

## Unusual Products from the Reaction of Substituted Benzenesulfonyl Azides with *N*-Methylindole

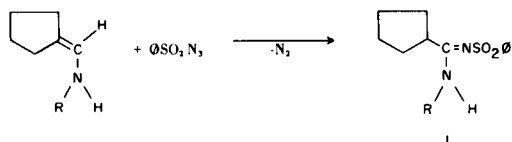
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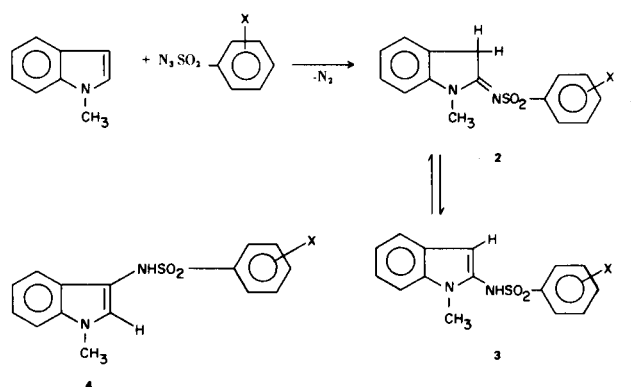
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Sir:

In this communication we wish to report the isolation and characterization of some unusual products obtained from the reaction of several substituted benzenesulfonyl azides with *N*-methylindole (1). On the basis of nmr spectroscopy, one series of products was found to exist in an amino-imino type of tautomeric equilibrium (in DMSO- $d_6$ ). Prior to this work, Fusco *et al.* (2) had reported that benzenesulfonyl azides add to open chain enamines in such a fashion that the enamine nitrogen and azide nitrogen are bonded to the same carbon atom as shown in the product (1). The addition of *p*-toluenesulfonyl azide to indole afforded similar results (3).



The reaction of several substituted benzenesulfonyl azides with *N*-methylindole was conducted by heating a solution of *N*-methylindole (0.01 mole) and the sulfonyl azide (0.015 mole) in *p*-dioxane (5 ml.) at 75-80° for 18-24 hours. Cooling and diluting the reaction mixture with ethanol (*ca.* 25 ml.) caused most of the 2-substituted product (2) to crystallize. Filtration and column chromatography of the filtrate over silica gel afforded the corresponding 3-substituted isomer (4). The position of the sulfonamido group in *N*-(1-methyl-2-indolinyldene)benzenesulfonamide (2) was established as shown by its acid hydrolysis to 1-methyloxindole and the corresponding benzenesulfonamide. In crystalline form, it existed mainly in the imino form (2). This observation was based on the ir spectrum (nujol) of 2 which showed the characteristic C=N absorption around 1600  $cm^{-1}$  and no absorption in the NH region. Its nmr spectrum using DMSO- $d_6$  (Varian A-60) as solvent indicated the existence of a tautomeric equilibrium between the imino (2) and amino (3) tautomers.



In the nmr spectrum, the *N*-methyl protons as well as the proton(s) at the 3 position of the indole ring of structures 2 and 3 showed significant differences in their chemical shifts. For instance, in 2 the *N*-CH<sub>3</sub> signal appeared at 3.4  $\delta$  and the two benzylic protons at the 3 position showed as a singlet near 4.2  $\delta$ . On the other hand, the *N*-CH<sub>3</sub> singlet of 3 appeared near 3.7  $\delta$  and the proton in the 3 position resonated as a singlet near 6.0  $\delta$ . These nmr assignments are consistent with those reported by Bailey *et al.* (4) for similar tautomers. The relative ratios of the peaks at 4.2  $\delta$  (structure 2) and 3.7  $\delta$  (structure 3) were used to calculate the equilibrium ratios of these two tautomers in solution.

The other major product isolated from the reaction of benzenesulfonyl azides with methylindole was found to be the abnormal *N*-(1-methylindol-3-yl)benzenesulfonamide (4). This isomer was shown by ir and nmr spectroscopy to exist entirely in the amino form 4 in crystalline form as well as in solution (DMSO- $d_6$  and deuteriochloroform). The ir spectrum (nujol) showed strong NH absorption around 3200  $cm^{-1}$  and no C=N absorption near 1600  $cm^{-1}$ . The nmr spectrum (DMSO- $d_6$ ) showed an exchangeable (deuterium oxide) one proton singlet at 10  $\delta$  and only one *N*-methyl singlet 3.7  $\delta$ . The proton at the 2 position of the indole ring appears in the aromatic region.

In order to substantiate the structure assigned to compound 4, two model compounds, 5 and 6, were prepared

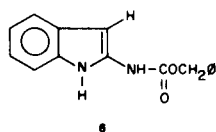
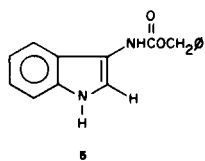
TABLE I

Isolated Yields of Compounds **2** and **4**. Relative Equilibrium Ratios of Tautomers **2** and **3** as Determined by Nmr Spectroscopy using DMSO-d<sub>6</sub> and DMSO-d<sub>6</sub>-Deuteriochloroform (15%) as Solvents

Substituent(s) X	Yield (%)		Relative Equilibrium Ratios of Tautomers <b>2</b> and <b>3</b>			
	<b>2</b>	<b>4</b>	in DMSO-d <sub>6</sub>		in DMSO-d <sub>6</sub> -d <sub>6</sub> -CDCl <sub>3</sub> (15%)	
			<b>2</b>	<b>3</b>	<b>2</b>	<b>3</b>
4-OCH <sub>3</sub>	47	24	80	20	86	14
4-CH <sub>3</sub>	44	22	81	19	87	13
4-NHCOCH <sub>3</sub>	67	5	81	19	87	13
-----	54	22	84	16	88	12
2,4,6-trimethyl	34	15	87	13	91	9
4-Cl	60	16	88	12	90	10
4-Br	49	12	89	11	90	10
3-NO <sub>2</sub> -4-Cl	82	8	90	10	94	6
3,4-dichloro	63	14	90	10	93	7
2,4,6-tri-isopropyl	32	24	91	9	94	6
4-NO <sub>2</sub>	72	21	91	9	94	6
3-NO <sub>2</sub>	74	6	92	8	93	7
2-NO <sub>2</sub>	75	14	95	5	97	3

All compounds **2** and **4** were isolated as crystalline compounds, which furnished satisfactory C,H and N analyses.

by Curtius rearrangement of the corresponding carbonyl azides in the presence of benzyl alcohol (5). The physical constants of compound **5** were in agreement with the literature values (5). Compound **6** was prepared analogously and characterized by satisfactory elemental analyses and spectral (ir and nmr) data. The nmr spectra (DMSO-d<sub>6</sub>) of compounds **5** and **6** contained two exchangeable (deuterium oxide) protons (NH) around 10.5  $\delta$ , which established that these compounds existed entirely in the amino form as shown.



In the nmr spectrum of compound **6**, the proton in the 3 position of the indole ring resonated as a doublet at 6.1  $\delta$  which was consistent with the nmr spectrum of compound **3**. The proton at the 2 position of the indole ring of compound **5** appeared in the aromatic region as

was observed for compound **4**. These results substantiate the position of the sulfonamido group in compound **4**.

The isolated yields of compounds **2** and **4**, as shown in the Table, indicated two trends. Electron withdrawing groups on the benzenesulfonyl azide gave higher total yields but lower percentages of the abnormal products (**4**).

Acknowledgement.

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