Nitration of Aromatic and Heteroaromatic Compounds by Dinitrogen Pentaoxide

Jan M. Bakke, Ingrid Hegbom, Elin Øvreeide and Kjersti Aaby

Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway

Bakke, J. M., Hegbom, I., Øvreeide, E. and Aaby, K., 1994. Nitration of Aromatic and Heteroaromatic Compounds by Dinitrogen Pentaoxide. – Acta Chem. Scand. 48: 1001–1006 © Acta Chemica Scandinavica 1994.

Nitration of benzene and monosubstituted benzenes in liquid SO_2 by dinitrogen pentaoxide at $-11\,°C$ gave the corresponding nitroarenes with substitution patterns similar to those obtained by nitrations with HNO_3–H_2SO_4. For acetophenone an o/m ratio of 0.94 was obtained. The yields were dependent on the substituents. With a 1:1 ratio of arene:N_2O_5 the yields varied from 73% for toluene to 0.4% for nitrobenzene as substrates. From competition experiments and the nitration of bibenzyl it was concluded that the reaction was faster than the macroscopic rate of mixing. The qualitative order of reactivity for PhX was $X = OCH_3 > CH_3 > H > Cl > CH_3CO > NO_2$. Nitration with N_2O_5 in liquid CO_2 gave similar results.

Nitration of pyrimidine, pyrrole, imidazole and indole with N_2O_5–SO_2 gave no nitrated products. With thiophene, 2- (34%) and 3-nitrothiophene (5%) together with 2,4-(16%) and 2,5-dinitrothiophene (8%) were obtained. With pyridine, mono- and di-methylpyridines, quinoline, isoquinoline and 4-phenylpyridine nitration of the pyridine ring was obtained. The yields varied from ca. 70% to 16%, except for 3,5-, 2,5- and 2,6-dimethylpyridine for which only traces of nitro-dimethylpyridines were obtained. The reaction with the pyridines appears to be intramolecular both in the SO_2 phase and in the water phase used for quenching the reaction. The reaction was proposed to proceed by a complex formed in liquid SO_2:

$$PyrH + N_2O_5 + SO_2 \rightarrow [PyrH \cdot SO_2 \cdot N_2O_5] \xrightarrow{H_2O} 3\text{-}NO_2\text{-}Pyr + HNO_3$$
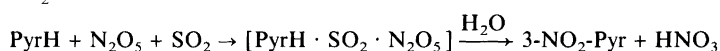
Dinitrogen pentaoxide (DNP) is a very reactive substance in nitration reactions.[1] It has been used for nitration of aromatic compounds in both non-polar and polar solvents and also with Lewis acids as catalysts.[2,3] Ingold and coworkers made a detailed kinetic investigation of the nitration of aromatic compounds by DNP in aprotic solvents. The results showed that at least two reaction mechanisms could operate: under non-ionising conditions, the undissociated DNP reacted with the aromatic compound. With catalysed ionising conditions, on the other hand, NO_2^+ was found to be the reactive species.[4] Titov has proposed an alternative mechanism involving free radical intermediates. This proposal was based on a detailed study of the products from the nitration with DNP in non-polar solvents.[5] Moodie investigated the nitration of highly deactivated aromatic compounds by DNP in nitric acid. In that case, NO_2^+ was found to be the major nitration agent. However, the mechanism was complex and several points are under further investigation.[6] Lately, Suzuki and coworkers have reported the nitration of aromatic and heteroaromatic compounds by dinitrogen tetraoxide and ozone.[7] These two substances

are known to react and give DNP[8] and this may also have been the nitration agent in their system.

We have presented some preliminary results on the use of DNP as a reagent for the nitration of aromatic compounds.[9] Here we report the results from nitrations with DNP in liquid carbon dioxide and sulfur dioxide. For some compounds the results obtained were very different from those obtained by the use of conventional nitration systems.

