Abnormal Displacement Reaction of 2-(Chloromethyl)-3,4-diphenylfuran with Aqueous Potassium Cyanide

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2-(Chloromethyl)-3,4-diphenylfuran reacted with aqueous potassium cyanide to give an α-angelica lactone derivative (V, 3,4-diphenyl-5-methyl-2(5*H*)furanone), which has never been isolated in such a reaction, as the main product.

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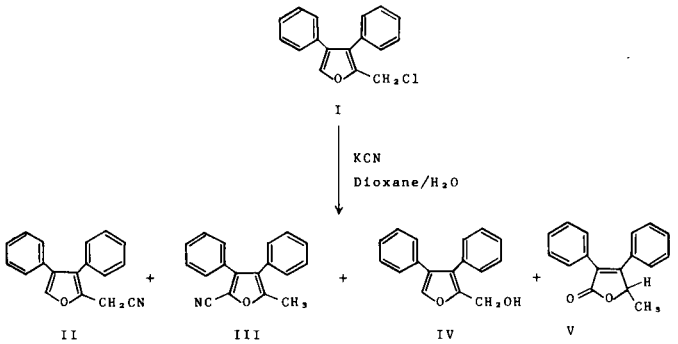
Sir:

Formation of an abnormal product, 5-cyano-2-methylfuran, by the reaction of 2-(chloromethyl)furan with aqueous potassium cyanide, has been known (1) and has attracted an interest of many chemists (2). We had an interest in how 2-(chloromethyl)-3,4-diphenylfuran (I), which possesses a conjugated system at the 3- and 4-positions of the furan ring, would behave in aqueous potassium cyanide. Thus, I (m.p. 69-70°) was prepared by reacting 3,4-diphenyl-2-furfuryl alcohol (3) with thionyl chloride. It was recognized that I was stable relative to 2-(chloromethyl)furan (4); I could be stored at room temperature for several days without observable deterioration.



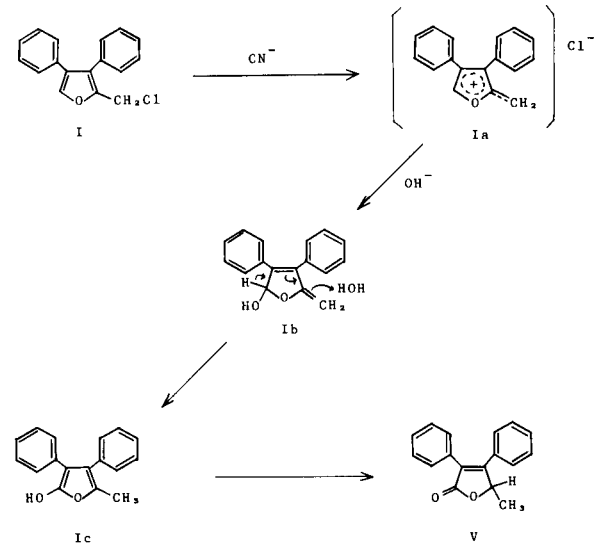
Scheme 1

Compound I was allowed to react with potassium cyanide in aqueous solution for 2 hours at 80° according to the method of Divald, *et al.* (2j), and the reaction mixture was chromatographed over silica gel (Wako gel) with benzene as eluant to give four products: 2-cyanomethyl-3,4-diphenylfuran (II) (m.p. 68-70°, 2%); 5-cyano-3,4-diphenyl-2-methylfuran (III) (m.p. 127-128°, 20%); 3,4-diphenyl-2-furfuryl alcohol (IV) (3) (trace); and 3,4-diphenyl-5-methyl-2(5*H*)furanone (V) (m.p. 137-138°, 77%) (Scheme 1).

Of these products, II, III, and IV correspond to three compounds (2j) obtained by the reaction of 2-(chloromethyl)furan with potassium cyanide in aqueous solution. Compounds of type V have so far not been isolated in a similar reaction. The structure of V was identified by various spectral data as mentioned below.

