

assume that this transformation is mechanistically similar to that of **8** to **9**. Thus, initial excitation of **1** appears to produce an unreactive excited state which possesses a sufficient lifetime at 77°K to absorb a second photon, giving rise to a higher excited state having the proper symmetry for rearrangement to **7**.

Further studies of the chemistry of this ring system are in progress.

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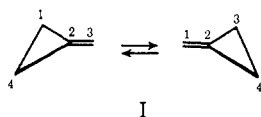
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## The Photochemical Methylenecyclopropane Rearrangement

Sir:

The relationship between thermal and photochemical energy surfaces for concerted isomerizations has become recognized as a subject of paramount theoretical importance.<sup>1</sup> In this context and reflecting current interest in the scope and mechanism of degenerate thermal rearrangements (*e.g.*, I) in the methylenecyclopropane series,<sup>2</sup> we now report the first example of a *reversible photochemical methylenecyclopropane rearrangement*. Our results to date on four members of this class (II–V) indicate that (1) reversible photoisomerization occurs between benzyldenecyclopropane (II) and 1-phenyl-2-methylenecyclopropane (III), (2) cheletropic<sup>3</sup> photofragmentations to olefins and vinylidenecarbenes compete to varying degrees with the photoisomerizations, (3) certain of the cheletropic fragmentations may occur from vibrationally excited primary photoproducts, (4) singlet excited states are involved in the photoisomerizations and photofragmentations, and (5) the observed photoisomerizations differ markedly from thermal pathways reported for these compounds in the literature.



Photolysis at 30° of a 1% acetonitrile solution of benzyldenecyclopropane (II)<sup>4</sup> under N<sub>2</sub> in a quartz

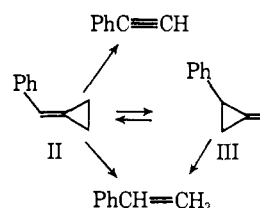
(1) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(2) For recent contributions defining the mechanism of the methylenecyclopropane rearrangement, see J. J. Gajewski, *ibid.*, **90**, 7178 (1968), and W. von E. Doering and H. Roth, *Tetrahedron*, **26**, 2825 (1970). The latter paper contains a thorough review of this field.

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 152–163.

(4) K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966). Com-

nmr tube using a 450-W high-pressure mercury source gave three new products as monitored by glpc.<sup>5</sup> After 30 min there was 54% loss of starting II accompanied by the formation of 18% 1-phenyl-2-methylenecyclopropane (III), 3% styrene, and 2% phenylacetylene. The identity of III was established by glpc collection from the photolysis mixture and comparison, by nmr and co-injection, with authentic III prepared from phenylallene and diazomethane using Ph<sub>3</sub>PCuCl catalysis.<sup>6</sup> When II was irradiated in a Pyrex tube using xanthone (0.07 M in C<sub>6</sub>H<sub>6</sub>) as triplet sensitizer (*E*<sub>T</sub> = 74 kcal) there was negligible loss of starting material and only traces of photoisomer III were detected.



Reversibility was demonstrated by photolysis of authentic III under the conditions employed for II. After 40 min there was 30% loss of III accompanied by the formation of 6% photoisomer II and 11% styrene. Longer irradiations of either II or III led to extensive material loss (by glpc) apparently from side reactions of the starting methylenecyclopropanes to high molecular weight by-products. Attempted xanthone photosensitization of III led to disappearance of starting material but neither II nor styrene could be detected.

