

A New Diazo Transfer Reaction

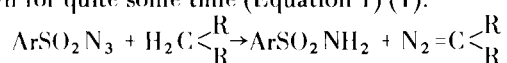
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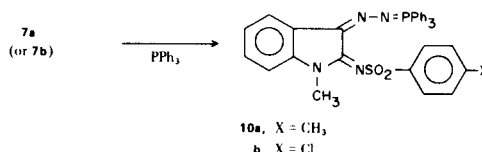
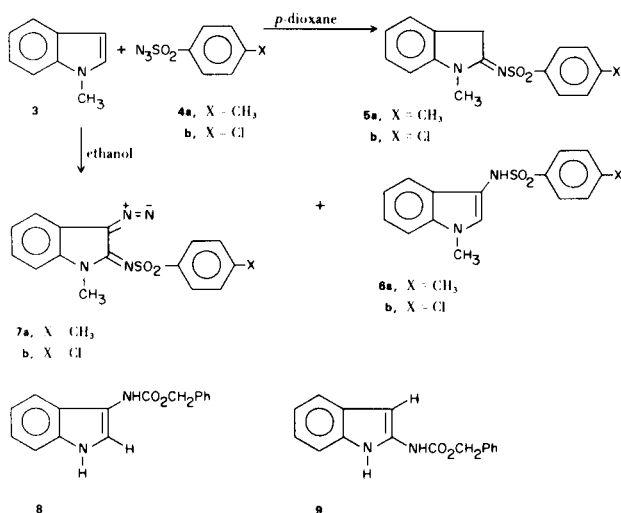
Sir:

The transfer of the diazo group from arylsulfonyl azides (**1**) to an active methylene compound (**2**) has been known for quite some time (Equation 1) (1).



Nearly all of the reported examples have involved the transfer of a diazo group to the α -carbon of carbonyl compounds (1). In addition, the transfer of diazo group from sulfonyl azides generally requires the presence of a base catalyst (1).

In this communication we wish to report the first example of a diazo transfer reaction to an amidine. The course of the reaction of arylsulfonyl azides with 1-methylindole (**3**) using *p*-dioxane was different than that using ethanol as solvent. For instance, the additions of sulfonyl azides **4a-b** to compound **3** in *p*-dioxane at 75° for 18-24 hours yielded the 2-substituted compounds **5a-b** as the major products and the 3-substituted compound **6a-b** as the minor products. The location of the sulfonamido group at the 2-position on the indole ring in compounds **5a-b** was established by their acid hydrolysis to 1-methyloxindole and the corresponding arylsulfonylamides. The structural assignments of compounds **6a-b**



were based on nmr spectral analogies with two model compounds **8** and **9**, prepared by Curtius rearrangement of the corresponding indole 2- or 3-carbonylazides in benzyl alcohol (2). The formation of compounds similar to **5a-b** was also reported by Bailey *et al.* (3) from the reaction of *p*-toluenesulfonyl azide with indole and 1,3-dimethylindole.

The reaction of sulfonyl azides **4a-b** with **3** using ethanol as the solvent gave the corresponding *N*-(3-diazo-1-methyl-2-indolylidene)benzenesulfonamides (**7a-b**). The reactions were followed by thin layer chromatography, which showed the formation of small amounts of the amidines **5a** and **5b** as intermediates which led to the diazo compounds **7a-b** as final products. This observation was further substantiated by the conversion of compound **5a** to **7a** in the presence of ethanol and the sulfonyl azide **4a**. The diazo compounds **7a-b** were light sensitive and difficult to isolate in pure form. However, treatment of these compounds with triphenylphosphine (4) afforded crystalline triphenylphosphine derivatives **10a-b** which were stable and gave satisfactory elemental (C, H and N) analyses. To the best of our knowledge this is the first example of a diazo transfer reaction to an amidine such as **5a-b**. In addition compounds **7a-b** were formed without the aid of any added catalyst unlike the normal diazo transfer reactions which are base catalyzed. According to Regitz (1) the rate of the triethylamine catalyzed diazo transfer reaction decreases with decreasing polarity of the solvent. Perhaps the same reasoning can be used to explain the reason why the diazo compounds **7** are formed in ethanol and not in *p*-dioxane because ethanol is more polar than *p*-dioxane. When an ethanol solution of the 2-sulfonamido derivative **5b** was heated with a differently substituted sulfonyl azide **4a**, the same diazo compound **7b** was obtained.

Acknowledgment.

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