Synthetically Attractive Indolization Processes and Newer Methods for the Preparation of Selectively Substituted Indoles

Ulf Pindur* and Reinhard Adam

Department of Pharmacy, University of Mainz, Saarstrasse 21,
D-6500 Mainz, Federal Republic of Germany

Received April 2, 1987

The synthetically interesting processes available for indolization reactions are discussed and illustrated in tabular form and particular emphasis is placed on the more recent methods.

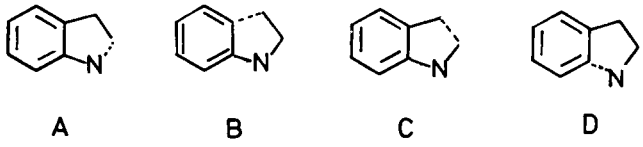
J. Heterocyclic Chem., **25**, 1 (1988).

Introduction.

The indole skeleton, when selectively functionalized, is a building block for the preparation of numberous alkaloids and substances with pronounced biological activities [1]. The search for efficient syntheses of indoles has been both a target and a problem in organic synthesis for nearly a century. Beginning with the classical Fischer and Reissert method, there is, thus, still a major need for versatile and, especially, regiospecific methods for the preparation of indole derivatives. In the present review, recent variants of indolization reactions for the preparation of synthetically attractive indoles are summarized. In general, work published in the period 1981 to 1986 has been surveyed. Reference has also been made to individual, trend-setting synthetic reports from the older literature. For a review on the older methods, see Ref. [2] and on some selected, more recent methods, see Refs. [3,4]. A review on the oldest indolization reaction, the Fischer indole synthesis, has been published recently [5].

The majority of indolization reactions start from selectively functionalized arenes. The arrangement of this article is based on the processes **A**, **B**, **C**, and **D**. In this roughly mechanistic classification of the processes, the respective key step in the indolization is indicated by a dashed bond (- - -) in the formulae **A** - **D** (Tables 1-4).

Table 5 lists new syntheses of indoles which cannot be directly classified as types **A** - **D**, either because the mechanisms have not yet been clarified or because they are based on completely different strategies such as, for example, benzoanellation.



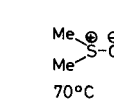
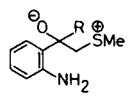
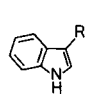
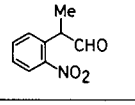
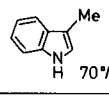
A B C D

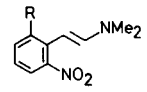
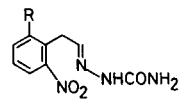
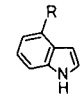
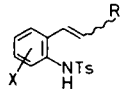
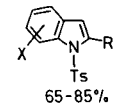
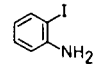
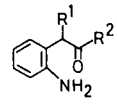
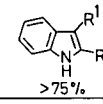
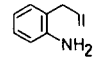
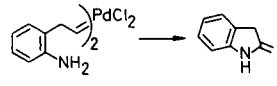
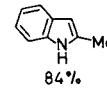
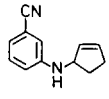
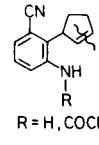
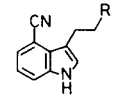
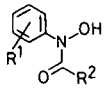
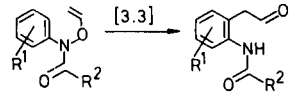
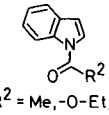
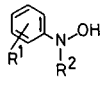
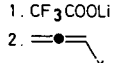
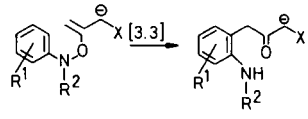
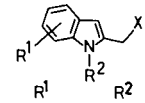
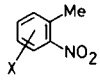
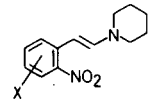
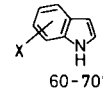
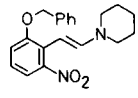
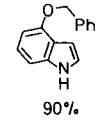
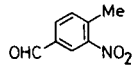
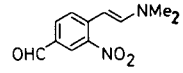
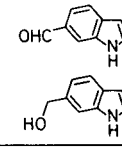
Indolization Processes.

