JOC *Article*

Molecular Rearrangement. 36. Selective α-CH Oxidation of Alkylarenes by Nitrogen Dioxide on Thermolysis with Nitramines

Mahmoud Z. A. Badr

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

m.z.badr@acc.aun.edu.eg

Received April 16, 2004

Thermolysis of 2,4,6-trichloro-*N*-nitroaniline **1** and *N*-methyl-2,4-dinitro-*N*-nitroaniline **2** each with primaryl alkylbenzenes led to the formation of acylbenzenes. Similar reactions with secondary alkylbenzenes afforded a mixture of acetophenone and aliphatic aldehydes. Use of *tert*-butylbenzene in this reaction yielded formaldehyde and 2,3-diphenyl-2,3-dimethylbutane. The mechanisms of the studied reactions are discussed.

Introduction

A literature search reveals that photooxidation of various organic compounds with nitrogen dioxide has attracted the interest of several research groups. For example, photolysis of *N*,*N*-dimethylaniline with nitrogen dioxide was reported to result in photooxidative dealkylation and the formation of *N*-methylformanilide.[1] Alcohols were also reported to undergo photooxidation when photolyzed with nitro compounds.[2] Furthermore, photoexcited nitro compounds caused α-carbon oxidation of *N*-alkylarylamines into the respective *N*-formanilide and other oxidiation products.[4] The rate of abstraction of hydrogen from hydrocarbons with nitrogen dioxide was also reported.[3] In addition, dialkyl sulfide and dialkyl disulfides were reported to undergo photooxidation upon photolysis with nitrogen dioxide in air to yield the respective sulfoxides.[5] Photooxidation of alkanes with nitrogen dioxide resulted in β-oxidation and formation of aldehydes and ketones.[6]

Here, we report the results of the study of thermolysis of primary, secondary, and tertiary alkylbenzenes with *N*-nitroarylamines. The main objective of such a study is to shed some light on the mechanism of thermal oxidation of alkylbenzenes and to elucidate the effect of structure on it.

Results and Discussion

Thermolysis of 2,4,6-trichloro-*N*-nitroaniline **1** with *N*,*N*-dimethylaniline gave a mixture of 2,4,6-trichloroaniline, *N*-methyl-*N*-nitrosoaniline, *N*-methylaniline, and formaldehyde together with nitrogen and nitric oxide gases. Thermolysis of the *N*-methyl-2,4-dinitro-*N*-nitroaniline **2** with *N*,*N*-diethylaniline yielded *N*-ethylaniline, *N*-methyl-2,4-dinitroaniline, acetaldehyde, and nitric oxide. The formation of these products may result via homolysis of the N−N bond in arylamino and nitrogen dioxide radical pairs[7-9] which lead to oxidation of the molecules in the medium.

In an earlier paper, it was indicated that production of carbonyl compounds upon thermolysis of *N*-alkyl-*N*-nitroanilines, proceeds through the intermediate *N*-arylimine which suffered hydrolysis on workup or by water byproduct in the course of reaction to produce parent aniline and aldehyde.[7]

As in the present studied reactions no water was produced, it is not unreasonable to suggest that nitrogen dioxide radicals oxidize selectively on the *N*-alkyl or alkyl groups of the arene systems to afford the carbonyl compounds produced.

The carbonyl compounds formed by thermolysis of both of *N*,*N*-dimethyl- and *N*,*N*-diethylanilines with *N*-nitroanilines must follow a pathway different from that reported before.[7] Both the aryl amino and nitrogen dioxide radicals as oxidative species abstract α-hydrogen from *N*,*N*-dialkylaniline to give *N*-alkyl-*N*-arylalkyl radical, which couple with nitrogen dioxide to give the intermediate aryl-*N*-α-nitroalkane. The latter isomerize to the respective alkyl nitrite.[10-13]

Alternatively, coupling of the α-alkyl radical with nitrogen dioxide may give directly the α-alkylnitrite

---

(1) Döpp, D.; Heufer, J. *Tetrahedron Lett.* **1982** *33*, 1553. Dopp, D.; Heufer, J. *J. Photochem.* **1986**, *32*, 243.

(2) Rees, Y.; Williams, G. H. *Adv. Free Radical Chem.* **1969**, *3*, 199.

