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Partial Reduction of Dinitroarenes to Nitroanilines with Hydrazine Hydrate[†]

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Dinitroarenes containing substituents such as hydroxyl and amine groups could be conveniently reduced with 3 molar equivalents of hydrazine hydrate in presence of Raney nickel catalyst in ethanol/1,2-dichloroethane solvent mixture to give a product wherein one of the two nitro groups was reduced to the amino group. The yields of the partial reduction products are good. Under similar conditions alkoxyl substituents in the *o,p*-position to the nitro groups were displaced by the hydrazino group to give 2,4-dinitrophenylhydrazine as the main product. The details of the reduction reaction are described.

We reported the high reduction ability of hydrazine hydrate in presence of Raney nickel in ethanol/1,2-dichloroethane solvent mixture to reduce nitroarenes under mild conditions.[1] The reaction conditions and solvent system are ideal for the reduction of nitro compounds having limited solvent solubility. The scope of the method has been extended for the reduction of one of the two nitro groups of dinitroarenes. The results of the partial reductions are discussed here.

Usually partial reduction is carried out in aqueous medium by using sodium sulfide under alkaline conditions (Zinin reduction) or tin(II) chloride under acidic conditions. The latter has a tendency to reduce the less hindered nitro group. The dinitro compounds such as 2,4-dinitrophenol, its ethers and 2,4-dinitroaniline derivatives undergo reduction with sulfide reagents at the nitro group ortho to the phenolic or ether oxygen or amino substituent.[2] Ruthenium-on-carbon catalyst, which can be used for the partial reduction of 2,4-dinitroaniline to 4-nitro-*o*-phenylenediamine with hydrazine, was shown to be useful for the synthesis of 1-*N*-substituted 4-nitro-*o*-phenylenediamines.[3] Use of Raney nickel catalyst under identical conditions yielded a complex mixture. Catalytic hydrogenation of 2,4-dinitroaniline at 2.72 atm in presence of 5% rhodium on alumina catalyst and ammonia in DMF yielded 4-nitro-*o*-phenylenediamine in 87% yield.[4] 4-Nitro-*o*-phenylenediamine has commercial utility as an analytical reagent, as an ingredient of hair dyes and as a drug and dye intermediate.

Results and Discussion

We found that 1,3-dinitrobenzene (**1a**) could be conveniently reduced to *m*-nitroaniline (**2a**) by using 3 mol of hydrazine hydrate per mol of **1a** in presence of Raney nickel catalyst in ethanol/1,2-dichloroethane solvent mixture at 50—60 °C.[1] The yield of **2a** exceeded 90%. The procedure is advantageously used for the partial reduction of dinitroarene derivatives containing various substituents. Ethanol/1,2-dichloroethane (1:1) mixture was used as the solvent. In general, the ortho nitro group in 2,4-dinitroarylamine derivatives was preferentially reduced, giving 2-amino-4-nitroarylamine derivatives as the main products. The less hindered para-nitro groups was reduced to a small extent. The results are summarised in Table 1. It can be seen that the yield of the partial reduction products by our method are excellent.

Reduction of 2,4-dinitrophenol (**1b**) with 3 molar equivalent of hydrazine hydrate in presence of Raney nickel in ethanol/1,2-dichloroethane (1:1) at 50—60 °C for 4 h gave 2-amino-4-nitrophenol (**2b**) and 4-amino-2-nitrophenol (**2c**) in 92% and 7% isolable yields respectively. Similarly, 2,4-dinitroaniline (**1c**), under identical conditions for 6 h gave 4-nitro-*o*-phenylenediamine (**2d**) and 2-nitro-*p*-phenylenediamine (**2e**) in 95% and 3% isolable yields. Quantitative yield of 2-amino-*N*-ethyl-4-nitro-aniline (**2f**) was obtained from *N*-ethyl-2,4-dinitroaniline (**1d**). With *N*-isopropyl-2,4-dinitroaniline (**1e**), however, the reduction was effected only upto the hydroxylamine stage. The hitherto unknown 2-hydroxy-*N*-isopropyl-4-nitroaniline (**2g**) was isolated in quantitative yield. With *N*-phenyl-substituted amino compounds such as 2,4-dinitrodiphenylamine (**1f**), the yield of the ortho-amino product, 2-amino-4-nitrodiphenylamine (**2h**) fell down to 70% and that of the isomeric para-amino product, 4-amino-2-nitrodiphenylamine (**2i**) increased to 29%. Thus, in the cases described so far, nitro group in the ortho position to amino or hydroxyl substituent was preferentially reduced giving ortho-amino derivatives as major or sole products. Apparently the hydrogen bonding between the amino or the hydroxyl substituent and the ortho-nitro group plays a decisive role in these cases. If such a hydrogen bonding is not possible, as in the case of 2,4-dinitrotoluene (**1j**), the reduction of the para-nitro group was predominant resulting in 88% of 2-nitro-*p*-toluidine (**2n**) and only 10% of 4-nitro-*o*-toluidine (**2o**). Sodium sulfide also selectively reduces the para-nitro group of 2,4-dinitrotoluene.[5,6] The reduction of 2,6-dinitro-*p*-creasol (**1g**) yielded 2-amino-6-nitro-*p*-cresol (**2j**) in 98% yield. During the partial reduction of 3,5-dinitrobenzoic acid, hydrazine salt of 3,5-dinitrobenzoic acid (mp 170 °C, lit,[7] 168 °C) was found to be an intermediate product, which could be isolated and characterized. Ultimately, 3-amino-5-nitrobenzoic acid (**2k**) was isolated in 85% yield. As a representative example of naphthalene series, the partial reduction of 1,5-dinitronaphthalene (**1i**), using 3 molar equivalents of hydrazine hydrate was studied. The reduction product consisted of 20.33% 5-nitro-1-naphthylamine (**2l**), 47.26% 1,5-naphthalenediamine (**2m**) and 32.41% of the starting 1,5-dinitronaphthalene (**1i**). The product analysis was carried out by using IATROSCAN TH

