Tetrahedron Vol 28, pp. 3271 to 3276 Pergamon Press 1972. Printed in Great Britain

CATALYTIC HYDROGENATION OF BENZO[2.1.3]OXADIAZOLES

V. CERÉ, D. DAL MONTE and E. SANDRI

Facoltá di Chimica Industriale dell' Universitá Viale Risorgimento, 4-40136
Bologna - Italy

(*Received in the UK* 22 *February* 1972; *Accepted for publication* 7 *March* 1972)

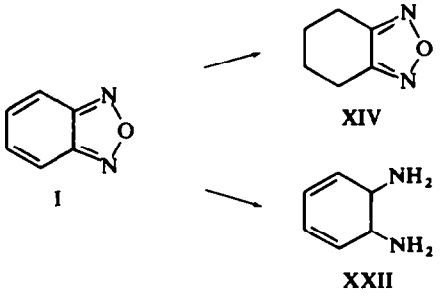
Abstract—Hydrogenation of benzo[2.1.3]oxadiazole and its chloro derivatives, yields 4,5,6,7-tetrahydrobenzo[2.1.3]oxadiazole together with small amounts of 1,2-phenylenediamine. Benzo[2.1.3]oxadiazoles substituted with no reduction-sensitive groups are hydrogenated either to the corresponding 1,2-phenylenediamines or to mixtures containing the 4,5,6,7-tetrahydro derivatives.

The NMR and UV spectra of seven new tetrahydrobenzo[2.1.3]oxadiazoles are recorded together with other physical properties.

CATALYTIC hydrogenation of benzofurazans* have not been reported, apart from the reduction of angular bisfurazanobenzene to 4,5-diaminobenzofurazan.[1,†]

In continuation of our studies,[2–5] we reduced benzofurazans (I-XIII) under standard conditions. The results are given in Table 1. The reduction may take place either in the homocylic or in the heterocyclic ring; in some cases a further hydrogenation of the 4,5,6,7-tetrahydro derivative can yield ammonia and unidentified basic compounds.

Benzofurazan (I) gives mainly the 4,5,6,7-tetrahydro derivative (XIV); 1,2-phenylenediamine (XXII), produced by the hydrogenolytic opening of the heterocyclic ring, is formed with yields of about 10%.



* For convenience we shall hereafter refer to benzo-2,1,3-oxadiazole by the alternative name of benzofurazan.

† Some examples of selective hydrogenation of reduction-sensitive groups in substituted benzofurazans have been reported.[2–4]

4- and 5-Chlorobenzofurazans (VI, XI) give the same products as the parent compound, with almost identical yields; the hydrogenolysis of the carbon-halogen bond occurs at about the same rate as the hydrogenation of benzofurazan, as shown by the composition of the reduction products after the absorption of one molar equivalent of hydrogen.

TABLE 1. HYDROGENATION OF BENZO[2.1.3]OXADIAZOLES ON 10% Pd-C

Benzo-[2.1.3]-oxadiazole reduced			Conds[a]	Time (hr)	Reduction products[b]			
					1,2-PhD		THBO	
No	Subst	Prepn Ref			Subst	%[c]	Subst	%[c]
I	H	9	A	1	H	9	H	80
II	4-CH_3	10	A	6	3-CH_3	14	4-CH_3	70
III	4-COOH	5	A	12	—[d]	—	4-COOH	85
IV	4-COOEt	new	A	12	—[d]	—	4-COOEt	65
V	4-OCH_3	12	A	12	3-OCH_3	95	—	—
VI	4-Cl	11	A	1	H	5	H	85
VII	5-CH_3	9	A	5	4-CH_3	47	5-CH_3	37
VIII	5-COOH	5	B	12	4-COOH	27	5-COOH	55
IX	5-COOEt	new	B	12	4-COOEt	59	5-COOEt	26
X	5-OCH_3	9	A	12	4-OCH_3	98	—	—
XI	5-Cl	9	A	1	H	6	H	85
XII	4,7-diCH_3	new	C	24	3,6-diCH_3	9	4,7-diCH_3	82
XIII	5,6-diCH_3	8	A	12	4,5-diCH_3	99	—	—

[a] "A" indicates the standard conditions (*cf* text). "B" and "C" indicate that 0·01 mol of the benzo-2,1,3-oxadiazole were reduced with 1 g and 3 g of 10% Pd-C respectively.

