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PHOTOCHEMICAL REACTIONS OF 1-PHENYL-2-PROPYN-1-ONE IN ALCOHOLS: FORMATION OF FURANS

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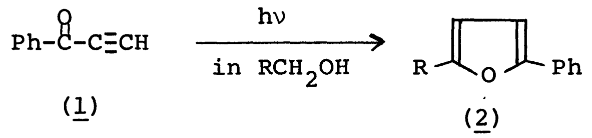
Irradiation of 1-phenyl-2-propyn-1-one (1) in various alcohols afforded 2-alkyl-5-phenyl furans (2a-d) via cyclization of the intermediate (4), 1:1-addition product of (1) and each alcohol.

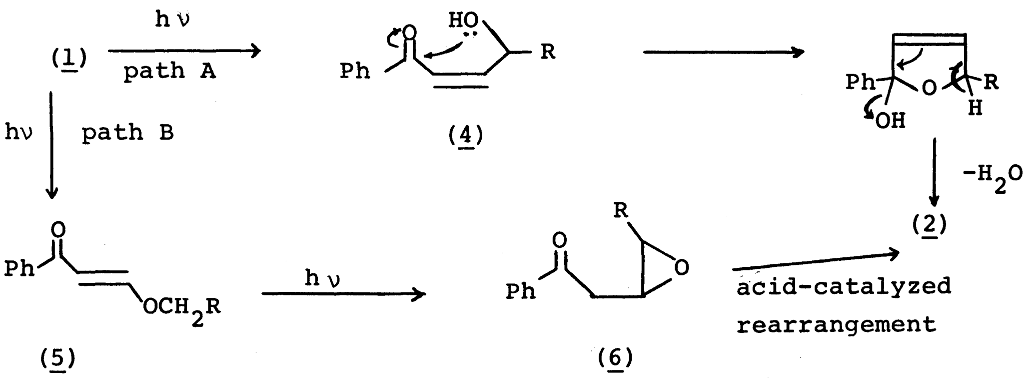
Photochemical addition reaction of alcohols with conjugated enones or olefins have been reported.[1)] However, the reaction of acetylenic ketones have not yet been given attention. We now report the photochemical formation of the furan derivatives from 1-phenyl-2-propyn-1-one (1).

When 1-phenyl-2-propyn-1-one (1) in methanol was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon for 24 hr at room temperature, 2-phenylfuran (2a) (20% based on 1), bp 62°C/2 mmHg (lit.[2)] 94°C/10 mmHg), was obtained as the sole product and recovered 1 (20%), purified by column chromatography on silica gel. Irradiation of 1 in ethanol, 1-propanol, and 2-methyl-1-propanol under the same conditions gave the corresponding furans (2b) (20%), (2c) (27%), and (2d) (18%), respectively. Irradiation of 1 in alcohols with a low-pressure mercury lamp through a quartz filter under the same conditions also gave the similar results.



a: R=H
b: R=Me
c: R=Et
d: R=iso-Pr

Hydrolysis of 2b in acetic acid produced 1-phenylpenta-1,4-dione (3). This result is in best accord with 2-alkyl-5-phenyl furan for the structure of 2b.[3)] The structures of 2a[2)] and 3[4)] were confirmed by direct comparison of spectra with authentic samples and those of other photo-products were elucidated by using spectral data and elemental analysis. The formation of the furan derivatives may be explained by two possible reaction paths (Scheme 1). In path A, 1:1-addition intermediate (4) of 1 and alcohol, which is formed initially by α-hydrogen abstraction of alcohol by the excited carbonyl oxygen of 1, gives the final product by intramolecular cyclization and dehydration. The NMR spectrum of the photolysate of 1 in ethanol showed a doublet at δ 1.2 assignable to methyl protons, the multiplet at δ 3.6 due to methine proton, and a broad singlet at ca. δ 3.8 attributable to hydroxy proton (exchangeable with D_2O) in a 3:1:1 integral ratio for the structure of 4 (R=Me), accompanied by the peaks corresponding to 2b and unreacted 1. In path B, the intermediate (5) involved in the addition reaction where the ether is formed photochemically as 1:1-addition product[5] gives the β,γ-epoxyketone (6), which seems to arise via δ-hydrogen abstraction by the excited carbonyl oxygen of 5; acid catalyzed rearrangement[6] of 6 would lead to 2. Irradiation of 1-phenyl-3-ethoxy-2-propen-1-one (5, R=Me), which was prepared independently[7], in ethanol under the same conditions for 24 hr gave the furan (2b) in very poor yield (<3%). This suggests that the furan is formed mainly through path A.



Scheme 1

References and notes

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2) D. C. Ayres and J. R. Smith, J. Chem. Soc. (C), 1968, 2737.

3) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry", W. A. Benjiamin, Inc., New York, (1968), p 105.

4) H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N. Sugiyama, J. Chem. Soc. (Perkin I), 1975, 298.

5) Exposure of 1 to ethanol in the dark at room temperature for 76 hr resulted in the complete recovery of 1.

6) A. Padwa reported that β,γ-epoxyketone, trans-1,4-diphenyl-3,4-epoxy-butan-1-one gave 2,5-diphenylfuran by acid-catalyzed reaction (J. Amer. Chem. Soc., 87, 4025 (1965))

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