Synthesis of Dimethoxy- and Dioxano-annellated Benzofuroxans from *o*-Dinitroarenes

S. V. Eswaran* and S. K. Sajadian

St. Stephen's College, Delhi University,
Delhi-110007, India

Received November 24, 1987

Thermolysis of 4,5-dinitroveratrole **1a** in the presence of sodium azide and dimethylsulfoxide gives the new 5,6-dimethoxybenzofuroxan, **2a**, whereas 3,4,5-trinitroveratrole led to the new 5(7),6-dimethoxy-4-nitrobenzofuroxans **2e**, **3e** *via* a nucleophilic substitution of a nitro group by azide ion and pyrolytic ring closure. This method provides a simpler route to the known 1,3-benzodioxano[5,6-*c*]furoxan, **2b** and 1,4-benzodioxano[6,7-*c*]furoxan **2c**, as well.

J. Heterocyclic Chem., **25**, 803 (1988).

Introduction.

Benzofuroxans have interesting biological and pharmacological activity [1], *e.g.* furazanobenzofuroxan has been considered as a possible vasodilator [2]. The chemistry of benzofuroxans have been reviewed extensively [3,4]. The antileukemic and immonsuppressive activity of 4-nitrobenzofuroxans may be linked to their ability to form Meisenheimer complexes on reaction with cellular thiols and amines [5]. To obtain a better understanding of the mechanism of their antileukemic activity, the formation of benzofuroxan-methoxide adducts has been studied in detail [6]. Benzofuroxans have been used for monitoring anion transport in human red blood cells [7] and for studying lateral diffusion of phospholipids in liposomes and vesicles derived from membranes [8]. It is a convenient chromophoric oxidising agent for thiol groups in enzymes and other proteins [9]. It has been shown recently that benzofuroxan reacts with the catalytic site (SH group) of the enzyme cathepsin B[10].

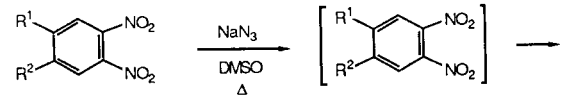
Benzofuroxans are commonly prepared by pyrolysis [11], of *o*-nitrophenylazides, the latter being obtained from either azide displacement of the corresponding *o*-nitroaryl halides or from the *o*-nitroanilines by diazotisation and azide displacement. However, when these two methods are ineffective, benzofuroxans can then be prepared by alkaline hypochlorite oxidation [12] of *o*-nitroanilines. We have come across an earlier example, describing the synthesis of a substituted benzofuroxan from an *o*-dinitroarene [11]. These workers synthesised 5-chloro-6-nitrobenzofuroxan from 2,4,5-trinitrochlorobenzene by displacement of a nitro group (rather than the chlorine atom) with an azide ion, followed by pyrolysis in acetic acid.

We describe below synthesis of two new and two other known benzofuroxans based on the corresponding *o*-dinitroarenes.

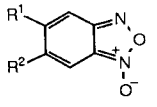
A Simple Route to Benzofuroxans.

During our studies on the preparation of new nitrophenylazides *via* preferential displacement of a nitro group by the azide ion [13], we found that nitration of *m*-hemipinic acid (4,5-dimethoxyphthalic acid) at 0° led to electrophilic *ipso*-substitution of the carboxyls by the nitro groups and resulted in the formation of 4,5-dinitroveratrole **1a**, which was also prepared by direct nitration of veratrole itself [14]. Thermolysis of **1a** in sodium azide-dimethylsulfoxide gave 5,6-dimethoxybenzofuroxan **2a** in good yield [15], *via* the intermediate 4-azido-5-nitroveratrole (Scheme I).