[b] 1,2-PhD, 1,2-phenylenediamine; THBO,4,5,6,7-tetrahydrobenzo[2.1.3]oxadiazole.

[c] The percentage of 1,2-phenylenediamine refers to the amount present in the reduction mixture (determined spectrophotometrically and reported as the average of at least two measurements); the percentage of 4,5,6,7-tetrahydrobenzo[2.1.3]oxadiazole refers to the yield after separation of the diamine.

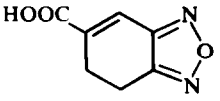
[d] The basic substance isolated is not the 1,2-phenylenediamine.

Likewise the hydrogenation of methyl, carboxy and ethoxycarbonylbenzofurazans (II–IV, VII–IX) results in the formation of tetrahydro derivatives. The 1,2-phenylenediamine could not be detected among compounds isolated from the reduction mixture of 4-carboxy and 4-ethoxycarbonylbenzofurazan. These compounds yielded a basic product (structure was not determined) which results from further hydrogenation of 4-carboxy and 4-ethoxycarbonyl-4,5,6,7-tetrahydrobenzofurazan respectively.

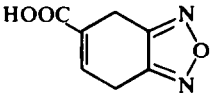
The ratio of tetrahydro derivative to 1,2-phenylenediamine in 4-methylbenzofurazan is higher than in the 5-methyl isomer. The effect of the position of the substituent is still larger in dimethyl derivatives. Thus, the heterocyclic ring is preferentially hydrogenated in 5,6-dimethylbenzofurazan (XIII), while the homocyclic ring is saturated in the 4,7-dimethyl isomer (XII).

5-Carboxybenzofurazan, when reduced under standard conditions gives, in addition to 4-carboxy-1,2-phenylenediamine and the 5-carboxy-4,5,6,7-tetrahydro derivative,

a third product corresponding to $C_7H_6N_2O_3$ and with the NMR spectrum compatible with structure A or B. The formation of this product is negligible when the reduction is carried out with a larger amount of catalyst.



A



B

The reduction of 4- and 5-methoxybenzofurazans (V, X) yields almost exclusively 3- and 4-methoxy-1,2-phenylenediamine respectively. The catalyst preparations proved to be reproducible in their behaviour. Changes in the ratio of tetrahyoho derivative to 1,2-phenylene diamine may take place when using palladium–charcoal catalyst with different characteristics. The nature of the catalyst may appreciably affect the direction of the hydrogenation: thus, 5% rodium or platinum on charcoal (contrary to palladium) reduces benzofurazan almost exclusively to 1,2-phenylenediamine. The structures assigned to the reduction products were supported either by comparison with compounds obtained by independent syntheses (1,2-phenylenediamines or their derivatives; 4,5,6,7-tetrahydrobenzofurazan) or by UV and NMR spectra (Table 2).

TABLE 2. UV AND NMR SPECTRA OF 4,5,6,7-TETRAHYDROBENZO[2.1.3]OXADIAZOLES

THBO[a]		NMR ($CDCl_3$, δ in ppm)[b]		UV (EtOH/H_2O, 1:9 v/v)[c]
No	Subst.	CH_2 of homocyclic ring	Other signals	λ_{max} in mμ (log ε)
XIV	H	1·7–2·1 m(4H), 2·7–3·1 m(4H)	–	216–7(3·57)[d], 218i(3·56), 225i(3·44), 231i(3·10)
XV	4-CH_3	1·3–2·3 m(4H), 2·7–3·4 m(3H)	CH_3: 1·41d(3H): J = 7 c/s	217(3·60), 220i(3·59), 225i(3·49), 231i(3·17)
XVI	4-COOH	1·7–2·5 m(4H), 2·8–3·1 m(2H), 3·9–4·3 m(1H)	COOH[f]: 11·2s	217–20(3·54)
XVII	4-COOEt	1·7–2·4 m(4H), 2·8–3·1 m(2H), 3·7–4·5 m(1H)	COOEt: 1·30t(3H), 4·35q(2H): J = 6·6 c/s	217(3·57), 220i(3·56), 225i(3·46)
XVIII	5-CH_3	1·0–3·4 m(7H)	CH_3: 1·16d(3H): J = 5 c/s	217(3·59), 219i(3·58), 225i(3·47), 232i(3·09)
XIX	5-COOH	1·9–3·4 m(7H)	COOH[f]: 10·8s(br)	217(3·61), 219i(3·60), 225i(3·49), 232i(3·11)
XX	5-COOEt	1·7–3·5 m(7H)	COOEt: 1·30t(3H), 4·23q(2H): J = 6 c/s	216–7(3·62), 219i(3·61), 225i(3·49), 231i(3·15)
XXI	4,7-diCH_3	1·5–2·2 m(4H), 2·8–3·5 m(2H)	CH_3: 1·36d(6H): J = 7 c/s	217(3·58), 220i(3·57), 230i(3·28)

[a] THBO,4,5,6,7-tetrahydrobenzo[2.1.3]oxadiazole. With the exception of compound n° XIV, all other compounds are new.