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TABLE 1. PARTIAL REDUCTIONa) OF DINITROARENES **1** WITH HYDRAZINE HYDRATE/RANEY NICKEL

Substrate **1** No.		Time h	Product **2**		Yieldb) %	Mp θ_m/°C Found	Mp θ_m/°C Ref.
1a,	$1,3\text{-}(NO_2)_2C_6H_4$	3	**2a**,	$3\text{-}NO_2C_6H_4NH_2$	94	113—114	(113—114)1)
1b,	$2,4\text{-}(NO_2)_2C_6H_3OH$	4	**2b**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OH$	92	141	(142—143)15)
			2c,	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3OH$	7	130	(131)16)
1c,	$2,4\text{-}(NO_2)_2C_6H_3NH_2$	6	**2d**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3NH_2$	95	200	(200)17)
			2e,	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3NH_2$	3	140	(140—141)18)
1d,	$2,4\text{-}(NO_2)_2C_6H_3NHC_2H_5$	6	**2f**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3NHC_2H_5$	98	139	(140)19)
1e,	$2,4\text{-}(NO_2)_2C_6H_3NHCH(CH_3)_2$	4	**2g**,	$2\text{-}NHOH\text{-}4\text{-}NO_2C_6H_3NHCH(CH_3)_2$	100	165	c)
1f,	$2,4\text{-}(NO_2)_2C_6H_3NHPh$	4	**2h**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3NHPh$	70	134	(134)20)
			2i,	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3NHPh$	29	80	(80—81)21)
1g,	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3C_6H_2OH$	6	**2j**,	$2\text{-}NH_2\text{-}4\text{-}CH_3\text{-}6\text{-}NO_2C_6H_2OH$	98	118	(119)22)
1h,	$3,5\text{-}(NO_2)_2C_6H_3COOH$	8	**2k**,	$3\text{-}NH_2\text{-}5\text{-}NO_2C_6H_3COOH$	85	210	(210—212)23)
1i,	$1,5\text{-}(NO_2)_2C_{10}H_6$	8	**2l**,	$5\text{-}NO_2\text{-}C_{10}H_6NH_2$	20.33	118	(118—119)24)
			2m,	$1,5\text{-}(NH_2)_2C_{10}H_6$	47.26	188	(188)25)
1j,	$2,4\text{-}(NO_2)_2C_6H_3CH_3$	4	**2n**,	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3CH_3$	88	78	(78)26)
			2o,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3CH_3$	10	107	(107)27)

a) Dinitroarene **1**: hydrazine hydrate ratio 1:3, 0.3 g of catalyst; 10 ml of solvent $C_2H_5OH/ClCH_2CH_2Cl$ (1:1 v/v) per g of **1**. Temperature 50—60 °C. b) Yield of isolated products. c) Characterized by spectral and elemental analysis.

TABLE 2. PARTIAL REDUCTIONa) OF DINITROPHENOL ETHERS **3** WITH HYDRAZINE HYDRATE/RANEY NICKEL

Substrate **3** No.		Time h	Productb)		Yieldc) %	Mp θ_m/°C Found	Mp θ_m/°C Ref.
3a,	$2,4\text{-}(NO_2)_2C_6H_3OCH_3$	4	**4a**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OCH_3$	8	118	(118)28)
3b,	$2,4\text{-}(NO_2)_2C_6H_3OC_2H_5$	4	**4b**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OC_2H_5$	6	96	(96)13)
3c,	$2,4\text{-}(NO_2)_2C_6H_3O(CH_2)_2OH$	4	**4c**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3O(CH_2)_2OH$	1	105	(105)8)
3d,	$2,4\text{-}(NO_2)_2C_6H_3O(CH_2)_2OCH_3$	4	**4d**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3O(CH_2)_2OCH_3$	1	94	(95)29)
3e,	$2,4\text{-}(NO_2)_2C_6H_3OCH(CH_3)_2$	4	**4e**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OCH(CH_3)_2$	1	63	(62.5—63.5)13)
3f,	$2,4\text{-}(NO_2)_2C_6H_3O(CH_2)_2CH_3$	4	**4f**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3O(CH_2)_2CH_3$	0.8	48	(47.5—48.5)13)
3g,	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_3(Cl)_2\text{-}2,4$	3	**4g**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OC_6H_3Cl_2\text{-}2,4$	0.5	125	d)
3h,	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_5$	3	**4h**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OC_6H_5$	0.5	105	(107)30)
3i,	$2,4\text{-}(NO_2)_2C_6H_3OCH_2\text{-}CH(OH)CH_2OH$	3	**4i**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3\text{-}OCH_2CH(OH)CH_2OH$	1	117	(117)8)
3j	$2,4\text{-}(NO_2)_2C_6H_3OCH_2C_6H_5$	3	**4l**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OCH_2C_6H_5$	1	105	(105)13)

