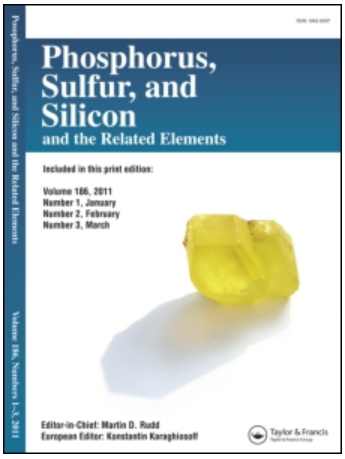

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N-BROMOBIS(*P*-TOLUENESULFONYL)AMINE AS A NOVEL AND MILD REAGENT FOR CONVERSION OF OXIMES TO CARBONYL COMPOUND

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N-*Bromobis(*p-*toluenesulfonyl)amine (NBBTA) is a novel and efficient reagent for the conversion of oximes to their corresponding carbonyl compounds in good yields under mild conditions.*

Keywords: Carbonyl compounds; deprotection; NBBTA; oximes

Regeneration of carbonyl compounds from their oximes is an important reaction because oxime serves as an efficient protective group for aldehydes and ketones, and these are used extensively for the purification of carbonyl compounds. A number of methods have been reported for the transformation of oximes to the corresponding carbonyl compounds,[1–16] and newer methods are continuously added. Some of these methods require the use of strong bases, acids or oxidizing agents, i.e., conditions that may be incompatible with sensitive substrate molecules and may thus lead to the formation of side products. Further these methods have drawbacks such as the use of expensive or less easily available reagents, vigorous reaction conditions, prolonged standing and high temperature, complicated reaction procedures, and tedious work-up in the isolation of pure products. Some of them are corrosive, toxic, and have low yields.

RESULTS AND DISCUSSION

We now report a convenient method for the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds using a new reagent (NBBTA) **2** that is prepared from *p*-toluenesulfonyl chloride (Scheme 1).

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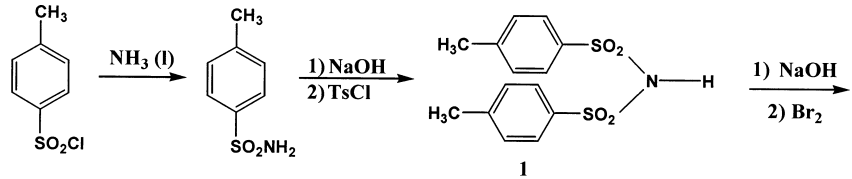

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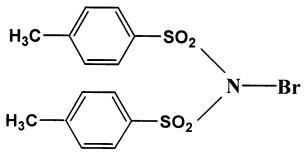


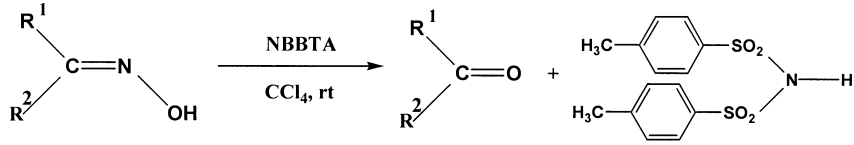
NBBTA 2

SCHEME 1

The advantages of NBBTA are as follows:

1. The preparation of *N*-bromobis(*p*-toluenesulfonyl)amine is easy.
2. NBBTA is stable for a long time in atmospheric condition.
3. After reaction of NBBTA with substrate, the sulphonamide is recovered and can be reused many times without decreasing the yield.
4. NBBTA is regarded as pure.

The reaction of oximes **(3)** with NBBTA in CCl_4 afforded carbonyl compounds **(4)** without side products (Scheme 2).



3 4

SCHEME 2

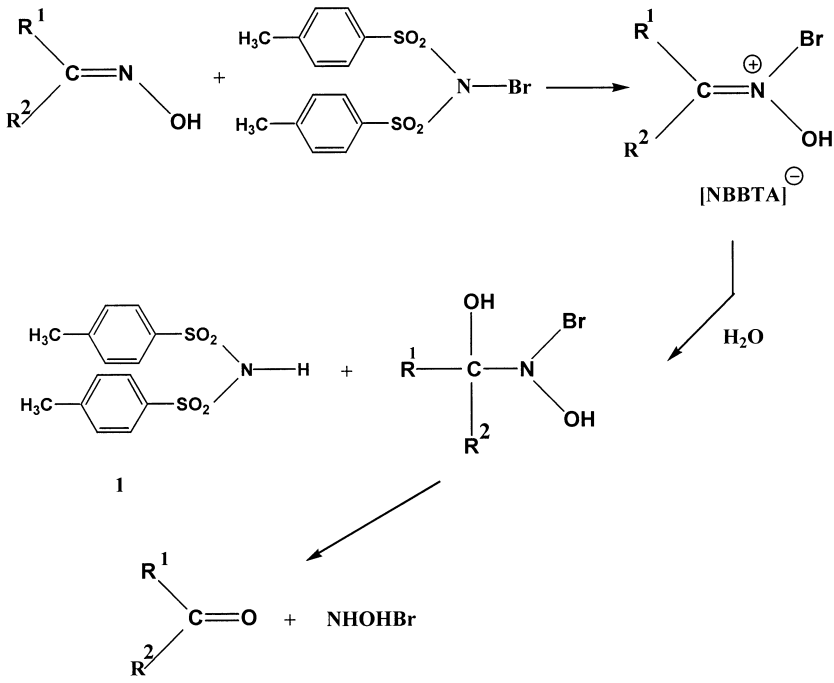
We suggest the following mechanism for the conversion (Scheme 3).

