

The Thermal Decomposition of Primary Aromatic Nitramines

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THE acid-catalysed rearrangement of primary aromatic nitramines has been studied in detail¹ whereas the thermal decomposition has received little attention.²

The thermal decomposition of primary aromatic nitramines in aromatic solvents has been found to

produce biaryls, *e.g.* 4-nitrophenylnitramine in nitrobenzene gave a mixture of biaryls from which 4,4'-dinitrobiphenyl was isolated. The decomposition is accompanied by the evolution of nitrogen (identified by mass spectrometry³) and the formation of water. Decomposition of nitramines

in octan-2-ol gives the substituted aromatic hydrocarbon, nitrogen, water, and methyl n-hexyl ketone (Table).

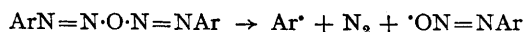
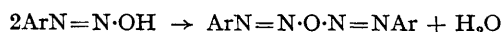
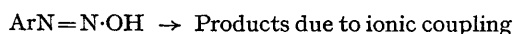
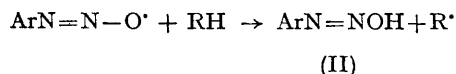
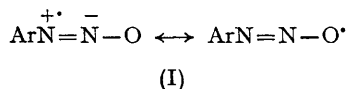
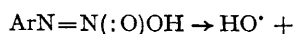
Since water and nitrogen are produced and not nitrogen oxides, we suggest that homolysis of the N-O bond of the *aci* form of the nitramine occurs

TABLE
Products from the decomposition of primary aromatic nitramines in octan-2-ol at 120°

| Substituted phenylnitramine | Yield of nitrogen ^a | Yield of methyl n-hexyl ketone ^{a,b} | Substituted hydrocarbon ^a (%) | Yield of water ^d (%) |
|-----------------------------|--------------------------------|---|--|---------------------------------|
| 4-nitro | 72.5 | 59 | Nitrobenzene (48.5) | 80 |
| 4-methyl | 71.5 | 33 | Toluene (45) | 56 |
| 2,4-dinitro | 67.5 | 30 | 1,3-Dinitrobenzene (21) ^c | 69 |
| 2,5-dichloro | 70.0 | 27 | 1,4-Dichlorobenzene (50) | 100 |
| 2,4,6-trinitro | 95.0 | 63 | | 100 |
| 2,4,6-trimethyl | 75.0 | 23 | 1,3,5-Trimethylbenzene (43) | 95 |
| 2,4,6-tribromo | 51.0 | 27 | 1,3,5-Tribromobenzene (11) ^c | 50 |

^a Yields determined by gas liquid chromatography; ^b Yields based on 1 mole of nitramine oxidises 2 moles of alcohol; ^c Yield of isolated material; ^d Yield based on 1 mole of nitramine gives 2 moles of water.

The biaryl and substituted aromatic hydrocarbon formation shows that aryl radicals are produced. A mechanism which accounts for the observed products is shown below:



with the formation of a hydroxyl and an aryl diazotate radical (I). Aryl diazotate radicals have previously been shown to be intermediates in the Gomberg reaction⁴ and in the thermal decomposition of *N*-nitrosoacylarylamines.⁵ The observation by Bamberger,⁶ which we have confirmed, that the decomposition of phenylnitramine in the presence of 2-naphthol gives benzene-1-azo-2-naphthol, supports the suggested formation of the diazonium hydroxide (II). Huisgen and Horeld have shown⁷ in a similar way that phenyldiazoacetate is formed in the decomposition of *N*-nitrosoacylarylamines. The yield of nitrogen for decomposition in aromatic solvents was highest when the nitramine was 2,4,6-trisubstituted, thus precluding C-coupling of the diazonium hydroxide (II) with unreacted nitramine, a probable side-reaction in the decomposition of less substituted nitramines.

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¹ D. V. Banthorpe and J. A. Thomas, *J. Chem. Soc.*, 1965, 7149 and references cited.

² E. Bamberger and K. Landsteiner, *Ber.*, 1893, 26, 482.

³ S. Harvey and I. R. Nightingale, unpublished results.

⁴ C. Ruchardt and E. Merz, *Tetrahedron Letters*, 1964, 2431.

⁵ G. Binsch, E. Merz, and C. Ruchardt, *Chem. Ber.* 1967, 100, 247; cf. G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 1967, 89, 3054.

⁶ E. Bamberger, *Ber.*, 1897, 30, 1248.

⁷ R. Huisgen and G. Horeld, *Annalen*, 1949, 562, 137.