Oxidation Using Quaternary Ammonium Polyhalides VII[1]. Oxidation of Primary Amines and Hydrazo Compounds by Use of Benzyltrimethylammonium Tribromide

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Abstract

The reactions of primary amines and hydrazo compounds with benzyltrimethylammonium tribromide in aqueous sodium hydroxide or in water gave the corresponding nitriles and azo compounds in satisfactory yields, respectively.

1. Introduction

Halogen is known to oxidize some nitrogen compounds. For example, the reaction of primary amines with alkaline hypobromite gives nitriles[2], hydrazo compounds are transfered to azo compounds by bromine[3], hydroxylamines are oxidized to nitroso compounds by aqueous sodium hypobromite[4], furthermore, the reaction of oximes with bromine in aqueous potassium hydroxide gives bromonitro compounds[5].

During the course of our investigation on the synthetic utility of benzyltrimethylammonium tribromide (BTMA Br_3), we have found that this reagent is an effective oxidizing agent[1,6-10]. In this paper, we wish to report on the oxidation of primary amines (**1**) to nitriles (**2**) and the oxidation of hydrazo compounds (**3**) to azo compounds (**4**) by the use of BTMA Br_3.

2. Results and Discussion

2.1 Oxidation of Primary Amines (1) to Nitriles (2)

Preparative methods of nitriles **2** have already been shown in many literatures[11]. As one of these methods, primary amines **1** at a primary carbon can be dehydrogenated to **2**. The reaction has been carried out in a variety of ways: by treatment with IF_5[12], lead tetraacetate[13], nickel peroxide[14], silver(II) picolinate[15], CuCl-O_2-pyridine[16], *N*-bromosuccinimide and triethylamine[17], or Cl_2-

$$\underset{(1)}{RCH_2NH_2} \xrightarrow{-H_2} \underset{(2)}{R-C\equiv N}$$

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$NaHCO_3$ followed by CsF[18].

Well, the reaction of **1** with 2-equiv of BTMA Br_3 in aqueous NaOH (4-equiv) at 40℃ gave **2** as light yellow oil in fairly good yields. The results are summarized in Table 1, and the reaction scheme can be represented as

$$\mathbf{1} + 2\mathrm{BTMA\ Br_3} + 4\mathrm{NaOH} \longrightarrow \mathbf{2} + 2\mathrm{BTMA\ Br} + 4\mathrm{NaBr} + 4\mathrm{H_2O}.$$

An end point of the reaction can be detected by decolorization of the orange red reagent. Some viscous products are formed at initial reaction. These products are probably RCH_2NHBr and/or RCH_2NBr_2. Lower yield of nitrile is obtained when reaction temperature is kept so high because produced nitrile may be hydrolyzed into carboxylate by alkali. In the case of the reaction of lower primary amines with BTMA Br_3, it is necessary to select the extracting solvent since the lower products are relatively soluble in water. Consequently, it turned out that diethyl ether was best solvent.

Table 1 Oxidation of Amines **1** with BTMA Br_3[a] in NaOHaq at 40℃

	Procuct **2**	Reaction	Bp ℃/mmHg		Yield[c]
	$CH_3(CH_2)_nCN$	time/h	found	reported	%
a	n = 2	7	-	117/760[19]	-[d]
b	3	10	139/760	141.55-141.57[20]	-[d]
c	4	10	163/760	158-160/739[21]	33
d	5	8	182/760	184.5/760[22]	63
e	6	10	196/760	82.5/10[23]	65
f	7	10	220/760	100/11[23]	70
g	8	11.5	232/760	238.9/760[24]	72

a) Two-equiv. of BTMA Br_3 to **1** was used. b) Two-equiv. of NaOH to BTMA Br_3 was used. c) Yeild of isolated product. d) Mixture was obtained.

