SHORT PAPER

Solvent-free cyclotrimerization of isocyanates catalysed by sodium or potassium piperidinedithiocarbamate or nitrite under conventional or microwave heating: preparation of aryl or alkyl isocyanurates[†]

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A solvent-free method for the efficient preparation of symmetrically trisubstituted aryl or alkyl isocyanurates from isocyanates catalysed by sodium or potassium piperidinedithiocarbamate or the readily available sodium or potassium nitrite under conventional or microwave heating is described.

The cyclic trimers of isocyanates, perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) are important in polyurethanes industry.[1] These classes of compounds, which are characterized by outstanding thermal stability, have the potential to improve thermal resistance, flame retardation and chemical resistance of modified polyurethanes.[2]

The most common method employed for the preparation of symmetrically trisubstituted isocyanurates involves the catalytic trimerization of isocyanates. This transformation has been accomplished by a broad range of catalysts, such as (1) Lewis bases: *N,N,N′,N′,N′′*-pentamethyldipropylenetriamine,[3] triethylamine under high pressure,[4] proazaphosphatrane and its derivatives,[5] pyridine in ethylene oxide, styrene oxide or epichlorohydrin solution,[6] N-methylmorpholine in the presence of ethanol[7] and DABCO in dipolar aprotic solvents,[8] (2) anions: salts of carboxylic acid,[9] fluoride salts[10] and cyanate,[11] (3) organometallics: tri-*n*-butylantimony and triisobutylarsenic oxides,[12] 2-tributylstannylpropanol,[13] organic tin (II)[14a] and (IV)[14b] compounds and Ti(bipyridyl)₃.[14c] However, most of these conventional methods usually require severe conditions due to low activity of the catalyst, formation of byproducts such as dimer or carbodiimides because of poor selectivity of the catalyst, lengthy reactions and use of reagents which are not readily accessible.

Here we wish to report a convenient solvent-free method for the synthesis of aryl and alkyl isocyanurates from isocyanates promoted by readily available reagents, which serve as catalysts under conventional or microwave heating. Thus, it was found that when a mixture of phenyl isocyanate (**1a**) and a catalytic amount of sodium piperidinedithiocarbamate (**2**) was heated in the absence of solvents triphenyl isocyanurate (**3a**) was isolated as the only product of the reaction (Scheme 1). To determine the optimal conditions, the reaction was performed under different condition with respect to catalyst concentration and its efficiency, reaction time and temperature. It was found that when the concentration of (**2**) is 0.5 mol % the trimerization of (**1a**) reaches the maximum amount in 25 min at 110 °C producing 91 % of the corresponding isocyanurate (**3a**). Examination of IR spectrum of the crude product reveals the absence of any absorption bond characteristic of carbodiimide (N=C=N, 2110–2150 cm⁻¹). This was confirmed by TLC comparison of the crude product and authentic samples of carbodiimide and the corresponding dimer, diphenyl diazetidinedione.[8]


R— NCO   +

1a Phenyl
  b 4 -chlorophenyl
  c 4 -methoxyphenly
  d 1-naphthyl
  e ethyl
  f cyclohexyl
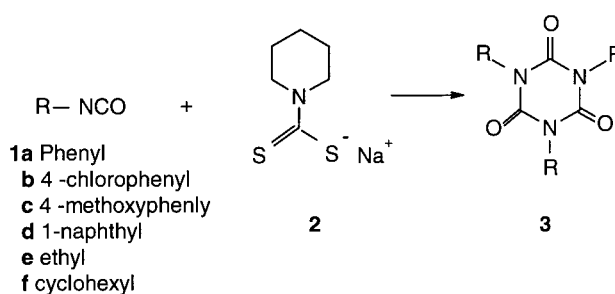
Scheme 1

The optimal condition such as 0.5 mol % of the catalyst (**2**) and reaction temperature at 110 °C was applied for a number of aryl and alkyl isocyanates(**1a–f**), except in the case of ethyl isocyanate (**1e**) which the reaction was performed at 50°C. The results are summarized in Table 1.

Potassium piperidinedithiocarbamate (**4**) can be easily prepared from piperidine, carbon disulfide and potassium hydroxide.[16] Like its sodium salt, (**4**) showed also excellent activity as a selective catalyst for the trimerization of aryl and alkyl isocyanates. The results are shown in Table 1.

Trimerization of aryl and alkyl isocyanates catalysed by (**2**) and (**4**) at reaction temperature, 110°C, proceeds in a homogeneous system. In these reactions the catalytic activity of (**4**) is fairly higher than that of (**2**). In both cases, the catalyst was removed easily from the solid isocyanurate by triturating of the crude product with water or by first dissolving the product in an organic solvent and then filtration.