(3) Denisov, E. T.; Derisova, T. G.; Geletii, V. Yu.; Balavouane, J. *Kinet. Catal.* **1998**, *39* (2), 312.

(4) Takami, M.; Matsuura, T.; Saito, I. *Tetrahedron Lett.* **1974**, (8), 661.

(5) Martinez, E.; Albuladejo, J.; Jimenez, E.; Notario, A.; Aranda, A. *Chem. Phys. Lett.* **1999**, *308*, 37.

(6) Otsuka, K.; Takahashi, R.; Yamanaka, I. *J. Catal.* **1999**, *185*, 182.

(7) Barnes, J.; Hickinbottom, W. J. *J. Chem. Soc.* **1961**, 2616; Naud, D. L.; *J. Chem. Soc., Perkin Trans. 2* **1996**, 1321.

(8) (a) Badr, M. Z. A. *J. Photochem. Photobiol.* **2004**, *132*, 163. (b) Gowenlock, B. B.; Pfab, J.; Young, V. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 915. (c) Naud, D. L.; Brower, K. R. *J. Org. Chem.* **1992**, *57*, 3303.

(9) Solovskii, D. *Catal. Rev. Sci. Eng.* **1990**, *32*, 1. Cavani, F. C.; Trifiro, F. *Stnd. Sci. Catal.* **1997**, *110*, 19.

(10) Dewar, M. J. S.; Ritchie, J. P. J. *Org. Chem.* **1985**, *50*, 1031.

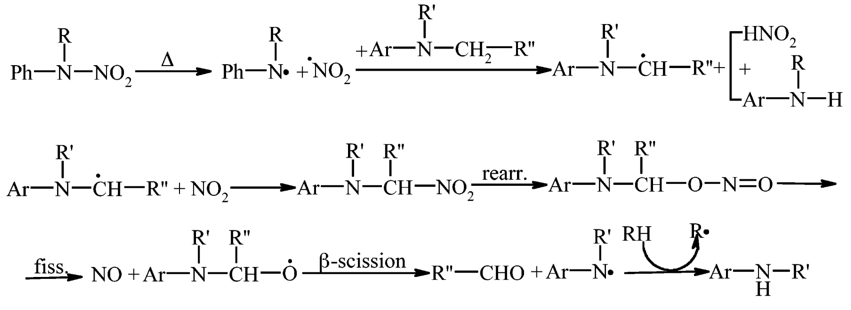
(11) Saito, I.; Takami, M.; Matsuura, T. *Tetrahedron Lett.* **1975**, *36*, 3155.

(12) Ioki, Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1240.

(13) Chapman, O. L.; Cleveland, P. G.; Hoganson, E. D. *J. Chem. Soc., Chem. Commun.* **1966**, 101.

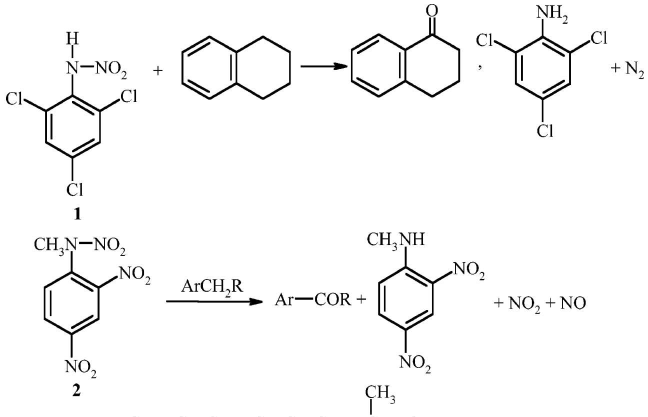
10.1021/jo040176+ CCC: $27.50

SCHEME 1



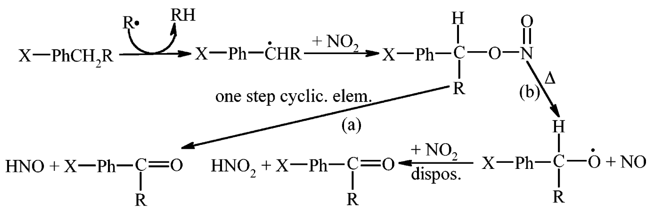
(a - R' = CH_3, R'' = H; b - R' = C_2H_5, R'' = CH_3)

