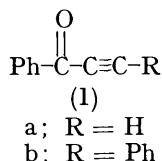


Photochemical Reactions of Acetylenic Ketones ¹

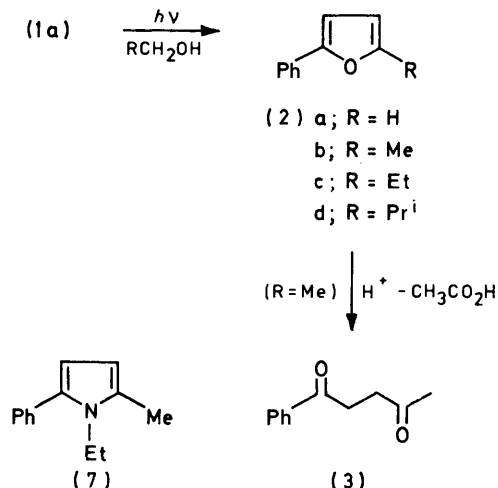
By Takehiko Nishio* and Yoshimori Omote, Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki, 300-31, Japan

The photochemical reactions of acetylenic ketones (1a and b) have been examined. Irradiation of 1-phenylprop-2-yn-1-one (1a) in alcohols gave 2,5-disubstituted furans (2a-d) in 18-27% yield *via* cyclization of the intermediate, the C-C bonded 1 : 1 adduct of (1a) and the alcohol, while irradiation of (1a) and *NN*-diethylamine in benzene gave the pyrrole (7) in 61% yield *via* cyclization of the intermediate, the C-N bonded 1 : 1 adduct of (1a) and the amine. Irradiation of 1,3-diphenylprop-2-yn-1-one (1b) and *NN*-dialkylamines afforded the C-C bonded 1 : 1 adducts (8a-c) in 30-40% yield.

PHOTOCHEMICAL addition reactions of alcohols and amines to multiple bonds have been studied extensively.² However, additions of alcohols and amines to acetylenic ketones have received little attention. Pfau *et al.*³ reported the photochemical synthesis of 4-hydroxy-4-methylpent-2-enoic acid γ -lactone from propiolic acid with propan-2-ol, and Shono *et al.*⁴ recently reported the photochemical [2 + 2]cycloaddition reaction of 4-phenylbut-3-yn-2-one and alkenes. We now report the photochemical reactions of acetylenic ketones (1a and b) the formation of 2,5-disubstituted furans (2a-d) from (1a) and alcohols, and the isolation of the C-C bonded 1 : 1 adducts (8a-c) of (1b) and *NN*-dialkylamines.



When 1-phenylprop-2-yn-1-one (1a) in methanol was irradiated in a Pyrex vessel with a high-pressure mercury lamp under argon for 24 h at room temperature, 2-



phenylfuran (2a) [20% yield based on (1a)] was obtained as the sole product. This compound was identified by direct comparison with an authentic sample.⁵ Irradiation of the acetylenic ketone (1a) in ethanol, propan-1-

† Exposure of (1a) to ethanol in the dark at room temperature for 76 h resulted in complete recovery of (1a).