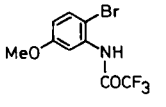
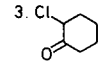
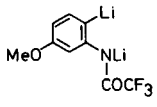
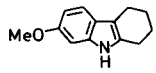
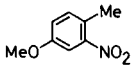
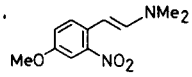
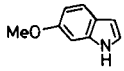
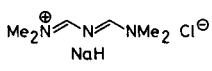
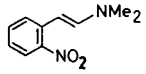
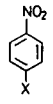
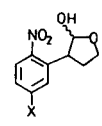
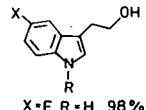
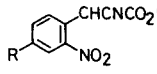
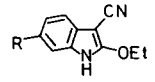
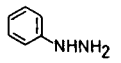
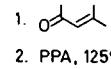
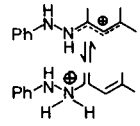
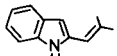
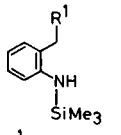
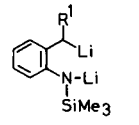
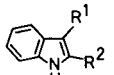
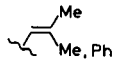
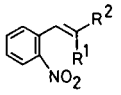
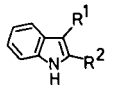
Type **A** (Table 1), the most highly developed indolization process, exhibits a broad synthetic flexibility, especially for the construction of indole derivatives substituted at position 2 and on the benzene ring. Both donor- and acceptor-substituted derivatives are easily accessible in this way. The palladium-catalyzed indolization of *o*-alkenyltosylanilines (Entry 4) and the heteroCope variants (Entries 8,9) have particularly wide scopes of application. Modified Leimgruber-Batcho processes represent very elegant methods for the synthesis of 4-substituted indoles (Entries 3,10). A convenient, one-pot preparation of 6-indolecarbaldehyde and 6-indolemethanol proceeds through an analogous reaction (Entry 11). Carbocyclic [*b*]anellated indole derivatives can be obtained through organometallic routes from the reactions of *N*-trifluoroacetyl-*o*-bromoanilines with 2-chlorocyclohexanone (or 2-chlorocyclopentanone) (Entry 12). Substituted tryptophol derivates are elegantly accessible from silyl enol ethers and nitroarenes (Entry 15). The synthetically attractive 2-vinylindoles can be obtained by a modified Fischer method (Entry 17) or by the preparatively more flexible heteroCope methodology (Entry 20).

Table 1

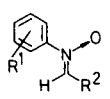
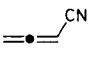
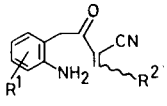
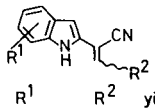
Type A

Entry	Starting material	Reagent, Conditions	Intermediate Mechanism	Product	Lit.
1				 R: Me 80%; Ph 69%; CO_2H 48%	6
2		CO/H_2, 160°C/160 atm, Rh-C		 70%	7

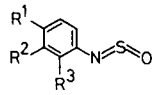
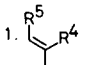
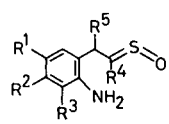
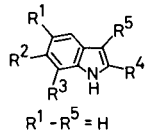
3		1. $H_2NNHCONH_2$ 2. H_2/Pd-C		 R / yield [%] Me 81 MeO 82 CO_2Me 82	8
4		Li_2PdCl_4, EtOH, 36 hours, reflux		 65-85% R = X = H R = $-C_4H_9$, X = H R = Ph, X = H R = Ph, X = 5-Me R = C_4H_9, X = 5-NO_2	9
5		 liq. NH_3, t-BuOK, hv, -33° C		 >75% R^1 = H, R^2 = H, Me, Pr^i; R^1, R^2 = $-(CH_2)_4-$	10
6		1. $PdCl_2(MeCN)_2$ THF 2. Et_3N -HCl, -PdH		 84%	11
7		1. TFA, $PhCH_3$, 85°C 2. O_3, CH_2Cl_2, -78°C 3. MeSMe, rt, 12 hours 4. Ag_2O, EtOH -CHO → -COOEt	 R = H, $COCF_3$	 R = CHO 66% COOEt 36%	12
8		 Li_2PdCl_4 0° → 70°C		 R^2 = Me, -O-Et, -Ph, $-CH=CH_2$, $-CH_2-CH_2Cl$; R^1 = H 51-95% R^1 = H; R^2 = CH_2Cl 52% R^1, R^2 = H 12%	13
9		1. CF_3COOLi 2.  HCOOH		 R^1 / R^2 / X / yield [%] 5-Me / COMe / CN / 70 5-Me / COMe / $PO(OEt)_2$ / 95 H / CO_2CH_2Ph / SOMe / 85 5-CO_2Me / COMe / SOPh / 85	14
10		1. TPM 2. $TiCl_3$		 60-70% X = 4-OAlk, 5-OAlk 4-CH_2Ph, 5-CH_2Ph, 4-Cl, 4-CN	15
		Ni_2B, EtOH $N_2H_4 \cdot H_2O$, Δ		 90%	16 17
11		1. DMFDMA, THF · Py 2. $TiCl_3$		 22% 20%	18