SCHEME 2



R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH(CH_3)-CH_3$

SCHEME 3



(a- R=H, X=P-CH_3; b-R=CH_3; c-R=CH_3, X=P-CH_3; d- R=CH_3, X=3,5 $(CH_3)_2$; e- R=C_2H_5; f-R=C_3H_5; g-R=$CH(CH_3)_2$)

which suffers O−N bond homolysis to yield the corresponding *N*-alkoxy and nitric oxide radicals.[14] The *N*-α-alkoxy radical suffers *β*-scission[14,15] into aldehyde (formaldehyde, acetaldehyde) and the *N*-arylamino radical, which then abstracts hydrogen to produce the arylamine, (Scheme 1).

On the other hand, thermolysis of the *N*-nitroaniline **2** with *p*-xylene gave *p*-tolualdehyde, *N*-methyl-2,4-dinitroaniline, formaldehyde, and nitric oxide. Thermolysis of the *N*-nitroaniline **2** with mesitylene gave 3,5-dimethylbenzaldehyde, *N*-methyl-2,4-dinitroaniline, formaldehyde, nitrogen dioxide, and nitric oxide. In these cases, the *N*-nitroamines underwent N−NO_2 homolysis to give the respective radicals which affect oxidative hydrogen abstraction from methyl group of the methyl arene to yield the corresponding benzyl radical. The latter couples in a consecutive step with nitrogen dioxide to give the α-arylmethylnitrite,[7,9,16] which undergoes fission into nitric oxide and arylalkoxy radicals. Disposition of the latter afforded the aryladehyde.[17]

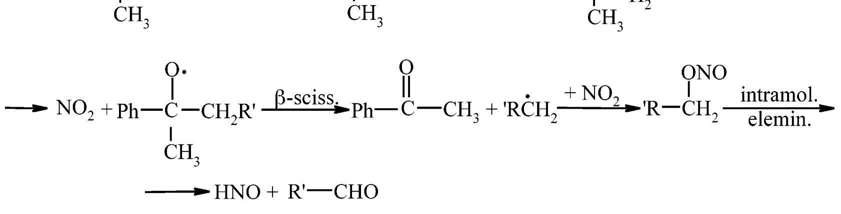
An alternative pathway involving one step cyclic elimination[8b] of the aralkyl nitrite that results in *β*-scission leading to the corresponding arylaldehyde nitrous acid, *N*-alkylaniline, and nitric oxide[10] (Scheme 1).

The formation of formaldehyde in the above thermolysis may result from the *N*-methylnitroaniline byproduct through process of hydrogen abstraction, coupling of the aryl-*N*-α-methyl radical with nitrogen dioxide, and fission of the nitrite product followed by *β*-scission of *N*-methoxy radical to yield formaldehyde and the arylamino radical (Scheme 1).

Next, thermolysis of the *N*-nitroaniline **1** with tetralin was examined. In our hands, the reaction grave α-tetralone, 2,4,6-trichloroaniline, and nitrogen gas. Similarly, heating of **2** with ethylbenzene, *p*-ethyltoluene, *n*-propylbenzene, *n*-butylbenzene, and isobutylbenzene, respectively, afforded the respective acylarenes together with *N*-methyl-2,4-dinitroaniline, nitric oxide, and nitrogen dioxide (Scheme 2).

These results indicate that nitrogen dioxide radical abstracts hydrogen selectively from the α-carbon atom bonded to the benzene ring to generate highly resonance stabilized substituted α-benzy radical which couple with nitrogen dioxide to generate α-alkylnitrite. The α-alky-

SCHEME 4



(R' = H; R' = CH_3)

TABLE 1. Thermolysis of the 2,4,6-Trichloro-*N*-nitroaniline 1 with Alkylarenes (% Yield)

alkylarene	nitramine (mol/*T* (°C)/ time (h))	carbonyl product	2,4,6-trichloro-aniline (%)	byproduct	gases	residue
tetralin (50 mL)	0.02/140/3	α-tetralone[e] (20%)	75		N_2	oil residue + alkylarene
N,*N*-dimethylaniline (20 mL)	0.02/135/1	formaldehyde	72	*N*-methyl- *N*-nitroso-aniline[a] (20%) + *N*-methylaniline	N_2	tar + alkyl-arene
dodecane (20 mL)	0.01/180/1		81	2,4,6-trichloro-phenol[b] + 2-nitrododecane (5%)[c]	N_2 (0.50 mol)	tar + alkane
in silica gel (12 g)	0.01/140/2		20	2,6-dichloro-4-nitroaniline[d]	N_2O	red tar

