Tetrahedron Letters No.48, pp. 4995-4998, 1968. Pergamon Press. Printed in Great Britain.

CONTRAST BETWEEN THERMAL AND PHOTOCHEMICAL REVERSE DIELS-ALDER REACTIONS INVOLVING KETENES

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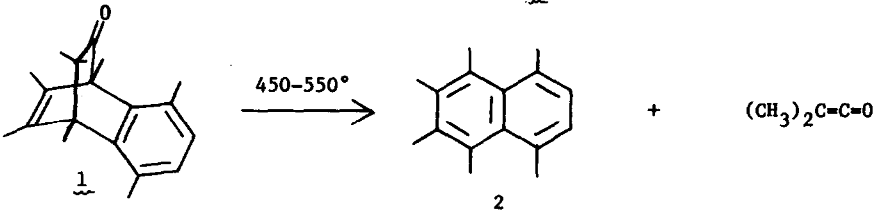
(Received in USA 28 June 1968; received in UK for publication 2 September 1968)

Thermal elimination of dimethyl ketene from 1, a reverse Diels-Alder reaction, proceeds quantitatively, but requires temperatures which might be considered unusually high (450-550°),[2] particularly when the aromaticity of the product (2) is taken into account.[3,17] Accordingly,



1

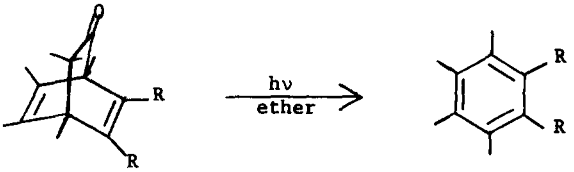
2

we investigated this type of reaction photochemically. Whereas the photochemistry of a number of bicyclo-β,γ-enones has been extensively studied,[4,5] only recently has there been a report of a related system where the pi-electrons of more than one double bond can interact equally with the carbonyl group.[6]

Hexamethyl-2,4-cyclohexadienone[7] readily gave bicyclo[2.2.2]octadienones 3 and 4 with dimethyl acetylenedicarboxylate and diphenylacetylene.[8,9] Irradiation of a 1% ether solution of 3 through a Corex filter with a Hanovia L 450-w lamp for two hours provided an 80% yield of

3, $R{=}CO_2CH_3$

4, $R{=}C_6H_5$

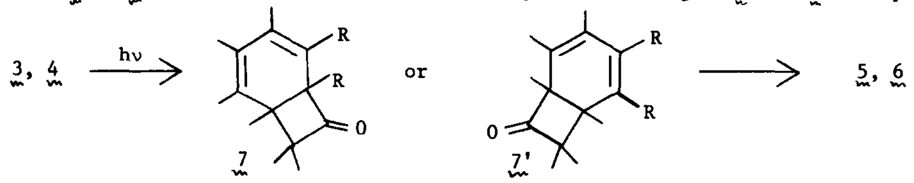


5, $R{=}CO_2CH_3$

6, $R{=}C_6H_5$

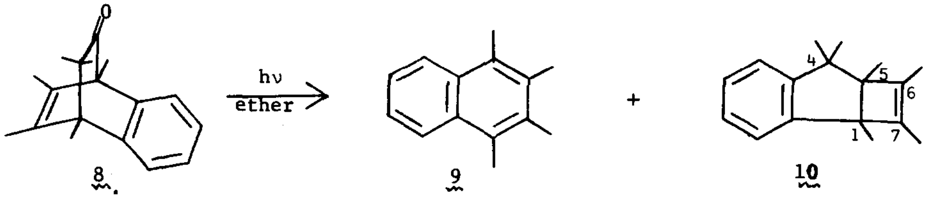
dimethyl 3,4,5,6-tetramethylphthalate, 5. Irradiation of 4 under identical conditions gave an 83% yield of 3,4,5,6-tetramethyl-1,2-diphenylbenzene, 6. Dimethylketene formed during the reaction was trapped as the anilide.