Results and discussion

Nitrations in liquid SO_2. Sulfur dioxide is a liquid from ca. -75 to $-10\,°C$ at atmospheric pressure and it has a dielectric constant $\varepsilon = 17.6$ ($-20\,°C$, $\varepsilon_{vacuum} = 1$).[10] It is thus more polar than solvents like chloroform or diethyl ether but less than aprotic solvents like N,N-dimethylformamide and dimethyl sulfoxide. Organic compounds are soluble in liquid SO_2, except for saturated hydrocarbons. Sulfur dioxide forms complexes with a number of compounds, including amines, ethers, alcohols and

aromatic compounds.[11,12] It has been used as a solvent in organic chemistry both for mechanistic investigations and organic preparations.[13] In our preliminary report, the combination of N_2O_5 and SO_2 showed particularly interesting properties as a nitration system.[9]

Nitration of aromatic compounds. We have reacted benzene and a number of substituted benzenes with N_2O_5 in liquid SO_2. The results are given in Table 1. The substitution pattern of the products was close to those reported for nitrations with HNO_3–H_2SO_4 or other methods involving NO_2^+, that is, with a high positional selectivity. For acetophenone a higher o/m ratio was obtained than that from HNO_3–H_2SO_4 (0.94 vs. 0.3). Such a high o/m ratio was also observed in the nitration of acetophenone with N_2O_4–O_3.[7] As N_2O_4 and O_3 react to give DNP,[8] this may also have been the nitrating agent in that case. To estimate the relative reactivity of the aromatic compounds towards DNP, we also conducted a series of competition experiments (Table 2). The substrates were allowed to compete with benzene or chlorobenzene for 10 mol % of DNP. The dependence of the reactivity on the substituents was qualitatively as expected for electrophilic nitrations. However, from the partial rate factors (Table 3) it is evident that the substrate selectivity for this reaction was lower than for the nitration with HNO_3–H_2SO_4.[14a] Correlation of the partial rate factors (Table 3) with Hammett σ^+ values gave $\rho^+ = -9.1$ ($r = 0.973$) for the HNO_3–H_2SO_4 nitrations and $\rho^+ = -3.9$ ($r = 0.947$) for reactions with DNP–SO_2. In Table 3, the partial rate factors for toluene and chlorobenzene were calculated from the results of the competition experiments with benzene. Owing to low reactivity, the partial rate factors for acetophenone and nitrobenzene had to be obtained from the competition reactions with chlorobenzene and the relative rate of reaction $k_{chlorobenzene}k_{benzene} = 0.3$. This made the precision of the Hammett correlation lower than desired. Nevertheless, the results showed that the DNP–SO_2 nitration system has a lower substrate selectivity than that of HNO_3–H_2SO_4. Reactions with low intermolecular and high intramolecular selectivity have been observed, e.g., for nitrations with NO_2BF_4 in sul-

Table 1. Reaction of benzene and monosubstituted benzenes (6.4 mmol) with N_2O_5 (6.4 mmol) in SO_2 (l) (25 ml) at $-30°C$.

		Isomer ratio		
Substituent	Yield (%)	ortho	meta	para
H	40			
Cl	65	34	1	66
CH_3CO	60	47	50	3
CN	4	18	78	4
NO_2	0.3	2	93	5
CH_3	73	61	5	35
CH_3O	35[a]	46	0	54

[a] In addition, a 25% yield of dinitroanisole (2,6-:2,4-dinitroanisole 11:89) was obtained.

Table 2. Competition reactions between pairs of monosubstituted benzenes (or benzene) (0.2 mmol each) for N_2O_5 (0.07 mmol) in SO_2 (l) (25 ml).

Competing pair of substances	Yields (%)
Anisole/benzene	7[a]/3.6
Toluene/benzene	9/7
Chlorobenzene/benzene	3/10
Acetophenone/benzene	0/14
Benzonitrile/benzene	0/10
Anisole/chlorobenzene	8[b]/3
Toluene/chlorobenzene	10/4
Acetophenone/chlorobenzene	0.3/12
Benzonitrile/chlorobenzene	0/7
Nitrobenzene/chlorobenzene	0.02/15

[a] 4.5% mono- and 2.4% dinitroanisole.
[b] 5.0% mono- and 2.7% dinitroanisole.

Table 3. $\log_{10}$ partial rate factors ($\log_{10} f$) for the nitration of benzene derivatives (PhX) with N_2O_5 in liquid SO_2 and CO_2. Calculated from the data in Tables 1 and 2.