a) Dinitrophenol ether **3**: hydrazine hydrate ratio 1:3; 0.3 g of catalyst; 10 ml of solvent $C_2H_5OH/ClCH_2CH_2Cl$ (1:1 v/v) per g of **3**. Temperature 50—60 °C. b) The rest of the product amounting 91—99% is 2,4-dinitrophenylhydrazine (**5**) isolated in every case; mp 200 °C (Ref. 31, 200 °C). c) Yield isolated product. d) Characterized by spectral and elemental analysis.

10 TLC/FID analyzer (Iatron Laboratories, Inc., Japan). Apparently, the initially formed partially reduced product undergoes parallel reduction reaction to give **2m** in organic solvent medium.

Using the same conditions as mentioned above, alkyl and aryl ethers of 2,4-dinitrophenol were allowed to react with 3 molar equivalents of hydrazine hydrate in presence of Raney nickel catalyst. The reactions resulted in rapid replacement of the alkoxyl or the aryloxyl groups with the formation of 2,4-dinitrophenylhydrazine (**5**) as the predominant product. The results are summerised in Table 2. Partial reduction products having amino groups in ortho positions to the alkoxyl or the aryloxyl substituents were isolated in yields ranging from 0.5 to 8%. In general, the bulkier groups (such as 2-hydroxyethoxy, 2-methoxyethoxy, propoxy, isopropoxy 2,4-dichlorophenoxy, phenoxy, 2,3-dihydroxypropoxy, and benzyloxy groups of **3c**—**3j** are replaced with ease with the formation of 2,4-dinitrophenylhydrazine (**5**). The yields of the corresponding partial reduction products **4c**—**4i** and **4l** ranged from 0.5 to 1%. The compound **4f**, known as P4000, is the sweetest material known and is 4000 times sweeter than sucrose.8) In the case of **3a** and **3b** with less bulkier methoxyl and ethoxyl substituents, the yields of 4-nitro-*o*-anisidine (**4a**) and 4-nitro-*o*-phenetidine (**4b**) were 8% and 6% respectively. The formation of **5** involves nucleophilic substitution reaction similar to the reaction of amines with 2,4-dinitrophenyl ethers, resulting in the formation of 2,4-dinitroanilines.8—10) The 2,4-dinitrophenylhydrazine (**5**), which is formed in high yields within 4 h, has a tendency to undergo subsequent reaction, if prolonged further, resulting in the formation of side products as indicated by TLC. Under basic reaction conditions, triazoles and other products arising from partial and complete reduction of **5** are produced.11) Apparently, the catalyst played no role, when 2,4-dinitrophenyl ethers were allowed to react with hydrazine under our conditions. When 2,4-dinitrophenyl ethers **3a**, **3b**, **3c**, **3e**, and **3g** were allowed to react with 3 molar equivalents of hydrazine hydrate in the absence of catalyst in ethanol/1,2-dichloroethane solvent at 60 °C for 4 to 6 h the expected 2,4-dinitriphenylhydrazine (**5**) was obtained as the sole product. There was no trace of any side product.

In order to study the role of solvent, 1,3-dinitrobenzene (**1a**) was allowed to react with 3 molar equivalents of 20, 40, 60, and 80% hydrazine hydrate in aqueous medium at 90 °C for 16—18 h. The yields (based on TLC/FID analysis using IATROSCAN TH 10) of *m*-nitroaniline (**2a**) were 74, 86, 100, and 100% respectively. Since 60% hydrazine hydrate gave quantitative yield of **2a**, it was used for the noncatalytic reduction of other dinitroarenes. The results are summerised in Table 3. The partially reduced products, 2-amino-4-nitrophenol (**2b**) and 2-nitro-*p*-toluidine (**2n**) were obtained in 98% and 92% yields from 2,4-dinitrophenol (**1b**) and 2,4-dinitrotoluene (**1j**) respectively. The reductions were, however, slow and took 16 to 18 h for completion. In the case of *N*-ethyl-2,4-dinitroaniline (**1d**), the yield of **2f** was 70%. The success of this method is noteworthy in the case of 1,5-dinitronaphthalene (**1i**). The yield of the partially reduced product, 5-nitro-1-naphthylamine (**2l**) was 80%. The rest of the product consisted of the starting material **1i**. Apparently in this case, the partially reduced product **2l** falls out of the reaction medium and is inaccesible for further reduction to **2m**. Such a partial reduction of 1,5-dinitronaphthalene by noncatalytic hydrazine hydrate in the absence of solvents has been reported in a patent.[12] Mononitro compounds such as *p*-nitrotoluene (**6**) or difficultly soluble dinitro compounds such as bis(3-nitrodiphenyl) sulfone (**7**) were not reduced under similar conditions even after 36 h. Their complete insolubility in aqueous 60% hydrazine hydrate is responsible for the nonreducibility. The dinitrophenol ethers **3a**, **3b**, **3e**, **3f**, **3g**, and **3i**, as expected yielded 2,4-dinitrophenylhydrazine (**5**) quantitatively within 0.5 h even at 65 °C. Lower concentrations of hydrazine hydrate (*e.g.* 20%) also yielded **5** quantitatively at 90 °C for 2 h. Alkaline sulfide reductions of 2,4-dinitriphenol ethers are known to give the corresponding partial reduction products.13)

