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THERMOLYSIS OF BENZHYDRAZONES IN THE PRESENCE OF COPPER

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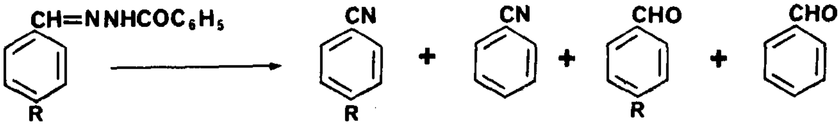
Abstract: Benzhydrazone derivatives of aromatic aldehydes, in the presence of copper, undergo thermolysis to give nitriles.

Aldehydes react with benzhydrazide (C_6H_5 $CONHNH_2$) in hot ethanol to give crystalline benzhydrazones.[1-23] Fahmy[24,25] et al have reported a brief study of the thermolysis of benzhydrazones although yields were not quoted and copper was not used.

We wish to report that benzhydrazones undergo thermolysis, in the presence of copper, to give the corresponding nitriles with aldehydes as byproducts.[26]

The following procedure is representative: the aldehyde benzhydrazone (1, 0.08 mol) and reprecipitated copper metal (8g) were heated at atmospheric pressure in a Claisen flask fitted with a short Vigreux side arm, condenser and receiver. When the temperature of the mixture reached about 220° thermolysis occurred. Heating was maintained until distillation had stopped, the final temperature in the flask being about 320°. A typical reaction time was 40 minutes. The distillate was redistilled at atmospheric pressure and all the distillate was collected until the vapour temperature rose above the boiling point of the higher boiling nitrile expected. A small amount of water codistilled. The distillate was dissolved in carbon tetrachloride and filtered to remove traces of insoluble solid. The solution was analysed by gas liquid chromatography using a Carbowax 20M column with nitrogen as carrier gas and a column temperature of 218°. The results are presented in Table I.[27]



1 2 3 4 5

a. R = H; b. R = CH_3O; c. R = Cl; d. R = CH_3; e. R = F

TABLE I. PRODUCTS

Benzhydrazone [a]	Products (% yield) [b]
1a	3 (73), 5 (7)
1b	2b (20), 3 (33), 4b (2), 5 (1)
1c	2c (24), 3 (21), 4c (1), 5 (2)
1d	2d (29), 3 (28), 4d (5), 5 (3)
1e	2e (34), 3 (24), 4e (9), 5 (2)

[a] Prepared by the published procedure.[1-5] [b] Yields are not optimised. [c] 2a = 3 and 4a = 5.

Minor quantities of the corresponding aldehydes 4 and 5 were produced along with the nitriles and it is possible that they are formed by atmospheric oxidation. Yields in the absence of copper were greatly reduced. The mode of action of the copper is not known and alternative 'catalysts' are being studied. Preliminary indications are that anhydrous copper sulphate may be used instead of copper metal. Steam distillation of the pyrolysis distillates did not increase the recoveries. Non-volatile products are being examined with a view to obtaining information about the reaction mechanism. Evidently, benzonitrile is produced irrespective of the nature of the substituent R, and the product ratios do not appear to depend on the electronic properties of R. A possible intermediate in this reaction is the 2,5-diaryl-1,3,4-oxadiazole formed by dehydrogenation and cyclisation of the benzhydrazone. Copper should aid initial cyclisations of this type. This possibility was ruled out by heating 2,5-diphenyl-1,3,4

-oxadiazole with copper and it was found that pyrolysis did not occur even at 345°.[28] The possibility that the aldehydes could, at least in part, be unchanged starting material has been ruled out by using recrystallised benzhydrazones. Indeed recrystallisation of the benzhydrazones before pyrolysis does not appear to be necessary. The products were identified using chromatographic standards, infrared spectroscopy and ^{1}H-nuclear magnetic resonance spectroscopy.[29,30]

Attempts so far to extend the use of this reaction to aliphatic benzhydrazones (those of pentanal, nonanal and decanal) have not been successful, very little pyrolysate being produced under these conditions.

It is hoped that this reaction will form a basis for the conversion of aromatic aldehydes to nitriles in essentially one step, because isolation of the intermediate benzhydrazones is not necessary in principle.[31]

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26. Cleaning of the distillation flasks was facilitated by mixing the reactants with 8g of sand. The sand appeared to have no effect on the reaction.
27. The chromatographic column consisted of 5% Carbowax 20 M on Chromosorb G (60/80 mesh); column length 2.2 m and column diameter 2 mm. The carrier gas was nitrogen and the flow rate 35 cm^{3} min^{-1}.
28. The oxadiazole was obtained from Aldrich Chemical Co. Ltd., Gillingham, Dorset, England.
29. The product mixture analysis results were confirmed using a Carbowax 20M capillary column (length 10 m, internal diameter 0.2 mm and 0.4 µm film) linked to an electron impact mass spectrometer (Hewlett-Packard 5995 system) with helium as carrier gas.
30. Quantitative analysis of the pyrolysis product mixture from 1a was also checked by infrared spectroscopy. The relative areas of the carbonyl stretch peak for 3 (at 1701 cm^{-1}) and the nitrile stretch peak for 5 (at 2227 cm^{-1}) were determined using a Perkin-Elmer model 983G spectrometer. Infrared analyses of the pyrolysis products from 1b, 1c, 1d and 1e were not possible owing to peak overlap.
31. By ^{1}H-nuclear magnetic resonance monitoring (Jeol FX90Q) we have found that formation of the benzhydrazones from the aldehyde and benzhydrazide occurs at room temperature when dimethyl sulphoxide is used as solvent instead of ethanol. Benzhydrazones of lower aliphatic aldehydes are most conveniently prepared by refluxing the aldehyde with benzhydrazide in toluene solvent in a Dean and Stark apparatus so as to enable removal of water as the reaction proceeds.

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