12		1. MeLi 2. t-BuLi 3. 		 69%	19
13		1. $(MeO)_2CHNMe_2$,  DMF, 105°C 2. H_2/Pd-C/$MeCO_2Et$		 76%	20
14		 NaH			21
15		 1. , TASF 2. DDQ 3. DIBAL 4. Pd/C/H_2		 X=F, R=H 98% X= Cl, R=OH 48%	22
16		Zn, MeOH H_2SO_4 rt	R = CF_3CO	 77-79%	23
17		1.  , HAc, Δ 2. PPA, 125°C, 20minutes		 26%	24
18	 R^1=H, Me	1. n-BuLi n-Hexane, Δ, 6hours 2. R^2COOEt, THF, -78°C		 32-65% R^2=Me, i-Pr, C_5H_{11}  Me, Ph	25
19		CO, 220°C 80 atm PhMe $Fe(CO)_5$ $Ru_3(CO)_{12}$, Toluene		 18.1 - 74.9%	26

R^1	R^2	R^1	R^2
H	H	H	2-Pyr
H	Me	Me	Me
H	COOMe	Ph	Me
H	Ph		

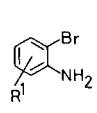
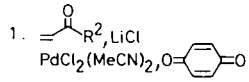
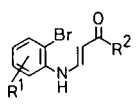
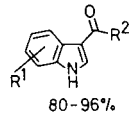
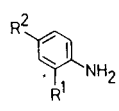
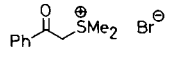
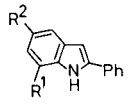
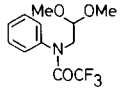
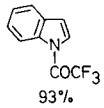
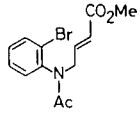
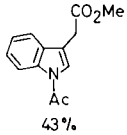
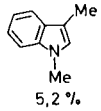
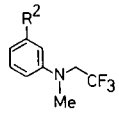
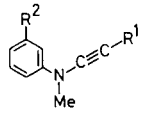
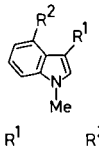
20		 0°C, 48h			27

R^1	R^2	yield [%]
5-Me	Ph	65
7-Me	Ph	65
5-Me	Py-2	75
5-OMe	Ph	55

21		1.  2. H_2O, $KHSO_4$ 3. 110°C		 R^1-R^5 = H 75% R^1 = MeO, R^2-R^5=H 52% R^1 = Br, R^2-R^5=H 49% R^1 = H, R^2=OMe, R^3-R^5=H 25%	28

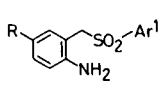
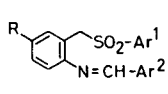
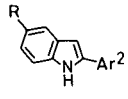
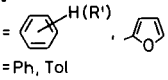
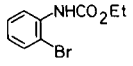
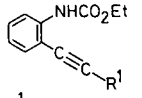
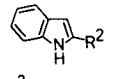
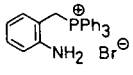
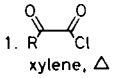
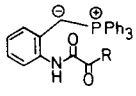
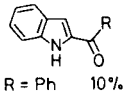
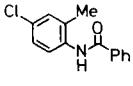
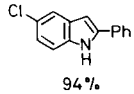
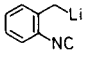
Type **B** (Table 2) represents an indolization process proceeding through formation of the indole 3/3a bond. Some of these processes exhibit a wide synthetic flexibility (Entries 1,2,7). Whereas the method illustrated in Entry 1 makes an elegant access to 3-acetyl- and 3-ethoxycarbonyl-substituted indoles possible, the method of Entry 2 offers a new route to 2-phenylindoles. The reaction exemplified by Entry 7 involves a new intramolecular, carbanionic addition to acetylenes. The 2-lithioindole formed as an intermediate in this process can be further functionalized by reaction with electrophiles.

