

THE PHOTOCHEMISTRY OF A PHENYLPROPENYL ALLENE; SUPPRESSION OF THE DI- $\pi$ -METHANE REARRANGEMENT IN AN ALLENIC SYSTEM

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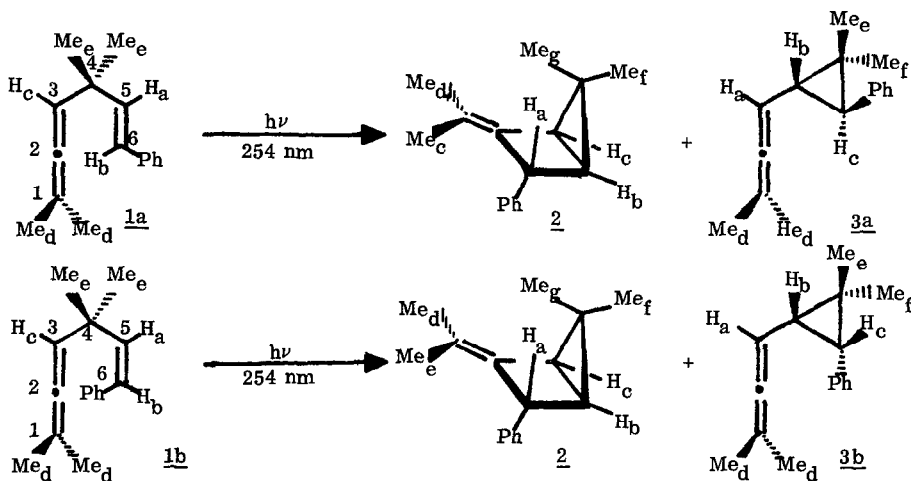
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(Received in USA 18 June 1973; received in UK for publication 31 August 1973)

Recently, several studies have appeared<sup>2</sup> which focus on the question of the importance of C-4 substitution on the singlet di- $\pi$ -methane rearrangement. It has been demonstrated that the presence of gem-dimethyl substitution at C-4 appears to favor the di- $\pi$ -methane rearrangement<sup>2</sup> (vinyl cyclopropane formation) while the absence of methyls and the presence of hydrogens at C-4 tend to favor formation of bicyclo[2.1.0]pentane (housane) derivatives.<sup>2a, b, c</sup> As a continuation of our studies involving the di- $\pi$ -methane rearrangement<sup>3</sup>, we have had occasion to study the effect of unusual hybridization at C-2 on the course of the rearrangement. We wish to report our preliminary results on the photochemistry of the allenes 1a and 1b where it is observed that the di- $\pi$ -methane rearrangement, specifically of 1a, is suppressed in favor of what is presumed to be the symmetry allowed  $\pi^2_s + \pi^2_s$  intramolecular cycloaddition.

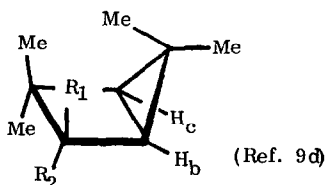


Direct irradiation<sup>4</sup> of 1a<sup>5</sup>, 6a,b ( $J_{ab} = 15.5$  Hz)<sup>6c</sup> in *t*-butyl alcohol for 5 min (7.5% conversion) gives primarily the bicyclo[2.1.0]pentane 2<sup>6</sup> and a minor product assigned the allene cyclopropane structure 3a (4.9:1, respectively). Similarly, direct irradiation of 1b ( $J_{ab} = 12.5$  Hz) gives predominantly 2 along with a compound tentatively assigned 3b<sup>7a</sup>, the epimer of 3a<sup>7b</sup>. For preparative purposes irradiations were conducted in benzene (30 min) where similar results were obtained although the ratio 2:3a is reduced to 1.9:1. In contrast to the direct irradiation studies, sensitized irradiation using acetone as a solvent sensitizer gave rise to geometric isomerization (*cis*:*trans* from 1a, 7.5:1; from 1b, 5.6:1) without skeletal reorganization. This indicates that both the di- $\pi$ -methane rearrangement products 3a and 3b and the bicyclo[2.1.0]pentane 2 are formed by way of the singlet rather than triplet state. Furthermore all appear to be primary photoproducts based upon data obtained in the low conversion runs.

