New Rearrangements in the Pyrolysis of Nitrocarbodi-imides

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On flash vacuum pyrolysis the nitrobiphenylcarbodi-imide (**4**) gave benzimidazo[1,2-*f*]phenanthridine (**8**), and the nitronaphthylcarbodi-imide (**11**) gave benz[*cd*]indazole *N*-oxide (**12**), in new rearrangements involving the nitro groups.

Thermolysis of 2-nitrodiphenylcarbodi-imide (**1**) gives 2-phenylbenzotriazole (**3**) and carbon dioxide almost quantitatively, *via* the benzotriazinone *N*-oxide (**2**).[1] In view of this very efficient, though unexpected, interaction between the carbodi-imide and the *ortho*-nitro group, we have investigated the analogous naphthalene (**11**) and biphenyl (**4**) compounds in which the carbodi-imide and nitro groups are 1,3- and 1,4-related respectively, and find that these undergo different, new rearrangements.

The carbodi-imides were prepared in high yield from the corresponding thioureas, m.p. 186—188 °C and m.p. 155—156 °C respectively, by treatment with 2-chloro-1-methylpyridinium iodide and triethylamine.[2] They were thermally much more stable than (**1**), presumably because the initial, favourable cyclisation reaction proposed for (**1**)[1] is not available in (**11**), and would have a higher activation energy in (**4**). They were unchanged after heating in 1,2,4-trichlorobenzene (215 °C) for a few hours, and they gave complex mixtures when decomposed in the melt at 270 °C; they were therefore subjected to flash vacuum pyrolysis.

At 750 °C and 0.015 mmHg, the carbodi-imide (**4**) decomposed cleanly to give, after chromatography, benzimidazo-[1,2-*f*]phenanthridine (**8**) (45%), m.p. 153—155 °C, lit.,[3] m.p. 155 °C, the identity of which was confirmed by comparison with an authentic specimen.† Formation of (**8**) from (**4**), with the formal loss of nitrous acid, suggests an initial cyclisation of the carbodi-imide group on to the nitro-substituted position of the biphenyl to give the tetrahedral intermediate (**6**). This intermediate could readily dissociate into nitrogen dioxide and the highly stabilised organic radical (**7**), which could cyclise again to give the observed product (**8**) on aromatisation. The apparent selectivity for closure on to the nitro-substituted position suggests some attractive interaction between the

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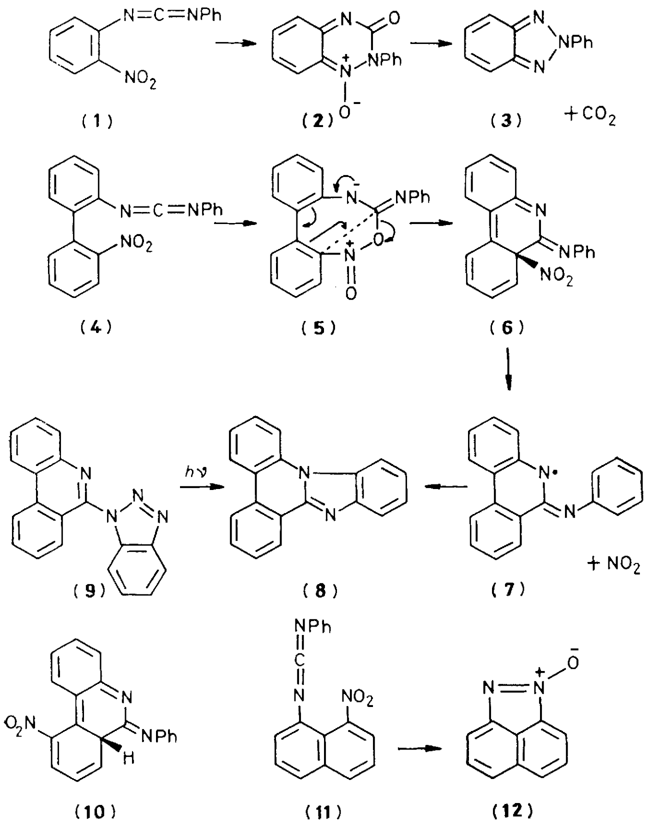
† Since none of the literature methods[3,7,8] for the preparation of benzimidazo[1,2-*f*]phenanthridine (**8**) was entirely suitable, we devised a simple alternative route to it. Condensation of 6-chlorophenanthridine with 2-nitroaniline, reduction of the nitro group, and diazotisation of the resulting amine readily gave the phenanthridinobenzotriazole (**9**), m.p. 215—217 °C; photolysis of this in acetonitrile gave the benzimidazole (**8**) in good yield.



carbodi-imide and nitro groups, the extreme of which could be O—C bond formation to give (**5**) by a process analogous to that proposed on the way from (**1**) to (**2**).[1] Intermediate (**5**) could then collapse to (**6**) as shown. Interaction between the carbodi-imide and nitro groups could also be favoured by the known propensity for 2,2′-disubstituted biphenyls to adopt the *cisoid* conformation, in the gas and in condensed phases.[4] If the carbodi-imide group in (**4**) had cyclised on to the unsubstituted 2′-position to give (**10**), we would have expected some 6-anilino-10-nitrophenanthridine to be formed by rapid hydrogen shifts; none of this compound was detected by direct comparison of the pyrolysate with authentic 6-anilino-10-nitrophenanthridine, m.p. 144—147 °C, made from 10-nitrophenanthridone,[5] by successive treatment with phosphorus oxychloride and aniline.

Some evidence in support of the decisive influence of the nitro group in (**4**) is found in the flash vacuum pyrolysis of the compound with the nitro group omitted. Under exactly the same pyrolysis conditions as used for (**4**), 2-phenyldiphenylcarbodi-imide was largely unchanged; 72% was recovered and only 4% of the cyclisation product, 6-anilinophenanthridine, was obtained. Thus the nitro group in (**4**) controls the direction of ring closure and provides a lower-energy pathway for it, as in the mechanism proposed.

The naphthyl-carbodi-imide (**11**) sublimed very slowly and so was pyrolysed, as above, but on a small scale (10 mg). It gave benz[*cd*]indazole *N*-oxide (**12**)[6] in good yield (70%) though the other volatile component, probably phenyl isocyanate, was not identified. The *N*-oxide (**12**) could reasonably be formed by transfer of oxygen from the nitro to the carbodi-imide group, as in the formation of (**5**) above; but since the charged, *peri*, nitrogen atoms are not now conjugated they interact through space to form an N–N bond, and phenyl isocyanate can then be eliminated.

Thus, intramolecular nucleophilic attack by the oxygen of the nitro group upon the carbodi-imide carbon appears to be general; but after this initial attack the reactions of (**1**), (**4**), and (**11**) diverge to form five-membered heterocyclic rings by three different pathways.

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