[a] *N*-methyl-*N*-nitrosoaniline:[25] colorless oil, bp 130 °C/12 Torr; $^{20}_{\mathrm{nD}}$ 1.5769; ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 3H, CH_3), 7.5−7.8 (m, CH, ArH). [b] 2,4,6-Trichlorophenol:[26] mp 66 °C (EtOH); IR (cm^{-1}) 3570 (OH, shifted in D_2O); ^{1}H NMR ($CDCl_3$) δ 4.8 (s, 1H, OH), 6.8−7.3 (d, 2H, ArH); MS *m*/*z* 196 (M^{-1}, 100), 198 (M^{+1}, 89). [c] 2-Nitrododecane:[27] bp 120 °C/1.4Torr; $^{20}_{\mathrm{nD}}$1.4407; IR (film) (cm^{-1}) 1580−1365 (NO_2); ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3H, CH_3CH_2), 1.51 (d, 3H, CH_3-CH), 4.48 (q, 1H, CH), 1.40−1.62 (m, 18H, $9CH_2$). [d] 2,6-Dichloro-4-nitroaniline:[28] yellow crystals; mp 194 °C (EtOH); IR (cm^{-1}) 3790, 3350 (NH_2); ^{1}H NMR (DMSO) δ 2.8 (s, 2H, NH_2), 6.9−7.2 (2H, ArH); MS *m*/*z* 207 (M^+, 100). [e] α-Tetralone: bp 116 °C/6 Torr; $^{20}_{\mathrm{nD}}$ 1.5685; IR (cm^{-1}) 1680 (C═O); ^{1}H NMR ($CDCl_3$) δ 2.1, 2.5, 2.9 (t, $3CH_2$), 7.2−7.9 (m, 4H, ArH).

TABLE 2. Thermolysis Product of the *N*-Methyl-2,4-dinitro-*N*-nitroaniline 2 with Alkylarenes

alkylarene	nitramine (mol/*T* (°C) /time (h))	carbonyl product (% yield)	2,4- dinitro-aniline (% yield)	byproduct (% yield)	gases	residue
p-xylene	0.02/140/2	*p*-tolualdehyde[a] (18)	78	formaldehyde[b]	NO_2^+, NO	tar + arene
mesitylene	0.03/170/4	2,5-dimethylbenz-aldehyde[c] (20)	95	formaldehyde	NO_2^+, NO	tar + arene
ethylbenzene	0.03/140/4	acetophenone (18)[d]	82		NO_2^+, NO	tar + arene
p-ethyltoluene	0.02/160/2	*p*-methylaceto-phenone[e] (22)	85		NO_2^+, NO	tar + arene
N,*N*-diethylaniline (DMA)	0.02/135/2	acetaldehyde[f] (18)	78	*N*-ethylaniline (23)	NO_2^+, NO	tar + DMA (10%)
n-propylbenzene	0.02/140/4	propiophenone[g] (20)	80		NO_2^+, NO	tar + arene
isoproylbenzene	0.03/140/2	acetophenone[d] (18)	82	formaldehyde	NO_2^+, NO	tar + arene
n-butylbenzene	0.02/140/2	*n*-butyrophenone[h] (21)	79		NO_2^+, NO	tar + arene
isobutylbenzene	0.02/140/3	isobutyrophenone[i] (20)	76		NO_2^+, NO	tar + arene
sec-butylbenzene	0.02/140/2	acetophenone[d] (19)	80	formaldehyde	NO_2^+, NO	tar + arene
tert-butylbenzene	0.03/140/2	formaldehyde[b]	79	bicumyl[k] (14)	NO_2^+, NO	tar + arene
dodecane (50 mL)	0.04/150/2	paraformaldehyde[j] (0.5)	81	*m*-dinitrobenzene (5)[l] + 2-nitrododecane (5)[m]	N_2, 0.24 mol (73%) + NO (12%)	tar + alkane

