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FURTHER ASPECTS OF THE THERMAL REARRANGEMENT OF 1-ARYL-2-CYANO-3,3-DIPHENYLDIAZETIDIN-4-ONES[a]

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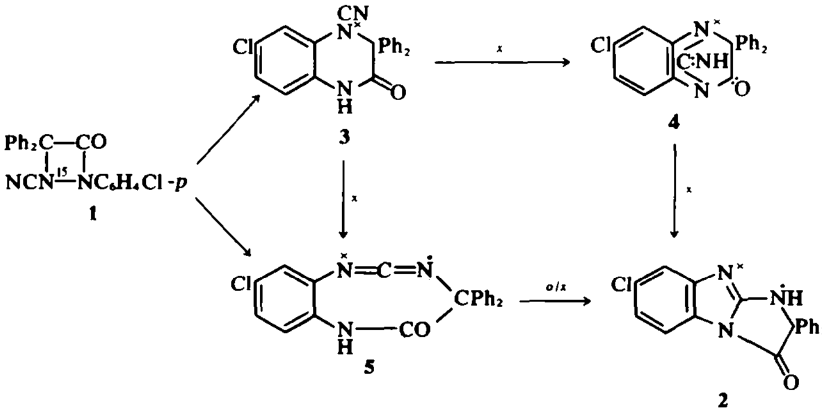
Abstract—The title reaction has been shown by a ^{15}N labelling study to proceed *via* a [3.3]-sigmatropic rearrangement. The 1,2-migration of halogen atoms has been observed during the rearrangement of 1-(2′,6′-dichlorophenyl)- and 1-(2′,4′,6′-tribromophenyl)-2-cyano-3,3-diphenyldiazetidin-4-ones.

At the time of the original description[1] of the facile rearrangement of 1-aryl-2-cyano-3,3-diphenyldiazetidin-4-ones (*e.g.* **1**) to imidazo[1.2-a]benzimidazoles (**2**) two basically different mechanisms were considered for this transformation. This first of these entailed an ortho-semidine rearrangement of **1** to **3**. This intermediate could then undergo intramolecular cyclisation to **4** followed by an N-to-N-migration giving **2**. It has not proved possible to synthesise **3**, but the dimethyl analogue (**6**) is thermally stable at 100° higher than that at which the pyrazolidinone (**7**) rapidly rearranges to **8**.[2] However, this does not exclude rearrangement of **3** to the cyclic carbodiimide **5** by an N-to-N migration, and subsequent intramolecular cyclisation to **2**. The alternative mechanism considered proceeded *via* a [3.3]-sigmatropic rearrangement of the diazetidinone (**1**) to **5**. Although the results[3] of a kinetic study of the rearrangement were discussed in relation to the latter mechanism, they did not clearly differentiate between these various mechanistic possibilities.

However, as reference to Scheme 1 shows, these mechanisms predict different locations of N-2 of the diazetidinone in the resulting imidazo[1.2-a]benzimidazole. Recently acquired access to a suitable assay system has enabled us to carry out the appropriate labelling experiment.

p-Chloroaniline was diazotised using ^{15}N-enriched sodium nitrite and the diazonium salt converted into *p*-chlorobenzenediazocyanide. Addition to this of diphenylketen gave the diazetidinone (**1**) with N-2 enriched with ^{15}N. The product (**2**) of thermal rearrangement was then degraded by an established series of reactions[1] indicated in Scheme 2. The N-15 enrichment of 1·84% present in the diazetidinone was maintained upto and including the derived 2-amino-5-chlorobenzimidazole. Deamination to 5-chlorobenzimidazolid-2-one resulted in complete loss of the ^{15}N-enrichment, showing that the amino-nitrogen atom was derived from N-2 of the diazetidinone. This clearly establishes that conversion of **1** to **2** proceeds via a [3.3]-sigmatropic rearrangement to **5**, followed by intramolecular cyclisation.

In the course of preliminary quantitative studies on this rearrangement by differential scanning



SCHEME 1.

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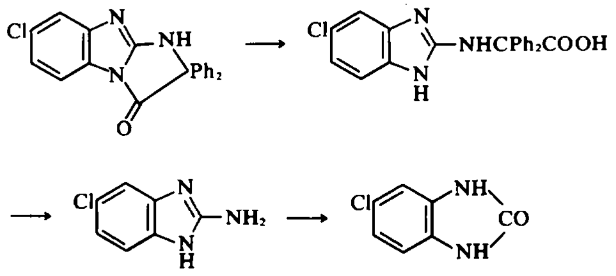
[a] A preliminary account of part of this work has already appeared: C. W. Bird, *Chem. Commun.* 1486 (1969).



