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Molecular rearrangements, part 33, photolysis and thermolysis of arylnitramines☆

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Abstract

Ultraviolet irradiation of arylnitramines in 2,6-di-*tert*-butylphenol results in the transfer of the nitro group intermolecularly to produce the corresponding 4-nitrophenol together with nitroanilines in addition to oxidation products, diphenoquinone and the diphenolic compounds. Thermolysis of arylnitramines or *N*-alkylarylnitramines at controlled temperatures either alone or in phenolic solvent, produce the corresponding *p*- and/or *o*-nitroanilines together with 4-nitrophenol, diphenoquinone and diphenol in addition to crystals of their dimeric product quinhydrone. No dimerization products of the arylamino radicals are detected. However, evolution of nitrogen, nitrogen dioxide and water drops are detected. Thermolysis of primary arylnitramines in β-naphthol results in separation of free radicals substitution product, 1-arylazo-2-naphthols as major products with evolution of nitrogen dioxide. However, such rearrangement products are not produced with secondary *N*-alkylarylnitramines. Other products of homolytic substitution of halogen by nitro group are identified.

Keywords: *N*-Methyl and arylnitramines; Photo and thermal changes; Tetra-*tert*-butylbiphenol; Diphenoquinone; Quinhydrone; 1-Arylazo-2-naphthols; *ipso*-Substitution

The mechanistic study of *N*-nitroarylamines thermolysis had received less attention than those of acid catalyzed rearrangements [1]. Thermolysis of arylnitramines in fused systems had shown to fragment at faster rates than those of C- and O-nitrocompounds [2]. Thermolysis of *N*-methyl-N, 4-dinitroaniline either alone or in 2,6-dialkylphenol [3], had resulted into homolysis of the nitramine to give *N*-methyl-2,4-dinitroaniline and 4-nitrodialkylphenol. *N*-nitro-1-naphthylamine thermolysis or photolysis in toluene or polar solvents [4] was inferred to undergo heterolytic fission into nitrite anion and arylamino cation. Recent kinetic studies [5], have supported the N–NO_2 bond homolysis of the arylnitramines on thermolysis into the arylamino and NO_2 radicals leading to the rearranged products. Photolysis of the arylnitramines was recently demonstrated to rearrange in neutral solvents [6], which was started by N–NO_2 bond fission into radical pair. The present work throws more light on the mechanistic behavior of *N*-nitroarylamines on their photolysis and thermolysis in dialkylphenol as a reagent sensitive for oxidative species in the medium, together with the aryl substituents effect on the type of products.

Ultraviolet irradiation of the 4-nitro-*N*-nitroaniline and 2,6-di-*tert*-butylyphenol in acetone, give the products, 4-nitro-2,6-di-*tert*-butylphenol, *p*-nitroaniline and 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone. Also, photolysis of the *N*-methyl-4-nitro-*N*-nitroaniline and the dialkylphenol in acetone, separate *N*-methyl-*p*-nitroaniline and 4-nitrodialkylphenol together with the corresponding diphenoquinone (Table 1). In each case, part of the original nitramine has been recovered unchanged. Products of *N*-nitroanilines photolysis under our conditions suggest that the process may be iniated by acetone excited triplet state which undergoes energy transfer to the nitramine that change to its excited triplet state which suffers preliminary homolysis of *N*–NO_2 bond into nitro and arylamino free radical pair in solvent cage. The radicals separated out of solvent cage exert rearrangement and/or oxidation potential on the phenol to separate nitrophenol and arylamine and corresponding diphenoquinone. However, partial reversible recombination of radicals in cage regenerates starting nitramine. Direct excitation of the nitramine by absorption of light followed by homolysis of N–NO_2 bond can not be excluded [6].

$$\mathrm{ArN(NO_2)R} \overset{h\nu}{\leftrightarrows} \underbrace{[\mathrm{ArN^{\bullet}R} + \mathrm{NO_2}]}_{\text{Solvent cage}} \rightarrow \text{products}$$

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Table 1
Products (%) of photolysis of nitramines in acetone (100 ml) together with 2,6-di-*tert*-butylphenol

Nitramines (0.01 mol)	Phenol (mol) irradiation time	a	b	c	Others
1	(0.01) 288 h	11%	2%	5%[a]	Recovered nitramine
2	(0.015) 139 h	15%	N-CH_3-*p*-NO_2-aniline, 20%	1%	Recovered nitramine

Starting nitramine: (**1**) 4-nitro-*N*-nitroaniline; (**2**) *N*-methyl-4-nitro-*N*-nitroaniline. *Products*: (a) 4-nitro-2,6-di-*tert*-butylphenol; (b) 4-nitroaniline; (c) tetra-*tert*-butyl-4,4′-diphenoquinone.

[a] With few crystals of quinhydrone.

