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SHORT COMMUNICATIONS

p-Terphenyl as Unexpected By-Product in the Synthesis of 2,5-Diphenylpyrrole from Acetophenone Oxime and Phenylacetylene

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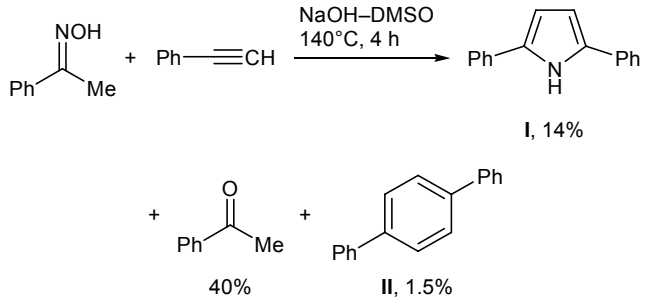
The synthesis of 2,5-diphenyl-1*H*-pyrrole (**I**) from acetophenone oxime and phenylacetylene in superbasic systems MOH–DMSO (where M is an alkali metal) [1–4] is attractive due to its simplicity (one-step process) and accessibility of initial compounds, despite poor yield of the target product (14–18%); furthermore, alternative methods [5–7] include many steps, and the overall yields of pyrrole (**I**), calculated for all steps, are comparable with the that obtained in the reaction of acetophenone oxime and phenylacetylene (Scheme 1).

Scheme 1.



The main factor responsible for the low yield of pyrrole **I** is formation of an appreciable amount of acetophenone (up to 40%); however, the latter can be subjected to oximation and brought again into the synthesis of pyrrole **I**. Therefore, the real yield of **I**, calculated on acetophenone as primary initial compound, is considerably higher. Further optimization of this reaction implies study on other side processes. While performing studies in this line we isolated from the reaction mixture (NaOH–DMSO, 140°C, 4 h) an unexpected product, *p*-terphenyl (**II**) with a yield of 1.5% (Scheme 1). Special experiments showed that *p*-terphenyl (**II**) is not formed from acetophenone oxime or phenylacetylene taken separately under analogous conditions. On the other hand, we obtained 1.7% of *p*-terphenyl in the reaction of acetophenone with NaOH in DMSO (140°C, 4 h; Scheme 2).

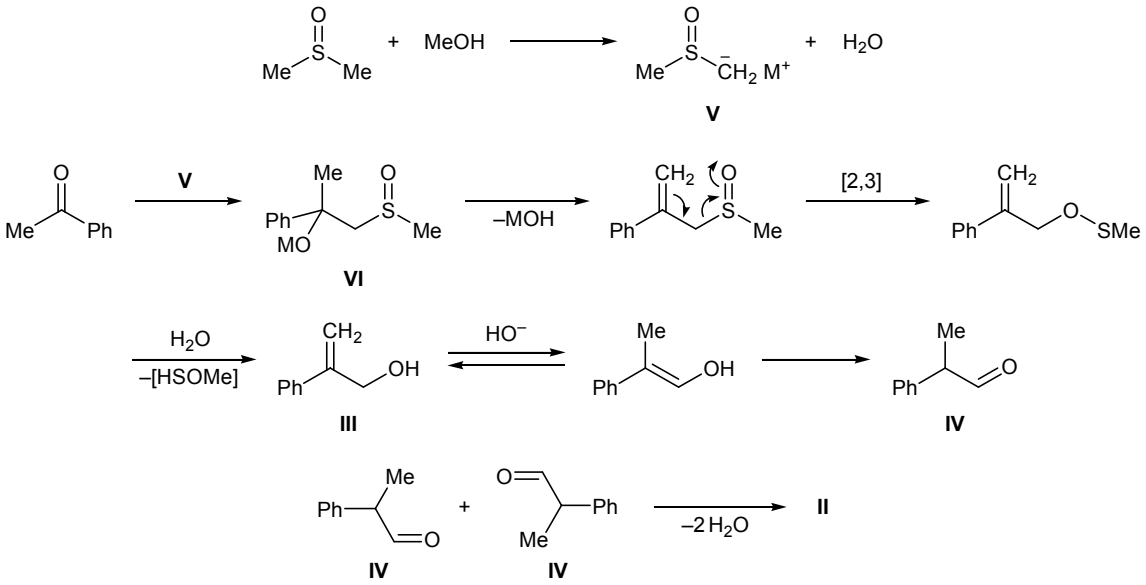
Scheme 2.

II

M = Na (yield 1.7%), K (14.6%).

Presumably, acetophenone in the system NaOH–DMSO undergoes hydroxymethylation [8–14] to produce substituted allyl alcohol **III**, and prototropic isomerization of **III** gives aldehyde **IV**. Dimerization of aldehyde **IV** (like aldolization–crotonization) leads to *p*-terphenyl (**II**) (Scheme 3). The adduct of DMSO with acetophenone, compound **VI**, was isolated previously and characterized as hydroxy derivative (after neutralization of the reaction mixture) [15]. The proposed mechanism is also consistent with the fact that no *p*-terphenyl (**II**) was detected among products formed in the synthesis of pyrrole **I** according to Scheme 1 in less basic LiOH–DMSO system; presumably, this system cannot ensure generation of dimsyl anions in a sufficient concentration. However, the other steps in Scheme 3, especially dimerization of aldehyde **IV**, require additional proofs, including isola-

Scheme 3.



tion of substituted allyl alcohol **III**; the reaction mechanism will be the subject of our further studies.

