The Mechanism of Formazan Formation

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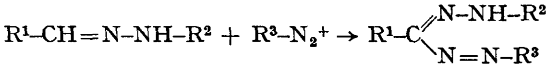
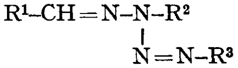
THE reaction of diazonium compounds with arylidenearylhydrazines (I) leads to the formazans (II). By carrying out the reaction under carefully controlled conditions at pH 6—8, Busch and Schmidt[1] and later Hauptmann and Perisse[2] isolated a light yellow intermediate formulated as the tetrazene (IIIa). This intermediate was shown to isomerise to the deep red formazan even in the solid state and very rapidly in basic solution. However the intermediate has not been shown unambiguously to be the tetrazene (IIIa) and we present evidence to show that this structure is, in fact, incorrect.



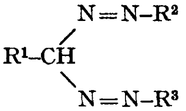
$$R^1\text{–}CH{=}N\text{–}NH\text{–}R^2 + R^3\text{–}N_2^+ \rightarrow R^1\text{–}C\begin{cases}N\text{–}NH\text{–}R^2\\ N{=}N\text{–}R^3\end{cases}$$

(I) (II)



$$R^1\text{–}CH{=}N\text{–}\underset{\displaystyle N{=}N\text{–}R^3}{\underset{|}{N}}\text{–}R^2$$

(IIIa)



$$R^1\text{–}CH\begin{cases}N{=}N\text{–}R^2\\ N{=}N\text{–}R^3\end{cases}$$

(IIIb)

An attempt to synthesise 1-benzylidene-2,4-diphenyltetrazene (IIIa; $R^1 = R^2 = R^3 = Ph$) by the reaction of 1,3-diphenyltetrazene and benzaldehyde failed,[3] the only product isolated being a small amount of 1,3,5-triphenylformazan (II; $R^1 = R^2 = R^3 = Ph$). The 1,3-diphenyltetrazene [$PhN(N{=}NPh)\text{–}NH_2$] used was prepared by coupling benzenediazonium chloride and phenylhydrazine at the imino-nitrogen.[4] Some tetrazenes of the type (IIIa) *e.g.*, 1-benzylidene-4-(*p*-nitrophenyl)-2-benzyltetrazene (IIIa; $R^1 = Ph$, $R^2 = p\text{-}NO_2C_6H_4$, $R^3 = C_6H_5CH_2$)[3] and 1-benzylidene-2-phenyl-4-(1'*H*-5'-tetrazolyl)tetrazene (IIIa; $R^1 = R^2 = Ph$, $R^3 =$ 1'*H*-5'-tetrazole)[5] have been prepared unambiguously by a comparable reaction sequence. These do not rearrange in basic solution to give the formazans.

The formulation (IIIa) is also inconsistent with the observed[2] acid cleavage reactions. When the intermediate is treated with ethanolic hydrochloric acid, a hydrazone and a diazonium salt are obtained which may differ from those used originally to form the intermediate. Thus if $R^2\text{–}N_2^+$ is less electrophilic than $R^3\text{–}N_2^+$ then $R^2\text{–}N_2^+$ and $R^1\text{–}CH{=}N\text{–}NH\text{–}R^3$ are obtained on cleavage of the intermediate from $R^3\text{–}N_2^+$ and (I). This exchange reaction is difficult to visualise in terms of the tetrazene formulation (IIIa) for the intermediate, but if the intermediate is in fact the more symmetrical bisarylazo-compound (IIIb) then it should be easily cleaved to give diazonium salts containing either R^2 or R^3.

That the so-called tetrazene intermediate is, in fact, the bisarylazo-compound (IIIb) (rather than IIIa), was confirmed by n.m.r. spectroscopy. We have found that the signal for the methine proton in compounds of type (I) of *ca.* τ 2·3 (an assignment confirmed by deuteration) is relatively insensitive to substituents in either ring, and only a small shift (0·2 p.p.m.) to higher fields results on the insertion of a methyl group on the imino-nitrogen. The τ-value expected for this proton in the tetrazene should therefore be close to 2·3 p.p.m. The absorption for the intermediate (III; $R^1 = R^2 = R^3 = Ph$), prepared by the reaction of benzenediazonium acetate and benzylidenephenylhydrazine in alcohol[2] is at τ 3·75 (in acetone solution with tetramethylsilane as internal reference), consistent with the α-benzyl proton of (IIIb).[6] After approximately 10 min. at room temperature this signal had disappeared and the resultant spectrum is close to that of 1,3,5-triphenylformazan. The ultraviolet data are also consistent with structure (IIIb), showing the two bands characteristic of simple phenylazoalkanes with maxima at 282 mμ (ϵ_{max} = 20,100) assigned to a $\pi \rightarrow \pi^*$ transition and 410 mμ (ϵ_{max} = 400) ($n \rightarrow \pi^*$), the molar extinction coefficients being approximately double those expected[7] for the presence of a single azo-bond. Moreover the same intermediate (n.m.r., u.v., and m.p.) is obtained by the reaction of benzylidenephenylhydrazine (I; $R^1 = R^2 = Ph$) and *p*-tolyldiazonium ion as from benzylidene-*p*-tolylhydrazine (I; $R^1 = Ph$, $R^2 = p\text{-}MeC_6H_4$) and benzenediazonium ion. This identity of intermediates prepared in these two ways is again evidence that the structure (IIIb) is correct. The rearrangement of the intermediate to the formazan thus, rather than involving an intramolecular[2,8] transfer of the diazo-function from nitrogen to carbon, is merely an azo–hydrazone conversion.

We have measured the rates of reaction between benzenediazonium chloride and arylidenearylhydrazines variously substituted in both rings in 40 : 60 v/v t-butyl alcohol : water at pH 7 by following the disappearance of the diazonium ion polarographically at a dropping-mercury electrode. Substituents in the hydrazine ring have a larger effect ($\rho = -1{\cdot}3$) than those in the aldehyde ring ($\rho = -0{\cdot}38$). This is similar to the effect observed[9] in the bromination with methine attack of hydrazones which leads to hydrazidic bromides. Even though the reagent and the solvent conditions are quite different for both reactions, the ratio of the substituent responses for both rings, as measured by the ρ-values, which reflects the relative distribution of the charges developed in the transition states of the reactions are quite similar (3·4 for diazonium ion attack, 3·5 for bromination) suggesting that the site of reaction, namely the methine carbon, is the same in both reactions. Thus diazonium ion attack rather than proving an exception[10] to the general pattern observed in the halogenation, oxidation,[7] or reaction with ethyl azodicarboxylate[6,11] of hydrazones is consistent with the other data.

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