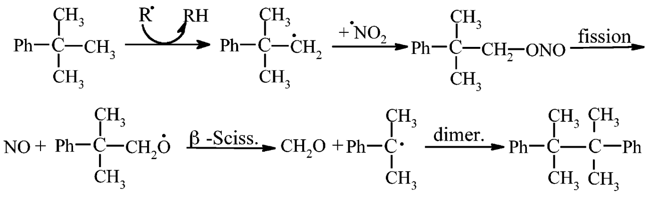
[a] 2,4-Dinitrophenyl hydrozone (2,4-DNPH), orange-red crystals (benzene), mp 243 °C.[29] [b] 2,4-DNPH (petroleum ether), mp 167 °C, semicarbzone, mp 168 °C.[30] [c] Semicarbazone (EtOH), mp 218 °C.[31] [d] 2,4- DNPH (EtOH), mp 249 °C.[30] [e] 2,4-DNPH, red crystals (EtOH), mp 259 °C.[30] [f] 2,4- DNPH (EtOH), mp 162 °C.[30] [g] 2,4- DNPH, red crystals (EtOH), mp 192 °C.[30] [h] 2,4- DNPH (EtOH), mp 192 °C.[30,32] [i] 2,4-DNPH, orange crystals (EtOH), mp 163 °C.[33] [j] Paraformaldehyde, white powder, mp 123 °C; 2,4-DNPhH, prisms (petroleum ether), mp 167 °C, semicarbazone (petroleum ether), mp 189 °C.[30] [k] 2,3-Dimethyl-2,3-diphenylbutane (bicumyl),[34] white needles (EtOH), mp 115 °C, MS *m*/*z* = 238 (M^+), ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 12H, $4CH_3$), 7.3−7.8 (m, 10H, ArH). Anal. Calcd for $C_{18}H_{22}$: C, 90.75; H, 9.25. Found: C, 90.66; H, 9.30. [l] *m*-Dinitrobenzene, mp 92 °C (EtOH).[35] [m] 2-Nitrododecane, bp 120 °C/ 1.4 Torr, n_D^{20} 1.4407. Anal. Calcd for $C_{12}H_{25}NO_2$: C, 66.97; H, 11.62; N, 6.51. Found: C, 70.01; H, 11.79; N, 6.46. 2-Nitrododecane + MeOH−KOH 10% + H_2O_2 (in excess) heated at 70 °C for 6 h, collected, mixture extracted with (petroleum ether) to separate 2-dodecanone: bp 100 °C/2.5 Torr, n_D^{20} 1.4332; semicarbazone (EtOH), mp 124 °C.[36]

lnitrite undergoes elimination of HNO molecule to produce the corresponding carbonyl compound[10] (Scheme 3, route a).

An alternative multistep unimolecular dissociation of the alkylnitrite and disposition of the intermediate radicals[3,8] into the aryl alkyl ketone can also be suggested (route b, Scheme 3).

Thermolysis of *N*-nitroaniline **2** with isopropylbenzene and *sec*-butylbenzene yielded formaldehyde and acetaldehyde, respectively, together with acetophenone as byproduct in both cases. The formation of such products can be rationalized by the mechanistic pathway depicted in Scheme 4.

SCHEME 5



Finally, thermolysis of *N*-nitroaniline **2** with *tert*-butylbenzene was studied. In this case, the reaction gave 2,3-dimethyl-2,3-diphenylbutane (bicumyl), *N*-methyl-

---

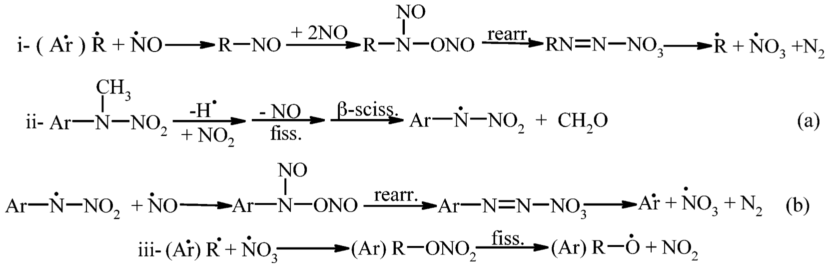
(14) Furlan, A. *Chem. Phys. Lett.* **1999**, *309*, 157. Effrenhauser, C. S.; Feder, P.; Huber, J. R. *J. Phys. Chem.* **1990**, *94*, 296. Untch, A.; Schinke, R.; Cotting, R.; Huber, J. R. *J. Chem. Phys.* **1993**, *99*, 9553.