Recently it was shown that if nitro compounds containing *N*- or *O*-benzyl groups were added to a refluxing mixture of excess of hydrazine hydrate, Raney nickel and methanol, nitro groups got reduced to the amino groups; but the benzylamino or the benzyloxy groups were unaffected. Thus 2,4-dinitrophenyl benzyl ether (**3j**) gave 2,4-diaminophenyl benzyl ether with 10 molar equivalents of hydrazine hydrate.14) We carried out the same reaction under identical conditions by using 3 molar equivalents of hydrazine hydrate and obtained 2,4-diaminophenyl benzyl ether in 43% yield (isolated as dihydrochloride, mp 134 °C), the rest of the product consisted of unreacted starting material. Apparently the mode of addition of the nitro compounds and other reaction conditions play an important role in the selective reduction of dinitroarenes. Thus, when 2,4-dinitroanisole, **3a** (**3a**: hydrazine hydrate ratio 1:3, 0.3 g Raney nickel, 0.01 mol **3a** and methanol 40 ml per g of **3a**, 4 h reaction time) was added to hydrazine hydrate, methanol and Raney nickel mixture at 0 °C, about 95% of unreacted **3a** and 5% 2-amino-4-nitroanisole (**4a**) were isolated. At 28—30 °C, there was 94% formation of **5** and the rest a complex mixture giving a series of spots on silica gel TLC plate. At 40—50 °C, the formation of **5** was 86% and that of **4a** was 8.8% (isolated yield). There was also evidence for the formation of other complex reduction products as noticed by TLC analysis. When **3a** was added to a refluxing mixture of methanol, hydrazine hydrate and Raney nickel, formation of **5** was not noticed. Only 2,4-diaminoanisole was isolated as dihydrochloride, mp 248 °C (mixed mp with an authentic sample was not depressed) in 46% yield. Under identical conditions, **3j** was reduced with 3 molar equivalents of hydrazine hydrate to give a product consisting of 44% of unreacted **3j**, and 43% of 2,4-diaminophenyl benzyl ether isolated as dihydrochloride. Finally, a mixture of methanol, hydrazine hydrate and Raney nickel was refluxed for 10—12

TABLE 3. REDUCTION a) OF NITROARENE (**6**), DINITROARENES (**7** AND **1**) and DINITROPHENOL ETHERS (**3**) WITH 60% AQ. HYDRAZINE HYDRATE ALONE

Substrate No.	Time h	Temperature °C	Product	Yield b) %	Mp θ_m/°C Found	 Ref.
6, $4\text{-}NO_2C_6H_4CH_3$	36	90	No reduction	—	—	—
7, $(3\text{-}NO_2C_6H_4)_2SO_2$	36	90	No reduction	—	—	—
1b	18	90	**2b**	98	141	(142—143)15)
1d	18	90	**2f**	70 c)	139	(140)19)
1i	16	90	**2l**	80 d)	118	(118—119)24)
1j	16	90	**2n**	92	78	(78)26)
3a, **3b**, **3e**, **3f**, **3g**, **3i**	0.5	65	**5**	100	200	(200)31)
3a e)	2	90	**5**	100	200	(200)31)

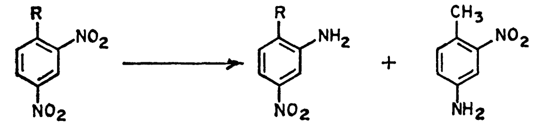
a) Substrate: hydrazine hydrate ratio, 1:3. b) Yield of isolated product. c) 30% unreacted **1d** is isolated. d) 20% unreacted **1i** is isolated. e) 20% aq. hydrazine hydrate is used.

min, dinitroarenes **3a**, **3d**, **3f**, **3g**, and **3j** (1 mol per 3 mol of hydrazine) were added to the cooled mixture at 5 °C, and stirred for 45 min at that temperature. Hydrazine hydrate in this case probably has decomposed to hydrogen and nitrogen (along with ammonia) in the beginning, leaving most of the alkoxyl of aryloxyl group unaffected. Here, thus, we could isolate partially reduced products without the replacement of *O*-