Irradiation under N<sub>2</sub> of a 10% acetonitrile solution of diphenylmethylenecyclopropane (IV)<sup>7</sup> by a low-pressure mercury source led in 5.5 hr to 22% disappearance of starting material and formation of 6% 1,1-diphenyl-2-methylenecyclopropane (V) plus 0.11% of 1,1-diphenylethylene; these products were also observed using a 450-W source. Isomer V was identified by glpc collection and comparison by nmr and mass spectra and co-injection with an authentic sample prepared by photolysis of diphenyldiazomethane in liquid allene.<sup>8</sup> Attempted photoreversal from V by similar irradiation of a 1.5% solution for 45 min caused 8% loss of starting V and formation of 7% 1,1-diphenylethylene as the only new glpc peak. Irradiation of an acetone solution of IV above 290 nm failed to effect photosensitized conversion to V. Likewise, xanthone (0.1 M in C<sub>6</sub>H<sub>6</sub> under N<sub>2</sub>) did not produce the

pound II, purified by silica gel chromatography and short-path distillation below 30° at 0.3 mm, was homogeneous by glpc and exhibited the reported nmr spectrum. *Cf.* E. E. Schweizer and J. G. Thompson, *Chem. Commun.*, 666 (1966).

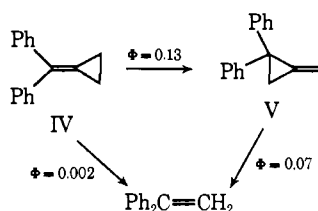
(5) Glpc analyses were conducted using 6 ft × 1/8 in. columns of 10% UCON on Chromosorb W98 and columns of 10% SE-30 on ABS at oven temperatures of 100° for II and III, 140–160° for III and IV.

(6) R. Noyori, H. Takaya, Y. Nakanishi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969). Pure III was homogeneous by glpc and showed the expected nmr signals in CDCl<sub>3</sub> at δ 1.21 (1 H, m), 1.73 (1 H, t), 2.60 (1 H, t), 5.54 (2 H, q), and 7.16 (5 H, s).

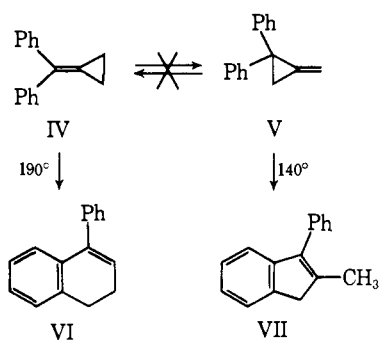
(7) K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 3267 (1966). Compound IV was recrystallized from petroleum ether to constant mp 65.0–65.5°, and showed ir, uv, and nmr spectra identical with those in the literature. Pure IV was homogeneous to glpc and contained no trace of isomer V.

(8) M. Jones, M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970). Nearly pure V was separated from nitrogen-containing by-products by preparative tlc over silica gel and characterized by the nmr signals in CDCl<sub>3</sub> at δ 1.91 (2 H, t), 5.59 (1 H, t), 5.78 (1 H, t), and 7.25 (10 H, s). Glpc analysis showed no contamination by IV.

sensitized photoisomerization of IV to V nor the reverse reaction. Quantum yields<sup>9</sup> for the direct photolyses were insensitive to added 0.3 M piperylene and are given in the equations.



The observed photoisomerizations have formal analogy as photochemical 1,3-sigmatropic shifts, notably in the 1,3-benzyl migration reported by Sanford and Hammond<sup>10</sup> and the recently described degenerate photorearrangement of 1,2-dimethylenecyclobutanes.<sup>11</sup> Unlike the case of the dimethylenecyclobutanes, however, the photoisomerizations observed for IV and V differ sharply from their thermal rearrangements, namely the reported formation of the dihydronaphthalene VI from IV at 190° and of the indene VII from V at 140°; no thermal interconversion between IV and V could be detected.<sup>12,13</sup>



Formation of phenylacetylene, styrene, and 1,1-diphenylethylene, respectively, from II, III, and V is consistent with cheletropic fragmentation of each electronically excited methylenecyclopropane to an olefin and a vinylidene carbene.<sup>14</sup> Such a photofragmentation resembles the well-known cleavage of arylcyclopropanes to olefins and carbenes<sup>15a</sup> and has parallel in the direct or Hg(6<sup>3</sup>P<sub>1</sub>)-sensitized photolysis of methylenecyclopropane itself to ethylene and acetylene in the gas phase.<sup>15b</sup>

(9) Quantum yields were measured at low conversions using a "merry-go-round" apparatus in a Rayonet photochemical reactor equipped with eight low-pressure 2537-Å uv lamps. The light intensity of the merry-go-round lamp was measured using the photochemical conversion of cyclopentanone to 4-pentenol as the actinometer; cf. P. Dunion and C. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965), and J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970). Quantum yields of products from IV and V were independent of oxygen concentration and, in the case of IV, were constant through one-third conversion of starting material.

