A New Nitro Group Interaction: Conversion of *o*-Nitrophenylcarbodi-imides into Benzotriazoles

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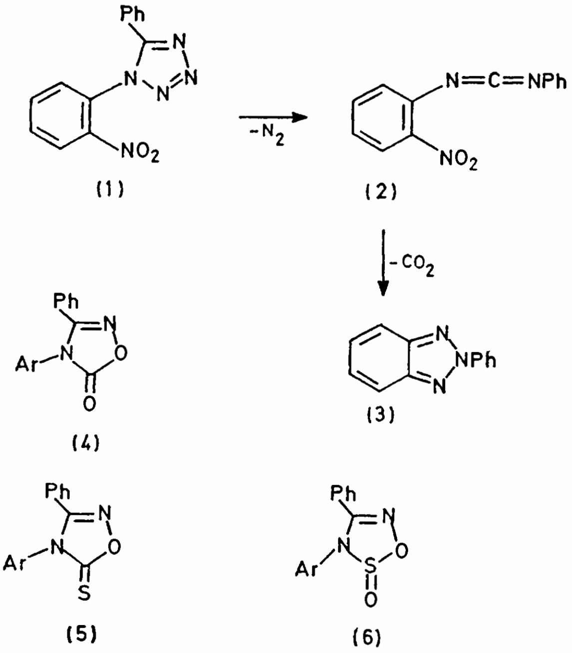
Summary 2-Nitrodiphenylcarbodi-imide, generated by thermolysis of the heterocyclic precursors (**1**), (**4**), (**5**), and (**6**), and prepared by oxidation of 2-nitrodiphenylthiourea, is rapidly transformed in high yield into 2-phenylbenzotriazole (**3**) and carbon dioxide, in a new *o*-nitro group interaction.

1,5-Diphenyltetrazole loses nitrogen on thermolysis[1] or photolysis[2] to give 2-phenylbenzimidazole and diphenylcarbodi-imide, the former by imidoyl nitrene cyclisation and the latter by 1,2-phenyl shift, either in the nitrene or simultaneously with the initial nitrogen loss. We have found these reactions to be general, and both occur even when the *ortho* positions of the 1-phenyl ring are substituted. Cyclisation of the nitrene then gives a 3a*H*-benzimidazole intermediate from which the products isolated are derived by various competing sigmatropic shifts.[3]

Thermal and photochemical decomposition of variously substituted tetrazoles usually gives the same products though in different proportions, but we now find that when the 1-aryl group has an *ortho*-nitro substituent a new and unexpected thermolysis reaction, not observed photochemically, leads to the ultimate formation of a 2-substituted benzotriazole in high yield. Thermal decomposition of 1-*o*-nitrophenyl-5-phenyltetrazole (**1**),[4] neat (rather violent), diluted with sand, or in solution (boiling bromobenzene, *o*-dichlorobenzene, acetophenone, or nitrobenzene), gives 2-phenylbenzotriazole (**3**) (80—90%); reaction times vary from several minutes at the highest temperature to several hours at the lowest. The tetrazole (**1**) decomposed much faster than 1,5-diphenyltetrazole under the same conditions. Transformation of (**1**) into (**3**) requires the loss of nitrogen, as expected for a tetrazole, and either carbon dioxide or carbon monoxide and oxygen. Chemical tests and mass spectral measurements showed that nitrogen and carbon dioxide were formed to the total exclusion of carbon monoxide.



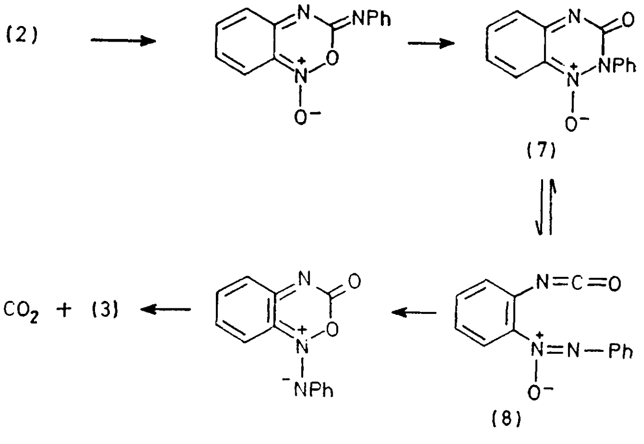
(1) (2) (3) (4) (5) (6)

