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QUATERNARY AZO COMPOUNDS

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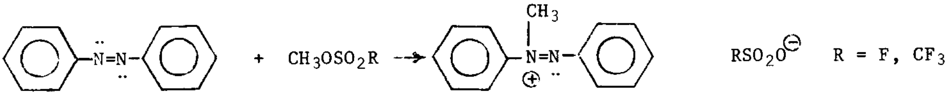
Trifluoromethanesulphonic acid and fluorosulphonic acid are two of the strongest known monobasic acids[1]. The strongly electron-attracting CF_3SO_2- and FSO_2- groups facilitate alkyl-oxygen fission and the alkyl esters of both acids are, as would be expected, very powerful alkylating agents. Several papers have been published describing their use in the alkylation of amines, amides, nitriles, ethers and alcohols [2,3,4]. Ethyl trifluoromethanesulphonate has been found to alkylate benzene at room temperature[4].

This paper reports the facile quaternisation of aromatic azo compounds by methyl trifluoromethanesulphonate and by methylfluorosulphonate to give the previously unknown N-methyl-1,2-diphenyldiazenium salts in yields of 60-90%.



A number of these salts were prepared from azobenzene and its alkyl, alkoxy and halo derivatives (Table 1).

The effect of ring substituents on the reactivity of the poorly nucleophilic azo nitrogen atoms was quite marked. Generally, the quaternisation of unsymmetrically substituted azobenzenes containing relatively neutral or electron-donating substituents gave a mixture of both quaternary structural isomers while electron-withdrawing groups in the ring completely deactivated the adjacent nitrogen atom to quaternisation. Thus 4,4'-dichloroazobenzene and 4,4'-dinitroazobenzene did not react with methyl fluorosulphonate while 4-chloroazobenzene gave only one isomer.

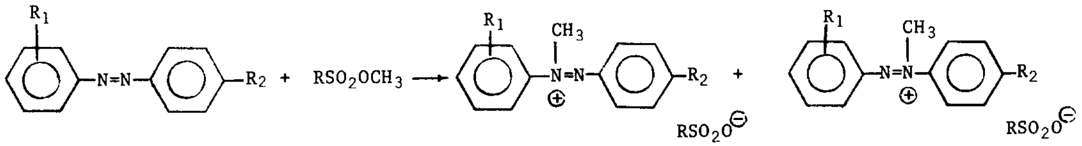
In the general procedure for the quaternisation, 2g of the azo compound was refluxed for 5 minutes in 15 ml of the ester then allowed to cool to room temperature, filtered, and the solid product washed with 20 ml of dry ether. The quaternary azo salts, though sensitive to atmospheric moisture, could be stored indefinitely in a desiccator over phosphorus pentoxide.

The structure of the products was determined by elemental analysis and N.M.R. spectroscopy.

Difficulty was experienced in finding a suitable solvent for spectroscopic analysis since those solvents sufficiently polar to dissolve the quaternary azo salts also reacted with them. Solutions in deuterochloroform or deuteroacetonitrile were satisfactory if used immediately.

Table 1

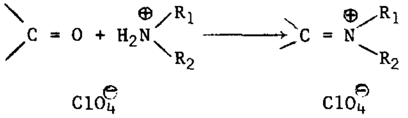
N.M.R. DATA: as δ from TMS

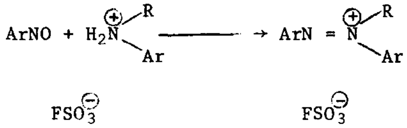


1.	$R_1 = R_2 = H$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.68s (3H)[a]	
2.	$R_1 = R_2 = H$	$R = CF_3$	$\overset{\oplus}{N}\text{-CH}_3$: 4.68s (3H)	
3.	$R_1 = H$; $R_2 = CH_3$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.68s (3H) R_2 : 2.50s (3H)	$\overset{\oplus}{N}\text{-CH}_3$: 4.68s (3H) R_2 : 2.57s (3H)
4.	$R_1 = H$; $R_2 = Cl$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.62s (3H)	
5	$R_1 = H$: $R_2 = OCH_3$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.55s (3H) R_2 : 3.97s (3H)	$\overset{\oplus}{N}\text{-CH}_3$: 4.60s (3H) R_2 : 4.09s (3H)
6.	$R_1 = 2\text{-CH}_3$; $R_2 = H$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.66s (3H) R_1 : 2.70s (3H)	$\overset{\oplus}{N}\text{-CH}_3$: 4.66s (3H) R_2 : 2.63s (3H)
7.	$R_1 = 4\text{-CH}_3$, $R_2 = CH_3$	$R = CF_3$	$\overset{\oplus}{N}\text{-CH}_3$: 4.72s (3H) R_1 : 2.50s (3H) R_2 : 2.42s (3H)	
8.	$R_1 = 4\text{-CH}_3$, $R_2 = CH_3$	$R = F$	$\overset{\oplus}{N}\text{-CH}_3$: 4.75s (3H) R_1 : 2.51s (3H) R_2 : 2.43s (3H)	

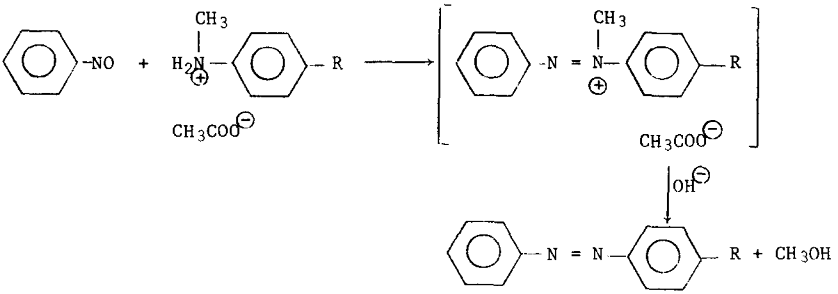
a. Proton integration values were found by comparison with the total integration of the aromatic protons.

In an attempt to prepare the quaternary azo salts by an alternate route, the reaction of nitrosobenzene with both N-methylaniline fluorosulphonate and N-methylaniline trifluoromethanesulphonate was studied. This reaction would be analogous to the preparation of ternary iminium salts by the reaction of ketones with the acid salts of secondary amines[5].





When N-methylaniline trifluoromethanesulphonate and nitrosobenzene were warmed together in the absence of solvent, a highly exothermic reaction took place resulting in the formation of tarry products. The problem of finding a mutual solvent inert to the product was again encountered and no quaternary azo compounds have yet been isolated from this reaction. When N-methylaniline was reacted with nitrosobenzene in acetic acid an exothermic reaction took place from which a good yield of azobenzene was obtained by pouring into water and extracting with chloroform. The dealkylation of N-methylaniline could be explained by the intermediacy of a quaternary azo compound :-



Bamberger[6] has reported the reduction of aryl nitroso compounds to azo compounds by secondary amines. However, the reaction of N-benzyl-p-toluidine and nitrosobenzene in acetic acid gave 4-methylazobenzene as the major product, supporting the proposed quaternary pathway.

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