Thermal Decomposition of Liquid α-Nitrotoluene

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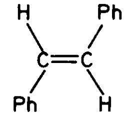
Liquid α-nitrotoluene decomposes on heating into benzonitrile, benzaldehyde, benzaldehyde oxime, oxides of nitrogen, and water. Prolonged heating (over 2 h) at 125 °C leads to *N,N'*-dibenzoyl-*N*-phenylhydrazine, α-nitrostilbene, 3,4,5-triphenylisoxazole, 1,3,5-triphenyl-1,2,4-triazole, 3,5-diphenyl-1,2,4-oxadiazole, benzamide, benzylideneaniline, benzanilide, and *trans*-stilbene. The product distribution depends on the temperature and duration of heating.

Earlier work has shown that when di-t-butyl peroxide is heated with benzyl cyanide at 125 °C for 36 h, both $(\pm)$- and *meso*-1,2-dicyano-1,2-diphenylethane are formed.[1] In an attempt to prepare the analogous dinitroethanes by the peroxide method from α-nitrotoluene, it was found that instead of the expected *meso*- and $(\pm)$-diastereoisomers, a variety of other solid products was formed, mostly those named in the Table. It was suspected that these compounds were formed through the thermal decomposition of α-nitrotoluene itself. Benzaldehyde oxime, benzaldehyde, and benzonitrile have been previously detected [2] as products of electron-impact-induced decomposition when α-nitrotoluene was pyrolysed in the inlet system of a mass spectrometer at 230 °C. Bibenzyl, water, and benzene were also formed, the bibenzyl probably as a result of the catalytic action of a glass surface. When subjected to gas chromatography,[3] α-nitrotoluene showed three peaks, attributable to benzonitrile, benzaldehyde, and α-nitrotoluene itself. The extent of decomposition was dependent on the injector temperature and the contact time.

We have studied the thermal decomposition in greater detail by monitoring the products at intervals when liquid α-nitrotoluene is heated in a sealed system in an oxygen-free atmosphere of argon over an extended period. On prolonged heating at 125 °C an unexpected variety of products is formed.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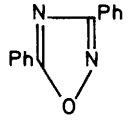
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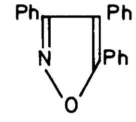
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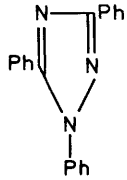
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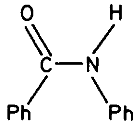
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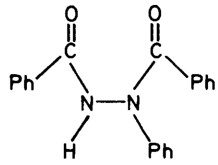
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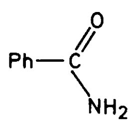
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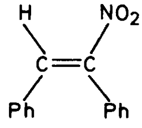
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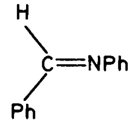
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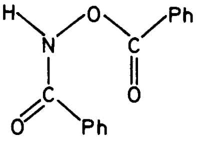
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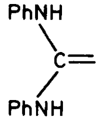
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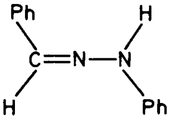
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Experimental

Prolonged heating of α-nitrotoluene at 125 °C (30 h) followed by cooling led to an orange-brown sticky semi-solid. Passage through a column of alumina (Art 1077 neutral; chloroform–hexane as eluant) and recrystallisation with ethanol gave (in order of elution) traces of *trans*-stilbene (1), m.p. 124—125 °C; 3,5-diphenyl-1,2,4-oxadiazole (2), m.p. 107—108 °C (0.2 g); 3,4,5-triphenylisoxazole (3), m.p. 213—214 °C (0.3 g); traces of 1,3,5-triphenyl-1,2,4-triazole (4), m.p. 98—99 °C; benzanilide (5), m.p. 162—163 °C (0.2 g); *NN'*-dibenzoyl-*N*-phenylhydrazine (6), m.p. 177—178 °C (1.8 g); and benzamide (7), m.p. 128—129 °C (0.3 g). About 2 g of water was produced. The compounds isolated as solids were identified with the aid of elemental analysis and mass and n.m.r. spectra, and confirmed by comparing m.p.s and i.r. spectra with those of authentic samples.[4]

