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One Facile Preparation of N-Aroyl-N′-arylsulfonylhydrazines by Oxidation of Aromatic Aldehyde N-Arylsulfonylhydrazones with bis(Trifluoroacetoxy)iodobenzene

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One Facile Preparation of *N*-Aroyl-*N*′-arylsulfonylhydrazines by Oxidation of Aromatic Aldehyde *N*-Arylsulfonylhydrazones with bis(Trifluoroacetoxy)iodobenzene

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Abstract: *N*-aroyl-*N*′-arylsulfonylhydrazines can be obtained by oxidation of aromatic aldehyde *N*-arylsulfonylhydrazones with bis(trifluoroacetoxy)iodobenzene in acetone at room temperature in mild to good yields.

Keywords: Aromatic aldehyde, *N*-aroyl-*N*′-arylsulfonylhydrazine, *N*-arylsulfonylhydrazone, bis(trifloroacetoxy)iodobenzene, oxidation

INTRODUCTION

Many studies of the oxidation of aldehyde *N*-sulfonylhydrazones have been reported. Bhati has described the oxidation of some arylidene-toluene-*p*-sulfonylhydrazones by lead tetra-acetate to α-sulfonylhydraonobenzyl acetates (**2**) as crystals.[1] In 1966, Butler comfirmed Bhati's work, and compounds (**3**) were obtained from compounds (**2**), which is believed to

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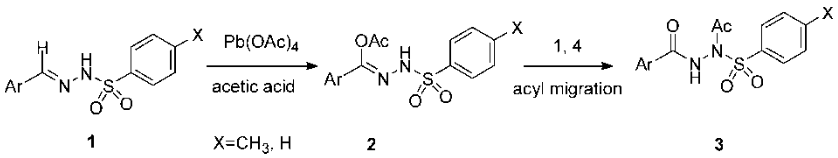


Scheme 1.

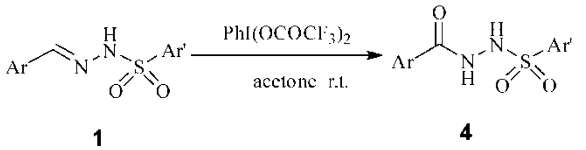
occur when compounds **2** rapidly rearrange to compounds **3** through 1,4-acyl migration (Scheme 1).[2] Furthermore, aldehyde sulfonylhydrazones can be oxidized to their parent carbonyl compounds by Dess-Martin periodinane (DMP),[3] H_2O_2/K_2CO_3,[4] thallium triaceatate,[5] N-bromosuccinimide (NBS),[6] uranium hexafluoride,[7] and Br_2.[8] Uiurg et al. found oxidation of aromatic tosylhydrazones leads to benzoic acid when poly(bis-1,2-phenylene)diselenide was used as a catalyst.[9] In addition, intramolecular 1,3-dipolar cycloadducts through nitrilesulfonimides, oxidized from aldehyde sulfonylhydrazones, react with dipolarophile.[10] Herein, we report that aromatic aldehyde *N*-sulfonylhydrazones (**1**) react smoothly with the organic iodine(III) reagent, bis(trifloroacetoxy)iodobenzene (BTI), at room temperature to efficiently afford *N*-acyl-*N*′-sulfonylhydrazines (**4**) in mild to good yields (Scheme 2).

RESULTS AND DISCUSSION

Commercially available BTI is commonly used as an efficient oxidizing reagent in organic synthesis. Many applications of BTI have been reported,[11–16] a reflection both of its mild reactivity along with a low by-product profile. In the current report, similar advantages of this reagent, mild reactivity and cleanly prepared products, were observed (Table 1).

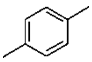
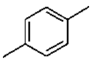
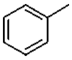
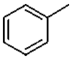
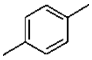
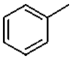
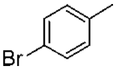
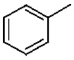
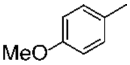
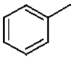
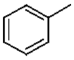
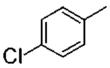
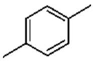
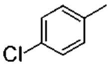
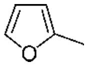
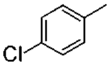
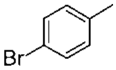
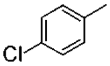
Oxidation of the aromatic aldehyde *N*-arylsulfonylhydrazones implicated that all the reactions proceeded rapidly and finished within 10 min. The oxidative yield was lower than others when the starting material contained a furan ring, whereas other functional groups had little influence.

