J. prakt. Chem. 334 (1992) 497 – 504

Journal für praktische Chemie
Chemiker-Zeitung

Vicarious Nucleophilic Hydroxylation of Aromatic Nitro Compounds with Organic Hydroperoxides

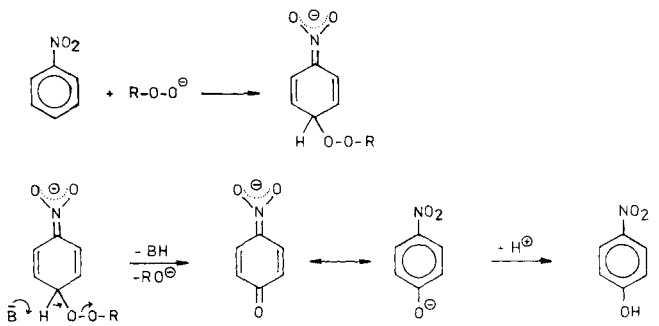
Thomas Brose, Felix Holzscheiter, Gunter Mattersteig, Wilhelm Pritzkow and Volkmar Voerckel

Merseburg, Technical University, Department of Chemistry

Dedicated to Professor Dr. Dr. h. c. Alfred Rieche on the Occasion of his 90th Birthday

Abstract. Nitrobenzene, α-nitronaphthalene, m-dinitrobenzene, 1,3,5-trinitrobenzene, m-nitrobenzophenone, m-nitrobenzonitrile, methyl m-nitrobenzoate and m-nitro diphenylsulphone can be hydroxylated with cumene or tert-butyl hydroperoxide in dipolar aprotic solvents in the presence of strong bases. The hydroxyl group is introduced preferably in p-position to the nitro group. Attempts to hydroxylate benzophenone, anthraquinone, 2-ethyl anthraquinone, anthraquinone 2-sulphonate, benzonitrile and diphenyl sulphone under the same conditions failed. 1-Nitroanthraquinone delivered 1-hydroxy, 1,2-dihydroxy and 1,4-dihydroxy anthraquinone.

Two independent papers dealing with the vicarious nucleophilic hydroxylation of aromatic nitro compounds with organic hydroperoxides in the presence of strong bases (Formula Scheme 1) were published 1990 [1, 2]. *Makosza* used liquid ammonia as the solvent [1], we accomplished the hydroxylation either in two-phase systems in the presence of phase transfer catalysts or in dipolar aprotic solvents [2]. We have extended our studies, and this paper deals with the hydroxylation of several aromatic nitro compounds with cumene or tert-butyl hydroperoxide in the dipolar aprotic solvents dimethyl formamide (DMF), dimethyl acetamide (DMA), dimethyl sulphoxide (DMSO), hexamethyl phosphoric acid triamide (HMPT) and tetramethyl urea (TMU). Potassium tert-butoxide, sodium methoxide and potassium hydroxide were used as bases. In all cases a small amount of the disodium salt of ethylene diamine tetraacetic acid was added in order to avoid a catalytic decomposition of the hydroperoxides by traces of transition metal ions [3].



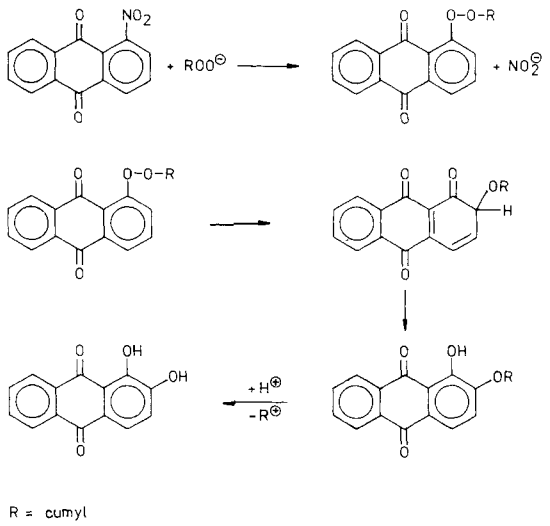
Formula Scheme 1 Mechanism of the vicarious nucleophilic hydroxylation of aromatic nitro compounds

The results of our studies are collated in Tables 1 and 2. It is clear that the vicarious nucleophilic hydroxylation of aromatic nitro compounds is a relatively fast reaction giving high yields already after about 1 h at 0 – 20 °C. Extended reaction times, especially at temperatures above 20 °C lead to a decrease of the yield. Both hydroperoxides used give comparable yields.

In the cases of nitrobenzene, 1-nitronaphthalene, m-nitro benzophenone, methyl m-nitrobenzoate, m-nitro benzonitrile and m-nitro diphenylsulphone the hydroxylation takes place preferably in p-position to the nitro group.

