1319. *The Rearrangement of Aromatic* N-*Nitroamines. Part VI.*[1] *The Thermal and Photochemical Rearrangements of* N-*Methyl*-N-*nitro-1-naphthylamine*

By D. V. Banthorpe and J. A. Thomas

N-Methyl-*N*-nitro-1-naphthylamine in solution in toluene, methanol, ethanol, methyl cyanide, or acetone rapidly rearranges to form 2- and 4-nitro-isomers on heating to 100° and also on exposure to ultraviolet radiation at 20°. Tar is generally formed, but the thermal reaction in toluene is clean and is first-order in the substrate. Pyrolysis of the melt at 75—80° gives small quantities of rearrangement products together with much tar and oxides of nitrogen.

Although the thermally and photochemically induced decompositions in all the solvents studied were more complex than the acid-catalysed processes in aqueous media, *e.g.*, some cross-nitration of added scavengers occurred, there is no evidence for radical mechanisms, and heterolytic fission and intramolecular migration to the 4-position *via* a 2-linked intermediate, similar to the route proposed for acid-catalysed migration, is believed to take place.

THE thermally-induced rearrangement of aromatic hydrazo-compounds has been extensively studied,[2] but little is known about the analogous reaction of *N*-nitroarylamines. Such decomposition of *N*-nitroaniline has been briefly mentioned[3] and a product investigation of the pyrolyses of *N*-methyl-4,*N*-dinitroaniline in the melt and in dichloroethane was interpreted on the basis of radical processes, which partly led to 2-nitro-isomers.[4] Certain *N*-nitroanilines are known to discolour on exposure to light,[5] but no study of any photochemical decomposition has been made. We now record a preliminary investigation of the thermally and photochemically induced rearrangements and disproportionations of *N*-methyl-*N*-nitro-1-naphthylamine (I).

An *N*-methylated substrate was chosen to avoid possible complications due to the existence of an *aci*-form, and to eliminate self-promoted acid-catalysed decomposition: the latter type of reaction could be appreciable because *N*-nitroanilines have pK_a values comparable to those of carboxylic acids.[6]

RESULTS

Thermal Decomposition.—Compound (I) decomposed smoothly in the absence of light and oxygen at 100° in several solvents of widely different polarity and also in the melt at 75—80°. There was usually considerable tar formation, but the reaction in toluene was clean and this solvent was used, unless otherwise specified, in the experiments to be described. The 2- and 4-nitro-isomers were recovered in yields of about 35 and 45% of the total reaction, together with traces of nitric oxide, dinitrogen tetroxide, formaldehyde, benzoic acid, and benzaldehyde from product analysis of the decomposition in toluene in sealed tubes under nitrogen. Paper chromatography also indicated a few yellow bands which were probably mono- and di-nitro-derivatives of *N*-methyl-1-naphthylamine present to the extent of a few percent (unfortunately few of these isomers have been reported in the literature), and also traces of 2- and 4-nitro-1-naphthylamine. No amine formed from denitration of the substrate could be detected although less than 3% decomposition of the substrate to form this would have been easily recognised. If (I) was boiled in toluene in an open vessel less rearrangement (*ca.* 30%) occurred but more tar and nitric oxide was formed. The pyrolysis of the melt was much less smooth, and tar and oxides of nitrogen were formed and only a few percent of rearrangement products, mainly the 2-isomer, could be isolated.

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[1] Part V, preceding Paper.
[2] D. V. Banthorpe and E. D. Hughes, *J.*, 1964, 2849, and references therein.
[3] E. Bamberger and K. Landersteiner, *Ber.*, 1893, **26**, 471.
[4] T. J. Barnes and W. J. Hickinbotham, *J.*, 1961, 2616.
[5] A. E. Bradfield and K. J. P. Orton, *J.*, 1929, 915.
[6] G. S. Sabyanon *et al.*, *Sbornik Statei Obshchei Khim.*, 1953, **2**, 1315 (*Chem. Abs.*, 1955, **49**, 4554).

