A Useful Methodology for the Synthesis of 2-Methyl-4-nitrobenzimidazoles

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Cyclocondensation of 3-nitro-1,2-benzenediamines **2** with 2,4-pentanedione provides a convenient route for the preparation of 2-methyl-4-nitrobenzimidazoles **3**. A discrepancy in the literature regarding the 5-chloro-, 5-methoxy- and 5-methyl derivatives of the title compounds is discussed.

In connection with the work related to some very potent food mutagens,[2] we have prepared starting from 4-nitro-2,1,3-benzoselenadiazoles **1** a number of novel 4-halo-3-nitro-1,2-benzenediamines, which on reaction with α-dicarbonyls afford the corresponding previously unknown 6-halo-5-nitroquinoxalines.[3,4] We would like now to report that the simple condensation of 2,4-pentanedione (acetylacetone) with diamines **2** leads exclusively and efficiently to the 4-nitro derivatives of 2-methylbenzimidazoles **3**.

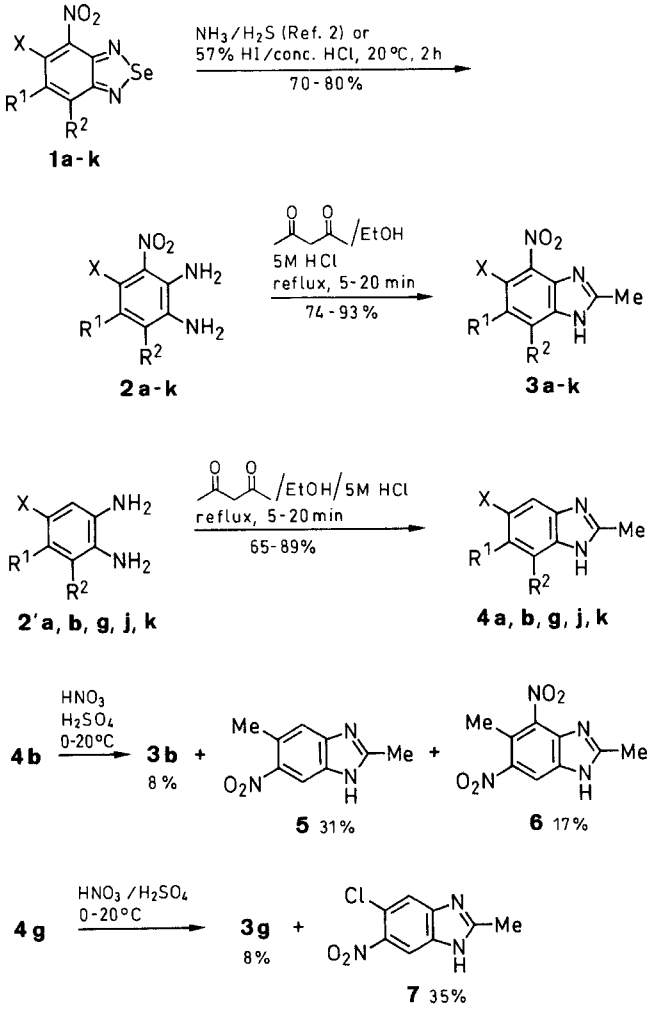
2-Methylbenzimidazoles have been usually prepared by heating 1,2-benzenediamines with acetic acid, preferably in aqueous mineral acid as described by Phillips,[5] or with its anhydride, acid chloride, ester, nitrile etc.[6] Catalase-mediated cyclizations have also yielded 2-methylbenzimidazoles.[7] Further, 1,2-benzenediamines have been treated with 1,3-biscarbon electrophiles to afford 1,5-benzodiazepines.[8] However, the concomitant formation of benzimidazoles in the reaction of diamines with β-diketones,[9] β-oxo esters[10] and 2-hydroxypyrones[11] has been observed.