Scheme I



1a, R^1, $R^2 = OCH_3$
1b, R^1, $R^2 = O-CH_2-O$
1c, R^1, $R^2 = O-CH_2-CH_2-O$
1d, R^1, $R^2 = OH$



2a, R^1, $R^2 = OCH_3$
2b, R^1, $R^2 = O-CH_2-O$
2c, R^1, $R^2 = O-CH_2-CH_2-O$

rapid degenerate equilibrium

Marquet *et al.* [16] recently suggested that 5,6-dimethoxybenzofuroxan **2a** may be an intermediate in the formation of 5,6-dimethoxybenzofurazan, by photoaromatic substitution of 4,5-dinitroveratrole **1a** in the presence of *n*-butylamine. The authors state that the furazan could

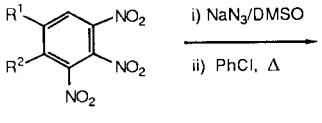
arise either by reduction of the furoxan or *via* the corresponding *o*-nitrosohydroxylamine.

1,3-Benzodioxano[5,6-*c*]furoxan **2b** has now been synthesised by us *via* thermolysis of 5,6-dinitro-1,3-benzodioxane **1b** in the presence of sodium azide-dimethylsulfoxide. This furoxan **2b** has been reported earlier [17], but the author did not discuss its method of preparation.

1,4-Benzodioxano[6,7-*c*]furoxan **2c** was prepared earlier [18] from alkaline hypochlorite oxidation of 6-amino-7-nitro-1,4-benzodioxane, which itself was obtained in six steps. Along with this was reported the failure to prepare this furoxan **2c** by pyrolysis of 6-azido-7-nitro-1,4-benzodioxane in various solvents and at different temperatures. We have now successfully prepared the same furoxan **2c** from 6,7-dinitro-1,4-benzodioxane **1c** *via* azide displacement and followed by pyrolysis of the crude intermediate azide in toluene or chlorobenzene.

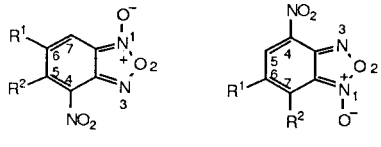
In our hands nitration of *m*-hemipinic acid at room temperature gave 3,4,5-trinitroveratrole **1e**. Reaction of **1e** with sodium azide-dimethylsulfoxide gave the crude mono-azide which on thermolysis in chlorobenzene yielded the new isomeric 5(7),6-dimethoxy-4-nitrobenzofuroxans **2e**, **3e** (Scheme II), from which pure 6,7-dimethoxy-4-nitrobenzofuroxan **3e** could be isolated by preparative thin layer chromatography.

Scheme II



1 e

1e, $R^1, R^2 = OCH_3$



2 e 3 e

2e,3e, $R^1, R^2 = OCH_3$

Discussion of Spectra.

The ir spectra of the intermediates in the above reactions exhibited an intense band at 2100 cm^{-1} for the azide group, whereas the benzofuroxans showed characteristic bands in the region 1580-1620 cm^{-1} for the benzofuroxans. The uv spectrum of **2a**, **2b** and **2c** showed four maxima between 315-370 nm while the new nitrobenzofuroxans **2e**, **3e** showed three maxima between 300-480 nm.

The proton magnetic resonance spectrum of 5,6-dimethoxybenzofuroxan **2a** in deuterated chloroform at room temperature showed a sharp signal at δ 3.97 for the methoxy groups. In addition two broad signals, one at δ 6.68 (due to H-4) and the other at δ 6.46 (due to H-7, adjacent to the *N*-oxide group), each for one aromatic proton were also seen. These coalesced at 41° into a new broad signal which now appeared, centred at δ 6.52. Based on the above variable temperature pmr studies of **2a**, the activation energy (ΔG^*) for this rapid degenerate equilibrium was calculated [19] to be 15.5 Kcal/mole.