Table 2 Type B

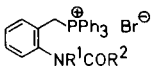
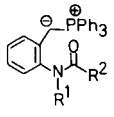
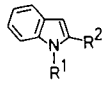
Entry	Starting material	Reagent, Conditions	Intermediate, Mechanism	Product	Lit.
1		1.  2. $Pd(OAc)_2$, Tol_3P, Et_3N, MeCN 100°C, sealed tube	 68-85%	 80-96% R^1 = H, 3-, 4-, 5- COOMe, 5-OMe R^2 = Me, OEt	29
2		 $PhNEt_2$. △, 3hours		 R^1, R^2 = H 60 % R^1=Me, R^2=H 72 % R^1=Me, R^2=Me 75 %	30
3		$(CF_3CO)_2O$ CF_3CO_2H, 56°C		 93%	31
4		Pd° 125°C		 43%	32
5		Cyclodehydrogenation porous catalyst (silica, alumina) 710-750°C		 50 %	33
6		1. $Ni(PPh_3)_4$ 2. O_2		 5,2 %	34
7		1. R^1Li 2. $H^\oplus$		 R^1 / R^2 / yield [%]: n-Bu / OMe / 60; sec-Bu / OMe / 50	35

Indolizations of Type **C** (Table 3) are used principally for the specific preparation of differing 2-substituted indoles. From the point of view of the mechanism, the reactions are mostly modified Madelung variants (Entries 1,3,4,5,6). Of these cyclization processes which are all regio-controlled, the "Le Corre" method is especially worthy of mention (Entry 6). This procedure offers a very elegant access to a series of 2-substituted indole derivatives and has also been used successfully by us for the preparation of a series of 2-vinylindoles.

Table 3 Type C

Entry	Starting material	Reagent, Conditions	Intermediate, Mechanism	Product	Lit.
1		1. Ar^2-CHO p-TSA, C_6H_6 30 minutes, △ 2. NaOH, DMSO		 74-92% R=H, Ar^2=  R=Cl, Ar^1=Ph, Tol R=Ph	36
2		1. R^1-C≡CH, Et_3N, $Pd(PPh_3)_2Cl_2$ 100°C, 3 hours, 2. NaOEt, EtOH	 R^1=$SiMe_3$, n-Bu, Ph	 R^2 = H 93% R^2 = n-Bu 74% R^2 = Ph 82%	37
3		 1. xylene, △ 2. t-BuOK, toluene, △		 R = Ph 10% R = Me 5%	38
4		$NaNH_2$, 200-400°C or n-BuLi(LDA), THF, 20°C		 94%	39
5		1. RX, diglyme, -78°C 2. LTMP(LDA), -78°C 3. -78°C ⟶ RT 4. H_2O			40

R	yield [%]
H	100
Me	95
i-C_4H_9	78

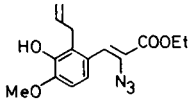
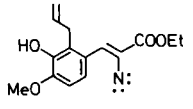
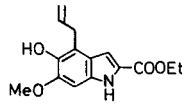
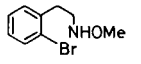
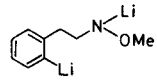
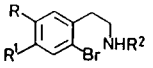
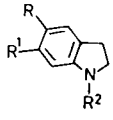
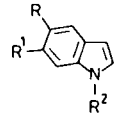
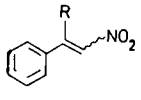
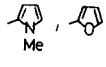
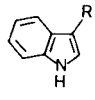
Entry	Starting material	Reagent, Conditions	Intermediate, Mechanism	Product	Lit.
6		MeONa or t-BuOK, toluene, △			41

R^1	R^2	yield [%]
H	Me	96
H		93
H	Ph	97

In indolization processes of Type **D** (Table 4), the N/7a bond is formed for construction of the indole system. This strategy is particularly attractive in the cases of the thermolysis of azidocinnamates and the sodium hydride/copper(I) halide-catalyzed cyclization of 2-(2-bromophenyl)-ethylacetamides since wide ranges of the required starting materials are available (Entries 1,3).