All attempts to accomplish vicarious nucleophilic hydroxylation of benzophenone, anthraquinone, 2-ethyl anthraquinone, anthraquinone 2-sulphonate, benzonitrile and diphenyl sulphone under the conditions used for nitro aromatics were unsuccessful. Most of the starting compounds were recovered unchanged. Only benzonitrile reacted, but only benzamide, no product of the hydroxylation of the aromatic nucleus, was isolated.

1-Nitro anthraquinone reacted with cumene hydroperoxide in the presence of strong bases in dipolar aprotic solvents. In this case the 1-nitro group was substituted by a hydroxy group, but besides 1-hydroxy anthraquinone also the 1,2- and the 1,4-dihydroxy compounds were formed (Tabelle 3). The mechanism of the reactions taking place is not clear. It is known



Formula Scheme 2 Reaction of 1-nitro anthraquinone with cumene hydroperoxide: possible mechanism for the formation for 1,2-dihydroxy anthraquinone. An analogous mechanism is possible for the formation of 1,4-dihydroxy anthraquinone

Table 1 Reaction of aromatic nitro compounds with organic hydroperoxides in the presence of strong bases using dipolar aprotic solvents (nitro compound : hydroperoxide : base = 1 : 1 : 2.4)

starting compound	hydroper-oxide[a)]	solvent	base	temperature °C	time h	reaction product (yield in %)
nitrobenzene	CHP	DMSO	t-BuOK	15/20	10	4-nitrophenol (40)
	CHP	HMPT	t-BuOK	−5/+5	12	4-nitrophenol (50)
m-dinitro	CHP	DMSO	t-BuOK	15/20	0.75	2,4-dinitrophenol (55)
benzene	CHP	DMSO	t-BuOK	15/20	1.0	2,4-dinitrophenol (60)
	CHP	DMSO	t-BuOK	15/20	1.5	2,4-dinitrophenol (52)
	CHP	DMSO	t-BuOK	15/20	2.5	2,4-dinitrophenol (62)
	CHP	DMSO	t-BuOK	15/20	4.0	2,4-dinitrophenol (53)
	CHP	DMSO	t-BuOK	15/20	5.5	2,4-dinitrophenol (47)
	t-BHP	DMSO	t-BuOK	15/20	1.7	2,4-dinitrophenol (58)
	t-BHP	DMSO	t-BuOK	25	2.0	2,4-dinitrophenol (31)
	CHP	DMSO	MeONa	10/15	2.5	2,4-dinitrophenol (15)
	CHP	DMF	t-BuOK	−10/0	1.0	2,4-dinitrophenol (80)
	CHP	DMA	t-BuOK	−5/+5	1.0	2,4-dinitrophenol (33)
	CHP	HMPT	t-BuOK	−5/+5	0.5	2,4-dinitrophenol (55)
	CHP	HMPT	t-BuOK	−5/+5	0.75	2,4-dinitrophenol (65)
	CHP	HMPT	t-BuOK	15/20	1.0	2,4-dinitrophenol (85)
	CHP	HMPT	t-BuOK	15/20	1.5	2,4-dinitrophenol (92)
	CHP	HMPT	t-BuOK	15/20	4.0	2,4-dinitrophenol (60)
	t-BHP	HMPT	t-BuOK	20/25	1.6	2,4-dinitrophenol (56)
1,3,5-trinitro	CHP	DMSO	t-BuOK	12/20	0.25	2,4,6-trinitrophenol (30)
benzene	CHP	HMPT	t-BuOK	−5/+5	0.25	2,4,6-trinitrophenol (50)
1-nitro-	CHP	DMSO	t-BuOK	15	1.0	4-nitro-naphth-1-ol (55)
naphtalene	CHP	DMSO	t-BuOK	25	1.0	4-nitro-naphth-1-ol (50)
	CHP	DMSO	t-BuOK	25	3.0	4-nitro-naphth-1-ol (53)
	t-BHP	DMSO	t-BuOK	25	2.1	4-nitro-naphth-1-ol (51)
	t-BHP	DMSO	t-BuOK	15/20	5.5	4-nitro-naphth-1-ol (51)
	CHP	HMPT	t-BuOK	−5/+5	0.5	4-nitro-naphth-1-ol (50)
	CHP	HMPT	t-BuOK	5/10	0.25	4-nitro-naphth-1-ol (58)
	CHP	HMPT	t-BuOK	5/10	0.5	4-nitro-naphth-1-ol (42)
	CHP	HMPT	t-BuOK	5/10	0.75	4-nitro-naphth-1-ol (37)
	t-BHP	HMPT	t-BuOK	25	2.1	4-nitro-naphth-1-ol (28)

