SHORT PAPER

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Solid-state synthesis of aryl 2-nitrophenyl ureas[†]

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A simple and efficient solid-state synthesis for aryl 2-nitrophenyl ureas at room temperature is described for the first time.

Keywords: solid-state, aryl 2-nitrophenyl ureas

Previous studies have shown that *N*, *N′*-diarylurea derivatives have certain cytokinin activity[1, 2] and bacteriostatic activity.[3] There are several methods reported see the synthesis of *N*, *N′*-diarylurea derivatives as follows: the addition reaction of an aromatic amine with phenylisocyanate,[4,5] the reaction of an aromatic amine with benzazides,[6, 7] the acylation reaction of an anilino amide,[8] the condensation reaction of an anilino acyl halide,[9] *etc*. The shortcoming of all the existing methods is that they need a large amount of volatile or poisonous solvents (such as benzene, toluene and acetone), long reaction times and redundant procedure.

In an effort to overcome these disadvantages, we have developed a rapid, efficient and solid-state organic synthesis of aryl 2-nitrophenyl ureas. Seven aryl 2-nitrophenyl ureas have been synthesised in excellent yields (81-95%) (Scheme 1). This novel method has a number of advantages, such as short reaction times, easy separation and purification and environmental acceptability.

Experimental:

Melting points were determined with a Kofler micro melting point apparatus without correction. IR spectra were recorded on a Bio-Rad Win-IR spectrophotometer in KBr.

Caution: The grinding of nitrocompounds in a mortar is potentially hazardous and due precautions should be taken against possible overheating/explosion. Reactions were performed on a small scale.

2-nitrophenylisocyanate (1mmol) was ground together with an aromatic amine (1mmol) in an agate mortar for 10–30 minutes at room temperature.

The progress of the reaction was monitored by thin-layer chromatography. After the reaction was completed, the resulting mixture was dissolved in 95% ethanol (12ml) with a few drops of DMF, warmed and filtered promptly. The products separated and were collected by filtration. After recrystallisation from acetone or ethanol, the products were dried under vacuum. The results are listed in Table 1.

The melting point of **2b** does not accord with that of the literature. Therefore, the following data for 2b were determined: ^{1}H NMR[$(CD_3)_2SO$], δ(ppm), 9.58–9.94 (2H, NH), 7.17–8.25(8H, Ar-H); *m/z*: 335(M^+), 170, 155, 138. Found: C, 46.55; H, 3.13; N,12.64%; $C_{13}H_{10}BrN_3O_3$ requires: C, 46.57; H, 2.99; N, 12.54%.

^{1}H NMR spectra were measured on a Mercury 300 Spectrophotometer using TMS as internal standard and $(CD_3)_2SO$ as solvent. Mass spectra were recorded on a KYKY QP-1000A. Elemental analyses were performed on a Elementar Vario EL instrument.

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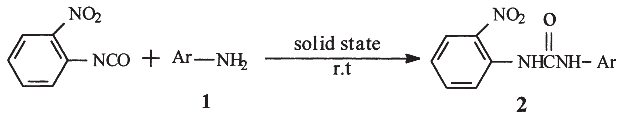

Ar:

a	4-chlorophenyl	e	3-nitrophenyl
b	4-bromophenyl	f	2-nitrophenyl
c	4-iodophenyl	g	4-methylphenyl
d	4-nitrophenyl		

Scheme 1

Table 1 Solid-state synthesis of substituted aryl 2-nitrophenyl ureas

Entry	Reaction times/min	Colour and shape	Yield/%	M.p./°C Found	Lit.	IR/KBr/cm^{-1} N–H	C=O
2a	20	Yellow needles	90	205–207	208.6–209.2[5]	3335	1668
2b	20	Yellow needles	87	215–217	207–208[7]	3336	1666
2c	10	Pale yellow needles	94	222–224	223–224[10]	3328,3286	1651
2d	30	Yellow needles	91	270 (dec.)	270–275 (dec.)[11]	3335	1611
2e	15	Orange sticks	81	243–245	246–247.2[5]	3381	1729
2f	15	Pale yellow needles	82	226–228	225[11]	3298	1659
2g	25	Pale yellow sticks	95	192–193	191–193[12]	3326,3302	1652

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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