[b] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

[c] i, inflection.

[d] Previous values reported: λ_{max}^{MeOH}: 220 mμ (log ε, 3·56)[6]; λ_{max}^{EtOH}: 217 mμ (log ε, 3·30), inflections at 220, 225 and 233 mμ.[13]

[f] The singlet disappears by adding D_2O.

The preparation of 4,5,6,7-tetrahydrobenzofurazan *via* cyclohexane-1,2-dione dioxime[6] or *via* 2-nitrocyclohexane-1-one-oxime[7] is laborious so that when the yields are sufficiently high, the catalytic reduction is a better route for the preparation of these compounds.

The reduction, under analogous conditions, of the N-oxides (benzofuroxans) of I-V, VII–X, XII and XIII leads exclusively to the corresponding 1,2-phenylenediamines.

EXPERIMENTAL

M.ps and b.ps. are uncorrected.

UV spectra were measured for 10^{-4} M solns in EtOH-H_2O (1 :9 v/v) with a Beckman DU-2 spectrophotometer. NMR spectra were measured for solns in $CDCl_3$, unless otherwise stated, with a Jeol C-60 HL instrument (TMS as internal reference).

Products. Benzofurazans (I–III, V–VIII, X and XI) were prepared by methods described previously (Refs in Table 1) and had m.ps. corresponding to those in the literature. Compound XIII was obtained by reduction of the corresponding benzofuroxan[14] to quinone dioxime followed by dehydration with boiling alkali[10]: m.p. 84–5° (lit.[8], 83–5°).

4,7-Dimethylbenzofurazan (XII). A soln of 4,7 dimethylbenzofuroxan[14] (16·4 g) and triphenylphosphine (27 g) in anhydrous xylene (500 ml) was refluxed for 5 hr.[15] The mixture was evaporated to dryness under reduced pressure and the residue was distilled, the fraction with b.p. 95–105°/4 mm being collected. The product was sublimed to give a material with m.p. 37·5–39·5°. Two crystallizations from n-heptane gave a product melting at 38·5–39·5°, b.p. 88–9°/3 mm; NMR: δ 2·59 (6H singlet) and 7·04 (2H singlet). (Found: C 64·63; H, 5·38; N, 18·90. $C_8H_8N_2O$ requires: C, 64·85; H, 5·44; N, 18·91%).

5-Ethoxycarbonylbenzofurazan (IX) was prepared by esterification of 5-carboxybenzofurazan[5] (16·4 g) with dry HCl (20 g) and abs EtOH (100 ml). The mixture was refluxed for 1 hr and, after removal of solvent, the residue, washed with 5% $NaHCO_3$, was purified by crystallization from n-heptane; m.p. 45–6°; NMR: δ 1·48 (3H triplet), 4·51 (2H quartet), 7·8–8·3 (2H multiplet and 8·6–8·7 (1H multiplet). (Found: C, 56·30; H, 4·15; N, 14·48. $C_9H_8N_2O_3$ requires: C, 56·25; H, 4·19; N, 14·58%).

4-Ethoxycarbonylbenzofurazan (IV) was prepared by the procedure described for the 5-derivative and crystallized from n-heptane, m.p. 41–2°; NMR: δ 1·50 (3H triplet), 4·56 (2H quartet), 7·3–7·8 (1H multiplet) and 8·0–8·4 (2H multiplet). (Found: C, 56·17; H, 4·22; N, 14·57. $C_9H_8N_2O_3$ requires: C, 56·25; H , 4·19; N, 14·58%).

