Conversion of Aryl Hydrazonates into Hydrazides. A New O to N Aryl Migration

By A. F. HEGARTY, J. A. KEARNEY, M. P. CASHMAN, and F. L. SCOTT

(*Chemistry Department, University College, Cork, Ireland*)

Summary Thermal rearrangement of aryl hydrazonates yields *NN*-diarylhydrazides, a Chapman-like rearrangement in the hydrazone series.

THE reaction of the chloride (**1**) with substituted phenols in benzene using triethylamine as catalyst gave the novel aryl hydrazonates (**2**). The hydrazonates may be recrystallised below 60° (*e.g.* from hexane). At higher temperatures rearrangement occurs with quantitative formation of the hydrazide (**4**). This reaction is a new O → N aryl migration, analogous to the Chapman rearrangement[1] of imidic ethers.

Yields of rearranged product were optimised by maintaining the hydrazonate (**2**) in the absence of solvent for 10 min at 200°. In an inert solvent, *e.g.* toluene, rearrangement could be effected, however, under milder conditions, *i.e.* 4 h at 100°. Preliminary kinetic studies on the rearrangement have shown a small substituent effect, the rate being accelerated by electron withdrawing groups X in (**2**).

It is interesting that the rearrangement occurs such that the carbon on the migrating ring which was attached to oxygen is attached to nitrogen in the hydrazide. This was shown by the identity of the product formed on rearrangement of both the *p*-nitrophenyl (**2**; X = NO_2) and phenyl compounds (**3**; X = NO_2). Thermal rearrangement of both gave the same hydrazide (**4**; X = NO_2). Other pairs of hydrazonates (**2**) and (**3**) (with X = Br or Cl) similarly gave a single rearranged product (**4**; X = Br or Cl).

The conditions required for the rearrangement of (**2**) are markedly milder than those for the Chapman rearrangement (which typically requires pyrolysis at 280—300°). Assuming that the mechanisms of both reactions are similar (an intramolecular nucleophilic attack by nitrogen on the *O*-aryl group) then the ease of reaction of compounds (**2**) presumably reflects the involvement of a five- (rather than four-) membered transition state. Alkyl imidates rearrange only under forcing conditions and then by an intermolecular mechanism;[2] attempts to effect the analogous rearrangement of alkylhydrazonates were unsuccessful.[3,4]

The *NN*-disubstituted hydrazides (**4**) can readily be hydrolysed in acidic or basic conditions to the corresponding 1,1-diarylhydrazines. This provides a more convenient route to these hydrazines (which may carry two different aryl substituents) than nitrosation and reduction of the corresponding amines (which are themselves difficult to obtain).

The scope and mechanism of the rearrangement are under active study.

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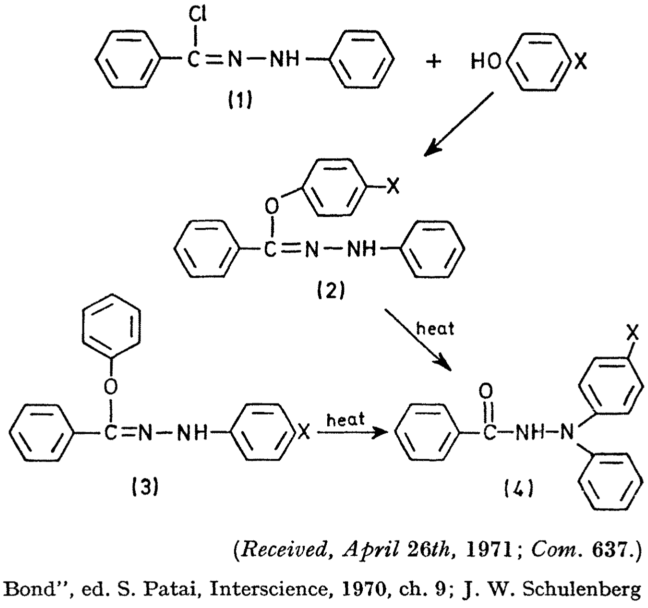

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[1] C. G. McCarty, "The Chemistry of the Carbon–Nitrogen Double Bond", ed. S. Patai, Interscience, 1970, ch. 9; J. W. Schulenberg and S. Archer, *Org. Reactions*, 1965, **14**, 1.

[2] K. B. Wiberg, T. M. Shryne, and R. R. Kinter, *J. Amer. Chem. Soc.*, 1957, **79**, 3160.

[3] J. B. Aylward and F. L. Scott, *J. Chem. Soc.* (*C*), 1970, 968.

[4] The isolation of *N'N'*-(diphenyl)benzhydrazide in the reaction of 3,5-diphenyltetrazole with phenol at elevated temperatures probably also involves the intermediate formation of (**2**; X = H) (R. Huisgen, J. Sauer, and M. Seidel, *Ber.*, **1961**, **94**, 2503).