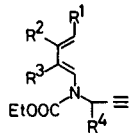
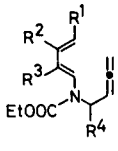
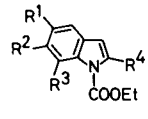
Table 4

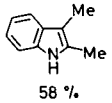
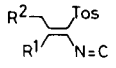
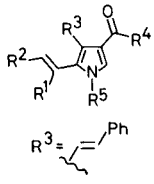
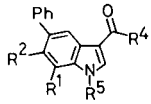
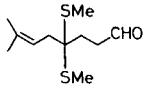
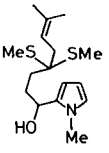
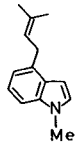
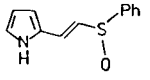
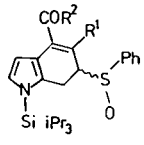
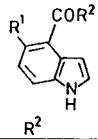
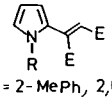
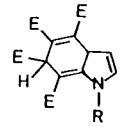
Type D

Entry	Starting material	Reagent, Conditions	Intermediate, Mechanism	Product	Lit.
1		thermolysis; decalin 190°C, 0.1 hours		 28%	42
2		1. MeLi 2. n-BuLi, hexane 3. 15°C/ 2-3 hours 4. H_2O 5. Ac-Cl, Py, Et_2O		 78 %	43
3	 R = R^1 = MeO, R^2 = Ac R = MeO, R^1 = H, R^2 = Ac R = R^1 = MeOH, R^2 = CO_2Me	1. 50% NaH/DMF 2. Cu Hal 3. Mg^0 or MgO_2, CH_2Cl_2		 65 - 88 %	44
4	 R = 	$PO(OEt)_3$ 160 °C	 30, 40%		45

The methods listed in Table 5 have to be classified as special cases with regard to the mechanisms. The methods illustrated in Entries 1, 3, 4, 5, and 6 involve pericyclic processes centered upon the construction of the benzene ring of the indole system. The Diels-Alder process (Entry 1) as well as the reactions of 1-tosylalkenyl isocyanides with Michael acceptors (Entry 3) are characterized by particularly wide synthetic scopes. Entry 6 represents a special case for the simple preparation of a 3a,6-dihydroindole.

Table 5

Entry	Starting material	Reagent, Conditions	Intermediate Mechanism	Product	Lit.
1	 R^1, R^2, R^3 = H, Me, Et R^1 - R^2 = -$(CH_2)_4$- R^4 = H, CH_2Ph	1. CH_2O, i-Pr_2NH, CuBr 2. 160°, 6-12 hours 3. DDQ (MnO_2) 20°C		 36-80%	46

2	PhNHR	HO(CH2)2OH, $RuCl_2(PPh_3)_3$	 R = Me, Et 34-51%		47
	$PhNH_2$	HO(CHMe)2OH, $RuCl_2(PPh_3)_3$	 58 %		
3		1.  t-BuOK, THF 2. MeI 3. DDQ, triglyme or benzene, 1 hour, 80° C			48
				R^1 R^2 R^4 R^5 yield[%] $-(CH_2)_3-$ Ph Me 83 $-(CH_2)_4-$ Ph Me 95 $-(CH_2)_5-$ Ph Me 92	
4		1. p-TSA, MeCN, rt  2. p-TSA, MeCN, 50°C		 61%	49
5		1. iPr_3SiOTf, NaH, DMF 2. $R^1-\equiv-COR^2$ xylene/Δ 3. $n-Bu_4NF$, THF, 20 °C			50
				R^1 R^2 yield[%] H OEt 88 Ph OEt 74 H H 84	
6	 R = 2-MePh, 2,6-$(Me)_2$Ph E = COOMe	E−≡−E AcOH, Et_2O Δ, 24 hours		 8, 47 %	51

Conclusions.

This review presents an up-to-date summary of the newer methods for the preparation of indole derivatives. Emphasis has been placed on procedures with pronounced synthetic flexibilities and also the limitations of the reaction principles have been delineated. As a result of the intensive synthetic developments of the last 20 years and, in particular, the discovery of new and selective reagents, especially of the organometallic type, indole derivatives are now accessible that could not be obtained by the classical procedures.