The efficient reaction of substituted 1,2-benzenediamines with 2,4-pentanedione to form 2-methylbenzimidazoles has apparently not been appreciated as an alternative to Phillips' procedure, which sometimes suffers from long reaction times and undesired side reactions, e.g. alkylations. Some isolated examples have, however, appeared in the literature. For instance, the sulfate of 4,5,6,7-tetrachloro-2-methylbenzimidazole has been synthesized by treating an ethanolic solution of the appropriate diamine with 2,4-pentanedione in the presence of sulfuric acid.[12] 2-Methylbenzimidazole itself has been isolated in 30% yield by treating 1,2-benzenediamine with 2,4-pentanedione in *o*-xylene.[13] The reaction apparently involves an acid cleavage (retro-Claisen condensation) of the β-dicarbonyl compound, in the present case with the formation of acetone.[14]

Nitration of a benzimidazole substituted with a strong electron-donating group (amino or hydroxy group) at position 5 outweighs the inherent greater reactivity of position 6, thus affording mainly the 4-nitro derivative. That is, benzimidazole itself and its, e.g. 5-methoxy, 5-methyl and 5-nitro derivatives are mainly nitrated at the 6-position.[6,15] The methodology we report herein provides an easy and unambiguous way to obtain exclusively the 4-nitro derivatives of 2-methylbenzimidazoles, especially of those which are not readily obtainable by direct nitration. We found that neither the number of the substituents in **2** (cf. **2e** to **2f** and **2i** to **2j**) nor their nature (cf. **2c** to **2g**) had any significant influence on the yield or reaction time. Diamine **2k**, with both nitro groups conjugated with one of the amino groups, gave **3k** in 74% yield within 20 minutes. Additionally, the method works satisfactorily without isolation of the intermediate diamine or triamine. For example, reduction of **1f** with ammonium sulfide, followed by filtration and treatment of the filtrate with 2,4-pentanedione and 5 M hydrochloric acid gave **3f** in 50% isolated yield. Evidently, the presence of a 3-nitro substituent in **2** is not imperative for a successful condensation as demonstrated by the easy formation of **4g** and the more substituted **4j** from the corresponding diamines **2'g** and **2'j**, respectively. However, the presence of a chloro or a nitro substituent does favour the formation of the corresponding benzimidazoles. For example, **4g** and the isomers **3a** and **4k** were obtained in much higher yield than **4a** and **4b** from the corresponding diamines.

Although it is well documented[6,15] that only strong electron-donating groups at the 5-position of benzimidazoles direct the nitro substituent mainly to the 4-position, compounds **3b**, **3d** and **3g** have been reported[16] to be the major nitration product from 5-methyl-, 5-methoxy- and 5-chloro-2-methylbenzimidazoles, respectively. No spec-

tral data were given and no other nitro products were mentioned.[16] By repeating the patented procedure we found that **4b** afforded 2,5-dimethyl-6-nitrobenzimidazole (**5**), 2,5-dimethyl-4,6-dinitrobenzimidazole (**6**) and the 4-nitro derivative **3b** in 31, 17 and 8% isolated yield, respectively. Nitration of **4g** gave 5-chloro-2-methyl-6-nitrobenzimidazole (**7**) and the 4-nitro derivative **3g** in 35 and 8% isolated yield, respectively. The melting points of the reported[16] **3b, 3d** and **3g** differed greatly from those prepared by the unambiguous methodology presented herein via **2b, 2d** and **2g**. The intermediate diamines **2d**[17] and **2g**[3] have also been useful in the synthesis of 2-methyl-7-methylamino-8-nitroquinoxaline, the structure of which was confirmed by an independent synthetic pathway.[18] To the best of our knowledge 4-bromo-3-nitro- and 4-methyl-3-nitro-1,2-benzenediamines, 5-chloro-2-methyl-6-nitro-,[19] 2,5-dimethyl-4,6-dinitrobenzimidazoles and benzimidazoles **3f, 3h–3j** and **4j** have not been described before.



