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PHOTOCHEMISTRY OF 4,5,6,7-TETRAHYDROINDAN-2-ONE

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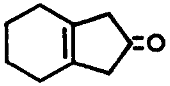
In the course of a study[1] on photorearrangements of β,γ-unsaturated ketones, we examined the photochemistry of 4,5,6,7-tetrahydroindan-2-one (1). Although 1 did not yield rearrangement products, its behavior is unusual in that loss of carbon monoxide is very inefficient and photoreduction of the carbon-carbon double bond occurs.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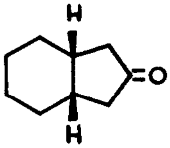
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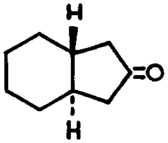
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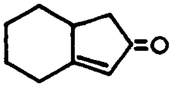
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Irradiation of 0.031 M 1 in isooctane at 313 mμ with an incident intensity of 0.1 millieinsteins hr^{-1} for 60 hours[2] resulted in disappearance of 90% of the starting material as determined by vpc (3% OV-17 on Gas Chrom Q at 90°) but only 20% of the theoretical amount of CO was formed. In benzene under similar conditions, 77% of 1 disappeared and 49% CO was evolved. After correction for the low absorbance of 1 ($\varepsilon = 7$ at 313 mμ), the CO quantum yield in benzene was calculated to be about 0.02. Quenching of excited 1 by a photoproduct cannot be the reason for the low quantum yield because this figure was still only 0.04 when the irradiation in benzene was carried to less than 5% conversion of 1. The higher CO quantum yield at low conversion is explained by a general increase in uv absorbance which was noted in irradiated benzene solutions of 1. This effect particularly was marked in isooctane where the reaction mixture eventually became yellow. The observed CO actually came from 1 and not from a secondary photolysis since the absorbance in benzene had not changed significantly by the time 1.5% of the CO had been evolved. Furthermore, if a secondary photolysis were important, one would have expected a CO quantum yield of less than 0.02 in the low conversion experiment.

To learn what excited state was responsible for photodecarbonylation, triplet quenching experiments were carried out. 0.10 M cis piperylene in benzene decreased the CO yield by a factor of 2.1 and the rate of disappearance of **1** by 2.6 with the concomitant formation of trans piperylene. Thus decarbonylation occurs significantly from this triplet state.

1,2-dimethylenecyclohexane (**2**), the expected product of photodecarbonylation, was identified in irradiated benzene and isooctane solutions of **1** by comparison of its vpc retention time and mass spectrum with that of an authentic sample. No significant new vpc peaks were seen on 3% OV-17 at 100° and 220° in irradiated benzene solutions of **1**. In isooctane, ethanol, isopropanol, and methylene chloride, however, vpc showed two new peaks which had retention times very similar to that of the starting material. These products gave nearly identical breakdown patterns in the mass spectrometer[3] with a base peak at $m/e = 94$ and a parent peak at $m/e = 138$, corresponding to addition of two mass units to **1**. Apparently photoreduction had occurred but surprisingly, neither of the products was the expected alcohol 4,5,6,7-tetrahydroindan-2-ol (**3**) as shown by comparison with known **3**. Column chromatography of the mixture obtained by irradiating **1** in isooctane (silica gel with 10% ethyl acetate in hexane as eluent) allowed isolation of the products.

The major product, which had the longer retention time on vpc, showed a carbonyl band at 1757 cm^{-1} in the ir, while the salient features of its nmr spectrum were a sharp singlet at $\delta = 2.1$ ($-CH_2-CO-$) and a broad singlet at $\delta = 1.5$. Although not enough of the minor product could be isolated for an nmr, its ir carbonyl band appeared at 1759 cm^{-1}. In view of the spectral similarity of the two products, they were tentatively assigned as the ring junction isomers cis and trans hydrindanone-2 (**4** and **5** respectively).

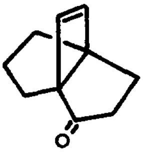
The structures were confirmed by independent synthesis. Rhodium catalyzed hydrogenation of o-phenylenediacetic acid followed by pyrolysis[4] with acetic anhydride gave a mixture of two ketones. These were separated by preparative vpc and identified by preparation of their oximes. Oxime of **4** mp 75-76.5°, reported[4] 80°; oxime of **5** mp 159.5-160°, reported[4] 161°. The nmr, mass spectrum, ir spectrum, and vpc retention time of **4** coincided with that of the major photoisomer from irradiation of **1** while **5** had the same vpc retention time, mass spectrum, and ir spectrum as the minor photoproduct.

The vpc yields of **4** and **5** based on the amount of starting **1** were 9% and 3% respectively when 78% of **1** had reacted. However the concentration of **4** and **5** build up to a steady state value early in the reaction so that their maximum combined yield based on reacted **1** is 26%. vpc on OV-17 at 220°C of irradiated isooctane solutions of **1** showed at least seven low yield, long retention time products which discouraged attempts at characterization.

The excited state of **1** leading to photoreduction also appears to be the triplet, since oxygen and piperylene strongly inhibit product formation.

Irradiation of the conjugated ketone **6** under the conditions used for **1** did not lead to detectable amounts of **4** or **5**, implying that **6** is not an intermediate in the photoreduction of **1**.

The photoreduction of the double bond in **1** has its only analogy in a report of Cargill and co-workers[6] that another β,γ-unsaturated ketone **7** undergoes this reaction. Although



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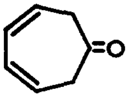

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the mechanism is not yet understood, the postulate that the triplet state of **1** has free radical character at the ring junction carbon atoms can explain the observed photoreduction accompanied by many higher molecular weight materials in hydrogen donating solvents and the absence of well-defined products in benzene.

It is of interest to compare the behavior of **1** with that of **8**, a compound which superficially at least is of the same symmetry. Preliminary measurements[7] indicate that the CO quantum yield in the latter is about 0.25, nearly an order of magnitude higher than the value for **1**. Moreover, from our work and that of Schuster,[8] it appears that singlet decarbonylation in **1** is much slower relative to intersystem crossing than it is in **8**. Three other systems[9-11] analogous to **1** have been shown to undergo photodecarbonylation but as has already been noted,[12] this reaction is facilitated in each case by some feature such as ring strain, heavy α-substitution, or carrying out the irradiation in the gas phase. It will be of interest to learn what excited state is responsible for loss of CO in these cases.

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2. Irradiation was done at 25° in a photochemical merry-go-round apparatus with a Hanovia 450 watt mercury lamp and a potassium chromate filter.
3. A LKB Model 9000 gas chromatograph-mass spectrometer was used. The only difference in the spectra was that in the major product, the m/e = 96 peak was about one-half as intense as the m/e = 95 peak while in the minor component, they were of equal intensity.
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