(15) Wang, J.; Brower, K. R. *J. Org. Chem.* **1997**, *62*, 9048.

(16) Grossi, L.; Strazzai, S. *J. Org. Chem.* **1999**, *64*, 8076.

(17) Iyima, S.; Yudasaka, M.; Yamada, R.; Bandaw, S.; Suenaga, S.; Kokai, F.; Takahashi, K. *Chem. Phys. Lett.* **1999**, *309*, 165.

SCHEME 6



2,4-dinitroaniline, formaldehyde, nitrogen dioxide, and nitric oxide. Since *tert*-butylbenzene has no α-CH, the most plausible rationalization for the products formation is by hydrogen abstraction from *β*-CH_3 to separate the α,α-dimethyl benzyl-α-methyl radical, which couples with nitrogen dioxide to generate the α-methylnitrite. The latter undergo O−NO bond fission into primary *β*-alkoxy radical and nitric oxide. The alkoxy radical suffer *β*-scission to generate formaldehyde and the highly stabilized tertiary cumyl radical,[18] which dimerize to bicumyl, as depicted in Scheme 5.

To study and determine the quantity of gases evolved during the thermolysis of *N*-nitroanilines a control experiment was performed where the *N*-nitroaniline **1** is heated in dodecane to give the products 2,4,6-trichloroaniline, 2,4,6-trichlorophenol, and 2-nitrododecane, and the gas evolved was collected and analyzed quantitatively by GLC and identified to be only nitrogen up to 0.50% mol.

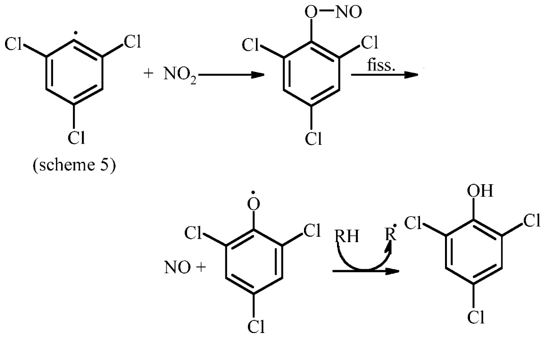
Similarly, thermolysis of *N*-nitroaniline **2** in dodecane gave paraformaldehyde (white sublimate at condenser wall), *N*-methyl-2,4-dinitroaniline, and *m*-dinitrobenzene, and the gases collected were analyzed quantitatively by GLC and were identified to be nitrogen (75%) and nitric oxide (12%).

Paraformaldehyde is suggested to be formed from the *N*-methyl group of the *N*-nitroaniline **2**, which suffers abstraction of hydrogen to give the aryl *N*-methyl radical which couples with nitrogen dioxide into *N*-methylnitrite. The latter undergoes fission into nitric oxide and *N*-methoxy radical, which undergoes *β*-scission into *N*-anilino radical and formaldehyde. Polymerization of the latter forms paraformaldehyde.

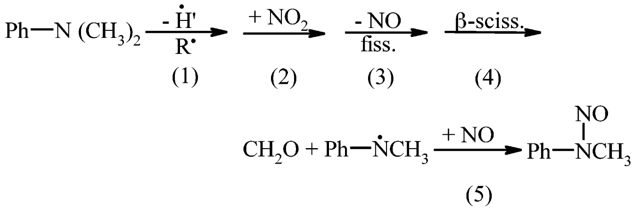
Formation of nitrogen can be rationalized in terms of the formation of the intermediate *N*-nitro-*N*-nitrsoalkane (or arene) which rearranges to the corresponding (aryl)-alkyldiazonium nitrate.[19,20] The diazo compound undergoes homolysis to alkyl and nitrate radicals and nitrogen (Scheme 6).