The infrared spectrum showed some principal features of the product **4a**, strong bands at 3343 cm^{-1} and 3256 cm^{-1}, which may be assigned



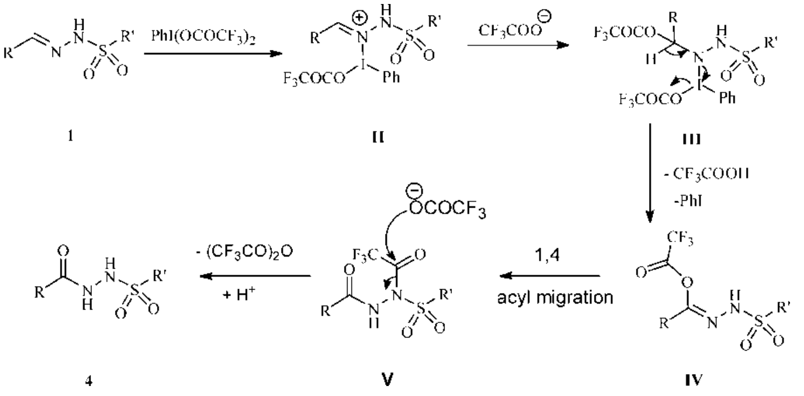
Scheme 2.

Table 1. Conversion of aromatic aldehyde arylsulfonylhydrazones into *N*-aroyl-*N*′-arylsulfonylhydrazines

Entry	Ar	Ar′	Reaction time (min)	Isolated yield (%)
4a			3	83
4b			3	88
4c			3	77
4d			3	80
4e			3	84
4f			2	76
4g			2	65
4h			2	45
4i			7	82

to –NH-; a carbonyl stretching band at 1681 cm^{-1} and a sulfonyl stretching band at 1328 cm^{-1} and 1166 cm^{-1}. In addition, the proton NMR showed two protons in the low field at 8.52 ppm and 9.92 ppm. All the data suggested the product **4a** may be *N*-(4-methylbenzenesulfonyl)-*N*′-(4-methyl-benzoyl)hydrazine. *N*-(4-methylbenzenesulfonyl)-*N*′-(4-methyl-benzoyl)hydrazine, prepared from *p*-methylbenzenesulfonyl chloride reacting with benzenesulfonyl chloride,[17] showed the same physical and chemical properties with **4a**.

A proposal for the reaction mechanism is shown in Scheme 3. The hydrazone **1** can be oxidized to nitronium ion **II**, which reacts with trifluoroacetic acid anion and eliminates iodobenzene and trifluoroacetic acid to afford **IV**. The intermediate **V** comes from **IV** through 1,4-acyl migration and is attacked by trifluoroacetic acid anion to eliminate trifluoroacetic anhydride and form product **4**.



Scheme 3.

CONCLUSION

The present method provides a rapid and productive synthesis of *N*-aroyl-*N*′-arylsulfonylhydrazines. This method is particularly advantageous, involving the use of easily handled BTI as a mild reaction reagent, which produced the desired products in good yields and a short period of time.

EXPERIMENTAL

Melting points were determined on a X-4 micro hot stage and are uncorrected. IR spectra were recorded on FTS 3000 instrument (BIO-RAD). ^{1}H NMR spectra were recorded on Bruker AV 400-MHz instrument using acetone-d_6 as a solvent, and chemical shifts (δ) are in ppm relative to TMS. All solvents were dried.

General Procedure

A dried round-bottomed flask was charged with aldehyde *N*-sulfonylhydrazones (1 mmol),[18] bis(trifluoroacetoxy) iodobenzene (BTI, 1.2 mmol), and anhydrous acetone (5 mL). This mixture was stirred at room temperature and monitored by TLC. When the reaction was complete, purification of the product directly by flash chromatography (silica gel, ethyl acetate–petroleum ether) three times afforded the products as solids.

Data

4a: *N*-(4-methylbenzenesulfonyl)-*N*′-(4-methyl-benzoyl)hydrazine mp: 201–202°C; IR (KBr): 3343, 3256, 1681, 1328, 1166 cm^{-1}; ^{1}H NMR: δ ppm

2.35 (s, 6H), 7.23–7.25 (d, 2H, $J = 8.0$ Hz), 7.29–7.31 (d, 2H, $J = 8.0$ Hz), 7.66–7.68 (d, 2H, $J = 8.4$ Hz), 7.78–8.00 (d, 2H, $J = 8.0$ Hz), 8.52 (s, 1H), 9.92 (s, 1H).