The pmr spectrum of furoxan **2b** in deuterated chloroform exhibited a two proton signal for the methylene group at δ 6.08 and signals due to the aromatic protons at δ 6.74 and δ 6.52, the higher field signal being attributed to the aromatic proton adjacent to the *N*-oxide group. Variable temperature pmr studies in deuteriochloroform gave a coalescence temperature of 61° with a new signal appearing at δ 6.58 for the aromatic protons ($\Delta G^* = 16.6$ Kcal/mole). The pmr spectrum of **2c** showed a signal at δ 6.8 for two aromatic protons and a signal at δ 4.36 for the methylene protons, as has been described earlier [18]. The ΔG^* was reported to be 13.1 Kcal/mole.

The pmr spectrum of the isomeric 5(7),6-dimethoxy-4-nitrobenzofuroxans **2e**, **3e** in deuteriochloroform at 30° showed two signals at δ 8.26 and δ 6.67 for the aromatic protons and peaks at δ 4.24, 4.13 and 4.01 for the methoxy groups. The signal at δ 6.67 could be assigned to the aromatic proton at 7-position of **2e** which is shielded by the adjacent *N*-oxide group of the furoxan ring, whereas the peak at δ 8.26 could be assigned to the aromatic hydrogen at 5-position of isomer **3e**. This proton appears downfield due to the deshielding influence of the adjacent nitro group at 4-position. The observed ratio of the intensities for the two peaks at δ 6.67 and δ 8.26 was found to be 56:43. Hence the 5-methoxy isomer **2e** slightly predominated. Further, the signal at δ 4.01 was common for both the isomers **2e** and **3e**. This could be, therefore, easily assigned for the methoxy group at 6-position. The peaks at δ 4.24 and δ 4.13 could be assigned respectively to the methoxy at 7-position in **3e**, and the 5-methoxy group in **2e** as the former is adjacent to the nitro group while the latter is adjacent to the *N*-oxide group. The ratio of intensities of the signals at δ 4.13 and δ 4.24 again indicated that the isomer **2e** slightly predominated. These pmr assignments for **2e**, **3e** were further confirmed by the isolation of one of the isomers **3e**, by preparative thin-layer chromatography. The pmr spectrum of **3e** in deuterated chloroform showed a signal for the aromatic proton at δ 8.26 and a signal at δ 4.01 for the 6-methoxy group and at δ 4.24 for the 7-methoxy group. Thus both the signals at δ 4.13 (due to the 5-methoxy) and δ 6.67 (due to the aromatic proton) of isomer **2e**, seen earlier in the spectrum of **2e**, **3e**, were no longer observed in the spectrum of

3e. Variable temperature pmr studies in deuterated dimethylsulfoxide of both 5(7),6-dimethoxy-4-nitrobenzofuroxans **2e**, **3e** and 6,7-dimethoxy-4-nitrobenzofuroxan **3e** did not show any change up to 110° and decomposition occured only above 120°. Thus isomeric **2e**, **3e** do not rearrange into one another on heating. Dry heating of isomer **3e** at 130° for 10 minutes did not result in any Boulton-Katritzky type of rearrangement [20] into the other isomer **2e**.

Mass spectral fragmentation pattern of benzofuroxans and nitrobenzofuroxans have been discussed recently [21]. The mass spectra of all our benzofuroxans showed an intense molecular ion peak, as well as the $(M-16)^+$ and intense $(M-60)^+$ peaks characteristic of the furoxan ring. The isomeric **2e**, **3e** and the isomer **3e** showed in addition a weak $(M-90)^+$ peak due to loss of N_2O_2 and NO groups, characteristic of nitrobenzofuroxans. The mass spectrum of **2c** has been reported earlier [18].

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Shimadzu IR-435. The pmr spectra were recorded on Jeol JNM-FX 200 FT NMR (199.5 MHz). The uv spectra were recorded on a Shimadzu UV-260. The C,H,N analyses were recorded on Heraus CHN-RAPID.

4,5-Dinitroveratrole (**1a**).