The use of a more active system, KOH–DMSO (140°C, 4 h) allowed us to raise the yield of *p*-terphenyl (**II**) to 14.6% (Scheme 2).

To conclude, we have revealed a new reaction, one-step conversion of acetophenone into *p*-terphenyl in superbasic systems MOH–DMSO. This reaction essentially supplements fundamental chemistry of fatty aromatic ketones, and its further optimization could make it valuable as a simple and selective synthesis of *p*-terphenyls.

***p*-Terphenyl (II).** *a*. A mixture of 20.4 g (0.15 mol) of acetophenone oxime and 6.0 g (0.15 mol) of sodium hydroxide in 200 ml of dimethyl sulfoxide was stirred at 100–105°C until the corresponding oxime sodium salt was obtained (2 h). The mixture was heated to 140°C, and a solution of 16.85 g (0.165 mol) of phenylacetylene in 25 ml DMSO was added dropwise under stirring over a period of 3.5 h. The mixture was stirred for 0.5 h more, cooled to room temperature, diluted with 600 ml of water, and extracted with diethyl ether (7×100 ml). The extracts were combined, washed with water (4×100 ml), and dried over potassium carbonate. The solvent was distilled off, and the residue, a brown viscous liquid containing some crystals, was filtered through a glass filter. The crystals were washed with cold diethyl ether and dried to obtain 0.52 g (1.5%) of light brown lustrous crystals with mp 210–212°C (from hexane); published data: mp 212–213°C (Aldrich 1996–1997, p. 1367). IR spectrum, ν, cm^{-1}: 3060, 3034, 1945, 1879, 1595, 1576, 1480, 1415, 1403, 1075, 1002, 838, 747, 688. ^{1}H NMR spectrum, δ, ppm: 7.66 s (4H, C_6H_4), 7.63 m (4H, *o*-H), 7.44 m (4H, *m*-H), 7.34 m (2H, *p*-H). ^{13}C NMR spectrum, δ_C, ppm: 140.8 (C^i), 140.2 (C^1, C^4), 128.9 (C^m), 127.6 (C^2, C^3, C^5, C^6), 127.4 (C^p), 127.2 (C^o). Mass spectrum, *m*/*z* (I_{rel}, %): 231 $[M + H]^+$ (18), 230 $[M]^+$ (100), 215 (4), 202 (6), 152 (6), 115 (25), 101 (12), 88 (5), 76 (5), 51 (4). Found, %: C 93.66; H 6.24. $C_{18}H_{14}$. Calculated, %: C 93.87; H 6.13. *M* 230.11.

The filtrate was distilled under reduced pressure to isolate 7.31 g (40%) of acetophenone, 2.97 g of unreacted acetophenone oxime (conversion 86%), and 4.73 g (14%) of 2,5-diphenyl-1*H*-pyrrole.

b. A mixture of 1.5 g (37.5 mmol) of NaOH and 50 ml of DMSO was heated to 140°C under stirring, 4.50 g (37.5 mmol) of acetophenone was added dropwise under stirring over a period of 10 min, and the mixture was stirred for 4 h at that temperature. The mixture was cooled to room temperature, 30 ml of DMSO was distilled off, and the residue was diluted with 75 ml of water and extracted with diethyl ether (6×25 ml). The extracts were combined, washed with water (3×30 ml), and dried over potassium carbonate. The solvent was removed to obtain 3.80 g of a dark brown viscous liquid containing some fine crystals. The crystals were filtered off through a glass filter and washed with cold diethyl ether to obtain 0.145 g (1.7%) of *p*-terphenyl.

c. Following an analogous procedure (method *b*), from 4.50 g (37.5 mmol) of acetophenone and 2.44 g

(37.5 mmol) of KOH in 50 ml of DMSO (140°C, 4 h) we obtained 0.545 g (6.3%) of *p*-terphenyl. According to the GC–MS data, the residue (2.40 g) after isolation of *p*-terphenyl contained an additional amount of compound **II**, 0.72 g (30%); overall yield 14.6%.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz for ^{1}H and 100.6 MHz for ^{13}C) using $CDCl_3$ as solvent and hexamethyldisiloxane as internal reference. The IR spectrum was measured in KBr on a Bruker IFS25 instrument. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP5050A system (quadrupole mass analyzer, a.m.u. range 34–650; SPB–5ms capillary column, 60 m × 0.25 mm × 0.25 μm; carrier gas helium, flow rate 0.7 ml/min; injector and ion source temperature 240°C, gas inlet pressure 300 kPa; oven temperature programming from 60 to 250°C at a rate of 10 deg/min).

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