The infrared (ir) spectrum of V indicated the bands for a C=O group and a C=C group at 1750 and 1660 cm^{-1}, respectively. The mass spectrum showed m/e 250 corresponding to the molecular weight of V. The ultraviolet (uv) spectrum of V displayed two abosrption maxima at 222 nm (ε 23,500) and 248 nm (ε 14,500) in ethanol, which were similar to the maxima of *cis*-stilbene (5). In addition, the nuclear magnetic resonance (nmr) spectrum (δ ppm in deuteriochloroform) showed the following signals: ten protons on two phenyl groups (7.33, multiplet); one proton at the 5-position (5.51, quartet, $J_{CH_3'H\text{-}5}$ = 6.5 Hz); and three protons of the methyl group (1.35, doublet, $J_{CH_3'H\text{-}5}$ = 6.5 Hz). Elemental analytical values also agreed with the composition of V.

As mentioned above, the uv spectrum of V suggested that V contained a *cis*-stilbene structure and the nmr spectrum showed closely similar signals as those (H-5, 5.46, quartet, $J_{CH_3'H\text{-}5}$ = 7 Hz; 5-CH_3' 1.53, doublet, $J_{CH_3'H\text{-}5}$ = 7 Hz) of 4-*t*-butyl-5-methyl-2(5*H*)furanone reported by Divald, *et al.* (2j). Therefore, it seems certain that V is 3,4-diphenyl-5-methyl-2(5*H*)furanone.



Scheme 2

0022-152X/79/061293-02$02.25

A possible mechanism for the formation of V is proposed in Scheme 2. First the 3,4-diphenylfurylium ion (Ia) would be formed, as stated by Divald, *et al.* (2j). Then the hydroxide ion attacks the 5-position of Ia in competition with the cyanide ion to form Ib. In addition, 3,4-diphenyl-5-hydroxy-2-methylfuran (Ic) is formed from Ib by the elimination of a proton in 5-position and the addition of a proton from water to the methylene group, followed by proton transfer to give V.

Divald and others (2) have also discussed the possibility of the reaction with hydroxide ion of the solvent in the reaction of 2-(chloromethyl)furan but they did not isolate 5-hydroxy-2-methylfuran because it is unstable and results in the opening of the furan ring to give products that polymerize. However, as Ic possesses the conjugated system in the 3- and 4-position, the more stable α-angelica lactone derivative (V), which has never been isolated in such a reaction, could be isolated.

The solvolysis of I in water was further carried out. Compound I was recovered by the reaction at room temperature, but when the reaction was carried out at 80°, V was obtained in a good yield. This isolation of V seems to support the fact that cyanide ion and hydroxide ion competitively attack the 5-position of the furan ring.

REFERENCES AND NOTES

(1) T. Reichstein, *Ber.*, **63**, 749 (1930).

(2a) M. M. Runde, E. W. Scott and J. R. Johnson, *J. Am. Chem. Soc.*, **52**, 1284 (1930); (b) T. Reichstein and H. Zshokke, *Helv. Chim. Acta.*, **15**, 249 (1930); (c) E. W. Scott and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 2549 (1932); (d) K. Yu. Novitskii, Kh. Gresl and Yu. K. Yur'ev, *Zh. Org. Khim.*, **1**, 539 (1965); (e) K. Yu. Novitskii, Kh. Gresl and Yu. K. Yur'ev, *Khim. Geterotsikl. Soedin.*, **6**, 829 (1966); (f) Y. Oshiro, H. Tanisake and S. Komori, *J. Synth. Org. Chem.* Japan, **24**, 950 (1966); (g) F. Yamamoto, M. Hiroyuki and S. Oae, *Heterocycles*, **3**, 1 (1975); (h) S. Divald, M. C. Chun and M. C. Joullié, *Tetrahedron Letters*, 777 (1976); (i) T. M. Crasp and M. V. Sargent, *Aust. J. Chem.*, **27**, 905 (1975); (j) S. Divald, M. C. Chun and M. C. Joullié, *J. Org. Chem.*, **41**, 2835 (1976); (k) J. R. Carson, J. T. Hortestein, B. E. Marynoff and A. J. Molinari, *ibid.*, **42**, 1096 (1977).

(3) S. Yoshina and K. Yamamoto, *J. Pharm. Soc. Japan*, **95**, 219 (1975).

(4) W. R. Kimer and G. H. Reichter, *J. Am. Chem. Soc.*, **51**, 3131 (1929).

(5) R. M. Silverstein and C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley & Sons, New York, N. Y., 1963 p. 165.