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OXIDATIVE CONVERSION OF ARYLHYDRAZONES INTO ARYLNITRILES

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The oxidation of arylhydrazones with mercuric oxide in ether to give diazoalkanes or their decomposition products is well known[1]. A little ethanolic potassium hydroxide is usually added to speed up the reaction.

In connection with another research we oxidised various hydrazones (see table) in boiling solvents such as benzene, diethyl ether, furan, dioxan or petrol with yellow mercuric oxide in presence of a few drops of ethanolic potassium hydroxide and obtained the corresponding diazoalkane. However, with 1,2-dimethoxyethane, diglyme, ethanol or tetrahydrofuran as the solvent the main product was the corresponding nitrile (see table). Ketohydrazones (e.g. from various acetophenones) notwithstanding the solvent gave invariably the diazo-compound. Formally, the conversion of a hydrazone into a nitrile involves loss of ammonia but it was found that approximately 1 mole of nitrogen was liberated for every 2 moles of hydrazone consumed. When the progress of the oxidation of a hydrazone in dimethoxyethane was followed by infrared spectroscopy it was found that a diazoalkane peak was formed first ($C=N_2$ at 2070 cm^{-1}), then slowly disappeared giving way to a nitrile band (CN at 2220 cm^{-1}), the reaction being complete in about 4 hr. Also, similar treatment of an aryldiazomethane yielded the nitrile but more slowly.

We believe the mechanism of this new nitrile preparation to involve a tautomeric equilibrium of the diazomethane with its imine ($1 \rightleftharpoons 2$). The parent isodiazomethane ($CN\ NH_2$) derived from diazomethane (CH_2N_2) in presence of potassium hydroxide was described recently by Müller[2]. Formation of (2) would obviously be favoured by base as well as by increased polarity of the solvent which was invariably more polar (D 7) than that used for the preparation of diazoalkanes (D 7). The fact that ketohydrazones which cannot undergo tautomerism form diazo-compounds only and that with aldehyde hydrazones the reaction will not proceed beyond diazoalkane formation in absence of alkali supports the intermediacy of the nitrilimine (2).

It is possible to envisage 3 distinct ways in which the tautomers (1 and 2) could interact (routes a, b, c) to give either the 1-amino-1,2,3-triazole (4) or the 4-amino-1,2,4-triazole (5) or the linear tetrazene (9). We found, however, that the triazole (4; Ar = Ph) was unaffected by mercuric oxide under the reaction conditions which agrees with its reported resistance[3] towards both Fehling s and ammoniacal silver solutions. While route a is thus excluded we are not able to distinguish between the pathways (b and c) both of which appear feasible. The oxidative fragmentation of the 1-amino-1,3,4-triazole (5) to give nitriles and nitrogen is in keeping with results obtained by Rees and his group[4] and has in fact been recently demonstrated for the compounds (5; Ar=H, Ph, Me)[5]. On the other hand interaction between the tautomers (1 and 2) to give a linear tetrazine (9) which subsequently fragments under basic conditions to yield an arylcyanide with evolution of nitrogen is also compatible with experimental observations.

Other pathways were considered: for instance formation of the *N*-aminotriazole (5) from unreacted hydrazone and iso-diazomethane. However, since the diazoalkanes in presence of alkali are capable of nitrile formation (*cf.* above) this possibility was discounted.

Results of further work to define the synthetic scope of this novel method of nitrile preparation will be published elsewhere.

