542. *Hydrazones. Part VI.*[1] *The Hydrazidic Halide → Acylhydrazide Transformation*

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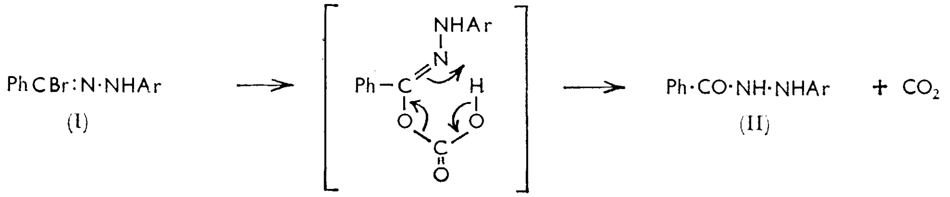
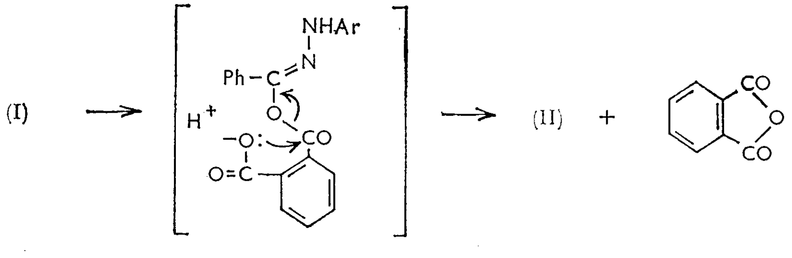
Although, formally, hydrazidic halides ($\mathrm{RCX{:}N{\cdot}NHR'}$) are related to acylhydrazides ($\mathrm{RCO{\cdot}NH{\cdot}NHR'}$), there appear to be no methods on record for converting the former into the latter. Normal acidic or alkaline hydrolytic procedures are unattractive because of the known or likely occurrence of secondary reactions.[2] We now report two simple methods that appear to be general for effecting this conversion.

First, *N*-α-bromobenzylidene-*N*′-(2,4-dibromophenyl)hydrazine (I) reacts with potassium hydrogen carbonate in dry dimethylformamide to give *N*-benzoyl-*N*′-(2,4-dibromophenyl)hydrazine (II) and carbon dioxide. Decarboxylation of the intermediate α-hydrogen carbonate, formed possibly *via* the diarylnitrilimine, can occur directly with nitrogen participation, or *via* the anion, by processes akin to those involved in the decarboxylation of β-keto-acids.[3]



(Ar = 2,4-dibromophenyl)

Secondly, the hydrazine (I) reacts with potassium hydrogen phthalate in dry acetonitrile to give the hydrazine (II) and phthalic anhydride. In this case, ionisation of the intermediate α-hydrogen phthalate is followed by attack of the nucleophilic carboxylate ion on the juxtaposed carbonyl group, leading to elimination of phthalic anhydride, as, for example, in the reaction of phthalic acid with carbodi-imides.[4]



In a sense, the second method represents an abnormal mode of acylolysis, and it is possible that in the acetolysis of the hydrazine (I), and other hydrazidic halides (cf.[1,2]), a similar attack of acetate ion on the intermediate α-acetate occurs as a side reaction; the

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[1] Part V, J. M. Burgess and M. S. Gibson, *J.*, 1964, 1500.

[2] F. D. Chattaway and A. J. Walker, *J.*, 1925, **127**, 975.

[3] Cf. E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, 1959, 346; B. Capon, *Quart. Rev.*, 1964, **18**, 45.

[4] Cf. H. G. Khorana, *Chem. Rev.*, 1953, **53**, 145.

isolated product, *N'*-acetyl-*N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine, is, however, certainly formed by intramolecular acetylation, as the hydrazine (II) is not acetylated by acetic anhydride (one equiv.) under these conditions. The corresponding acylhydrazides have not been reported as by-products in acetolyses of hydrazidic halides, but separation might be difficult in many cases because of the physical similarities to the *N'*-acetyl compounds; detection of the hydrazine (II) in samples of *NN'*-dibenzoyl-*N'*-(2,4-dibromophenyl)hydrazine presents similar problems.

Experimental.—Microanalyses are by Mr. V. Manohin.

Reaction of N-*α-bromobenzylidene*-N'-(2,4-*dibromophenyl*)*hydrazine with potassium hydrogen carbonate.* (*a*) A stirred mixture of *N*-α-bromobenzylidene-*N'*-(2,4-dibromophenyl)hydrazine (14·6 g.),[2] potassium hydrogen cabonate (6·75 g.) and dry dimethylformamide (200 ml.) was heated under reflux to 150° for 30 min. and then at 150° for 15 min.; evolution of carbon dioxide began at *ca.* 40°. The brown mixture was allowed to cool, and then poured into water (200 ml.) and acetic acid (2 ml.) with vigorous stirring. The pale brown solid (10 g.; 80%) was collected, washed, and dried. Three crystallisations from acetonitrile (charcoal) gave *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine as colourless elongated plates, m. p. 173—174° (lit.,[2] 172°) (Found: C, 42·3; H, 2·6; N, 7·8%. Calc. for $C_{13}H_{10}Br_2N_2O$; C, 42·2; H, 2·7; N, 7·6%); $\nu_{max.}$ (Nujol mull) 1635 cm.$^{-1}$.

