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Bis(1-Benzyl-3,5,7-Triaza-1-Azoniatricyclo[3.3.1.1^{3,7}] Decane) Peroxodisulfate: A Mild and Efficient Oxidation of Organic Compounds Under Anhydrous and Aprotic Conditions

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BIS(1-BENZYL-3,5,7-TRIAZA-1-AZONIATRICYCLO[3.3.1.1^{3,7}] DECANE) PEROXODISULFATE: A MILD AND EFFICIENT OXIDATION OF ORGANIC COMPOUNDS UNDER ANHYDROUS AND APROTIC CONDITIONS

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Abstract: Bis(1-benzyl-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane) peroxodisulfate was readily prepared as an white solid from commercically available hexamethylenetetramine and potassium peroxodisulfate. This reagent could be used as a stable, mild and efficient oxidizer to produce the corresponding carbonyl compounds from hydroxyl compounds or hydrazones or oximes and disulfides from thiols under anhydrous and aprotic conditions. The yields were almost quantitative, and the reaction time was very short.

The oxidation of organic compounds under anhydrous and aprotic conditions is very important in modern organic synthesis. The peroxodisulfate ion is one of the strongest oxidizing agents. The early investigations[1] on application of peroxodisulfate ion in organic synthesis as a oxidant were performed in aqueous acidic or basic solution or in the presence of transition metal ions. In the recent decades, much attention has given to the synthesis and application of new peroxodisulfate compounds such as tetrakis(pyridine) silver(Ⅱ) peroxodisulfate[2], tetrabutylammonium peroxodisulfate[3] and benzyltriphenylphoshonium peroxodisulfate[4], which used for the oxidation of organic compounds under aprotic conditions in organic solvants.

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We have recently prepared polymer supported peroxodisulfate[5] for the oxidative transformation of organic compounds. Unfortunately, these reagents suffered from at least one of the following disadvantages: 1) cost of preparation, 2) hygroscopicity, 3) photosensitive, 4) instability, 5) long reaction time. In this paper we introduce bis(1-benzyl-3,5,7-triaza-1-azoniatricyclo[3.3.1.$1^{3,7}$]decane) peroxodisulfate which was readily prepared as an white solid from commercically available hexamethylenetetramine and potassium peroxodisulfate. This reagent could be used as a stable, rapid, cheap, mild and efficient oxidizer to produce the corresponding carbonyl compounds from hydroxyl compounds or hydrazones or oximes and disulfides from thiols under anhydrous and aprotic conditions.

Experimental

All yields refer to isolated products unless reported as GC or LC yields, and all oxidation products were characterized by comparison of their spectra and physical date with authentic samples. IR spectra were run on a IR – 440 infrared spectrometer. ^{1}H NMR spectra were recorded on a Varian EA 360 spectrometer.

Preparation of N-benzylhexamethylenetetramine bromide

To a saturatd solution of HMTA (16.0 g, 0.11 mol) in a minimum amount of ethanol was added benzylbromide (19.0 g, 0.11 mol) dropwise. The mixture was stirred 1 h at room temperature. The white solid precipitated. The crystals were collected, washed with ethanol and dried to obtain 26.3 g of N-benzylhexamethylenetetramine bromide, yield 75 %. IR υ/cm^{-1} 3045, 2977, 1460, 1363, 1270, 1233, 1110, 1002, 924, 757, 705. ^{1}H NMR (D_2O)δ 7.7(m, 5H,), 4.60(s, 2H), 3.95(s, 6H), 3.73(s, 6H). Found: C, 50.38; H, 6.27; N, 18.22. Calcd for $C_{13}H_{19}N_4Br$: C, 50.17; H, 6.15; N, 18.00.

Preparation of bis (1*-benzyl-*3, 5, 7*-triaza-*1*-azoniatricyclo* [3. 3. 1. $1^{3,7}$] *decane*) *peroxodisulfate*

N-benzylhexamethylenetetramine bromide (20 g, 0.057 mol) and potassium peroxodisulfate (15.4 g, 0.057 mol) were dissoved in a minimum amount of water, respectively, and mixed at room temperature. A white precipitate separated out immediately. After vigorous stirring for 30 min, the precipitate was filtered, washed with water and dried to give 26.1 g of the oxidizer, yield 70 %. IR υ/cm^{-1} 3045, 2977, 1467, 1300, 1266, 1233, 1110, 1062, 1002, 924, 813, 757, 701. ^{1}H NMR (DMSO-d_6) δ 7.70 (m, 5H,), 4.75 (s, 2H), 3.98 (s, 6H), 3.76 (s, 6H). Modified iodometry was used to measure the content of peroxodisulfate ions. Found: C, 47.38; H, 5.65; N, 16.80; S_2O_8, 29.03. Calcd for $C_{26}H_{38}N_8O_8S_2$: C, 47.69; H, 5.84; N, 17.11; S_2O_8, 29.34.

