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# THE PHOTOLYSIS OF 1-PHENYLCYCLOHEXENE IN 2-PROPANOL

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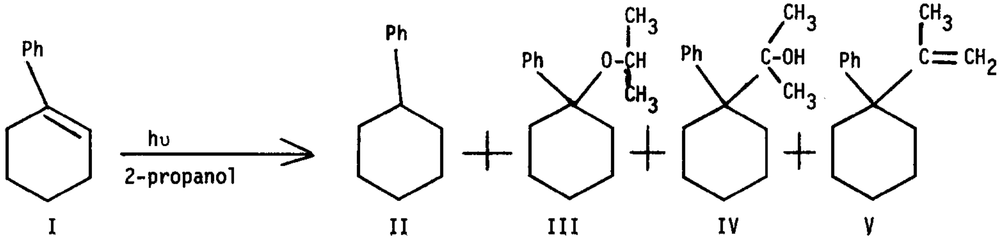
Reports of hydrogen abstraction reactions originating from olefinic $(\pi,\pi^*)$ triplet excited states are rare[1a,b]. The photolyses of 1- substituted cyclohexenes are reported to give products mainly resulting from ionic addition[2a,b]. Recently we reported that 1-phenylcyclohexene (I) when irradiated in methanol yielded minor products which could be envisioned as forming via a hydrogen abstraction mechanism originating from an excited triplet state of I[3].

In the desire to show that hydrogen abstraction reactions resulting from an excited $(\pi,\pi^*)$ triplet state could be made the major pathway for photolysis reactions we irradiated solutions of I in 2-propanol[4], a better hydrogen donor than methanol. Irradiation of degassed solutions of I in 2-propanol (0.03M) at 2537Å or 3000Å for 72 hours yielded 1-phenylcyclohexane (II), 39%, 1-isopropoxy-1-phenylcyclohexane (III), 7%, dimethyl-1-phenylcyclohexylcarbinol (IV), 23%, unsym-methyl-1-phenylcyclohexylethylene (V), 9%, dimers of 1-phenylcyclohexene, 22% and pinacol.



The yields (%) are based on reacted (I). The products were separated by alumina column chromatography and identified by superimposing their ir spectra with those of known samples. Irradiation of a solution of I ($E_T$ = 62 kcal/mole)[5] in 2-propanol at 3500Å using 3-methoxyacetophenone[6] as a sensitizer yielded the products II→V in the above ratios, but only traces of the dimeric products. Chemical sensitization was ruled out by an experiment which demonstrated that the quantum yield for reaction of VI in 2-propanol at 3500Å was less than the quantum yield for the sensitized reaction. 1,3-Cyclohexadiene ($E_T$ = 52.5 kcal/mole) quenched the photolysis at 3000Å. These experiments tend to indicate that the photolysis proceeded via an excited ($\pi,\pi^*$) triplet state although prior to decay to a reactive trans-cyclohexene derivative cannot be ruled out.

If one assumes that product II is formed via a hydrogen abstraction reaction[7] and product V results from IV by loss of a molecule of water, better than 90% of the non-dimeric product can be visualized as forming via a hydrogen abstraction pathway. To show that ionic addition is possible with 2-propanol, irradiation of degassed solutions of I in 2-propanol containing 1% $H_2SO_4$ for 1 hour at 2537Å and 3000Å showed only the presence of III.

## REFERENCES

1. (a) H.M. Rosenberg and M.P. Serve', J. Am. Chem. Soc. 92, 4746 (1970);
   (b) T.S. Cantrell, Chem. Commun., 1633 (1970).
2. (a) J.A. Marshall, Accounts Chem. Res. 2, 33 (1969) and references therein;
   (b) P.J. Kropp, J. Am. Chem. Soc. 91, 5783 (1969).
3. H.M. Rosenberg and M.P. Serve', J. Org. Chem., 37, 141 (1972).
4. Solutions of I in 2-propanol were degassed using a freeze-thaw sequence and irradiated in a Rayonet (RPR-100) photochemical reactor.
5. D.F. Evans, J. Chem. Soc., 1351 (1957).
6. The quantum yield for photoreduction of 3-methoxyacetophenone ($E_T$ = 72.4 kcal/mole) in 2-propanol is 0.006. See N.C. Yang, D.S. McClure, S.L. Murov, J.J. Houser and R. Dusenbery, J. Am. Chem. Soc., 89, 5466 (1967).
7. J.A. Marshall and A.R. Hochstetler, Chem. Commun. 296 (1968).