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N,*N*′-Diiodo-*N*,*N*′-1,2-ethanediylbis(*p*-toluenesulfonamide) as a reagent for conversion of aldehydes to methyl esters

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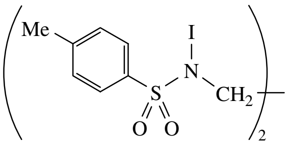
_N_,_N_′-Diiodo-_N_,_N_′-1,2-ethanediylbis(_p_-toluenesulfonamide) (NIBTS) can be used for the oxidation of aldehydes to the corresponding methyl esters with high efficiency in a single step.

The selective oxidation of aldehydes to esters is very important in organic chemistry.[1] For example, NIS is used for the oxidation of aldehydes to esters.[2] Ester formation can be performed under various conditions,[3] which are not always satisfactory in yield and/or simplicity of operation. The presence of strong acids, bases or catalysts and the application of heat or electricity are required.[1(*a*)] Simple processes for esterification under mild conditions are very desirable.



NIBTS **1**

Scheme 1

Here we report a convenient method for the conversion of aldehydes to the corresponding methyl esters with high efficiency in a single step[1(*b*),4] using a new reagent *N*,*N*′-diiodo-*N*,*N*′-1,2 ethanediylbis(*p*-toluenesulfonamide) **1** (NIBTS)[5] (Scheme 1).[†]

The advantages of NIBTS are as follows: (i) the preparation of NIBTS is easy; (ii) NIBTS is stable for six months under atmospheric conditions; (iii) after reaction of NIBTS with a substrate, the sulfonamide is recovered and can be reused many times without decreasing the yield.

The oxidation of aldehydes to esters with NIBTS under ambient conditions is shown in Scheme 2.[‡]

The results of the conversion of various aldehydes to esters are presented in Table 1.

Since NIBTS contains two iodine atoms, which are attached to nitrogen atoms, this reagent can *in situ* release I^+, which can act as an electrophilic species.[5,6] Therefore, the following mechanism can be suggested for the conversion of aldehydes to esters (Scheme 3). Initially formed methyl hemiacetal **3** is oxidised by NIBTS to corresponding hemiacetal hypoiodite **4**.[7] The subsequent elimination of hydrogen iodide produces the observed product.[8] The reaction is performed in the dark to prevent the light induced homolytic decomposition of the intermediate hypoiodite.[9]

Note that α,β-unsaturated aldehydes such as crotonaldehyde (Table 1, entry 12) converted to an ester with high chemoselectivity without addition of the reagent to the C=C bond. Furthermore, functional groups such as chloro, methoxy and

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[†] The IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively.

Procedure for preparation of N,N′*-1,2-ethanediylbis(*p*-toluenesulfonamide).* *p*-Toluenesulfonyl chloride (30 g) was placed in a three-necked round bottom flask and melted. Then, ethylenediamine (8 ml) was added dropwise (for 30 min). The mixture was heated at 90 °C for 2 h. Then, it was cooled to room temperature and 100 ml of distilled water was added and filtered off. Crude product was recrystallised from ethanol.

Procedure for the preparation of N,N′*-diiodo-*N,N′*-1,2-ethanediylbis-(*p*-toluenesulfonamide)* **1**. *N*,*N*′-1,2-ethanediylbis(*p*-toluenesulfonamide) (1 g, 0.006 mol) was dissolved in an excess of a sodium hydroxide solution (6 M) at room temperature and transferred to a beaker. Iodine (10 g) dissolved in carbon tetrachloride (15 ml) was added to the solution with vigorous stirring at –10 °C and immediately a yellow precipitate was formed. The product (yellow precipitate) was collected on a Buchner funnel and washed with cold distilled water (10 ml) and then dried in a vacuum desiccator at room temperature for 6 h. The reaction gives **1** (0.9 g, 90%). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.40 (s, 6H), 2.70 (s, 4H), 7.50–7.76 (dd, 8H). ^{13}C NMR (DMSO) δ: 20.2 (Me), 45.1 (CH_2), 126.20–141.19 (four peaks of benzene carbons). IR (KBr, ν/cm^{-1}): 1600, 1460, 1340, 1150.