When the decomposition in toluene was carried out in the presence of large molar excesses of hydroquinone, a large amount of reaction was diverted from rearrangement and the profile of the spectrum of the products from 300 to 500 mμ was drastically changed. The addition of aniline or anisole caused little change in the spectrum, but additional bands, due to small amounts of products of nitration of these additives appeared on the paper chromatogram. Following the previous investigation,[4] the effect of added 2,6-dimethylphenol (a feebly acidic compound) and *NN*-diethylaniline were studied. A small yield of 2,6-dimethyl-4-nitrophenol and considerable quantities of *NN*-diethyl-4-nitroaniline (corresponding to a trapping of about 15% of the reactions) were isolated, together with traces of acetaldehyde. In these experiments, considerable quantities (*ca.* 10%) of the amine formed by denitration of (I) were detected.

The presence of radical scavengers such as cyclohexene and *p*-cymene caused negligible change in the spectrum of products in the range 300—500 mμ, and added acrylonitrile did not polymerise under the reaction conditions. No electron spin resonance (e.s.r.) signal was detected when the decomposition in toluene was conducted at 100° between the pole-pieces of the magnet of the spectrometer, and repeatedly scanned up to one half-life of the reaction; nor when aliquot portions were removed, frozen in liquid nitrogen, and examined. Thus, a standing concentration of less than 10^{-9}M of free radicals, if any, could have been present.

A survey of the products of thermal decomposition in various solvents was made. The percentage formation of the 2-isomer in the two main products is shown in Table 1. This isomer was separated completely by the paper-chromatographic methods used, but the 4-isomer was contaminated with other, more lightly coloured, substances (but with no tar), and a complete separation could not be achieved with several solvent systems and papers. Such contamination is appreciable and the consequence would be to underestimate the percentage of the 2-isomer, as recorded, by about 10—20%. The net recovery of products in all these runs was 30—60%.

TABLE 1

Rearrangement products from thermal and photochemical decompositions

Solvent	Methanol	Ethanol	Methyl cyanide	Toluene	Acetone
Thermal: 2-isomer (%) *	53	58	55	34	51
Photochemical: 2-isomer (%) *	66	68	66	64	57

* (2-Isomer + 4-isomer) = 100%.

The kinetics of rearrangement in toluene at 100° were measured by following the increase in optical density at the wavelength of maximum absorption of the reaction products. As found for the thermal rearrangement of hydrazo-compounds,[2] the kinetics were only reproducible to about ±10% from run to run, probably owing to the difficulty of excluding traces of oxygen (see Discussion) and to slightly variable amounts of tar formation; but acceptable first-order plots were obtained and measurements over a range of initial concentrations showed the reaction to be first-order in substrate. Results are in Table 2. Kinetic studies were not made in other media owing to tar formation, but visually the rate of decomposition was found to decrease appreciably in an order methanol > ethanol $\gg$ methyl cyanide $\sim$ acetone > toluene.

TABLE 2

Kinetics of decomposition of *N*-methyl-*N*-nitro-1-naphthylamine in toluene at 100·0° ± 0·2°

10^4[Substrate]$_0$	1·04	2·09	3·13	4·18	5·22
10^4k_1 (sec.$^{-1}$)	8·3	10·0	9·5	9·5	9·5

Photochemical Decomposition.—This was studied in the same solvents at 20°. Decomposition was rapid on exposure to radiation with a lower cut-off at about 360 mμ, and much tar was formed, although there was negligible decomposition over periods of days on exposure to daylight at room temperature. Products were essentially those of the thermal reaction, but with a reduced (*ca.* 30%) proportion of rearrangement products; and addition of scavengers produced similar effects. Again, no amine formed from denitration of (I) was detected. The proportions of the main rearrangement products are recorded in Table 1: again the 4-isomer was slightly contaminated, and so the percentage of 2-nitro-compound is underestimated.

DISCUSSION

The only previous study[4] of this type of thermal rearrangement led to the proposal of a radical mechanism. However, we have several results which do not support homolysis.

(i) There is no direct evidence for radicals; *viz.*, the e.s.r. measurements, the failure of the reaction to initiate polymerisation, and the ineffectiveness of radical traps such as cyclohexene, *p*-cymene, and toluene. The latter would almost certainly destroy any radicals of more than transient existence generated by the homolysis of (I), with the formation of the readily detectable benzyl radical.

(ii) The 2-nitro-isomer is predominantly formed and the products are similar to those of the acid-catalysed reaction. An intermolecular radical process would be expected (if it could survive in the presence of toluene) to give almost equal quantities of the 2-, 4-, 5-, and 7-nitro-isomers and an intramolecular radical process would give as much of the 5- and 7-isomers as of the 4-isomer; for all these types would probably involve radical pairing at the encounter rate.[1]* An intermolecular process would also give significant amounts of benzidine-like products, and would be largely supressed by the addition of anisole, aniline, *NN*-diethylaniline, or 2,6-dimethylphenol.