On the other hand, thermolysis of the 2,4-dinitro-*N*-nitroaniline **1** with the 2,6-di-*tert*-butylphenol at controlled temperature to overcome side reactions of primary products [7], where nitrogen and nitrogen dioxide are evolved, together with the products, 4-nitro-2,6-dialkylphenol, 2,4-dinitroaniline, 4,4′-dihydroxy-3,5,3′,5′-tetra-*tert*-butylbiphenyl and the corresponding 4,4′-diphenoquinone (Table 2). Thermolysis of the 4-bromo-*N*-nitroaniline **2** with the 2,6-dialkylphenol produce, 4-bromo-2-nitroaniline, 4-nitroaniline, 4-nitrodialkylphenol, 4,4′-dihydroxy-tetra alkylbiphenyl and its corresponding diphenoquinone in addition to few crystals of their condensation adduct, quinhydrone.

Thermolysis of the *N*-methyl-*N*-nitroaniline **3** with the dialkylphenol produce, *N*-methyl-*p*-nitroaniline, 4-nitrodialkylphenol, 4,4′-dihydroxybiphenyl and the corresponding diphenoquinone.

Similarly, heating the *N*-methyl-2,4-dinitro–*N*-nitroaniline **4** with the dialkylphenol, evolves nitrogen and NO_2 in cold trap, and give the products, 4-nitrodialkylphenol, *N*-methyl-2,4-dinitroaniline and tetralkyl diphenoquinone and crystals of quinhydrone. On the other hand, thermolysis of the 4-bromo-*N*-methyl-*N*-nitroaniline **5** in the dialkylphenol produce, *N*-methyl-4-bromo-2-nitroaniline, *N*-methyl-2,4-dinitroaniline, 4-nitrodialkylphenol, 4,4′-tetraalkyldiphenoquinone and crystals of the quinhydrone. It is noteworthy that by using lower temperature for the rearrangements, the yield of the nitrophenolic product increases preferably on the expense of the corresponding diphenol or diphenoquinone (Scheme 1).

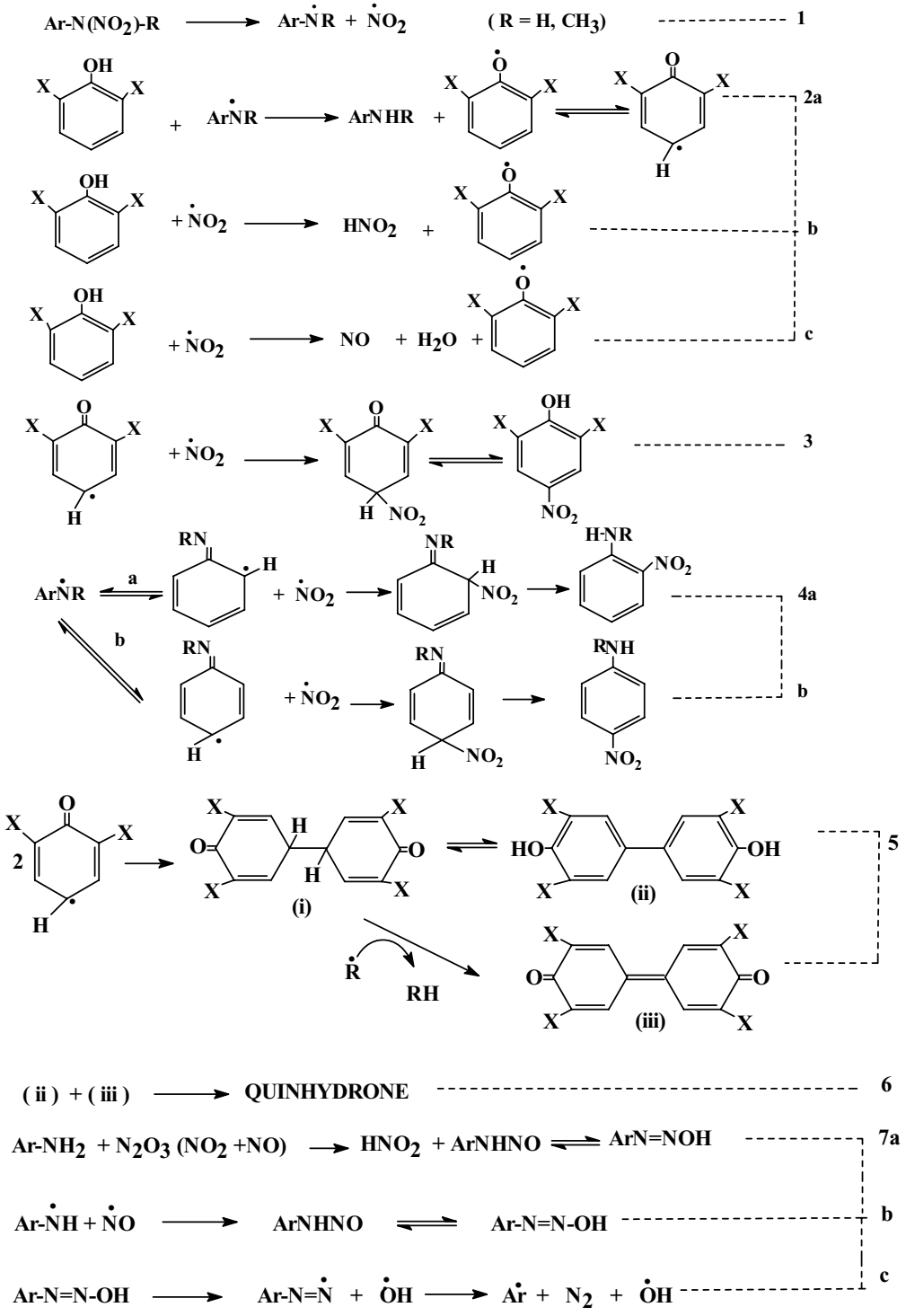
That the *N*–nitro group of the nitramine is transferred to different molecules under suitable conditions strongly suggest that the migration brought about photochemically and thermally is not intramolecular but involves fission of *N*–NO_2 bond into arylamino and nitro radicals [3,5,8]. The later substitute on the aromatic nucleus by intermolecular pathway. Both of nitrogen dioxide and aryl amino radicals effect oxidative hydrogen abstraction from the phenolic nucleus to produce, arylamine and nitrous acid in addition to phenoxy radical intermediates. The major reaction processes can be summarized by Eqs. (1)–(6). Such mechanism have to be expected on the bases of relative stabilization energy of radicals Ph $N^{\bullet}H$ and Ph $N^{\bullet}CH_3$ being calculated of the order 56.7 and 55.8 kcal/mol, respectively [9]. Hydrogen abstraction by arylamino radical is considered as the main course of the reaction since most of the nitro groups are coupled with the phenoxy radicals. The rearrangement of nitramine to nitroaniline at 4- or 2-positions may proceed through intermolecular pathway in which phenoxy radicals competes with mesomeric 4- and 2-aminoaryl radicals in coupling with NO_2. An alternative unfavorable suggestion is that the hydrogen abstraction from phenol may be effected by nitrous acid byproduct to separate nitric oxide, water and phenoxy radical. Such assumption is considered as a minor path, where nitric oxide should be consumed in side reactions and where absence of any nitrosation products is a clue for that fact. Production of dihydroxybiphenyl may be generated from dimerization of resonance *p*-hydroxyphenyl radical into the intermediate, 1,1′-dihydrodiphenoquinone (i) which either isomerise to the corresponding dihydroxy biphenyl (ii) and/or preferably suffer dehydrogenation by radicals and oxidative species in the medium into the corresponding diphenoquinone(iii) [3] Eq. (5). Existence of both of arylamino and aryloxy radicals in reaction pathway are proved in other homolysis reactions by ESR studies [10]. There is no evidence for dimerization of anilino radicals, due to instability of probable N–N dimer formation under experimental conditions used [10]. Also, it was recorded that acetylamino radicals (Ar-$N^{\bullet}$COR) do not dimerize into hydrazine derivatives but preferably attack on carbon to generate C–N bonded compounds [11].