[a)] CHP: cume hydroperoxide; t-BHP: tert-butyl hydroperoxide

Table 2 Reaction of aromatic nitro compounds bearing a second electron-withdrawing substituent with organic hydroperoxides in the presence of strong bases using dipolar aprotic solvents (nitro compound : hydroperoxide : base = 1 : 1 : 2,4)

starting compound[a]	hydro-peroxide[b]	solvent	base	temperature °C	time h	reaction product[c] (yield)
8	CHP	DMSO	t-BuOK	15/20	2.0	**9** (44): **10** (11)
	CHP	HMPT	t-BuOK	15	2.0	**9** (48); **10** (12)
	t-BHP	DMSO	t-BuOK	15/25	2.0	**9** (44); **10** (11)
	t-BHP	HMPT	t-BuOK	15	2.0	**9** (48): **10** (12)
	CHP	DMSO	KOH	25	2.0	**9** (28); **10** (7)
	CHP	HMPT	KOH	25	2.0	**9** (32); **10** (8)
4	CHP	DMSO[d]	t-BuOK	0/10	2.0	**3** (20)
	CHP	HMPT	t-BuOK	−5/+5	0.5	**3** (70)
	CHP	HMPT	t-BuOK	−5/+5	2.0	**3** (65)
	CHP	DMF	KOH	−5/+5	3.0	**3** (35)
	CHP	HMPT	KOH	−5/+5	3.0	**3** (45)
6	CHP	DMF	t-BuOK	−5/+5	2.0	**5** (55)
	CHP	DMSO	t-BuOK	20	1.0	**5** (45)
	CHP	HMPT	t-BuOK	−5/+5	1.0	**5** (48)
	CHP	HMPT	t-BuOK	−5/+5	2.0	**5** (45)
11	CHP	DMSO	t-BuOK	20/30	2.0	**12** (40); **13** (8)
	CHP	DMF	t-BuOK	−5/+5	2.0	**12** (58); **13** (22)
	CHP	DMA	t-BuOK	−5/+5	2.0	**12** (32); **13** (9)
	CHP	TMU	t-BuOK	−5/+5	2.0	**12** (57); **13** (23)

[a] **8**: m-nitro benzophenone; **4**: m-nitrobenzoic acid methylester; **6**: m-nitro benzonitrile; **11**: m-nitro diphenylsulphone (see Formula Scheme 3)
[b] CHP: cumene hydroperoxide; t-BHP: tert-butyl hydroperoxide
[c] **9**: 2-hydroxy-5-nitro benzophenone; **10**: 4-hydroxy-3-nitro benzophenone; **3**: methyl 2-hydroxy-5-nitrobenzoate; **5**: 2-hydroxy-5-nitro benzonitrile; **12**: 2-hydroxy-5-nitro diphenylsulphone; **13**: 4-hydroxy-3-nitro diphenylsulphone (see Formula Scheme 3)
[d] DMSO/tetrahydrofurane (3 : 1)

Table 3 Reaction of 1-nitro anthraquinone with cumene hydroperoxide and strong bases in dipolar aprotic solvents (1-nitro anthraquinone: hydroperoxide : base = 1 : 1 : 1,2)

solvent	base	temperature °C	time h	reaction product[a] (yield in mole − %)
DMF	t-BuOK	−5/+5	3	A_1 (53); A_2 (25); A_3 (11); A (11)
DMSO	t-BuOK	15/25	3	A_1 (45); A_2 (35); A_3 (10)
	KOH	15/25	10	A_1 (55); A_2 (32); A_3 (13)
HMPT	t-BuOK	15/20	3	A_1 (45); A_2 (35); A_3 (8)
	t-BuOK	−5/+5	0.25	A_1 (35); A (55)
	t-BuOK	−5/+5	0.5	A_1 (23); A_2 (23); A (54)
	t-BuOK	−5/+5	1.0	A_1 (55); A_2 (17); A_3 (10; A (18)
	KOH	15/20	10	A_1 (55); A_2 (23); A (22)

[a] A_1: 1-hydroxy anthraquinone; A_2: 1,2-dihydroxy anthraquinone; A_3: 1,4-dihydroxy anthraquinone; A: unchanged 1-nitro anthraquinone

that aromatic nitro groups can be substituted by strong nucleophils [4 – 6], but in our case a compound with a peroxy group directly connected with an aromatic nucleus is to be expected; such compounds are instable [7] and should rapidly rearrange [8, 9]. In our case the cumyl ether of 1,2-dihydroxy anthraquinone is to be expected (Formula Scheme 2). It is possible that 1,2- and 1,4-dihydroxy anthraquinone are formed according to the reaction path shown in Formula Scheme 2, but the formation of 1-hydroxy anthraquinone remains unexplained.

We thank the "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie" for financial support and Mr. G. Holst for looking through the English manuscript.