1–4	R^1	R^2	X	1–4	R^1	R^2	X
a	H	H	H	**g**	H	H	Cl
b	H	H	Me	**h**	Me	H	Cl
c	H	H	OH	**i**	H	H	Br
d	H	H	OMe	**j**	Me	Me	Br
e	H	H	NHMe	**k**	NO_2	H	H
f	Me	Me	NHMe				

The possible acetylation byproducts from, e.g. **2c, 2e** and **2f** under Phillips' conditions[5] were avoided by this methodology. Benzimidazoles with a hydroxy group in the benzene ring have been previously prepared by hydrobromic acid cleavage of the corresponding methyl ethers[20] obtained using Phillips' conditions,[5] by the Udenfriend oxidation[21] and by bioconversion with micromycetes.[22] Benzimidazoles with an amino substituted benzene ring have been prepared by reduction of the corresponding nitrobenzimidazoles,[23] likewise obtained from nitro-1,2-benzenediamines under Phillips conditions.[5]

In conclusion, treatment of diamines **2** with 2,4-pentanedione instead of acetic acid or one of its derivatives leads exclusively to **3** in an efficient and straightforward manner. Some of these derivatives are inaccessible by nitration of the substituted 2-methylbenzimidazoles.

Melting points were taken using a Mettler FP5 instrument and are uncorrected. ^{1}H NMR spectra were obtained on a Varian VXR-400 spectrometer at 20°C and referenced to the solvent [$\delta(CHCl_3)$ 7.26]. Mass spectra were obtained on a Finnigan 4021 instrument with DEI ionisation and an ion source temperature of 250°C. Ions containing isotopes other than ^{79}Br or ^{35}Cl are not listed. Flash liquid chromatography (FC) was performed on silica gel (230–400 mesh ASTM, Merck). All reactions and purifications were monitored by TLC (UV detection) on aluminium sheets coated with silica 60 F_{254} (Merck).

5-Bromo-3,4-dimethyl-1,2-benzenediamine (**2'j**) was prepared by bromination of commercial (Aldrich) 2,3-dimethyl-6-nitroaniline followed by reduction with sodium dithionite.[24] 1,2-Benzenediamine and its 4-chloro- (**2'g**), 4-methyl- (**2'b**) and 3-nitro derivative (**2a**) were obtained commercially (Aldrich). Diamines **2b, 2c,**[25] **2g,**[3] **2h,**[3] **2i, 2j**[24] and **2k**[26] were prepared from **1b,**[27] **1c,**[25] **1g,**[28] **1h,**[24] **1i,**[29] **1j,**[24] and **1k**[26] by reduction with 57% HI in HCl[3] as described below for **2i**. Diamines **2d,**[17,30] **2e**[31] and **2f**[24] were prepared by ammonium sulfide reduction of **1d,**[30] **1e**[31] and **1f**[24] as described previously.[2]

4-Bromo-3-nitro-1,2-benzenediamine (2i):
To a suspension of **1i**[29] (13 g, 42 mmol) in conc. HCl (300 mL) was added dropwise 57% HI (30 mL, 0.4 mol) with vigorous stirring. The stirring was continued at r.t. for 2 h (TLC, eluent: CH_2Cl_2/EtOAc, 1:1). A 5% aq $NaHSO_3$ solution (240 mL) was added to the dark red mixture, which was warmed to ca. 80°C and filtered hot. The filtrate was cooled to 4°C and the needle-like hydrochloride was collected and washed with 1 M HCl (200 mL). Pure **2i** was obtained by crystallization from EtOH/conc. NH_4OH, (5:1); yield: 7.7 g (79%); mp 146–147°C.

$C_6H_6BrN_3O_2$ (232.0) calc. C 31.06 H 2.61 N 18.11
found 31.0 2.6 18.0

^{1}H NMR ($CDCl_3$): δ = 3.5, 4.5 (2 br s, 2 × NH_2), 6.68, 6.92 (ABq, 2H, J = 8.3, H-5,6).

MS (70 eV): m/z (%) = 231 (M^+, 53), 214 (15), 213 (9), 185 (16), 184 (11), 134 (99), 105 (100).

4-Methyl-3-nitro-1,2-benzenediamine (2b):
This compound was prepared from **1b** as described above for **2i**; yield: 82%; mp 132–134°C.

$C_7H_9N_3O_2$ (167.2) calc. C 50.30 H 5.43 N 25.14
found 49.9 5.4 24.8

^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3H, CH_3), 3.3, 4.9 (2 br s, 2 × NH_2), 6.51, 6.76 (ABq, 2H, J = 7.8, H-5, 6).

MS (70 eV): m/z (%) = 167 (M^+, 79), 150 (38), 149 (34), 133 (13), 132 (10), 120 (34), 119 (48), 77 (100).