Heating the 2,4,6-trichloro-*N*-nitroaniline **6** at controlled temperature, with di-*tert*-butylphenol under nitrogen atmosphere, nitrogen gas is evolved and collected together with water drops, in cold traps, ethanol/carbon dioxide and liquid nitrogen respectively, in addition to the main products, 2,4,6-trichloroaniline, 4-nitro-2,6-di-*tert*-butylphenol and low yield of diphenoquinone. In order to study the nature and quantity of gases evolved in nitramine thermolysis, a control experiment is performed in which the 2,4,6-trichloro-*N*-nitroaniline is heated with the dialkylphenol in an atmosphere of carbon dioxide and the evolved gases are collected in azotemeter containing potassium hydroxide solution (30%). Assuming that one mole of nitramine gives one mole of nitrogen, the results obtained show that the gas ratio evolved to be in the range of (0.14%) yield. Similarly, thermolysis of the 2,4,6-trichloro-*N*-methyl-*N*-nitroaniline **7** with di-*tert*-butylphenol at the same above conditions, no water is separated and the only gas evolved is nitrogen, which is collected in liquid nitrogen trap, up to (0.05%) yield, together with the main products, 4-nitrodialkylphenol and recovered starting nitramine, however, without formation of diphenol nor diphenquinone. In other control experiment, the 2,4,6-trichloro-*N*-nitroaniline **6** (0.02 mol) is