Experimental

Starting Compounds

Nitrobenzene and m-dinitrobenzene were commercial products. The other starting compounds were prepared according to instructions from literature: α-nitronaphthalene [10]; 1,3,5-trinitrobenzene [11]; methyl m-nitrobenzoate [12]; m-nitro benzophenone [13 – 16]; m-nitro benzonitrile [17]; m-nitro diphenyl-sulphone [18 – 21]; 1-nitro anthraquinone [22, 23].

Cumene hydroperoxide was an industrial intermediate from the Leuna-Werke AG; after distillation (Kp: 44 – 46 °C/ 0.5 Pa) from a water bath the purity was 95 – 96 %. tert-Butyl hydroperoxide was an industrial product from the Chemische Fabrik Eilenburg; after distillation from a water bath using a 15 cm Vigreux column (Kp: 34 – 37 °C/ 2.3 kPa) the purity was 90 – 95 %.

Test Substances

The two nitro phenols (o- and p-isomer), 2,4-dinitro phenol, 2,4,6-trinitro phenol, 1-hydroxy, 1,2-dihydroxy and 1,4-dihydroxy anthraquinone were commercial products. The other test substances needed for the identification and determination of the hydroxylation products were prepared according to instructions from literature: 2,6-dinitro phenol [24]; 4-nitro 1-naphthol [25 – 27]; 1-nitro 2-naphthol [25, 26, 28]; methyl 2-hydroxy-5-nitrobenzoate [29]. 2-Hydroxy-5-nitro benzophenone was prepared by Friedel-Crafts acylation [15] of benzene with 2-methoxy-5-nitrobenzoyl chloride [30 – 32]. In this reaction a demethylation took place. 4-Hydroxy-3-nitro benzophenone was obtained by Friedel-Crafts acylation [15] of benzene with 4-methoxy-3-nitrobenzoyl chloride [33]. Also in this case a demethylation took place. A mixture of 2-hydroxy-5-nitro and 2-hydroxy-3-nitro benzonitrile was obtained by nitration of 2-hydroxy benzonitrile [34]. The mixture was separated by column chromatography (length: 120 cm; diameter: 1 cm; adsorbent: silica gel (Merck); solvent: benzene/methanol (95 : 5)). 2-Hydroxy-3-nitro benzontrile (F: 144 °C [35]) appeared as the first and 2-hydroxy-5-nitro benzonitrile (F: 190 °C [34]) as the second compound in the eluate. All test substances prepared were characterized by their melting points and their ^{13}C-n.m.r. spectra (Table 8).

Vicarious Nucleophilic Hydroxylation of Aromatic Nitro Compounds,

1st method. 12 mmol of the base, a spatula-tipful of EDTA and 15 ml of the solvent are put into a 100 ml Erlenmeyer flask equipped with a magnetic stirrer, a dropping funnel and a drying tube. Into this mixture a solution of 5 mmol nitro compound and 5 mmol hydroperoxide is given dropwise under vigorous stirring at the temperature wanted. After a definite time the reaction mixture is poured into 20 ml aqueous sulphuric acid (20 %) and cooled to – 20 °C. After addition of 100 ml ice-water the mixture is extracted four times with 50 ml methylene chloride each time. The combined methylene chloride phases are washed twice with 20 ml water each time and dried over sodium sulphate. The solvent is removed in vacuo, and the residue is weighed. An exactly weighed part is etherified with diazomethane and a definite amount of α-bromo naphthalene (internal standard) is added. The yields of the products (methyl) ethers of the phenols formed in the vicarious nucleophilic hydroxylation) are determined by gaschromatography.

2nd method. The reaction is accomplished as in the 1st method until the pouring into 20 % aqueous sulphuric acid, but the double amount of all the reaction partners is used. To the acidified reaction mixture 75 ml ice-water are added. The solution is decanted from the brown tar. In some cases reaction products crystallize from the aqueous solution and can be isolated by filtration. The aqueous solution (or the filtrate) is extracted four times with 50 ml methylene chloride each time. The combined organic phases are washed twice with 50 ml water each time and dried over sodium sulphate. The solvent is removed by distillation from a water bath, the residue is combined with the crystals filtered off before the extraction with methylene chloride and recrystallized from water/acetone (4 : 1). The suspension is stored for 12 h in a refrigerator at 0 °C, then the crystals precipitated are filtered off, dried in a vacuum exsiccator over calcium chloride and exactly weighed. The identification was accomplished by melting and mixed melting point, by ^{13}C-n.m.r. spectroscopy, by gas chromatography and by GC/MS analysis (after etherification with diazomethane).