Table 4. Partial reduction[a)] of dinitrophenol ethers (**3**) with hydrazine hydrate/Raney nickel

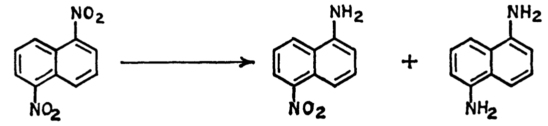
Substrate No.	Product		Yield[b)] %	Mp θ_m/°C Found	Ref.
3a	**4a**,		33	118	(118)[28)]
	9a,	$(2\text{-}CH_3O\text{-}5\text{-}NO_2C_6H_3)_2N_2O$	22.9	210	c)
3d	**4j**,	$2\text{-}NHOH\text{-}4\text{-}NO_2C_6H_3OCH_2CH_2OCH_3$	30	116	c)
	9b,	$[2\text{-}(CH_3OCH_2CH_2O)\text{-}5\text{-}NO_2C_6H_3]_2N_2O$	36	178	c)
3f	**4f**		10	48	(47.5—48.5)[13)]
	9c,	$[2\text{-}(CH_3CH_2CH_2O)\text{-}5\text{-}NO_2C_6H_3]_2N_2O$	24	106	c)
3g	**4g**		22.5	125	c)
	4k,	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3OC_6H_3Cl_2\text{-}2,4$	20	86	c)
3j	**4l**,	$2\text{-}NH_2\text{-}4\text{-}NO_2C_6H_3OCH_2C_6H_5$	6	105	(105)[13)]
	9d,	$[2\text{-}(C_6H_5CH_2O)\text{-}5\text{-}NO_2C_6H_3]_2N_2O$	31	205	c)

a) Substrate: Hydrazine hydrate ratio 1:3; 0.3 g of catalyst; 40 ml of methanol per g of **3**. Temperature 4—5 °C, time 45 min. b) Yield of isolated products. c) Compounds characterized by spectral and elemental analysis.

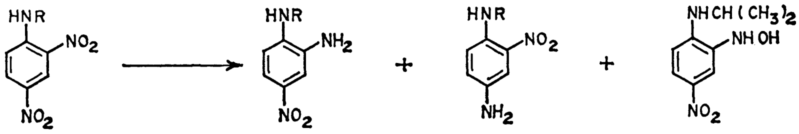


1a, 1j 2a, 2o 2n

R = H, CH3

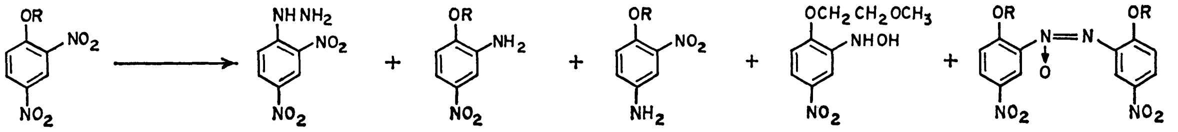


1i 2L 2m



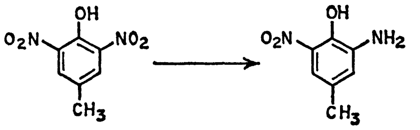
1c, 1d, 1e, 1f 2d, 2f, 2h 2e, 2i 2g

R = H, C_2H_5, i-C_3H_7, C_6H_5

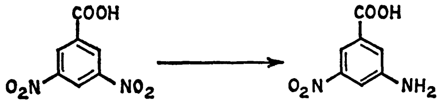


1b, 3a-3j 5 2b, 4a-4i, 4l 2c, 4k 4j 9a-9d

R = H, CH_3, C_2H_5, $(CH_2)_2OH$, $(CH_2)_2OCH_3$, i-C_3H_7, n-C_3H_7, 2,4-$Cl_2C_6H_3$, C_6H_5, $CH_2CHOHCH_2OH$, $CH_2C_6H_5$

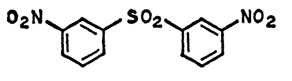


1g 2j



1h 2k

6



7

alkyl or *O*-aryl groups (Table 4). The reduction of **3a** gave 2-amino-4-nitroanisole (**4a**) in 33% yield. Under similar conditions, the yields of 2-amino-4-nitro-1-propoxybenzene (**4f**), 2-amino-4-nitro-2′,4′-dichlorodiphenyl ether (**4g**) and 2-amino-4-nitrophenyl benzyl ether (**4l**) were 10, 22.5, and 6% respectively. The 2,4-dinitrophenyl 2-methoxyethyl ether (**3d**), however, gave only 2-hydroxyamino-4-nitrophenyl 2-methoxyethyl ether (**4j**) in 30% yield. In the case of **3a**, **3d**, **3f**, and **3j**, we could additionally isolate the hitherto unknown pale yellow azoxy compounds, 2,2′-disubstituted 5,5′-dinitroazoxybenzenes, **9a**—**9d** as major products in 22.9, 36, 24, and 31% yields respectively. Such azoxy compounds were not isolated during the reduction of dinitroarenes **1**. The compound **3g** yielded the para-nitro reduction product, 4-amino-2-nitro-2′,4′-dichlorodiphenyl ether (**4k**) in 20% yield. About 49% of **3g** and 53% of **3j** were recovered unreacted. All the unknown compounds were characterized by their spectral and analytical data.