ol, and 2-methylpropan-1-ol under the same conditions gave the corresponding furans (2b) (20%), (2c) (27%), and (2d) (18%), respectively. The n.m.r. spectrum of (2b) indicated the presence of a methyl group [δ 2.30 (3 H)] and a phenyl group [δ 7.1-7.85 (5 H)]. The signals of the furan ring protons [δ 5.98 (1 H, q, J 1.4, 4 Hz) and 6.48 (1 H, d, J 4 Hz)] showed that the furan was 2,5-disubstituted.⁶ Furthermore, the furan (2b) was hydrolysed in acetic acid to yield 1-phenylpentane-1,4-dione (3). The product (2b) was therefore identified as 2-methyl-5-phenylfuran. The structures of other furans were also elucidated on the basis of spectral data and elemental analyses. A reasonable mechanism for the formation of the furan is presented in Scheme 1. In this postulated mechanism (path A), the C-C bonded 1 : 1 adduct (4) of (1a) and an alcohol, which is formed initially by α -hydrogen abstraction of alcohol by the excited carbonyl oxygen of (1a), gives the final product by cyclization. Attempts to isolate the intermediate (4; R = Me) were unsuccessful, but the n.m.r. spectrum of the photolysate of (1a) in ethanol showed a doublet at δ 1.2 assignable to methyl protons, a multiplet at δ 3.6 due to a methine proton, and a broad singlet at δ ca. 3.8 attributable to a hydroxy-proton (exchangeable with D₂O) in a ca. 3 : 1 : 1 integral ratio for structure (4; R = Me), accompanied by the peaks corresponding to (2b) and unchanged (1a). In path B, the intermediate (5) involved in the addition reaction where the ether is formed photochemically † gives the $\beta\gamma$ -epoxyketone (6), which seems to arise *via* δ -hydrogen abstraction by the excited carbonyl oxygen of (5); the acid-catalysed rearrangement ‡ of (6) would lead to (2). Meanwhile, irradiation of 1-phenyl-3-ethoxyprop-2-one (5; R = Me), which was prepared independently⁸ in ethanol under the same conditions for 24 h, gave the furan (2b) in very low yield (<3%). These results might suggest that the furan is formed mainly through path A.

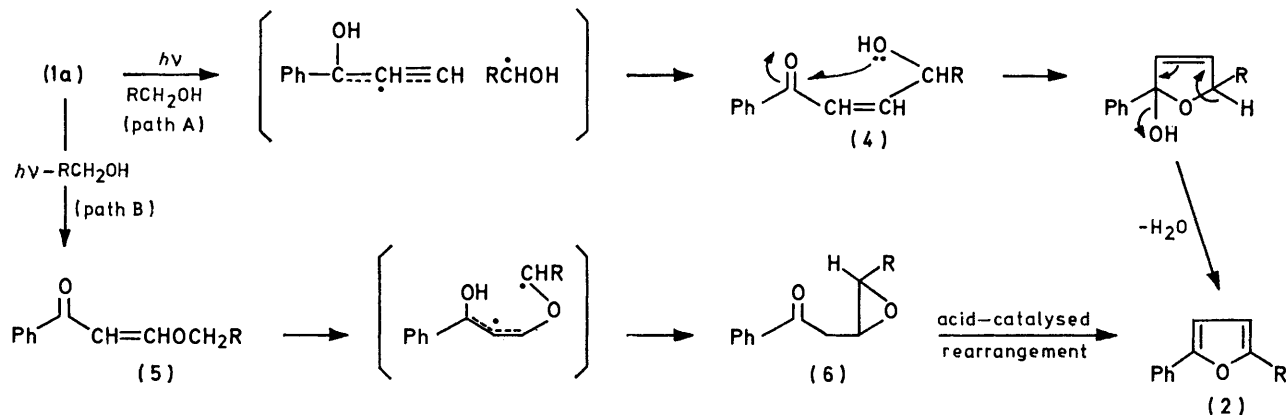
Irradiation of a solution of (1a) and diethylamine in benzene afforded *N*-ethyl-2-methyl-5-phenylpyrrole (7) in 61% yield [based on (1a)]. The formation of (7) can be explained by photochemical cyclization of the C-N bonded 1 : 1 adduct, 3-diethylamino-1-phenylprop-2-en-

‡ Padwa⁷ reported that the β,γ -epoxyketone, *trans*-3,4-epoxy-1,4-diphenylbutan-1-one, gave 2,5-diphenylfuran by acid-catalysed reaction.