In the case of m-nitro diphenyl sulphone we did not prepare the two hydroxylation products by independent methods but identified them by ^{13}C-n.m.r. spectroscopy of the mixtures obtained in our hydroxylation experiments. Knowing that 2-hydroxy-5-nitro diphenylsulphone was the main product and 4-hydroxy-3-nitro diphenylsulphone the side product in all cases the assignment of the two product peaks in the gas chromatogram of the reaction mixture (after etherification with diazomethane) and also the exact gaschromatographic analysis was possible. We used m-nitro diphenyl sulphone as the internal standard. The work-up of the reaction mixtures took place principally according to method 1, but the main part of the reaction product obtained after removal of the methylene chloride was treated several times with a 20 % aqueous solution of sodium hydroxide. The combined aqueous extracts were acidified with aqueous sulphuric acid and the phenolic compounds extracted with methylene chloride. After the removal of the methylene chloride the residue consisting of the phenols formed was weighed and a ^{13}C-n.m.r. spectrum was taken.

The reaction of 1-nitro anthraquinone with cumene hydroperoxide was accomplished according to the 2nd method, but in this case the reaction mixture was analyzed by high performance liquid chromatography (HPLC). The main products were separated by column chromatography (length: 120 cm; diameter: 1 cm; adsorbent: silica gel (Merck); solvent: cyclohexane/acetone (65 : 35)). 1-Hydroxy anthraquinone together with a small amount of 1,4-dihydroxy anthraquinone appeared as the first and 1,2-dihydroxy anthraquinone as the second compound. The compounds were isolated by evaporation of the solvent. They were exactly weighed and identified by ^{13}C-nmr spectroscopy. 1,2-Dihydroxy anthraquinone was also identified by its melting point and the mixed melting point with an authentic sample.

Gaschromatographic Analyses

The nitro phenols formed in the hydroxylation experiments could not be analyzed directly by gaschromatography. They

Table 4 Gaschromatographic analyses of the hydroxylation mixtures of m-dinitrobenzene and α-nitronaphthalene (3 m column with 12 % SE 30 on Inertone-N-super; 230 °C; 3 l h^{-1} H_2; heat conductivity detector)

compound	retention time (min)
m-dinitrobenzene	4.7
α-bromo naphthalene[a]	6.0
2.6-dinitro anisol	6.1
α-nitronaphthalene	8.5
2.4-dinitro anisol	12.5
1-nitro-2-methoxy naphthalene	16.0
4-nitro-1-methoxy naphthalene	23.0

[a] internal standard

were transformed into the corresponding methyl ethers by reaction with an ether solution of diazomethane. Two columns were used for the analyses of the methylated reaction mixtures (Tables 4 and 5).

HPLC Analyses

The HPLC analyses were accomplished with an apparatus of the firm Knauer with UV detector. In all cases the gradient technique was used with acetonitrile and water as the solvents. Columns with a length of 250 mm and a diameter of 4 mm were used. The exact conditions and the R_f-values of the compounds separated and analyzed are given in Table 6.

Thin-layer Chromatography

In most cases the crude reaction products were analyzed by thin-layer chromatography using commercial Silufol plates from the firm Kavalier (Votice, ČSFR). The conditions and the R_f values are given in Table 7. The spots became yellow or brown in an atmosphere of ammonia; they became visible under UV radiation.

^{13}C-n.m.r. Spectroscopy

The ^{13}C-n.m.r. spectra of the test substances and of the reaction products (sometimes binary or ternary mixtures) were taken either with the Bruker-spectrometer HX 90R (22.635 MHz) or with the Tesla-spectrometer BS 587 A (20.062 MHz) in acetone-D_6, DMSO-D_6 or $CDCl_3$. Hexa-

Table 5 Gaschromatographic analyses of the hydroxylation mixtures of nitrobenzene, m-nitro benzonitrile, m-nitrobenzoic acid methyl ester, m-nitro benzophenone, α-nitronaphthalene and m-nitro diphenylsulphone (1 m column with 10 % Dexsil 410 on Inertone-N-super; 3 l h^{-1} Ar)

compound	temperature program[a]	retention time (min)
nitrobenzene	A	4.8
o-nitroanisol		11.9
p-nitroanisol		12.8
azoxy benzene		20.6
m-nitrobenzonitrile	B	4.6
2-methoxy-5-nitro benzonitrile		9.5
methyl m-nitrobenzoate	B	4.3
methyl 2-methoxy-3-nitrobenzoate		5.7
methyl 2-methoxy-5-nitrobenzoate		9.3
m-nitro benzophenone	C	5.4
2-methoxy-5-nitro benzophenone		13.0
4-methoxy-3-nitro benzophenone		14.7
α-nitronaphthalene	D	2.3
1-nitro-2-methoxy naphthalene		5.7
4-nitro-1-methoxy naphthalene		9.1
m-nitro diphenylsulphone	E	2.6
4-methoxy-3-nitro diphenylsulphone		5.8
2-methoxy-5-nitro diphenylsulphone		7.3