Features of the present method are: (1) the preferential formation of 2-amino-4-nitroanilines from the corresponding dinitroanilines, (2) the formation of 2,4-dinitrophenylhydrazine (**5**) by the replacement of *O*-alkyl or *O*-aryl groups in 2,4-dinitrophenyl ethers by hydrazino group; and (3) the simplicity of the work-up procedures.

Experimental

Melting points were uncorrected. IR spectra were recorded on a Perkin-Elmer infrared spectrometer-model 137B, ^{1}H NMR spectra on a Varian T-60 spectrometer using TMS as internal standard. Mass spectra were determined on CEC-2L-11OB spectrometer.

*Reduction of Dinitroarenes **1** and **3**. General Procedure*: A mixture of dinitroarene (0.1 mol), 1:1 (v/v) ethanol/1,2-dichloroethane (10 ml per g of **1** and **3**), and hydrazine hydrate (0.3 mol) is stirred for 10 min at 28—30 °C. Raney nickel (0.3 g) is added with stirring in three portions over a period of 40 min. The reaction is vigorous and the temperature increases to 50—60 °C. (Temperature is not allowed to rise above 60 °C). After 30 min, when the reaction has subsided, stirring is continued for 3 to 8 h at 50—60 °C (Tables 1 and 2). Complete conversion of the dinitroarene can be confirmed by TLC analysis on silica gel using benzene/ethanol (19:1) as eluent and colour development with iodine vapours. The catalyst is removed by filtration. The solvent is evaporated and the residue is crystallized from ethanol (**1a**—**1e**; **1g**—**1i**) and from pet.ether/benzene (**1f**). The filtrates were chromatographed to give minor aminonitroarenes, **2c**, **2e**, and **2i**. In case of **1i**, the product mixture is analyzed by IATROSCAN TH 10 TLC/FID analyzer using benzene:ethanol (99:1, v/v) as solvent to give 1,5-dinitronaphthalene (**1i**) 32.41%, 5-nitro-1-naphthylamine (**2l**), 20.33%, and 1,5-naphthalenediamine (**2m**), 47.26%. The reduction product from **1j** is chromatographed on silica gel (eluent, benzene) to give **2n** and **2o** respectively. The aminonitroarenes **2a**—**2f** and **2h**—**2o** are characterized by mp, mixed mp and elemental micro analysis. The orange product, 2-hydroxyamino-*N*-isopropyl-4-nitroaniline (**2g**) is isolated from the reduction of *N*-isopropyl-2,4-dinitroaniline (**1e**); mp 165 °C. IR (nujol) 3345, 3200, 1585, 1535, 1445, 1370, 1300, 1280 1240, 1220, 1155, 1120, 1100 cm^{-1}; ^{1}H NMR (pyridine) δ 1.26 (s, 3H), 1.40 (s, 3H), 4.1 (q, 1H); (DMSO), 4.63 (d, 1H, exchangeable with D_2O), 4.93 (s, 1H exchangeable with D_2O), 5.6 (s, 1H, exchangeable with D_2O), 6.33 (d, 1H), 7.10—7.4 (m, 2H); MS *m/e* 211. Found: C, 50.62; H, 6.52; N, 19.82%. Calcd for $C_9H_{13}N_3O_3$: C, 51.17; H, 6.20; N, 19.89%.

Dinitrophenylhydrazine (**5**), a major product from dinitrophenol ethers (**3a**—**j**) (Table 2) is isolated by crystallisation from ethanol, mp 200 °C (Lit,[34] mp 200 °C). The filtrate is evaporated and the residue is chromatographed on silica gel (eluent, benzene) to obtain minor partial reduction products (**4**). They are characterized (**4a**—**4f**; **4h**, **4i**, **4l**) by mp (mixed mp with authentic sample is not depressed). The unknown 2-amino-4-nitro-2′,4′-dichlorodiphenylether (**4g**) is characterized by spectral and microanalytical data. IR (Nujol) 3425, 3300, 3200, 1625, 1570, 1510, 1460, 1380, 1340, 1270, 1250, 1230, 1140, 1100, 1050, 865 cm^{-1}. ^{1}H NMR (CH_3CN) δ 4.57 (br s, 2H), 6.66—7.53 (m, 6H); MS *m/e* 299. Found: C, 47.81; H, 2.96; N, 9.33%. Calcd for $C_{12}H_8Cl_2N_2O_3$: C, 48.18; H, 2.69; N, 9.36%.