[‡] *General procedure for conversion of aldehydes to methyl esters with NIBTS.* A mixture of benzaldehyde (0.106 g, 1 mol), methanol (10 ml), NIBTS (0.620 g, 0.5 mol) and sodium carbonate (0.333 g, 3.1 mol) was stirred at room temperature for 2.5 h. The reaction was performed in the dark to prevent the light-induced homolytic decomposition of intermediate hypoiodite **4**. The reaction was monitored by TLC (carbon tetrachloride–acetone, 9:1). After completion of the reaction, 3 ml of $Na_2S_2O_3\cdot5H_2O$ (5%) was added to destroy remaining NIBTS or hypoiodite species. The resultant mixture was extracted with 2×10 ml of a solution of 50% diethyl ether in hexane. The organic layer was dried with $MgSO_4$. The removal of the solvent under reduced pressure gave the crude product. The crude product was chromatographed on a silica gel column with 1% ethyl acetate in hexane. The evaporation of the solvent gave methyl benzoate (90%).

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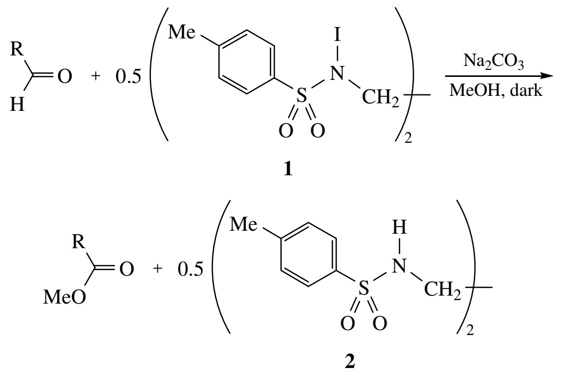


Scheme 2

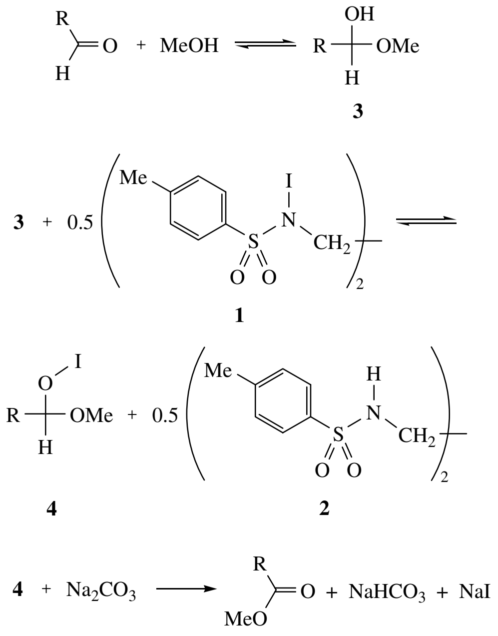
Table 1 Oxidation of aldehydes to esters with NIBTS at room temperature.

Entry	Substrate	Time/h	Yield of ester[a] (%)
1	Benzaldehyde	2.5	90
2	4-Chlorobenzaldehyde	24	80
3	4-Bromobenzaldehyde	24	78
4	4-(Dimethylamino)benzaldehyde	36	65
5	4-Methoxybenzaldehyde	36	78
6	2-Chlorobenzaldehyde	36	72
7	Butyraldehyde	36	80
8	4-Methylbenzaldehyde	36	87
9	3-Methylbenzaldehyde	40	85
10	Propionaldehyde	40	80
11	Isobutyraldehyde	42	78
12	Crotonaldehyde	18	70

[a] Products were characterised by their physical properties, comparison with authentic samples and by spectroscopic methods.

alkyl were also inert to this reagent, and no by-products were observed.

The advantages of our reagent over common reagents in the direct oxidation of aldehydes to esters are shown in Table 2.



Scheme 3

Table 2 Comparison of the results obtained by our method with previously published data.

Substrate	Conditions	Yield (%)
Benzaldehyde	Trichloroisocyanuric acid	82[10]
	H_2O_2, $HCl_{aq.}$	82[11]
	NIS	89[2]
	Electrochemical	80[12]
4-Methylbenzaldehyde	Electrochemical	82[12]
4-Chlorobenzaldehyde	Electrochemical	83[12]

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