ISSN 1070-4280, *Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 9, pp. 1416–1417. © Pleiades Publishing, Ltd., 2010.*
Original Russian Text © O.V. Petrova, I.A. Ushakov, L.N. Sobenina, A.I. Mikhaleva, B.A. Trofimov, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 9, pp. 1412–1413.

SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
N.S. Zefirov on occasion of his 75th anniversary

Formation of *N*-Benzylbenzamide from Benzyl Phenyl Ketone Oxime in a System C_2H_2–KOH–DMSO. Key Role of Acetylene

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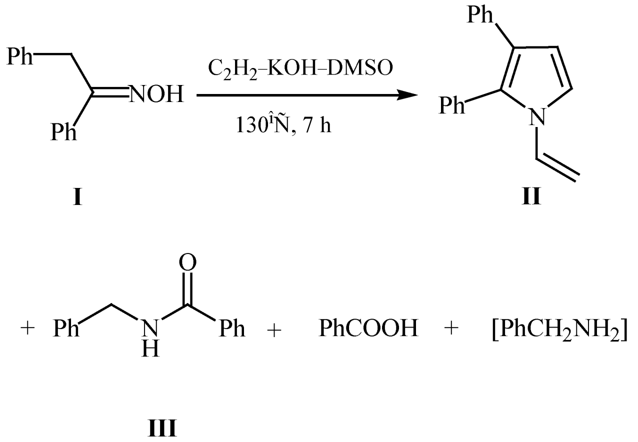
Received April 14, 2010

DOI: 10.1134/S1070428010090265

Oximes rearrange into amides under the action of strong acids (Beckmann rearrangement) [1]. Only seldom this rearrangement occurs in the presence of bases, for instance, that of benzoquinosylidone *E*- and *Z*-oximes [2]. The preparation of benzamide from benzaldoxime in the system KOH–DMSO was described through hydration of the intermediate nitrile [3].

In the course of the synthesis of 1-vinyl-2,3-diphenylpyrrole (**II**) from benzyl phenyl ketone oxime (**I**) and acetylene by Trofimov reaction [4–6] in the system KOH–DMSO at the atmospheric pressure (130°C, 7 h) alongside the expected pyrrole **II** (yield 14–34%) N-benzylbenzamide (**III**) was obtained (14–24%) (Scheme1).

Scheme 1.



Besides after acidifying the reaction mixture benzoic acid was isolated (up to 56%).

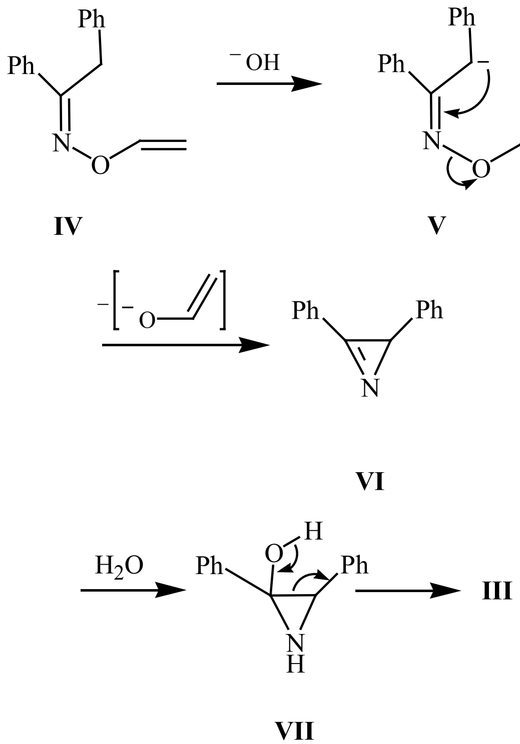
Special experiment showed that amide **III** was not a product of oxime **I** rearrangement under the action of KOH–DMSO (at heating oxime **I** under the same conditions without acetylene it was nearly completely recovered, to 95–97%). Obviously the key role in the formation of amide **III** from oxime **I** belonged to acetylene.

Apparently O-vinyloxime **IV**, the intermediate in the synthesis of pyrroles from oximes and acetylene, was deprotonated by the superbase KOH–DMSO forming carbanion **V** that further replaced intramolecularly the vinyloxy anion with the closure of the azirine ring **VI** (Scheme 2). Its hydration into hydroxyaziridine **VII** followed by a rearrangement resulted in amide **III**.

The stage of azirine formation from O-vinyloxime under the action of the superbase was suggested recently for the understanding of the assembling of 4-methylene-3-oxa-1-azabicyclo[3.1.0]hexanes from ketoximes, ketones, and acetylene [7]. In essence this stage resembles the azirine synthesis from oximes or their ethers by Hoch–Campbell reaction [1, 8].

This reaction fundamentally supplements the common

Scheme 2.



views on the reactivity of ketoximes.

***N*-Benzylbenzamide (III)**. A mixture of 5.50 g (26 mmol) of oxime **I** and 1.45 g (26 mmol) of KOH in 20 ml of DMSO was stirred at 130°C, and acetylene was passed through for 7 h at a rate 40–45 ml/min. On cooling to room temperature 15 ml of DMSO was distilled off at a reduced pressure. The residue was diluted with water (40 ml) and extracted with ether (6 × 30 ml), the combined extracts were thrice washed with water (30 ml) and dried with potassium carbonate. On removing the solvent the red-brown transparent oily substance (3.83 g) was subjected to column chromatography on aluminum oxide (eluent first hexane, then a mixture hexane–dichloromethane, 10 : 1). We obtained 0.902 g (14%) of 1-vinyl-2,3-diphenylpyrrole (**II**), mp 109–110°C (mp 109–110°C [3]), and 1.314 g (24%) of *N*-benzylbenzamide (**III**), mp 105–106°C (mp 104–106°C [9]). IR, ^{1}H and ^{13}C NMR spectra were similar to those published in [10].

The water layer was acidified with diluted (1 : 3) HCl till pH ~2–3 and extracted with ether (3 × 30 ml), the combined extracts were thrice washed with water (3 × 20 ml), dried with Na_2SO_4. On removing ether we obtained 1.79 g (56%) of benzoic acid as fine white crystals, mp 120–121°C (from water) (mp 121–125°C [11]).

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX 400 [operating frequencies 400.13 (^{1}H) and 100.6 (^{13}C) MHz], solvent $CDCl_3$, internal reference HMDS. IR spectra were recorded on a spectrophotometer Bruker IFS-25 from pellets with KBr.

The study was carried out under the financial support of the program of the President of the Russian Federation for the support of the leading scientific schools (grant NSh 3230-2010.3).

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