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# PHOTOLYSIS OF HEXAMETHYLCYCLOHEXANE-1,3,5-TRIONE

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Recently the photolysis of tetramethylcyclobutane-1,3-dione has been reported (1). Besides some fragmentation to dimethylketene, this compound easily splits off one to two moles of carbon monoxide, giving tetramethylethylene and derivatives of tetramethylcyclopropanone. In the present paper a similarly fast and nearly quantitative decarbonylation of hexamethylcyclohexane-1,3,5-trione (I) (2) is reported.

Thirty grams of I, dissolved in 300 ml. of ether, was irradiated in a quartz apparatus with a mercury high pressure immersion lamp (Hanau Q 700). The photolyte was monitored by periodic gas chromatographic analyses. Initially, one mole of carbon monoxide was liberated per mole of I consumed; however, the product of this photolysis was itself converted photochemically to two new compounds. All three products were isolated by preparative gas chromatography and identified by IR and NMR spectra*. The primary decarbonylation product was hexamethylcyclopen-

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* Correct elemental analyses were obtained for all new compounds.

tane-1,3-dione (V)*; the secondary products, formed in approximately 2·1 ratio, were 4-hydroxy-2,2,3,3,5-pentamethyl-4-hexenoic acid γ-lactone (VII)* and hexamethylcyclobutanone (X)*. In contrast to the photolysis of tetramethylcyclobutane-1,3-dione, no fragmentation to dimethylketene was observed in these experiments. The concentration of V reached a maximum after 4 hours of irradiation, when 83% of I had reacted. After 8 hours I was completely consumed. Only trace amounts of side products were formed. Based on peak areas on the gas chromatogram, the products formed gave full account for the amount of I consumed.

If irradiation was extended beyond complete conversion of I, mass balance was no longer achieved. Product V was completely converted after 16 hours of total exposure, but at this time X was also consumed by another slow photoreaction, and even the concentration of VII decreased slightly. Such an overexposed solution consisted mainly of VII (about 65% yield relative to I) and small quantities of three low boiling products, which were identified as 2,2,3,3-tetramethyl-4-iso-

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* V: m.p. 51°C., $\nu_{max}(CCl_4)$ 1728, 1270, 1062 $cm^{-1}$. $\lambda_{max}$(EtOH) 215 mμ (ε 235) and 292 mμ (ε 41). NMR ($CCl_4$, TMS as internal standard): $\delta$ = 1.04 (12H), 1.15 (6H) p.p.m.

VII: m.p. 45°C., $\nu_{max}(CCl_4)$ 1790, 1700, 1285, 1135, 1098, 1053 $cm^{-1}$. NMR ($CCl_4$): $\delta$ = 1.04 (6H), 1.19 (6H), 1.72 (6H) p.p.m.. NMR($C_6D_6$): $\delta$ = 0.88 (12H), 1.46 (3H), 1.68 (3H) p.p.m.

X: m.p. 45°C., $\nu_{max}(CCl_4)$ 1775, 1262, 1150, 1122, 1022 $cm^{-1}$. NMR($CCl_4$): $\delta$ = 1.09 (18H) p.p.m., NMR($C_6D_6$): $\delta$ = 0.84 (6H), 0.96 (12H) p.p.m.

propylideneoxetane (IX)*, hexamethylcyclopropane (XII)*, and tetramethylethylene (XIII). The exact origins of these side products were not determined, except that photolysis of pure X converted it partly to XII and XIII.

The reactions reported here can be rationalized by the scheme shown on the next page. The products V, X and XII arise from three succesive decarbonylations of I, which are assumed to involve the diradicals III, VIII and XI, although a concerted mechanism cannot be rigorously excluded. The rate of decarbonylation of I was found to be 3.7 times slower in methanol than in cyclohexane. Such a strong solvent dependence is not likely to exist for a concerted mechanism. On the other hand, it was not possible to obtain direct evidence for the existence of intermediate diradicals, since no addition products were formed in presence of cyclohexene or maleic anhydride in the photolyte. This behaviour, as well as the absence of recombination products of the postulated diradicals with each other, might be due to a cage effect. Evidence for a diradical mechanism has recently been presented for the gas phase decarbonylation of 2,6-dimethylcyclohexanone (3).

