

## Photochemical Reactions of $\beta$ -Aminovinyl Phenyl Ketones and Related Compounds

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Photochemical reactions of some  $\beta$ -aminovinyl ketones and related compounds have been examined. Irradiation of the  $\beta$ -*NN*-dialkylaminovinyl phenyl ketones (1a—g) yielded the corresponding pyrroles (2a—g'), while ketones (1h—m) were inert. Irradiation of the ( $\beta$ -benzoylviny)ltrialkylammonium chlorides (7a and b) afforded the 1,4-diketones (8a and b) respectively. Irradiation of  $\beta$ -ethoxyvinyl phenyl ketone (5) gave an intractable mixture, while the corresponding thioketone (6) was photochemically inactive. Photolysis of the 2-dialkylaminobenzo-phenones (9a and b) gave the corresponding indoles (10a and b) respectively, accompanied by dealkylation products. The formation of the pyrrole was presumed to occur from the  $n\text{-}\pi^*$  triplet state. The mechanisms of these photochemical reactions are discussed.

PHOTOCHEMICAL reactions of conjugated enones and dienones have been studied extensively.<sup>1</sup> However those of  $\beta$ -aminovinyl ketones have received little attention. Previously, one of us reported the photochemical isomerization of a 2,3-dihydro-4-pyridone

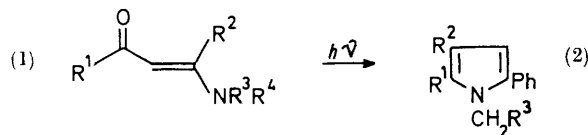
<sup>1</sup> A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, New York, 1969.

derivative,<sup>2a</sup> and Yamada *et al.*<sup>2b</sup> recently reported the photochemical synthesis of benzazocine derivatives

<sup>2</sup> (a) C. Kashima, M. Yamamoto, Y. Sato, and N. Sugiyama, *Bull. Chem. Soc. Japan*, 1969, **42**, 3596; (b) K. Yamada, T. Konakahara, S. Ishihara, H. Kanamori, T. Itoh, K. Kimura, and H. Iida, *Tetrahedron Letters*, 1972, 2513; (c) H. Aoyama, T. Nishio, Y. Hirabayashi, H. Hasegawa, H. Noda, and N. Sugiyama, *J.C.S. Chem. Comm.*, 1972, 775.

from cyclic  $\beta$ -*N*-phenylaminovinyl ketones. We now report the photochemical synthesis of some pyrroles from  $\beta$ -*NN*-dialkylaminovinyl phenyl ketones, and some related reactions.

When  $\beta$ -*NN*-dimethylaminovinyl phenyl ketone (1a) in benzene was irradiated in a Pyrex vessel with a high pressure mercury lamp, 1-methyl-2-phenylpyrrole (2a) (37%) was obtained. This compound was identified by direct comparison with an authentic sample.<sup>3</sup>



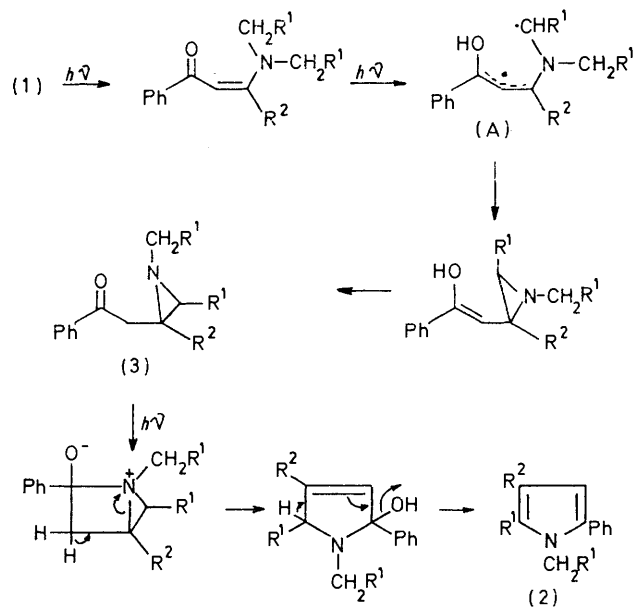
- a; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Me  
 b; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Et  
 c; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Pr<sup>n</sup>  
 d; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Bu<sup>n</sup>  
 e; R<sup>1</sup> = Ph, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = Et  
 f; R<sup>1</sup> = Ph, R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = Pr<sup>n</sup>  
 g; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = Me, R<sup>4</sup> = Et  
 h; R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = Me  
 i; R<sup>1</sup> = Ph, R<sup>2</sup> = Me, R<sup>3</sup> = H, R<sup>4</sup> = CH<sub>2</sub>Ph  
 j; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = CH<sub>2</sub>Ph  
 k; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup>, R<sup>4</sup> = [CH<sub>2</sub>]<sub>4</sub>  
 l; R<sup>1</sup> = Ph, R<sup>2</sup> = H, R<sup>3</sup>, R<sup>4</sup> = [CH<sub>2</sub>]<sub>2</sub>O[CH<sub>2</sub>]<sub>2</sub>  
 m; R<sup>1</sup> = Me, R<sup>2</sup> = H, R<sup>3</sup> = R<sup>4</sup> = Et