[a] A: 100 – 300° C/6 K min^{-1}; flame ionization detector
B: 180 – 270° C/6 K min^{-1}; flame ionization detector
C: 250 °C; flame ionization detector
D: 220 °C; flame ionization detector
E: 280 °C; heat conductivity detector

Table 6 HPLC analyses of the hydroxylation mixtures of m-nitro benzophenone, 1,3,5-trinitrobenzene and 1-nitroanthraquinone (column length 250 mm; column diameter 4 mm; UV detection at 254 nm; gradient elution)

stationary phase	solvent (eluent)	compound	retention time (min)
RP 18	MeCN/H_2O 30 : 70	4-hydroxy-3-nitro benzophenone	1.5
(5μm)	after 56 min 100 : 0	2-hydroxy-5-nitro benzophenone	4.5
	volume rate 1.2 ml min^{-1}	m-nitro benzophenone	28.1
ES-RP 18	MeCN/H_2O 30 : 70	2,4,6-trinitrophenol	1.4
(6μm)	after 40 min 100 : 0	1,3,5-trinitrobenzene	9.3
	volume rate 1.8 ml min^{-1}		
Lichrospher	MeCN/H_2O 50 : 50	1,2-dihydroxy anthraquinone	9.0
RP 18	after 50 min 90 : 100	1-nitro anthraquinone	9.8
(7μm)	volume rate 1.4 ml min^{-1}	1-hydroxy anthraquinone	11.9
		1,4-dihydroxy anthraquinone	15.1

Table 7 Thin-layer chromatography of the hydroxylation mixtures of 1-nitronaphthalene, m-nitro benzophenone and m-nitro benzonitrile (Silufol plates of the firm Kavalier)

solvent	compound	R_f-value
$CHCl_3$/EtOH (99 : 1)	4-nitro-1-hydroxy naphthalene	0.02
	1-nitro-2-hydroxy naphthalene	0.79
	1-nitronaphthalene	0.84
cyclohexane/acetone (65 : 35)	4-hydroxy-3-nitro benzophenone	0.53
	2-hydroxy-3-nitro benzophenone	0.62
benzene/methanol (95 : 5)	2-hydroxy-5-nitro benzonitrile	0.20
	2-hydroxy-3-nitro benzonitrile	0.77
benzene/cyclohexane/acetone (30 : 45 : 25)	2-hydroxy-5-nitro diphenylsulphone	0.25
	4-hydroxy-3-nitro diphenylsulphone	0.47
	m-nitro diphenylsulphone	0.51

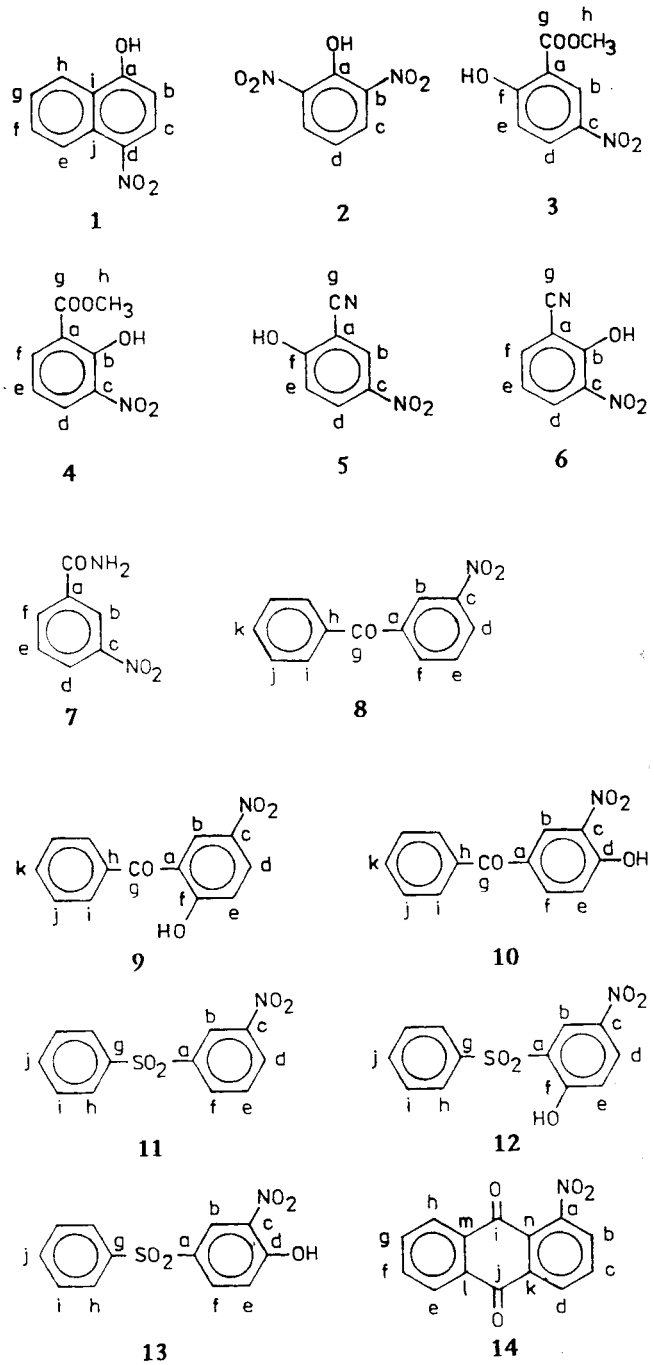
methyl disiloxane ($\delta = 1.91$ ppm) was used as the internal standard. The spectra of most of our compounds were already known [36]. In these cases the spectra taken by us agreed with those published. In the other cases the spectra taken were compared with those estimated from the spectra of the parent compounds with the aid of increment systems [37 – 39].