Table. 2-Methylbenzimidazoles **3a–k** and **4a,b,g,j,k** Prepared

Product	Yield[a] (%)	mp (°C) (aq EtOH)	Molecular Formula[b] or Lit. mp (°C)	MS (70 eV) *m/z* (%)	^{1}H NMR ($CDCl_3$) δ, *J* (Hz)
3a	75	216–217	219–220[33] 217–218[34]	177 (M^+, 100), 131 (85), 130 (5), 129 (2), 119 (10), 116 (7), 104 (29), 90 (30)	2.74 (s, 3H, CH_3), 7.34 (t, 1H, J = 8.1, H-6), 8.02, 8.12 (2d, 1H each, J = 8, H-5, 7), 10.3 (br s, 1H, NH)
3b	93	234–235	173–175[16]	191 (M^+, 40), 174 (57), 146 (27), 145 (29), 144 (14), 105 (35), 103 (36), 77 (100)	2.70, 2.84 (2s, 3H each, CH_3 at C-2, 5), 7.19, 7.84 (ABq, 2H, J = 8.1, H-6, 7), 10.3 (br s, 1H, NH)
3c	79	254 (dec)	254–256[15]	193 (M^+, 100), 175 (57), 160 (4), 145 (11), 130 (7), 119 (13), 104 (23)	2.68 (s, 3H, CH_3), 6.99, 7.89 (ABq, 2H, J = 8.8, H-6, 7), 10.2 (br s, 1H, NH), 10.8 (s, 1H, OH)
3d	75	203–204	106–107[16] 204–205[17] 203–204[35]	207 (M^+, 87), 192 (6), 160 (42), 147 (7), 131 (82), 118 (6), 104 (61), 76 (100)	2.67 (s, 3H, CH_3), 4.07 (s, 3H, OCH_3), 6.99, 7.89 (ABq, 2H, J = 8.8, H-6, 7), 10.3 (br s, 1H, NH)
3e	89	238–240	225–227[36]	206 (M^+, 100), 189 (5), 172 (14), 160 (16), 159 (47), 158 (21), 132 (55), 131 (44)	2.62 (s, 3H, CH_3), 3.12 (d, 3H, J = 5.2, $NHCH_3$), 6.66, 7.79 (ABq, 2H, J = 9, H-6, 7), 8.7, 10.5 (2 br s, 1H each, NH-1, 5)
3f	50[c]	230–232	$C_{11}H_{14}N_4O_2$ (234.3)	234 (M^+, 76), 220 (22), 199 (32), 188 (20), 187 (42), 172 (34), 160 (35), 57 (100)	2.36, 2.61, 2.63 (3s, 3H each, CH_3 at C-2, 6, 7), 3.06 (s, 3H, NCH_3), 8.1, 10.3 (2 br s, 1H each, NH-1, 5)
3g	81	197–199	224–226[16] $C_8H_6ClN_3O_2$ (211.6)	211 (M^+, 100), 195 (1), 181 (3), 165 (80), 153 (15), 138 (3), 124 (49)	2.71 (s, 3H, CH_3), 7.42, 7.82 (ABq, 2H, J = 8.4, H-6, 7), 10.3 (br s, 1H, NH)
3h	80	221–223	$C_9H_8ClN_3O_2$ (225.6)	225 (M^+, 100), 195 (4), 179 (76), 167 (15), 152 (5), 138 (14), 111 (45)	2.57 (s, 3H, CH_3 at C-6), 2.69 (s, 3H, CH_3 at C-2), 7.82 (br s, 1H, H-7), 10.1 (br s, 1H, NH)
3i	81	188–190	$C_8H_6BrN_3O_2$ (256.1)	255 (M^+, 93), 209 (65), 197 (9), 168 (33), 156 (3), 130 (52), 89 (100)	2.71 (s, 3H, CH_3), 7.63, 7.76 (ABq, 2H, J = 8.5, H-6, 7), 10.3 (br s, 1H, NH)
3j	83	239–241	$C_{10}H_{10}BrN_3O_2$ (284.1)	283 (M^+, 66), 266 (2), 253 (6), 237 (18), 204 (12), 158 (51), 117 (33), 89 (100)	2.58, 2.68, 2.72 (3s, 3H each, CH_3 at C-2, 6, 7), 10.1 (br s, 1H, NH)
3k	74	251–252	249–251[37]	222 (M^+, 78), 192 (6), 176 (28), 146 (15), 130 (30), 129 (28), 62 (100)	2.81 (s, 3H, CH_3), 8.89, 9.06 (2d, 1H each, J = 1.8, H-5, 7), 10.6 (br s, 1H, NH)
4a[d]	65	175–176	176[5]	132 (M^+, 100), 131 (74), 117 (0.4), 105 (3), 104 (10), 92 (9), 91 (5), 90 (10), 87 (2), 85 (12), 83 (19)	2.47 (s, 3H, CH_3), 7.09 (m, 2H, H-5, 6), 7.38 (d, 1H, J = 7.1, H-4 or H-7), 7.48 (d, 1H, J = 7.9, H-7 or H-4), 12.1 (br s, 1H, NH)
4b[e]	58	202–204	203–204[38]	146 (M^+, 86), 145 (100), 144 (3), 131 (7), 118 (2), 116 (1), 105 (6), 104 (16), 91 (3), 78 (18), 77 (24)	2.46, 2.60 (2s, 3H each, CH_3 at C-2, 5), 7.03 (d, 1H, J = 8.3, H-6 or H-7), 7.30 (s, 1H, H-4), 7.42 (d, 1H, J = 8.3, H-7 or H-6), 8.9 (br s, 1H, NH)
4g[e]	82	211–212	197–200[39] 210–211[40]	166 (M^+, 100), 165 (52), 131 (27), 124 (6)	2.63 (s, 3H, CH_3), 7.18 (dd, 1H, J = 2.0, 8.5, H-6), 7.43 (d, 1H, J = 8.5, H-7), 7.52 (d, 1H, J = 1.0, H-4)
4j[d]	89	224–225	$C_{10}H_{11}BrN_2$ (239.3)	238 (M^+, 66), 223 (13), 159 (100)	2.37, 2.47, 2.48 (3s, 3H each, CH_3 at C-2, 4, 5), 7.52 (s, 1H, H-7), 12.2 (br s, 1H, NH)
4k[d]	86	220–221	221[5]	177 (M^+, 100), 147 (20), 146 (6), 145 (3), 132 (6), 131 (60), 104 (29), 90 (45), 63 (98)	2.56 (s, 3H, CH_3), 7.63 (d, 1H, J = 9.0, H-7), 8.06 (dd, 1H, J = 2.3, 9.0, H-6), 8.36 (d, 1H, J = 2.4, H-4), 12.9 (br s, 1H, NH)