- (2)  
 a; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H  
 b; R<sup>1</sup> = R<sup>3</sup> = Me, R<sup>2</sup> = H  
 c; R<sup>1</sup> = R<sup>3</sup> = Et, R<sup>2</sup> = H  
 d; R<sup>1</sup> = R<sup>3</sup> = Pr<sup>n</sup>, R<sup>2</sup> = H  
 e; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me  
 f; R<sup>1</sup> = R<sup>3</sup> = Et, R<sup>2</sup> = Me  
 g; R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me  
 g'; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H

Irradiation of the enones (1b–f) under the same conditions gave the corresponding pyrroles (2b) (40%), (2c) (46%), (2d) (19%), (2e) (11%), and (2f) (18%) respectively, while (1g) gave a 3:1 mixture of (2g) and (2g') (combined yield 27%). The n.m.r. spectrum of (2b) indicated the presence of a methyl group [ $\delta$  2.30 (3H, s)], an ethyl group [ $\delta$  1.18 (3H, t) and 3.90 (2H, q)], and a phenyl group [ $\delta$  7.34 (5H, s)]. The signals of the pyrrole ring protons [ $\delta$  5.93 (1H, d) and 6.08 (1H, d, *J* 4 Hz)] showed that the pyrrole was 1,2,5-trisubstituted.<sup>4</sup> The product (2b) was therefore identified as 1-ethyl-2-methyl-5-phenylpyrrole. The structures of the other pyrroles were also elucidated on the basis of spectral data and elemental analyses (see Experimental section). The enones (1h–m) however, did not yield the corresponding pyrroles under the same conditions.

A reasonable mechanism for the formation of the pyrroles is presented in Scheme I. In this postulated

mechanism, an aziridinyl ketone (3) is formed initially. Jorgensen and Yang have reported analogous photocyclization of  $\beta$ -substituted  $\alpha\beta$ -unsaturated ketones to cyclopropyl ketones.<sup>5</sup> An attempt to synthesize (3; R<sup>1</sup> = R<sup>2</sup> = H) from 3,4-dichlorobutyrophenone and methylamine<sup>6</sup> was unsuccessful, the product being 1-methyl-2-phenylpyrrole (2a). The intermediacy of (3; R<sup>1</sup> = R<sup>2</sup> = H) in the reaction could not be confirmed. A zwitterionic intermediate similar to that in Scheme 1 has been postulated by Padwa *et al.*<sup>7</sup> for the photochemical reaction of a 2-arylozazetidine. A mechanism as shown in Scheme 2, involving photochemical isomerization<sup>8</sup> of a pyrrole (4), was disproved because (4; R<sup>1</sup> = R<sup>2</sup> = H)<sup>9</sup> did not isomerize to (2a) on irradiation.



SCHEME 1

The photochemical reactions of (1a–g) were completely quenched by the addition of 1,3-pentadiene, and they also proceeded in *n*-hexane but not in methanol or acetonitrile.<sup>10</sup> These facts suggested that the  $\delta$ -hydrogen abstraction proceeded *via* the  $n$ - $\pi^*$  triplet state.