A cold mixture of fuming nitric and concentrated sulphuric acid (1:1, 10 ml) was added dropwise over 15 minutes with stirring to *m*-hemipinic acid, 1 g (4.4 mmoles) kept in an ice-acetone bath. The reaction mixture was allowed to stand for 15 minutes, poured into ice water and filtered. The yellow solid obtained was purified by column chromatography using silica gel. Elution with benzene-petroleum ether (60:40) gave a solid which was crystallized from methanol to give **1a**, 0.35 g (35%) as yellow needles, mp 129° (lit [16] mp 128-130°). The same compound was later also obtained by direct nitration of veratrole.

5,6-Dimethoxybenzofuroxan (**2a**).

To a solution of **1a**, 7 g (0.03 mole) in dimethylsulfoxide, 110 g (1.41 moles) was added, followed by sodium azide 7.0 g (0.107 mole). The mixture was heated in a water bath at 80-90° for four hours. The reaction mixture was poured into ice-water and the solid collected by filtration. Crystallization from ethyl acetate afforded pale yellow needles of **2a**, 3.75 g (62%) mp 212° dec; ir (potassium bromide): 1628 cm^{-1}, 1582, 1518, 1500, 1440, 1338, 1260, 1220; uv (chloroform): λ max 241.8 nm (ε 4081), 315 (5250), 329.4 (5515), 352.8 (5395), 367.8 (4313); ^{1}H-nmr (deuteriochloroform): δ 6.68 (br, aromatic, 1H), 6.46 (br, aromatic, 1H), 3.97 (s, $-OCH_3$, 6H); ms: m/z (relative intensity) 197 (M+1, 10.2), 196 (M^+, 100), 180 (M-16, 3.8), 136 (M-60, 84.1), 121 (20.4), 93 (36.6), 82 (22.3), 50 (17.5).

Anal. Calcd. for $C_8H_8N_2O_4$: C, 48.97; H, 4.08; N, 14.28. Found: C, 49.0; H, 4.2; N, 14.1.

4,5-Dinitropyrocatechol (**1d**).

Compound **1d** was prepared as described [22] mp 166° (lit mp 166.5-167.5°); ir (potassium bromide): 3300 cm^{-1}, 1595, 1500, 1435, 1325, 1290, 1205, 1025; uv (methanol): λ max 336 nm (ε 2111), 272 (5582), 245.2 (4932), 205 (9708); ^{1}H-nmr (acetone-d_6): δ 10.24 (br, OH, 2H). 7.54 (s, aromatic, 2H).

Anal. Calcd. for $C_6H_4N_2O_6$: C, 36.0: H, 2.0; N, 14.0. Found: C, 36.0; H, 2.3; N, 13.8.

6,7-Dinitro-1,4-benzodioxane (**1c**).

According to the method described [23] a mixture of **1d**, 2 g (10 mmoles), *N,N*-dimethylformamide 30 ml, ethylene bromide, 17.4 g (93.7 mmoles), potassium carbonate, 6.0 g (43.4 mmoles) and cupric oxide 0.2 g was stirred and refluxed for 8 hours. It was allowed to stand overnight at room temperature and then poured into ice-water. The orange solid was collected by filtration and washed with water followed by 5% aqueous hydrochloric acid and finally with water. It was dried and crystallised from ethyl alcohol to give **1c**, 1.2 g (53%) as orange needles, mp 133° (lit [24] mp 132-133°); ir (potassium bromide): 1580 cm^{-1}, 1480, 1320, 1260 1190, 1050; uv (chloroform): λ max 304.2 nm (ε 5332), 245.2 (13512); ^{1}H-nmr (deuteriochloroform): δ 7.45 (s, aromatic, 2H) 4.43 (s, OCH_2, 4H).

Anal. Calcd. for $C_8H_6N_2O_6$: C, 42.47; H, 2.65; N, 12.38. Found: C, 42.72; H, 2.63; N, 12.37.

1,4-Benzodioxano[6,7-c]furoxan (**2c**).