[a] Yield of isolated product from **2**.
[b] Satisfactory microanalyses obtained: C ±0.2, H ±0.3, N ±0.2.
[c] Overall yield for **1f** → **3f** without isolation of **2f**.
[d] In DMSO-d_6 with TMS as internal standard.
[e] When recorded in DMSO-d_6 the NH signal was observed at δ = 12.0 for **4b** and at δ = 12.3 for **4g**.

Benzimidazoles 3a–k and 4a,b,g,j,k; General Procedure:
To a solution of diamine **2** (1 mmol) in hot EtOH (15 mL) and 5 M HCl (4 mL) was added 2,4-pentanedione (200 mg, 2 mmol). The mixture was refluxed for 5–20 min (TLC, eluent: CH_2Cl_2/EtOAc, 1:1), cooled to r.t. and neutralized with conc. aq $NaHCO_3$. The precipitate was collected and the filtrate extracted with $CHCl_3$ (3 × 15 mL) to obtain a further amount of the product. All benzimidazoles were recrystallized from 75% EtOH. Benzimidazoles **4a** and **4b** were purified by flash chromatography (CH_2Cl_2/EtOAc, 1:1) before recrystallization.

Nitration of 4b and 4g:
The nitration of **4b** and **4g** was carried out according to the patented procedure using equimolecular amount of HNO_3 in conc. H_2SO_4 at 0–20 °C.[16] The products were purified by flash chromatography on silica gel (eluent: EtOAc).