(10) E. Sanford and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 3497 (1970).

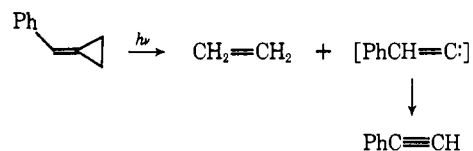
(11) J. J. Gajewski and C. N. Shih, *ibid.*, **92**, 4457 (1970).

(12) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970).

(13) Because of local symmetry in compounds II-V such plausible photoisomerizations as cis-trans rotation about the exocyclic double bond, or an interchange of CH<sub>2</sub> groups within III and V would remain undetected in our studies.

(14) E.g., K. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, **87**, 1142 (1965), and references cited therein.

(15) (a) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind. (London)*, 1562 (1966); (b) R. K. Brington, *J. Phys. Chem.*, **72**, 321 (1968).



More remarkable, however, is the "abnormal" formation of styrene from II and of 1,1-diphenylethylene from IV since these products cannot arise directly from the starting materials by the above type of photofragmentation. It is clear that the formation of 1,1-diphenylethylene from IV does not involve hydrogen transfer from solvent since we find that preparative photolysis of IV-*d*<sub>2</sub> (containing a CD<sub>2</sub> in place of a CH<sub>2</sub>) yields a ca. 1:1 mixture of Ph<sub>2</sub>C=CH<sub>2</sub> and Ph<sub>2</sub>C=CD<sub>2</sub> by glpc-mass spectral analysis. Nor does the 1,1-diphenylethylene arise from an impurity in IV since careful recrystallization of IV does not affect the quantum yield. The possibility that the 1,1-diphenylethylene results from a secondary photoreaction of the primary photoproduct V was precluded by the fact that the quantum yield of 1,1-diphenylethylene from IV is invariant over conversions ranging from 1.5 to 10% production of V. Therefore at low conversions the 1,1-diphenylethylene must arise subsequent only to electronic excitation of IV to its singlet, yet neither this singlet nor an acyclic intermediate of the trimethylenemethane type<sup>16</sup> are structurally reasonable as immediate precursors of 1,1-diphenylethylene. A clue to the possible origin of 1,1-diphenylethylene from IV may lie in the work of Frey who showed that addition of methylene (from photolysis of CH<sub>2</sub>N<sub>2</sub> or ketene by 310-370-nm light) to allene in the gas phase produces not only the expected methylenecyclopropane but also ethylene and acetylene, the latter pair presumably from cheletropic fragmentation of vibrationally hot methylenecyclopropane arising from the initial cycloaddition.<sup>17</sup> It is possible, therefore, that the "abnormal" olefins in our series arise from hot ground states of primary photoproducts which undergo, in part, carbene-olefin fragmentations before collisional deactivation by solvent.<sup>18</sup> Experimental consequences of this and alternative hypotheses are presently under investigation.

(16) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

(17) H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961); cf. W. von E. Doering, J. C. Gilbert, and P. A. Leermakers, *Tetrahedron*, **24**, 6863 (1968).

(18) For an example of possible "hot ground-state" intermediates in solution photochemistry and a discussion of theoretical limitations on this hypothesis, see E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, **86**, 5050 (1964). Vibrationally hot intermediates have been invoked in the degenerate photorearrangement of 1,2-dimethylenecyclobutanes by Gajewski and Shih.<sup>11</sup>

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