

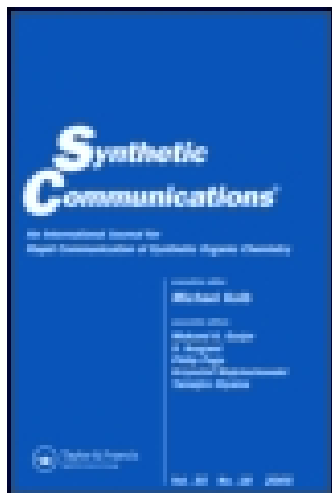
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### A New Synthesis and Application of N, N'-Dibromo-N, N' -1,2-Ethylene bis(2,5-Dimethyl Benzene Sulfonamide); As a Novel Selective Bromination Agent for Aromatic Compounds

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**A NEW SYNTHESIS AND APPLICATION OF N,  
N'-DIBROMO-N, N'-1,2-ETHYLENE BIS(2,5-DIMETHYL  
BENZENE SULFONAMIDE); AS A NOVEL SELECTIVE  
BROMINATION AGENT FOR AROMATIC COMPOUNDS.**

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**Abstract:** Reaction Between Novel Compound; N, N' dibromo-N, N'-1,2- ethylene bis(2,5- dimethyl benzene sulfonamide) and aromatic compounds in the carbontetrachloride produces bromo aromatic compounds. In the case of benzene rings that contain mono activated substituted, only para - bromo isomer was formed. At the presence of benzoyl peroxide in the reaction mixture  $\alpha$  - Hydrogen from alkyl side chain was substituted with bromine.

Alkyl halides and arylhalides have prominent role in formation of carbon - carbon bonds and in the interconversion of functional groups.

The introduction of the halogens on to aromatic rings by electrophilic substitution is an important synthetic procedure. Chlorine and bromine are reactive toward aromatic hydrocarbons, but Lewis acid catalysts are normally used to achieve desirable rate,<sup>1,2</sup>.

A wide variety of aromatic compounds can be brominated. Highly reactive ones, such as anilines and phenols, may undergo bromination at all activated positions.

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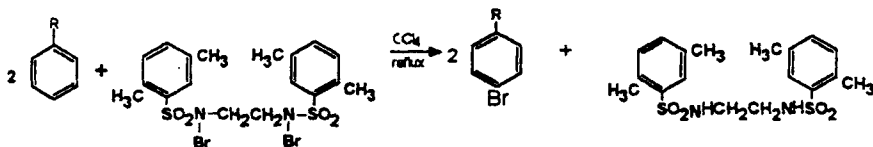
\* To whom correspondence should be addressed

The bromination of benzene and toluene is first order in both bromine and the aromatic substrate in trifluoroacetic acid solution<sup>3</sup>, but the rate law becomes more complicated in presence of water<sup>4</sup>. N-Bromo Succinimide (NBS) has been used extensively, especially for allylic and benzylic bromination<sup>5, 6, 7</sup>.

N-Bromo Succinimide in carbon tetrachloride reacts with cumene to give bromides.<sup>8</sup> When an ortho - para directing group is on a ring, it is usually difficult to predict how much of the product will be the ortho isomer and how much the para isomer. Indeed, these proportions may depend greatly on the reaction conditions<sup>9</sup>. Another important factor is the steric effect. If either the group on the ring or the attacking group is large, then steric hindrance inhibits formation of the ortho product and increase the amount of the para isomer<sup>10,11</sup>. A few groups are so large that they direct almost entirely para.

According to this idea, we synthesised a novel compound N, N' - dibromo -N, N' -1,2-ethylene bis (2,5 - dimethyl benzenesulfonamide), that is able to brominate aromatic rings containing ortho - para directing group almost entirely para. (scheme 1)

Scheme 1



This reagent is also able to brominate the benzylic position selectively. (scheme 2)

Scheme 2

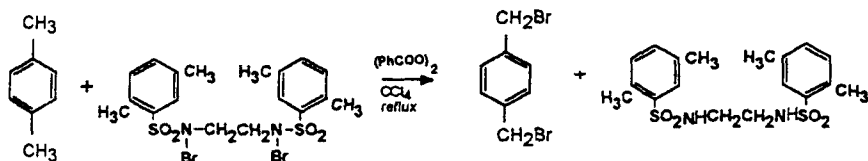


Table 1 shows the results of reactions of N, N' -dibromo -N, N' -1,2- ethylene bis(2,5-dimethylbenzene sulfonamide) with different aromatic compounds.