From 4b:
2,5-Dimethyl-4-nitrobenzimidazole **(3b)**; yield: 8%; R_f = 0.37 (Table).

2,5-Dimethyl-6-nitrobenzimidazole **(5)**; yield: 31%; R_f = 0.16; mp 207–208 °C (Lit.[32] 200–201 °C).

^{1}H NMR ($CDCl_3$): 2.68, 2.71 (2 s, 3H each, CH_3 at C-2 and C-5), 7.38, 8.29 (2 s, 1H each, H-4, 7).

MS (70 eV): *m/z* (%) = 191 (M^+, 33), 174 (84), 146 (26), 145 (17), 144 (13), 119 (22), 105 (35), 77 (91), 51 (100).

2,5-Dimethyl-4,6-dinitrobenzimidazole **(6)**; yield: 17%; R_f = 0.60; mp 217–218 °C.

$C_9H_8N_4O_4$ (236.2)	calc.	C 45.77	H 3.41	N 23.72
	found	45.7	3.4	23.7

^{1}H NMR ($CDCl_3$): δ = 2.76, 2.82 (2 s, 3H each CH_3 at C-2 and C-5), 8.35 (s, 1H, H-7).

MS (70 eV): *m/z* (%) = 236 (M^+, 25), 219 (60), 202 (30), 201 (37), 189 (3), 167 (5), 160 (21), 144 (35), 76 (100).

From 4g:
5-Chloro-2-methyl-4-nitrobenzimidazole **(3g)**; yield: 8%; R_f = 0.53 (Table).

5-Chloro-2-methyl-6-nitrobenzimidazole (**7**); yield: 35%; mp 233–235 °C; $R_f = 0.39$.

$C_8H_6ClN_3O_2$	calc.	C 45.41	H 2.86	N 19.86
(211.61)	found	45.3	2.8	19.7

^{1}H NMR (CD_3OD/TMS): $\delta = 2.62$ (s, 3 H, CH_3), 7.69, 8.11 (2 s, 1 H each, H-4, 7).

MS (70 eV): m/z (%) = 211 (M^+, 93), 195 (2), 181 (56), 165 (51), 153 (38), 138 (26), 124 (49), 97 (100).