Table 2
Thermolysis products (%) yield

Nitramine (mol)	Phenol (mol, temperature °C) time	a	b	c	d	e	f	Gases ix	Tar residue
1 (0.01)	(0.025, 200 °C) 2 h	60%	–	2,4-di-NO_2, 55% (i)	1%	4%	–	$N_2 + NO_2$	4%
2 (0.01)	(0.025, 125 °C) 1 h	45%	2-NO_2-4-Br, 17% (iii)	*p*-NO_2, 4% (ii)	2%	4%	0.4%	$N_2 + NO_2$	6%
3 (0.01)	(0.025, 130 °C) 1 h	40%	–	N-CH_3-*p*-NO_2, 35% (iv)	2%	6%	0.53%	$N_2 + NO_2$	4%
4 (0.01)	(0.025, 130 °C) 3 h	50%	–	N-CH_3-2,4-di-NO_2, 30% (v)	1.5%	4%	0.6%	$N_2 + NO_2$	3.5%
5 (0.01)	(0.025, 130 °C) 1 h	40%	N-CH_3-2-NO_2-4-Br, 20% (vi)	N-CH_3-2,4-di-NO_2, 3% (v)	2%	5%	0.4%	$N_2 + NO_2$	3%
6 (0.01)	(0.025, 150 °C) 1 h	82%	–	2,4,6-tri-Cl_3, 30% (vii)	–	0.5%	–	N_2 only 0.14% + H_2O drops (x)	4%
7 (0.01)	(0.025, 140 °C) 1 h	40%	–	–	–	–	–	N_2 only	viii + 2%

Starting nitramines: (**1**) 2,4-dinitro-*N*-nitroaniline; (**2**) 4-bromo-*N*-nitroaniline; (**3**) *N*-methyl-*N*-nitroaniline; (**4**) *N*-methyl-2,4-dinitro-*N*-nitroaniline; (**5**) 4-bromo-*N*-methyl-*N*-nitroaniline; (**6**) 2,4,6-trichloro-*N*-nitroaniline; (**7**) 2,4,6-trichloro-*N*-methyl-*N*-nitroaniline. *Products*: (a) 4-nitro-2,6-di-*tert*-butylphenol mmp. 176–178 °C. MS: $m/z = 251$ (M^+); (b) 2-nitroaniline, mmp.75–76 °C; IR (KBr) cm^{-1}, 3480, 3340 (NH_2), 1490, 1370(C–NO_2); 1,2-nitrophenylazo-2-naphthol; Brown crystals (pyridine), mmp. 213 °C; (c) 4-nitroaniline; Brownish crystals, mmp. 149 °C, IR (KBr) cm^{-1}, 3480, 3350 (NH_2), 1500, 1350 (C–NO_2); 1-4-nitrophenylazo-2-naphthol, mmp. 259 °C; MS *m/z* 293 (M^+); (d) 4,4′-dihydroxy-3,5,3′,5′-tetra-*tert*-butylbiphenyl, mmp. 187 °C. MS: $m/z = 410$ (M^+); (e) 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone, mmp. 249.5 °C. MS: $m/z = 408$ (M^+); (f) quinhydrone, mmp. 223 °C. (dimeric adduct of diphenol and diphenoquinone, experimental section); (g) *byproducts separated*: (i) 2,4-dinitroaniline, mmp. 180 °C; IR (KBr) cm^{-1}, 4410, 3400 (NH_2), 1500, 1340 (C–NO_2); (ii) 4-nitroaniline, mmp.148–149 °C; (iii) 4-bromo-2-nitroaniline; Orange crystals (pet-ether (60–80)), mmp. 112 °C. IR (KBr) cm^{-1}, 3470, 3400 (NH_2), 1500, 1360 (C–NO_2); (iv) *N*-methyl-4-nitroaniline, mmp.154.5 °C. IR (KBr) cm^{-1}, 3350 (NH_2), 1570 (C–NO_2); (v) *N*-methyl-2,4-dinitroaniline, mmp. 179.5 °C. IR (KBr) cm^{-1}, 3350 (NH), 1470, 1330 (C–NO_2); (vi) *N*-methyl-4-bromo-2-nitroaniline, mmp. 97.5 °C; (vii) 2,4,6-trichloroaniline mmp. 75 °C, *N*-formanilide: White crystals (ethanol), mmp. 180 °C, IR (KBr) cm^{-1}, 3200 (NH), 1653 (C=O). Anal. Calcd. for: $C_7H_4Cl_3NO$: C, 37.4; H, 1.8; Cl, 43.7, N, 6.2; Found: 37.5; H, 2.03; Cl, 43.97; N, 6.3%; (viii) recovered original nitramine **7** in high percent + nonresolvable tar; (ix) NO_2 brown gas give (+ve) brucine test [29a] and (−ve) no decolourization of acid $KMnO_4$; NO is absent since no decolourization of acidic $KMnO_4$ [28] is observed. Nitrogen gas collected was identified by GLC. (x) H_2O drops gave orange-red colour with 1% dry dioxan + dipicrylamine test (+ve) [29b].