(*b*) A solution of potassium hydrogen carbonate (4·0 g.) in water (30 ml.) was added dropwise to a stirred solution of *N*-α-bromobenzylidene-*N'*-(2,4-dibromophenyl)hydrazine (8·66 g.) in ethanol (200 ml.) under reflux. The reddish-brown solution was boiled for 15 min. and cooled, and glacial acetic acid (1·2 ml.) was added. The solution was then concentrated *in vacuo* to *ca.* 100 ml., and poured into water (200 ml.) with stirring, when crude *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine (5 g., 68%) separated as a pale greenish solid (colourless elongated plates, m. p. 170—171°, after one crystallisation from ethanol).

Reaction of N-*α-bromobenzylidene*-N'-(2,4-*dibromophenyl*)*hydrazine with potassium hydrogen phthalate.* A stirred mixture of *N*-α-bromobenzylidene-*N'*-(2,4-dibromophenyl)hydrazine (2·17 g.), potassium hydrogen phthalate (2·04 g., AnalaR) and dry acetonitrile (50 ml.) was refluxed for 3 hr., and then filtered hot from suspended potassium salts. When the filtrate was cooled, *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine (0·9 g.) separated as elongated plates, m. p. and mixed m. p. 173—174°. Evaporation of the mother-liquor gave a pale pink solid A (1·30 g.), whose infrared spectrum resembled that of a 3 : 4 mixture of phthalic anhydride and *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine; the latter was the only detectable component by thin-layer chromatography (Merck Kieselgel G; 10% ethyl acetate in benzene; development with iodine, which does not spot phthalic anhydride). A sample of A (0·25 g.) was crystallised from acetonitrile (2·5 ml.), giving *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine (0·07 g.), m. p. 173—174°; the quantity of this compound estimated as recoverable by crystallisation is thus 1·26 g. (68%). Another sample of A (0·25 g.) was sublimed *in vacuo* 100—170°/4 mm.) giving phthalic anhydride (0·135 g.), m. p. and mixed m. p. 132—133°; the total amount of phthalic anhydride estimated as recoverable by sublimation is thus 0·7 g. (94%).

Hydrolysis of N-*benzoyl*-N'-(2,4-*dibromophenyl*)*hydrazine.* A mixture of *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine (2 g.), ethanol (20 ml.) and concentrated hydrochloric acid (20 ml.) was refluxed for 2 hr.; the solution was cooled, and 2,4-dibromophenylhydrazine hydrochloride (1·4 g., 86%) separated as needles, m. p. 190—195° (decomp.), after subliming as prisms above *ca.* 120°; it was characterised by conversion into *o*-nitrobenzaldehyde 2,4-dibromophenylhydrazone, which crystallised from acetonitrile as orange needles, m. p. 205° (lit.,[2] 205°).

The acidic mother-liquor from the hydrolysis was made alkaline by addition of 40% sodium hydroxide solution, and the ethanol then removed by distillation *in vacuo*. Acidification precipitated benzoic acid (0·4 g., 61%), which crystallised from water as leaflets, m. p. and mixed m. p. 120—121°.

NN'-*Dibenzoyl*-N'-(2,4-*dibromophenyl*)*hydrazine.* (*a*) A mixture of *N*-α-bromobenzylidene-*N'*-(2,4-dibromophenyl)hydrazine (8·66 g.), anhydrous sodium benzoate (5·76 g.), and dry acetonitrile (100 ml.) was boiled under reflux with stirring for 24 hr. The hot suspension was filtered, and the residue washed with acetonitrile. The solution was allowed to cool, the solid (4·25 g.) collected, and the filtrate then concentrated *in vacuo* to yield a second crop (1·95 g.; total 65%). From acetonitrile, NN'-*dibenzoyl*-N'-(2,4-*dibromophenyl*)*hydrazine* crystallised as colourless rhomboids, m. p. 172—173° (Found: C, 50·5; H, 2·8; N, 6·1. $C_{20}H_{14}Br_2N_2O_2$

requires C, 50·6; H, 2·95; N, 5·9%); $\nu_{max.}$ 1660, 1670sh, and 1695 cm.$^{-1}$ (C=O). A mixed m. p. with a sample from method (*b*) below showed no depression.

(*b*) A mixture of *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazine (2·65 g.), dry benzene (40 ml.), and benzoyl chloride (1·5 ml.) was boiled under reflux until evolution of hydrogen chloride ceased (14 hr.); the volume of liquid was then reduced *in vacuo* to *ca.* 15 ml. The product (2·46 g., 73%) separated when the liquid was chilled. *NN'*-Dibenzoyl-*N*-(2,4-dibromophenyl)hydrazine crystallised from acetonitrile as rhomboids, m. p. 172—173° (Found: C, 50·8; H, 3·0; N, 5·8%). *NN'*-Dibenzoyl- and *N*-benzoyl-*N'*-(2,4-dibromophenyl)hydrazines display similar chromatographic properties (Kieselgel G), but the infrared spectra are distinctive, and a depression in m. p. to 135—160° was observed when the two were mixed.

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