Radical Cation Initiated Cycloaddition Reactions Between 2-Vinylindoles and β-Substituted Enaminonitriles

Christoph F. Gürtler, Siegfried Blechert* and Eberhard Steckhan

Abstract: Electron transfer initiated cycloaddition reactions between 2-vinylindoles, acting as heterodienes, and β-substituted enaminonitriles lead to different cycloaddition products depending on the substituents. Initiated by potentiostatically controlled electrolysis, an anellation of a cyclopropanated five-membered ring system to the diene yielding cyclopropapyrrolo[1,2-*a*]indoles can be achieved in just one reaction step. Interestingly, the formation of a cyclopropane ring system takes place in reaction mechanisms which involve radicals and radical cations. In addition to these products, [4+2]-cycloaddition products with subsequent [1,4] dialkylamino shifts can also be formed. The formation of both products can be attributed to new reaction pathways via radical cation intermediates.

Keywords
cycloadditions · domino reactions · electrochemistry · electron transfer · radical ions

Introduction

Numerous organic reactions can be attributed to electron transfer (ET) processes, which are amongst the most important elementary reactions in chemistry.[1] In addition to intensified mechanistic/theoretical investigations[2] of ET reactions in all areas of chemistry, there is an increasing interest in the preparative potential of these reactions.[3, 4]

Recently we reported hetero [4+2]-cycloaddition reactions with dienes and dienophiles of electronically similar structure, which were performed by electron transfer catalysis with transformation of the diene to a radical cation. Initiation of the reaction by potentiostatically controlled electrolysis proved to be a very useful and mild method of forming the radical cation from the diene. The electron-deficient radical cation and an electron-rich component react to form a radical cation as a cycloadduct, which, in the catalytic case, can undergo back electron transfer with the starting material. Compounds of higher oxidation level can be formed by a one-electron oxidation of the product radical cation, which normally takes place under conditions of anodic oxidation.

The versatility of 2-vinylindoles,[5] especially in the synthesis of heterocycles and natural compound synthesis, has been demonstrated in our recent work.[6] We have previously reported the reaction of the electron-rich (in terms of the Diels–Alder reaction) 2-vinylindoles with several cyclohexadienes and styrenes.[7] This provides an efficient route to highly substituted carbazole derivatives. Similar reactions with enaminoesters[8] led, by an elimination process, directly to carbazoles or heteroaromatic compounds such as pyrido[1,2-*a*]indoles. If α-acceptor-substituted enamines such as acceptor-substituted 1,4,5,6-tetrahydropyridines and β-aminomethacrylates or -nitriles are employed, then preparatively interesting tetracycles of the indolo[1,2-*a*]hexahydro[1,8]naphthyridine type containing the alkaloid pyrrocoline skeleton (e.g. goniomitine) are accessible (Scheme 1).[9] This type of reaction could also be extended to sterically more demanding dienophiles such as enaminolactones. Recently we were successful in introducing amide-substituted 2-vinylindoles into the hetero[4+2]-cycloaddition reaction; this opens a pathway to the skeleton of β-carboline alkaloids.[6]

Results and Discussion

Within the framework of previous investigations on electron transfer initiated cycloaddition reactions, we reported on electrochemically initiated [4+2]-cycloaddition reactions between 2-vinylindoles and α-alkyl substituted enamines as donor-acceptor substituted dienophiles.[10] We have already demonstrated that the proposed reaction pathways for the radical-cation cycloaddition reactions of these dienophiles with dienes of similar electronic structure are very sensitive to steric effects.[6] When we attempted to extend this new type of reaction to β-alkyl-substituted enamines we discovered new reaction pathways

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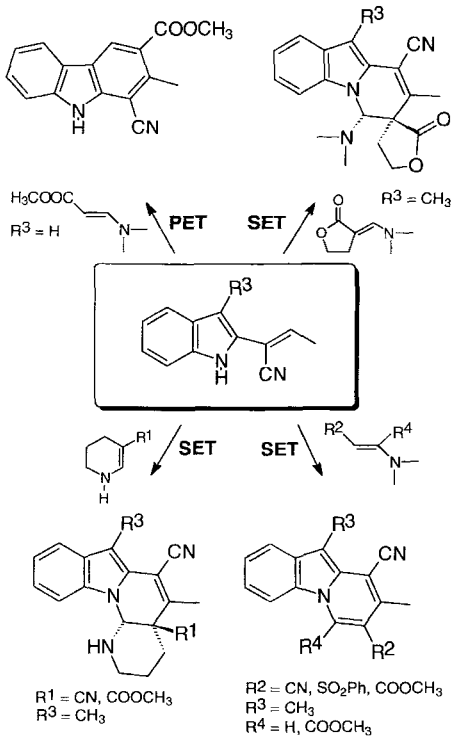
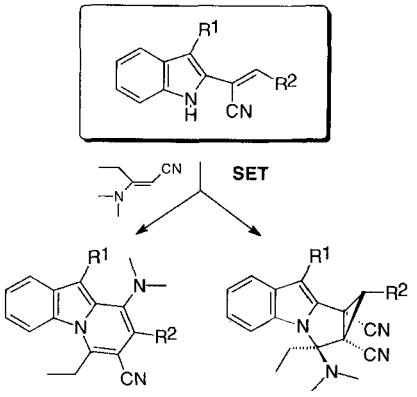