SCHEME 2.

calorimetry it was found that the 2,6-dichlorophenyldiazetidinone (**9a**) underwent an exothermic transformation (T_{max} *ca* 150°). On a preparative scale brief heating of **9a** in refluxing bromobenzene gave the dichloroimidazobenzimidazole (**11a**), whose structure was established by its formation from 2,5-dichlorophenyldiazetidinone (T_{max} *ca* 120°). The formation of any other chlorinated imidazobenzimidazoles from **9a** could be not be detected.

IR examination of the reaction mixture resulting from rearrangement of **9a** showed the presence of compounds absorbing strongly at 2210 cm^{-1} and weakly at 2150 cm^{-1}. The compound responsible for the former absorbtion was identified as 2,6-dichlorophenyl isocyanate which was conveniently characterised as its methyl carbamate. The other absorption may have been due to the expected N-cyanodiphenylketimine but attempts to isolate a pure material were unsuccessful. Diphenylketen, which would be expected[4] to be formed by fission of the diazetidinone ring in the alternate sense, could not be detected (no band at 2050 cm^{-1}). 2,4,6-Tribromophenyldiazetidinone (**9**) underwent thermal transformation into a tribromoimidazobenzimidazole which we assume to be the 5,7,8-tribromo-isomer (**11b**).

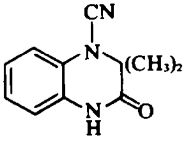
Thus in these transformations the initial sigmatropic rearrangement of the diazetidinones to **10** is followed by an intramolecular 1,2-halogen shift. The fragmentation of **9** to the aryl isocyanate also probably proceeds *via* **10** since comparable diazetidinones, incapable of forming such intermediates, have far greater thermal stabilities.

The foregoing 1,2-halogen shifts appear to be the first encountered in sigmatropic thermal rearrangements. Only reductive displacement of halogen has been encountered previously in the thermal rearrangement of allyl phenyl ethers.[5] Formal 1,3-shifts of chlorine and bromine have been observed[6] in the Lewis acid catalysed rearrangements of allyl 2,6-dihalophenyl ethers to 2-allyl-4,6-dihalophenols, although the actual pathway probably includes an S_N2^1 reaction.

EXPERIMENTAL

^{15}N *Labelling experiments.* The reactions precisely duplicated those previously described[1] except that sodium nitrite, enriched *ca* 2% in ^{15}N, was used in the preparation of *p*-chlorobenzenediazocyanide. All compounds obtained had m.ps and IR spectra identical to those previously recorded.

For quantitative estimation of ^{15}N the compounds were pyrolysed with a mixture of copper oxide and copper acetate[7] in a stream of purified CO_2 to yield N_2 and some



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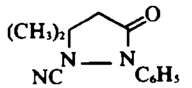

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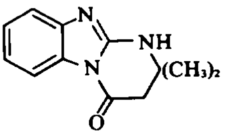

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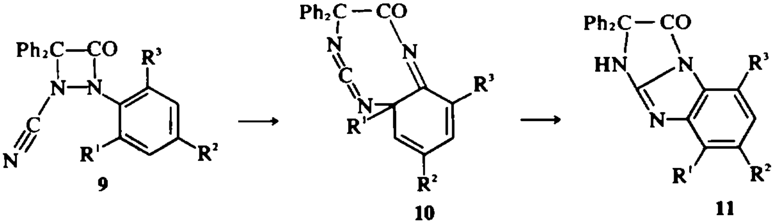

9 **10** **11**

a: $R^1 = R^3 = Cl$; $R^2 = H$
b: $R^1 = R^2 = R^3 = Br$

of its oxides, which were reduced by means of hot copper by Dumas' method.[8] The N_2 was collected in a high vacuum system by allowing the gases to flow (*ca* 10 ml min^{-1}) through a capillary into a liquid N_2 trap, whence the uncondensed N_2 gas flowed into a previously evacuated reservoir. After completion of the pyrolysis (*ca* 1 h) the cold trap and reservoir were isolated from the combustion train, and the collected N_2 gas purified by repeated circulation over copper and copper oxide at 900°.[9] Mass spectroscopic analyses were carried out with an AEI MS 20 double collection, isotope ratio mass spectrometer. The relative isotopic abundance ratios $^{14}N^{14}N/^{14}N^{15}N$ were measured relative to a standard N_2 source. Reproducibility was approximately ±0·02%.