	Conditions					
	N_2O_5–SO_2			HNO_3–H_2SO_4[14]		
X	ortho	meta	para	ortho	meta	para
Cl	-0.51	-2.05	0.07	-1.17	-2.74	-0.61
CH_3	0.37	-0.71	0.43	1.65	0.35	1.78
CH_3CO	-1.95	-1.92	-2.84	-4.99	-4.56	-5.81
NO_2	-4.61	-2.95	-4.22	-7.97	-6.79	-8.14

folane.[15] However, with fast reactions, the macroscopic rate of mixing may be slower than the rate of reaction. The results therefore may not give a correct picture of the substrate selectivity.[16] A test for this was presented by Ridd, in which an excess of bibenzyl is reacted with the nitrating agent. A higher dinitrobibenzyl/mononitrobibenzyl ratio than that expected from statistical considerations was considered evidence for such a situation. Accordingly, we nitrated bibenzyl with an approximately equimolar amount of DNP in liquid SO_2. The results are given in Table 4. If the mixing was fast compared with the rate of nitration, the statistical composition of the products would depend on the initial ratio $R = 2[\text{Bibenzyl}]/[N_2O_5]$.[16] From Table 4, it is evident that the observed ratio [dinitrobibenzyl]/[mononitrobibenzyl] (7.8) was higher than that expected from a statistical distribution

Table 4. Product composition from the reaction of bibenzyl (0.25 M) with N_2O_5 (0.29 M, $R = 1.72$) in SO_2 at $-30°C$. For comparison, the statistical distribution of products are included. For details see the text.

Compounds	Experimental composition (%)	Statistical composition (%)
Bibenzyl	65	18
Mononitrobibenzyl	4	49
Dinitrobibenzyl	31	34

(0.7). This strongly suggests that the rate of reaction was fast on the macroscopic mixing time scale. Therefore, the results from the competition experiments gave only qualitative information on the substrate selectivity. In conclusion on this part, it is obvious that the combination DNP-SO_2 is a reactive nitration system for aromatic compounds. The order of reactivities was the same as for systems with NO_2^+ as the nitration agent and so were the isomer ratios (except for acetophenone). It should be noted that the yields from the less reactive compounds were low even when the intermolecular selectivity was low. This may have been due to the low reaction temperature.

Nitration of heteroaromatic compounds. We have reacted a number of heteroaromatic compounds with DNP in SO_2. The results are given in Tables 5 and 6. For pyrimidine, pyrrole, imidazole and indole no, or only traces of nitrated products was obtained. With thiophene, four products were obtained, 2-(34%) and 3-nitrothiophene (5%), 2,4-dinitrothiophene (16%) and 2,5-dinitrothiophene (8%). The ratio of 2-nitro-/3-nitrothiophene (6.8) was almost the same as that obtained with benzoyl nitrate in acetonitrile (6.2).[17] Also, on nitration of 2-nitrothiophene with fuming nitric acid, 2,4- and 2,5-dinitrothiophene (1:1) were obtained.[18] Thus, DNP-SO_2 gave a similar type of product mixture as that obtained with other nitration systems.

However, on nitration of pyridines, quinoline and isoquinoline the results were different from those obtained earlier. The direct nitration of pyridine and monoalkyl pyridine gives only low yields of the corresponding nitropyridines: nitration of pyridine with HNO_3-H_2SO_4 gave 3% of 3-nitropyridine[19] and the use of KNO_3-H_2SO_4 at 330°C gave 1% of the same compound.[20] 2-Methylpyridine gave 2% 5-nitro-2-methylpyridine with the same reactants at 160°C.[21] Even as late as 1992 a patent was obtained for a process for the nitration of pyridine with N_2O_4-O_3 with a yield of 3-nitropyridine of only 3%.[22] Nitration by conventional methods of compounds with both pyridine and aromatic rings such as phenylpyridines, quinolines and isoquinolines results in nitration of the aromatic ring system: 4-phenylpyridine and HNO_3-H_2SO_4 gave 4-(2'-nitrophenyl)pyridine

Table 5. Nitration of heteroaromatic compounds (12.5 mmol) with N_2O_5 (25.0 mmol) in SO_2 (liq., 25 ml).