(iii) Only a few percent of the reaction led to nitric oxide, formaldehyde, benzoic acid, or benzaldehyde, the known products of attack of nitrogen dioxide on *N*-methyl groups or on toluene.[4] Similarly, little acetaldehyde but rather *C*-nitro-anilines were formed from attack on added *NN*-diethylaniline.

(iv) The rate of decomposition was significantly faster in the more polar media.

The thermal rearrangement of hydrazo-compounds in protic media is considered to be initiated by hydrogen bonding to the feebly basic imino-nitrogen,[7] and thence to simulate an acid-catalysed reaction. Even in aprotic solvents the products are similar to those of the acid-promoted reaction, and the rearrangement, which is intramolecular, is believed to utilise the heterolytic route favoured by acid catalysis.[2] Homolytic reactions typically appear by default under conditions where heterolytic fission is discouraged. As solvation (other than hydrogen bonding to the more basic nitrogen) exerts a minor influence on the formation of the cyclic transition states of the " cartwheel " mechanism favoured for acid-catalysed rearrangement,[8] it seems that heterolysis may not be greatly inhibited in the solvents that we have used, and so homolysis may not be allowed to predominate.

Accordingly, we suggest that rearrangement products from the thermal reaction of (I) may be formed intramolecularly in a manner similar to that proposed for the acid-catalysed reactions; *e.g.*, by a " cartwheel " mechanism. This suggestion is consistent with the observations (i)—(iv) above. The N–N bond in (I) is predisposed to heterolyse to nitrite ion, for by this means the electrons move towards the more electronegative nitrogen atom, and the positive charge which is generated is delocalised into the benzene ring. In acid-catalysed fission, this heterolysis is greatly aided by the bond-weakening due to adjacent-charge repulsion, but its direction is not reversed. At elevated temperatures or under ultraviolet irradiation, the bond will tend to heterolyse in its preferred direction, even in the absence of acid, and the separating fragments can perform concerted cartwheels to the 2- or 4-ring positions. Such a process can occur in protic or aprotic media, but hydrogen bonding to the nitrogen aids the reaction in the former instance, and so the reaction is faster in ethanol or methanol than in toluene, acetone, or methyl cyanide at a particular temperature; but the products of rearrangement are similar in all these media.

As in acid-catalysed processes, the bond-making and -breaking contributing to the cartwheel may become uncoupled and complete heterolyses to a nitrite ion and an aromatic cation may take place. In protic media of high dielectric constant, dissociation and tar formation may occur. In aprotic media of low dielectric constant, such as toluene, the

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* The 2-isomer would be expected to predominate owing to a proximity effect in an intramolecular radical reaction.

[7] H. Shine and J. C. Trisler, *J. Amer. Chem. Soc.*, 1960, **82**, 4054.

[8] D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J.*, 1964, 5349.

lack of solvating power does not affect the progress of the intramolecular rearrangement, but it does prevent dissociation and a caged ion-pair results. This ion-pair probably largely collapses to the 4-nitro-derivative (cf. the facility of 4-substitution in 1-naphthylamine), and the high proportion of 4-isomer and a lack of tar and disproportionation products results, which is alone characteristic of the reaction in toluene. The fate of the expelled hydrogen in this and in the direct rearrangement is obscure.

Nitration of added hydroquinone and anilines is not unambiguous evidence for intermolecular rearrangement,[9] despite an assertion to the contrary.[4] At high temperatures (I) may be directly acting as a nitrating (but not an oxidising) agent towards such susceptible additives.

Our main evidence refers to the thermal reaction, but the photochemical decomposition may proceed similarly. The small difference in products may be due to differences in side reactions or to the different temperatures at which the reactions were conducted. The high proportion of the 2-isomer, the low recovery of rearrangement products and the occurrence of tars in all solvents used, including toluene, could result from extensive ion-pair formation and subsequent escape of the fragments from the solvent cage and reaction with substrate, solvent, or reaction products. All these processes would be favoured, as compared with the thermal rearrangement, by the need to dissipate the excess of energy imported by the captured photons. The consistently higher proportions of 2-isomer in the photochemically induced decomposition in all solvents, as compared with the thermal rearrangement, is also compatible with a facilitated disproportionation of the 2-linked nitrito-intermediate previously postulated for the acid-catalysed rearrangement [8] and now in an energetically excited state. This disproportionation prevents further migration to the 4-position.