Samples of the reaction mixture were withdrawn at various time intervals while the heating progressed and subsequently subjected to g.l.c.–mass spectrometric analysis. Samples withdrawn after 2 h heating revealed five g.l.c. peaks, and corresponding mass spectra with molecular ions of *m/z* 106, 103, 122, 121, and 225. These were shown to be consistent with the presence of benzaldehyde, benzonitrile, benzoic acid, benzamide (7), and α-nitrostilbene (8) by comparison with the mass spectra of authentic samples. The mass spectrum of benzonitrile from the decomposition of α-nitrotoluene showed an ion with *m/z* 119, which we believe was derived from benzonitrile *N*-oxide (PhCNO) formed by the dehydration of α-nitrotoluene during pyrolysis in the mass spectrometer. On cooling samples of the reaction mixture, crystals of *NN'*-dibenzoyl-*N*-phenylhydrazine (6) were deposited.

From samples withdrawn after 5 h, eight g.l.c. fractions were obtained; four of these were identical with those detected earlier, and the other four gave mass spectra with molecular ions of *m/z* 181, 222, 197, and 297. Comparison with the mass spectra of authentic samples established that these were due to benzylideneaniline (9), 3,5-diphenyl-1,2,4-oxadiazole (2), benzanilide (5), and 1,3,5-triphenyl-1,2,4-triazole (4). On cooling the reaction samples, crystals of benzoyl benzohydroxamate (10) and of *sym*-diphenylurea (11) were detected. A summary of the overall results is given in the Table.

Discussion

Initial Products.—Earlier work [2,3] has shown that α-nitrotoluene decomposes initially into water, benzonitrile,

Table. Thermal decomposition of phenylnitromethane at 125 °C

Initial products of decomposition	Products detected after 2 h heating	Additional products detected after 5 h heating	Products isolated as solids/liquids on cooling after 30 h heating
Benzonitrile	Benzonitrile	Benzylideneaniline (9)	*trans*-Stilbene (1)
Nitric oxide	Benzaldehyde	Benzanilide (5)	3,5-Diphenyl-1,2,4-oxadiazole (2)
Water	Benzoic acid	3,5-Diphenyl-1,2,4-oxadiazole (2)	3,4,5-Triphenylisoxazole (3)
Benzaldehyde	Benzamide (7)	1,3,5-Triphenyl-1,2,4-triazole (4)	1,3,5-Triphenyl-1,2,4-triazole (4)
Benzaldehyde oxime	α-Nitrostilbene (8)	Benzoyl benzohydroxamate (10)	Benzanilide (5)
Benzonitrile *N*-oxide (?)	*NN'*-Dibenzoyl-*N*-phenylhydrazine (6) (on cooling)	*sym*-Diphenylurea (11)	*NN'*-Dibenzoyl-*N*-phenylhydrazine (6)
			Benzamide (7)
			Water

benzaldehyde oxime, and benzaldehyde, as well as oxides of nitrogen which dissolve in the water providing the acid conditions which may be necessary for further reaction to give the products obtained. Our experiments show that further reaction takes place to produce the compounds listed in colums 2, 3 and 4 in the Table. Benzonitrile may be formed by direct dehydration of α-nitrotoluene, or partly by dehydration of benzaldehyde oxime as suggested by Allen and Happ[2] and partly from benzonitrile *N*-oxide as suggested by Nibbering and de Boer.[5] Allen and Happ tentatively attributed an ion *m*/*z* 119 observed in the pyrolysis products to *o*-hydroxybenzonitrile. Our g.l.c.–mass spectrometric analysis of the benzonitrile derived from the decomposition of α-nitrotoluene also showed the presence of an ion with *m*/*z* 119 (10%), 103 (80), 77 (72), and 51 (100), in accord with the presence of a small amount of benzonitrile *N*-oxide rather than *o*-hydroxybenzonitrile, formed during pyrolysis in the mass spectrometer. We prefer this interpretation because none of the products (1)—(10) from the decomposition reaction contained an *ortho*-hydroxy group. If benzonitrile *N*-oxide were present as an intermediate, the formation of 3,5-diphenyl-1,2,4-oxadiazole might be explained as from a 1,3-cycloaddition of benzonitrile and benzonitrile *N*-oxide.[6] Benzoic acid must have resulted from the oxidation of benzaldehyde by nitric oxide, and the presence of benzamide is likely to be due to the hydration of benzonitrile.[7]