Substrate	Yield (%)	Position of NO_2
Pyridine	63	3
4-Phenylpyridine	37	3
Quinoline	16	3
6-Methoxyquinoline	69	5
Isoquinoline	28	4
Pyrimidine	0	
Pyrrole	Tars	
Imidazole	Complex mixture	
Indole	Complex mixture	
Thiophene	63	2/3/2,4/2,5

(20%), 4-(3'-nitrophenyl)pyridine (33%) and 4-(4'-nitrophenyl)pyridine (47%).[23] With quinoline and isoquinoline, the same method gave mixtures of the 5- and 8-nitroderivatives.[24]

These results show that the pyridine ring is strongly deactivated for nitration. This is common to all electrophilic substitution: partial rate factors for electrophilic substitution of pyridine is in the order of 10^{-6} and of pyridinium ions as low as 10^{-20}.[25]

From Tables 5 and 6, it is evident that the DNP-SO_2 nitration system represents an important new method for the introduction of the nitro group into the pyridine ring system. Pyridine and monoalkylpyridines were nitrated with good yields. The nitration generally took place in the 3- or 5-position of the ring. The only exception was for 2-methylpyridine which gave two products, 3-nitro- and 5-nitro-2-methylpyridine in a 1:9 ratio. Surprisingly, 3,5-, 2,6- and 2,5-dimethylpyridine were not nitrated or gave a low yield only (2,6-dimethyl-3-nitropyridine, 1%). It is known that methyl groups activate the pyridine nucleus towards electrophilic substitutions, 2,6-dimethylpyridine was nitrated by the use of HNO_3-H_2SO_4 (81%)[26] and 2,4-dimethylpyridine was nitrated in the 3-position (25%) and in the 5-position (25%).[27] We will return to this point later.

For quinoline and isoquinoline, the pyridine ring was nitrated in preference to the carbocyclic ring systems. Again, the nitration took place in the β-position relative to the ring nitrogen atom. Nitrations of these compounds with HNO_3-H_2SO_4 gave substitution in the carboxylic ring only and in the positions expected for an electrophilic aromatic substitution.[24] 6-Methoxyquinoline was nitrated in the 5-position with DNP-SO_2 and not in the 3-position as for quinoline itself. Nitration of quinoline with HNO_3-Ac_2O gave a 6% yield of 3-nitroquinoline. with isoquinoline, the same method gave 4-nitroisoquinoline (14%).[28]

From Table 5 it is evident that the nitration by DNP is liquid sulfur dioxide represents a new method for the nitration of substances containing a pyridine ring. For the first time it is possible to nitrate pyridine, monoalkylpyridines and phenylpyridines directly and with acceptable to good yields. Some of the dimethylpyridines are nitrated with better results than those obtained before (2,3-, 2,4- and 3,4-dimethylpyridine) while others are not nitrated by DNP-SO_2. For quinolines and isoquinolines the yields are less satisfactory. However, compared with available methods,[28] the present system is not without interest.

The mechanism for the nitration of the pyridine system is currently under investigation. It appears to be different from that of the standard methods as the nitronium ion was not the nitration agent; nitronium tetrafluoroborate in SO_2 did not react with pyridine. Furthermore, N-nitropyridinium nitrate (from DNP and pyridine) was not the nitration agent as it is known not to react with pyridine in SO_2.[29]

The reaction may be intramolecular, both in the SO_2 phase and in the water phase used for quenching of the

reaction, when pyridine was reacted with DNP–SO$_2$ for 10 min and 4-methylpyridine added to the SO$_2$ solution, only 3-nitropyridine and unchanged 4-methylpyridine were isolated. The same result was obtained when 4-methylpyridine was added to the water phase before quenching the reaction mixture of pyridine and DNP–SO$_2$. Analogous results were obtained when the reactions were started with 4-methylpyridine and pyridine added.

The product from the reaction in SO$_2$ was not 3-nitropyridine. When the SO$_2$ solution was evaporated, the residue decomposed with evolution of nitric oxides (brown gases) and pyridine, and only 8% 3-nitropyridine was recovered. The quenching of the reaction mixture with water was thus a necessary part of the formation of the nitropyridines.

The nitrations of the dimethylpyridines (Table 6) showed that neighbouring α and β positions in the pyridine ring had to be unsubstituted; 2,5-, 2,6- and 3,5-dimethylpyridine gave only traces of nitrated products. This was not an electronic effect as, e.g., 2,4-dimethylpyridine gave 64% of 5-nitro-2,4-dimethylpyridine. However, whether this is because an N-α-β migration takes place or if the effect is of steric nature is not known at present.