Furthermore, it was found that under anhydrous conditions sodium nitrite (**5**) is able to catalyse the formation of isocyanurates from isocyanates. To find the optimal reaction conditions, a systematic study of its catalytic performance with respect to the concentration ratio of phenyl isocyanate, as the model compound, to the catalyst, reaction time and temperature was performed. These experiments demonstrated that
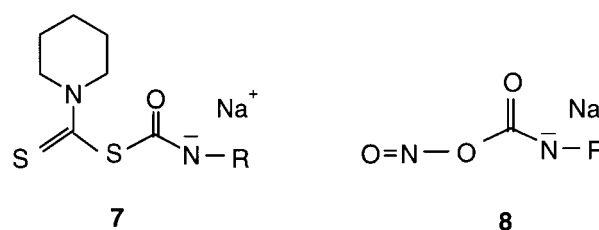
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[†] This is a Short Paper, there is therefore, no corresponding material in *J Chem. Research (M)*.

7   **8**

Scheme 2

Table 1 Synthesis of isocyanurates from isocyanates catalysed by sodium or potassium piperidinedithiocarbamate or nitrite

			A. Conventional heating				B. Microwave irradiation[a]	
			0.5 mol % of **2**[b]	0.5 mol % of **4**[c]	10 mol % of **5**[d]	10 mol % of **6**[e]	0.5 mol % of **2**[b]	4 mol % of **5**[d]
Entry	Product	R_1	t/min^f (T/°C) Yield(%)[g]	t/min^f (T/°C) Yield(%)[g]	t/min^f (T/°C) Yield(%)[g]	t/min^f (T/°C) Yield(%)[g]	P/W (t/min)[f] Yield(%)[g]	P/W (t/min)[f] Yield(%)[g]
1	**3a**	ph	25 (110) 91	22 (110) 93	22 (140) 98	10 (140) 80	210 (5) 97	385 (10) 99
2	**3b**	4-Cl–C_6H_4	15 (110) 83	14 (110) 86	8 (140) 75	5 (140) 60	210 (4) 89	385 (8) 87
3	**3c**	4- CH_3O–C_6H_3	28 (110) 86	25 (110) 84	30 (140) 76	26 (140) 64	210 (8) 86	385 (11) 82
4	**3d**	1-Naphthyl	45(110) 73	38 (110) 72	32 (140) 75	10 (140) 77	385 (10) 81	385 (16) 84
5	**3e**	C_2H_5	4 (50) 76	3 (50) 75	8 (50) 78	5 (50) 71	210 (4) 84	385 (5) 87
6	**3f**	Cyclohexyl	105 (110) 70	98 (110) 74	90 (140) 72	65 (140) 67	385 (15) 71	385 (20) 79

To control the reaction the irradiation was carried out in two or three stages, with a cooling period between each irradiation.
[b]Sodium piperidinedithiocarbamate. [c]Potassium piperidinedithiocarbamate. [d]Sodium nitrite. [e]Potassium nitrite. [f]Reaction time.
[g]Yield of pure, isolated product based on isocyanates.

when the reaction temperature is set at 140°C and 10 mol % of the catalyst was employed, the trimerization of (**1a**) is complete in 22 min. By reducing the temperature or the mol % of the catalyst a longer reaction time or lower yield was obtained. For example at room temperature and with a 5 mol % of (**5**) after 24 h a 56 % of (**3a**) was isolated and at 140°C with 8 mol % of (**5**) after 26 min the yield of the isolated product was 79 %.

Consequently, the optimal condition such as 10 mol % of the catalyst (**5**) and reaction temperature at 140 °C was applied for a number of aryl and alkyl isocyanates. Except in the case of ethyl isocyanate (**1e**) which the reaction was performed at 50°C. The results are summarized in Table 1. In our hands, dry sodium nitrite was a free-flowing powder. Although its mixture with isocyanates at 140°C (in these reactions acts as a heterogeneous catalyst), is colourless, but at nearly half the reaction time it turns yellow and before solidification to deep red. The results with potassium nitrite (**6**) are also summarized in Table 1. In this case, as it was expected the catalyst is more reactive (the nitrite anion is more loosely interacted with the K⁺, consequently it is more nucleophilic), this is shown by shorter reaction time. In comparison with (**5**) the lower yield of potassium salt (**6**) is due to sticky behaviour of its dried fine particles, which prevents its complete contact with the molecules of the isocyanates.

The mechanism for these isocyanurate formations involves the initial nucleophilic attack by the hard bases, piperidinedithiocarbamate or nitrite anion, to the isocyanates as hard heterophiles. This will result in the formation of intermediate (**7**) and (**8**) respectively (Scheme 2). Successive addition of two molecules of the corresponding isocyanates to (**7**) and (**8**) and finally cyclization of the resulting intermediate with the elimination of dithiocarbamate or nitrite anion will proceed to produce the cyclized products.

Finally, we examined the performance of (**2**) and (**5**) under microwave irradiation in a closed Teflon vessel without employing any solvent. It was found that the reaction of isocyanates (**1a–f**) with 0.5 mol % of (**2**) or 4 mol % of (**5**) results in the rapid formation of isocyanurates (**3a–f**) in high yield. The results are summarized in Table 1.

