Oxidation of 1,2-bis (cyanoalkyl) hydrazines to azobisnitriles using trichloroisocyanuric acid

S.A. Mohite[a], Uday V. Desai[a]*, D.M. Pore[a], R.B. Mane[a] and P.P. Wadgaonkar[b]

[a]*Department of Chemistry, Shivaji University, Kolhapur- 416 004, India*

[b]*Polymer Division, National Chemical Laboratory, Pune- 411 008, India*

Azobisnitriles were synthesised in excellent yields by oxidation of the corresponding 1, 2-bis (cyanoalkyl) hydrazines using trichloroisocyanuric acid in acetonitrile medium at room temperature.

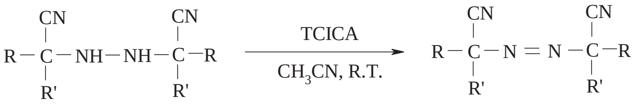
Keywords: trichloroisocyanuric acid, oxidation, azobisnitriles

Azobisnitriles constitute an important class of organic compounds and are used commercially as initiators in several free radical polymerisation reactions, and also as blowing agents for the production of polymer foams.[1-3]

The symmetrical azobisnitriles are conventionally prepared by reaction between a ketone and hydrazine to form azines, which on reaction with hydrogen cyanide, yield 1,2-bis (cyanoalkyl) hydrazines as intermediates. The oxidation of 1, 2-bis (cyanoalkyl) hydrazines with a variety of oxidants such as chlorine, bromine, potassium dichromate, sodium dichromate, potassium permanganate, oxygen–ozone mixture, sodium hypochlorite solution, hydrogen peroxide–KBr–H_2SO_4 reagent system, as well as Oxone–KBr in aqueous medium[4] yields azobisnitriles.[3]

However, many of these oxidants suffer from drawbacks such as formation of toxic / undesirable waste (dichromates and permanganate), difficulty in handling (halogens, hypochlorites) and are non-economical (oxygen–ozone). Therefore, the development of a protocol using a non-toxic and an inexpensive reagent, which is easier to handle and does not form a toxic waste, is desirable.

Trichloroisocyanuric acid (TCICA) is a readily available, stable, non-volatile solid, which is easier to handle and is inexpensive. It is used commercially as a disinfectant, as a source of chlorine and as an oxidant.[5,7] It has earlier been used as a cohalogenating agent,[8] for oxidation of alcohols to carbonyls[9] and selenols to diselenides[10], for dehydrogenation of indoles[11] and for conversion of aldehydes to esters,[12] *etc.*



$$\mathrm{R-\underset{R'}{\overset{CN}{C}}-NH-NH-\underset{R'}{\overset{CN}{C}}-R \xrightarrow[CH_3CN,\ R.T.]{TCICA} R-\underset{R'}{\overset{CN}{C}}-N=N-\underset{R'}{\overset{CN}{C}}-R}$$

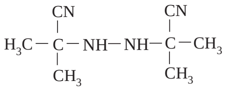
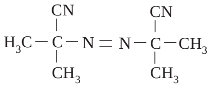
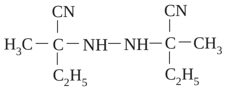
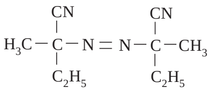
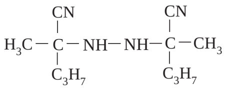
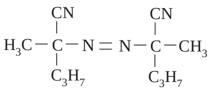
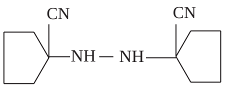
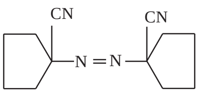
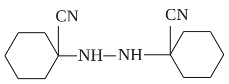
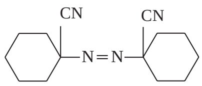
R' = $-CH_3$, $-C_2H_5$, n-C_3H_7 and R = R'= $-(CH_2)_4-$ and $-(CH_2)_5$

Scheme 1

In continuation of our ongoing programme directed towards the synthesis of azobisnitriles,[4] we report herein the usefulness of TCICA as an oxidant for the conversion of 1, 2-bis (cyanoalkyl) hydrazines to azobisnitriles in acetonitrile medium at room temperature (Scheme 1).