TABLE 3. U.V. SPECTRA OF 1,2-PHENYLENEDIAMINES

1,2-phenylenediamine			λ_{max}^{MEOH} in mμ (log ε)[a]
No	Subst.	Prepn Ref	
XXII	H	[b]	239(3·82), 293*(3·53)
XXIII	3-CH_3	17	230sh(3·84), 291*(3·46)
XXIV	3-COOH	18	230–5(4·08), 347(3·63)
XXV	3-COOEt	new	237(4·11), 257i(3·75), 347(3·69)
XXVI	3-OCH_3	19	235i(3·88), 285*(3·17)
XXVII	4-CH_3	20	230i(3·80), 299*(3·51)
XXVIII	4-COOH	21	235sh(4·09), 278–81(3·92), 313*(3·90)
XXIX	4-COOEt	22	282(3·97), 317*(3·98)
XXX	4-OCH_3	23	305–6*(3·59), 365sh(2·63)
XXXI	3,6-diCH_3	24	235i(3·89), 289*(3·38)
XXXII	4,5-diCH_3	25	230i(3·89), 300*(3·55)

[a] Starred values are those used for quantitative measurements; i, inflection; sh, shoulder.

[b] Reagent grade.

10% *Palladium on charcoal* was prepared as described by Mozingo,[16] using Merck Lab. charcoal and Carlo Erba $PdCl_2$.

Hydrogenation of benzofurazans and estimation of 1,2-phenylenediamines. The substrate (0·01 mol) in MeOH* (200 ml), on Pd-C (0·6 g)† was shaken under hydrogen at room temp and pressure until absorption ceased. For compounds I, VI and XI the reduction was stopped as soon as the absorption of hydrogen underwent a marked fall: a further slow hydrogenation of 4,5,6,7-tetrahydrobenzofurazan (previously formed) is thus avoided.

The catalyst was filtered off and washed repeatedly with MeOH under N_2. The filtrate and washings were combined and the yield in 1,2-phenylenediamine was estimated by recording the optical density of the solutions at the wavelengths reported in Table 3. (The solns from reduction of VI and XI were previously treated with 20 ml of 4% KOH in MeOH to remove HCl).

Before the spectrophotoscopic measurements, a comparison was made between the spectrum of the reduction mixture and that of the suitable 1,2-phenylenediamine in the 290–350 mμ region, where the 4,5,6,7-tetrahydrobenzofurazans do not absorb.

Separation and identification of the reduction products. The filtrate and the washings combined, were evaporated under reduced pressure at 30° and the residue, with 150 ml of ether, was extracted with dilute (1:2) HCl (3 × 30 ml). The acidic extract and the ethereal soln was evaporated and the residue used for identification of 1,2-phenylenediamines (A) and 4,5,6,7-tetrahydrobenzofurazans (B) respectively.

(A) The residue arising from reduction of IX, when treated with 5% $NaHCO_3$ was found identical (m.p. mixed m.p., IR spectrum) with XXIX.[22] The residue from the reduction of VIII proved to be 4-carboxy-1,2-phenylenediamine, since when treated with NaOAc aq and then with a boiling aqueous solution of SeO_2 it gave 5-carboxy-benzo[2.1.3]selenadiazole.[26] The residue from IV§, when treated with 5% $NaHCO_3$ and extracted with benzene, gave a red gummy material which did not contain 3-ethoxycarbonyl-1,2-phenylenediamine. The IR spectrum of the gummy material corresponds to that of the compound obtained by independent catalytic reduction of XVII. Similar behaviour was found in the residue from reduction of III*.

The residues from the acidic extract of reduced I, II, V–VII, X XIII, was treated with 5% $NaHCO_3$ and the diamine was extracted with benzene. The benzene soln was dried, and acetylated with Ac_2O (reflux for 2 hr). The diacetyl derivative was identified by comparison with autentic samples. The reduced benzofurazan, the obtained diacetyl-1,2-phenylenediamine, the relevant literature or its characteristics are reported below: I, VI, XI; PhDA‖; 27.V: 3-OCH_3-PhDA; 28.VII: 4-CH_3-PhDA; 29.XIII: 4,5-diCH_3-PhDA; 30.II: 3-CH_3-PhDA; crystallized from xylene, m.p. 197–8°; (Found: C, 63·90; H, 6·78; N, 13·41. $C_{11}H_{14}N_2O_2$ requires: C, 64·06; H, 6·84; N, 13·58%). X; 4-OCH_3-PhDA; crystallized from xylene, m.p. 185–6°; (Found: C, 59·65; H, 6·12; N, 12·52. $C_{11}H_{14}N_2O_3$ requires: C, 59·45; H, 6·35; N, 12·60%). XII: 3,6-diCH_3-PhDA; crystallized from EtOH, m.p. 298–90°; (Found: C, 65·47; H, 7·37; N, 12·68. $C_{12}H_{16}N_2O_2$ requires: C, 65·43; H, 7·32; N, 12·72%).