Scheme 1.

heated in dry dodecane (20 ml), where 2,4,6-trichloroaniline is produced and the gas evolved is collected in liquid nitrogen trap and identified as nitrogen only up to (0.45%). However, heating the 2,4,6-trichloro-*N*-methyl-*N*-nitroaniline **7** under the above same conditions gives only nitrogen gas (0.25%). However, both of the above two experiments are not processed further. Formation of nitrogen gas and water byproducts from primary arylnitramines rearrangement favour the assumption that diazocompound intermediate must be formed as precursor [12]. These may be rationalized to be formed through different paths, for less extent by coupling of primary arylamino radical with trace of nitric

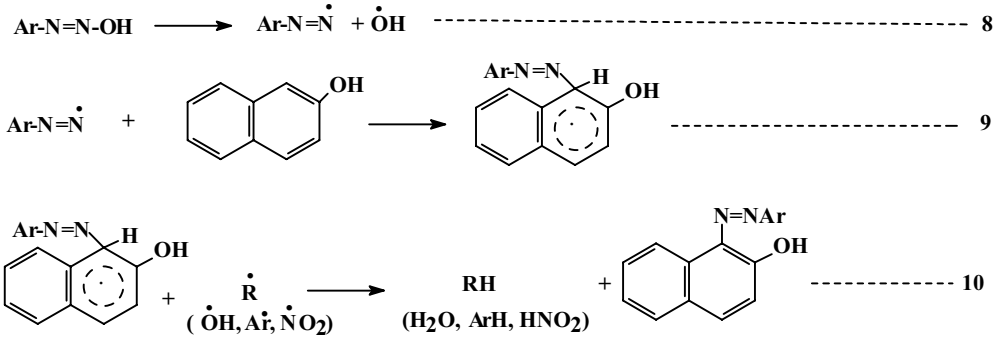
Table 3
Thermolysis products of nitramine in β-naphthol (yield %)

Nitramine (mol)	β-Naphthol (mol, temperature, h)	Yield (%)	Gas	Others
4-Nitro-*N*-nitroaniline (0.005)	(0.05 mol, 120 °C) 2 h	1,4-Nitrophenyl-azo-2-naphthol (39%)	NO_2	Excess β-naphthol + Tar
2,4-Dinitro-phenyl-*N*-nitroaniline (0.01)	(0.05 mol, 145 °C) 2 h	1,2,4-Dinitrophenyl-azo-2-naphthol (40%)	NO_2	Excess β-naphthol + Tar
2,4,6-Trichloro-*N*-nitroaniline (0.01)	(0.05 mol, 140 °C) 2 h	1,2,4,6-Trichlorophenyl-azo-2-naphthol (85%)	NO_2	Excess β-naphthol + Tar
2,4,6-Trichloro-*N*-methyl-*N*-nitroaniline (0.01)	(0.05 mol, 185 °C) 1.5 h	Negative	NO_2	Excess β-naphthol + Tar

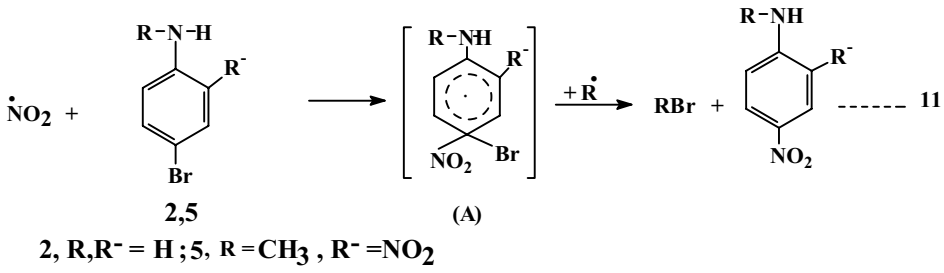
oxide Eq. (7b), however, most favorably by oxidative disproportionation of dinitrogen trioxide and primary arylamine, where the intermediate *N*-nitrosophenylnitramine tautomerize to its isomeric aryldiazonium hydroxide Eq. (7a), which at thermal conditions used undergoes homolytic fission into hydroxyl and arylazo radicals. The arylazo radical will subsequently decompose thermally into nitrogen molecule and aryl radical [13] Eq. (7c). The aryl radicals interfere in side radical reactions. The hydroxyl radicals abstract hydrogen to generate water molecules.

On the other hand, the above assumptions can not explain the formation of nitrogen gas from pyrolysis of the *N*-methyl-*N*-nitroanilines. The only acceptable rationalization [6] is the aryl radical catalyzed disproportionation of nitric oxide to give nitrogen gas and nitrogen dioxide. However, separation of nitric oxide is not a general path since neither of nitrosoarylamine nor 2,6-dialkyl-1,4-benzoquinone-4-oxime [7] are detected under our experimental conditions. On the other hand, thermolysis of each of the nitramines 4,6 and the 4-nitro-*N*-nitroaniline in β-naphthol, give rise to nitrogen dioxide only in addition to the corresponding 1-arylazo-2-naphthol as the only product together with excess β-naphthol and tar residue. However, on thermolysis of the 2,4,6-trichloro-*N*-methyl-*N*-nitroaniline **7** in β-naphthol, there is no production of azodye, but tary residue and trace nitrogen dioxide (Table 3). β-Naphthol differs from 2,6-di-*tert*-butylphenol in that the former is not nitrated by nitrogen dioxide while the later do not couple with diazo compounds [14]. Separation of 1-arylazo-2-naphthols in good yields from the primary *N*-nitramines under our, non-ionic, non-polar, but at free radical conditions, may be suggested to be proceeded by radical substitution of the arylazoyl radical on the highly electron rich 1-center of 2-naphthol molecule followed by hydrogen atom abstraction from the resonance stabilized benzohydroxycylohexadienyl radical intermediate [15a], Eqs. (8)–(10). In favour of such assumption is the absence of 2,2′-dinaphthol byproduct from any probable hydrogen abstraction-coupling processes [15b] (Scheme 2).

