

Microwave Assisted Facile Cleavage of 2,4-Dinitrophenylhydrazones to the Corresponding Carbonyl Compounds with *N,N'*-Dibromo-*N,N'*-1,2-ethanediybis(*p*-toluenesulphonamide)

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Received: 14 October 2001 / Accepted: 25 May 2002 / Published: 31 May 2002

Abstract: Deprotections of 2,4-dinitrophenylhydrazones to their corresponding carbonyl compounds have been carried out in good yields by using *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluenesulphonamide) (**BNBTS**, **2**) under microwave irradiation.

Keywords: Microwave, BNBTS, reagents, synthesis.

Introduction

Carbonyl compound derivatives such as 2,4-dinitrophenylhydrazones and oximes are important intermediates in organic synthesis because of their use in the characterization and purification [1-3] of such compounds and the important role they play as protective groups for this functionality [4-7]. Consequently, the regeneration of carbonyl compounds from the corresponding 2,4-dinitrophenylhydrazones under mild conditions is an important process in synthetic organic chemistry. Several such procedures for regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones have been reported, for example: with Dowex-50 cation exchange resin [5], clayfen [6], potassium bromate [7], etc.

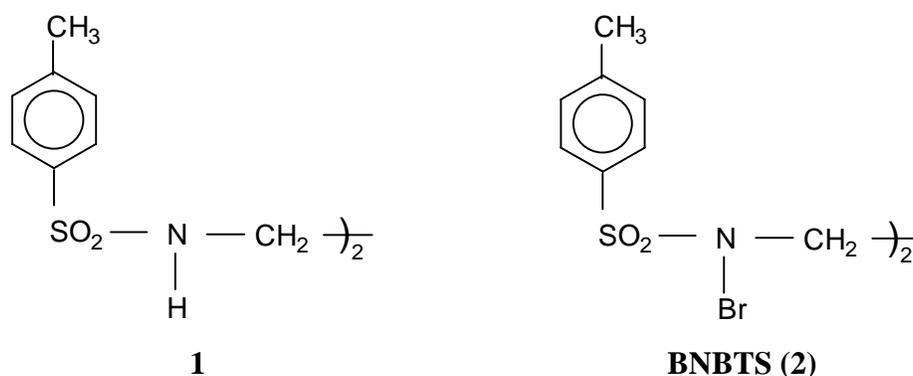
Although some are carried out under mild conditions most of these regenerations are often hazardous or use very toxic, expensive, or not readily available reagents, or reagents which need to be

freshly prepared [8-10]. Thus, there is still a need to develop new and facile procedures for the regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones.

Result and Discussion

We have previously reported a convenient method for the deoxygenation of ketone and aldehyde oximes to their corresponding carbonyl compounds [11] using the new reagent **BNBTS** (**2**), prepared from *N,N'*-1,2-ethanediylbis(*p*-toluenesulphonamide) (**1**) (**Figure 1**) [12]. Herein, we wish to report a mild and convenient method for the clean, fast and economical oxidative deprotection of 2,4-dinitrophenylhydrazones with this reagent under microwave irradiation.

Figure 1.



2,4-Dinitrophenylhydrazones **3** reacted with **BNBTS** (**2**) in CH_2Cl_2 under microwave irradiation to afford the corresponding carbonyl compounds **4** without any detectable byproducts (Scheme 1). The products of the reaction with **BNBTS** were isolated simply by filtering off compound **1** and evaporating the solvent from the filtrate. The results of the conversion of various 2,4-dinitrophenylhydrazones to their corresponding ketones and aldehydes are presented in **Table 1**.

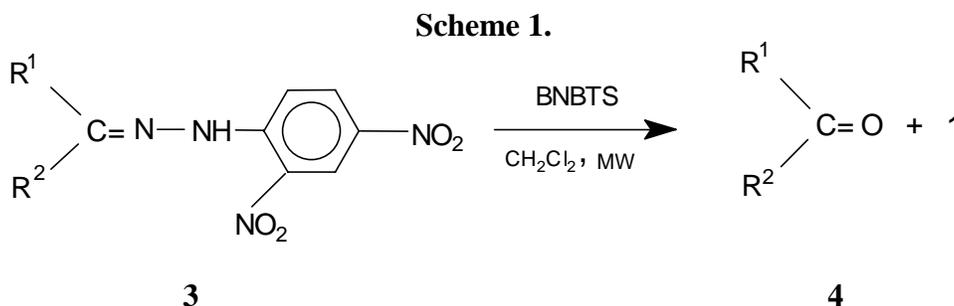


Table 1. Cleavage of 2,4-dinitrophenylhydrazones with BNBS under microwave irradiation

Entry	R ¹	R ²	Product ^a	Reaction Times (min)	Yield(%)
1	CH ₃	C ₆ H ₅	Acetophenone	50	91
2	CH ₃	p-ClC ₆ H ₅	<i>p</i> -Chloroacetophenone	60	92
3	CH ₃	p-MeOC ₆ H ₅	<i>p</i> -Methoxyacetophenone	50	94
4	CH ₃	p-BrC ₆ H ₅	<i>p</i> -Bromoacetophenone	50	93
5	C ₆ H ₅	C ₆ H ₅	Benzophenone	60	90
6	C ₆ H ₅	p-ClC ₆ H ₅	<i>p</i> -Chlorobenzophenone	30	92
7	H	C ₆ H ₅	Benzaldehyde	50	89
8	H	p-ClC ₆ H ₅	<i>p</i> -Chlorobenzaldehyde	40	95
9	H	p-MeC ₆ H ₅	<i>p</i> -Tolualdehyde	50	92
10	H	o-MeOC ₆ H ₅	<i>o</i> -Methoxybenzaldehyde	40	92
11	C ₆ H ₅	C ₆ H ₅ CH(OH)	Benzoin	50	91

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

Conclusions

From the results obtained, we find that the described procedure and the reaction conditions are simple. The reagent (BNBS) is stable and the recovered reagent can be reused.

Acknowledgements

The authors are grateful to Bu-Ali Sina University Research Council for partial financial support of this work.

Experimental

General

IR spectra was recorded using a Shimadzu 435-U-04 spectrophotometer (KBr Pellets). The 2,4-dinitrophenylhydrazones were prepared by a standard procedure [13]. The purity of compounds was checked by TLC (silica gel 60 F₂₅₄/CHCl₃ and CCl₄/UV). A Shivaki Co. microwave (220 v, 700 w, RF output 2450 MHz) was used for the microwave irradiations.

General procedure for facile cleavage of 2,4-dinitrophenylhydrazones with BNBS under microwave irradiation.

A mixture of 2,4-dinitrophenylhydrazone (5 mmol), dichloromethane (15 mL) and **BNBS** (5 mmol) was introduced in a flask and was refluxed under irradiated in a microwave oven at a power output of 700 W for the appropriate time as indicated in **Table 1**. After irradiation, cold water was

added to hydrolyze the intermediate, and the insoluble sulfonamide **1** was removed by filtration and washed with cold dichloromethane (10 mL). The organic layer was separated from the aqueous layer, combined with the washes and dried with MgSO₄. Dichloromethane was removed 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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Sample Availability: Samples of entries **1**, **5**, **7** and **11** are available from MDPI