The non-reactivity of (1h and i) in photolysis can be explained in terms of their intramolecular hydrogen bonds,<sup>11,12</sup> while the inertness of (1j–m) toward photolysis cannot be explained at present.

<sup>3</sup> A. Holy and Z. Arnold, *Coll. Czech. Chem. Comm.*, 1965, **30**, 346.

<sup>4</sup> T. J. Batterham, 'N.M.R. Spectra of Simple Heterocycles,' John Wiley, New York, 1973.

<sup>5</sup> N. J. Jorgensen and N. C. Yang, *J. Amer. Chem. Soc.*, 1963, **85**, 1698.

<sup>6</sup> The synthesis of 1-(azirin-2-yl)propan-2-one from 4,5-dichloropentan-2-one and ammonia (at 100°), and that of 2-methylpyrrole from the same reagents (at 200°) have been reported: P. Rosenmund and K. Grubel, U.S.P. 3,687,962/1972 *Chem. Abs.*, 1973, **78**, 136,045).

<sup>7</sup> A. Padwa, F. Albrecht, P. Singh, and E. Vega, *J. Amer. Chem. Soc.*, 1971, **93**, 2928.

<sup>8</sup> H. Hiraoka, *Chem. Comm.*, 1970, 1306; 1971, 1610.

<sup>9</sup> S. Hauptmann and J. Weisflog, *J. prakt. Chem.*, 1972, **314**, 353; the pyrrole (4a) is easily distinguishable from (2a) on the basis of the n.m.r. spectra (see Experimental section).

<sup>10</sup> Similar solvent effects in photochemical hydrogen abstraction of ketones have been reported: G. Porter and P. Suppan, *Proc. Chem. Soc.*, 1964, 191; *Trans. Faraday Soc.*, 1965, **61**, 1664.

<sup>11</sup> N. M. Brown and D. C. Nonhebel, *Tetrahedron*, 1968, **24**, 5655.

<sup>12</sup> A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2051.



*J* 2.2 Hz, H-3 and -4), 6.70 (1H, t, *J* 2.2 Hz, H-5), and 7.34 (5H, s, C<sub>6</sub>H<sub>5</sub>);  $\lambda_{\text{max}}$  (EtOH) 279 nm ( $\epsilon$  11,000).

(ii) 1-Ethyl-2-methyl-5-phenylpyrrole (2b) had b.p. 125–130° at 3 mmHg;  $\nu_{\text{max}}$  (film) 3050, 1600, 1510, 755, and 700 cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 1.18 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 2.30 (3H, s, 2-CH<sub>3</sub>), 3.90 (2H, q, NCH<sub>2</sub>), 5.93 (1H, d, *J* 4 Hz, H-3), 6.08 (1H, d, *J* 4 Hz, H-4), and 7.34 (5H, s, C<sub>6</sub>H<sub>5</sub>);  $\lambda_{\text{max}}$  (EtOH) 286 nm ( $\epsilon$  11,600) (Found: C, 84.2; H, 8.35; N, 7.4. C<sub>13</sub>H<sub>15</sub>N requires C, 84.3; H, 8.15; N, 7.55%).

(iii) 2-Ethyl-5-phenyl-1-propylpyrrole (2c) had b.p. 110–115° at 3 mmHg;  $\nu_{\text{max}}$  (film) 3055, 1603, 1510, 745, and 695 cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 0.72 (3H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.30 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.50 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.63 (2H, q, 2-CH<sub>2</sub>), 3.80 (2H, t, NCH<sub>2</sub>), 5.93 (1H, d, *J* 3.5 Hz, H-3), 6.08 (1H, d, *J* 3.5 Hz, H-4), and 7.34 (5H, s, C<sub>6</sub>H<sub>5</sub>) (Found: C, 84.7; H, 8.95; N, 6.45. C<sub>15</sub>H<sub>19</sub>N requires C, 84.45; H, 9.0; N, 6.55%).