To a solution of **1c**, 0.5 g (2.2 mmoles) in dimethylsulfoxide 11.0 g (141.0 mmoles) was added sodium azide 1.0 g (15.3 mmoles). The mixture was warmed at 60-70° for 30 minutes. It was then poured into ice-water. The yellow solid obtained was filtered and dried. It was crystallised from carbon tetrachloride to give the yellow crude azide, 0.4 g (81%)(ir, 2100 cm^{-1}). The crude azide (0.3 g) on thermolysis in toluene, 15 ml (100-110°, 4 hours) gave a crude product, which was purified by column chromatography (silica gel) using benzene as eluent and finally crystallised from benzene to give **2c**, 0.13 g (40%) as yellow needles, mp 203° dec (lit [18] mp 203-204° dec).

5,6-Dinitro-1,3-benzodioxane (**1b**).

Reaction of **1d** with methylene iodide, and potassium carbonate using the procedure described above for **1c** gave compound **1b**, mp 101° (lit [25,26] mp 101°); ir (potassium bromide): 1495 cm^{-1}, 1420, 1325, 1260, 1165, 1020; uv (chloroform): λ max 331.2 nm (ε 4142), 244.6 (14310); ^{1}H-nmr (deuteriochloroform): δ 7.30 (s, aromatic, 2H), 6.26 (s, OCH_2, 2H).

Anal. Calcd. for $C_7H_4N_2O_6$: C, 39.62; H, 1.88; N, 13.2. Found: C, 39.5; H, 2.1; N, 12.9.

1,3-Benzodioxano[5,6-c]furoxan (**2b**).

To a solution of **1b**, 0.3 g (1.6 mmoles) in dimethylsulfoxide 6.6 g (84.6 mmoles) was added sodium azide, 0.9 g (13.8 mmoles). The mixture was heated in a water bath at 80-90° for six hours. It was then poured into ice-water and the dark yellow solid obtained was filtered and crystallised from benzene and petroleum ether to give **2b**, 0.08 g (31 %) as yellow leaflets, mp 171° dec; ir (nujol mull); 1610 cm^{-1}, 1570, 1195, 1175; uv (chloroform): λ max 240.6 nm (ε 3730), 300 (5958), 315.8 (7355), 331.8 (7417), 351.6 (7380), 369.8 (6014); ^{1}H-nmr (deuteriochloroform): δ 6.74 (s, aromatic, 1H), 6.52 (s, aromatic, 1H), 6.08 (s, OCH_2, 2H); ms: m/z (relative intensity) 181 (M+1, 6.5) 180 (M^+, 100), 164 (M-16, 68.1), 120 (M-60, 83.8), 76 (8.6), 62 (23.6), 55 (15.7).

Anal. Calcd. for $C_7H_4N_2O_4$: C, 46.66; H, 2.22; N, 15.55. Found: C, 46.9; H, 2.5; N, 15.6.

3,4,5-Trinitroveratrole (**1e**).

A mixture of fuming nitric acid and concentrated sulphuric acid (1:1, 10 ml) was added slowly over 10 minutes with stirring to *m*-hemipinic acid (1 g, 4.4 mmoles) at room temperature and then poured into ice-water. The yellow solid was collected by filtration, dried and crystallised from methanol to give 0.45 g (37%) of compound **1e**, as pale yellow needles (The same compound was also obtained by the direct nitration of veratrole) mp 142° (lit [22] mp 144.5°-145.5°); ir (potassium bromide): 1525 cm^{-1}, 1330, 1290, 1235, 1185, 1070, 1015; uv (chloroform): λ max 245.6 nm (ε 12140), 293.6 (5948), 320 (5395); ^{1}H-nmr (deuteriochloroform): δ 7.64 (s, aromatic, 1H), 4.11 (s, $-OCH_3$, 3H), 4.10 (s, $-OCH_3$, 3H); ms: m/z (relative intensity) 274 (M+1, 7.0) 273 (M^+, 100), 243 (2.2), 181 (20.4), 166 (7.0), 138 (20.4), 123 (15.3), 110 (27.0), 93 (51.9), 77 (56.0), 75 (71.1), 58 (22.3), 53 (18.7).

