A Photochemical Vinylcyclopropane to Cyclopentene Rearrangement[1]

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Summary Photochemical conversion of the excited singlet state of isopropenylcyclopropane into 1-methylcyclopentene has been observed.

I report the photochemical conversion of isopropenylcyclopropane into 1-methylcyclopentene. In this rearrangement electronic excitation is localized exclusively in the vinylcyclopropane chromophore, and the reaction proceeds through the singlet state. This observation indicates that the prediction[2] of ready conversion of an excited singlet state vinylcyclopropane into a cyclopentene is correct.†

Samples of 0·2 M-isopropenylcyclopropane[4] in n-hexane were degassed by three freeze–pump–thaw cycles and sealed in 13 mm quartz tubes. The tubes were irradiated on a 450 w Hanovia medium-pressure mercury lamp while immersed in a cooling bath which maintained the temperature below 40°. The reaction was followed by g.l.c. on a 9 ft. 25% $\beta\beta'$-oxydipropiononitrile column at 25°. Aliquots of n-nonane were added to the samples after irradiation as an internal standard. The rate of disappearance of isopropenylcyclopropane was $(2\cdot0 \pm 0\cdot2)10^{-3}$ M hr.$^{-1}$ and was approximately of zero order. One major product was formed at the zero order rate of $(1\cdot1 \pm 0\cdot1)10^{-3}$ M hr.$^{-1}$, *i.e.* the chemical yield of the reaction was $55 \pm 7\%$. A number of minor products of both shorter and longer retention times as well as polymeric material were observed but not identified. From a preparative scale reaction in

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† Previous examples (ref. 3) of formal photochemical vinylcyclopropane to cyclopentene rearrangements do not provide cases which test whether this photoreaction proceeds as a suprafacial [1,3]-sigmatropic shift allowed by the Woodward–Hoffmann rules or involves a diradical intermediate. Two conditions required by the theoretical calculations of Hoffmann and Woodward are not necessarily fulfilled in these instances. First, the reactions may proceed through the triplet manifold and spin inversion will make the processes nonconcerted. Second, these reactions may not involve the excited state of the vinylcyclopropane if lower energy chromophores such as phenyl or ethoxycarbonyl are present in the molecules.

n-pentane the product was isolated in poor yield by g.l.c. on a 10 ft. 25% dimethylsulpholane column at 25°. This material was found to be identical in all respects—i.r. spectrum, n.m.r. spectrum, and g.l.c. retention time, with an authentic sample of 1-methylcyclopentene. Irradiations of 0·2 M-solutions of this product in degassed n-hexane under identical conditions led to disappearance of the cyclopentene at a zero order rate of $(4{\cdot}7 \pm 1{\cdot}1)10^{-4}$ M hr.$^{-1}$. Although a number of minor products were detected, isopropenylcyclopropane was not formed. Production of this compound at a rate of greater than $8{\cdot}0 \times 10^{-7}$ M hr.$^{-1}$ could have been observed under our analytical conditions.

Irradiations of 0·10 M-solutions of isopropenylcyclopropane in degassed n-hexane containing various triplet sensitizers were carried out. The intensities of light of either 313·0 or 253·7 nm were determined by ferric oxalate actinometry. The results are summarized in the Table. In the photoreactions sensitized with benzene and acetone traces of methylcyclopentene were observed; however, none was detected with naphthalene as sensitizer. Only traces of other products were observed in the benzene- and naphthalene-sensitized experiments; however, at least seven other products appear in the acetone-sensitized irradiations. These compounds have not been further investigated, but a number of products are expected from the photoreduction and oxetan formation reactions which compete with energy transfer. The limited success in the triplet-sensitized production of 1-methylcyclopentene strongly indicates that under direct irradiation the reaction proceeds from the excited singlet state of the vinylcyclopropane.

Sensitizer (M)	E_T (kcal mole^{-1})	ϕ − cyclopropane	ϕ + cyclopentene
Naphthalene (0·03)	60·9	0·00 ± 0·01	$\leqslant 1{\cdot}9 \times 10^{-4}$
Acetone (1·4)	78·0	0·24 ± 0·03	*ca.* $9{\cdot}3 \times 10^{-4}$
Benzene (1·1)	84·0	0·02 ± 0·01	*ca.* $1{\cdot}4 \times 10^{-4}$

Two pathways for this rearrangement are: (i) the excited singlet molecule may undergo cleavage of one of the cyclopropane bonds to give a diradical which may reclose to starting material or form the cyclopentene, or (ii) the reaction may proceed in a concerted manner by way of a suprafacial [1,3]-sigmatropic shift.

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[1] For previous paper in the series see: H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 2852.

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[3] For examples of formal photochemical vinylcyclopropane to cyclopentene rearrangements see: H, Prinzbach, H. Hageman, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, 1965, **98**, 2201; M. J. Jorgenson and C. H. Heathcock, *J. Amer. Chem. Soc.*, 1965, **87**, 5264; H. Kristinsson and G. S. Hammond, *ibid.*, 1967 ,**89**, 5970; P. J. Kropp, *ibid.*, p. 1126.

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