A Preparative Method for *o*-Diisocyanoarenes

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A general method for the preparation of *o*-diisocyanoarenes in moderate to good yields has been developed by the dehydration of *o*-di(formamido)arenes with trichloromethyl chloroformate at −78 °C to 0 °C.

A variety of aliphatic and aromatic isocyanides have been prepared by the dehydration of the corresponding *N*-substituted formamides according to Ugi's procedure.[1] Diisocyanides can be similarly prepared from the corresponding diformamides. However, *o*-diisocyanobenzene, which has been the only *o*-diisocyanoarene reported, is unstable and has been synthesized only in an impure form and in low yield.[1,2] Our attempts to prepare some substituted *o*-diisocyanoarenes using the literature procedure[1,2] gave the desired products also in low yields. Herein, we wish to report a much improved method for preparation of *o*-diisocyanoarenes from *o*-di(formamido)arenes.

The starting *o*-di(formamido)arenes **1** were best prepared in good yields by formylation of the corresponding *o*-diaminoarenes with phenyl formate[3] at room temperature. Other conventional formylating agents such as acetic formic anhydride and formic acid did not give the desired **1**. The preparation of o-diisocyanoarenes **2** was carried out by the dehydration of **1** with trichloromethyl chloroformate at low temperature beginning at −78 °C and warming to 0 °C. The reaction temperature is crucially important. For instance, when o-di(formamido)benzene **1a** was treated with trichloromethyl chloroformate in the presence of triethylamine at room temperature, only 26% yield of **2a** was obtained. On the other hand, the dehydration of **1a** beginning at −78 °C and raised to 0 °C provided **2a** in 92% isolated yield. Some new *o*-diisocyanoarenes were thus prepared in moderate to good yields, as shown in Table.

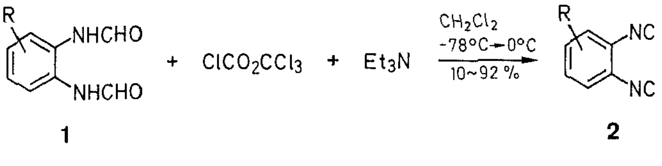

Table. Synthesis of *o*-Diisocyanoarenes **2**

Product	R	Yield (%)	mp (°C)	Molecular Formula[a]	IR (KBr) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ
2a	H	92	82–84[b]	$C_8H_4N_2$ (128.1)	2128	7.56 (s)
2b	4-Me	51	78–80[b]	$C_9H_6N_2$ (142.2)	2124	2.42 (s, 3H); 7.16–7.50 (m, 3H)
2c	4,5-Me$_2$	88	112–113[b]	$C_{10}H_8N_2$ (156.2)	2128	2.30 (s, 6H); 7.56 (s, 2H)
2d	4-MeO	67	97–100[b]	$C_9H_6N_2O$ (158.2)	2132	3.86 (s, 3H); 6.88–7.52 (m, 3H)
2e	4-MeO$_2$C	75	110[c]	$C_{10}H_6N_2O_2$ (186.2)	2132, 1730	3.98 (s, 3H); 7.49–8.19 (m, 3H)
2f	4-Cl	10	72–75[b]	$C_8H_3ClN_2$ (162.6)	2128	7.20–7.60 (m, 3H)
2g	benzo[e]	57	140[c]	$C_{12}H_6N_2$[d] (178.2)	2124	7.52–8.04 (m, 6H)

[a] Satisfactory microanalyses obtained: C ±0.28, H ±0.17, N ±0.29 (exception: **2d**, C −0.5).

[b] Decomposes on reaching the melting point.

[c] Darken during the measurement of melting point.

[d] Satisfactory high resolution MS obtained.

[e] 2,3-Diisocyanonaphthalene.

Synthetic applications including polymerization of the new *o*-diisocyanoarenes are now being investigated in our laboratory.

1,2-Diisocyano-4,5-dimethylbenzene (2c); Typical Procedure:
To a stirred mixture of 1,2-di(formamido)-4,5-dimethylbenzene (**1c**; 2.24 g, 11.7 mmol) and Et_3N (9.2 mL, 66 mmol) in CH_2Cl_2 (9 mL) is added trichloromethyl chloroformate (2.1 mL, 17 mmol) in CH_2Cl_2 (37 mL) over 30 min at −78 °C. The mixture is gradually warmed to 0 °C overnight with stirring, and then cooled to −15 °C. An ice-cold 10% aq. Na_2CO_3 (50 mL) is added dropwise to the mixture and then warmed up to room temperature. The organic phase is separated, extracted with an ice-cold 10% aq. Na_2CO_3, and dried ($MgSO_4$). The solvent is evaporated and the crude product is chromatographed on a Florisil column using hexane/CH_2Cl_2 (1:1) as an eluent to afford **2c** as a yellow solid; yield: 1.60 g (88%); mp 112–113 °C (dec) (Table).

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