Ar = $C_6H_4NO_2$-*o*

Of the many pathways which can be considered for this transformation, the simplest appears to involve the carbodi-imide (**2**) and we now show that (**2**) is indeed an intermediate. The *para*-nitro isomer[4] of (**1**) gave the analogous carbodi-imide as its major (and stable) thermolysis product. 1-(2,4-Dinitrophenyl)-5-phenyltetrazole[5] decomposed in the same way as (**1**), though faster still, to give 5-nitro-2-phenylbenzotriazole[6] (60%). The oxadiazolone (**4**),[7] the oxadiazolethione (**5**), m.p. 126—128 °C, and the oxathiadiazole 2-oxide (**6**), m.p. 102—104 °C, which can rearrange to the same cardbodi-imide on extrusion of CO_2, COS, and SO_2, respectively, all gave 2-phenylbenzotriazole (**3**) on thermolysis.

The very stable oxadiazoles (**4**) and (**5**) required strong heating (255 °C) in boiling diphenyl ether or in the melt and gave the benzotriazole (**3**) in low yield only (*ca.* 10%), the major product being that of nitrene cyclisation, 4-nitro-2-phenylbenzimidazole. However, the oxathiadiazole 2-oxide (**6**) decomposed rapidly under much milder conditions, in boiling bromobenzene or in the melt at 130 °C, to give benzotriazole (**3**) in very high yield; formation and decomposition of the carbodi-imide (**2**) can be clearly monitored spectroscopically. 3,4-Diaryloxathiadiazole 2-oxides like (**6**) are known to give carbodi-imides almost quantitatively on heating.[8] Finally, the nitrocarbodi-imide (**2**), m.p. 19—21 °C, ν 2160 cm^{-1}, has been prepared independently from 2-nitrodiphenylthiourea and mercury(II) oxide and found to rearrange completely to 2-phenylbenzotriazole and carbon dioxide on brief heating in bromobenzene.

Thus, the *o*-nitro group in (**1**) facilitates formation of the carbodi-imide and then intercepts it very efficiently. *o*-Nitro groups are known to act as nucleophiles in intramolecular displacement reactions[9] and the preparation of many heterocyclic systems is based upon acid and base catalysed *o*-nitro cyclisation reactions.[10] For the conversion of the carbodi-imide (**2**) into benzotriazole (**3**) we propose a sequence of electrocyclic ring closing and opening reactions (Scheme). In support of this, a red crystalline intermediate, m.p. 121—124 °C, has been isolated by thermolysis of the carbodi-imide (**2**), or oxathiadiazole 2-oxide (**6**), at a slightly lower temperature in toluene. On longer heating in toluene or on heating in bromobenzene or in the melt, the red compound gives 2-phenylbenzotriazole almost quantitatively. On the basis of spectroscopic evidence, it is tentatively assigned structure (**7**), ν 1695 cm^{-1} (KBr disc, Nujol mull). In solution this carbonyl absorption diminishes and a new absorption at 2260 cm^{-1} (CCl_4), attributed to the isocyanate group in (**8**), appears. Removal of solvent leaves a solid with the original i.r. spectrum, demonstrating the reversibility (**7**) $\rightleftharpoons$ (**8**).



SCHEME

The only arylcarbodi-imide with an *o*-nitro group previously recorded is the symmetrical 2,2′-dinitrodiphenyl compound,[11] but there is no report of this undergoing rearrangement. We find that on brief heating in the melt at 150 °C or in bromobenzene this carbodi-imide is similarly converted into 2-(*o*-nitrophenyl)benzotriazole in high yield (85%). 4-Methoxy-2′-nitrodiphenylcarbodi-imide and 2,6-dimethyl-2′-nitrodiphenylcarbodi-imide also rearrange thermally to give the corresponding 2-arylbenzotriazoles.

(*Received*, 24*th May* 1979; *Com.* 550.)

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