$$PhCH_2NO_2 \xrightarrow{\text{rearrangement}} PhCONHOH$$

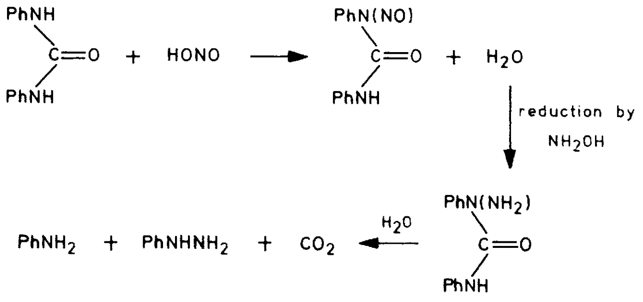
$$PhCONHOH + PhCONHOH \xrightarrow{\text{nitrous acid}} \underset{(10)}{PhCONHOCOPh} + NH_2OH$$

$$PhCONHOCOPh \longrightarrow PhNCO + PhCO_2H$$

$$PhCONHOH \longrightarrow PhNCO + H_2O \longrightarrow PhNH_2 + CO_2$$

$$PhNH_2 + PhNCO \longrightarrow (PhNH)_2CO$$

Scheme 1.



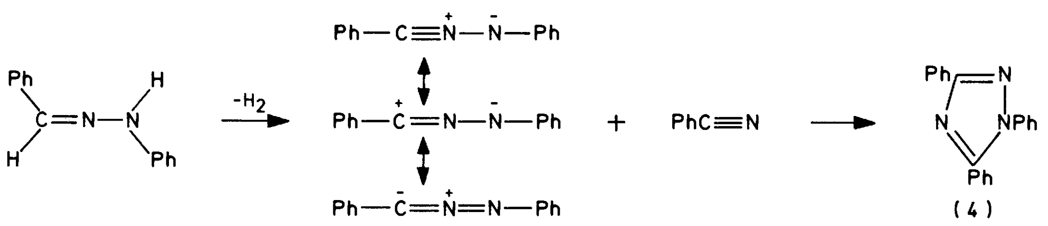
Scheme 2.

Subsequent Products.—One of the intermediate products obtained after heating α-nitrotoluene for some time is benzoyl benzohydroxamate (10).[8] This compound probably plays an important role in determining the subsequent products. Meyer[9] found that heating nitroparaffins with hydrochloric acid in sealed tubes gave hydroxylamine. He correctly surmised that the intermediate was a hydroxamic acid. Support for this comes from the observation that neutral nitromethane, when subjected to u.v. irradiation, rearranges to formohydroxamic acid, while formohydroxamic acid itself, under similar irradiation, partially rearranges to *aci*-nitromethane.[10] In the case of α-nitrotoluene, Bamberger and Rust[11] found that rearrangement to benzohydroxamic acid occurred to the extent of 2%. We may further assume that in the presence of nitrous acid, benzohydroxamic acid then undergoes ' self condensation ' to produce benzoyl benzohydroxamate (10) and hydroxylamine (Scheme 1). When (10) is heated, the Lossen rearrangement[12] takes place giving phenyl isocyanate and benzoic acid. Phenyl isocyanate is also probably formed as an intermediate in the destructive distillation of benzohydroxamic acid to give carbon dioxide and aniline.[13] Thus the presence of phenyl isocyanate would explain the formation of *sym*-diphenylurea (11) in the mixture after it had been heated for some time (Scheme 1). If aniline is formed as an intermediate, the formation of benzylideneaniline (9) by reaction with benzaldehyde is easily understood.