*Reduction of Nitroarene (**6**), Dinitroarenes (**1b**, **1d**, **1i**, **1j**, and **7**) and Dinitrophenol Ethers (**3a**, **3b**, **3e**, **3f**, **3g**, **3i**) with 60% Hydrazine Hydrate Alone.* A mixture of 2,4-dinitrophenol (**1b**) (0.05 mol), and 60% hydrazine hydrate (0.15 mol) is stirred for 10 min at 28—30 °C. Temperature is then raised to 90 °C in 45 min and stirring is continued for 18 h at 90 °C on water bath. Complete conversion of the nitroarene (**1b**) can be confirmed by TLC analysis on silica gel using benzene/ethanol (19:1) as eluent and colour development with iodine vapours. The dark red coloured reaction mixture is neutralized with dilute hydrochloric acid, when 2-amino-4-nitrophenol (**2b**) gets precipitated out. The solid filtered and crystallized from ethanol. Yield 7.53 g (98%), mp 141 °C (Lit,[16] mp 142—143 °C); mixed mp not depressed. Similar reactions of **1d**, **1i**, and **1j** give **2f**, **2l**, and **2n** in 70, 80, and 92% yields respectively (Table 3). In the case of **6** and **7**, there is no reduction and starting material can be recovered even after 36 h heating at 90 °C. The dinitrophenol ethers under similar treatment give 2,4-dinitrophenylhydrazine exclusively at 65 °C in 0.5 h.

*Reduction of Dinitrophenol Ethers (**3a**, **3d**, **3f**, **3g**, **3j**) in Methanol at 5 °C.* A mixture of methanol (40 ml), 80% hydrazine hydrate (1.9 ml) and Raney nickel (0.3 g) is refluxed for 10—12 min and cooled to 5 °C. To this cold solution is added 2,4-dinitroanisole (**3a**) (1.98 g, 10 mmol) in methanol (40 ml) under stirring. The reaction is continued for additional 45 min. Complete conversion of **3a** can be confirmed by TLC analysis on silica gel using benzene/ethanol (19:1) as eluent and colour development with iodine vapours. The catalyst is removed by filtration. The solvent is evaporated and the residue is chromatographed on silica gel (eluent, benzene). The aminonitrophenolic ethers (**4a**, **4f**, **4g**, **4l**) are characterized by mp, mixed mp and microanalysis. The unknown partial reduction product, 2-hydroxyamino-4-nitrophenyl 2-methoxyethyl ether (**4j**) mp 116 °C, from **3d** is characterized by spectral and microanalytical data. IR (Nujol) 3280, 3180, 1510, 1460, 1333, 1290, 1270, 1200, 1140, 1120, 1080, 1030, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3H), 3.8 (t, 2H), 4.16—4.54 (m, 3H, 1H exchangeable with D_2O), 4.72 (br s, 1H, exchangeable with D_2O), 7.08—7.40 (m, 1H), 7.92—8.72 (m, 2H). MS *m/e* 228. Found: C, 47.68; H, 5.58; N, 12.01%. Calcd for $C_9H_{12}N_2O_5$: C, 47.37; H, 5.20; N, 12.27%. The hitherto unknown compound 4-amino-2-nitro-2′,4′-dichlorodiphenyl ether (**4k**), mp 86 °C, isolated from **3g** is characterized by spectral and microanalytical data. IR (Nujol) 3480, 3365, 3300, 1625, 1580, 1510, 1460, 1380, 1340, 1270, 1250, 1230, 1140, 1100, 1050, 865 cm^{-1}; ^{1}H NMR (CH_3CN) δ 3.77 (brs, 2H), 6.43—7.23 (m, 6H); MS *m/e* 299. Found: C, 48.20; H, 3.07; N, 9.73%. Calcd for: $C_{12}H_8N_2Cl_2O_3$: C, 48.18; H, 2.69; N, 9.36%.

The major products, 2',2'-disubstituted 5,5'-dinitroazoxybenzenes (**9a**, **9b**, **9c**, **9d**) were isolated from **3a**, **3d**, **3f**, and **3j** respectively by column chromatography on silica gel column using benzene as eluent. They were characterized as follows:

2,2'-Dimethoxy-5,5'-dinitroazoxybenzene (**9a**), mp, 210 °C. IR (Nujol) 3090, 1600, 1525, 1450, 1340, 1290, 1145, 1090, 1020, 895, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.26 (d, 6H), 7.16—7.56 (m, 3H), 8.36—9.23 (m, 3H). MS *m/e* 348. Found: C, 48.08; H, 4.00; N, 16.16%. Calcd for $C_{14}H_{12}N_4O_7$: C, 48.28; H, 3.47; N, 16.08%.

2,2'-Bis(2-methoxyethoxy)-5,5'-dinitroazoxybenzene (**9b**), mp 178 °C. IR (Nujol) 3100, 2850, 1600, 1590, 1450, 1340, 1290, 1280, 1200, 1140, 1125, 1080, 1040, 940, 860, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 6H), 4.0 (m, 4H), 4.56 (m, 4H), 7.20—7.66 (m, 3H), 8.33—8.93 (m, 3H); MS *m/e* 436. Found: C, 50.10; H, 4.89; N, 12.31%. Calcd for $C_{18}H_{20}N_4O_9$: C, 49.54; H, 4.62; N, 12.84%.