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(2) Nyhammar, T.; Grivas, S. *Acta Chem. Scand.* **1986**, *B40*, 583. Jägerstad, M.; Skog, K.; Grivas, S.; Olsson, K. *Mutation Res.* **1991**, *259*, 219.
(3) Tian, W.; Grivas, S. *J. Heterocycl. Chem.* **1992**, *29*, 1305.
(4) Grivas, S.; Tian, W.; Andersson, R. *J. Chem. Res.* **1992**, (S) 328, (M) 2701.
(5) Phillips, M.A. *J. Chem. Soc.* **1928**, 172.
(6) Theobald, R.S. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Coffey, S.; Ansell, M.F. Eds.; Elsevier: Amsterdam, 1986; Vol. IV^c, p 197.
Wright, J.B. *Chem. Rev.* **1951**, *49*, 397.
(7) Kamal, A.; Hashim, R. *Heterocycles* **1990**, *31*, 969.
(8) Gagan, J.M.F. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Ansell, M.F. Ed.; Elsevier: Amsterdam, 1979; Vol. IV^k, p 270.
(9) Lloyd, D.; McDougall, R.H.; Marshall, D.R. *J. Chem. Soc.* **1965**, 3785.
Drewes, S.E.; Upfold, U.J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1901.
(10) Israel, M.; Jones, L.C.; Modest, E.J. *Tetrahedron Lett.* **1968**, 4811.
Solomko, Z.F.; Tkachenko, V.S.; Kost, A.N.; Budylin, V.A.; Pikalov, V.L. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1976**, *11*, 470.
(11) Abbassi, M.El.; Djerrari, B.; Essassi, E.M.; Fifani, J. *Tetrahedron Lett.* **1989**, *30*, 7069.
(12) Burton, D.E.; Lambie, A.J.; Lane, D.W.J.; Newbold, G.T.; Percival, A. *J. Chem. Soc. (C)* **1968**, 1268.
(13) Glatt, H.H.; Csunderlik, C.; Bacalglu, R.; Malureanu-Munteanu, M.; Glatt, I. *Bull. Stiint. Teh. Inst. Politeh. "Traian Vuia" Timisoara, Ser. Chim.* **1984**, *29*, 83; *Chem. Abstr.* **1985**, *103*, 104933.
(14) Badger, G.M.; Clark-Lewis, J.W. In *Molecular Rearrangements*; De Mayo, P. Ed.; Wiley: New York, 1963; Vol. 1, p 617.
(15) Kuznetsov, Yu.V.; Stolyarova, L.G.; Lezina, V.P.; Smirnov, L.D. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, 2142.
(16) Belgian Patent 611895, Farbenwerke Hoechst (1961), *Chem. Abstr.* **1962**, *57*, 13765.
(17) Gillespie, H.B.; Engelman, M.; Spano, F.; Graff, S. *J. Am. Chem. Soc.* **1957**, *79*, 2245.
(18) Grivas, S.; Olsson, K. *Acta Chem. Scand.* **1985**, *B39*, 31.
(19) Japanese patent 58190944, Konishiroku Photo Industry Co Ltd. (1983); *Chem. Abstr.* **1984**, *100*, 112174.
(20) Smith, S.A.; Markwell, R.E. European Patent 178413, Beecham Group PLC (1985); *Chem. Abstr.* **1986**, *105*, 42814.
(21) Cole, E.R.; Crank, G.; Sheikh, A.-S. *Tetrahedron Lett.* **1974**, 2925.
(22) Chapelle, F.; Steinman, R.; Seigle-Murandi, F.; Cuong, L.D. *Appl. Microbiol. Biotechnol.* **1986**, *23*, 430.
(23) Hoover, J.R.E.; Day, A.R. *J. Am. Chem. Soc.* **1955**, *77*, 4324.
(24) Grivas, S.; Tian, W.; Ronne, E.; Lindström, S.; Olsson, K., *Acta Chem. Scand.*, in press.
(25) Tian, W.; Grivas, S.; Olsson, K. *J. Chem. Soc., Perkin Trans 1*, in press.
(26) Elvidge, J.A.; Newbold, G.T.; Percival, A.; Senciall, I.R. *J. Chem. Soc.* **1965**, 5119.
(27) Pesin, V.G.; Muravnik, R.S. *Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser.* **1964**, 725; *Chem. Abstr.* **1965**, *63*, 4279.
(28) Bird, C.W.; Cheeseman, G.W.A.; Sarsfield, A.A. *J. Chem. Soc.* **1963**, 4767.
(29) Pesin, V.G.; D'yachenko, S.A.; Khaletskii, A.M. *J. Gen. Chem. USSR (Engl. Transl.)* **1964**, *34*, 3807.
(30) Grivas, S.; Tian, W. *Acta Chem. Scand.*, in press.
(31) Grivas, S. *Acta Chem. Scand.* **1986**, *B40*, 404; this communication was printed again and included in the November issue of volume *B40*.
(32) Maron, D.; Salzberg, D. *Ber. Dtsch. Chem. Ges.* **1912**, *44*, 2999.
(33) Piotrovskii, L.B. *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 1458.
(34) Rabinowitz, J.L.; Wagner, E.C. *J. Am. Chem. Soc.* **1951**, *73*, 3030.
(35) Ishiwata, S.; Shiokawa, Y. *Chem. Pharm. Bull.* **1969**, *17*, 1153.
(36) Bashir, M.; Kingston, D.G.I.; Carman, R.J.; Van Tassell, R.L.; Wilkins, T.D. *Heterocycles* **1990**, *31*, 1333.
(37) Ficken, G.E.; Fry, D.J. *J. Chem. Soc.* **1963**, 736.
(38) Green, H.; Day, A.R. *J. Am. Chem. Soc.* **1942**, *64*, 1167.
(39) Isikdag, I.; Ucucu, U.; Demirayak, S.; Cakir, B. *J. Fac. Pharm. Gazi* **1989**, *6*, 31; *Chem. Abstr.* **1989**, *112*, 4345.
(40) Itaya, M. *Yakugaku Zasshi* **1962**, *82*, 1; *Chem. Abstr.* **1962**, *57*, 9840.