From these points, it appears that a complex is formed in SO$_2$ between DNP and pyridine. As the nitration of pyridine did not take place in liquid CO$_2$ (see below), it is reasonable to assume that SO$_2$ also is part of the complex. The complexation of pyridine with SO$_2$ is well known.[30] This complex then reacts with water to give nitropyridine [eqn. (1)].

$$PyrH + SO_2 + N_2O_5 \rightarrow [PyrH \cdot SO_2 \cdot N_2O_5]$$

$$\xrightarrow{H_2O} 3\text{-}NO_2\text{-}Pyr + HNO_3 \tag{1}$$
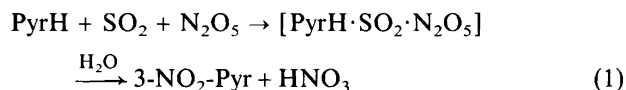
Nitrations in liquid carbon dioxide. Carbon dioxide is a liquid from -57 to $+31\,^\circ$C with corresponding pressures 4.2 and 74 bar. In this state it is non-polar and weakly acidic.[31,32] Organic substances in general are soluble in it. However, only low molecular weight polar compounds are soluble in CO$_2$. Liquid carbon dioxide has found limited use as a reaction medium, although it has been extensively used for extractions and chromatography, especially in the supercritical state. Isaacs and Keating have used it as a solvent for Diels–Alder reactions in both the

liquid and supercritical state and it has also been used for electrochemical reactions and for photoisomerisations.[32,34]

We performed the nitrations in a stainless steel reactor. A nitromethane solution of DNP was placed in the reactor together with a magnetic stirring bar and liquid CO$_2$ was pumped in at 60–65 bar. A chloroform solution of the substrate was then pumped in by means of an HPLC pump. At the end of the reaction, the contents of the reactor were expanded into a water–ice mixture and worked up.

The results from the nitration of a series of aromatic compounds are given in Table 7. Owing to difficulties in obtaining a reproducible volume of CO$_2$, the concentrations of the reactants are also given. However, for several of the compounds in Table 7, experiments at different concentrations showed that the yields and isomer distribution was not very dependent on the concentrations.

The isomer distributions in Table 6 are approximately the same as those obtained by nitrations with, e.g., HNO$_3$–H$_2$SO$_4$. However, in this medium a high o/m ratio was also obtained from acetophenone. In competition experiments, the results were very dependent on the rate of pumping the reactants into the DNP–CO$_2$ solution. Obviously here the situation was analogous to that in SO$_2$, the rate of reaction being fast compared with the rate of macroscale mixing. The competition experiments were therefore of qualitative value only and showed the reactivity sequence for PhX: X = H > Cl $\approx$ CH$_3$CO > CN > NO$_2$. Due to its insolubility in CO$_2$, bibenzyl could not be nitrated in this solvent and Ridd's test was therefore not performed. However, from the results in Table 7, the nitration with DNP in liquid CO$_2$ gave results similar to those obtained with more conventional nitration systems. The mechanism may have been the same as for nitrations with DNP in non-polar organic solvents.[4,5] Attempts to use NO$_2$BF$_4$ as a nitration agent failed owing to its insolubility in liquid CO$_2$.

We also reacted a series of heteroaromatic compounds with DNP in liquid CO$_2$. Pyridine, pyrrole, indole and imidazole all gave either intractable tars or complicated reaction mixtures. Thiophene gave a mixture of products:

Table 6. Nitration of methyl- and dimethyl-pyridines (12.5 mmol) with N$_2$O$_5$ (25.0 mmol) in SO$_2$ (liq., 25 ml).

Substrate	Yield (%)	Position of NO$_2$ group
2-Methylpyridine	70	5/3 (9/1)
3-Methylpyridine	30	5
4-Methylpyridine	54	3
3,5-Dimethylpyridine	0	
3,4-Dimethylpyridine	58	5
2,6-Dimethylpyridine	1	3
2,5-Dimethylpyridine	<3	3/4 (1:4)
2,4-Dimethylpyridine	66	5
2,3-Dimethylpyridine	46	5

Table 7. Reaction of benzene and monosubstituted benzenes (12.5 mmol) with N$_2$O$_5$ (12.5 mmol) in CO$_2$ (l) at 22 $^\circ$C.