1-one, * of (1a) and diethylamine from the fact that 2,5-disubstituted pyrroles were formed by photolysis of 3-dialkylamino-1-phenylprop-2-en-1-ones.⁹

Irradiation of a solution of 1,3-diphenylprop-2-yn-1-

postulated in the photoreaction of (1b) with amines to give the C-C bonded 1:1 adducts (8a-c) (Scheme 2). The formation of dibenzoylmethane (9) is presumed to proceed through the hydrolysis of another type of C-N

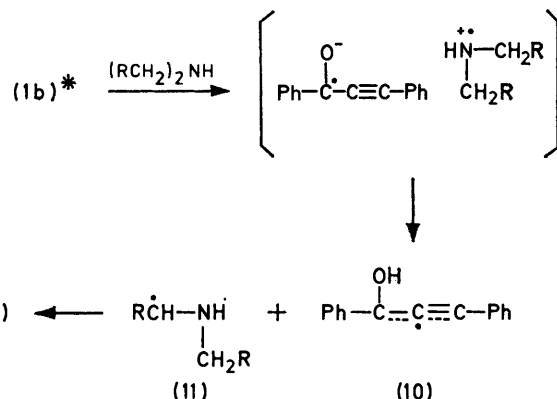
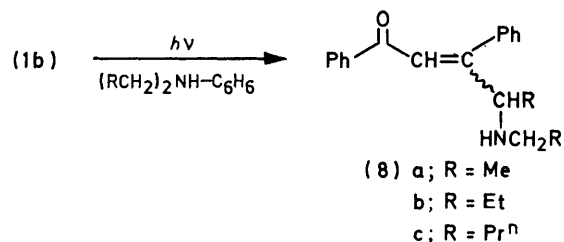


SCHEME 1

one (1b) and diethylamine in benzene afforded the C-C bonded 1:1 adduct, 4-ethylamino-4-methyl-1,3-diphenylbut-2-en-1-one (8a) [30% yield based on (1b)], and dibenzoylmethane (9) (10%), purified by silica gel column chromatography using benzene as eluant. The structure of (8a) was elucidated on the basis of spectral data (see Experimental section). Similarly, irradiation of (1b) and the other dialkylamines in benzene afforded the C-C bonded 1:1 adducts (8b and c) in 35 and 40% yield, respectively, accompanied by (9).

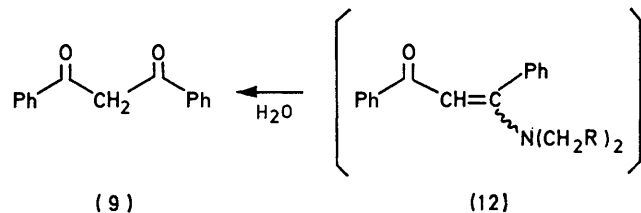
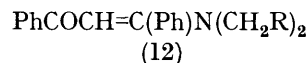
Photoreaction of ketone triplets with amines generally proceeds by way of a charge-transfer complex followed

bonded 1:1 adduct, the β -aminoenone (12), of (1b) and the amine, during the purification by column chromatography. The β -aminoenone (12) could not be obtained



SCHEME 2

even when a mixture of (1b) and diethylamine was heated in a sealed tube at 100 °C for 15 h.



by transfer of an α -hydrogen atom of the amine to the carbonyl oxygen atom, leading to radicals.¹⁰ Analogously, the similar intermediates (10) and (11) may be

* The C-N bonded 1:1 adduct, 3-diethylamino-1-phenylprop-2-en-1-one, was obtained upon leaving a solution of (1a) and diethylamine in benzene at room temperature in quantitative yield.

EXPERIMENTAL

All b.p.s are uncorrected. A Ushio 450-W high-pressure mercury lamp was used as an irradiation source.

Irradiation of 1-Phenylprop-2-yn-1-one (1a) in Alcohols.—A solution of (1a) (400 mg) in an alcohol (40 ml) was irradiated in a Pyrex vessel under argon for 15–24 h at room temperature. After removal of the solvent, the residual oil was chromatographed on silica gel. Elution with benzene yielded the furan (2).