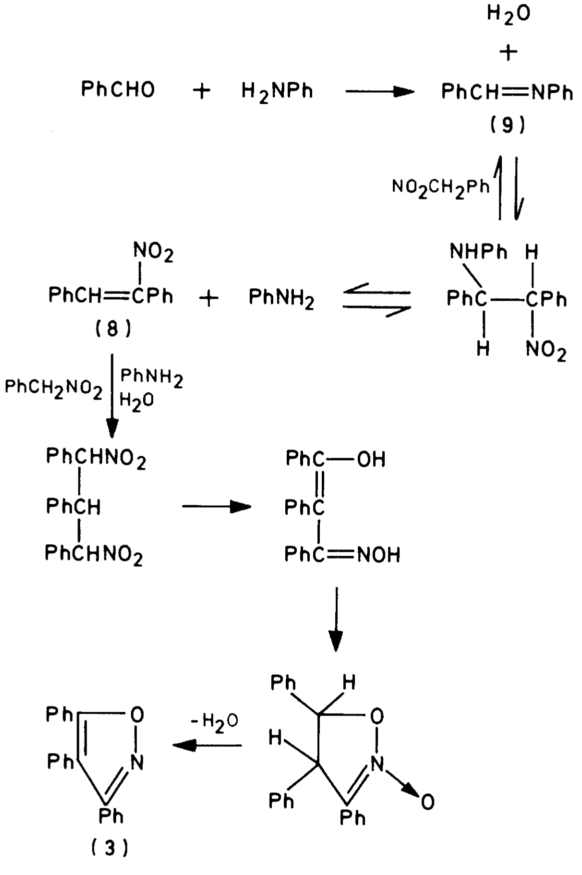
In the presence of nitrous acid and hydroxylamine, *sym*-diphenylurea would yield phenylhydrazine[14] (Scheme 2). This would then react with benzaldehyde in the presence of acid to form benzaldehyde phenylhydrazone (12).

An explanation for the formation of 1,3,5-triphenyl-1,2,4-triazole (4) presents some difficulty. The reaction could involve the 1,3-cycloaddition of a nitrile imine (derived from benzaldehyde phenylhydrazone) and benzonitrile (Scheme 3). This mechanism requires abstraction of hydrogen from benzaldehyde phenylhydrazone, but under the conditions of the experiment it is not clear how this can be achieved.

The mode of formation of *N*,*N'*-dibenzoyl-*N*-phenylhydrazine (6) is also not clear cut. It is possible that during the Lossen rearrangement of benzoyl benzohydroxamate (10), homolytic scission of the central N–O bond occurs, leading to benzoyl radicals before benzoic acid and phenyl isocyanate are formed. Benzoyl radicals react easily with benzaldehyde phenylhydrazone to yield *NN'*-dibenzoyl-*N*-phenylhydrazine.[4a]



Scheme 3.



Scheme 4.

Benzanilide could be formed by the reaction of aniline with benzohydroxamic acid.[15]

The presence of α-nitrostilbene (8) and benzylideneaniline (9) suggests that the formation of 3,4,5-triphenylisoxazole (3) follows the Knoevenagel reaction. According to Robertson,[16] the Knoevenagel reaction of benzaldehyde and α-nitrotoluene, catalysed by a primary amine (aniline in this case) to give (3), may be written as in Scheme 4. Heim [17] and Robertson [16] originally suggested that 3-nitro-1,2,3-triphenylpropene was one of the intermediates of the reaction, but Nielsen and Archibald [18] later showed that this compound was not involved.

Nielsen and Archibald also detected the presence of *trans*-stilbene (1) in repeating the reaction of Heim,[17] and postulated that *trans*-stilbene was formed from nitrostilbene under the conditions present.

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