The rearrangement of V to the lactone VII presumably proceeds via the mesomeric diradical VI. An analogous

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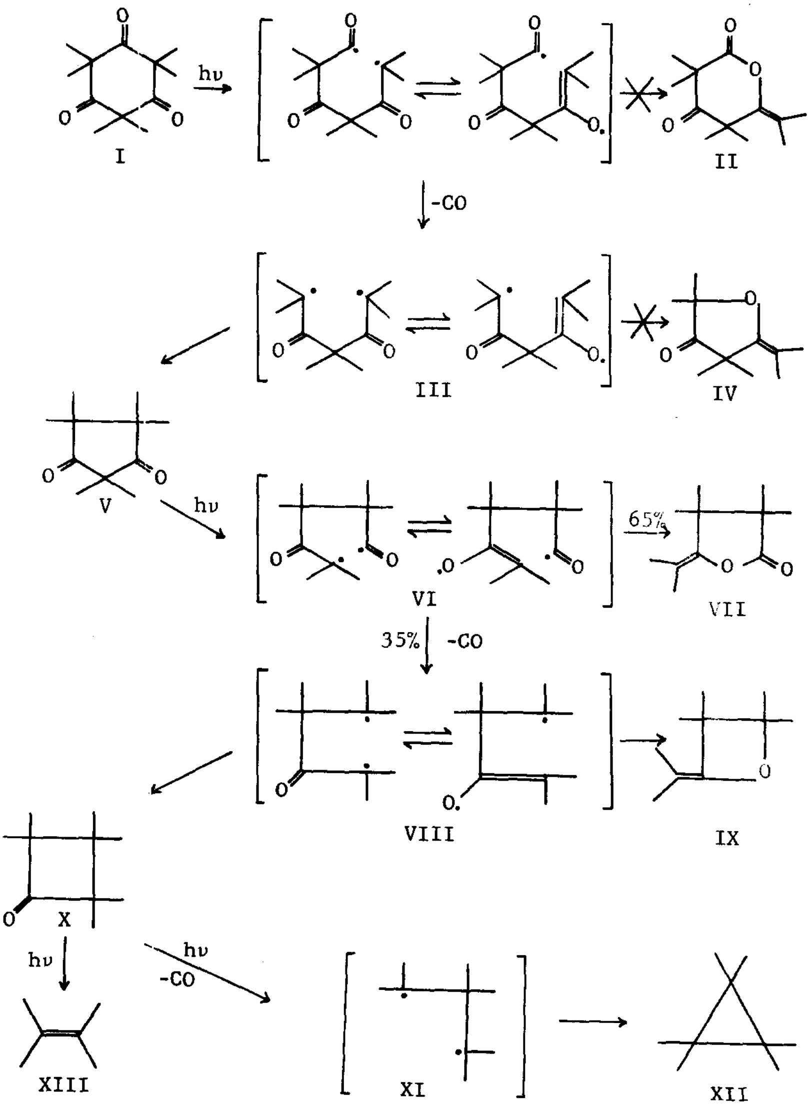
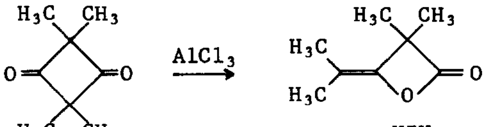
* IX: $\nu_{max}(CCl_4)$ 1730 (C=C), 1162, 1100, 1062, 950, 830 $cm^{-1}$. NMR($CCl_4$): $\delta$ = 1.24 (6H), 1.30 (6H), 1.38 (3H), 1.45 (3H) p.p.m.
XII: $\nu_{max}(CCl_4)$ 1465, 1380, 1110, 926 $cm^{-1}$. NMR($CCl_4$): $\delta$ = 0.94 p.p.m.



I
hν
II
-CO
III
IV
V
hν
VI
65%
VII
35%
-CO
VIII
IX
X
hν
hν
-CO
XI
XII
XIII

rearrangement has been reported for 2,2,5,5-tetramethylcyclohexane-1,3-dione (4). It is conceivable that the oxetane IX arises through a similar mechanism from the diradical VIII, although its formation from V was not experimentally verified. It is surprising that no rearrangement of I to the lactone II nor to the cyclic ether IV takes place; likewise, no lactone XIV is found in the photolysis of tetramethylcyclobutane-1,3-dione, although it can be prepared easily by rearrangement catalyzed by Lewis acids (5).



XIV

Benzophenone was found ineffective as sensitizer for the decarbonylation of I and V and for the rearrangement of V, nor did flushing with nitrogen prior to exposure affect the rates of reaction. This indicates that these photoreactions probably occur from excited singlet states.

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