General procedure for oxidation of organic compounds

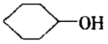
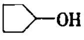
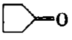
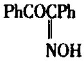
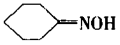
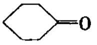
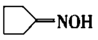
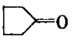
To a solution of a substrate (10 mmol) in acetonitrile was added the above-prepared oxidant (7.2 g, 11 mmol). The mixture was stirred under reflux until TLC showed complete disapearance of the substrate, which required 0.5 ~ 1 h (Table 1). The mixture was cooled and filtered. Silica gel (15 g) was added to the filtrate. The mixture was stirred for 5 min and the solid removed by fitration, followed by washing with acetonitrile (2×30 mL). Evaporation of the solvent gave the product, which was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent (9:1), yield 90 ~ 100 %.

Results and Discussion

Bis(1-Benzyl-3, 5, 7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane) peroxodisulfate was readily prepared from HMTA, benzylbromide and potassium peroxodisulfate in two steps. The starting materials were commercially available and inexpensive. This reagent was a stable white powder which was not hygroscopic. This reagent was soluble in DMF and DMSO, and slightly soluble in acetonitrile and water.

The oxidation of organic compounds with bis(1-Benzyl-3, 5, 7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane) peroxodisulfate proceeded smoothly in refluxing acetonitrile (the results are shown in Table 1), almost no further oxidations were observed. Primary and secondary benzylic alcohols and cycloalkanols were oxidized to their corresponding carbonyl compounds in high yields. When the reagent reacted with allylic alcohols, only

Table 1. Bis(1-Benzyl-3,5,7-triaza-1-azoniatricyclo[3.3.1.1^{3,7}]decane) peroxodisulfate for the oxidative transformation

Entry	Substrate	Product	Time(min)	Yield(%)[a]
1	$PhCH_2OH$	$PhCHO$	35	98
2	$PhCH(OH)CH_3$	$PhCOCH_3$	40	96[b]
3	$PhCH(OH)Ph$	$PhCOPh$	25	96
4	$4\text{-}NO_2PhCH_2OH$	$4\text{-}NO_2PhCHO$	30	95
5	$PhCH=CHCH_2OH$	$PhCH=CHCHO$	35	95[b]
6	$PhCH=CHCH(OH)CH_3$	$PhCH=CHCOCH_3$	35	96
7			45	97[c]
8			40	97[c]
9	$PhCH(OH)COPh$	$PhCOCOPh$	25	95
10	$4\text{-}CH_3OPhCH(OH)COPhOCH_3\text{-}4$	$4\text{-}CH_3OPhCOCOPhOCH_3\text{-}4$	30	97
11	$PhSH$	$PhSSPh$	10	98
12	$PhCH=NOH$	$PhCHO$	15	98[b]
13	$Ph_2C=NOH$	$PhCOPh$	15	98
14	 $PhCO\underset{\underset{NOH}{\Vert}}{C}Ph$	$PhCOCOPh$	20	97
15	$4\text{-}NO_2\text{-}PhC=NOH$	$4\text{-}NO_2PhCHO$	30	97[b]
16			20	100
17			3.5	100[c]
18	$Ph_2C=NNHPh$	Ph_2CO	25	97
19	$PhC(CH_3)=NNHPh$	$PhCOCH_3$	20	96
20	$Ph_2C=NN(CH_3)_2$	Ph_2CO	25	98
21	$PhC(CH_3)=NN(CH_3)_2$	$PhCOCH_3$	25	98
22	$PhCH=NNHCONH_2$	$PhCHO$	20	94
23	$PhC(CH_3)_2=NNHCONH_2$	$PhCOCH_3$	40	94
24	$Ph_2C=NNHPh(NO_2)_2\text{-}2,4$	Ph_2CO	45	94
25	$PhCH=NNHPh(NO_2)_2\text{-}2,4$	$PhCHO$	50	93
26	$PhCH(CH_3)=NNHPh(NO_2)_2\text{-}2,4$	$PhCOCH_3$	60	90

[a] Refers to isolated yield. [b] Detrmined by LC. [c] Determined by GC.

α,β-unsaturated carbonyl compounds were produced. It showed that the reagent was a selective oxidizer for alcohols and a inefficient oxidizer for carbon – carbon double bonds. α-Hydroxyketones have been converted to their correspounding diketone in excellent yields. Carbon – carbon bond cleavage was not observed. The mildness of the reagent had been shown by the oxidation of thiols to its disulfides in high yields.

Formation of crystalline hydrazones and oximes were a widely used very efficient method for the protection, isolation, purification and characterization of aldehydes and ketones. Thus the generation of aldehydes and ketones from their hydrazone and oximes derivatives constituted an important process. The classical procedure for the coversion of hydrazones or oximes to the corresponding carboyl compounds involved hydrolysis under acidic conditions and was not suitable for acidic-sesitive and asymmetric compounds[6]. Hydrazones and oximes were converted to the carbonyl compounds with bis(1-benzyl-3, 5,7-triaza-1-azoniatricyclo[3.3.1.$1^{3,7}$]decane) peroxodisulfate in almost quatitative yields. It provided us a efficient method for removal of the protecting groups when carbonyl compounds were transformed to hydrazones and oximes.

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