Tetrahedron Letters No.5, pp. 379-382, 1969. Pergamon Press. Printed in Great Britain.

THE PHOTOSENSITIZED REARRANGEMENT OF BENZOBICYCLO[2.2.2]OCTADIENONES

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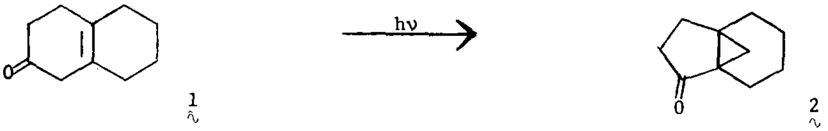
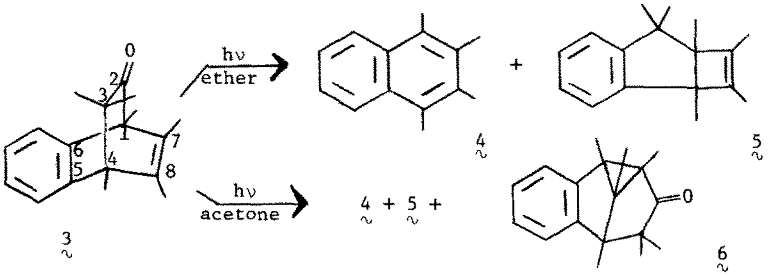
(Received in USA 8 November 1968; received in UK for publication 17 December 1968)

While the most common photochemical transformation of medium-sized monocyclic β,γ-unsaturated ketones involves a 1,3-acyl shift and migration of the allylic double bond,[2] 3-cyclohexenones such as 1 have been observed[3] to photochemically rearrange with 1,2-acyl migration, to yield conjugated cyclopropyl ketones (2). The multiplicity of this photorearrangement has not been reported. We have examined the photochemistry of a related bicyclo system, 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one, 3.[4] Our results permit deductions regarding the multiplicity of the excited states in these rearrangements, and the competition between these and di-π-methane photorearrangements.[5]