Anal. Calcd. for $C_8H_7N_3O_8$: C, 35.16; H, 2.56; N, 15.38. Found: C, 35.3; H, 2.8; N, 15.2.

5(7),6-Dimethoxy-4-nitrobenzofuroxans (**2e**, **3e**).

To a solution of 3,4,5-trinitroveratrole **1e**, 3.0 g (10.9 mmoles) in dimethylsulfoxide (55 g, 705.1 mmoles) was added sodium azide (3.0 g, 46.1 mmoles). The mixture was allowed to stand for five and a half hours at room temperature. It was then poured into ice-water. The yellow solid obtained was filtered and dried to give the crude azide, 1.9 g (ir 2100 cm^{-1}). The crude azide (1.9 g) was dissolved in chlorobenzene (15 ml) and refluxed at 130° for 10 minutes. Most of the solvent was distilled under reduced pressure and the resultant dark brown mixture was purified by column chromatography over silica gel using benzene as eluent. The orange band was separated and finally the compound was crystallised from benzene-petroleum ether to give 0.5 g (19% based on **1e**) of **2e**, **3e** as orange red needles mp 108°; ir (Nujol mull): 1625 cm^{-1}, 1580, 1500, 1400, 1340, 1308, 1265, 1190, 1145, 1100, 1005; uv Chloroform): λ max 222.6 nm (ε 19647), 317.4 (2730), 401.8 (4029), 460 (1154); ^{1}H-nmr (deuteriochloroform): δ 8.26 (s, aromatic, 1H), 6.67 (s, aromatic, 1H), 4.24 (s, OCH_3 at C-7), 4.13 (s, OCH_3 at C-5), 4.01 (s, OCH_3 at C-6); ms: m/z (relative intensity) 242 (M + 1, 7.7), 241 (M^+, 76.5), 225 (M-16, 7.9), 207 (1.3), 196 (4.0),, 181 (M-60, 31.5), 166 (11.7), 165 (8.0), 151, (M-90, 6.1), 136 (11.0), 123 (14.1), 108 (12.0), 93 (37.5), 77 (48.3), 75 (100), 69 (18.1), 63 (13.0), 53 (14.1), 51 (26.1).

Anal. Calcd. for $C_8H_7N_3O_6$: C, 39.8; H, 2.90; N, 17.42. Found: C, 39.9; H, 3.2; N, 17.2.

6,7-Dimethoxy-4-nitrobenzofuroxan (**3e**).

The isomeric compounds **2e**, **3e**, (60 mg, 0.24 mmoles) were dissolved in chloroform and subjected to the preparative silica gel thin layer chromatography using toluene-ethyl acetate (8:2) as a solvent. The lower band on elution and crystallisation from ethyl acetate-petroleum ether gave 15 mg (25%) of **3e** as red needles mp 142°; ir (Nujol mull): 1625 cm^{-1}, 1575, 1500, 1400, 1340, 1300, 1260, 1140, 1095; uv (chloroform): λ max 253.8 nm (ε 3965), 303.6 (2445), 440.8 (3828), 484.6 (3673); ^{1}H-nmr (deuteriochloroform): δ 8.26 (s, aromatic, 1H), 4.24 (s, OCH_3, 3H), 4.01 (s, OCH_3, 3H); ms: m/z (relative intensity) 242 (M + 1, 8.5), 241 (M^+, 50), 225 (M-16, 5.2), 196 (1.3) 181 (M-60, 26.4), 166 (5.2), 151 (M-90, 2.3), 136 (7.2), 123 (13.8), 108 (10.5), 93 (28.9), 75 (44.1), 77 (20.3), 69 (2.6), 63 (3.2), 51 (1.8).

Anal. Calcd. for $C_8H_7N_3O_6$: C, 39.8, H, 2.90; N, 17.42. Found: C, 39.8; H, 3.4; N, 17.0.

