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THE DI-π-METHANE REACTION OF 4-BENZYL-5,5-DIMETHYL-2(5H)-FURANONE

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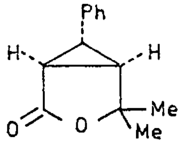
Upon irradiation of 6-*exo*-phenyl-4,4-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (1) in acetonitrile with λ 254 nm[1] a primary product 2 [(δ, $CDCl_3$, p.p.m.) 7.38 (m,5, arom), 5.45 (t,1, vinyl H,J=2 Hz), 3.58 (d,2, $-CH_2-$, J=2 Hz), 1.50 (s,6, *gem*-CH_3)] and a secondary product 3 [(δ, $CDCl_3$, p.p.m.) 7.38 (s,5, arom), 2.4 (m,1, cyclopropyl H), 1.5 (m,2, cyclopropyl H), 1.54 (s,3, $-CH_3$), 1.25 (s,3, $-CH_3$)] were obtained. On the basis of the ^1H n.m.r. data 2 and 3 were assigned to be 4-benzyl-5,5-dimethyl-2(5H)furanone and 4,4-dimethyl-5-phenyl-3-oxabicyclo[3.1.0]hexan-2-one respectively.

The formation of 3 can be explained by a di-π-methane reaction of 2. The rearrangement of 2 to 3 could also be effected upon acetone photosensitized irradiation of 2: irradiation of 10 mg 2 in 0.5 ml acetone with λ 300 nm for 24 hr afforded 20% conversion of 2 to 3.



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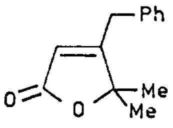

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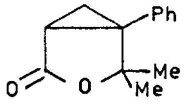

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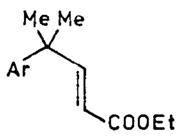
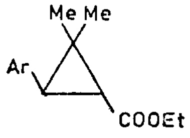
Our results are complementary and of interest in relation to the conclusion drawn by Hixson *et al.*[2] from both his photochemical study on ethyl 4-(1-naphthyl)-4,4-dimethyl-butenoate (4a) and on that by Hammond *et al.*[3] on ethyl 4-phenyl-4,4-dimethylbutenoate (4b). The di-π-methane reaction of 4b to yield 5b



4a, Ar= 1-naphthyl
b, Ar= phenyl



5a, Ar= 1-naphthyl
b, Ar= phenyl

could only be effected upon direct irradiation (λ 254 nm), but not upon the acetone photosensitized irradiation (λ 300 nm). The photoreaction of 4a to yield 5a could be effected both by direct irradiation (λ > 300 nm) and upon the xanthone photosensitized irradiation of 4a. Hixson explained the difference in behaviour of 4a and 4b in terms of energy localisation. Upon the xanthone sensitized irradiation of 4a the triplet energy was considered to be localized in the naphthyl moiety, whereas with 4b the triplet energy would be localized in the α,β-unsaturated ester group from which it could possibly be dissipated by facile E-Z isomerization (the "free rotor effect"[4]) before the di-π-methane reaction can take place.

The present findings with 2 (in which the "free rotor effect" cannot operate because the C=C bond is contained in a five membered ring) firmly substantiate the suggestion made by Hixson that the "free rotor effect" in 4b is responsible for the non-occurrence of the di-π-methane reaction of the triplet excited state of 4b.

References

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