Substituent	Yield (%)	Isomer ratio ortho	meta	para	Concentration of reactants/M
H	64				0.93
Cl	43	26	0.5	74	0.24
CH$_3$CO	47	43	52	5	0.43
CN	25	22	69	9	0.28
NO$_2$	46	11	87	2	0.69
CH$_3$	19[a]	50	2	48	0.35
CH$_3$O	17[b]	35	0	65	0.27

[a] In addition, an 18% yield of dinitrotoluenes (2,4-:2,6-dinitrotoluene 5:1) was obtained. [b] In addition, a 13% yield of 2,4-dinitroanisole was obtained.

2-nitrothiophene (6%), 3-nitrothiophene (1%), 2,4-dinitrothiophene (39%) and 2,5-dinitrothiophene (23%).

From the results presented here, the nitration by DNP in liquid CO_2 gave results very similar to those obtained by nitration with DNP in non-polar organic solvents. No special effects were observed, in contrast with those from the reactions in liquid SO_2.

Conclusion. The nitration of aromatic compounds with DNP in liquid SO_2 showed this system to be very reactive and to give products of compositions similar to those obtained by conventional nitration systems. However, nitration of pyridine compounds gave in general good yields of the corresponding β-nitropyridines. The nitration agent in that case was not NO_2^+ and the reaction appears to be intramolecular.

The nitration of aromatic compounds by DNP in liquid CO_2 gave results similar to those obtained by nitration with DNP in non-polar organic solvents. Pyridines were not nitrated by this system.

Experimental

The preparation of DNP and the manipulation of liquid SO_2 has been reported.[9] The reactions with the results in Tables 1–6 were performed as before,[9] except that the reactions in SO_2 were run at constant temperature (-30°C). The reaction mixtures were analysed by GC and the yields obtained by the internal standard method. For pyridine and pyridine derivatives, the yields were also determined from isolated, crystallised products. The products were identified by comparison of their physical properties (m.p., IR, ^1H and ^{13}C NMR and MS spectroscopy) with those of authentic samples. For new compounds or compounds which were difficult to obtain, the spectroscopic data were sufficient to determine the structure. The reactions in liquid CO_2 were performed in a 100 ml stainless steel autoclave with a ca. 75 ml glass reaction tube inside. The autoclave was equipped with two ports for admission of liquid CO_2 and the substrate, one port with a tube to the bottom of the autoclave for discharging the reaction mixture and one port for a safety valve (90 bar). At the start of the reaction DNP was added to the Ar-filled autoclave, either as crystals or dissolved in purified nitromethane[35] (5 M). These two procedures gave the same results. The autoclave was then closed and liquid CO_2 was pumped in by a high pressure pump (Chematron AB, Östersund, Sweden). The amount of CO_2 was checked by weighing the autoclave. The volume could also, in many cases, be checked by inspection of the reaction vessel after the reaction as a thin layer of light brown material appeared on its inside. The substrate was then pumped in as a chloroform solution (25–50 vol.%) by means of a Chrompack ISOS HPLC pump. Usually 5 ml of the solution were pumped in over 2.5 min but to check the role of the mixing the pumping was also performed for 0.5 and 1.0 min.

