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CHEMISTRY

2,4,5-Triphenylimidazole as an Indicator of Intermediate Formation of 2,3-Diphenyl-2*H*-azirine in the Synthesis of 1-Vinyl-2,3-Diphenylpyrrole from Benzyl Phenyl Ketoxime and Acetylene

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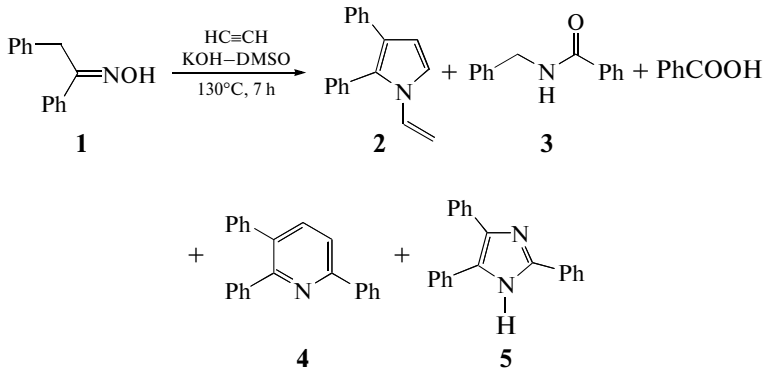
The assemblage of pyrrole ring from ketoximes and acetylenes in superbasic systems like KOH–DMSO (the Trofimov reaction) [1–3] attracts the growing interest of synthetic chemists because of its simplicity and versatility, as well as the possibility to obtain in one preparative step pyrroles and *N*-vinylpyrroles from ketones and acetylenes, even avoiding preliminary preparation of ketoximes [4, 5]. Depending on reaction conditions and initial reactant structures, other heterocyclic compounds are formed sometimes along with pyrroles, for example, pyridylpyrroles [6], carbolines [7], 4-methylene-3-oxa-1-azabicyclo[3.1.0]hexanes [8], and minor byproducts that, nonetheless, can provide valuable information on the reaction mechanism.

Recently, upon treatment of a reaction mixture obtained in the synthesis of 1-vinyl-2,3-diphenylpyrrole (**2**) from benzyl phenyl ketoxime (**1**) and acetylene in a KOH–DMSO system (130°C, 7 h) at atmospheric pressure, we isolated N-benzylbenzamide (**3**) (12%) [9], benzoic acid (55%), and 2,3,6-triphenylpyridine (**4**) (1.5%) [10], along with target compound **2** (17%), Scheme 1.



Scheme 1.

We showed that amide **3** did not result from the classical Beckmann rearrangement because the amide could not be detected (^{1}H NMR) in the reaction mixture when the reaction was carried out in the absence of acetylene. Its formation was explained presumably by the transformation of intermediate 2,3-diphenyl-2*H*-azirine (**6**, Scheme 2).

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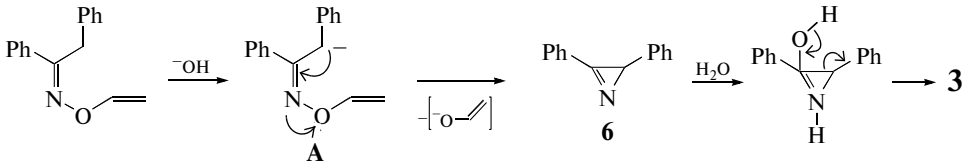

Scheme 2.

2,3-Diphenyl-2*H*-azirine on heating is known to form 2,4,5-triphenylimidazole, along with other products [11]. The careful examination of the reaction mixture obtained in the synthesis of pyrrole **2** allowed us to isolate imidazole **5** (yield 1%, Scheme 1), along with other products **2**–**4**; this finding proves the previously postulated formation of azirine **6** from ketoxime **1** and acetylene in a KOH–DMSO superbasic system (Scheme 2).

The ease of formation of azirine **6** in this case seems to result from the enhanced CH acidity of the methylene group of oxime **1** located between the oxime function and the benzene ring: stable carbanion **A** forms, which is simultaneously of benzylic and α-carbonyl type.

Thus, the systematic elaboration of the reaction of ketoxime **1** and its substituted or heterocyclic analogues with acetylene in KOH–DMSO superbasic systems promises to open a fundamentally new route to 2,3-aryl(hetaryl)-2*H*-azirines. These compounds, if necessary, can be used as intermediates without preliminary isolation (similar to the described above synthesis of amide **3**).

EXPERIMENTAL

^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker DPX-400 spectrometer (operating at 400.13, 100.61, and 40.55 MHz, respectively) in $CDCl_3$ solutions, using hexamethyldisiloxane as the internal reference. IR spectra were obtained on a Bruker ISF-25 spectrophotometer as KBr pellets. Mass spectra were recorded on a Shimadzu GCMS-QP5050A mass spectrometer at an ionizing voltage of 70 eV.