Table 1: The reactions of N, N' - dibromo -N, N' -1,2- ethylene bis(2,5- dimethylebenzene sulfonamide)with different aromatic compounds:

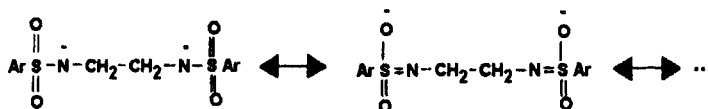
No.	substrates <sup>a</sup>	products	para (%)	total yield (%)	time/min	T/°c
1	Benzene	Bromobenzene	-	59.3	90	77
2	Anisole	Bromoanisole	100	80	20	77
3	Acetanilid	Bromoacetanilide	100	80	30	77
4	p-Xylene	Bromo p-xylene	-	80	30	77
5	Aniline	Bromoaniline	100	90.2	15	25
6	N, N-Dimethylaniline	Bromo-N,N-dimethyl aniline	100	91	15	25
7	Phenol	Bromophenol	100	90.5	15	25
8	para-N,N-Dimethyl-amino benzaldehyde	2- Bromo - para N, N - dimethylamino benzaldehyde	-	81.96	20	50
9	Toluene	Benzylbromide	-	61	90	77
10	p-Xylene	$\alpha,\alpha'$ -Dibromo p-xylene	-	62	90	77
11	o-Xylene	$\alpha,\alpha'$ -Dibromo o-xylene	-	61.5	90	77
12	m-Xylene	$\alpha,\alpha'$ -Dibromo m-xylene	-	60	90	77

<sup>a</sup> ccl<sub>4</sub> as a usable solvent.

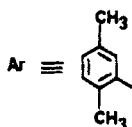
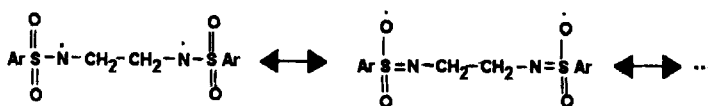
According to these results , reveals that N, N' - dibromo -N, N' -1,2- ethylene bis(2,5-dimethylbenzene sulfonamide) is an effecting bromination agent. In electrophilic aromatic substitution reactions, this reagent selectively brominate only para position, and in the presence of radical initiator benzylic position is brominated. One of the main factor of this reagent is releasing Br<sup>+</sup> and Br<sup>o</sup> very easily. The reason is resonance effect of anion and

free radical with  $\text{SO}_2$  group which make them very stable. Simple presentation of the stabilities of the sulfonamide anion and radical are shown in schemes 3 and 4.

Scheme 3



Scheme 4



Because of the bulky molecule, this reagent is selectively brominated only para position and also because of the steric effect, the ortho position is strictly prevented to be brominated but the para position is freed of this problem.

The advantages of the novel method of the bromination are as follows:

- 1) The novel bromination reagent is solid and the reaction's procedure is very simple (Does not need special safety).
- 2) The reagent is acting selectively. (para and benzylic positions)
- 3) Simplicity of the separation of reaction mixture.
- 4) Reaction time are very short (specially in electrophilic reactions with strong electron releasing groups).
- 5) Excellent yield.
- 6) If other functional groups present in aromatic ring of the substrates, does not react with this reagent (eg. aldehyde groups attached to the substrate ring does not oxidize with this reagent whereas  $\text{Br}_2$  molecule oxidize this group).

- 7) The starting material is recovered easily and can be reused many times without reducing the yield.

### EXPERIMENTAL

**General:** IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a 90 MHz Jeol FT-NMR Spectrometer, respectively. NMR chemical shifts were measured relative to TMS (int; 1H).

#### *Preparation of N, N' - 1,2 - ethylene bis (2,5 - dimethyl benzenesulfonamide)*

65g (0.3186 mol) of p-xylene sulfonyl chloride was placed in a beaker. The beaker was heated on a water bath (80°C) until it changed to a liquid. 10.62 ml (0.1593 mol) of ethylene diamine was added dropwise to the reactant and the mixture was stirred with a glass rod. The mixture was heated (80°C) and stirred for 30 minutes. The mixture was cooled and 100 ml water was added. The product was collected on a Buchner funnel, washed with a little cold water. The product was recrystallized from ethanol. The yield of pure N, N' - 1,2-ethylene bis (2,5 - dimethyl benzenesulfonamide), m.p. 143-144°C, was 56.5g (89.5%). IR spectrum (KBr pellets): 3300, 1310, 1140, 1370 - 1460 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>COCD<sub>3</sub>, TMS): δ 2.549 (s, 3H), 2.357 (s, 3H), 2.990 (s, 2H), 6.568 pm (br., 1H), 7.275 - 7.703 (m, 3H). Anal.: calc'd for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>O<sub>4</sub>: C, 54.53%, H, 6.11%, N, 7.07%, S, 16.14%. Found: C, 54.43%, H, 6.12%, N, 7.1%, S, 16.13%.

