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PHOTOREARRANGEMENT OF ALKYL SUBSTITUTED PHENYLCYCLOPROPANES TO OLEFINS

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During the course of our studies on the photofragmentation of epoxides in the presence of olefins[1] and on the photocyclization of propenes,[2] we found that the primary products, namely cyclopropanes, were subsequently converted to olefins upon extended irradiation in dilute solution. Related transformations of arylcyclopropanes to olefins have been reported earlier;[3] however in the case of the alkyl substituted phenylcyclopropanes I described herein, the conversion is exceedingly efficient and in the majority of cases the reaction takes a novel and unexpected course.

The results accumulated to date suggest that the initial step[4] in the rearrangement of I is invariably homolysis of the weakest bond of the cyclopropane ring followed by intramolecular 1,4-transfer of a 1°-hydrogen atom from the methyl group to give a terminal olefin (Path A) or 1,2-migration of a 3°-hydrogen atom to give the conjugated olefin (Path B; R_2 = H).[5]

The ring-opening proceeds exclusively by Path A in all cases with the exception of Ia and Ib (Table I) where reaction

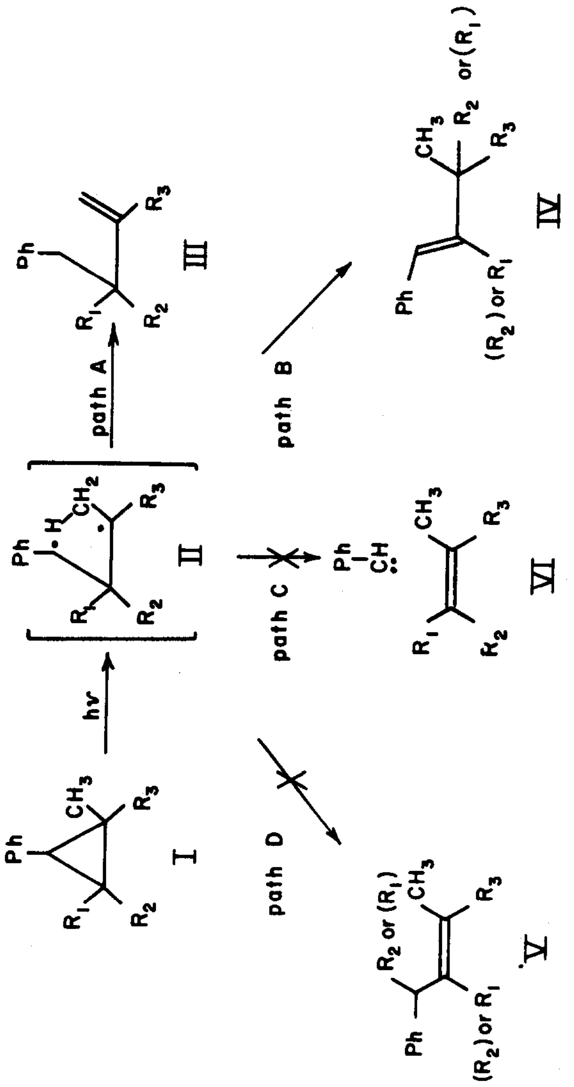
I
hν
II
path A
III
path B
IV
path C
VI
path D
V
Ph
CH₃
R₁
R₂
R₃
CH₂
H
(R₂) or R₁
R₂ or (R₁)

TABLE I

	CYCLOPROPANE I	R_1	REACTION COURSE	OLEFINIC PRODUCT III OR IV
a*	*cis*-2,3-dimethyl-1-phenylcyclopropane	$R_1=CH_3$	B	*cis*- or *trans*-1-phenyl-2-methyl-butene-1
		$R_2=R_3=H$	A	3-methyl-4-phenylbutene-1
b	*trans*-2,3-dimethyl-1-phenylcyclopropane	$R_2=CH_3$	B	*cis*- or *trans*-1-phenyl-2-methyl-butene-1
		$R_1=R_3=H$	A	3-methyl-4-phenylbutene-1
c	2,2-dimethyl-1-phenylcyclopropane	$R_3=CH_3$ $R_1=R_2=H$	A	2-methyl-4-phenylbutene-1
d*	2-methyl-2-ethyl-1-phenylcyclopropane	$R_3=C_2H_5$ $R_1=R_2=H$	A	2-ethyl-4-phenylbutene-1
e	2,2,3-trimethyl-1-phenylcyclopropane	$R_2(\text{or } R_1)=R_3=CH_3$ $R_1(\text{or} R_2)=H$	A	2,3-dimethyl-4-phenylbutene-1
f	2,2,3,3-tetramethyl-1-phenylcyclopropane	$R_1=R_2=R_3=CH_3$	A	2,3,3-trimethyl-4-phenylbutene-1

*An approximately equimolar mixture of *syn* and *anti* isomers was employed.

by both Paths A and B are observed and the latter predominates. Other possible competing reactions such as fragmentation of II to phenylcarbene and olefin VI (Path C)[6,7,8] and hydrogen or alkyl migrations (Path D) which might be anticipated by analogy with known conversions[2,3] do not occur under the conditions employed. Indane formation has also been excluded within the limits of our analytical procedure. One minor product remains to be identified in the case of Ia and Ib, however.

