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Substituent Effects in the Reaction of Arenediazonium Salts with Methylamine

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Summary The formation of isolable 1-aryl-3-methyltriazenes in the coupling reaction of arenediazonium salts with methylamine is favoured by the presence of electron-withdrawing substituents in the aryl group.

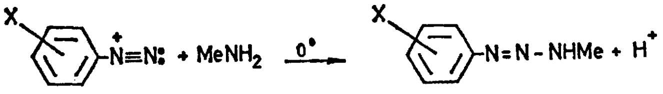
TRIAZENE synthesis by diazo-coupling to nitrogen is often cited in organic chemistry text-books[1] as being generally applicable to primary and secondary, aliphatic or aromatic, amines. However, reviews of diazo-chemistry[2] suggest that coupling with a primary aliphatic amine [reaction (1)] leads to formation of a penta-azadiene (**2**) and that the

$$\mathrm{ArN_2^+ + RNH_2 \rightarrow ArN{=}N{-}NHR} \xrightarrow[\textbf{(1)}]{\mathrm{ArN_2^+}} \underset{\textbf{(2)}}{\mathrm{ArN{=}N{-}NR{-}N{=}NAr}} \qquad (1)$$

intermediate triazene (**1**) cannot usually be isolated. We report here that 1-aryl-3-alkyltriazenes (**1**) are formed readily and in good yield by direct N-coupling, only when the aryl group is substituted with a strongly electron-withdrawing group.

Addition of excess of aqueous methylamine to cold solutions of the diazonium salts (**3**, **a**—**g**), followed by immediate isolation of the resulting precipitates, afforded the 1-aryl-3-methyltriazenes (**4**, **a**—**g**)† in yields of 60—85%; the products were characterised by their i.r., n.m.r. and mass spectra. Although the yield of triazene is greatly reduced when methylamine is not in excess, no penta-azadiene formation was evident in any of these reactions. The *meta*- and *para*-substituted triazenes (**4**, **b**—**e**, **g**), although susceptible to decomposition in protic solvents, are stable yellow crystalline solids, whereas the *ortho*-isomers (**4**, **a** and **f**) decompose in the solid state or in solution. The *ortho*-alkoxycarbonyl compounds, *e.g.* (**4f**) cyclise when set aside, affording benzotriazinones.[3]

The behaviour of the diazonium salts (**3**, **a**—**g**) contrasts with the previously reported[4] reactions of diazonium salts containing electron-donating substituents (*e.g.* OMe), which yield only the penta-azadiene under similar conditions, and with the formation of mixtures of triazene and penta-azadiene in the reactions of *p*-toluene- and *p*-bromobenzene-diazonium chlorides with methylamine.[5] Thus there is a distinct difference between the influence of electron-withdrawing and -donating substituents on the outcome of the coupling reaction (1), which is not readily explainable in terms of the reactivity of the diazonium ion.



(3) **(4)**

a; X = *o*-NO_2
b; X = *m*-NO_2
c; X = *p*-NO_2
d; X = *p*-CN
e; X = *p*-COMe
f; X = *o*-CO_2Et
g; X = *p*-CO_2Me

The electrophilic character of the diazonium ion is increased by the presence of electron-withdrawing substituents in the aryl group,[6] and the initial coupling reaction

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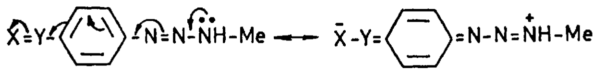
† M.p.s as follows: (**a**) 43—44° (decomposed when recrystallised); (**b**) 95—96° (from light petroleum); (**c**) 111—113° (benzene); (**d**) 135·5—136° (benzene–light petroleum); (**e**) 90—92° (benzene-light petroleum); (**f**) 35—36° (aq. EtOH);[3] (**g**) 94—96° (benzene).[8]

with the amine should be favoured. However, the second coupling reaction between triazene and diazonium ion will also be enhanced by an increase in diazonium ion reactivity; clearly the effect of the substituent on the nucleophilic reactivity of the triazene must be the predominant factor in preventing penta-azadiene formation. Delocalisation of electron density at the alkyl-bearing nitrogen due to resonance (2) will reduce the nucleophilicity of the triazene unit, thus rendering it less reactive in the coupling reaction; electron withdrawal by inductive effect may be a significant contribution only in the case of the *meta*-NO$_2$ substituent. Conversely, an electron-donating substituent should favour penta-azadiene formation, in accordance with previous observations.[4]



(2)

Our findings correlate with the recently reported results of Matrka *et al.*,[7] concerning the kinetics of protolysis of 3-methyl-1-phenyltriazene and some of its *para*-substituted derivatives in acid aqueous medium.

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