Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Sep 2006.

To cite this article: Shanti N. Sawhney, Pawan Sharma, Kiran Bajaj & Asha Gupta (1993) A New Synthesis of 2-Arylbenzothiazoles from 1,2,3-Benzodithiazole-2-Oxides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:2, 263-270, DOI: 10.1080/00397919308009777

To link to this article: http://dx.doi.org/10.1080/00397919308009777

SYNTHETIC COMMUNICATIONS, 23(2), 263-270 (1993)

A NEW SYNTHESIS OF 2-ARYLBENZOTHIAZOLES FROM 1,2,3-BENZODITHIAZOLE-2-OXIDES

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Abstract: The reaction of 6-substituted-1,2,3-benzodithiazole-2-oxides (3a-3d) with aromatic aldehydes, carboxylic acids, and their chlorides in the presence of an organic base provides a new method for the synthesis of 6-substituted-2-arylbenzothiazoles (4a-4d) without involving the preparation of intermediate 2-aminobenzenethiols.

Of the several processes known for the preparation of benzothiazoles, the most commonly used process involves the use of 2-aminobenzenethiols as starting materials. However, with the exception of 2-aminobenzenethiol (abbreviated as 2-ABT) which is available commercially, all the substituted 2-ABTs have to be synthesized which are quite difficult to prepare, store, and use due to their foul smell and oxygen sensitive nature. 2-Aminobenzenethiols prepared, have to be employed in the form of their derivatives such as acid

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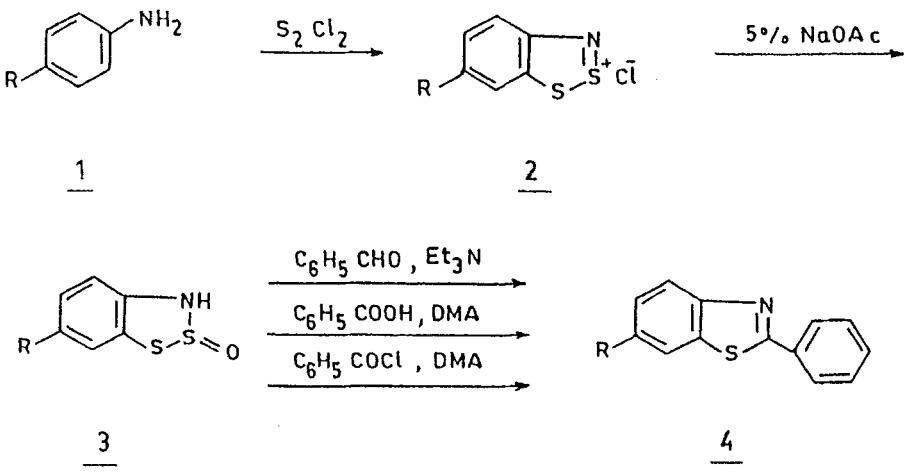
salts, alkali salts, zinc salts or disulphides. These precursors generate the free 2-ABTs under suitable conditions. Moreover, the yields of benzothiazoles prepared from the use of the above salts and derivatives are generally poor.

No efforts appear to have been made towards evolving a method to synthesize benzothiazoles from the Herz compounds without involving the use of 2-ABTs. During the present investigation we have developed a new, simple, and versatile method for the preparation of benzothiazoles in high yields from 1,2,3-benzodithiazole-2-oxides without resorting to the preparation of intermediate 2-ABTs.

The new procedure involves the treatment of 6-substituted-3H-1,2,3-benzodithiazole-2-oxides (hydrolysed Herz compounds) (3) with aldehydes (method A), carboxylic acids (method B) or acid chlorides (method C) in the presence of an appropriate organic base. The reaction gives 6-substituted-2-arylbenzothiazoles (4) in 49-69% yield (Scheme 1). The reaction of 6-substituted-3H-1,2,3-benzodithiazole-2-oxides (3) and an aromatic aldehyde was performed in 50% methanol in the presence of triethylamine. However, the reaction of compound 3 with carboxylic acid under these conditions did not proceed as desired and the reactants remained unchanged. The reaction of benzoyl chloride with 3 can not be carried out in 50% methanol as it requires non-hydroxylic solvent. So the reaction of 3 with benzoic acid and benzoyl chloride was carried out in N,N-dimethylaniline which acts as a base and solvent.



a , R = Cl b , R = OCH_3

c , R = Br d , R = F

Scheme 1

The required Herz compounds (2) were prepared by the slow action of sulphur monochloride on appropriate p-substituted aniline in the presence of acetic acid according to the literature procedure[1,2]. However, hydrolysis of the Herz compounds (2) to 6-substituted-3H-1,2,3-benzodithiazole-2-oxides (3) by stirring with water[3-7] did not proceed smoothly. The major difficulty in this process was the isolation and purification of the hydrolysed product 3. The hydrolysis of 2 was achieved by treatment with 5% sodium acetate solution giving 6-substituted-3H-1,2,3-benzodithiazole-2-oxides (3) in 62-80% yield.