Formation of displacement product of the *p*-bromo substituent by the nitro group during thermolysis of the 4-bromo-*N*-nitroaniline **2** with the dialkylphenol where 4-nitroaniline (4%) is separated. On the other hand, thermolysis of the 4-bromo-*N*-methyl-*N*-nitroaniline **5** with the dialkylphenol gives *N*-methyl-2,4-dinitroaniline (3%) byproduct. Separation of such substitution byproducts on thermolysis under our free radical conditions, although of low yields, however they are of mechanistic importance. In both nitramines, the bromine atom is resident at para-position to the amino group and also in the second nitramine is meta to nitro group. The major reaction condition is non ionic and absence of polar solvents. Consequently, the mechanism cannot be considered to constitute paths of nucleophilic substitution [16] nor an electron transfer and halogen ion expulsion from arene radical anion [17]. The most acceptable mechanism for that thermal radical substitution of the bromine atom by the nitro group, from each of the



Scheme 2.



Scheme 3.

4-bromoaniline and the 4-bromo-*N*-methyl-2-nitroaniline although at low yield, it may be rationalized to go through homolytic ipso substitution reaction where the nitrogen dioxide radical attacks the ring at the highly electron deficient carbon center attached to the highly electronegative bromine atom leading to the cyclohexadienyl radical σ complex intermediate (A) [13,18], which is stabilized by electron donating *p*-amino or *N*-methyl-*p*-amino group to the ring substitution center. Abstraction of the bromine atom from the intermediate radical (A) by radicals will separate the final *p*-nitro substitution products, Eq. (11) (Scheme 3).

The fate of the hydroxyl radical Eqs. (7c) and (8) is abstraction of hydrogen atom from any hydrogen donor to produce the water molecules which are collected in ethanol/carbon dioxide trap in a control experiment.

1. Experimental

Melting points were obtained with a hot-stage apparatus calibrated with known samples. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model SP8000. GLC was carried out on a Perkin-Elmer, Gas chromatograph, Sigma 3B, equipped with thermal conductivity detector, and argon gas carrier, and using a i.d. 3Q × 3 mm column packed with molecular sieve 5A (60–80 mesh). TLC was carried out on glass plates covered with silica gel (100–150 mesh) and eluted with ether/benzene (1:1, v/v) or petroleum ether (60–80) or (40–60). Column chromatography was carried out using silica gel (100–150 mesh), (80–120 mesh) or Merck Kieselgel 60, 0.040–0.063 nm (230–400 mesh ASTM) with benzene as solvent. Mass spectral determination of some products was carried out on a Hitachi RMU 6E mass spectrometer and by a high resolution double focusing mass spectrometer, model MS-902 made by AET, UK.

Ultraviolet irradiation was carried out in an immersion well using Hanovia high pressure mercury lamp 700 W with water cooling jacket. All experiments were flushed with nitrogen before proceeding. All products were identified by elemental analyses, TLC, IR, H NMR, MS, and mixed m.p. with authentic samples whenever possible and summarized in Tables 1–3.

1.1. Photolysis of the arylnitramines

A solution of the nitramine (0.01 mol) and 2,4-di-*tert*-butyl-phenol (0.015 mol) in acetone (100 ml) was irradiated under nitrogen atmosphere for periods of 228 h (nitramine) and 139 h (*N*-methylnitramine) at room temp (25 °C). The acetone was evaporated and the residue dissolved in ether/benzene mixture (v/v). Extraction with dilute sodium hydroxide (2N) gave on acidification a precipitate from which some original nitramine was extracted. Recrystallization of the precipitate from ethanol gave 4-nitrodialkylphenol up to 15%. Extraction with dilute hydrochloric acid and neutralization, where solid was separated which on crystallization gave the corresponding nitroaniline. Evaporation of ether/benzene solvent gave a brownish solid, part of which was recrystallized from glacial acetic acid to separate 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone.

The remaining part was solvated in pet-ether (60–80) and eluted by column chromatography on silica gel (100–150 mesh), where the corresponding nitroaniline was collected together with few crystals of diphenoquinone. The results are summarized in Table 1.