Two alternative mechanisms can be suggested for these conversions: (a) direct photoelimination of dimethylketene, either concerted or stepwise; or (b) photorearrangement to the cyclobutanone 7 or 7'[10] which then eliminates dimethyl ketene to give 5 and 6. Many other



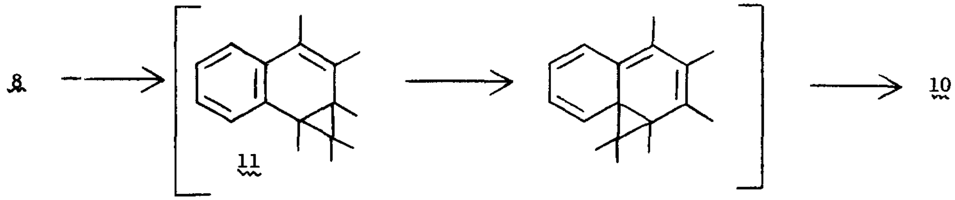
β,γ-unsaturated ketones undergo photorearrangements formally analogous to path b.[4] When a solution of 3 in methyltetrahydrofuran was irradiated for short intervals at -100° in a sodium chloride cavity cell, the ketene was detected[11] by its intense ir absorption at 2135 cm^{-1}. Thus for path b to be plausible, elimination of ketene from 7 or 7' must be efficient at -100°.

Irradiation (6 hr) of a 1% ether solution of 8[12] through a Corex filter with a Hanovia L 450-w lamp proceeded with 86% conversion to provide 82% of 1,2,3,4-tetramethylnaphthalene and

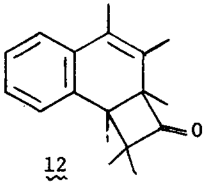


13% of 1,4,4,5,6,7-hexamethyl-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, 10.[13] The elemental analysis and mass spectrum (parent peak at m/e 226) of 10 indicated that it was formed by the loss of carbon monoxide from 8. The ultraviolet spectrum of 10 in 95% ethanol had maxima at 274 (ε 1910), 267 (ε 1980), and 211 mμ (ε 8580) with shoulders at 262 (ε 1470) and 330 mμ (ε 4860).[14] The nmr spectrum showed singlets at τ 8.95 (3H, methyl at C-1), 8.83 (3H, methyl at C-5), and 8.75 (6H, gem-methyls at C-4), quartets at τ 8.53 and 8.59 (3H each, methyls at C-7 and C-6, J = 1.2 Hz), and a singlet at τ 3.05 (4H, aromatic protons).[15]

The formation of 10 from 8 can be accounted for by the initial production of the benzonorcaradiene 11 which then photochemically rearranges to provide 10. An analogous photo-



rearrangement of the type 11 ⟶ 10 has been observed.[14] Either the photochemical elimination of carbon monoxide from an intermediate cyclobutanone 12[16] or the elimination of carbon monoxide from the diradical 13 or 13', followed by appropriate rebonding, would account for the formation of 10.



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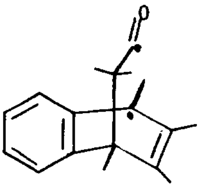

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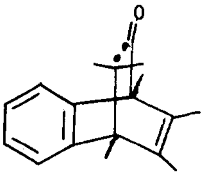

13'

The ease with which ketenes are formed by this photochemical reverse Diels-Alder reaction is in marked contrast to the high temperature required for the thermal reaction. If the reaction is a concerted reverse 2 + 4 cycloaddition these results would be contrary to expectation.[17] Since the photochemical excitation involves the carbonyl group, it may be necessary to include the carbon-oxygen double bond in the electron count for cycloadditions involving ketenes.

Further studies to determine the nature of the excited state and the scope of this photoreaction are in progress.

Acknowledgement. We are indebted to the National Science Foundation for generous support.

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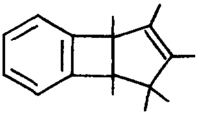
13. The alternative structure **10'**, although also plausible mechanistically, seems less likely by comparison of uv and nmr spectra with those of model compounds, but chemical proof is desirable.



10'

14. *Cf.* 4,4-dicyano-2,3-benzobicyclo[3.2.0]hepta-2,6-diene, λ_{max}^{MeCN} 273 mμ (ε 570), 266 (550), 260 (370), and 214 (8000); E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1967).

15. The nmr assignments follow from the preparation of labeled **10** from variously methyl-d_3 substituted **8**.[12]

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18. That ketenes undergo thermal 2 + 2 cycloadditions is well documented; see H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, 1967, Chapter II. The reaction is probably concerted (R. Montaigne and L. Ghosez, *Angew. Chem. Internat. Edit.*, **7**, 221 (1968)). Ketenes are not reactive as dienophiles in the Diels-Alder reaction (H. Ulrich, *loc. cit.*).