Acknowledgements.

We are grateful to University Grants Commission, New Delhi for the grant of a project and a fellowship (to S.K.S.). We thank Dr. Dinesh, USIC, Delhi University, Prof. Dr. W. Schäfer, Max-Planck-Institute for Biochemistry, Munich, Dr. K. V. C. Rao, VSSC, Thumba, Trivandrum and Prof. R. P. Gandhi, I.I.T., Delhi for spectra.

REFERENCES AND NOTES

[1] P. B. Ghosh, B. Ternai and M. W. Whitehouse, *Med. Chem. Rev.*, **1**, 159 (1981).

[2] P. B. Ghosh and B. J. Everitt, *J. Med. Chem.*, **17**, 203 (1974).

[3] A. Gasco and A. J. Boulton, "*Adv. Heterocyclic Chem.*, **29**, 251 (1981).

[4] R. M. Paton, in "Comprehensive Heterocyclic Chemistry", Vol **6**, A. R. Katritzky, ed, Pergamon Press, Oxford, New York, 1984, p 393.

[5] P. B. Ghosh, B. Ternai and M. W. Whitehouse, *J. Med. Chem.*, **15**, 255 (1972).

[6] E. Buncel, N. Chuaqui-Offermanns and A. R. Norris, *J. Chem. Soc., Perkin Trans.* I, 415 (1977).

[7] O. Eidelmen and Z. I. Cabantchik, *Anal. Biochem.*, **106**, 335 (1980).

[8] L. H. Smith, H. M. McConnell, B. A. Smith and J. W. Parce, *Biophys. J.*, **33**, 139 (1981).

[9] M. Shipton and K. Brocklehurst, *Biochem. J.*, **167**, 799 (1977).

[10] F. Willenbrock and K. Brocklehurst, *Biochem. J.*, **238**, 103 (1986).

[11] A. S. Bailey and J. R. Case, *Tetrahedron*, **3**, 113 (1958).

[12] P. B. Ghosh and M. W. Whitehouse, *J. Med. Chem.*, **11**, 305 (1968).

[13] S. V. Eswaran and S. K. Sajadian, 10th International Congress of Heterocyclic Chemistry, Waterloo, Canada, Abstract P5-143 (1985).

[14] D. S. Wulfman and C. F. Cooper, *Synthesis*, 924 (1978).

[15] S. V. Eswaran and S. K. Sajadian, 11th International Congress of Heterocyclic Chemistry, Heidelberg, West Germany, Abstract P.12.68, p 441.

[16] J. Marquet, M. Moreno-Mañas, A. Vallribera, A. Virgili, J. Bertran, A. Gonzalez-Lafont and J. M. Lluch, *Tetrahedron*, **43**, 351 (1987).

[17] W. Dürckheimer, *Ann. Chem.*, **756**, 145 (1972).

[18] P. M. Hadjimihalakis, *J. Heterocyclic Chem.*, **13**, 1327 (1976).

[19] A. J. Boulton, A. R. Katritzky, M. J. Sewell and B. Wallis, *J. Chem. Soc. (B)*, 914 (1967).

[20]A. J. Boulton and A. R. Katritzky, *Rev. Chem. Acad. Rep. Pop. Roum.*, **2**, 691, (1962).

[21] A. P. Chafin and E. D. Erickson, *Org. Mass Spectrom.*, **20**, 276 (1985).

[22] J. Ehrlich and M. T. Bogert, *J. Org. Chem.*, **12**, 522 (1947).

[23] S. McLean, M. SieLin and J. Whelan, *Can. J. Chem.*, **48**, 951 (1970).

[24] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **111**, 929 (1917).

[25] Beilstein's Handbuch, Band **XIX**, Syst. No. 2672, p 21 (1934).

[26] G. K. Hughes and E. Ritchie, *Aust. J. Chem.*, **7**, 104 (1954).