The results of the conversion of various ketoximes and aldoximes to ketones and aldehydes are presented in Table I. The products of the reaction with NBBTA were isolated simply by filtering of **1** and evaporating the solvent from the filtrate. The method has advantage in terms of yields, simplicity of reaction conditions, short reaction times and no

TABLE I Oxidative Cleavage of Oximes with NBBTA

Entry	R^1	R^2	Product[a]	Reaction times (h)	Yield (%)
1	CH_3	C_6H_5	Acetophenone	2.5	93
2	CH_3	*p*-$MeOC_6H_5$	*p*-Methoxyacetophenone	2.0	91
3	C_6H_5	C_6H_5	Benzophenone	2.0	95
4	C_6H_5	*p*-ClC_6H_5	*p*-Chlorobenzophenone	2.0	90
5	H	C_6H_5	Benzaldehyde	2.5	92
6	H	*o*-ClC_6H_5	*o*-Chlorobenzaldehyde	2.0	90
7	H	*o*-OHC_6H_5	*o*-Hydroxybenzaldehyde	2.5	91
8	H	*p*-ClC_6H_5	*p*-Chlorobenzaldehyde	2.0	90
9	C_6H_5	$C_6H_5CH(OH)$	Benzoin	3.0	91
10	C_6H_5	C_2H_5	Propiophenone	3.5	89
11	CH_3	C_6H_{13}	2-Octanone	4.0	91
12			Cyclohexanone	3.0	92

[a]Products were characterized by their physical constants, comparison with authentic samples, and IR spectra.



SCHEME 3

side products. The recovered starting material **(1)**, was rebrominated and used many times without reducing the yield.

CONCLUSIONS

From the results obtained, we find that the described procedure and the reaction conditions are simple. NBBTA is stable and the recovered regent can be reused.

EXPERIMENTAL

General

The oximes were prepared by a standard procedure. Commercial *p*-toluenesulfonyl chloride was used as received. *p*-Toluenesulfonylamine was prepared according to the literature. The purity of the compounds was checked by TLC.

Procedure for the Preparation of *N*-Bromobis(*p*-toluenesulfonyl)amine

Bis (*p*-toluenesulfonyl)amine (10 g, 0.06 mmol) was dissolved in a slight molar excess of chilled sodium hydroxide solution (3 M) at room temperature and was transfered to a beaker. 3 ml of bromine dissolved in 15 ml of carbon tetrachloride were added to the solution with vigorous stirring and immediately a yellow precipitate was formed. The product (yellow precipitate) was collected on a Büchner funnel and it was washed with 30 ml of distilled cold water and then dried in a vacuum dessicator at room temperature for 6 h. The reaction gives the product in 9 g (90%) yield. Melting point was 103–106°C. IR (KBr): ν 1600, 1470, 1340, 1150 cm^{-1}. ^1H NMR (acetone-d^6): δ 2.42 (s, 6H), 7.50–7.76 (dd, 8H). ^{13}C NMR (acetone-d^6): δ 20.15 (CH_3), 126.13–141.21 (benzene carbons).

General Procedure for Deoximation with *N*-Bromobis(*p*-toluenesulfonyl)amine

A mixture of oxime (5 mmol), carbon tetrachloride (10 ml), and *N*-bromobis(*p*-toluenesulfonyl)amine **2** was stirred at room temperature for the specified time (Table I). The reaction was monitored by TLC. After completion of the reaction, water was added to hydrolyze the intermediate, and the insoluble sulfonamide **1** was removed by filteration

and washed with cold carbon tetrachloride (5 ml). Removal of the solvent under reduced pressure gave the crude product. Solid products were recrystallized from diethyl ether, oily products were dissolved in ether and the ether solution washed, dried, and concentrated.

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