Scheme 1. Reactions of 2-vinylindoles as versatile dienes with various dienophiles.

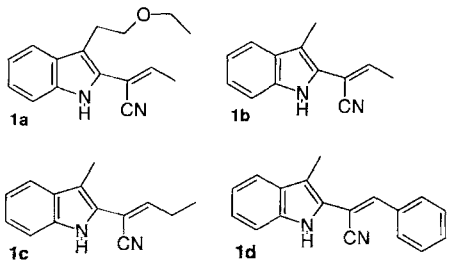
leading to unusual cyclopropapyrrole derivatives and products of a hetero [4 + 2]-cycloaddition reaction with a subsequent [1,4] dialkylamino shift (Scheme 2).



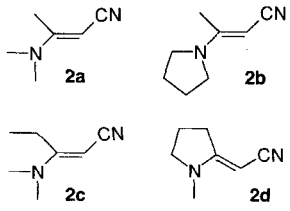
Scheme 2. Formation of cyclopropapyrrolo[1,2-*a*]indoles and pyrido[1,2-*a*]indoles starting from 2-vinylindoles and enaminonitriles.

The 2-vinylindoles employed as dienes are readily accessible[11] in great structural variety by a method of synthesis developed by our group.[5] This method permits a simple variation of the substituents of the side chain (aryl, alkyl) of the vinylic double bond and the alkyl chain attached at the 3-position of the indole nucleus. These vinyl acrylonitriles are rather electron-rich dienes; this was established from their oxidation potentials, which range from 690 to 750 mV (vs. $Ag/AgNO_3$).

The cyano-substituted indolylacrylates **1a**, **1b** and **1c**, acting as the diene, were reacted with β-alkyl-substituted enamines



(**2a–c**) containing a 1,2-donor-acceptor substituted double bond. The dienophiles are easily obtainable in quantitative yield by a Michael addition of the donor (e.g. dimethylamine or pyrrolidine) to an allene (2,3-pentadienonitrile). The oxidation potentials of the dienophiles range from 820 to 850 mV (vs. $Ag/AgNO_3$).



By potentiostatically controlled electrochemical initiation[12] of the cycloaddition reaction, which selectively generates the radical cation of the diene, we obtained either highly substituted pyrido[1,2-*a*]indoles as the products of a [4 + 2]-cycloaddition reaction with subsequent [1,4] dialkylamino shift or cyclopropapyrrolo[1,2-*a*]indoles (Scheme 3). In one case, both types of products were formed.

From studies of dienophiles with different steric demands, we observed that the formation of cyclopropapyrrole derivatives and the products of a [4 + 2]-cycloaddition with subsequent [1,4] dialkylamino shift depended on steric influences. In addition, variation of the diene and the dienophile afforded the cyclopropapyrrole derivative **9** as the only reaction product in 41% yield. Compound **8** was obtained as a mixture of *cis*/*trans*-diastereomers (with respect to the arrangement of the dimethylamino moiety and the cyclopropane ring) in a ratio of 4:1. The cyclopropapyrrole derivative **7** was formed along with **6** by the [4 + 2]-cycloaddition reaction with subsequent [1,4] dialkylamino shift. In the case of compound **6** we observed that a higher dilution of the diene permitted the formation of the rearranged product, which, under the conditions of higher concentration, formed only in trace amounts relative to the cyclopropapyrrole derivative **7**. When **2a** was used as a dienophile containing a methyl side chain, a cycloaddition product with subsequent rearrangement (compound **3**) could be obtained selectively in 37% yield.

The cyclopropapyrrole derivatives **7**, **8a,b** and **9** were formed exclusively if the dienophile contained an ethyl sidechain, whereas the formation of [4 + 2]-cycloaddition products with subsequent rearrangement (compounds **3**, **4** and **5**) took place if the dienophile contained a methyl group (with **6** being the only exception).