(i) 2-Phenylfuran (2a) was identical with authentic material, b.p. 62 °C at 2 mmHg (lit.,⁵ 94 °C at 10 mmHg); ν_{max} (film) 3 050, 1 600, 1 480, 755, and 685 cm^{-1} ; δ (CDCl_3) 6.40 (1 H, q, J 2.5, 4 Hz, 4-H), 6.60 (1 H, d, J 4 Hz, 3-H), and 7.1–7.8 (6 H, m, C_6H_5 and 5-H); m/e 144 (M^+), 115, and 105.

(ii) 2-Methyl-5-phenylfuran (2b) had b.p. 82 °C at 2 mmHg (lit.,¹¹ m.p. 38–39 °C); ν_{\max} (film) 3 050, 1 585, 1 480, 775, and 685 cm^{-1} ; δ (CDCl_3) 2.30 (3 H, s, CH_3), 5.98 (1 H, q, J 1.4, 4 Hz, 3-H), 6.48 (1 H, d, J 4 Hz, 4-H), and 7.1–7.85 (5 H, m, C_6H_5); m/e 158 (M^+), 115, and 105.

(iii) 2-Ethyl-5-phenylfuran (2c) had b.p. 103 °C at 2 mmHg; ν_{\max} (film) 3 030, 1 603, 1 485, 755, and 685 cm^{-1} ; δ (CDCl_3) 1.25 (3 H, t, CH_2CH_3), 2.70 (2 H, q, CH_2CH_3), 6.03 (1 H, q, J 1.4, 4 Hz, 3-H), 6.60 (1 H, d, J 4 Hz, 4-H), and 7.1–7.75 (5 H, m, C_6H_5); m/e 172 (M^+), 157, 115, and 105 (Found: C, 83.65; H, 7.0. $\text{C}_{12}\text{H}_{12}\text{O}$ requires C, 83.7; H, 7.0%).

(iv) 2-Isopropyl-5-phenylfuran (1d) had b.p. 105 °C at 2 mmHg; ν_{\max} (film) 3 030, 1 600, 1 490, 760, and 685 cm^{-1} ; δ (CDCl_3) 1.29 [6 H, d, $\text{CH}(\text{CH}_3)_2$], 3.00 [1 H, septet, $\text{CH}(\text{CH}_3)_2$], 6.01 (1 H, q, J 1, 3.5 Hz, 3-H), 6.50 (1 H, d, J 3.5 Hz, 4-H), and 7.05–7.75 (5 H, m, C_6H_5); m/e 186 (M^+), 171, 115, and 105 (Found: C, 83.6; H, 7.4. $\text{C}_{13}\text{H}_{14}\text{O}$ requires C, 83.8; H, 7.6%).

Hydrolysis of 2-Methyl-5-phenylfuran (2b).—A solution of (2b) (50 mg) and sulphuric acid (one drop) in acetic acid (2 ml) was refluxed for 2 h. Then the mixture was poured into ice-water and extracted with ether. The extract was washed with aqueous sodium hydrogencarbonate and water and dried (MgSO_4). The solvent was distilled off *in vacuo* and the residual oil was chromatographed on silica gel using benzene as eluant, giving 1-phenylpentane-1,4-dione (3), identical with an authentic sample.⁹

Irradiation of (1a) and Diethylamine in Benzene.—A solution of (1a) (400 mg) and diethylamine (1 ml) in benzene (40 ml) was irradiated under the same conditions as described above for 15 h. After removal of the solvent, the residual oil was chromatographed on silica gel. Elution with benzene yielded *N*-ethyl-2-methyl-5-phenylpyrrole (7), which was identical with an authentic sample.⁹

Irradiation of 1,3-Diphenylprop-2-yn-1-one (1b) and Dialkylamine in Benzene.—A solution of (1b) (500 mg) and dialkylamine (1 ml) in benzene (40 ml) was irradiated under the same conditions as described above for 15 h. After removal of the solvent, the residual oil was chromatographed on silica gel. Elution with benzene yielded the C–C bonded 1 : 1 adduct (8) and dibenzoylmethane (9).