4b: *N*-benzenesulfonyl-*N*′-benzoylhydrazine mp: 193°C (lit.[19] 170°C); IR (KBr): 3311, 3139, 1670, 1341, 1170 cm^{-1}; ^{1}H NMR: δ ppm 7.41–7.46 (m, 2H), 7.48–7.52 (m, 3H), 7.58–7.63 (m, 1H), 7.75–7.78 (m, 2H), 7.92–7.95 (m, 2H), 8.67 (s, 1H), 10.01 (s, 1H).

4c: *N*-benzenesulfonyl-*N*′-(4-methyl-benzoyl)hydrazine mp: 156–157°C; IR (KBr): 3342, 3127, 1663, 1341, 1169 cm^{-1}; ^{1}H NMR: δ ppm 2.34 (s, 3H), 7.23–7.25 (d, 2H, $J = 8.0$ Hz), 7.47–7.51 (m, 2H), 7.57–7.62 (m, 1H), 7.65–7.67 (d, 2H, $J = 8.4$ Hz), 7.91–7.93 (m, 2H), 8.65 (s, 1H), 9.98 (s, 1H).

4d: *N*-benzenesulfonyl-*N*′-(4-bromo-benzoyl)hydrazine mp: 202–204°C (lit.[19] 200–202°C); IR (KBr): 3338, 3147, 1681, 1320, 1173 cm^{-1}; ^{1}H NMR: δ ppm 7.49–7.53 (m, 2H), 7.59–7.64 (m, 3H), 7.68–7.70 (d, 2H, $J = 8.4$ Hz), 7.91–7.93 (m, 2H), 8.65 (s, 1H), 10.05 (s, 1H).

4e: *N*-benzenesulfonyl-*N*′-(4-methoxy-benzoyl)hydrazine mp: 179–181°C (lit.[19] 189–190°C); IR (KBr): 3240, 3100, 1650, 1330, 1160 cm^{-1}; ^{1}H NMR δ: ppm 3.84 (s, 3H), 6.94–6.97 (m, 2H), 7.47–7.51 (m, 2H), 7.58–7.60 (m, 1H), 7.74–7.76 (d, 2H, $J = 8.8$ Hz), 7.90–7.92 (d, 2H, $J = 6.8$ Hz), 8.59 (s, 1H), 9.88 (s, 1H).

4f: *N*-benzoyl-*N*′-(4-chloro-benzenesulfonyl)hydrazine mp: 194°C; IR (KBr): 3253, 1652, 1349, 1164 cm^{-1}; ^{1}H NMR: δ ppm 7.43–7.47 (m, 2H), 7.53–7.56 (m, 3H), 7.76–7.78 (m, 2H), 7.91–7.94 (m, 2H), 8.01 (s, 1H), 10.03 (s, 1H).

4g: *N*-(4-methylbenzoyl)-*N*′-(4-chloro-benzenesulfonyl)hydrazine mp: 210–212°C; IR (KBr): 3254, 1651, 1346, 1164 cm^{-1}; ^{1}H NMR: δ ppm 2.47 (s, 3H), 7.35–7.37 (d, 2H, $J = 8.0$ Hz), 7.59–7.62 (m, 2H), 7.64–7.69 (m, 2H), 7.96–7.98 (dd, 2H, $J = 2.0$ Hz, $J = 2.8$ Hz), 8.07 (s, 1H).

4h: *N*′-4-chlorobenzenesulfonylfurane-2-carbohydrazide mp: 198–200°C; IR (KBr): 3292, 3140, 1660, 1349, 1167 cm^{-1}; ^{1}H NMR: δ ppm 6.64–6.66 (dd, 1H, $J = 1.6$ Hz, $J = 3.6$ Hz), 7.14–7.15 (d, 1H, $J = 3.6$ Hz), 7.62–7.65 (m, 2H), 7.70–7.73 (m, 1H), 7.93–7.97 (m, 2H), 8.28 (s, 1H), 9.24 (s, 1H).

4i: *N*-(4-bronobenzoyl)-*N*′-(4-chlorobenzenesulfonyl)hydrazine mp: 209–210°C; IR (KBr): 3329, 3146, 1641, 1380, 1175 cm^{-1}; ^{1}H NMR: δ ppm 7.55–7.58 (m, 2H), 7.63–7.66 (m, 2H), 7.70–7.72 (m, 2H), 7.91–7.94 (m, 2H), 8.86 (s, 1H), 10.12 (s, 1H).

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