The cyclopropapyrrole derivatives may be formed by a [4 + 2]-cycloaddition reaction with ring contraction. We attribute the formation of the cyclopropane ring system to a new domino process involving radical cation/radical intermediates. We propose that there are two reaction pathways starting from the key intermediate **a** (Scheme 4). Intermediate **a** may be formed by a radical attack of the vinylic terminus of the 2-

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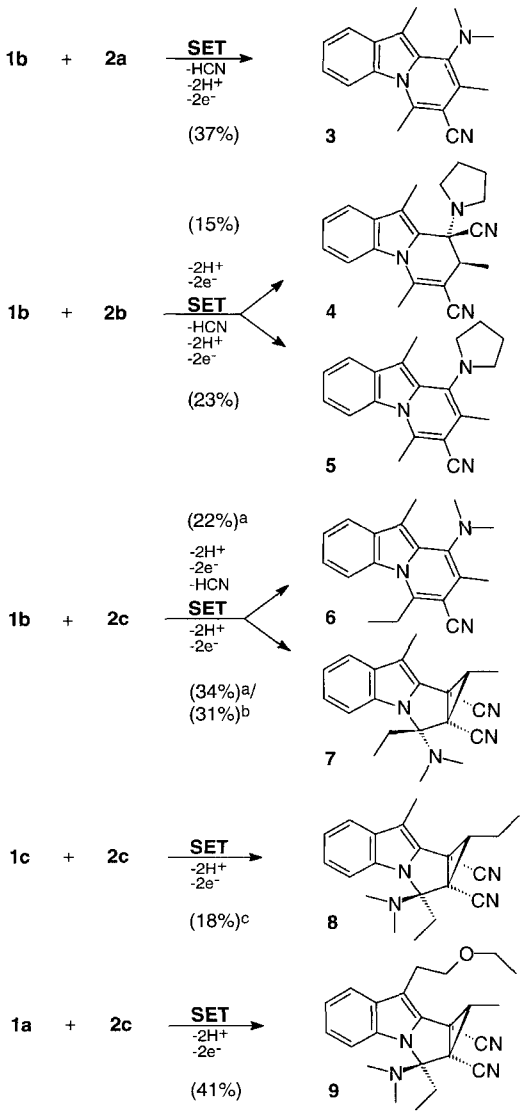
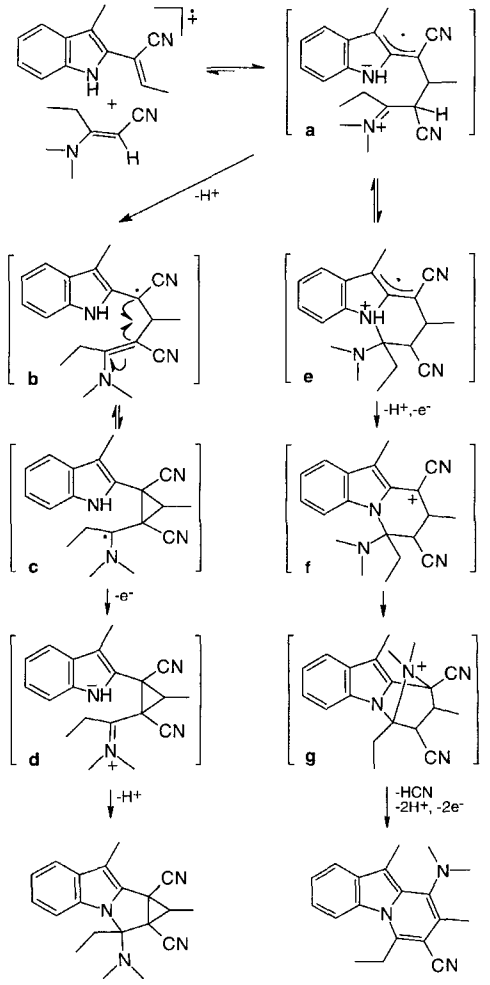


Scheme 3. Products of the electron transfer initiated cycloaddition reaction of 2-vinylindoles with several enaminonitriles. a) Rel. concentration of **1a** = 1: **4** (22%) + **7** (34%); b) rel. concentration of **1a** = 1.5: **7** (31%); c) **8a** (14%) + **8b** (4%).



Scheme 4. Proposed mechanisms for electron transfer initiated cycloaddition reactions between 2-vinylindoles and several enaminonitriles.

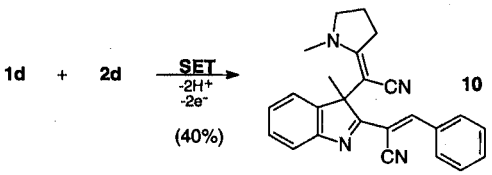
vinylindole radical cation on the β-alkyl-substituted enamine followed by an intramolecular electron transfer. Alternatively, a nucleophilic addition of the enamine to the vinylogous iminium radical cation of the 2-vinylindole may take place.