(i) 4-Ethylamino-4-methyl-1,3-diphenylbut-2-en-1-one (8a) had b.p. 200 °C at 2 mmHg (decomp.); ν_{\max} (film)

3 050, 1 660, 1 600, 1 495, 750, and 690 cm^{-1} ; δ (CDCl_3) 1.05 (3 H, t, CH_2CH_3), 1.30 (3 H, d, CHCH_3), 2.9–3.5 (2 H, m, CH_2CH_3), 4.46 (1 H, q, >CHCH_3), 6.10 (1 H, s, $\text{CH}=\text{C}<$) and 6.9–8.1 (11 H, m, $2 \times \text{C}_6\text{H}_5$ and NH, 1 H disappeared on treatment with D_2O); m/e 279 (M^+).

(ii) 4-Ethyl-1,3-diphenyl-4-n-propylaminobut-2-en-1-one (8b) had b.p. 150 °C at 1 mmHg (decomp.); ν_{\max} (film) 3 050, 1 655, 1 590, 1 490, 750, and 690 cm^{-1} ; δ (CDCl_3) 0.71 (3 H, t, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91 (3 H, t, CH_2CH_3), 1.0–2.0 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$ and CH_2CH_3), 2.6–3.6 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.17 (1 H, t, $\text{CH}<$), 6.08 (1 H, s, $\text{CH}=\text{C}<$), and 6.8–8.25 (11 H, m, $2 \times \text{C}_6\text{H}_5$ and NH).

(iii) 4-n-Butylamino-1,3-diphenyl-4-n-propylbut-2-en-1-one (8c) had b.p. 135 °C at 1 mmHg (decomp.); ν_{\max} (film) 3 050, 1 660, 1 590, 1 480, 750, and 700 cm^{-1} ; δ (CDCl_3) 0.6–1.1 (6H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.1–1.8 (8 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.6–3.7 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) 4.23 (1 H, t, $\text{CH}<$), 6.09 (1 H, s, $\text{CH}=\text{C}<$), and 6.8–8.1 (11 H, m, $2 \times \text{C}_6\text{H}_5$ and NH).

The results of elemental analysis of the C–C bonded 1 : 1 adducts (8) were not in accord with the calculated values since (8) decomposed during purification.

[8/1336 Received, 19th July, 1978]

REFERENCES

- ¹ Preliminary report; see T. Nishio and Y. Omote, *Chem. Letters*, 1976, 103.
- ² O. L. Chapman, 'Organic Photochemistry', Marcel Dekker, New York, 1967, vol. 2; D. Bryce-Smith, 'Photochemistry', The Chemical Society, London, 1970–1976, vols. 1–7.
- ³ M. Pfau, D. Dulu, and M. Vilkas, *Compt. rend.*, 1960, **251**, 2188.
- ⁴ K. Fujita, K. Yamamoto, and T. Shono, *Nippon Kagaku Kaishi*, 1974, 86.
- ⁵ D. C. Ayres and J. R. Smith, *J. Chem. Soc. (C)*, 1968, 2737.
- ⁶ T. J. Batherhan, 'N.M.R. Spectra of Simple Heterocycles', Wiley, New York, 1973.
- ⁷ A. Padwa, *J. Amer. Chem. Soc.*, 1965, **87**, 4025.
- ⁸ L. Panizzi and M. S. Siene, *Gazzetta*, 1943, **73**, 335; T. Nishio and Y. Omote, *J. Synth. Org. Chem., Japan*, 1976, **34**, 515.
- ⁹ H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N. Sugiyama, *J.C.S. Perkin I*, 1975, 298; T. Nishio and Y. Omote, *Heterocycles*, 1977, **6**, 1.
- ¹⁰ S. G. Cohen, A. Parola, and G. H. Parson, *Chem. Rev.*, 1973, **73**, 141.
- ¹¹ J. P. Girault, P. Scribe, and G. Dana, *Bull. Soc. chim. France*, 1973, 1760.