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MECHANISM OF PHOTOCHEMICAL DIMERIZATION OF 2,4-CYCLOOCTADIENONE

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In an earlier report[1] we described the isolation and structural elucidation of two dimers (III and IV) obtained in high yield (85% combined) by the u.v. irradiation of 2,4-cyclooctadienone (I) in benzene. In this communication we report results which clarify three important mechanistic aspects of this dimerization: the nature of the excited state involved in the photochemical step, the structure of the dimer precursor and the mechanism of the dimerization itself.

The quantum yield[2] of disappearance of I in benzene (Φ_{dis}) using a 350 mμ source[3] was 0.28. When oxygen was bubbled through the solution during irradiation, Φ_{dis} was not affected. Similarly, 0.01-1.0 *M* concentrations of the triplet quencher 1,3-cyclohexadiene (E_T 53 kcal/mole)[4] had no effect on Φ_{dis}. The quantum yield of intersystem crossing of I as determined by the sensitized dimerization of 1,3-cyclohexadiene was found to be <0.01 relative to a value of unity for benzophenone.[5] These results suggest that the excited state in the photochemical step is either a singlet or a short-lived triplet. Triplet sensitization experiments were used to differentiate between these two possibilities.

Benzene solutions of I were irradiated in the presence of the following triplet sensitizers such that the sensitizer absorbed the indicated percentage of incident irradiation: xanthone (99%[6,7])(E_T 74.2 kcal/mole),[8] benzophenone (82%)(E_T 68.5 kcal/mole)[8] and Michler's ketone (99%) (E_T 61.0 kcal/mole).[8] In all these sensitized irradiations there was a very significant decrease in Φ_{dis} (<0.01). Although the triplet energy of I has not been determined it would be expected to be below that of at least the first two sensitizers. Thus, the photochemically reactive state of I must be an excited *singlet*.

Next, it was necessary to determine the nature of the photochemical reaction and the structure of the dimer precursor. A toluene solution[9] of I was irradiated at -78° for two hours and then divided into two portions. To one was added a 15-fold excess of the trapping reagent 2,3-dimethyl-1,3-butadiene (DMBD)[10] and both samples were allowed to warm slowly to room temperature. The portion without the diene gave a 40% yield of dimers III and IV and 60% of unreacted I while the other portion gave a *decreased* yield of dimers (32%), unreacted I (62%) and a low melting Diels-Alder adduct, V[11] (6%): i.r. (CCl_4) 1700, 693 cm^{-1}; n.m.r. ($CDCl_3$) τ 4.4-4.7 (2H, m, -CH=CH-), 7.2-8.5 (12 H, m), 8.4 [apparent 6H, s, -C(CH_3)=C(CH_3)-]; mass spectrum, molecular ion at m/e 204. Irradiation of I at room temperature in the presence of a 15-fold excess of DMBD gave dimers III and IV (46%) and two adducts, V (15%) and VI (35%): i.r. (neat) 1700, 889 and 755 cm^{-1}; n.m.r. ($CDCl_3$) τ 4.0-4.5 (2H, m, -CH=CH-), 5.3-5.5 (2H, m, =CH_2), 6.9-9.1 (10 H, m), 8.4 (apparent 3H, s, $CH_3\text{-}\underset{|}{C}\text{=}$), 8.7 (apparent 3H, s, $CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}$); mass spectrum, molecular ion at m/e 204. Adduct VI must have been formed in a photochemical 2 + 2 addition[12] as it was not formed in the trapping experiment. The low temperature trapping experiment proved conclusively the existence of a highly reactive ground-state species, namely *trans*,*cis*-2,4-cyclooctadienone (II), formed by photoisomerization from an excited singlet state of I. Dienone II had the capability of undergoing ground-state reactions such as dimerization, isomerization back to I and addition to suitable trapping reagents such as dienes. Cantrell reported[13] the formation of *trans*-fused Diels-Alder adducts upon irradiation of I in furan and suggested II was the reactive species.

Finally, the dimerization itself must be discussed and an explanation provided for the formation of two dimers. Irradiation of I in benzene at concentrations of 0.08 and 0.38 *M* resulted in the same 44:56 ratio of dimers III:IV.[14] Similarly, irradiation of I in toluene (at R.T. or -78°), in methanol[15] or in the presence of 1,3-dienes at R.T. caused no change in the dimer ratio. Addition of trapping reagents such as dienes after irradiation of I at -78° also caused no change in this ratio but did result in a decreased yield of dimers (see above), indicating competition for the intermediate II. We conclude that the dimers must be formed from two molecules of II in a two-step thermal process in which the initially formed diradical, VII, closes in either a conrotatory or a disrotatory manner to give III or IV, respectively. A similar mechanism has been proposed for the thermal dimerization of *cis*,*trans*-1,3-cyclooctadiene.[16] Cantrell suggested[13] previously that dimerization of I proceeded *via* addition of an excited triplet of I to ground-state I.