Table 8 shows the chemical shifts estimated and those found for the compounds whose spectra could not be found in [36].

Table 8 ^{13}C-NMR spectra of those test and reaction products whose spectra could not be found in the literature (see Formula Scheme 3)

compound Nr.[a]	a	b	c	d	e	f	g	h	i	j	k	l	m	n
1, calc.	159.0	108.3	124.7	140.5	123.2	130.9	127.7	123.2	126.2	126.8				
1	159.7	106.2	125.6	137.3	122.7	129.9	127.4	122.8	124.0	127.0				
2,calc.	145.9	135.9	130.5	123.8										
2	148.5	139.0	130.7	119.2										
3,calc.	117.4	123.8	139.4	127.7	116.6	160.8	163.3	51.5						
3	115.2	126.8	139.4	129.8	118.7	164.2	166.5	52.9						
4,calc.	117.4	149.3	134.0	127.7	122.0	135.3	163.3	51.5						
4	119.1	153.1	135.3	130.4	119.1	135.5	168.0	53.0						
5,calc.	100.8	128.5	140.7	129.2	118.5	165.1	116.8							
5	99.9	130.2	139.6	130.5	117.0	165.8	115.3							
6,calc.	100.8	154.0	135.3	129.2	123.9	139.6	116.8							
6	104.7	154.4	137.2	130.4	120.2	140.2	114.9							
7,calc.	134.4	122.2	148.3	126.8	129.5	133.4								
7	135.9	122.3	148.0	125.9	130.1	133.9								
8,calc.	138.5	125.1	148.2	127.4	129.2	136.1	196.4	137.6	130.0	128.3	132.3			
8	139.6	124.6	148.0	127.1	130.7	135.9	194.2	137.1	130.4	129.2	133.7			
9,calc.	120.0	128.6	138.4	131.3	119.2	169.4	201.4	137.9	128.3	129.1	131.8			
9	126.6	125.9	139.4	128.0	117.2	161.8	194.4	136.7	129.6	128.9	133.8			
10,calc.	130.7	129.2	136.2	158.5	117.2	140.2	198.0	139.6	130.6	129.3	133.0			
10	132.5	127.6	136.6	155.7	119.2	136.0	192.8	136.8	129.3	128.5	132.5			
11,calc.	142.7	122.3	149.1	128.1	130.3	133.6	141.9	127.6	129.5	133.4				
11	142.8	122.1	148.2	128.2	131.8	134.3	139.9	127.8	129.8	133.5				
12,calc.	130.2	123.7	140.6	129.8	119.2	161.2	139.9	127.8	129.9	133.5				
12	126.8	125.5	140.0	130.9	118.4	161.5	138.7	128.1	129.0	133.7				
13,calc.	135.2	123.7	136.5	155.0	119.2	135.9	139.9	127.8	129.9	133.5				
13	131.0	125.5	136.5	156.0	120.5	133.7	140.9	127.2	129.7	133.3				
14,calc.	146.5	129.4	137.0	132.7	126.6	134.3	134.3	126.6	182.5	182.5	133.9	133.0	133.0	128.1
14	148.5	128.0	135.6	129.2	126.9	135.0	135.0	126.9	180.8	180.0	134.3	132.5	132.5	132.9

[a] see Formula Scheme 3



Formula Scheme 3 Numbering of the compounds and designation of their carbon atoms: see Table 8

