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UNEXPECTED FORMATION OF 2,4,6-TRIPHENYLPYRIDINE IN THE SYNTHESIS OF 2,5-DIPHENYL-PYRROLE FROM ACETOPHENONE OXIME AND PHENYLACETYLENE

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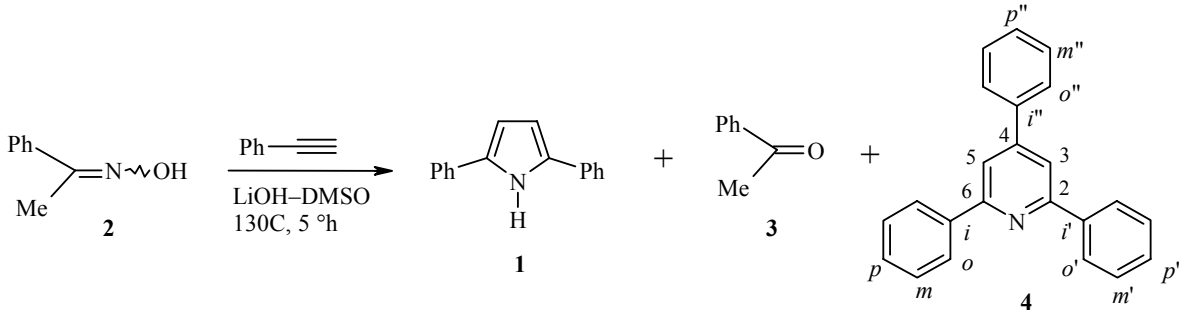
The synthesis of 2,5-diphenylpyrrole (**1**) [1, 2] (in special cases, 2,4-diphenylpyrrole [3]) from acetophenone oxime **2** and phenylacetylene in MOH–DMSO superbase systems (M = Li, Na, K) by means of the Trofimov reaction has gained preparative significance despite low yields of the desired product because the pyrrole obtained is a promising chemical intermediate. Further optimization of this synthesis will involve determining the structure of the sideproducts as well as reducing both the number and amount of such side-products. However, at present, we only know that a significant amount of acetophenone **3** [1] is formed during the reaction. In essence, acetophenone **3** is not a sideproduct since it may be reused after oximation in the same synthesis. Other components of the reaction mixture have not yet been identified.

In a study of this reaction in the 1:1 molar ratio LiOH–DMSO system at 130°C for 5 h, we unexpectedly isolated 2,4,6-triphenylpyridine (**4**) in 2.5% yield along with the expected 2,5-diphenylpyrrole **1** and acetophenone **3**.



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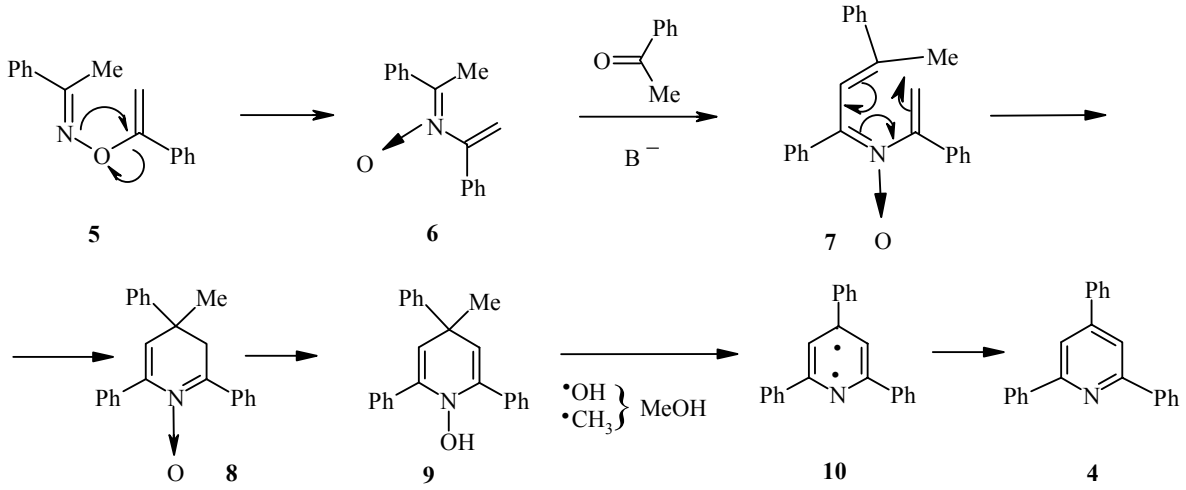
Intermediate O-vinyl oxime **5** rearranges to give nitrone **6** [4], which then condenses with acetophenone **3** to give trienic nitrone **7**. The electrocyclization of **7** leads to dihydropyridine N-oxide **8**, which rearranges to give N-hydroxydihydropyridine **9**. The 1,4-elimination of methanol through 1,4-diradical **10** (an analog of the 1,4-benzoid Bergman diradical [5, 6]) leads to pyridine **4**. Examples of the aromatization of dihydropyridines with the loss of methanol have been reported by Nedolya et al. [7, 8].