References

1. Fischer, J. W. In: Feuer, H. and Nielsen, A. T. Eds., *Nitro Compounds, Recent Advances in Synthesis and Chemistry*, VCH, New York, 1990.
2. Olah, G. A. In: Albright, L. F. and Hanson, C., Eds., *Industrial and Laboratory Nitrations*, ACS Symposium Series 22, Washington DC 1976.
3. Millar, R. W., Colclough, M. E., Golding, P., Honey, P. J., Paul, N. C., Sanderson, A. J. and Stewart, M. J. In: Field, J. E. and Gray, P., Eds., *Energetic Materials*, The Royal Society, London 1992.
4. Gold, V., Hughes, E. D., Ingold, C. K. and Williams, G. H. *J. Chem. Soc.* (1950) 2452.
5. Baryshnikova, A. N. and Titov, A. I. *Dokl. Akad. Nauk SSSR 114* (1957) 777.
6. Moodie, R. B. and Stephens, R. J. *J. Chem. Soc., Perkin Trans. 2* (1987) 1059; Moodie, R. B., Sanderson, A. J. and Willmer, R. *J. Chem. Soc., Perkin Trans. 2* (1990) 833; Moodie, R. B., Sanderson, A. J. and Willmer, R. *J. Chem. Soc., Perkin Trans. 2* (1991) 645.
7. Suzuki, H., Kozai, I. and Murashima, T. *J. Chem. Res. (S)* (1993) 156; Suzuki, H., Murashima, I. K. and Mori, T. *J. Chem. Soc., Perkin Trans. 1* (1993) 1591; Suzuki, H., Mori, T. and Maeda, K. *J. Chem. Soc., Chem. Commun.* (1993) 1335; Suzuki, H. and Murashima, T. *J. Chem. Soc. Perkin Trans. 1* (1994) 903.
8. Harris, A. D., Trebelas, J. C. and Johanssen, H. B. In: Young Tyree, S. Ed., *Inorganic. Synthesis*, Vol IX, McGraw Hill, New York 1967.
9. Bakke, J. M. and Hegbom, I. *Acta Chem. Scand. 48* (1994) 181.
10. Weast, R. C. *CRC Handbook of Chemistry and Physics*, 58th ed., CRC Press, Palm Beach 1978.
11. Lorimer, J. W., Smith, B. C. and Smith, G. H. *J. Chem. Soc., Faraday Trans. 1* (1975) 2232.
12. Andrews, L. J. and Keefer, R. M. *J. Am. Chem. Soc. 73* (1951) 4169.
13. Tokura, N. *Synthesis 12* (1971) 639.
14. Schofield, K. *Aromatic Nitration*, Cambridge University Press, Cambridge 1980: (a) chap. 12, (b) chap. 7.
15. Olah, G. A. *Acc. Chem. Res. 4* (1971) 240.
16. Christy, P. F., Ridd, J. H. and Stears, N. D. *J. Chem. Soc. B* (1970) 797.
17. Östman, B. *Ark. Kem. 19* (1962) 499.
18. Östman, B. *Acta Chem. Scand. 22* (1968) 2754.
19. Ege, S. *Organic Chemistry*, Health, Lexington 1984, p. 1827.
20. Kirpalt, A. and Reiter, E. *Ber. Dtsch. Chem. Ges. 58* (1925) 699.
21. Plazek, E. *Ber. Dtsch. Chem. Ges. 72* (1939) 577.
22. Suzuki, H., Murashima, T. and Tsukamoto, K. *Jpn. Kokai Tokkyo Koho* JP 04282368 A2 (1992); *Chem. Abstr. 118* (1993) 101821d.
23. De Sarlo, F. and Ridd, J. H. *J. Chem. Soc. B* (1971) 712.
24. Dewar, M. J. S. and Maitlis, P. M. *J. Chem. Soc.* (1957) 2521.
25. Katritzky, A. R. and Ridgewell, B. J. *J. Chem. Soc.* (1963) 3753, 3882.
26. Brawn, W. V. and Neil, R. H. *J. Org. Chem. 26* (1961) 3546.
27. Dodd, R. H., Doisy, X. and Potier, P. *Heterocycles 28* (1981) 1101.
28. Dewar, M. J. S. and Maitlis, P. M. *J. Chem. Soc.* (1957) 944.
29. Olah, G. A., Olah, J. A. and Overchuck, N. A. *J. Org. Chem. 30* (1965) 3373.

30. Oh, J. J., Hilling, K. W. II. and Kuczkowski, R. L. *J. Am. Chem. Soc. 113* (1991) 7480 and references cited therein.
31. Compressed Gas Association, *Handbook of Compressed Gases*, third ed., Reinhold, New York 1990.
32. Hyatt, J. A. *J. Org. Chem. 49* (1984) 5097.
33. Isaacs, N. S. and Keating, *J. Chem. Soc., Chem. Commun.* (1992) 876.

34. Dandge, D. K., Heller, J. P. and Wilson, K. V. *Ind. Eng. Chem. Prod. Res. Dev. 24* (1985) 162.
35. Perrin, D. D. and Armarego, W. L. F. *Purification of Laboratory Chemicals*, third ed. Pergamon, Oxford 1988.