A radical-cage process, similar to that proposed for the acid-catalysed rearrangement [10] but rejected on several grounds,[1,8] cannot be excluded for both these types of rearrangements; but the close similarity to the acid rearrangement, and especially points (ii), (iii), and (iv) detailed at the head of this section, cause us to prefer the heterolytic mechanism, especially for the thermal reaction. Greater solvent intervention, especially by toluene, would also be expected in a radical mechanism.

A good case has been made for homolytic processes in the thermal decomposition of *N*-methyl-4,*N*-dinitroaniline, although such fission could lead to the disproportionation products rather than to rearrangement. In this structure, the usual direction of heterolysis of the N–N bond is opposed by the electron-attracting 4-nitro-group, which favours fission to form a nitronium ion. A compromise between these two tendencies could well lead to homolysis of the bond and intermolecular rearrangement (in the melts and solvents used), with the formation of much formaldehyde and nitric oxide. It may be significant that no attempts were made to exclude oxygen and light in these experiments. Studies on the thermal decomposition of hydrazo-compounds show that traces of oxygen initiate homolytic processes,[2] and our experiments using open reaction vessels and melts gave tar and the side products characteristic of radical mechanisms of decomposition.

EXPERIMENTAL

The substrate had been previously prepared,[9] and solvents were purified and dried by standard methods. All glassware was washed with detergent, rather than chromic acid, in order to prevent adventitious introduction of protons.

Products. Solutions for product analysis were immersed in an opaque thermostat bath (dyed with nigrosine) at 100·0° ± 0·2° for 20 hr. Tubes containing the substrate (0·03 g.) in the organic solvent (3 ml.) were degassed by 3 cycles of a previously described vacuum-line procedure [2] and finally sealed under nitrogen. Aliquot portions for ultraviolet irradiation were similarly prepared, placed in a water-cooled quartz chamber at 20°, and exposed to a Mazda

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[9] D. V. Banthorpe, J. A. Thomas, and D. L. H. Williams, *J.*, 1965, 6135.

[10] W. N. White, D. Lazdins, and H. S. White, *J. Amer. Chem. Soc.*, 1964, **86**, 1517.

80-w mercury-vapour lamp, with the glass envelope removed, at a range of 2 ft. for about 6 hr. The described conditions ensured almost 100% decomposition for both thermal and photochemical reactions.

Tars were removed from the reaction products by the previously described [9] paper-chromatographic techniques and the isomer ratios were calculated. Several grades of papers and solvent systems were used, without success, to separate the 4-isomer completely. Large-scale product analyses were carried out by chromatography on alumina (Grade III, Brockmann) with benzene–light petroleum (b. p. 40—60°) mixtures. Scavengers were added at 5—10-molar excesses.

Minor reaction products were detected by removal of oxides of nitrogen, acetaldehyde, and formaldehyde in a stream of nitrogen, steam-distillation to separate benzaldehyde and toluene, and examination of the residue for rearrangement products, benzoic acid, etc., by alkali and acid extraction, and paper chromatography of the fractions. These products were identified by their infrared spectra and by the preparation of appropriate derivatives.

Kinetics. Kinetic tubes were sealed under nitrogen as described, and quenched at appropriate times by cooling to 20°. The optical density was measured at 408 mμ and, since the "infinity" value varied with time, the Guggenheim method was used to calculate rate constants. Results from a typical run are shown: the substrate concentration is $3{\cdot}13 \times 10^{-4}$M.

t (min.)	5	10	15	20	25	30
$\{\text{Log}_{10}(E^{t+\Delta} - E) + 1\}$	1·148	1·042	0·924	0·806	0·676	0·538

E^t and $E^{t+\Delta}$ are the optical densities of the reaction mixture at times t and $(t + \Delta)$ respectively, where $\Delta = 30$ min. A plot of $[\text{Log}_{10}(E^{t+\Delta} - E^t) + 1\}$ *vs.* t was linear, and k_1 was calculated as $(9{\cdot}5 \pm 0{\cdot}3) \times 10^{-4}$ sec.$^{-1}$.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower Street, London W.C.1.

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