The formation of pyridine **4** may be shown by the following scheme:



This reaction expands the basic chemistry of oximes and acetylenes and may stimulate further synthetic investigations.

The ^{1}H, ^{13}C, and ^{13}N NMR spectra were taken on a Bruker 400DPX spectrometer at 400, 100, and 40 MHz, respectively, in $CDCl_3$ with HMDS (δ 0.05 ppm) as the internal standard. The IR spectra were taken on a Bruker ISF-25 spectrometer. The mass spectrum was taken on a Shimadzu QP5050-A mass spectrometer.

Synthesis of 2,5-Diphenylpyrrole (1), Acetophenone (3) and 2,4,6-triphenylpyridine (4). A mixture of acetophenone oxime **2** (5.00 g, 37 mmol) and phenylacetylene (4.16 g, 42 mmol) was dissolved in DMSO (50 ml) and LiOH (0.88 g, 37 mmol) was added. The mixture was heated for 5 h at 130°C and then cooled. Water (100 ml) was added and the mixture was extracted with five 25 ml ether portions. The ethereal extracts were washed with water and dried over K_2CO_3. After removal of the ether, the residue was subjected to chromatography on an alumina column using gradient elution from hexane to 1:1 hexane–ether to give 1.08 g (13.3%) 2,5-diphenylpyrrole **1**, 1.24 g (28.0%) acetophenone **3**, and 0.28 g (2.5%) pyridine **4**.

2,4,6-Triphenylpyridine (4) was obtained as pale-yellow crystals, mp 132-134°C (hexane, 135-136°C [9]). IR spectrum (KBr), ν, cm^{-1}: 1594, 1550, 1527, 1494, 1398, 1361, 865, 757, 692. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.20 (4H, m, H-*o*'); 7.88 (2H, s, H-3, H-5); 7.74 (2H, m, H-*o*"); 7.54-7.43 (9H, m, H-*m*', H-*p*', H-*m*", H-*p*"). ^{13}C NMR spectrum, δ, ppm: 157.59 (C-2, C-6); 150.27 (C-4); 139.68 (C-*i*, C-*i*'); 139.17 (C-*i*"); 129.18, 129.10, 129.04, 128.99, (C-*p*", C-*p*', C-*p*, 2C-*m*"); 128.77 (2C-*m*', 2C-*m*); 127.36, 127.26, 127.20 (2C-*o*", 2C-*o*', 2C-*o*); 117.18 (C-3, C-5). ^{15}N NMR spectrum, δ, ppm: -83 (N-1). Mass spectrum, *m/z*: 307. Found, %: C 89.79; H 5.55; N 4.58. $C_{23}H_{17}N$. Calculated, %: C 89.87; H 5.57; N 4.56.

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