In conclusion, irradiation of I in benzene or toluene with a 350 mμ source resulted in singlet photoisomerization to give the strained dienone II, which dimerized in a thermal two-step process to give dimers III and IV. Noyori reported[17] irradiation of 2-cyclooctenone in methanol to give a methanol adduct *via trans*-2-cyclooctenone is not affected by diene quenchers and a recent review suggested[18] the reactive state in this isomerization may also be a singlet.

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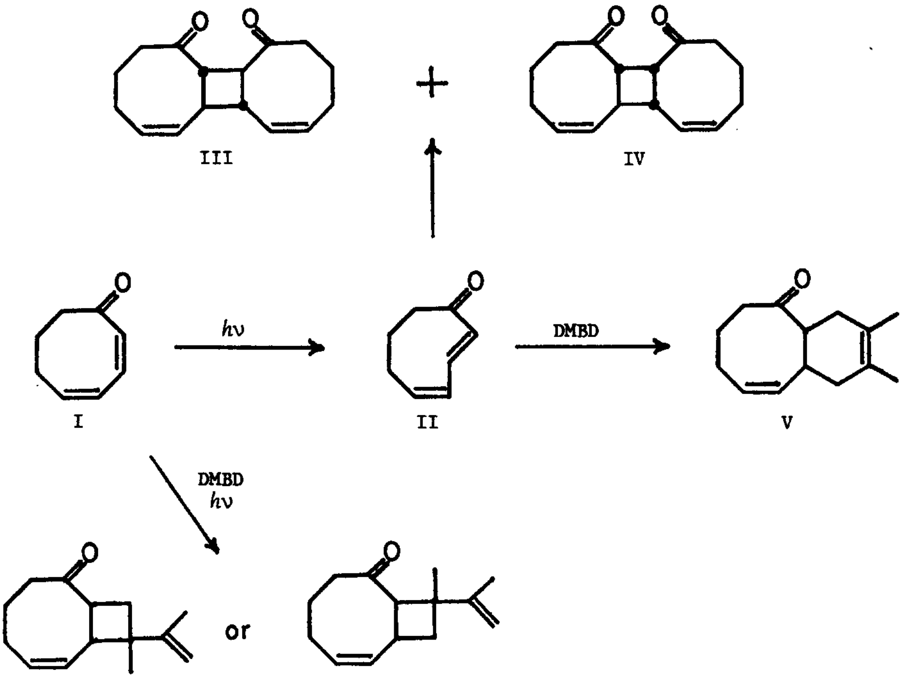


III

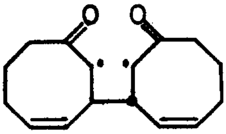
IV

I

II

V

VI



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2. Benzophenone-benzhydrol actinometer. W.M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, 84, 1368 (1962).
3. A Rayonet Model RPR-100 Reactor with sixteen 350 mμ lamps was used in conjunction with a MGR-100 "merry-go-round" apparatus to ensure uniform irradiation of all samples, which were placed in pyrex tubes. In benzene, λ_{max} for the $n \rightarrow \pi^*$ transition of I is at 343 mμ.
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5. D. Valentine, N.J. Turro and G.S. Hammond, *J. Amer. Chem. Soc.*, 86, 5202 (1964). See also: D.I. Schuster and D.J. Patel, *J. Amer. Chem. Soc.*, 90, 5145 (1968).
6. To ensure that self-quenching by the sensitizer[7] was not involved, the concentration of xanthone was varied such that it absorbed 90 and 62% of the irradiation and it was found that Φ_{dis} increased as expected.
7. (a) O.L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, 91, 5390 (1969).
   (b) P.S. Engel and B.M. Monroe, *Advan. Photochem.*, 8, 253, 303 (1971).
8. J.G. Calvert and J.N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p. 298.
9. A combined yield of 82% dimers was obtained when I was irradiated in toluene under normal conditions.
10. This diene was particularly useful as n.m.r. spectroscopy could readily distinguish between the 2 + 2 and the 2 + 4 adducts of I and DMBD. When other dienes such as piperylene were used as trapping agents the yield of adducts was higher but the structural assignments were not as straightforward.
11. This adduct was not formed when a toluene solution of I and DMBD was treated under similar conditions in the absence of light.
12. Similar cycloadditions of 1,3-dienes and enones have been reported: T.S. Cantrell, *Chem. Comm.*, 1656 (1970).
13. T.S. Cantrell and J.S. Solomon, *J. Amer. Chem. Soc.*, 92, 4656 (1970).
14. Dimer ratios were determined by g.l.c. on a 6' x 1/4" 20% SE 30 column at 240°. The two peaks overlap slightly and thus the determinations are accurate to ±3%.
15. Cantrell reported[13] the isolation of only one dimer upon irradiation of I in methanol but we have repeated this experiment using his conditions and have detected both dimers.
16. A. Padwa, W. Koehn, J. Masaracchia, C.L. Osborn and D.J. Trecker, *J. Amer. Chem. Soc.*, 93, 3633 (1971).
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18. "Photochemistry", Vol. 1, D. Bryce-Smith, Senior Reporter, The Chemical Society, London, 1970, p. 186.