#### *Preparation of N, N' - dibromo - N, N' - 1,2 - ethylene bis (2,5 - dimethyl benzenesulfonamide)*

10g (0.02525 mol) N, N' - 1,2 - ethylene bis (2,5 - dimethyl benzenesulfonamide) was dissolved in a slight molar excess of chilled sodium hydroxide solution (of approximately 3M strength) in room temperature and transfer the solution to a beaker. 3ml (0.0584 mol) of bromine dissolved in 15ml carbon tetrachloride was added to the solution with vigorous stirring and immediately yellow precipitate was formed. The product (yellow precipitate) was collected on a Buchner funnel and it was washed with 30 ml distilled cold water and then dried in a vacuum desiccator at room temperature for 6 hours. The yield of pure N,N' - dibromo - N,N' - 1,2 - ethylene bis (2,5 - dimethylbenzene sulfonamide), m.p. 96-98°C, was

11.3g (81%). The product was stable at standard condition and was not sensitive to air. The reagent was identified by NMR, IR spectroscopies and elemental analysis. IR spectrum (KBr pellets): 1320, 1165, 1490, 3050, 2980  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR spectrum ( $\text{CD}_3\text{COCD}_3$ , TMS): $\delta$  2.553 (s, 3H), 2.347 (s, 3H), 2.998 (s, 2H), 7.258-7.695 (m, 3H). Anal.: calc'd for  $\text{C}_{18}\text{H}_{22}\text{N}_2\text{Br}_2\text{S}_2\text{O}_4$ : C, 39.13%, H, 4.02%, N, 5.07%, S, 11.59% Found C, 39.23%, H, 4.03%, N, 5.12%, S, 11.7%.

***Bromination of benzene and activated benzene rings with N, N'-dibromo-N, N'-1,2- ethylene bis(2,5 - dimethylbenzene sulfonamide)***

***preparation of para-bromo anisole:***

In a 250 ml round - bottomed flask 8g (0.0145 mol) of N, N' - dibromo - N, N' - 1,2 - ethylene bis (2,5 - dimethylbenzene sulfonamide) and 30 ml of carbon tetrachloride were placed. The flask was cooled in ice- water and added, with stirring, 3.17 ml (0.029 mol) of anisole dropwise. The mixture was refluxed for 20 minutes. Then the flask was cooled, by this time all the solid should have risen to the surface of the liquid. The primary sulfonamide; [N, N' - 1,2 ethylene bis (2,5 - dimethylbenzene sulfonamide)] was filtered under suction. The carbon tetrachloride was removed on a water bath, and the para - bromo anisole was collected as a single product. The yield of product, b.p.214°C , was 80%

***preparation of para - bromo phenol :***

In a 250 ml round - bottomed flask ,8g(0.0145 mol) of N, N' - dibromo - N, N' - ethylene bis (2,5 - dimethylbenzene sulfonamide) and 30 ml of carbon tetrachloride were placed. The flask was cooled in ice - water and added, with stirring, 2.73 g(0.029 mol) of phenol dissolving in 60 ml carbon tetrachloride dropwise. The mixture was stirred for 15 minutes at room temperature. Then the flask was cooled, by this time all the solid should have risen to the surface of the liquid. The primary sulfonamide was filtered under suction. The carbon tetrachloride was removed on a water bath and the para - bromo phenol was collected as a single product. The yield of product, m.p. 63°C , was 4.54g (90.5%) By this method, benzene, acetanilide, p - xylene, aniline, N, N - dimethyl aniline and para -N, N-



dimethyl amino benzaldehyde were brominated and in the cases of acetanilide, aniline and N, N - dimehyl aniline , only para - bromo isomer were produced.

*preparation of  $\alpha$  ,  $\alpha'$  - dibromo - p - xylene:*

In a 250ml round - bottomed flask , 8 g(0.0145 mol) of N, N' - dibromo -N, N' -1,2-ethylene bis (2,5 - dimethylbenzene sulfonamide), 50ml of carbon tetrachloride and 500 mg benzoyl peroxide , previously dried by pressing between filter - papers were placed. 1.8 ml (0.0145 mol) p-xylene was added, with stirring, dropwise. The reaction mixture was refluxed for 1 hour. The flask was cooled, by this time all the solid should have risen to the surface of the liquid. The primary sulfonamide was filtered under suction. The carbon tetrachloride was removed on a water bath and the  $\alpha$ ,  $\alpha'$  - dibromo - p-xylene was collected as a product. The yield of product , m.p.141°C , was 2.37 g (62%). By this method , toluene , o-xylene and m-xylene were brominated and benzyl bromide,  $\alpha,\alpha'$  - dibromo o-xylene and  $\alpha$ ,  $\alpha'$  - dibromo - m - xylene were produced , respectively.

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