An alternative pathway involves coupling of the *N*-nitro-*N*-arylamino radical with nitric oxide to generate aryl-*N*-nitroso-*N*-nitrite, which rearranges to aryldiazonium nitrate, which then undergoes homolysis into aryl and nitrate radicals and nitrogen[21,22] (Scheme 6). The fate of the nitrate radical goes through coupling with alkyl or aryl radicals followed by fission (Scheme 6).

SCHEME 7



SCHEME 8



Production of 1,3-dinitrobenzene on heating the *N*-nitroaniline **2** in dodecane seems to be generated from the aryl radical (Scheme 6), which abstracts hydrogen to produce the *m*-dinitrobenzene.

Also, production of 2,4,6-trichlorophenol from heating the *N*-nitroaniline **1** in dodecane can be rationalized as shown in Scheme 7.

Formation of formaldehyde and *N*-methyl-*N*-nitrosoaniline from thermolysis of the *N*-nitroaniline **1** with *N*,*N*-dimethylaniline can be rationalized[23] as depicted in Scheme 8.

On the other hand, heating *N*-nitroaniline **1** alone, in the absence of oxidizable species, on silica gel gave 2,4,6-trichloroaniline, 2,6-dichloro-4-nitroaniline, and nitrogen dioxide. Formation of dichloronitroaniline can be rationalized to result via an ipso-substitution reaction[8a,24] of the 4-chloro substituent by the nitrogen dioxide radical

---

(18) Tanko, J. M.; Pacut, R. *J. Org. Chem.* **2001**, *123*, 5703. Gould, I. R.; Baretz, B. H.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 925. Gould, I. R.; Zimmit, M. B.; Turro, N. J.; Baretz, B. H.; Lehr, G. F. *J. Am. Chem. Soc.* **1985**, *107* , 4607.

(19) Donaruma, L. G.; Carmady, D. J. *J. Org. Chem.* **1957**, *22*, 635.

(20) Forrest, D.; Gowenlock, B. G.; Pfab, J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 576.

(21) Gowenlock, B. G.; Kresze, G.; Pfab, J. *Tetrahedron* **1973**, *29*, 3587; Brian, D. F.; Gowenlock, G.; Pfab, J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 576.

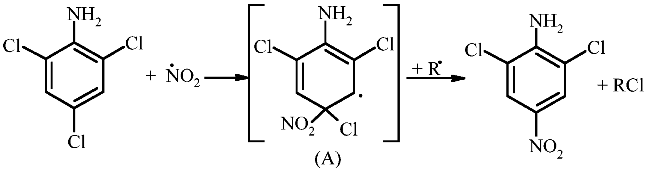
(22) Bolsman, T. A. B.; Deboer, T. H. J. *Tetrahedron* **1973**, *29*, 3579.

(23) Chow, Y. L.; Richard, H.; Snyder, R. W.; Lockhart, R. W. *Can. J. Chem.* **1979**, *57*, 2936.

(24) Pryor, W. A.; Echols, Y. T., Jr.; Smith, K. *J. Am. Chem. Soc.* **1966**, *88*, 1189. Ito, R.; Migita, T.; Morikawa, N.; Simmura, O. *Tetrahedron* **1965**, *21*, 955. Ivanora, G. M.; Voronova, L. K.; Deryagina, E. N.; Voronkov, M. G. *Zh. Org. Khim.* **1979**, *15* , 1232. Voronkov, M. G.; Deryagina, E. N.; Ivanova, G. M. *Zh. Org. Khim.* **1976**, *12*, 2179. Voronkov, M. G.; Deryagina, E. N.; Klochkova, L. G.; Ivanova, G. M. *Zh. Org. Khim.* **1977**, *13*, 2575.

(25) Hartman, W. W.; Roll, L. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 341.

SCHEME 9



through formation of cyclohexadienyl radical intermediate (A) followed by elimination of chlorine atom as depicted in Scheme 9.

Experimental Section

Melting points were obtained with a hot-stage apparatus calibrated with known samples. Column chromatography and TLC were carried out using silica gel (80−120 mesh) or Merck Kieselgel 60. All products were identified by elemental analysis, TLC, IR, ^{1}H NMR, MS, and mixed melting point with authentic samples wherever possible and are summarized in Tables 1 and 2.