Acetylene was passed at a flow rate of 40–45 mL/min through a mixture of 5.50 g (0.026 mol) of benzyl phenyl ketoxime (**1**) and 1.46 g (0.026 mol) of KOH in DMSO (20 mL) on heating at 130°C for 7 h. The reaction mixture was cooled, diluted with water (60 mL), and extracted with diethyl ether (5 × 30 mL). The ethereal extracts were washed with water and dried with potassium carbonate. After removal of the ether, the residue was fractionated on an Al_2O_3 column (eluent used was hexane, then hexane–diethyl ether, 5 : 1) to give 1.08 g (17%) of 1-vinyl-2,3-diphenylpyrrole (**2**), 0.65 g (12%) of *N*-benzylbenzamide (**3**), 0.12 g (1.5%) of 2,3,6-triphenylpyridine (**4**), and 0.07 g (1%) of 2,4,5-triphenylimidazole (**5**). The aqueous layer was acidified with diluted (1 : 3) HCl to pH ~2–3 and extracted with diethyl ether (3 × 30 mL). The ethereal extracts were washed with water and dried with Na_2SO_4. The ether was removed to give 1.74 g (55%) of benzoic acid, mp 120–121°C (water), [12]: mp 121–125°C. Spectral characteristics are identical to those described in literature [13].

1-Vinyl-2,3-diphenylpyrrole (2). Pale yellow crystals, mp 109–110°C (hexane), [1]: mp 109–110°C.

IR (ν, cm^{-1}): 3081, 1957, 1888, 1817, 1750, 1641, 1602, 1491, 1467, 1412, 1379, 1319, 1300, 1251, 1073, 1028, 965, 919, 910, 865, 774, 768, 737, 696, 610.

^{1}H NMR (δ, ppm, *J*, Hz): 7.35 (m, 2H, H-*o*, 2-Ph), 7.34 (m, 1H, H-*p*, 2-Ph), 7.28 (m, 2H, H-*m*, 2-Ph), 7.16 (m, 4H, H-*o*,*m*, 3-Ph), 7.09 (m, 1H, H-*p*, 3-Ph), 7.09 (m, 1H, H-5), 6.69 (dd, 1H, H-*x*, $^3J_{\text{H-}\alpha,\text{ H-}x}$ 8.8 Hz, $^3J_{\text{H-}\beta,\text{ H-}x}$ 15.7 Hz), 6.50 (d, 1H, H-4, $^3J_{\text{H-4, H-5}}$ 2.9 Hz), 5.12 (d, 1H, H-α, $^3J_{\text{H-}\alpha,\text{ H-}x}$ 8.8 Hz), 4.60 (d, 1H, H-β, $^3J_{\text{H-}\beta,\text{ H-}x}$ 15.7 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 136.0 (C-*i*, 3-Ph), 132.0 (C-*i*, 2-Ph), 131.6 (C-*o*, 2-Ph; C-α), 130.0 (C-2), 128.6 (C-*m*, 2-Ph), 128.2 (C-*m*, 3-Ph), 128.0 (C-*p*, 2-Ph; C-*o*, 3-Ph), 125.6 (C-*p*, 3-Ph), 124.0 (C-3), 117.0 (C-5), 110.6 (C-4), 98.2 (C-β).

N-Benzylbenzamide (3). Mp 105–106°C, [14]: mp 105–107°C. Spectral characteristics are identical to those described in literature [14].

2,3,6-Triphenylpyridine (4). White crystals, mp 98–100°C (hexane).

IR (ν, cm^{-1}): 3055, 3028, 1955, 1894, 1810, 1572, 1521, 1429, 1396, 1369, 835, 762, 745, 694, 629, 581.

^{1}H NMR (δ, ppm): 8.15 (m, 2H, H-*o*, 6-Ph), 7.77 (s, 2H, H-4,5), 7.48 (m, 4H, H-*o*, 2-Ph; H-*m*, 6-Ph), 7.41 (m, 1H, H-*p*, 6-Ph), 7.30 (m, 2H, H-*o*, 3-Ph), 7.28 (m, 2H, H-*m*, 3-Ph), 7.25 (m, 1H, H-*p*, 3-Ph), 7.24 (m, 2H, H-*m*, 2-Ph), 7.20 (m, 1H, H-*p*, 2-Ph).

^{13}C NMR (δ, ppm): 156.7 (C-2), 155.8 (C-6), 140.5 (C-*i*, 3-Ph), 140.1 (C-*i*, 2-Ph), 139.4 (C-4), 139.2 (C-*i*, 6-Ph), 134.5 (C-3), 130.3 (C-*o*, 3-Ph), 129.7 (C-*o*, 2-Ph), 129.0 (C-*p*, 2-Ph; C-*p*, 6-Ph),

128.8 (C-*m*, 6-Ph), 128.4 (C-*m*, 2-Ph), 127.9 (C-*m*,*p*, 3-Ph), 127.1 (C-*o*, 6-Ph), 118.6 (C-5).

^{15}N NMR (δ, ppm): –70.9.

MS (*m*/*z*): 307 $[M]^{\cdot+}$.

For $C_{23}H_{17}N$ anal. calcd. (%): C, 89.87; H, 5.57; N, 4.56. *M* 307.

Found (%): C, 89.79; H, 5.65; N, 4.48.

2,4,5-Triphenylimidazole (5). White crystals, mp 274°C (ethanol), [15]: mp 271–272°C. Spectral characteristics are identical to those described in literature [15].

MS (*m*/*z*): 296 $[M]^{\cdot+}$.

For $C_{21}H_{16}N_2$ anal. calcd. (%): C, 85.11; H, 5.44; N, 9.45. *M* 296.

Found (%): C, 85.21; H, 5.43; N, 9.34.

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