The structures of the photoproducts were established using pmr and ir spectral data. Their mass spectra confirm that they are isomeric with the precursor allenes. Retention of the allene moiety and loss of the styryl chromophore in 3a and 3b were confirmed by ir and pmr spectroscopy. The long range coupling between Me<sub>d</sub> and H<sub>a</sub> ( $J_{ad} = 3.0$  Hz), observed in the pmr spectra of 3a and 3b, as well as 1a and 1b ( $J_{cd} = 3.0$  Hz), is typical for related allenic systems.<sup>5b</sup> The stereochemistry tentatively assigned to 3a was established on the basis of the pmr double resonance experiments ( $J_{bc} = 6.5$  Ha)<sup>8</sup> and nuclear Overhauser effect studies.

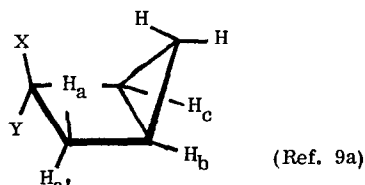
The structure 2 was arrived at by examination of the pmr spectrum which, aside from the aromatic protons, showed a broadened singlet at  $\delta$  3.17 (H<sub>a</sub>), a broadened doublet at 2.15 (H<sub>c</sub>), a sharp doublet centered at 1.61 (H<sub>b</sub>,  $J_{ab} < 0.5$  Hz;  $J_{bc} = 5.0$  Hz), in addition to four singlets at  $\delta$  1.60, 1.24, 1.21 and 1.01 assigned to Me<sub>d</sub>, Me<sub>b</sub>, Me<sub>f</sub> and Me<sub>g</sub>, respectively. The two lower field singlets are broadened and of lesser intensity relative to the two higher field singlets and this may be attributed to long range homoallylic coupling to H<sub>a</sub>. This observation was confirmed by double resonance experiments. Also, the protons whose signals are assigned to H<sub>a</sub> and H<sub>c</sub> were shown by double resonance to be coupled. The anti configuration assigned to 2 is consistent with the reported data since coupling has been observed for the analogous protons in closely related systems such as 4 - 6.<sup>9</sup> Additional confirmation of this structural assignment was obtained utilizing the nuclear Overhauser effect. NOe's of 13.3% and 4.5% were observed between the signals assigned to Me<sub>g</sub> and H<sub>a</sub>, and Me<sub>e</sub> and H<sub>a</sub>, respectively. Furthermore, if the bicyclo[2.1.0]pentane possessed the alternate epimeric structure 7, a coupling constant ( $J_{ab}$ ) of 2-4 Hz would be expected as is observed in the structurally similar model compounds 4 - 6. The thermal reversion of 2 to 1a ( $T > 200^\circ\text{C}$ ), a reaction which is not without precedent in bicyclo[2.1.0]pentane chemistry,<sup>10</sup> provides additional support for the assignment.

Several points regarding the preliminary observations presented here deserve comment. The unusual feature of the photochemistry observed for 1a and 1b is that the cycloaddition reaction leading to 2, represents the major reaction pathway and that the di- $\pi$ -methane process, affording 3a and 3b, represents the minor reaction mode. These results are to be contrasted with those obtained for the structurally related acyclic 1,4-diolefinic systems<sup>2a</sup>, where vinyl cyclopropane rather than bicyclo[2.1.0]pentane formation is the



$$\underline{4a} \text{ (R}_1\text{=H}_a\text{, R}_2\text{=Ph) } J_{ab} = 0.0 \text{ Hz}$$

$$\underline{4b} \text{ (R}_1\text{=Ph, R}_2\text{=H}_a\text{) } J_{ab} = 2.0 \text{ Hz}$$