2,2'-Dipropoxy-5,5'-dinitroazoxybenzene (**9c**), mp 106 °C. IR (Nujol) 3080, 1605, 1515, 1455, 1375, 1350, 1280, 1150, 1070, 1000, 900, 820, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 6H) 1.72—2.30 (m, 4H), 4.40 (t, 4H), 7.2—7.66 (m, 3H), 8.56—9.33 (m, 3H); MS *m/e* 404. Found: C, 52.95; H, 5.25; N, 13.24%. Calcd for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.29; N, 13.85%.

2,2'-Bis(benzyloxy)-5,5'-dinitroazoxybenzene (**9d**), mp 205 °C. IR (Nujol) 3080, 1600, 1530, 1415, 1345, 1275, 1142, 1085, 905, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.43 (d, 4H), 7.16—7.76 (m, 13H), 8.26—8.80 (m, 3H); MS *m/e* 500. Found: C, 62.25; H, 4.57; N, 11.41%. Calcd for $C_{26}H_{20}N_4O_7$: C, 62.40; H, 4.00; N, 11.20%.

References

1) N. R. Ayyangar, A. G. Lugade, P. V. Nikrad, and V. K. Sharma, *Synthesis*, **1981**, 640.

2) H. K. Porter, *Org. React.*, **20**, 455 (1973).

3) J. L. Miesel, G. O. P. O'Doherty, and J. M. Owen, "Catalysis in Organic Synthesis," ed by P. N. Rylander and H. Greenfield, Academic Press, New York, (1976), p. 273.

4) R. J. Alaimo and R. J. Storrin, "Catalysis of Organic Reactions," ed by W. R. Moser, Marcel Dekker Inc., New York, (1981), p. 473.

5) H. Limpricht, *Ber.*, **18**, 1400 (1885).

6) A. S. Wingrove and R. L. Caret, "Organic Chemistry," Harper and Row Publishers, New York (1981), p. 1122.

7) *Beilstein*, **9**, 414 (1942).

8) J. J. Blanksma and P. G. Fohr, *Recl. Trav. Chim.*, **65**, 711 (1946).

9) L. Bartolotti and A. Cerniani, *Bull. Sci. Fac. Chim. Ind. Bologna*, **14**, 33 (1956); *Chem. Abstr.*, **50**, 15182 (1956).

10) Y. Ogata and M. Okano, *J. Am. Chem. Soc.*, **71**, 3211 (1949).

11) C. C. Clark, "Hydrazine," Mathieson Chemical Corporation, Maryland, (1953), p. 32.

12) H. E. Oelinek and I. Zugravescu, Romanian Patent 49844 (1972); *Chem. Abstr.*, **79**, 146173 (1973).

13) P. E. Verkade, C. P. Van Dijk, and W. Meerburg, *Recl. Trav. Chim.*, **65**, 346 (1946).

14) F. Yuste, M. Saldana, and F. Walls, *Tetrahedron Lett.*, **23**, 147 (1982).

15) W. W. Hartman and H. L. Silloway, *Org. Synth.*, Coll. Vol. 3, 82 (1965).

16) P. Friedländer and M. Zeitlin, *Ber.*, **27**, 196 (1894).

17) K. P. Griffin and W. D. Peterson, *Org. Synth.*, **21**, 20 (1941).

18) B. M. Webster and P. E. Verkade, *Recl. Trav. Chim.*, **68**, 77, 83 (1949).

19) R. Foster, *J. Chem. Soc.*, **1957**, 4687.

20) W. Ozegowski, D. Krebs, and M. Wunderwald, *J. Prakt. Chem.*, **20**, 166 (1963).

21) A. T. Peters, *J. Appl. Chem. Biotechnol.*, **26**, 131 (1976).

22) H. Lindemann and S. Romanoff, *J. Prakt. Chem.*, **122**, 214 (1929); *Chem. Abstr.*, **24**, 91 (1930).

23) D. Pitre and E. Lorenzotti, *Chimica (Aarau)*, **19**, 462 (1965); *Chem. Abstr.*, **63**, 13128 (1965).

24) G. Schröeter, *Ber.*, **63**, 1308, 1317 (1930).

25) N. J. Leonard and A. M. Hyson, *J. Am. Chem. Soc.*, **71**, 1961 (1949).

26) E. Nölting and A. Collin, *Ber.*, **17**, 261 (1884).

27) A. G. Green and T. A. Lawson, *J. Chem. Soc.*, **59**, 1013 (1891).

28) C. Niemann, J. F. Mead, and A. A. Benson, *J. Am. Chem. Soc.*, **63**, 609 (1941).

29) J. F. Manning and J. P. Mason, *J. Am. Chem. Soc.*, **62**, 3136 (1940).

30) C. I. Brodrick, J. S. Nicholson, W. F. Short, and D. G. Wibberely, *J. Chem. Soc.*, **1953**, 1080.

31) A. I. Vogel, "A Text Book of Practical Organic Chemistry," 3rd ed., Longmans, London, (1956), p. 610.