(B) The residue after evaporation of the ethereal soln was purified to obtain analytically pure samples of the 4,5,6,7-tetrahydrobenzofurazans. The purification technique and physical properties are given below:‡

4,5,6,7-*Tetrahydrobenzofurazan* (XIV): distillation; b.p. 92°/5 mm; m.p. 26° (lit.: 26°[6]; 20·5°[7]; 24°[13]). 4-*Methyl*-4,5,6,7-*tetrahydrobenzofurazan* (XV): distillation; b.p. 92°/4 mm; $n_D^{25°}$ 1·4779‡ (Found: C, 60·76; H, 7·35; N, 20·19. $C_7H_{10}N_2O$ requires: C, 60·85; H, 7·29; N, 20·28%). 4-*Carboxy*-4,5,6,7-*tetrahydrobenzofurazan* (XVI): crystallization from ligroin (b.p. 80–120°)-toluene (1:1 v/v); m.p. 94–5°; pK_a^{pot} (in H_2O at 20°): 3.30. (Found: C, 49·82; H, 4·64; N, 16·71. $C_7H_8N_2O_3$ requires: C, 50·00; H, 4·80; N, 16·66%). 4-*Ethoxycarbonyl*-4,5,6,7-*tetrahydrobenzofurazan* (XVII): distillation; b.p. 158°/6 mm; $n_D^{25°}$ 1·4777. (Found: C, 55.04; H, 6·21; N, 14·19. $C_9H_{12}N_2O_3$ requires: C, 55·10; H, 6·16; N, 14·28%). 5-*Methyl*-4,5,6,7-*tetra*-

* Reagent P. A. Carlo Erba.

† Except where otherwise stated (see Table 1).

§ For benzofurazans IV and III, the hydrogenation solutions contain (in addition to the tetrahydro derivative and unidentified basic products) also ammonia which was removed together with MeOH by distillation under reduced pressure.

‖ PhDA, N, N′-diacetyl-1,2-phenylenediamine.

‡ The IR spectra were also measured and are available on request.

‡ Determined with an Abbè refractometer.

hydrobenzofurazan (XVIII): preparative gas chromatography; b.p. 95°/3 mm: $n_D^{25°}$ 1·4757. (Found: C, 60·92; H, 7·26; N, 20·13. $C_7H_{10}N_2O$ requires: C, 60·85; H, 7·29; N, 20·28%). 5-*Carboxy*-4,5,6,7-*tetrahydrobenzofurazan* (XIX): crystallization from ligroin (b.p. 80–120°)-toluene (1:1 v/v); m.p. 109–110°; pK_a^{pot} (in H_2O at 20°): 4·04. (Found: C, 49·90; H, 4·61; N, 16·62. $C_7H_8N_2O_3$ requires: C, 50·00; H, 4·80; N, 16·66%).

Reduction, when made under standard conditions, yielded (after separation of 4-carboxy-1, 2-phenylenediamine) a residue (m.p. 90–160°) which crystallized from H_2O (1·4 g from 50 ml) yielded a white product [m.p. 195–6° after two crystallizations from H_2O: NMR in $(CD_3)_2CO$: δ 3·7–4·0 (4H multiplet), 7·1–7·4 (1H multiplet) and 8·2 (1 COOH broad singlet which disappears on addition of D_2O); λ_{max} 208–10 mμ (log ε 4·03). (Found: C, 49·86; H, 3·90; N, 16·93. $C_7H_6N_2O_3$ requires: C, 50·61; H, 3·64; N, 16·86%)].

