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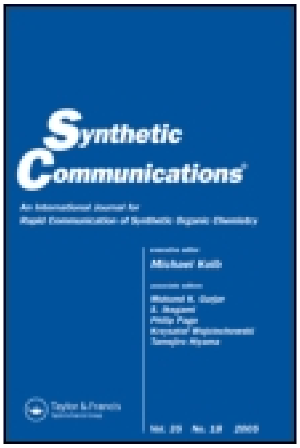

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OXIDATION OF ALKYLCYANOHYDRAZINES TO AZO-BIS NITRILES USING OXONE®-POTASSIUM BROMIDE IN AQUEOUS MEDIUM

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OXIDATION OF ALKYLCYANOHYDRAZINES TO AZO-*BIS* NITRILES USING OXONE®–POTASSIUM BROMIDE IN AQUEOUS MEDIUM

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ABSTRACT

Azo-*bis* nitriles were prepared in good yields and high purity by oxidation of corresponding 1,2-*bis*-dialkylcyano hydrazines using oxone-potassium bromide in aqueous medium.

The chemistry of azo-*bis* nitriles, a useful class of organic compounds, has been the subject of intensive studies. Commercially they are not only used as initiators for free radical polymerisation of common vinyl monomers like styrene, vinyl chloride, vinyl acetate, alkyl methacrylates, etc.,[1] but are also used as blowing agents for the production of polymer foams.[2]

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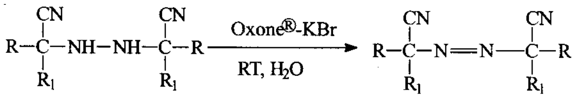


Scheme 1.

Routinely, symmetrical azo-*bis* nitriles are produced by the reaction between a ketone and hydrazine to form an azine, which on reaction with hydrogen cyanide yields the intermediate 1,2-*bis*-dialkylcyano hydrazine (I) which is then oxidised to symmetrical azo-*bis* nitrile (II) (Sch. 1).

The oxidation of intermediate hydrazino compound (I) to azo-*bis* nitrile has been achieved earlier using conventional oxidising agents like chlorine,[3] bromine,[4] potassium dichromate,[5] sodium dichromate,[6] potassium permanganate[7] and also by using oxidants like oxygen–ozone mixture,[8] sodium hypochlorite salt solution[9] and by using hydrogen peroxide in combination with bromine compound and sulphuric acid.[10] However, some of these oxidants are not acceptable from the viewpoint of environmental concerns.

Oxone® is a stable ternary composite of $KHSO_5$, $KHSO_4$ and K_2SO_4 in 2 : 1 : 1 molar ratio and its utility has been demonstrated for a variety of organic transformations.[11,12] We have recently reported bromination of activated arenes using alkali metal bromide and Oxone®[11] and also the oxidation of hydrazides to *N*,*N*′-diacyl hydrazines using Oxone® in aqueous medium.[12] In continuation of our work on Oxone®–KBr reagent system, we wish to report here its usefulness for the oxidation of 1,2-*bis*-dialkylcyano hydrazines (I) to azo-*bis* nitriles (II) (Sch. 1).

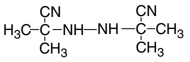
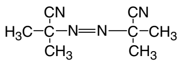
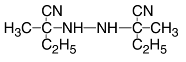
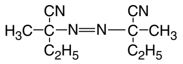
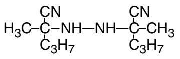
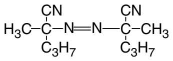
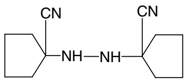
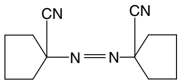
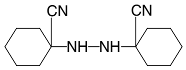
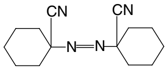
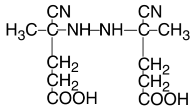
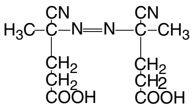
A variety of 1,2-*bis*-dialkylcyano hydrazines were smoothly oxidised using Oxone®–KBr reagent system to the corresponding azo-*bis* nitriles in good yields except for levulinic acid-based hydrazino compound in which case the yield was low. (Entry 6, Table 1).

In summary, Oxone®–KBr reagent system constitutes an useful and complimentary method for the oxidation of 1,2-*bis*-dialkylcyano hydrazines to the corresponding azo-*bis* nitriles.

EXPERIMENTAL

Oxone® (M/s Lancaster), potassium bromide and hydrazine sulphate (E.Merck), cyclohexanone, acetone, ethyl methyl ketone (Sd Fine Chem.) levulinic acid, cyclopentanone and methyl propyl ketone (Fluka) were used as received. All 1,2-*bis* dialkylcyano hydrazines were prepared by the standard procedure.[2,4]

Table 1. Oxidation of 1,2-*bis*-Dialkylcyanohydrazines to Azo-*bis* Nitriles Using Oxone®–KBr System

Entry	Substrate	Product	Yield (%)	M.P. °C (Lit. M.P. °C)
1	 $H_3C\text{-}C(CN)(CH_3)\text{-}NH\text{-}NH\text{-}C(CN)(CH_3)\text{-}CH_3$	 $H_3C\text{-}C(CN)(CH_3)\text{-}N{=}N\text{-}C(CN)(CH_3)\text{-}CH_3$	66	102–103 (103–104)[2]
2	 $H_3C\text{-}C(CN)(C_2H_5)\text{-}NH\text{-}NH\text{-}C(CN)(C_2H_5)\text{-}CH_3$	 $H_3C\text{-}C(CN)(C_2H_5)\text{-}N{=}N\text{-}C(CN)(C_2H_5)\text{-}CH_3$	64	52–55 (49–51)[2]
3	 $H_3C\text{-}C(CN)(C_3H_7)\text{-}NH\text{-}NH\text{-}C(CN)(C_3H_7)\text{-}CH_3$	 $H_3C\text{-}C(CN)(C_3H_7)\text{-}N{=}N\text{-}C(CN)(C_3H_7)\text{-}CH_3$	71	71 (73–74.5)[2]
4			89	82 (83–84)[13]
5			75	114 (114–115)[2]
6	 $H_3C\text{-}C(CN)(CH_2CH_2COOH)\text{-}NH\text{-}NH\text{-}C(CN)(CH_2CH_2COOH)\text{-}CH_3$	 $H_3C\text{-}C(CN)(CH_2CH_2COOH)\text{-}N{=}N\text{-}C(CN)(CH_2CH_2COOH)\text{-}CH_3$	26	113–118 (112–116)[1]

Typical Procedure: 1,1′-Azo *bis*-1-Cyclohexanenitrile

To a stirred suspension of 1,2-di-1-(1-cyano)-cyclohexylhydrazine (2.46 g, 0.01 mol) in water (30 mL) was added potassium bromide (1.18 g, 0.01 mol) followed by the solution of Oxone® (6.15 g, 0.01 mol) in water (20 mL) during a period of 30 min. The reaction mixture was stirred for additional 3 h and the resultant product was filtered at pump, washed with water and dried under vacuum. The crude product was recrystallized from petroleum ether. Yield: 1.82 g (75%).

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