$$\underline{5a} \text{ (X=H, Y=OH) } J_{ab} = 0.5 \text{ Hz}$$

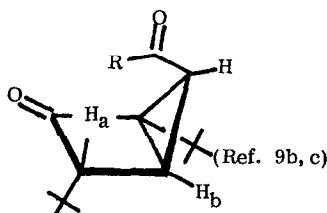
$$J_{ab}^{ac} = 1.0 \text{ Hz}$$

$$J_{a'b}^{ac} = 4.0 \text{ Hz}$$

$$\underline{5b} \text{ (X=OH, Y=H) } J_{ab} = 0.48 \text{ Hz}$$

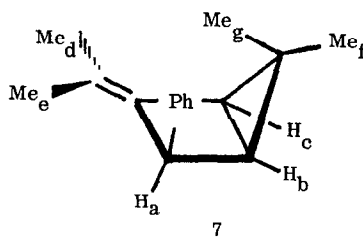
$$J_{ab}^{ac} = 1.0 \text{ Hz}$$

$$J_{a'b}^{ac} = 3.98 \text{ Hz}$$



$$\underline{6a} \text{ (R=Ph) } J_{ab} = 0.0 \text{ Hz}$$

$$\underline{6b} \text{ (R=t-Bu) } J_{ab} = 0.0 \text{ Hz}$$



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major reaction pathway.<sup>11</sup> Furthermore, it has been asserted<sup>2c</sup> that in the absence of *gem*-dimethyl substitution at the C-atom flanked by the  $\pi$ -moieties, bicyclo[2.1.0]pentane formation should dominate in 1,4-pentadienyl systems. In the case of 1a, the fact that only 3a is formed at low conversion parallels the previous observations in related systems<sup>2a, c, 3a, 12</sup> that di- $\pi$ -methane rearrangement proceeds in a highly stereoselective manner and suggests the reaction may be concerted. In addition, the formation of the bicyclo[2.1.0]pentane 2 having the anti configuration from 1a and 1b is consistent with principles based upon orbital symmetry considerations.<sup>13</sup> Two possible modes of disrotatory cyclization are available for 1a and 1b and stereochemical arguments may be invoked to account for thermodynamic control leading to preferential formation of 2; however, cyclization by sequential bond formation involving diradical intermediates is also mechanistically plausible. Finally, the formation of 2, having the anti configuration, as the sole bicyclic photoproduct from 1a and 1b, is to be contrasted with the formation of only 4b having the syn configuration from the related 1,4-diolefinic system.<sup>2a</sup> Possibly this apparent inconsistency may reflect subtle electronic and/or steric differences between the olefinic<sup>2a</sup> and allenic moieties.

**ACKNOWLEDGMENT** for partial support of this work is made to the National Science Foundation (Grant GP28171) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF 5471). We also wish to thank Dr. K. Ehrlich, Dr. E. Elder, and Mrs. J. Thompson for technical assistance.

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- (4) Irradiations were conducted in serum-capped Vycor test tubes employing a Rayonet RPR-100 Chamber Reactor equipped with 16 8-watt 254 nm or 350 nm lamps and a "merry-go-round" apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.). All samples were degassed by purging with nitrogen for a period of 45 min prior to irradiation.
- (5) (a) Compounds 1a and 1b were obtained as a ~1:1 mixture from 2,2,5-trimethyl-3,4-hexadien-1-ol<sup>5b</sup> using the Wittig reaction with benzylidenetriphenylphosphorane. The analytical and spectral properties of 1a and 1b are consistent with their assigned structures. Complete synthetic details will be presented in our full paper; (b) R. S. Bly and S. U. Koock, *J. Amer. Chem. Soc.*, **91**, 3292 (1969).
- (6) (a) Satisfactory combustion analyses and mass spectra were obtained for all new compounds with the exception of 3b; (b) all separations and purifications were achieved by glc utilizing either a 5 ft or 10 ft column of 30% SE 30 on Chromasorb P at a temperature of 140<sup>o</sup>; (c) all pmr data were obtained at both 60 and 100 MHz.
- (7) (a) The photochemistry of 1b is considerably more complex than the photochemistry of 1a. This is presumably due to the prior cis-trans isomerization of 1b to 1a which competes effectively with the rearrangement; however, during low conversion runs using 1b, formation of 2 appears to predominate over the di- $\pi$ -methane process; (b) while compound 3b has not been obtained pure, its nmr spectrum, as expected, was very similar to 3a, with distinct differences appearing in the aliphatic region.
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- (11) Bicyclo[2.1.0]pentyl systems may be formed as the major photoproducts from cyclic 1,4-dienes. See for example S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968).
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