In conclusion, the present study provides a new and simple method for the synthesis of 6-substituted-2-aryl-benzothiazoles from the hydrolysed Herz compounds without resorting to preparing the intermediate 2-ABTs. The procedure for the hydrolysis of the Herz compounds has also been improved by using 5% sodium acetate solution in place of water. The method provides a better alternative to the existing syntheses involving the use of 2-ABTs.

Experimental

6-Substituted-1,2,3-benzodithiazol-2-ium chlorides (Herz compounds) (2) were prepared according to the literature procedure.[1,2]

Hydrolysis of Herz compounds to 6-substituted-3H-1,2,3-benzodithiazole-2-oxides (3)

General Procedure

Appropriate 6-substituted-1,2,3-benzodithiazol-2-ium chloride (0.01 mol) was dissolved in 5% solution of sodium acetate (25 ml) and the solution stirred for 30 min. The product separated as a flocculent precipitate which was filtered, dried, and crystallized from benzene-acetic acid.

6-Chloro-3H-1,2,3-benzodithiazole-2-oxide (3a)

m.p. 114°(d) [Lit[8]. m.p. 113-114°(d)], yield 80%

IR (Nujol) cm^{-1} : 3120 (NH str.), 1104 (S=O str.).

6-Methoxy-3H-1,2,3-benzodithiazole-2-oxide (3b)

m.p. 150°, yield 72%, IR (Nujol) cm^{-1} : 3120 (NH str.), 1073 (S=O str.).

6-Bromo-3H-1,2,3-benzodithiazole-2-oxide (3c)

m.p. 115°, yield 62%, IR (Nujol) cm^{-1} : 3117 (NH str.), 1080 (S=O str.).

6-Fluoro-3H-1,2,3-benzodithiazole-2-oxide (3d)

m.p. 85°, yield 71%, IR (Nujol) cm^{-1} : 3200 (NH str.), 1100 (S=O str.).

Conversion of 6-chloro-3H-1,2,3-benzodithiazole-2-oxide (3a) to 6-chloro-2-phenylbenzothiazole (4a)

Method A : By the reaction of 3a with benzaldehyde

A solution of 6-chloro-3H-1,2,3-benzodithiazole-2-oxide (3a ; 1.03 g, 0.005 mol) and benzaldehyde (0.53 g, 0.005 mol) in 50% aqueous methanol (50 ml) was heated to reflux on a water bath. Triethylamine (5 ml) was added to the refluxing solution and refluxing continued for further 20 min. The solution was cooled and the solid which separated out was filtered, washed with a little cold ethanol, and crystallized from ethanol, m.p. 156° (Lit[9]. m.p. 156-157°), yield 68%. Mixed melting point with the authentic sample remained undepressed and IR spectra were superimposable. MS : M^{+}, m/z 245.0110/247.0720. Calcd. Mol. wt. 245.0069/247.0039.

Method B : By the reaction of 3a with Benzoic acid

A solution of 6-chloro-3H-1,2,3-benzodithiazole-2-oxide (3a; 1.03g, 0.005 mol) and benzoic acid (0.61 g, 0.005 mol) in N,N-dimethylaniline (12.5 ml) was refluxed for one hr. After cooling, it was poured into dil. hydrochloric acid (20 ml conc. HCl + 120 ml water) shaken well and allowed to stand overnight. The solid product which separated out was filtered, washed with water and dried. The crude product was washed with little acetone to remove last traces of dimethylaniline and crystallized from benzene-pet. ether, m.p. 156° (Lit[9]. m.p. 156-157°), yield 0.60 g (49%). Mixed melting point with sample obtained by method A undepressed and IR spectra were superimposable.

Method C : By the reaction of 3a with Benzoyl chloride

The procedure is same as in method B except that benzoyl chloride was used instead of benzoic acid, m.p. 156° (Lit[9]. m.p. 156-157°), yield 69%. Mixed melting point with sample obtained by method A underpressed and IR spectra were superimposable.

Other 6-substituted-2-phenylbenzothiazoles (4b-d) were prepared in a similar manner as described above.

6-Methoxy-2-phenylbenzothiazole (4b)

m.p. 115°, yield 55% (method A), 48% (method B), 51% (method C). Anal. Calcd. for $C_{14}H_{11}NOS$: C, 69.71; H, 4.56; N, 5.81. Found : C, 69.82; H, 4.51; N, 5.64. IR (Nujol) cm^{-1} : No absorption

in the region 3400-3100 and at 1073 (NH and S=O absent); ^{1}H nmr ($CDCl_3$) : δ 3.85 (s, 3H, OCH_3), 6.7-8.2 (m, 8H, aromatic protons).

6-Bromo-2-phenylbenzothiazole (4c)

m.p. 150° (Lit[10]. m.p. 152°), yield 52% (method A), 49% (method B), 54% (method C). Mixed melting point with the authentic sample remained undepressed and IR spectra superimposable.

6-Fluoro-2-phenylbenzothiazoles (4d)

m.p. 135° (Lit[11]. m.p. 134.5-135°), yield 54% (method A), 52% (method B), 58% (method C). Mixed melting point with the authentic sample remained undepressed and IR spectra superimposable.

Acknowledgements: The authors are grateful to the UGC, New Delhi for providing financial assistance to PS.

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(Received in USA 11 August, 1992)