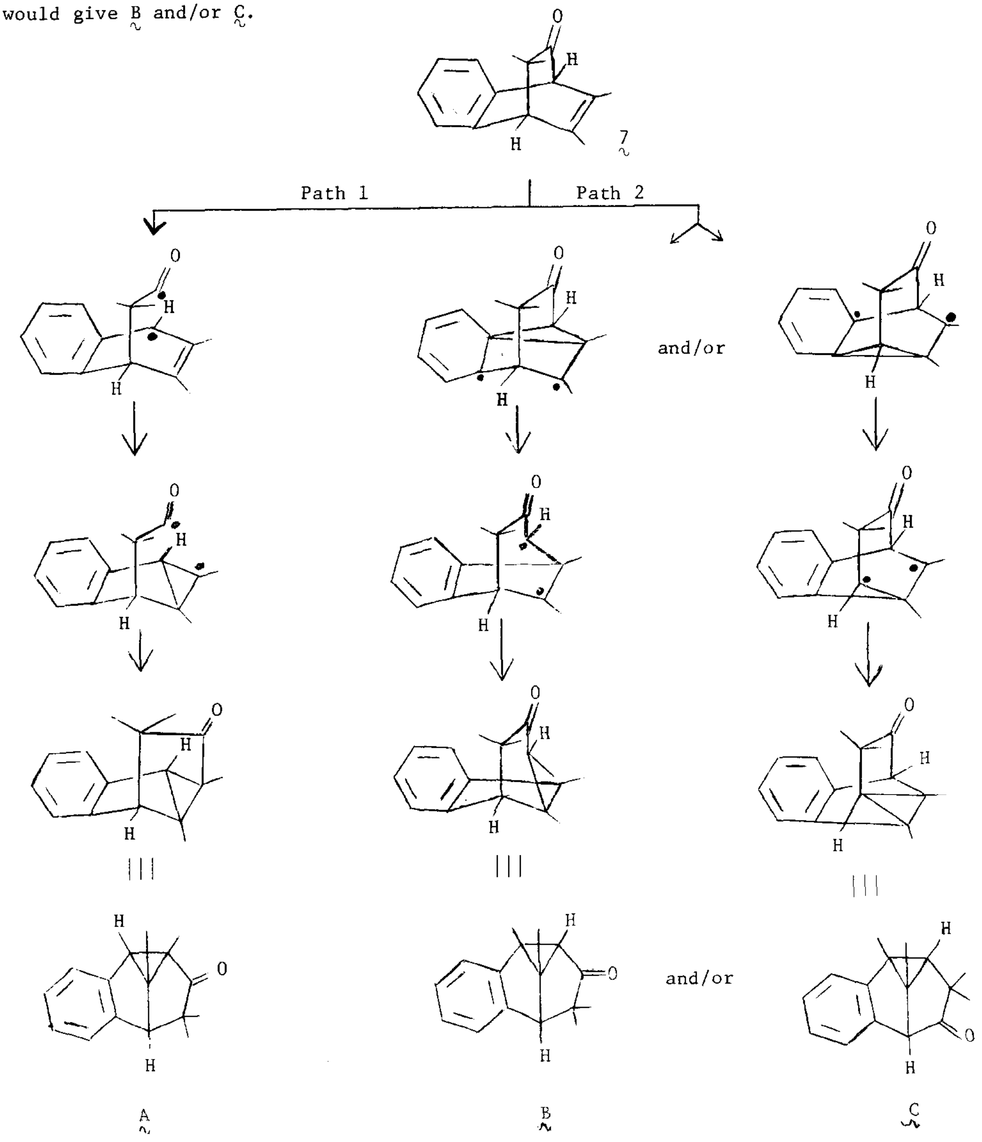


As recently reported by us,[6] irradiation of an ether solution of 3 through a Corex filter provides 1,2,3,4-tetramethylnaphthalene (82% yield) and 5 (13%). However, irradiation of 3 with acetone sensitization under identical conditions, when allowed to proceed to 91% conversion, gave 4 (45% yield), 5 (6%) and an isomeric ketonic product 6[7] (26%): mp 100-102°; $\nu_{C=O}^{CCl_4}$ 1720 cm^{-1}; $\lambda_{max}^{95\% \ EtOH}$ 278 (ε 1150) and 270 mμ (1370) with a shoulder at 263 mμ (1450); nmr

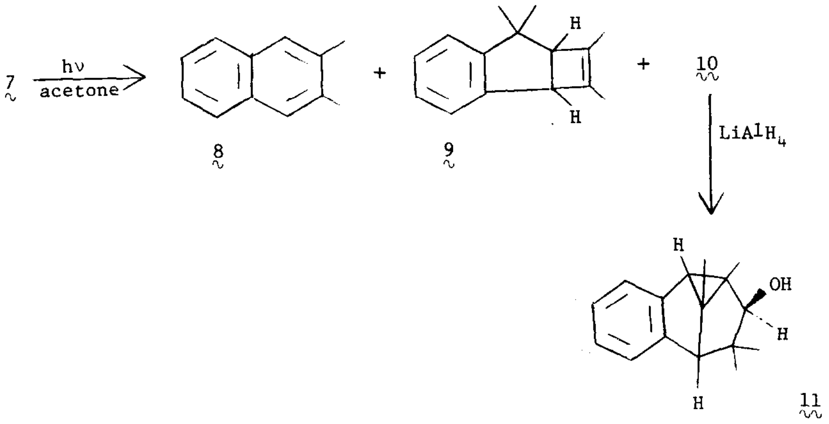


spectrum (CD$_3$CN): three-proton singlets at τ 9.44, 8.90, 8.74, 8.68, 8.63 and 8.57 and an aromatic multiplet τ 2.90-3.22 (4H).

As the formation of 6 only occurs with acetone sensitization, the reaction must proceed *via* the triplet. Two molecular pathways seem reasonable for the formation of 6 and 3: (1) acyl migration in 3 from C-1 to C-7 followed by rebonding between C-1 and C-8, analogous to the rearrangement 1→2, or (2) a regiospecific[8] di-π-methane rearrangement[5] in which only one of the two possible products which might be formed *via* benzo-vinyl bridging is observed. Differentiation between these mechanisms is possible *via* the ketonic photoproduct from tetramethyl ketone 7, for acyl migration (path 1) would provide A, while a di-π-methane rearrangement (path 2) would give B and/or C.



Acetone sensitized irradiation of 7[9] through a Corex filter with a Hanovia L 450-w lamp affords 2,3-dimethylnaphthalene (66% yield), 9[10] (6%) and an isomeric ketonic product 10 (9%): $\nu_{C=O}^{CCl_4}$ 1721 cm^{-1}, $\lambda_{max}^{95\%\ EtOH}$ 279 (ϵ 660) and 271 mμ (840) with a shoulder at 263 mμ (930); nmr spectrum: three-proton singlets at τ 9.38, 8.79, 8.65 and 8.44, sharp one-proton singlets at τ 7.80 and 6.97 and an aromatic multiplet τ 2.81-3.10 (4H).



Reduction of 10 with lithium aluminum hydride yields alcohol 11. A characteristic infrared absorption[4,11] at 3644 cm^{-1} defines the stereochemistry of the hydroxyl group, while the nmr spectrum: three-proton singlets at τ 9.22, 8.95, 8.80 and 8.57, <ins>sharp</ins> one-proton singlets at τ 8.20, 7.30 and 6.92 and an aromatic multiplet τ 2.90-3.13 (4H) requires a reduction product in which there are no protons on adjacent carbon atoms. Thus 10, the precursor of 11, must be ketone A and the formation of 6 and 3 occurs from the triplet *via* 1,2-acyl migration (path 1).

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