

Synthesis of Sulfonyl Azides from Sulfonyl Chlorides using Cyanuric Chloride

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ABSTRACT

A mild, efficient and convenient method for synthesis of sulfonyl azides from sulfonyl chlorides is described. In situ sulfonyl chlorides are prepared from sulfonyl chlorides. The sulfonyl chlorides were then further allowed to react with excess NaN_3 in the same pot.

Keywords : Sulfonyl Azides, Sulfonyl Chlorides, NaN_3 , N-Methyl

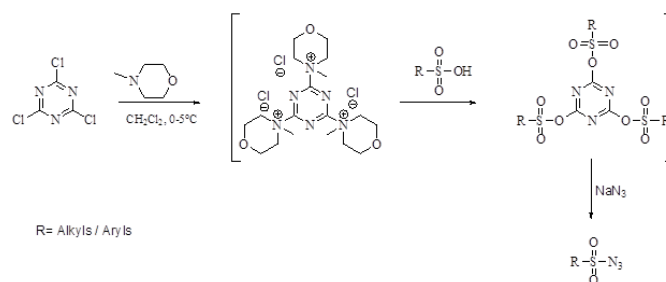
I. INTRODUCTION

Sulfonyl azides are valuable synthetic intermediate in organic chemistry. They can be prepared from sulfonyl chlorides. In situ sulfonyl chlorides can be prepared from corresponding thiols using number of methods, generally by bubbling Cl_2 gas into aqueous acids or a biphasic mixture containing thiols. Use of excess oxidant or aqueous acids was required in this methodology. (1) Sulfonyl azides are valuable reagent for variety of chemical transformation, they have been used as a valuable reagent for synthesis of α -diazocarbonyl reagents, (2,3,5,6) hydroazidation of olefins, (7) the aziridation of olefins, (8,9) the radical amination (4,10,11) and metal catalysed coupling reaction (8) owing to a wide range of applications.

Preparation of sulfonyl azides involves the reaction of sulfonyl chlorides with sodium azides (12). Sulfonyl chlorides are difficult to prepare and handled. Generally sulfonyl chlorides are prepared by treating sulfonyl acid with chlorinating agents like SOCl_2 (13), POCl_3 (14), PCl_5 (15), triphosgene (16) and cyanuric chloride (17). One pot synthesis of sulfonyl azides from sulfonyl chlorides was reported (18). Preparation of sulfonyl azides from thiols with chloramine-T, Bu_4NCl and water was reported (19). A mild, efficient and general method for the preparation of acyl azides from carboxylic acids and sodium azide using Cyanuric chloride was performed (20). One pot process for preparation of various sulfonyl azides by treating sulfonyl chlorides with triphenyl phosphine/ trichloroisocyanuric acid/ sodium azide at room temperature was described. A wide range of arenesulfonyl and alkanesulfonyl azides was obtained in

excellent yield under mild conditions. Cyanuric chloride and its derivatives like 4,6-dimethoxy derivative, 2-chloro-4,6-dimethoxy-1,3,5-triazine derivative found considerable applications in organic chemistry. Sulfonyl chlorides can be activated with cyanuric chloride and subsequently react with 18-crown-6 in acetone or NEt_3 in acetone (17). We now report the use of cyanuric chloride for the direct conversion of sulfonyl chlorides to sulfonyl azides. (scheme1)

The mechanism proceeds through activation of sulfonyl chloride by cyanuric chloride in presence of N-Methyl morpholine in dichloromethane. Various aryls, heteroaryls, alkylaryls, and alkyl sulfonyl chlorides on reaction with cyanuric chloride in presence of NaN_3 and N-Methyl morpholine undergoes smooth conversion to the corresponding sulfonyl azides in excellent yield (Table 1). Cyanuric chloride is inexpensive reagent and safe to handle in comparison to the recently reported use of hazardous and expensive triphosgene, thionyl chloride, and phosphorous pentachlorides.



Scheme 1.

II. RESULTS AND DISCUSSION

In this Strategy reactivity of Sulfonyl group enhances using 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride). The sulfonic acid was first allowed to react with 2,4,6-trichloro-1,3,5-triazine in dichloromethane in presence of N- Methylmorpholine. The resulting reaction mixture containing activated sulfonic acid was further sodium azide at room temperature gives sulfonyl azide in good to excellent yield. The results are summarized in table 1.

