

Intramolecular Photocycloaddition of *N*-Benzylstyrylacetamides. [2 + 2] Addition of Styrenes to Benzenes

Hiromu Aoyama,* Yoshiaki Arata, and Yoshimori Omote

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305 Japan

Irradiation of *N*-benzylstyrylacetamides gave tricyclic products *via* intramolecular [2 + 2] cycloaddition between the styryl and the phenyl groups.

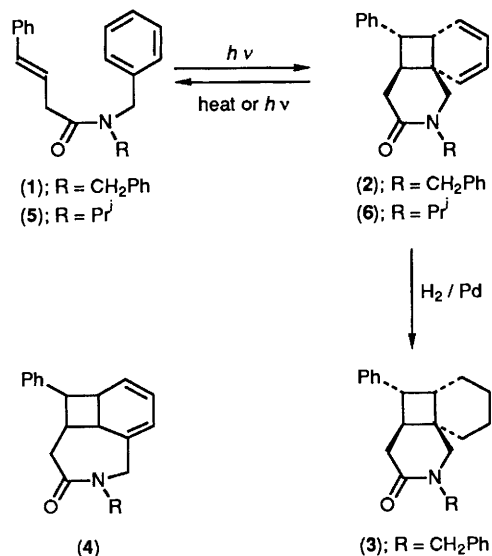
Photochemical reactions of styrenes have received much attention.¹ Styrenes undergo *cis-trans* isomerisation,² dimerisation,³ solvent-addition,⁴ and hydrogen abstraction.⁵ In relation to our studies on photoreactions of styrenes possessing a nitrogen-containing functional group,⁶ here we report intramolecular cycloaddition of *N*-benzylstyrylacetamides. This reaction represents the first example of [2 + 2] addition of styrenes to benzenes.⁷

When *N,N*-dibenzylstyrylacetamide (1) in methanol was irradiated with a low pressure mercury lamp, a tricyclic product (2) was obtained in 95% yield at 75% conversion. The structure of (2) was elucidated on the basis of spectral data and

elemental analysis. The structure was further supported by the chemical reactions: (2) reverted to (1) quantitatively on heating or irradiation, and catalytic hydrogenation of (2) gave a crystalline tetrahydro derivative (3) whose structure was determined from spectral data and elemental analysis. An alternative structure (4) was eliminated as the ¹³C NMR spectrum of the product showed the presence of a quaternary carbon and three tertiary carbons. The stereochemistry of (2) was tentatively assigned as shown in Scheme 1 since formation of a single stereoisomer suggested retention of the *trans* structure of (1). Similarly, irradiation of *N*-benzyl-*N*-isopropyl amide (5) gave (6) in 63% yield at 55% conversion.

Although the reaction of (1) was slightly sensitized by xanthone or Michler's ketone, the efficiency was quite low. Accordingly, the reaction by direct irradiation is presumed to involve a singlet reaction. The stereospecificity of the reaction is consistent with the singlet mechanism.

Photochemical cycloaddition of alkenes to benzenes has been studied extensively.⁸⁻¹¹ The [2 + 2] addition (*ortho* addition) of S₁ benzenes to S₀ alkenes is symmetry forbidden¹² and takes place efficiently only when mixing with charge transfer states occurs.¹³ Meanwhile, the addition of S₁ alkenes to S₀ benzenes is symmetry allowed.¹² The present reactions are presumed to proceed *via* excitation of the styrene moiety in view of the extinction coefficient at 254 nm [(1); ε 2 × 10⁴]. It is known that many [2 + 2] photocycloadditions proceed *via* exciplexes.¹⁴ The absorption and fluorescence spectra of (1) were almost the same as those of β-methylstyrene. This fact indicates the absence of interaction between the styryl group and the phenyl group in both the ground and singlet excited states, although intervention of nonemissive exciplexes in the photoreaction is not necessarily eliminated. Examples of cycloadditions of excited alkenes to benzenes are scarce, and have been limited to the reactions of alkenes bearing strongly electron-withdrawing substituents, to our knowledge.¹⁵ Photo-addition of β-methylstyrene to benzene or toluene did not



Scheme 1

occur even on prolonged irradiation so proximity effects are presumed to play crucial roles in the photoreaction of (1) or (5). Intramolecular photocycloadditions have been investigated extensively,¹⁶ and it is well known that interactions between two chromophores are particularly favourable when they are connected by chains with three intervening units.¹⁷ In the present case, the chain consists of four units. The frozen rotation of the CO-N bonds of these amides during the photoprocess may make the cycloaddition favourable.

