 (m)	6·22 (m) 5·66 (m)	6·56 (m) 5·54 (m)
	Phenyl protons	2·67 (bs)	2·7—3·2 (m)	2·68 (bs)

[a] A methanol solution ($3{\cdot}5 \times 10^{-2}$M) was externally irradiated in a Pyrex vessel using high pressure lamp (Toshiba H 400p).
[b] Calculation was done on the basis of the value 2·75 D for β-tetralone. [c] Abbreviations s, m, and bs mean singlet, multiplet, and broad singlet, respectively.

When the solvent is changed from methanol to acetone, acetic acid, benzene, and cyclohexane, the ratio of (II) + (III)/(IV) changes as follows: 12·8, 6·7, 5·7, 2·7, and 2·1. Increasing the concentration of the solution of (I) also resulted in some increase of the ratio of (II) + (III)/(IV). The photodimerization of (I) is retarded in the presence of triplet quenchers such as oxygen or biacetyl (E_T 55 kcal/mole). However, when the concentration of biacetyl is low, no change in the ratio of (II) + (III)/(IV) is observed, although the formation of the photoproducts is slow. Irradiation of (I) by light of wavelength greater than 340 nm also affords the same photodimers. These facts indicate that the photoreaction of (I) takes place *via* an n–π^* triplet state. We conclude that the photodimerization of (I) is different from that of coumarin,[2] but similar to that of cyclopent-2-enone and cyclohex-2-enone.[3] However, the formation of the *syn*-dimer (III) is of interest from a mechanistic viewpoint.

(*Received, December* 31*st*, 1969; *Com.* 1974.)

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