In the case of the hetero [4+2]-cycloaddition reaction with subsequent [1,4] dialkylamino shift, the expected ring closure starting from intermediate **a** takes place. The resulting cycloadduct radical is presumably oxidized to its cation[13] under the conditions of anodic oxidation. In contrast to the mechanism which we proposed previously for the formation of [4+2]-cycloaddition products with β-unsubstituted enamines, no formation of a vinylic double bond by loss of a proton in the cycloaddition product was observed. In this new reaction pathway, the cation **f** is proposed to be intramolecularly trapped by the dimethylamino moiety, leading to an intermediate bridged bicyclic five-membered ring system **g**, followed by aromatization. In the case of compound **4**, an intermediate was isolated that supports the proposed mechanism.

Starting from intermediate **a**, a different pathway is proposed for the formation of the cyclopropapyrrole cycloaddition products. We assume that formation of an intermediate tetrasubstituted double-bond system **b** results from the deprotonation of the highly acidic key intermediate **a**. For these cases, the deprotonation step is faster than the ring-closure step and therefore preferred. This is probably caused by the slightly greater steric demand of the ethyl substituent compared to the methyl group. The resulting double bond should be attacked by the indolyl radical to form a cyclopropane system and another α-amino radical **c**, which is instantaneously oxidized to its iminium ion **d**. Subsequent ring closure and deprotonation leads to a five-membered ring. Thus, the formation of the cyclopropapyrrole derivatives probably takes place by a radical cation/radical domino process[14] leading to an anellated cyclopropanated five-membered ring system to the diene. Remarkably, the formation of the cyclopropane ring occurs by a mechanism involving radicals.

In reactions with a 2-vinylindole bearing a phenyl group at the terminus of the vinylic double bond (**1d**), a change in the reactivity of the diene was expected to occur. Thus, the diene **1d** reacted with the dienophiles **2a–c** to give products with formation of a C–C bond via the radical cation of the diene. Unfortunately, the products were unstable and could not be isolated.

However, the cyclic dienophile **2d** reacted to give the stable addition product **10**. The result of this ET-initiated reaction can be explained by a radical attack by the 3-position of the indole nucleus on the dienophile to form an α-amino radical, which was instantaneously oxidized to the iminium ion under conditions of anodic oxidation. A double deprotonation led to the product containing an imine double bond in the indole nucleus and the regeneration of the double bond of the dienophile. This difference in reaction behaviour is attributed to a different electronic structure of the diene **1d** caused by the additional phenyl substituent (Scheme 5).



Scheme 5. Electron transfer initiated C–C bond formation.

Conclusion

Using β-substituted donor-acceptor-substituted dienophiles in reactions with indolylacrylonitriles we were able to open a pathway to cyclopropapyrrole derivatives and [4+2]-cycloaddition products with a subsequent [1,4] dialkylamino shift in just one reaction step. This is in contrast to the results obtained with α-alkyl-substituted dienophiles, such as acceptor-substituted 1,4,5,6-tetrahydropyridines. Remarkably, we observed the formation of a cyclopropane ring system by a radical mechanism. In reactions with β-substituted donor-acceptor-substituted dienophiles it was demonstrated that transformations of one component into its radical cation were very sensitive towards steric and electronic effects. By appropriate choice of the substitution pattern in the diene and dienophile component, a specific reaction pathway can be induced almost selectively. We have thus introduced new pathways in radical cation chemistry.

Experimental Section

Melting points: Leica Galan III. Melting points are uncorrected. MS spectra and high resolution mass spectra: Varian MAT711 and MAT955Q mass spectrometer (EI) with an ionization potential of 70 eV. Infrared spectra: Nicolet 750 FT infrared spectrometer. ^{1}H NMR spectra: Bruker AM400 and AC200; chemical shifts relative to $CDCl_3$. ^{13}C NMR spectra including DEPT: Bruker AM400 and AC200. Thin-layer chromatography was performed on Merck $^{60}F_{254}$ (0.2 mm) sheets which were visualized with ethanolic molybdophosphoric acid, UV light or a solution of *p*-methoxy benzaldehyde in ethanol/sulfuric acid. Preparative flash chromatography was performed on Merck (0.04–0.063 mm) silica gel using a positive air pressure. PE: light petroleum, b.p. 40–60 °C; MTBE: methyl *t*-butyl ether. Unless otherwise noted, all chemicals were of the highest purity commercially available and were used without further purification.