In conclusion, we have developed a mild efficient and general procedure for conversion of sulfonic acids to corresponding sulfonyl azides.

Table1. Synthesis of sulfonyl azides from sulfonic acids using cyanuric chloride.

Entry	Sulfonic acid	Sulfonyl azide	Time (min)	Yield (%) ^{a,b}	Ref. c
1	PhSO ₃ H	PhSO ₂ N ₃	40	88	_d
2	p-me[C ₆ H ₄]SO ₃ H	p-me[C ₆ H ₄]SO ₂ N ₃	55	83	_e
3	p-Ome[C ₆ H ₄]SO ₃ H	p-Ome[C ₆ H ₄]SO ₂ N ₃	50	74	18
4	p-Cl[C ₆ H ₄]SO ₃ H	p-Cl[C ₆ H ₄]SO ₂ N ₃	180	77	18
5	2,4-Cl ₂ [C ₆ H ₃]SO ₃ H	2,4-Cl ₂ [C ₆ H ₃]SO ₂ N ₃	180	82	21
6	p-NO ₂ [C ₆ H ₄]SO ₃ H	p-NO ₂ [C ₆ H ₄]SO ₂ N ₃	190	76	18
7	p-Br[C ₆ H ₄]SO ₃ H	p-Br[C ₆ H ₄]SO ₂ N ₃	190	78	21
8	C ₆ H ₅ -CH ₂ SO ₃ H	C ₆ H ₅ -CH ₂ SO ₂ N ₃	40	81	18
9	1-Naphthalene sulfonic acid	1-Naphthalenesulfonyl azide	50	76	21
10	2-Naphthalene sulfonic acid	2-Naphthalenesulfonyl azide	55	75	21
11	CH ₃ SO ₃ H	CH ₃ SO ₂ N ₃	60	80	21
12	CH ₃ -CH ₂ -SO ₃ H	CH ₃ -CH ₂ -SO ₂ N ₃	65	72	21
13	p-NHCOCH ₃ [C ₆ H ₄]-SO ₃ H	p-NHCOCH ₃ [C ₆ H ₄]-SO ₂ N ₃	65	74	21
14	m-NHCOCH ₃ [C ₆ H ₄]-SO ₃ H	m-NHCOCH ₃ [C ₆ H ₄]-SO ₂ N ₃	60	81	21

^aYield of pure isolated product. ^bProducts were characterized by their m.p. or b.p. with authentic samples. ^cPublished physical and spectral properties. ^dSpectroscopic data for 1 and 2 is given in experimental section.

General procedure for synthesis of sulfonyl azides-

To a solution of cyanuric chloride (3 mmol) in dichloromethane (25ml) N-Methyl morpholine was added at 0- 5°C with continuous stirring. A white suspension is formed. To this suspension sulfonic acid (9 mmol) in 10 ml dichloromethane was added and the stirring was continued for 3 Hrs. at room temperature and completion of reaction was checked by TLC. After completion of reaction mixture was washed with saturated solution of NaHCO₃ (3X10ml) and then with water (3x10ml). Organic layer was dried with Na₂SO₄, passed through short a silica gel, column and the solvent removed under reduced pressure to give pure sulfonyl azide.

Data for selected compounds. Benzenesulfonyl azide (Entry1, Table1): IR(cm⁻¹):1088, 1168(SO₂), 1372(SO₂), 2128(N₃), 3070, 3095. ¹H-NMR(300MHz, CDCl₃): 7.50 (t, 2H, J=7.3 Hz), 7.58 (t, 1H, J=7.3 Hz), 7.72(d, 2H, J=7.6 Hz)

p-Toluenesulfonyl azide (Entry2, Table1): IR(cm⁻¹):1085, 1170(SO₂), 1371(SO₂), 2127(N₃), 2920, 3059. ¹H-NMR (400MHz, CDCl₃): 2.49 (s, 3H), 7.43 (d, 2H, J=8 Hz), 7.86(d, 2H, J=8.5 Hz)

III. REFERENCES

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