The aqueous filtrate was evaporated; the residue crystallized repeatedly from ligroin-toluene (1:1 v/v) yielded a compound, identical with 5-carboxy-4,5,6,7-tetrahydrobenzofurazan described above. 5-*Ethoxycarbonyl*-4,5,6,7-*tetrahydrobenzofurazan* (XX): distillation; b.p. 163°/5 mm; $n_D^{25°}$ 1·4792. (Found: C, 49·95; H, 6·18; N, 14·21. $C_9H_{12}N_2O_3$ requires: C, 55·10; H, 6·16; N, 14.28%). 4,7-*Dimethyl*-4,5,6,7-*tetrahydrobenzofurazan* (XXI): preparative gas chromatography; b.p. 95°/4 mm; $n_D^{25°}$ 1·4727. (Found: C, 63·02; H, 8·11; N, 18·37. $C_8H_{12}N_2O$ requires: C, 63·13; H, 7·95; N, 18·41%). 3-*Ethoxycarbonyl*-1,2-*phenylenediamine* was prepared by the same procedure as 4-ethoxycarbonyl isomer[21] from 2-acetylamino-3-nitrobenzoic acid,[31] crystallized from n-heptane, m.p. 63–4°. (Found: C, 60·21; H, 6·52; N, 15·47. $C_9H_{12}N_2O_2$ requires: C, 59·99; H, 6·71; N, 15·55%).

Acknowledgments—We thank the Consiglio Nazionale delle Ricerche (Roma – Italy) for financial support.

REFERENCES

1 W. Borsche and H. Weber, *Liebigs Ann.* **489**, 270 (1931)
2 D. Dal Monte and E. Sandri, *Boll. Sci. Fac. Chim. Ind. Bologna* **26**, 127 (1968)
3 D. Dal Monte, E. Sandri and S. Pollicino, *Ibid.* **26**, 153 (1968)
4 D. Dal Monte, E. Sandri and P. Mazzaracchio, *Ibid.* **26**, 165 (1968)
5 D. Dal Monte, E. Sandri and W. Ceré, *Ann. Chim. Italy* **60**, 801 (1970)
6 N. Tokura, R. Tada and K. Yokoyama, *Bull. Chem. Soc. Japan* **34**, 270 (1961)
7 D. Klamann, W. Koser, P. Weyerstahl and M. Fligge, *Ber. Dtsch. Chem. Ges* **98**, 1831 (1965)
8 J. M. Prokipcak and P. A. Forte, *Canad. J. Chem.* **48**, 3059 (1970)
9 R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, *J. Am. Chem. Soc.* **76** 2233 (1954)
10 T. Zincke and P. Schwarz, *Liebigs Ann.* **307**, 28 (1899)
11 D. Dal Monte and E. Sandri, *Ann. Chim. Italy* **53**, 1697 (1963)
12 D. Dal Monte and E. Sandri, *Ibid.* **54**, 486 (1964)
13 G. Ohta, T. Takegoshi and K. Ueno, *Chem. Pharm. Bull. Tokyo* **13**, 1445 (1965)
14 F. B. Mallory, S. L. Manatt and C. S. Wood, *J. Am. Chem. Soc.* **87**, 5434 (1965)
15 J. H. Boyer and S. E. Ellzey, *J. Org. Chem.* **26**, 4684 (1961)
16 R. Mozingo, *Org. Syntheses*, Col. Vol. III, p. 685 Wiley N.Y. (1955)
17 E. Nölting and L. Stoecklin, *Ber. Dtsch. Chem. Ges* **24**, 565 (1891)
18 B. Schilling, *Ibid.* **34**, 904 (1901)
19 F. Montanari and R. Passerini, *Boll. Sci. Fac. Chim. Ind. Bologna* **11**, 42 (1953)
20 H. Limpricht, *Ber. Dtsch. Chem. Ges* **18**, 1404 (1885)
21 P. Griess, *Ibid.* **5**, 856 (1872)
22 J. A. Silk, *J. Chem. Soc.* 2059 (1956)
23 F. H. Bergeim, K. Losee and W. A. Lott, *J. Am. Chem. Soc.* **69**, 586 (1947)
24 E. Nölting and C. Geissmann, *Ber. Dtsch. Chem. Ges* **19**, 145 (1886)
25 E. Nölting, A. Braun and G. Thesmar, *Ibid.* **34**, 2251 (1901)
26 F. Heinemann, Ger. 261,412; Feb. 28, 1912. *Chem. Abstr.* **7**, 3200 (1913)
27 H. Rupe and A. Porai-Koschitz, *Chem. Zentr.* I, 102 (1904)
28 R. Meldola and J. V. Eyre, *J. Chem. Soc.* **81**, 993 (1902)
29 A. Bistrzycki and F. Ulffers, *Ber. Dtsch. Chem. Ges* **23**, 1878 (1890)
30 E. Nölting and G. Thesmar, *Ibid.* **35**, 638 (1902)
31 C. W. James, J. Kenner and W. V. Stubbings, *J. Chem. Soc.* **117**, 773 (1920)