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References

- 1 For reviews see: (a) P. J. Kropp, in 'Organic Photochemistry,' ed. A. Padwa, Dekker, New York, 1979, vol. 4; (b) J. J. McCullough, *Chem. Rev.*, 1987, **87**, 811.
 - 2 J. L. Goodman, K. S. Peters, H. Misawa, and R. A. Caldwell, *J. Am. Chem. Soc.*, 1986, **108**, 6803, see also ref. 1(a).
 - 3 W. G. Dauben, H. C. van Riel, J. D. Robbins, and G. J. Wagner, *J. Am. Chem. Soc.*, 1979, **101**, 6383, see also ref. 1(b).
 - 4 P. Wan and K. Yates, *J. Org. Chem.*, 1983, **48**, 869; S. L. Mattes and S. Farid, in 'Organic Photochemistry,' ed. A. Padwa, Dekker, New York, 1983, vol. 6; ref. 1(a).
 - 5 F. D. Lewis and G. D. Reddy, *J. Am. Chem. Soc.*, 1989, **111**, 6465; J. M. Hornback and G. S. Proel, *ibid.*, 1979, **101**, 7367.
 - 6 H. Aoyama, Y. Arata, and Y. Omote, *J. Chem. Soc., Chem. Commun.*, 1985, 1381; *J. Chem. Soc., Perkin Trans. 1*, 1986, 1165; *J. Org. Chem.*, 1987, **52**, 4639; H. Aoyama, T. Tomohiro, Y. Arata, and Y. Omote, *J. Phys. Org. Chem.*, 1988, **1**, 123.
 - 7 [2 + 2] Photocycloadditions of styrenes to electron-deficient alkenes or polynuclear aromatic compounds such as cyano-naphthalene have been reported: M. Yasuda, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 502; R. A. Caldwell and T. Maw, *J. Photochem.*, 1979, **11**, 165; H. Sakuragi, K. Tokumaru, H. Itoh, K. Terakawa, K. Kikuchi, R. A. Caldwell, and C. Hsu, *J. Am. Chem. Soc.*, 1982, **104**, 6796; ref. 1(b).
 - 8 D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1977, **33**, 2459.
 - 9 A. Gilbert, in 'Synthetic Organic Photochemistry,' ed. W. M. Horspool, Plenum, New York, 1984.
 - 10 A. Gilbert, in *Pure Appl. Chem.*, 1980, **52**, 2669.
 - 11 A. Gilbert and P. Yianni, *Tetrahedron*, 1981, **37**, 3275.
 - 12 D. Bryce-Smith, *Chem. Commun.*, 1969, 806; D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1976, **32**, 1309.
 - 13 D. Bryce-Smith, A. Gilbert, and J. Mattay, *Tetrahedron*, 1986, **42**, 6011; J. Mattay, *J. Photochem.*, 1987, **37**, 167; K. N. Houk, *Pure Appl. Chem.*, 1982, **54**, 1663.
 - 14 R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, 1980, **13**, 45.
 - 15 D. Bryce-Smith, A. Gilbert, N. Al-Jalal, R. R. Deshpande, J. Grzonka, M. A. Hems, and P. Yianni, *Z. Naturforsch., Teil B*, 1983, **38**, 1101; A. Gilbert and P. Yianni, *Tetrahedron Lett.*, 1982, **23**, 4611; I. W. J. Still and T. S. Leon, *ibid.*, 1979, 1097.
 - 16 H. Morrison, in 'Organic Photochemistry,' ed. A. Padwa, Dekker, New York, 1979, vol. 4; ref. 1(b); ref. 9.
 - 17 F. C. De Schryver, N. Boems, J. Huybrechts, J. Daemem, and M. Brackelaire, *Pure Appl. Chem.*, 1977, **49**, 237.
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