(iv) 1-Butyl-5-phenyl-2-propylpyrrole (2d) had b.p. 115–120° at 1 mmHg;  $\nu_{\text{max}}$  (film) 3060, 3030, 1600, 1510, 750, and 690 cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 0.75–1.99 (12H, m, methyls and methylenes), 2.62 (2H, t, 2-CH<sub>2</sub>), 3.88 (2H, t, NCH<sub>2</sub>), 5.97 (1H, d, *J* 3.5 Hz, H-3), 6.15 (1H, d, *J* 3.5 Hz, H-4), and 7.38 (5H, s, C<sub>6</sub>H<sub>5</sub>) (Found: C, 84.75; H, 9.65; N, 5.7. C<sub>17</sub>H<sub>23</sub>N requires C, 84.6; H, 9.6; N, 5.7%).

(v) 1-Ethyl-2,3-dimethyl-5-phenylpyrrole (2e) had b.p. 125–132° at 3 mmHg;  $\nu_{\text{max}}$  (film) 3070, 1605, 1510, 765, and 690 cm<sup>-1</sup>;  $\delta$  (CS<sub>2</sub>) 1.13 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.93 (3H, s, 3-CH<sub>3</sub>), 2.13 (3H, s, 2-CH<sub>3</sub>), 3.75 (2H, q, NCH<sub>2</sub>), 5.68 (1H, s, H-4), and 7.11 (5H, s, C<sub>6</sub>H<sub>5</sub>) (Found: C, 83.9; H, 8.55; N, 6.95. C<sub>14</sub>H<sub>17</sub>N requires C, 84.35; H, 8.6; N, 7.05%).

(vi) 2-Ethyl-3-methyl-5-phenyl-1-propylpyrrole (2f) had b.p. 85–90° at 2 mmHg;  $\nu_{\text{max}}$  (film) 3070, 1605, 1510, 750, and 680 cm<sup>-1</sup>;  $\delta$  (CS<sub>2</sub>) 0.70 (3H, t, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.13 (3H, t, CH<sub>2</sub>CH<sub>3</sub>), 1.52 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.97 (3H, s, 3-CH<sub>3</sub>), 2.54 (2H, q, 2-CH<sub>2</sub>), 3.70 (2H, t, NCH<sub>2</sub>), 5.72 (1H, s, H-4), and 7.18 (5H, s, C<sub>6</sub>H<sub>5</sub>) (Found: C, 84.2; H, 9.1; N, 6.0. C<sub>16</sub>H<sub>21</sub>N requires C, 84.55; H, 9.3; N, 6.15%).

(vii) 1-Ethyl-2-phenylpyrrole (2g) and 1,2-dimethyl-5-phenylpyrrole (2g') were not completely separated. Their structures were elucidated on the basis of n.m.r. spectra of mixtures of them [*cf.* the spectra of (2a) and (2b)]: (2g)  $\delta$  (CDCl<sub>3</sub>) 1.30 (3H, t, CH<sub>3</sub>), 3.94 (2H, q, CH<sub>2</sub>), 6.15 (2H, d, *J* 2.2 Hz, H-3 and -4), 6.73 (1H, d, *J* 2.2 Hz, H-5), and 7.33 (5H, s, C<sub>6</sub>H<sub>5</sub>); (2g')  $\delta$  (CDCl<sub>3</sub>) 2.28 (3H, s, 2-CH<sub>3</sub>), 3.48 (3H, s, NCH<sub>3</sub>), 5.90 (1H, d, *J* 4 Hz, H-3), 6.10 (1H, d, *J* 4 Hz, H-4), and 7.33 (5H, s, C<sub>6</sub>H<sub>5</sub>) {Found [for a mixture of (2g) and (2g')]: C, 83.85; H, 7.85; N, 8.3. Calc. for C<sub>12</sub>H<sub>13</sub>N: C, 84.15; H, 7.65; N, 8.2%}.

*Attempted Synthesis of 1-Methyl-2-phenylaziridine* (3; R<sup>1</sup> = R<sup>2</sup> = H).—A solution of 3,4-dichlorobutyric acid (1 g) in thionyl chloride (5 ml) was refluxed for 1 h and evaporated. The crude acyl chloride (1 g) in benzene (5 ml) was added to a mixture of aluminium chloride (1.5 g) and benzene (30 ml) at 5°. After stirring for 2 h the

reaction mixture was worked up as usual, and chromatographed on silica gel to yield 3,4-dichlorobutyrophenone (360 mg), m.p. 38–40°;  $\nu_{\text{max}}$  (film) 1687 and 752 cm<sup>-1</sup> (Found: C, 55.6; H, 4.65. C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>O requires C, 55.3; H, 4.65%).