REFERENCES AND NOTES

[1] U. Pindur and E. Akgün, *Chem. Z.*, **108**, 371 (1984); J. E. Saxton, "Indoles", Part Four, Wiley-Interscience, New York, Chichester, 1983; M. Suffness and G. A. Cordell, "The Alkaloids", A. Brossi, ed, Academic Press, New York, London, 1985; U. Pindur, L. Pfeuffer and C. Flo, *Chem. Z.*, **110**, 307 (1986).

[2] W. A. Remers, "Indoles", Part One, W. J. Houlihan, ed, Wiley-Interscience, New York, 1972.

[3] A. R. Katritzky, "Handbook of Heterocyclic Chemistry", Pergamon Press, Oxford, 1986.

[4] R. Livingstone, "Rodd's Chemistry of Carbon Compounds", Vol **IV**, Supplement A, M. F. Ansell, ed, Elsevier, Amsterdam, Oxford, New York, Tokyo, 1984.

[5] B. Robinson, "The Fischer Indole Synthesis", John Wiley & Sons, Chichester, New York, 1982.

[6] P. Bravo, G. Gaudiano and A. Umani-Ronchi, *Gazz. Chim. Ital.*, **100**, 652 (1970).

[7] E. Ucciani and A. Bonfand, *J. Chem. Soc., Chem. Commun.*, 82 (1981).

[8] L. I. Kruse, *Heterocycles*, **19**, 1119 (1981).

[9] A. Kasahara, T. Izumi and S. Murakami, *Bull. Yamagata Univ.*,

19, 39 (1986).

[10] R. Beugelsmans and G. Roussi, *J. Chem. Soc., Chem. Commun.*, 950 (1979).

[11] L. S. Hegedus, G. F. Allen and E. L. Waterman, *J. Am. Chem. Soc.*, **98**, 2674 (1976).

[12] S. J. Danishefsky and G. B. Phillips, *Tetrahedron Letters*, **25**, 3159 (1984).

[13] P. Martin, *Helv. Chim. Acta*, **67**, 1647 (1984); *Tetrahedron Letters*, **28**, 1645 (1987).

[14] S. Blechert, *Tetrahedron Letters*, **25**, 1547 (1984); *Helv. Chim. Acta*, **68**, 1835 (1985). New Variation: J. Wilkens, A. Kühling and S. Blechert, *Tetrahedron*, **43**, 3237 (1987).

[15] D. H. Lloyd and D. E. Nichols, *Tetrahedron Letters*, **24**, 4561 (1983).

[16] D. H. Lloyd and D. E. Nichols, *J. Org. Chem.*, **51**, 4294 (1986).

[17] Reaction with Raney nickel and hydrazine hydrate: W. Leimgruber and A. Batcho, *Org. Synth.*, **63**, 214 (1984).

[18] M. Somei, *Chem. Pharm. Bull.*, **34**, 4109 (1986).

[19] P. A. Wender and A. W. White, *Tetrahedron*, **39**, 3767 (1983).

[20] P. L. Feldman and H. Rapoport, *Synthesis*, 735 (1986).

[21] A. P. Kozikowski, H. Ishida and Y.-Y. Chen, *J. Org. Chem.*, **45**, 3350 (1980); J. T. Gupton, *Aldrichim. Acta*, **19**, 43 (1986).

[22] T. V. RajanBabu, B. L. Chenard and M. A. Petti, *J. Org. Chem.*, **51**, 1704 (1986).

[23] K. Konishi, I. Nishiguchi and T. Hirashima, *Chem. Express*, **1**, 287 (1986).

[24] J. Bergman and B. Pelcman, *Tetrahedron Letters*, **26**, 6389 (1985).

[25] A. B. Smith, III and M. Visnick, *Tetrahedron Letters*, **26**, 3757 (1985).

[26] C. Crotti, S. Cenini, B. Rindone, S. Tollari and F. Demartin, *J. Chem. Soc., Chem. Commun.*, 784 (1986).

[27] S. Blechert, *Ann. Chem.*, 673 (1985).

[28] J.-B. Baudin and S. A. Julia, *Tetrahedron Letters*, **27**, 837 (1986).