In conclusion, we have demonstrated that readily available sodium or potassium piperidinedithiocarbamate or nitrite ion functioned effectively as new homogeneous and heterogeneous catalysts for activation of aryl and alkyl isocyanates and were effective under conventional thermal heating or microwave irradiation. Furthermore, the reaction selectively only produced isocyanurate in a very clean reaction with sim-

ple work-up procedure. The extension of this study to other hard nucleophile including other type of countercation is currently under investigation.

Experimental

Isocyanates were purchased from either Aldrich or Fluka and were used as received. Sodium or potassium piperidinedithiocarbamate was prepared by a previously described procedure.[16] Freshly oven dried nitrite salts were used. IR spectra were recorded as KBr pellets on a Shimadzu IR-470 spectrometer. ¹H NMR spectra were obtained on a Bruker AC 80 or JEOL-EX-90 instrument. Mass spectra were recorded on Shimadzu QP-1100 mass spectrometer. Microwave irradiations were carried out in a National oven, Model 5250, at 2450 MHz. Melting points are uncorrected and were determined in open capillary tubes. For safety reasons all the experiments with microwave ovens should be performed in an efficient hood in order to avoid contact with vapours.

*Preparation of aryl or alkyl isocyanurates – The general procedure is illustrated with triphenyl isocyanurate (**3a**), (Method A):* In a flame dried 20 mL flask equipped with a condenser attached to a drying tube filled with dry calcium chloride, was placed (18.3 mg, 0.1 mmol) of sodium piperidinedithiocarbamate and (2.38 g, 20 mmol) of phenyl isocyanate. The mixture was stirred and heated in an oil bath at 110°C. After 25 min, the reaction mixture solidified into a white solid mass, which was cooled to room temperature and washed with ether (30 mL). Triturating of the crude product with water and finally recrystallization from acetone afforded the desire compound in 91%yield, mp 279–280 °C (lit.,[5] 279-279.5°C); v_{max}/cm^{-1} (KBr) 1709; δ_H (CDCl$_3$) 7.38–7.55 (m,15H, Ar–H).

*Preparation of tricyclohexyl isocyanurate (**3f**), (Method B):* A stirred mixture of cyclohexyl isocyanate (2.50 g, 20 mmol) and dried sodium nitrite (138 mg, 2 mmol) was heated at 140°C. At the beginning the reaction mixture was colourless, but after 25 min it turned yellow and after 50 min it went completely deep red. After 90 min the reaction mixture was cooled to room temperature and the solid mass thus formed was dissolved in 50 mL of ether. This solution was filtered, the filtrate was evaporated and the resultant yellowish residue recrystallised from ethanol to afford the pure tricyclohexyl isocyanurate in 72 % yield, mp 141–142 °C (lit.,[15] 142–143 °C); v_{max}/cm^{-1} (KBr) 2920, 1677, δ_H (CDCl$_3$) 1.12–2.43 (m, 30H), 4.35–4.82 (tt, 3H).

*Preparation of tri-1-naphthyl isocyanurate (**3d**), (Method C):* A mixture of naphthyl isocyanate (3.38 g, 20 mmol) and sodium piperidinedithiocarbamate (18.3 mg, 0.1 mmol) or sodium nitrite (55.2 mg, 0.8 mmol) was taken in a Teflon tube with secure screw cap and was then placed inside the microwave oven and irradiated for 5 min at 385 W. After 5 min (during this period it gently cools to about room temperature) it was irradiated again at the same power for another 5 min (see Table 2 for the time of irradiation for catalyst and individual compounds). The reaction mixture was allowed to cool to room temperature and the resultant residue washed with 50 mL ether. Trituration of the crude residue with water led to the title compound which was recrystallized from ethanol to give 81% of (**3d**), mp

339–341°C (lit.,[14b] 339-342°C); v_{max}/cm⁻¹ (KBr) 3046, 1715, 1415, δ_H (CDCl$_3$) 7.54–8.23 (m, 21H, Ar–H).

3b: mp 317–319 °C (lit.,[7] 318°C); v_{max}/cm⁻¹ (KBr) 3055, 1761, 1721, 1682, 1586;δ_H (CDCl$_3$) 7.27 (d, 6H,Ar–H), 7.51 (d. 6H. Ar–H).

3c: mp 260–262 °C (lit.,[5] 261–261.5°C); v_{max}/cm⁻¹ (KBr) 3040, 1712 ;δ_H (CDCl$_3$) 3.78 (s, 9H, 3 CH$_3$) 6.43 (d, 6H, Ar–H), 7.18 (d, 6H, Ar–H).

3e: mp 93–95 °C (lit.,[5] 93-94 °C); v_{max}/cm⁻¹ (KBr) 2970, 1674, 1458, δ_H (CDCl$_3$) 1.23 (t, 9H, 3 CH$_3$), 3.92 (q, 6H, 3 CH$_2$).

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