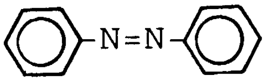
2.2 Oxidation of Hydrazo Compounds (3) to Azo Compounds (4)

There are a number of preparative methods of azo compounds **4**[25]. In particular, hydrazo compounds **3** are oxidized to **4** by several oxidizing agents, including NaOBr, HgO[26], $K_3Fe(CN)_6$ under phase transfer conditions[27], benzene-seleninic anhydride[28], MnO_2[29], $CuCl_2$, and air and NaOH[25].

$$\underset{(\mathbf{3})}{\mathrm{R{-}NH{-}NH{-}R^1}} \xrightarrow{-\mathrm{H_2}} \underset{(\mathbf{4})}{\mathrm{R{-}N{=}N{-}R^1}}$$

Now, the synthesis of **4** was achieved by marking use of BTMA Br_3 as oxidizing agent. That is, the reaction of **3** with a slightly excess of BTMA Br_3 in CH_2Cl_2-H_2O at room temperature gave **4** in satisfactory yields, the results are summarized in Table 2. The reaction scheme is as follows;

Table 2 Oxidation of Hydrazo Compounds with BTMA Br_3 at Room Temperature

	Product **4** R−N=N−R^1	Reaction time/h	Bp ℃/mmHg found	Bp ℃/mmHg reported	Yield[a)] %
a		0.5	67/760	67-68/760[30)]	91
b	$CH_3OCON=NCOOCH_3$	4	132-134/60	-	19
c	$C_2H_5OCON=NCOOC_2H_5$	7.5	135-136/25	108-110/15[31)]	60
d	$C_3H_7OCON=NCOOC_3H_7$	10	143/25	122/11[23)]	85
e	$C_4H_9OCON=NCOOC_4H_9$	10	174/25	142/11[23)]	89

a) Yield of isolated.

$$\mathbf{3} + \text{BTMA Br}_3 \longrightarrow \mathbf{4} + \text{BTMA Br} + 2\text{HBr}$$

In this reaction, *N*-monobromination of **3** with BTMA Br_3 and a subsequent dehydrobrominaiton must occurs.

Although BTMA Br_3-NaOHaq system was used as oxidation process instead of BTMA Br_3-H_2O system, the yield of product did not improve.

3. Experiment

3.1 Octanenitrile, $CH_3(CH_2)_6CN$ (2e); A typical procedure for the oxidation of primary amines: To a mixture of octylamine (0.65g, 5 mmol) and 4N-NaOH solution (5.03 ml, 20 mmol) was added little by little BTMA Br_3 (3.90 g , 10 mmol) and water (5 ml) under stirring. The reaction mixture was stirred for 10h at 40 ℃ until the initial orange color faded, and then was ice cooled. Organic layer was separated and washed with water (5 ml), and then extracted with diethyl ether (10 ml × 3). The combined organic solution was dried over $MgSO_4$ and evaporated in vacuo to give 2e as light yellow oil; yield 0.41 g (65%); bp 75 ℃/12 mmHg (lit.[23)], bp 198-200 ℃/760 mmHg); ^1H NMR δ= 0.93(3H, br.t, CH_3CH_2), 1.18-1.19(10H, m, $CH_3(CH_2)_6CH_2$), 2.40(2H, t, J= 14Hz, CH_2CN); IR (neat) 2210 $cm^{-1}(\nu_{C=N})$.

3.2 Propyl Azodicarboxylate (4d), $C_3H_7OCON=NCOOC_3H_7$; A typical procedure for the oxidation of hydrazo compounds: Substrate, propyl hydrazodicarboxylate (**3d**), was prepared by the method as described in the literature[32)]. BTMA Br_3 (1.46 g , 3.8 mmol) was added little by little to a mixture of 3d (0.51 g , 2.5 mmol), water (5 ml) and dichloromethane (5 ml). The reaction mixture was stirred for 10h at room temperature until the inithial orange color faded. Organic layer was separated, dried over $MgSO_4$, and then evaporated in vacuo to give 4d as yellow oil; yield 0.43 g (85%); bp 143℃/25 mmHg (lit.[23)], bp 122℃/11 mmHg); ^1H NMR δ= 1.20(6H, br.t, $2CH_3CH_2$), 1.60-2.10(4H, m, $2CH_3CH_2$), 4.40(4H, br.t, $2CH_2OCO$); IR (neat) $1780cm^{-1}(\nu_{C=O})$.

4. Summary

It turned out that BTMA Br_3 could be enough used as oxidizing agent for the oxidation of primary amines to nitriles and for the oxidation of hydrazo compounds to azo compounds instead of other known oxidizing agents.

The procedure for the oxidation of these substrates using BTMA Br_3 has a large merit in that this reagent can be treated safely and quantitatively owing to its stable solid character.

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