Chemical Compounds. Unless otherwise stated, the materials for synthesis and comparisons were used as commercially available: alkylarenes, alkanals, alkanones, arylalkylkanones, *N*,*N*-diethylaniline, *N*,*N*-dimethylaniline, *N*-ethylaniline, *N*-methylaniline, 2,6-dichloro-4-nitroaniline, 1,3-dinitrobenzene, 2,4,6-trichlorophenol, 2,4,6-trichloroaniline, 2,6-dichloro-4-nitrophenol. Other chemicals used or produced in the study are identified and analyzed as in Tables 1 and 2.

2,4,6-Trichloro-*N*-nitroaniline:[8a] white needles (petroleum ether); mp 134 °C.

***N*-Methyl-2,4-dinitro-*N*-nitroaniline:**[8a] yellow crystals (EtOH); mp 115 °C.

Thermolysis of the *N*-Nitroanilines in Arene Solvents. The *N*-nitroaniline (0.01−0.02 mol) and the arene (20 mL) were heated together under nitrogen atmosphere in the dark. The gases evolved were collected from the outlet into cold traps, ethanol−carbon dioxide, and liquid nitrogen successively, where nitrogen, nitric oxide, and nitrogen dioxide were analyzed by GC. Formaldehyde was passed through the hydrazine solution to produce the corresponding hydrazone. The dark mixture was steam distilled and part of the aqueous distilled treated with dinitrophenylhydrozine to precipitate the hydrazones of the carbonyl products. Extraction of water extract with ether may separate some of the arylamine products. Fractionation of the nonaqueous distillate and separation of the excess arenes gave the corresponding araldehyde or alkylaryl ketones. Extraction of the nonresolvable resides with glacial acetic acid and evaporation separated the corresponding arylamine product. Products of the *N*-nitroaniline **1** on heating with silica gel were separated and analyzed as above. All products were quantitatively analyzed by GC−MS using reference compounds as internal standards and by GLC by comparison of their retention times with those of known concentrations of authentic samples and by their mass spectra.

Thermolysis of the *N*-Nitroanilines in Dodecane. The *N*-nitroaniline and dodecane were heated together under a nitrogen atmosphere in the dark. The gases evolved were collected in cold traps, with ethanol−carbon dioxide and liquid nitrogen successively, where nitrogen and nitric oxide or nitrogen dioxide were quantitatively analyzed by gas chromatography. Formaldehyde was changed into the corresponding hydrazone. Praformaldehyde accumulated in the condenser on *N*-nitroaniline **2** thermolysis was collected and identified by hydrazone formation. The pyrolysis products were extracted with ether, which was extracted with sodium carbonate solution to extract phenolic products, and ether was evaporated and the oil residue fractionally distilled at reduced pressure to collect dodecane, trichlorophenol, trichloroaniline, and 1,3-dinitrobenzene. The oily residue was fractionated into dodecane and 2-nitrododecane, and the black residues were extracted with petroleum ethers to separate 2,4,6-trichloroaniline and *N*-methyl-2−4-dinitroanilines. All products were quantitatively analyzed by GC−MS and or by GLC.

Acknowledgment. This work was carried out with the financial support of the International bank. Part of this work was carried out at Boston College, Boston, MA.

JO040176+

---

(26) Strubell, W. *J. Prakt. Chem.* **1961**, *14*, 174.
(27) Haire, D. L.; Janzen, E. G. *Can. J. Chem.* **1982**, *60* , 1514.
(28) Higgons, D. J.; Stevensen, H. A. *Chem. Indust.* **1960**, 572.
(29) Smith, E. C.; Nichlols, M. L. *J. Org. Chem.* **1946**, *6*, 489.
(30) Johnson, G. D. *J. Am. Chem. Soc.* **1953**, *75, 2720.*
(31) Weiler, M. *Chem. Ber.* **1900**, *33*, 469.
(32) Morita, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 309.
(33) Maruyama, K. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 102.
(34) Kulkarni, V.; Cohen, T. *Tetrahedron* **1997**, *53* (36), 12089. Shipiro, I. O.; Nir, M.; Hoffmann, R. E.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1519.
(35) Wyler, A. *Helv. Chim. Acta* **1932**, *15*, 23.
(36) Grundmann, C. *Chem. Ber.* **1944**, *77*, 7 B, 82.