

We have repeated the thermal rearrangement of a series of hydrazonates (1, $Ar^1 = p\text{-MeC}_6\text{H}_4$, C_6H_5 and $p\text{-NO}_2\text{C}_6\text{H}_4$; $Ar^2 = \text{C}_6\text{H}_5$; $Ar^3 = p\text{-NO}_2\text{C}_6\text{H}_4$)⁴ at 200°. In our hands the products obtained in all cases were the N' , N' -diarylhydrazides 3, rather than N,N' -diarylhydrazides 2. This structural assignment is consistent with the following data. Hydrolysis of the rearrangement products in concentrated hydrochloric acid-ethanol gave in each case 1-phenyl-1-(p -nitrophenyl)hydrazine hydrochloride which was characterized as a benzaldehyde derivative, m.p. 139-140°. Aryl group migration did not occur during hydrolysis or the subsequent workup since reaction of the substituted hydrazine with benzoyl chloride regenerated N' -phenyl- N' -(p -nitrophenyl)benzhydrazide (3, $Ar^1 = Ar^2 = \text{C}_6\text{H}_5$; $Ar^3 = p\text{-NO}_2\text{C}_6\text{H}_4$).

Thermal rearrangement of the isomeric hydrazonate 4, in which the aryl groups attached to nitrogen and oxygen are reversed (relative to 1), gave the same product, namely 3, as did rearrangement of 1. This was true in all cases tested starting with the hydrazonates 1 and 4 (with $Ar^1 = Ar^2 = \text{phenyl}$ and $Ar^3 = p\text{-bromo}$, $p\text{-methyl}$, $p\text{-nitro}$ and $p\text{-chlorophenyl}$) which were heated in the absence of solvent at 200° for 10-60 min (Table). The identity of the hydrazides obtained by either route was established by m.p., mixed m.p.,

Table. The hydrazonates 1 and 4 and the rearrangement products (3).

| Ar^1 | Ar^2 | Ar^3 | M.p./°C. | | |
|-------------------------------------|-------------------------------------|-------------------------------------|---------------|---------------|-------------|
| | | | Hydrazonate 1 | Hydrazonate 4 | Hydrazide 3 |
| C_6H_5 | C_6H_5 | $p\text{-NO}_2\text{C}_6\text{H}_4$ | 175-178 | 134 | 178-180 |
| C_6H_5 | C_6H_5 | C_6H_5 | 154-155 | 154-155 | 190 |
| C_6H_5 | C_6H_5 | $p\text{-Cl-C}_6\text{H}_4$ | 137 | 104-108 | 168-170 |
| C_6H_5 | C_6H_5 | $p\text{-BrC}_6\text{H}_4$ | 154-156 | 98-100 | 205-206 |
| C_6H_5 | C_6H_5 | $p\text{-MeC}_6\text{H}_4$ | 181-183 | 108-110 | 171-173 |
| C_6H_5 | $p\text{-NO}_2\text{C}_6\text{H}_4$ | $p\text{-NO}_2\text{C}_6\text{H}_4$ | 178-180 | 278-280 | |
| $p\text{-ClC}_6\text{H}_4$ | C_6H_5 | C_6H_5 | 85-90 | | 194-196 |
| $p\text{-NO}_2\text{C}_6\text{H}_4$ | C_6H_5 | C_6H_5 | 146-147 | | 192-198 |

infrared spectra and, particularly, thin layer chromatography (on silica gel using benzene- n -hexane-triethylamine (in ratio 15 : 4 : 1) as mobile phase).

If aryl group migration had been to the adjacent nitrogen as claimed¹ then different products (viz. 2 and 5) would have been obtained from the various pairs of hydrazonates 1 and 4. Moreover the N-aryl groups are equivalent in the N',N'-diarylhydrazides (3) when $Ar^2 = Ar^3$ and non-equivalent in the alternative N,N'-diarylhydrazides (2 or 5). This was found to be so (by nmr spectroscopy) in the two cases that we have studied (3, $Ar^1 = Ar^2 = Ar^3 = C_6H_5$ and 3, $Ar^1 = C_6H_5$; $Ar^2 = Ar^3 = p-NO_2C_6H_4$).

In one case we have independently synthesised the N,N'-diarylhydrazide 2 (where $Ar^1 = Ar^2 = Ar^3 = C_6H_5$). This hydrazide is thermally stable at 200° for 10 min, under which conditions the rearrangement of 1 to 3 is rapid. When heated at 170° for 90 s, rearrangement of 1 to 3 had only partially proceeded. Analysis of the partially rearranged mixture by thin-layer chromatography showed the presence of just two compounds, 1 and 3 ($Ar^1 = Ar^2 = Ar^3 = C_6H_5$). N,N'-Diphenylbenzhydrazide (2, $Ar^1 = Ar^2 = Ar^3 = C_6H_5$) was absent (within the limits of detection). Thus the N,N'-diarylhydrazide 2 is not an intermediate in the thermal rearrangement of 1 to 3, aryl group migration to the terminal nitrogen occurring directly.

The isomerisation of 1 to 3 ($Ar^1 = Ar^2 = Ar^3 = C_6H_5$) may be carried out under much milder conditions than those required for the analogous Chapman rearrangement. Thus, for example, $t_{1/2}$ for this hydrazone in 4 : 1 dioxan water at 95° is ca. 5 min. Thermal rearrangement in the absence of solvent also occurs at ca. 100° less than that required for a similarly substituted imidoyl ether. These observations lend further support for the fact that rearrangement consists of aryl group migration from oxygen to the terminal nitrogen (which would involve a five-membered transition state) rather than to the adjacent nitrogen (via a strained four-membered transition state).

REFERENCES

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4. The m.p.s of these hydrazonates and rearranged products agree with literature¹ values.
5. The hydrazonates were prepared from the corresponding hydrazonyl chlorides or bromides using the method previously described³ or by direct reaction with the sodium salt of the phenol in benzene.