References

[1] M. Makosza, K. Sienkiewicz, J. Org. Chem. **55** (1990) 4979

[2] G. Mattersteig, W. Pritzkow, V. Voerckel, J. Prakt. Chem. **332** (1990) 569

[3] R. Hofmann, R. Hübner, G. Just, L. Krätzsch, A.K. Litkowez, W. Pritzkow, W. Rolle, M. Wahren, J. Prakt. Chem. (4) **37** (1968) 102

[4] J.R. Beck, Tetrahedron **34** (1978) 2057

[5] F. Effenberger, W. Streicher, Chem. Ber. **124** (1991) 157

[6] F. Effenberger, M. Koch, W. Streicher, Chem. Ber. **124** (1991) 163

[7] H. Kropf, Houben-Weyl: Methoden der Organischen Chemie, 4th edition, **E 13** (1988) 762

[8] H. Kropf, M. Ball, Liebigs Ann. Chem. **1976**, 2331

[9] E. Schmitz, O. Brede, J. Prakt. Chem. **312** (1970) 43

[10] H.E. Fiertz-David, R. Sponagel, Helv. Chim. Acta **26** (1943) 98

[11] H.T. Clarke, W.W. Hartmann, Org. Synth., Coll. Vol. I (1941) 541

[12] O. Kamm, J.B. Segur, Org. Synth., Coll. Vol. I (1941) 372

[13] O. Kamm, J.B. Segur, Org. Synth., Coll. Vol. I (1941) 391

[14] J. Munch-Petersen, Org. Synth., Coll. Vol. IV (1963) 715

[15] Organikum, 16th edition. Berlin. VEB Deutscher Verlag der Wissenschaften 1986, p. 325

[16] R. Geigy, W. Koenigs, Ber. Dtsch. Chem. Ges. **18** (1885) 2401

[17] J.J. Blanksma, E.M. Petri, Rec. Trav. Chim. Pays-Bas **66** (1947) 353

[18] V. Meyer, O. Stüber, Liebigs Ann. Chem. **165** (1873) 161

[19] F. Muth, in Houben-Weyl: Methoden der Organischen Chemie, 4th edition. Vol. 9, page 557

[20] J. Huismann (IG Farbenindustrie AG): DRP 701954 (1941) (Chem. Abstr. **36** (1942) 98)

[21] A. Schöberl, A. Wagner, in Houben-Weyl: Methoden der Organischen Chemie, 4th edition. Vol. 9, page 240

[22] T. Kameo, T. Hirashima, Kagaku to Kogyo (Osaka) **62** (1988), (3), 98 (Chem. Abstr. **109** (1988) 210651)

[23] W.H. Beiser, L.W. Jones, J. Am. Chem. Soc. **44** (1922) 2302

[24] H. Hübner, W. Schneider, Liebigs Ann. Chem. **167** (1873) 100

[25] J. Pinnow, Ber. Dtsch. Chem. Ges. **33** (1900) 417

[26] W.W. Hartmann, L.A. Smith, Org. Synth., Coll. Vol. II **1943**, 438

[27] H.H. Hodgson, E. Kilner, J. Chem. Soc. **125** (1924) 807

[28] W.W. Hartman, J.R. Byers, J.B. Dickey, Org. Synth. Coll. Vol. II **1943**, 451

[29] H.C. Barany, M. Pianka, J. Chem. Soc. **1946**, 965

[30] G.W. Raiziss, A. Proskouriakoff, J. Am. Chem. Soc. **44** (1922) 791

[31] C.W. Pohlmann, Rec. Trav. Chim. Pays-Bas **55** (1936) 746

[32] D.W. Mathieson, G. Newberg, J. Chem. Soc. **1949**, 1134

[33] W. Dy-Young, R.M. Herbst, J. Org. Chem. **17** (1952) 122F

[34] H. Lindemann, H. Thiele, Liebigs Ann. Chem. **449** (1926) 63

[35] S. Palazzo, B. Tornetta, Boll. Accad. Gioenia Catania /4/ **4** (1957) 205 (Beilsteins Handbuch der Organischen Chemie, 4. Ergänzungswerk, **10** (1983) 231)

[36] W. Bremser, L. Ernst, W. Fachinger, R. Gerhards, A. Hardt, P.M.E. Lewis, Carbon-13 NMR Spectral Data, Weinheim, VCH-Verlagsanstalt 1987

[37] H.O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR-Spektroskopie. Stuttgart, New York, Georg-Thieme-Verlag 1984
[38] E. Kleinpeter, R. Borsdorf, ^{13}C-NMR-Spektroskopie in der organischen Chemie, Berlin, Akademie-Verlag 1981
[39] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, 3rd Edition, Stuttgart, Georg-Thieme-Verlag 1987

Address for correspondence:

Prof. Dr. W. Pritzkow
Technical University of Merseburg, Institute of Technical Chemistry
Geusaer Straße
O-4200 Merseburg, Germany