Preparation and Thermolysis of a *cis*-Tetrazene

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Summary Lead tetra-acetate oxidation of *N*-aminophthalimide gives *trans*-1,4-diphthalyltetrazene, but in the presence of diphenyl sulphide the *cis*-tetrazene (II) is obtained, which on heating rearranges with nitrogen loss to give firstly the isocyanate (VIII) and then the benzoxazone (V).

THE oxidation of 1,1-disubstituted hydrazines provides a simple route to 2-tetrazenes.[1] Heterogeneous oxidation (mercuric oxide) has provided the only *cis*-tetrazene.[2] The products obtained by lead tetra-acetate oxidation of (I) are sensitive to changes in the reaction conditions.[3] We find that oxidation as described by Rees and his collaborators[4] gives *trans*-1,4-diphthalyltetrazene (70%). However in the presence of benzo[*b*]thiophen the corresponding *cis*-tetrazene (II), m.p. 160° (d.) was obtained (49%). Oxidation in the presence of diphenyl sulphide gave (II) in $>70\%$ yield.

The *cis*-*trans*-relationship of the two tetrazenes was established by partial conversion of the *cis*- into the *trans*-compound in boiling benzene, and is supported by the similar i.r. spectra (Nujol) of the two compounds which differ mainly in the carbonyl region where the *trans*-compound shows two bands (1743 and 1786 cm.$^{-1}$) and the *cis* four (1728, 1753, 1780, and 1806 cm.$^{-1}$).

While the role of diphenyl sulphide in this oxidation is being investigated, a simple explanation involves reaction of phthalimidonitrene with diphenyl sulphide to give the less-hindered sulphidimine (III)[5] which with a second molecule of the nitrene gives (IV) having the stereochemistry indicated. Loss of diphenyl sulphide then affords the *cis*-tetrazene (II). The second step of this sequence resembles the reaction of carbenes with sulphoxides,[6] and differs from the reaction of nitrenes with sulphoxides which yields sulphoximines.[5]

The explosive nitrogen loss observed on heating (II) to 160° prompted an investigation of its thermolysis. Heating (II) in boiling benzene (18 hr.) gave in addition to *trans*-tetrazene the benzoxazone (V), m.p. 196—198°, ν_{max} (Nujol) 1640, 1734, 1768, and 1785 cm^{-1}. The constitution of this compound is supported by hydrolysis (HCl–HOAc) to a mixture of the carboxylic acid (VI) and the dicarboxylic acid (VII). Reaction of (VI) with aqueous pyridine gives isatoic anhydride and phthalimide, whilst with diazomethane (VII) gives the known dimethyl ester.[7]

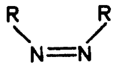
Information on the mechanism of the conversion (II) → (V) was provided by detection and isolation of the intermediate isocyanate (VIII). The solution obtained by heating (II) in boiling benzene (4·5 hr.) showed a strong i.r. band at 2300 cm^{-1}, and when (II) was decomposed by portionwise addition of the solid to a vessel maintained at 165° the isocyanate was the only isolable product. It was characterised as the urethan, m.p. 142—144° formed with ethanol, and on reaction with water gave isatoic anhydride and phthalimide.

The rearrangement (II) → (VIII) is depicted for brevity as a concerted process (IX) in which one phthalimido-group functions as an internal nucleophile. An analogous sequence involving a nitrene intermediate is also possible. The *trans*-tetrazene is unchanged on heating in boiling benzene and on decomposition at 260° gives only a trace of the isocyanate. Supplied with an external nucleophile (sodium ethoxide) the *trans*-compound undergoes a related Hofmann-type rearrangement giving phthalimide, and ethyl *o*-ethoxycarbonylphenylcarbamate. The conversion of (VIII) into (V) involves a 1,5-shift of the phthalimido-group to give (X) or a related biradical intermediate which then collapses to product (X; arrows).

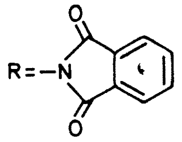
The conversion of (II) into (VIII) is related to a Wittig rearrangement and accompanying nitrogen loss described by Iffland.[8] These observations suggest that the chemistry of *cis*-tetrazenes merits further attention. Lead tetra-acetate oxidation in the presence of diphenyl sulphide may complement mercuric oxide in preparation of the *cis*-tetrazenes; mercuric oxide oxidation of (I) does not give the *cis*-tetrazene.

$R{-}NH_2$

(I)



(II)



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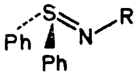
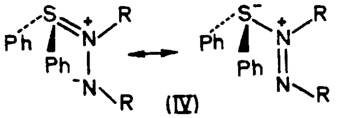
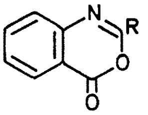


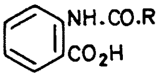
(III)



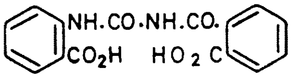
(IV)



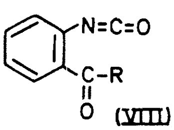
(V)



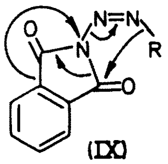
(VI)



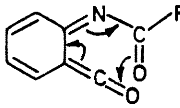
(VII)



(VIII)



(IX)



(X)

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