

Direct introduction of cyano group on furoxan ring

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Chemistry

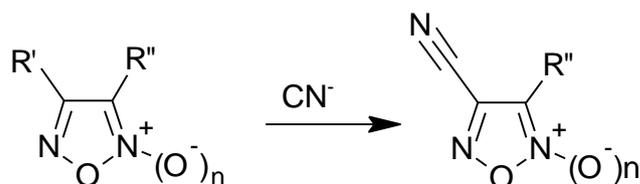
Anhydrous sodium sulfate (Na_2SO_4) was used as drying agent for the organic phases. Organic solvents were removed under reduced pressure at 30 °C. Synthetic-purity solvents dichloromethane, DMF and 40–60 petroleum ether (PE) were used. Dry DMF was obtained through storage over 4Å molecular sieves. The progress of the reactions was followed by thin-layer chromatography (TLC) on 5 × 20 cm plates Merck Kieselgel 60 F254, with a layer thickness of 0.20 mm.

4-Cyano-3-phenylfuroxan (2). To a solution of 3-phenyl-4-phenylsulfonylfuroxan (300 mg, 1.00 mmol) in dry DMF (10 ml), KCN (65 mg, 1.00 mmol) was added in one portion followed by 18-crown-6 (260 mg, 1.00 mmol). The mixture was stirred at room temperature for 1 h and then was poured into cold water (30 ml) and extracted with CH_2Cl_2 (2 × 25 ml). The organic phase was washed with water (20 ml), brine (20 ml), dried and evaporated. The obtained yellow oil was purified by flash chromatography (eluent PE : CH_2Cl_2 = 8 : 2) to give the target cyano derivative as a white solid. Yield 98 mg (58%). Analytically pure sample was obtained by crystallization from hexane. Mp 84-85 °C (C_6H_{14}), lit.¹ mp 81 °C. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.99 – 8.02 (m, 2H), 7.60 – 7.62 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 133.0 (^4C , Fx), 132.1 (CH of C_6H_5), 129.7 (2CH of C_6H_5), 126.4 (2CH of C_6H_5), 119.6 (C of C_6H_5), 112.6 (^3C , Fx), 108.4 (CN).

3-Cyano-4-phenylfuran (8). To a solution of 3-phenyl-4-phenylsulfonylfuran (290 mg, 1.00 mmol) in dry DMF (10 ml) KCN (65 mg, 1.00 mmol) was added in one portion followed by 18-crown-6 (260 mg, 1.00 mmol). The mixture was stirred at room temperature for 18 h, then poured into cold water (30 ml) and extracted with CH_2Cl_2 (2 × 25 ml). The organic phase was washed with water (20 ml), brine (20 ml), dried and evaporated. The obtained yellow oil was purified by flash chromatography (eluent PE : CH_2Cl_2 = 9 : 1) to give the target cyano derivative as a white solid. Yield 86 mg (50%). Analytically pure sample was obtained by crystallization from hexane. Mp 45-46 °C (C_6H_{14}), lit.² mp 40-41 °C. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.00 – 8.04

(m, 2H), 7.57 – 7.68 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 154.4 (³C, Fz), 132.4 (CH of C₆H₅), 130.6 (⁴C, Fz), 129.7 (2CH of C₆H₅), 127.7 (2CH of C₆H₅), 122.5 (C of C₆H₅), 108.3 (CN).

Table S1 Attempts to extend the procedure for differently substituted 4-phenylsulfonyl furoxans / furazans.



R'	R''	n	Conditions	Results
SO ₂ Ph	SO ₂ Ph	1	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	SO ₂ Ph	1	<i>n</i> Bu ₄ N ⁺ CN ⁻ / CH ₂ Cl ₂ / rt	decomposition
SO ₂ Ph	SO ₂ Ph	1	<i>n</i> Bu ₄ N ⁺ CN ⁻ / CH ₂ Cl ₂ / -15 °C	decomposition
SO ₂ Ph	SO ₂ Ph	1	<i>n</i> Bu ₄ N ⁺ CN ⁻ / CH ₂ Cl ₂ / -78 °C	no reaction
SO ₂ Ph	OEt	1	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	CH ₃	1	KCN / DMF / 18-crown-6 / rt	decomposition
NO ₂	CH ₃	1	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	SO ₂ Ph	0	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	SO ₂ Ph	0	<i>n</i> Bu ₄ N ⁺ CN ⁻ / CH ₂ Cl ₂ / rt	decomposition
SO ₂ Ph	SO ₂ Ph	0	<i>n</i> Bu ₄ N ⁺ CN ⁻ / CH ₂ Cl ₂ / -15 °C	decomposition
SO ₂ Ph	SCH ₂ Ph	0	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	OEt	0	KCN / DMF / 18-crown-6 / rt	decomposition
SO ₂ Ph	CH ₃	0	KCN / DMF / 18-crown-6 / rt	decomposition

Supplementary Part References

1. R. Fruttero, B. Ferrarotti, A. Serafino and A. Gasco, *Liebigs Ann. Chem.*, 1990, **4**, 335.
2. G. Ponzio, *Gazz. Chim. Ital.*, 1931, **61**, 943.