As a case study, when a mixture of 1,2-bis (cyanocyclohexyl) hydrazine (3 mmol) was stirred in acetonitrile with trichloroisocyanuric acid (1 mmol) 1, 1'-azobis-(1- cyclohexa-nenitrile) was obtained in excellent yield and purity. The method was then

Table 1 Oxidation of 1,2–bis(cyanoalkyl) hydrazines to azobisnitriles with TCICA in acetonitrile

No.	Substrate	Product [a]	Yield/%[b]	M.p./°C (Lit. M.p./°C)
1	 $\mathrm{H_3C-\underset{CH_3}{\overset{CN}{C}}-NH-NH-\underset{CH_3}{\overset{CN}{C}}-CH_3}$	 $\mathrm{H_3C-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-CH_3}$	93	103–105 (103–104)[2]
2	 $\mathrm{H_3C-\underset{C_2H_5}{\overset{CN}{C}}-NH-NH-\underset{C_2H_5}{\overset{CN}{C}}-CH_3}$	 $\mathrm{H_3C-\underset{C_2H_5}{\overset{CN}{C}}-N=N-\underset{C_2H_5}{\overset{CN}{C}}-CH_3}$	95	47 (49–51)[2]
3	 $\mathrm{H_3C-\underset{C_3H_7}{\overset{CN}{C}}-NH-NH-\underset{C_3H_7}{\overset{CN}{C}}-CH_3}$	 $\mathrm{H_3C-\underset{C_3H_7}{\overset{CN}{C}}-N=N-\underset{C_3H_7}{\overset{CN}{C}}-CH_3}$	87	75 (73–74.5)[2]
4			84	82 (83–84)[2]
5			92	116 (114–115)[1]

[a]All azobisnitriles are known compounds and were characterised by IR, ^{1}H NMR and ^{13}C NMR spectra.
[b]Yields refer to purified products.

---

* Correspondence. E-mail: uprabhu_desai@rediffmail.com

extended towards the oxidation of various 1,2-bis (cyanoalkyl) hydrazines and results are summarised in Table 1. In conclusion, we have developed a useful alternative protocol for the oxidation of 1,2-bis (cyanoalkyl) hydrazines to azobisnitriles using TCICA as an inexpensive and safe to handle oxidant

Experimental

Trichloroisocyanuric acid, (E.Merck), hydrazine sulfate, acetonitrile, cyclohexanone, methyl ethyl ketone (SD fine chemicals), cyclopentanone (Lancaster) and methyl propyl ketone (Fluka) were used as received. All the 1,2-bis (cyanoalkyl) hydrazines were prepared according to reported procedures.[2]

1,1'-Azobis (1-cyclohexanenitrile): typical procedure

To a well stirred solution of 1,2-bis (1-cyanocyclohexyl) hydrazine (0.74 g, 3 mmol) in acetonitrile (15 ml) was added TCICA (0.23 g, 1 mmol) in small portions and stirring was continued. On completion of reaction (TLC) the reaction mixture was filtered and the residue was washed with acetonitrile. Removal of solvent from the combined filtrate gave 1,1'–azobis (1-cyclohexanenitrile) as a white solid (0.68 g, 92 %), m.p. 116 °C (Lit[1] m.p. 114–115 °C).

Received 13 March 2004; accepted 3 August 2004
Paper 04/2384

References

1 C.S. Sheppard, *Encyclopedia of Polymer Science and Engineering*; H. F. Mark, N. M Bikales, C. G. Overberger and G. Menges Eds. 1985, 2, p.143, John Wiley and Sons, New York.
2 (a) C.G. Overberger, M.T. O’Shaughnessy and H.J. Shalit, *J. Am. Chem. Soc*., 1949, **71**, 2661; (b) C.G. Overberger, P.T. Huang and M.B. Berenbaum, *Org. Synth*., 1952, **32**, 16.
3 E.T. Denisov, T.G. Denisova and T.S. Pokidova, *Handbook of Free Radical Initiators*, Ch. 7: *Azo Compounds* p. 303, Wiley Interscience, New York, 2003.
4 B.V. Tamhankar, Uday V. Desai, R.B. Mane, P.P. Kulkarni and P.P. Wadgaonkar,. *Synth. Commun*. 2002, **32**, 3643 and references cited therein.
5 Y. Ura and G. Sakata, *Ullmann’s Encyclopedia of Industrial Chemistry*, 6th edn., Wiley VCH, Weinhein, 2001.
6 G. Pinto and B. Rohrig, *J. Chem. Educ*., 2003, **80**, 1.
7 U. Tilstam and H. Weinmann, *Org. Proc. Res. Dev*., 2002, **6**, 384.
8 G.F. Mendonca, A.M. Sanseverino and C.S. de Mattos Marcio, *Synthesis,* 2003, **1**, 45.
9 (a) L.D. Luca, G. Giacomelli and A. Porcheddu. *Org. Lett*., 2001, **3**, 3041; (b) C.J. Jenny, B. Lohri and M. Schalgeter, *US Patent*, 1998, **5**, 821, 374.
10 P. Zhong and M.P. Guo, *Synth. Commun*., 2001, **31**, 1507.
11 U. Tilstam, M. Harre, T. Heckrodt and H. Weinmann, *Tetrahedron Lett*., 2001, **42**, 5385.
12 G.A. Hiegel, C.D. Bayne, Y. Donde, G.S. Tamashiro and L.A. Hilberath, *Synth. Commun*., 1996, **26**, 2633.