Thermal rearrangement of 1-(2′,6′-*dichlorophenyl*)-2-*cyano*-3,3-*diphenyldiazetidin*-4-*one*. The diazetidinone (3·5 g) was dissolved in bromobenzene (15 ml) and heated under reflux for 5 min. The mixture was cooled, diluted with benzene (40 ml) and filtered to give 5,8-*dichloroimidazo*[1,2-a]*benzimidazole* (0·6 g) m.p. 326–330^{c} from nitrobenzene, ν_{max} 1770, 1660 cm^{-1}, (Found: C, 64·4; H, 3·4; N, 11·0. Calc. for $C_{21}H_{13}Cl_2N_3O$: C, 64·0; H, 3·3; N, 10·7%). The filtrate was evaporated *in vacuo* to remove the benzene and most of the bromobenzene. The residue was distilled, the main bulk boiling below 80° at 0·5 mm. The distillate which partially solidified had ν_{max} 2210 and was treated with methanol to give *methyl* 2,6-*dichlorophenylcarbamate*, m.p. 139–40°, ν_{max} 3,200, 1700 cm^{-1}, δ 3·8 (s, CH_3), 6·63 (br. N–H), 7·0–7·5 (m., aromatic H's). (Found: C, 44·0; H, 3·3; N, 6·3. Calc. for $C_8H_7Cl_2NO_2$: C, 43·7; H, 3·2; N, 6·4%).

Preparation and rearrangement of 1-(2′,5′-*dichlorophenyl*)-2-*cyano*-3,3-*diphenyldiazetidin*-4-*one*. 2,5-Dichlorobenzenediazocyanide was prepared by the general method of Le Fevre and Vine,[10] immediately dissolved in ether, dried over Na_2SO_4, and slowly treated with diphenylketen until the colour was almost discharged. The *diazetidinone* crystallized out on standing, m.p. 146°, 308–315° from ether, ν_{max} 2180, 1790 cm^{-1}. (Found: C, 64·2; H, 3·3; N, 11·0. Calc. for $C_{21}H_{13}Cl_2N_3O$: C, 64·0; H, 3·3; N, 10·7%).

The diazetidinone (0·5 g) was dissolved in xylene (10 ml) and briefly heated to reflux when 5,8-dichloroimidazo[1.2-a]benzimidazole (0·44 g) crystallised out and proved identical with the previously obtained sample.

Preparation and rearrangement of 1-(2′,4′,6′-*tribromophenyl*)-2-*cyano*-3,3-*diphenyldiazetidin*-4-*one* 2,4,6-Tribromobenzenediazocyanide[11] (7 g) in ethereal soln was slowly treated with diphenylketen (3·5 g) and then allowed to stand overnight. A solid (4 g) separated and was filtered off. It was set aside for future investigation as its IR spectrum had bands at 2100 and 1700 cm^{-1} showing it was not the desired diazetidinone. The filtrate was evaporated and the residue chromatographed on silica gel in carbon tetrachloride. Elution with benzene and crystallisation from $CHCl_3$–MeOH gave the *diazetidinone* m.p. *ca* 110° with partial resolidification finally giving a clear liquid phase *ca* 270°, ν_{max} 2210, 1800 cm^{-1}. (Found: C, 44·1; H, 1·9; N, 7·6; Br, 43·0. Calc. for $C_{21}H_{12}N_3OBr_3$: C, 43·8; H, 2·1; N, 7·5; Br, 42·7%).

The diazetidinone (0·5 g) was heated under reflux in xylene (10 ml) for 45 min. A solid (0·1 g) slowly separated and was recrystallised from xylene to give 5,7,8-*tribromoimidazo*[1,2-a]*benzimidazole*, m.p. 300–304°, ν_{max} 1780, 1650 cm^{-1}. (Found: C, 43·5; H, 2·2; N, 7·7; Br, 42·3. Calc. for $C_{21}H_{12}N_3OBr_3$: C, 43·8; H, 2·1; N, 7·5; Br, 42·7%). The IR spectrum of the mixture after filtration showed a strong band at 2280 cm^{-1} possibly due to 2,4,6-tribromophenyl isocyanate.

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