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NOVEL APPROACH TO SYNTHESIS OF *meta*-TERPHENYLS

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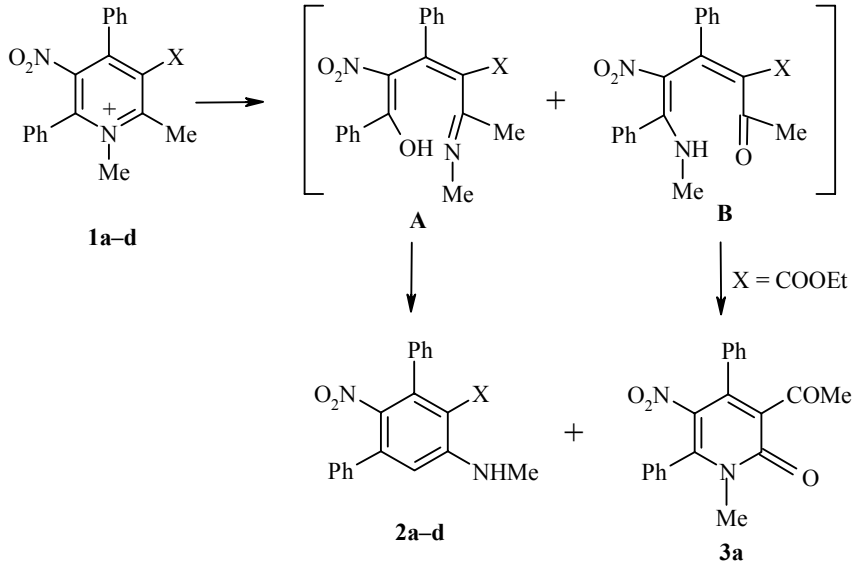
In studying the synthetic possibilities for isomerization recyclization of nitropyridinium salts we described earlier in [1], we have established that the reaction can be used to synthesize *meta*-terphenyls (*meta*-diphenylbenzenes).

Rearrangement of pyridinium salts **1a-d** when treated with an aqueous alcoholic base occurs at room temperature, and leads to diphenylbenzenes **2a-d** in 41-70% yield. Compounds **2a-d** are formed through the open form **A**, which is formed after attack by the hydroxyl anion on the position *ortho* to the nitro group. The benzene ring is formed by an intramolecular aldol–crotonic condensation of the benzoyl group (formed after opening of the pyridine ring) at the methyl group of the open form **A**. A byproduct of recyclization of salt **1a** is the pyridone **3a** (9% yield), which is formed from the open form **B** by intramolecular acylation of the ester group of the enamine moiety.

Recyclization of the salt **1b** occurs regiospecifically; the possible product of heterocyclization with participation of the cyano group [2, 3] is not observed.



1–3 a X = COOEt, **b** X = CN, **c** X = COMe, **d** X = CONHPh

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The *meta*-terphenyls with substituents on one ring that we synthesized cannot be obtained by other known methods.

Synthesis of *meta*-Terphenyls 2a-d. (General Procedure). A 10% aqueous NaOH solution (1.8 ml) was added to a suspension of the corresponding pyridinium salt **1a-d** (1 mmol) in ethanol (4 ml). The reaction mixture was stirred at room temperature for 3 h (for salts **1b,c**: 6 h), and then it was diluted with water. The precipitated crystals were filtered out, washed with water, and recrystallized from ethanol.

6-Methylamino-3-nitro-2,4-diphenylbenzoic Acid Ethyl Ester (2a). Yield of compound **2a** 42%. Yellow crystals with mp 183-185°C. Mass spectrum, *m/z* (*I*, %): 376 $M^{+\cdot}$ (100). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3420, 3030, 1680, 1520, 1360. ^1H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm (*J*, Hz): 0.66 (3H, t, *J* = 7.2, $COOCH_2\underline{CH_3}$); 2.93 (3H, d, *J* = 5.0, $NH\underline{CH_3}$); 3.81 (2H, q, *J* = 7.2, $COO\underline{CH_2}CH_3$); 6.59 (1H, s, H-5); 6.69 (1H, br. s, $\underline{NH}CH_3$); 7.24-7.41 (10H, m, 2,4-C_6H_5). Found, %: C 69.86; H 5.42. $C_{22}H_{20}N_2O_4$. Calculated, %: C 70.20; H 5.36.

3-Acetyl-1-methyl-5-nitro-4,6-diphenyl-2-pyridone (3a). Isolated by column chromatography on silica gel L 60/100, chloroform as eluent. Yield of compound **3a** 9%; mp 166-168°C. Mass spectrum, *m/z* (*I*, %): 348 $M^{+\cdot}$ (66.95). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3020, 1700, 1640, 1530, 1360. ^1H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm (*J*, Hz): 2.27 (3H, s, $COCH_3$); 3.31 (3H, s, N–CH_3); 7.25-7.56 (10H, m, 4,6-C_6H_5). Found, %: C 69.35; H 4.59. $C_{20}H_{16}N_2O_4$. Calculated, %: C 68.96; C 4.63.

6-Methylamino-3-nitro-2,4-diphenylbenzonitrile (2b). Yield of compound **2b** 62%; yellow crystals with mp 194-195°C. Mass spectrum, *m/z* (*I*, %): 329 $M^{+\cdot}$ (100). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3430, 3020, 2220, 1590, 1530, 1360. ^1H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm (*J*, Hz): 2.99 (3H, d, *J* = 4.8, $NHC\underline{H_3}$); 5.20 (1H, br. s, $N\underline{H}CH_3$); 6.58 (1H, s, H-5); 7.42-7.44 (10H, m, 2,4-C_6H_5). Found, %: C 72.86; H 4.59. $C_{20}H_{15}N_3O_2$. Calculated, %: C 72.94; H 4.59.

6-Methylamino-3-nitro-2,4-diphenylacetophenone (2c). Yield of compound **2c** 46%; yellow crystals with mp 158-160°C. Mass spectrum, *m/z* (*I*, %): 346 $M^{+\cdot}$ (100). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3440, 3030, 1640, 1510, 1340. ^1H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm (*J*, Hz): 1.65 (3H, s, $COC\underline{H_3}$); 2.90 (3H, d, *J* = 5.0, $NH\underline{CH_3}$); 6.59 (1H, s, H-5); 6.87 (1H, br. s, $\underline{NH}CH_3$); 7.31-7.44 (10H, m, 2,4-C_6H_5). Found, %: C 72.65; H 5.34. $C_{21}H_{18}N_2O_3$. Calculated, %: C 72.82; H 5.24.

6-Methylamino-3-nitro-2,4-diphenyl-N-phenylbenzamide (2d). Yield of compound **2d** 70%; yellow crystals with mp 193-194°C. Mass spectrum, *m/z* (*I*, %): 423 $M^{+\cdot}$ (100). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3420, 3020, 1660, 1520, 1360. ^1H NMR spectrum (DMSO-d_6, 200 MHz), δ, ppm (*J*, Hz); 2.84 (3H, d, *J* = 4.6, $NHC\underline{H_3}$); 6.12 (1H, br. s, $N\underline{H}CH_3$); 6.60 (1H, s, H-5); 7.16-7.49 (15H, m, $CONHC_6\underline{H_5}$, 2,4-C_6H_5); 10.12 (1H, s, $CON\underline{H}C_6H_5$). Found, %: C 73.91; H 5.12. $C_{26}H_{21}N_3O_3$. Calculated, %: C 73.74; H 5.00.

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