1.2. Thermolysis of the nitramines in 2,6-di-tert-butylphenol: general procedure

The nitramine (0.01 mol) and 2,6-di-*tert*-butylphenol (0.025 mol) were heated together under nitrogen atmosphere for time range, 1–2 h. The gases evolved were collected from outlet into cold traps, ethanol/carbon dioxide and liquid nitrogen successively, where nitrogen was confirmed by GLC, and nitrogen dioxide by passing in sodium hydroxide solution 30%. The dark mixture was steam distilled to recover excess 2,6-di-*tert*-butylphenol. The residue was dissolved in ether and extracted with, (a) dilute sodium hydroxide solution (2N), (b) dilute hydrochloric acid (33%, v/v). The alkali extract gave on acidification, yellow crystals of 4-nitro-2,6-di-*tert*-butylphenol, m.p. 157.5 °C. Neutralization of the acid extract followed by ether extraction gave the corresponding substituted arylamines. Evaporation of the original ether solution gave black tar residue. Some of the tar residue was boiled with water and filtered, the aqueous solution extracted with ether, which was evaporated and the solid residue crystallized from proper solvent to separate

the corresponding nitroaniline. The tar residue was extracted with petroleum ether (60–80) and chromatographed over silica gel (80–120 mesh) and eluted with petroleum ether (60–80). One fraction was collected and evaporated to separate yellow crystal from ethanol which was identified as 3,5,3′,5′-tetra-*tert*-butyl-4,4′-dihydroxybiphenyl mmp. 187.5 °C. In some experiments, on evaporation of the mother liquor from the above crystallization gave few crystals of quinhydrone, as purple black crystals (glacial acetic acid), mmp. 222–224 °C, which on reduction with sodium hydrosulphite, the only product separated was the dihydroxy-tetra-*tert*-butylbiphenyl as confirmed with reference sample on TLC plates (24–40 mesh), spectral and mmp. A second column chromatograph fraction was evaporated and the residue was crystallized from glacial acetic acid into brown crystals of 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone mmp. 249–250 °C. More crystals of nitroaniline were collected on evaporation of last fraction. All experimental results summarized in Table 2.

1.3. Thermolysis of the nitramines in β-naphthol

The nitramine (0.01 mol) and β-naphthol (0.05 mol) were heated in an oil bath, where nitrogen dioxide was evolved and heating continued at 140 °C for 2 h. The residue was crystallized from proper solvent to separate the corresponding 1-ary-azo-2-naphthol in high yield, which was characterized by its mmp. and spectral analysis with authentic samples. Acidification of alkaline extract, recovered excess β-naphthol . There was left non-resolvable black tar (Table 3).

1.4. Quantitative measures of gas evolved

The nature and quantity of gases evolved in the thermal decomposition of 2,4,6-trichlorophenylnitramine in 2,6-di-*tert*-butylphenol was carried out in an atmosphere of carbon dioxide and the evolved gases were collected in an Orsat azotometer fitted with three absorption pipettes, containing; ferrous sulphate solution (for nitric oxide), alkaline pyrogallol solution (for oxygen) and sodium hydroxide solution (30%) (for carbon dioxide and nitrogen dioxide), and remaining nitrogen gas was confirmed by GLC.

