An Unusual Ready Coupling of Diazonium Salts with Cations[1]

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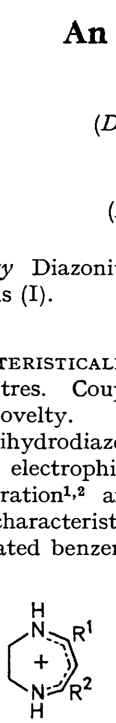
Summary Diazonium salts couple with dihydrodiazepinium cations (I).

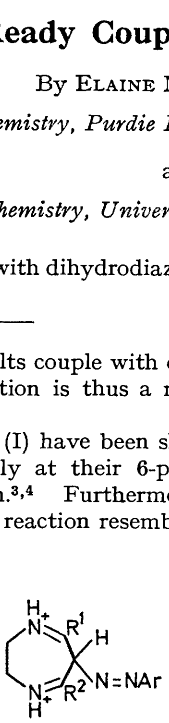
CHARACTERISTICALLY diazonium salts couple with electron-rich centres. Coupling with a cation is thus a rarity, if not a novelty.

The dihydrodiazepinium cations (I) have been shown to undergo electrophilic attack readily at their 6-positions, *e.g.*, nitration[1,2] and halogenation.[3,4] Furthermore, the kinetic characteristics of the latter reaction resemble those of activated benzene derivatives.


(I)

$Ac_2C{:}N{\cdot}NHAr$

(II)


(III)

Benzenediazonium salts react at once with these dihydrodiazepinium cations; an intense colour is formed on admixture. The presence of the arylazo-group, however, increases the susceptibility of the dihydrodiazepinium ring to hydrolysis and the products isolated are α-arylazo-derivatives of β-diketones. Thus, treatment of benzene-, *p*-bromobenzene-, and *p*-nitrobenzene-diazonium salts with 2,3-dihydro-5,7-dimethyl-1,4-diazepinium salts produced the corresponding 3-arylazo-acetylacetones (II), whose structure follows from their analyses, spectra, and comparison with the products obtained by reaction of the diazonium salts with acetylacetone.[5] In a typical reaction *p*-nitroaniline (0·70 g, 0·0051 mol), when diazotised and allowed to react in *ca.* 100 ml cooled aqueous hydrochloric acid solution at pH 1·5 with the diazepine (0·70 g base or 0·90 g hydrochloride, 0·0056 mol), gave *p*-nitrophenylazoacetylacetone (0·051 g, 64%, collected after 48 h).

That coupling involves the dihydrodiazepinium salt and is followed by hydrolysis, rather than the reverse, is clear, since control experiments showed that under the conditions used for coupling with (I; $R^1 = R^2 = Me$) no hydrolysis ensues, whilst under the conditions which have been used for the coupling of diazonium salts with acetylacetone[5] (cooled aqueous sodium acetate buffer, pH *ca.* 5) an unidentifiable dark red resinous material was formed and no normal coupling products were obtained from the dihydrodiazepinium salts.

There remains the possibility that coupling might involve the dihydrodiazepine base rather than its monocation. Since reaction always took place in the presence of an excess of mineral acid from the initial diazotisation of the arylamine (pH *ca.* 0), and because dihydrodiazepines are exceedingly strong bases (pK_a 13–14),[6] it is unlikely that the base form makes any large contribution to the rapid reaction.

Reaction presumably follows the initial course postulated for other electrophilic substitution reactions of (I), leading to a dication intermediate (III). This, or the substitution product formed by proton loss from the reaction centre in (III), will be highly susceptible to hydrolytic attack at the 5- and 7-positions because of the three adjacent strongly electron-withdrawing groups, though hydrolysis might be preceded by tautomerisation to the 6-oxodihydrodiazepine phenylhydrazone.

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[1] For previous part in the series see A. M. Gorringe, D. Lloyd, and D. R. Marshall, *J. Chem. Soc.* (*C*), 1970, 617.

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