The novel 1,4-hydrogen transfer (Path A) with formation of the terminal olefin is a reaction characteristic of the cyclopropanes I. In a typical experiment 2,2-dimethyl-1-phenylcyclopropane (Ic) in n-hexane (0.1M) was irradiated for 24 hours and gave 2-methyl-4-phenylbutene-1 (IIIc) in better than 80% yield. A kinetic study verified that the reaction was first order ($k = 3.4 \times 10^2 \text{ sec}^{-1}$)[9] and no quenching was observed upon irradiation of Ic in the presence of cis- and trans-piperylene.[10] These data suggest that a singlet π,π^* excited state mechanism is operative and that the 1,4-hydrogen transfer is intramolecular.

In view of the conversion of If to IIIf with 1,4-hydrogen transfer there can be little question that the terminal olefin is formed first and not as the result of initial formation and subsequent rearrangement of other olefins, i.e., no alternative intermediate olefin possessing the same skeletal structure of IIIf is possible in this case. Thus, while rearrangement must occur with transfer of a 1°-hydrogen atom a favorable five-membered transition state may be invoked. An alternative mechanism in which hydrogen is transferred initially to the ortho-position of the aromatic ring through a six-membered transition state can not be excluded.[11] The reaction bears some similarity to the thermal rearrangement of methyl *cis*-2-alkylcyclopropanecarboxylate[12] and related systems,[13] in which 1,5-transfer of hydrogen to oxygen occurs with concomitant ring opening. The selective transfer of a 1°-hydrogen in preference to a 2°-hydrogen in the case of Id is of interest and for the present is assumed to be dictated by geometrical factors. It is exceedingly interesting that radically different product distributions are obtained upon irradiation of the isomeric cyclopropanes Ia and Ib. In benzene (24 hours 0.1*M*) both Ia and Ib are converted to olefins IIIa(b) (Path A) and IVa(b) (Path B). The olefin IVa(b) is in both cases the major product, but the conversion of Ia to IIIa proceeds much more efficiently, when the *cis*-isomer is employed. The conversion of Ia and Ib occurs faster in benzene than in *n*-hexane, which leads us to believe that the 1,2-hydrogen transfer is benzene sensitized. The ability of benzene to function as a solvent-sensitizer has been discussed earlier.[3,14]

In each case the cyclopropane was synthesized from phenylcarbene generated photolytically from stilbene oxide and the appropriate olefin VI.[1] The olefins obtained from IIIa, b, c, d, and e were prepared independently in the Wittig manner from methylene or benzilidene triphenylphosphorane and the appropriate ketone or aldehyde. The olefin IIIf was characterized from nmr and infrared spectral data $\lambda_{max}^{CS_2}$ 893 cm^{-1}; nmr, τ 2.95 (5 H multiplet), τ 5.30 (1 H singlet), τ 5.42 (1 H singlet), τ 7.39 (2 H singlet), τ 8.18 (3 H singlet), τ 8.98 (6 H singlet).

The mechanistic implications of the data reported in this communication will be discussed in detail in a subsequent paper.

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3. G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson and C. S. Irving, *Tetrahedron Letters*, **34**, 2951 (1965).

4. For simplicity the reactions are formulated in a stepwise fashion, but in fact we favor concerted mechanisms for both Path A and Path B.

5. Very recently related conversions have been reported by J. A. Bell (*J. Am. Chem. Soc.*, **87**, 4966 (1965). It was found that the sensitized gas-phase photoisomerization of *cis*- and *trans*- 1,2-dimethylcyclopropane affords 3-methylbutene-1 and pentene-2 which correspond to our observed 1,4- and 1,2-hydrogen migrations. See also J. Zirner and S. Winstein, *Proc.* (London), 325 (1964) for a summary and discussion of photoinduced hydrogen migrations.

6. No detectable quantity of 7-phenylcycloheptatriene was produced upon irradiation of I in benzene.

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9. All irradiations were conducted in serum-capped quartz test tubes containing rigorously degassed benzene or *n*-hexane solutions employing an air cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 low pressure 8 W mercury lamps. The temperature was maintained at 38° during the course of the kinetic study of Ic and the diameter of the test tube was 13 mm.

10. G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

11. We wish to thank Professor D. E. McGreer for calling our attention to this possibility.

12. D. E. McGreer, N. W. K. Chiu and R. S. McDaniel, Proc. (London) 415 (1964).

13. R. M. Roberts, R. N. Greene, R. G. Landolt and E. W. Heyer, *J. Am. Chem. Soc.*, **87**, 2282 (1965).

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