[29] A. Kasahara, T. Izumi, S. Murakami, H. Yanai and M. Takatori, *Bull. Chem. Soc. Japan*, **59**, 927 (1986).

[30] H. Junjappa, *Synthesis*, 798 (1975); mechanism and further synthetic applications: K. C. Gupta, B. K. Saxena and P. Manglum, *Synthesis*, submitted.

[31] J. E. Nordlander, D. B. Catalane, K. D. Kotian, R. M. Stevens and J. E. Haky, *J. Org. Chem.*, **46**, 778 (1981).

[32] M. Mori, K. Chiba and Y. Ban, *Tetrahedron Letters*, 1037 (1977); L. S. Hegedus, P. R. Weider, T. A. Mulhern, H. Asaka and S. D. Andrea, *Gazz. Chim. Ital.*, **116**, 213 (1986).

[33] A. Gerecs, A. Mathe, T. Toth and M. Barta-Bukovecz, Hungarian Patent 16,696, 1979; *Chem. Abstr.*, **92**, P41760r (1980).

[34] M. Mori and Y. Ban, *Tetrahedron Letters*, 1803 (1976).

[35] F. Johnson and R. Subramanian, *J. Org. Chem.*, **51**, 5040 (1986).

[36] K. Wojciechowski and M. Makosa, *Bull. Soc. Chim. Belg.*, **95**, 671 (1986). A new Madelung variation to 3-substituted Indoles see: E. O. M. Orlemans, A. H. Schreuder, P. G. M. Conti, W. Verboom and D. N. Reinhoudt, *Tetrahedron*, **43**, 3817 (1987).

[37] T. Sakamoto, Y. Kondo and H. Yamanaka, *Heterocycles*, **24**, 31 (1986).

[38] L. Capuano, A. Ahlhelm and H. Hartmann, *Chem. Ber.*, **119**, 2069 (1986).

[39] W. J. Houlihan, V. A. Parrino and. Y. Uike, *J. Org. Chem.*, **46**, 4511 (1981).

[40] Y. Ito, K. Kobayashi and T. Saegusa, *J. Am. Chem. Soc.*, **99**, 3532 (1977).

[41] M. Le Corre, A. Hercouet and H. Le Baron, *J. Chem. Soc., Chem. Commun.*, 14 (1981); M. Le Corre, A. Hercouet, Y. Le Stanc and H. Le Baron, *Tetrahedron*, **41**, 5313 (1985).

[42] L. Henn, D. M. B. Hickey, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 2189 (1984); D. M. B. Hickey, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1113 (1986); a further variation for the synthesis of the left-hand unit for the anti-tumor agent CC-1065: C. J. Moody, M. Pass, C. W. Rees and G. Tojo, *J. Chem. Soc., Chem. Commun.*, 1062 (1986); P. T. Kim, R. Guilard, S. Samreth and R. Sornay, *J. Heterocyclic Chem.*, **18**, 1373 (1981); *J. Heterocyclic Chem.*, **18**, 1365 (1981).

[43] P. Beak, A. Basha, B. Kokko and D. Loo, *J. Am. Chem. Soc.*, **108**, 6016 (1986).

[44] T. Kametani, T. Ohsawa and M. Ihara, *J. Chem. Soc., Perkin Trans. 1*, 290 (1981).

[45] M. M. Campbell, N. Cosford, L. Zongli and M. Sainsbury, *Heterocycles*, **43**, 1117 (1987).

[46] K. Hayakawa, T. Yasukouchi and K. Kanematsu, *Tetrahedron Letters*, **27**, 1837 (1986).

[47] Y. Tsuji, K.-T. Huh and Y. Watanabe, *Tetrahedron Letters*, **27**, 377 (1986).

[48] J. Moskal and A. M. van Leusen, *J. Org. Chem.*, **51**, 4131 (1986); J. Moskal, R. van Stralen, D. Postma and A. M. van Leusen, *Tetrahedron Letters*, **27**, 2173 (1986).

[49] B. M. Trost, M. Reiffen and M. Crimmin, *J. Am. Chem. Soc.*, **101**, 257 (1979).

[50] J. M. Muchowski and M. E. Scheller, *Tetrahedron Letters*, **28**, 3453 (1987).

[51] W. E. Noland and K. J. Kim, *J. Org. Chem.*, **45**, 4582 (1980).