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Table

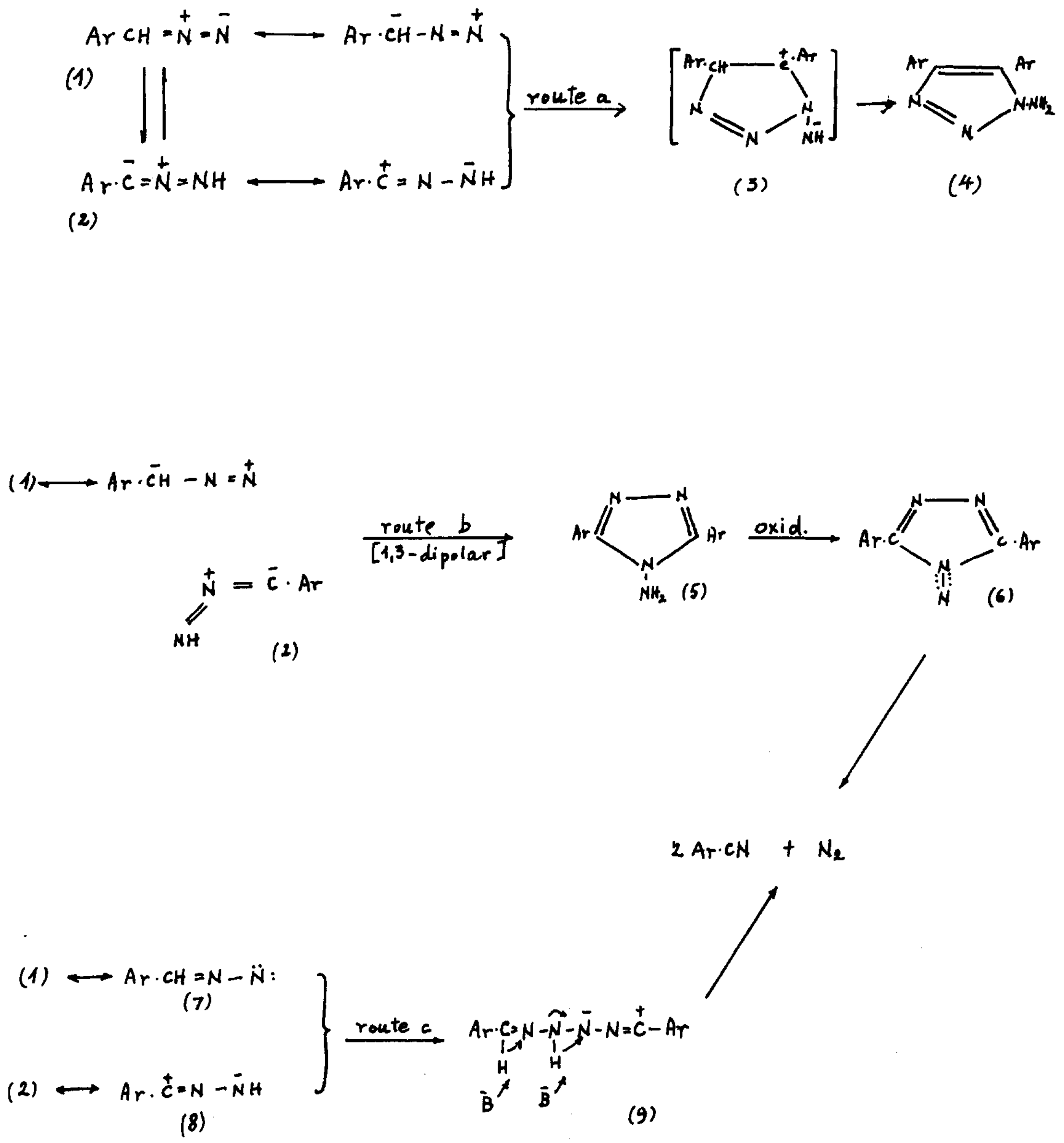
Products and Yields from the Oxidation of Aryl Aldehydehydrazones with Mercuric Oxide

Hydrazone	Solvent	Product	(Yield%)	m.p. (C^{o})
2,6-Dichlorobenzaldehyde	DME*	Nitrile	(80)	143^{o}
		Azine	(4)	153
	Diglyme	Nitrile	(65)	
	THF	Nitrile	(56)	
	Diethyl ether	Diazoalkane	(Quant.)	
4-Methoxybenzaldehyde	DME*	Nitrile	(55)	61
3-Nitrobenzaldehyde	DME*	Nitrile	(10)	117
		+ tar		
2-Chloro-5-nitrobenzaldehyde	DME*	Nitrile	(10)	106
		+ tar		
5-Nitro-2-piperidinobenzaldehyde	DME*	Nitrile	(40)	60
		Azine	(5)	279
4-Chlorobenzaldehyde	DME*	Nitrile	(40)	94
Benzaldehyde	DME*	Nitrile	(38)	190.7 (b.p.)
		Azine	(20)	93

*Dimethoxyethane

References

1. F. Staudinger and A. Gaule, Ber., 1916, 49, 1906.
2. E. Müller and W Kreutzmann, Annalen, 1934, 512, 264; E. Muller, R. Beutler and B Zeeh, ibid., 1968, 719, 72.
3. R.D. Stolle, Ber., 1926, 59, 1743.
4. C.D. Campbell and C.W. Rees, Proc. Chem. Soc., 1964, 296; R.S. Atkinson and C.W. Rees, J. Chem. Soc., 1969, 772.
5. K. Sakai and J.-P. Anselme, Tetrahedron Letters, 1970, 44, 3851.


(1)
(2)
route a
(3)
(4)
route b
[1,3-dipolar]
(5)
oxid.
(6)
2 Ar·CN + N₂
(7)
(8)
route c
(9)