A solution of 3,4-dichlorobutyrophenone (100 mg) and methylamine (1 ml) in ether (5 ml) was kept in a sealed tube at 5° for 1 h, when t.l.c. showed the disappearance of the original ketone. The solution was diluted with n-hexane (5 ml) and filtered to remove methylamine hydrochloride. The filtrate was evaporated to give an oil (90 mg). The n.m.r. spectrum of the oil showed no signals above  $\delta$  2.4; this indicated the absence of (3; R<sup>1</sup> = R<sup>2</sup> = H).<sup>4</sup> The oil was chromatographed on silica gel to yield (2a) (50 mg).

*Irradiation of 1-Methyl-3-phenylpyrrole* (4; R<sup>1</sup> = R<sup>2</sup> = H).—The pyrrole was prepared according to the literature;<sup>9</sup>  $\delta$  (CDCl<sub>3</sub>) 3.58 (3H, s, CH<sub>3</sub>), 6.37 (1H, t, *J* 2.5 Hz, H-4), 6.54 and 6.82 (each 1H, t, *J* 2.5 Hz, H-2 and -5), and 7.02–7.55 (5H, m, C<sub>6</sub>H<sub>5</sub>). Irradiation of (4; R<sup>1</sup> = R<sup>2</sup> = H) (50 mg) in benzene (20 ml) for 10 h resulted in the recovery of the original pyrrole.

*Irradiation of  $\beta$ -Benzoylvinyltriethylammonium Chloride* (7a).—A solution of (7a) (1 g) in ethanol (100 ml) was irradiated in a Pyrex vessel under nitrogen for 12 h. After removal of the solvent, the residue was extracted with benzene. The benzene solution was evaporated and the residue was chromatographed on silica gel, giving 1-phenylpentane-1,4-dione (8a).

*Irradiation of  $\beta$ -Benzoylvinyltri-*n*-propylammonium Chloride* (7b).—The irradiation was carried out as in the case of (7a), yielding 1-phenylhexane-1,4-dione (8b) (70 mg); b.p. 125–130° at 3 mmHg (lit.,<sup>23</sup> 115–117° at 0.1 mmHg);  $\nu_{\text{max}}$  (film) 3050, 1710, 1682, 1595, 745, and 690 cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 1.10 (3H, t, CH<sub>3</sub>), 2.55 (2H, q, CH<sub>2</sub>CH<sub>3</sub>), 2.84 and 3.28 (4H, A<sub>2</sub>B<sub>2</sub>m, CH<sub>2</sub>CH<sub>2</sub>), and 7.20–8.15 (5H, m, C<sub>6</sub>H<sub>5</sub>).

*Irradiation of 2-Dimethylaminobenzophenone* (9a).—A solution of (9a) (200 mg) in benzene (120 ml) was irradiated in a Pyrex vessel under nitrogen for 110 h. After removal of the solvent, the residue was chromatographed on silica gel to give 1-methyl-3-phenylindole (10a) (20 mg) and 2-methylaminobenzophenone (11a) (10 mg).

*Irradiation of 2-Ethylmethylaminobenzophenone* (9b).—A solution of (9b) (500 mg) in benzene (580 ml) was irradiated as in the case of (9a), yielding 1-ethyl-3-phenylindole (10b) (20 mg), (11a) (60 mg), and 2-ethylaminobenzophenone (11b) (50 mg);  $\nu_{\text{max}}$  (film) 3300, 3050, 1620, 1570, 755, and 690 cm<sup>-1</sup>,  $\delta$  (CDCl<sub>3</sub>) 1.34 (3H, t, CH<sub>3</sub>), 3.28 (2H, q, CH<sub>2</sub>), 6.35–6.80 (2H, m, aromatic), 7.15–7.70 (7H, m, aromatic), and 8.45b (1H, s, NH).

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<sup>23</sup> J. Ficini and J. P. Genet, *Tetrahedron Letters*, 1971, 1565.