

atoms or the local bond conformations, that determine the stability relations in a series of cyclics.

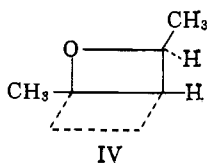
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cis-trans Isomerization of Olefins by Intramolecular Energy Transfer

Sir:

Recently, we reported¹ upon the photochemistry of *trans*-4-hexen-2-one (I). Among the plethora of isolable products was the isomeric *cis*-4-hexen-2-one (II), possibly a chemical consequence of intramolecular energy transfer² (irradiation by light absorbed only by the carbonyl group, resulting in reaction at the non-conjugated double bond). However, one can write plausible alternative mechanisms for this isomerization³; an unambiguous demonstration of intramolecular photosensitization required that substrates be devised for which internal energy transfer would be unequivocal. Two such systems have now been explored, with the carbonyl group acting as the donor moiety in one and phenyl filling this role in the other. Both exhibit the same phenomenon: *absorption of light at one site in the molecule results in a chemical reaction at a second, nonconjugated site.*

(a) *trans*-5-Hepten-2-one (III)⁴ was irradiated, using a Hanovia 450-watt high-pressure mercury arc with a Corex filter, so as to limit incident light to that which would effect only the carbonyl $n \rightarrow \pi^*$ transition. The reaction was followed by the withdrawal of aliquots and examination of these by vapor phase chromatography (v.p.c.). Two new peaks were observed to form,⁵ and these products were isolated by preparative v.p.c.; their mass spectra and elemental analyses indicated that they were isomers of the starting material. The infrared and nuclear magnetic resonance (n.m.r.) spectra of the first photoproduct allowed its assignment as the oxide IV, analogous to the trimethylene oxide obtained by Srinivasan⁶ from the photolysis of 5-hexen-2-one. Pyrolysis of IV gave exclusively the *trans*-unsaturated ketone, III.



The second photoproduct, V, had n.m.r. and mass spectra essentially identical with those of the original

(1) H. Morrison, *Tetrahedron Letters*, 3653 (1964).

(2) Intermolecular transfer of electronic excitation has been known for some time; cf. T. Förster, *Discussions Faraday Soc.*, 27, 7 (1959). Examples of intramolecular transfer are relatively few and limited to spectroscopic observations; cf. G. Weber, *Nature*, 180, 1409 (1957); O. Schnepf and M. Levy, *J. Am. Chem. Soc.*, 84, 172 (1962); P. Leermakers, G. Byers, A. Lamola, and G. Hammond, *ibid.*, 85, 2670 (1963).

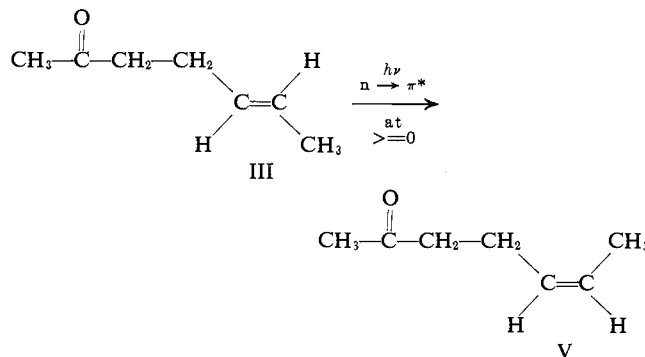
(3) Intermolecular energy transfer does not appear to be a factor in our systems since *trans*-2-hexene is not isomerized when included in the reaction mixtures.

(4) W. Kimel and A. Cope, *J. Am. Chem. Soc.*, 65, 1992 (1943).

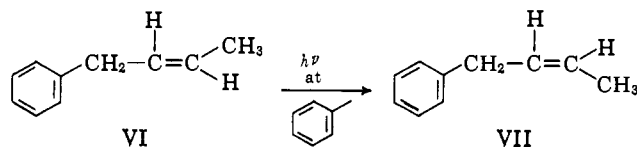
(5) Irradiation of 4 g. of III for 12 hr. produced IV and V in yields of ca. 30% each (by v.p.c.).

(6) R. Srinivasan, *J. Am. Chem. Soc.*, 82, 775 (1960).

ketone. However, its infrared spectrum showed a band at 14.4 μ (*cis*-disubstituted olefin), but lacked the 10.4 μ band (*trans*-disubstituted olefin) characteristic of III. An analogous change in infrared spectra was observed in the conversion of I to II. These data allow the assignment of *cis*-5-hepten-2-one as compound V and establish that internal photosensitization had occurred.



(b) *trans*-1-Phenyl-2-butene (VI) (Aldrich; 96% *trans* by v.p.c.) was irradiated through a filter solution so that the light admitted (248–282 $m\mu$) was absorbed only by the aromatic ring.⁷ After 2 hr., distillation followed by preparative v.p.c. provided, in addition to starting material, a single isomeric photoproduct, VII. The infrared, n.m.r., and mass spectra are consistent with its assignment as *cis*-1-phenyl-2-butene, again a product of internal energy transfer.⁹



These and other donor-acceptor systems are presently under investigation as possible probes for the geometric requirements of energy transfer; their potential utility in organic synthesis is also being explored.

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(7) Benzene, despite its high triplet energy ($E_t = 84$ kcal.), seems to have been neglected in the literature as a solution phase sensitizer, although its use in the gas phase has been reported; cf. R. Cundall and T. Palmer, *Trans. Faraday Soc.*, 56, 1211 (1960). Thus, whereas common ketone sensitizers ($E_t \sim 74$ kcal.) are inefficient in isomerizing simple olefins⁸ ($E_t \sim 80$ kcal.), we find that irradiation of a benzene solution of *trans*-2-hexene produces a photostationary mixture of *cis-trans* isomers within ca. 10 hr. Its ability to function as solvent as well as sensitizer promises to make benzene the agent of choice for effecting such isomerization.

(8) G. Hammond, N. Turro, and P. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962).

(9) The observation of a common photostationary mixture of VI and VII (1.0:1.0) for the intra- and intermolecular systems (benzene serving as donor in the latter case⁷) suggests that vibrational energy transfer, via internal conversion of the initial benzenoid excited state to a high vibrational level of its ground state, is not operable here. (Specific intermolecular energy transfer from benzene solvent to the aromatic ring of the olefin would also accommodate the data, however, and this question is still under study.)

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