1.5. Preparation of reference compounds

- 4-Nitro-*N*-nitroaniline [27]: Yellow crystals (benzene), m.p. 114.5 °C. IR (KBr) cm^{-1}, 3312 (NH), 1510, 1375 (C–NO_2), 1600, 1280(N–NO_2) ^{1}H NMR ($CDCl_3$): δ = 9.5 (s, 1H, NH), 7.4–7.9 (m.4H, ArH). Anal. Calcd. for $C_6H_5N_3O_4$: C, 39.3; H, 2.7; N, 22.97; Found: C, 39.5; H, 2.82; N, 22.8%.
- 2,4-Dinitro-*N*-nitroaniline: Yellow needles (ethanol), m.p. 104 °C ([19], m.p. 104 °C). IR (KBr) cm^{-1}: 3310 (NH), 1470, 1370 (C–NO_2), 1560, 1320 (N–NO_2).
- 4-Bromo-*N*-nitroaniline: Pale pink crystals (benzene/pet. ether (60–80)), m.p. 104 °C (dec.). IR (KBr) cm^{-1}, 3305 (NH), 1570, 1330 (N–NO_2). ^{1}H NMR ($CDCl_3$): δ = 9.64 (1H, NH), 7.8–8.6 (m, 4H, ArH). MS: m/z = 217 (M^+). Anal. Calcd. for, $C_6H_5BrN_2O_2$: C, 33.2; H, 2.3; Br, 36.8; N, 12.9; Found: C, 33.1; H, 2.7; Br, 37.1; N, 13.12%.
- *N*-Methyl-*N*-nitroaniline: Yellow crystals (pet-ether (40-60)), m.p. 39.5–40 °C ([6], m.p. 39 °C).
- *N*-Methyl-4-nitro-*N*-nitroaniline: Yellow crystals (ethanol), m.p. 140 °C (dec.) ([6], m.p. 138–139 °C).
- *N*-Methyl-2,4-dinitro-*N*-nitroaniline: Yellow crystals (ethanol), m.p. 116 °C ([21], 114.5–116 °C). IR (KBr) cm^{-1} 1520, 1330 (C–NO_2), 1600, 1257 (N–NO_2). ^{1}H NMR ($CDCl_3$): δ = 3.5 (s, 3H, CH_3) 8.2–8.8 (m, 3H, ArH).
- 4-Bromo-*N*-methyl-*N*-nitroaniline: White crystals (pet-ether (60–80)), m.p. 86–87 °C ([20], m.p. 84.5–85 °C).
- 2,4,6-Trichloro-*N*-nitroaniline: White needles (chloroform/pet-ether (60–80)), m.p. 134 °C (dec.) ([22], m.p. 135 °C). IR (KBr) cm^{-1} 3310 (NH), 1550, 1320 (NO_2). ^{1}H NMR (DMSO-d_6): δ = 7.2 (s, 2H, ArH), 9.35 (s, 1H, NH).
- 2,4,6-Trichloro-*N*-methyl-*N*-nitroaniline: separated by methylation of 2,4,6-trichloro-*N*-nitroaniline, with dimethylsulphate in sodium bicarbonate solution. White needles (ethanol), m.p. 88 °C. IR (KBr) cm^{-1} 1550, 1250 (NO_2). ^{1}H NMR (DMSO-d_6): δ = 3.4 (s, 3H, CH_3), 7.1 (s, 2H, ArH), MS: m/z = 256 (M^+). Anal. Calcd. for, $C_7H_5Cl_3N_2O_2$: C, 32.9; H, 2.0; Cl, 41.7; N, 10.9; Found: C, 32.68; H, 2.21; Cl, 42.0; N, 11.16%.
- 2,4-Dinitroaniline: Brown crystals (aqueous acetic acid), m.p. 180 °C ([25], m.p. 179–180 °C).
- 4-Bromo-2-nitroaniline: Orange brown crystals (aqueous acetic acid), m.p. 111–112 °C ([25], m.p. 109 °C).
- *N*-Methyl-4-nitroaniline: Yellow crystals (glacial acetic acid), m.p. 154 °C ([3], m.p. 150–151 °C).
- *N*-Methyl-2,4-dinitroaniline: Orange yellow crystals (glacial acetic acid), m.p. 180 °C ([3], m.p. 174–175 °C).
- *N*-Methyl-4-bromo-2-nitroaniline: Orange needles (pet-ether (60–80)), m.p. 97.5–98 °C. IR (KBr) cm^{-1}, 3350 (NH), 1520, 1330 (C–NO_2). ^{1}H NMR ($CDCl_3$): δ = 3.36 (s, 3H, CH_3), 7.47–8.1 (m, 4H, ArH). MS: m/z = 231 (M^+). Anal. Calcd. for, C_7 H_7 BrN_2O_2: C, 36.4; H, 3.0; Br, 34.6; N, 12.1; Found: C, 36.1; H, 3.16; Br, 34.82; N, 12.23%.
- 4-Nitro-2,6-di-*tert*-butylphenol: Yellow crystals (ethanol), m.p. 157.5–158 °C (dec.) ([7], m.p. 157.5 °C).
- 4,4′-Dihydroxy-3,5,3′,5′-tetra-*tert*-butylbiphenyl: Yellow orange needles (ethanol), m.p. 187.5 °C) ([24], 185 °C).
- 3,5,3′,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone: Redish brown needles (glacial acetic acid), m.p. 250 °C ([24], m.p. 244–246 °C).
- Quinhydrone (dimeric adduct of tetra-*tert*-butyl-4,4′-diphenoquinone and corresponding 4,4′-dihydroxy biphenyl): separated by dissolving equal weights of diphenoquinone and the diphenol in glacial acetic acid at 90 °C. Purple

black needles (glacial acetic acid), m.p. 223–225 °C. IR (KBr) cm^{-1}, 3820 (OH), 1770, 1740 (C=O). ^1H NMR (DMSO-d_6): $\delta = 1.21$ (s, 36H, $12CH_3$), 1.38 (s, 36H, $12CH_3$), 5.22 (s, 2H, 2OH, exchangeable with D_2O), 6.5–7.4 (m, 8H, ArH). Anal. Calcd. for, $C_{56}H_{82}O_4$: C, 82.2; H, 10.0; Found: C, 82.31; H, 9.9%.

- 1-4-Nitrophenylazo-2-naphthol: Dark reddish crystals (glacial acetic acid), m.p. 259 °C ([23], m.p. 258–259 °C).
- 1-2,4-Dinitrophenylazo-2-naphthol: Rust colourless crystals (pyridine), m.p. 325 °C ([26], m.p. 302 °C). IR (KBr) cm^{-1}, 3470 (OH). MS: $m/z = 338$ (M^+).
- 1-2,4,6-Trichlorophenylazo-2-naphthol: Orange red needless (glacial acetic acid), m.p. 151.5 °C ([22], m.p. 146 °C). IR (KBr) cm^{-1}, 3530, 3410, free and associated (OH). ^1H NMR (DMSO-d_6): $\delta = 5.61$ (s, 1H, OH, exchangeable with D_2O), 7.2–8.5 (m, 10H, ArH). MS: $m/z = 351$ (M^+). Anal. Calcd. for, $C_{16}H_9Cl_3N_2O$: C, 54.6; H, 2.6; Cl, 30.6; N, 8.0; Found: C, 54.42; H, 2.8; Cl, 30.41, N, 8.27%.

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