55. Photochemical Synthesis of 9-Methyl-tetracyclo$[5.3.0^{4,9}.0^{8,10}]$-decane-2,6-dione

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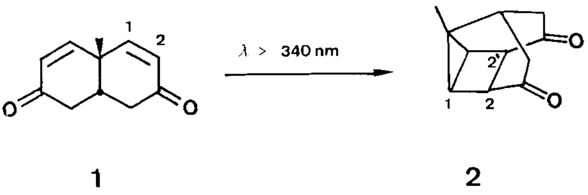
Summary

Irradiation ($\lambda > 340$ nm) of *cis*-8a-methyl-1,2,4a,7,8,8a-hexahydronaphthalene-2,7-dione (**1**) in benzene affords the title compound **2** *via* an intramolecular [2+2]-cycloaddition.

1,4-Dienes usually undergo the di-π-methane rearrangement on photochemical excitation [1]. Occasionally, an alternative path involving an intramolecular [2+2]-cycloaddition to yield a bicyclopentane derivative is followed [2-4]. A detailed analysis of the ^{1}H-NMR. and ^{13}C-NMR. spectra for the previously reported photoproducts was not possible. Their structures were assigned based on the absence of olefinic protons in the ^{1}H-NMR. spectrum, the symmetric carbon skeleton deduced from the ^{13}C-NMR., as well as the MS. analysis. We now report the synthesis of a tetracyclic diketone containing the bicyclopentane unit wherein such a complete NMR. analysis is feasible.

Irradiation of an Ar-degassed $5 \cdot 10^{-2}$M solution of the bis-enone **1** [5] in benzene or CH_2Cl_2 affords a single photoproduct as monitored by TLC. The product **2** was obtained in 74% yield after crystallization. The mass-spectrum of **2** ($M^+ = 176$, base peak at 120 m.u.) and the IR. spectrum ($\tilde{\nu}(C{=}O) = 1720$ cm^{-1} in CCl_4) suggest the formation of an isomeric saturated diketone *(Scheme)*.

Unambiguous proof for the proposed structure of **2** comes from the ^{1}H- and ^{13}C-NMR. spectra in $CDCl_3$. Due to the carbonyl groups adjacent to the cyclobutane ring the differences in chemical shifts of C(1) and C(2) and of H–C(1)



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and H–C(2) become significant, thus allowing their assignment[2]): H–C(1): 2.03 ppm (*d*×*d*); H–C(2): 3.13 ppm (*d*×*d*); C(1): 24.5 ppm (*d*); C(2): 46.6 ppm (*d*). Finally the magnitude of the coupling constants (J(H–C(1),H–C(2)) = 2.0 Hz; J(H–C(1),H–C(2')) = 1.6 Hz; J(C(1),H–C(1)) = 185 Hz; J(C(2),H–C(2)) = 150 Hz) fully agree with the values expected for a bicyclopentane unit constrained in such a polycyclic cage-structured molecule.

Irradiation of a similar solution of **1** in benzene, saturated with isobutene, in a merry go round apparatus leads again to the exclusive formation of **2**, but the rate of conversion is now about 20% slower. This result suggests that the primary intramolecular bonding step (the one forming the cyclopropane bond) is more efficient than the interaction of the enone with isobutene, and that - in terms of the accepted mechanism for enone-olefin cycloadditions [6] - the exciplex or the diradical formed from **1** and isobutene decays back to starting material, rather than forming a new cycloadduct.

Experimental Part

General remarks. Chemical shifts in the NMR. spectra are given in ppm relative to TMS (= 0 ppm) as internal standard.

Photolyses. Irradiations were carried out in a merry-go-round apparatus filtering the light of a 250 W mercury lamp ($\lambda > 340$ nm). A solution of 45 mg **1** in 5 ml benzene or CH_2Cl_2, degassed with Ar or saturated with isobutene, was irradiated for 12 h. After evaporation of the solvent, the residue was crystallized from cyclohexane to afford 33 mg **2**, m.p. 131-133°.

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[2]) For numbering see the *Scheme.*