UNEXPECTED FORMATION OF BIPHENYL AND TERPHENYL IN THE TROFIMOV SYNTHESIS OF PYRROLS FROM ALKYLPHENYLKETOXIMES AND ACETYLENE

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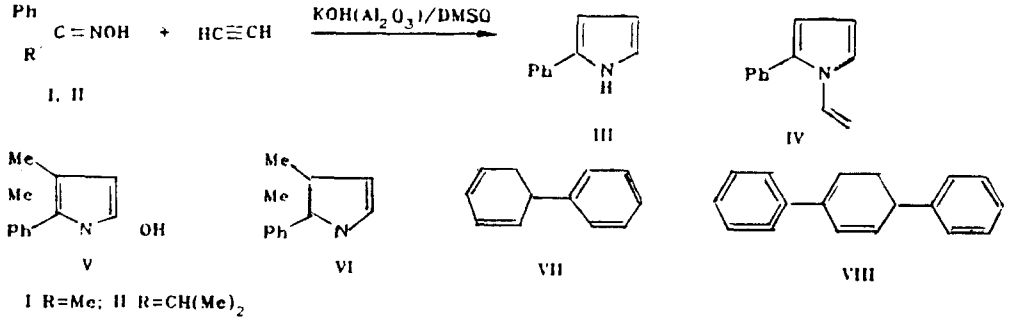
We find for the first time that, in the condensation of alkylphenylketoximes (I, II) with acetylene, along with the usual reaction products, viz., pyrrole (III) and its N-vinyl derivative (IV) (where R = Me) or hydroxypyrrole (V) and 3-H pyrrole (VI) [where R = $CH(Me)_2$] [2, 3], at 80-120°C in KOH–DMSO biphenyl (VII) is formed in 1% yield. In the reaction of methylphenylketoxime (I) with acetylene catalyzed by KOH–Al_2O_3*–DMSO [120°C, atmospheric pressure, molar ratio of (I) to KOH, 1:2], along with biphenyl (VII) (GLC), p-terphenyl (VIII) is formed in ~0.3% yield.



I R=Me; II R=$CH(Me)_2$

Biphenyl formation has been previously observed when the benzyl ether of acetophenone or benzophenone oximes are boiled in air at 200°C for 30 min, and when ketoximes or their ethers are heated in a nitrogen atmosphere at 200°C [4].

The structures of (VII, VIII) were confirmed by PMR spectra in $CDCl_3$; these lack any proton signals except those of the phenyl at 7.53 and 7.38 ppm. The mass spectrum of the biphenyl contains the peak of the molecule ion [M^+ 154], mp 70.5-71°C [5]. The mass spectrum of p-terphenyl contains the peak of the molecule ion [M^+ 230], mp 186-187°C; (VIII) is 99.5% pure according to GLC. According to [6], mp 214°C.

Compounds (VII, VIII) were separated from the mixture obtained after the reaction mixture was treated with water, and extracted with ether; the extract was dried over potash, solvent was removed, and the residue was chromatographed on plates covered with a layer of unattached Al_2O_3 (6:1 hexane–ether for biphenyl), or on an Al_2O_3 column (50:1 hexane–ethanol for p-terphenyl).

Biphenyl and terphenyl are also formed in the reaction of other alkylphenylketoximes with acetylene (as indicated by GLC).

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*20% of (I) by weight.

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