General Procedure: The reaction solution was potentiostatically electrolyzed at the potentials given below in an electrochemical cell (undivided) (max. volume 100 mL) under vigorous stirring. Anode: carbon (graphite), 20 cm^2; cathode: carbon (graphite), 20 cm^2; reference electrode: $Ag/AgNO_3$; separation of electrodes: 3 cm. Electrolysis started with a potential of 470 mV vs. $Ag/AgNO_3$. Prior to use, the electrodes were activated by ultrasonic treatment in acetonitrile. During electrolysis the current dropped from 20 mA to 2 mA. The current consumption is given with the individual compound. All reactions were monitored by TLC analysis. The reaction solutions darkened slightly. At the end of the reaction the electrodes were treated for 10 min with ultrasound in 60 mL of methanol, followed by acetonitrile. The combined solutions were evaporated under reduced pressure and then treated with brine. The aqueous layer was extracted five times with $CHCl_3$, dried over $MgSO_4$ and the solvent evaporated. Compounds were separated by chromatography on silica gel unless otherwise stated. With the exception of **8** yields are based on recovered material (min. 90% turnover).

The determination of configuration and regiochemistry was accomplished by NMR methods, especially 2D techniques (CH-COSY, COLOC-experiments), and NOE experiments.

7-Dimethylamino-9-cyano-6,8,10-trimethylpyrido[1,2-*a*]indole (3): 2-Vinylindole **1b** (71 mg, 0.36 mmol) and 3-(*N*,*N*-dimethylamino)-2-butenenitrile (1 mmol, 113 mg) in CH_3CN/CH_2Cl_2 (1:1) (+ 0.1 M $LiClO_4$, 100 mL) were electrolyzed for 90 min; the current decreased from 23 mA to 6 mA. Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:2) afforded 37 mg (37%) of **3** as a yellow solid. M.p. = 264 °C (cryst. from MTBE); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.12 (d, ^3J(H,H) = 8.0 Hz, 1H, H-4), 7.78 (d, ^3J(H,H) = 8.0 Hz, 1H, H-1), 7.44 (dd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 8.0 Hz, 1H, H-2), 7.28 (dd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 8.0 Hz, 1H, H-3), 3.18 (s, 3H, 6-CH_3), 2,88 (s, 6H, 9-$N(CH_3)_2$), 2.68 (s, 3H, 10-CH_3), 2.37 (s, 3H, 8-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 144.5 (s, C-6), 138.8 (s, C-9), 133.2 (s, C-9a), 132.4 (s, C-10), 131.3 (s, C-4a), 124.4 (s, C-8), 123.1 (d, C-2), 120.8 (d, C-3), 118.6 (d, C-1), 118.5 (s, 7-CN), 115.1 (d, C-4), 103.4 (s, C-10), 96.5 (s, C-7), 42.5 (q, 2C, 9-$N(CH_3)_2$), 21.3 (q, 6-CH_3), 15.9 (q, 8-CH_3), 9.1 (q, 10-CH_3); IR (CCl_4): $\tilde{\nu}$ = 926 (m), 2213 (s), 1479 (m), 1459 (s), 1417 (vs), 1127 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 360, 340, 320 (sh), 270, 240 (sh), 235 (sh), 205 nm; MS (70 eV, EI): *m/z* (%): 277 (100), [M^+] 262 (36), [$M^+ - CH_3$] 234 (38), 233 (60%), 57 (36%); HRMS calcd for $C_{18}H_{19}N_3$ 277.1579, found 277.1579.

9-(1-Pyrrolidino)-7,9-dicyano-6,8,10-trimethyl-8,9-dihydropyrido[1,2-*a*]indole (4) and **9-Pyrrolidino-7-cyano-6,8,10-trimethylpyrido[1,2-*a*]indole (5)**: 3-Methyl-2-[2-(3-methyl)-indolyl]acrylonitrile **1b** (20 mg, 0.1 mmol) and *N*-(1-cyano-1-propylene)pyrrolidine (33 mg, 0.24 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 50 mL) were electrolyzed for 240 min at 450 mV (current consumption = 84 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:8) afforded 5 mg of the dihydropyrido[1,2-*a*]indole **4** (15%) and 7 mg of the aromatized product **5** (23%) to give a total yield of 38%.

9-(1-Pyrrolidino)-7,9-dicyano-6,8,10-trimethyl-8,9-dihydropyrido[1,2-*a*]indole (4): White solid; m.p. = 201 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.68 (d, ^3J(H,H) = 7.5 Hz, 1H, H-1), 7.60 (d, ^3J(H,H) = 7.5 Hz, 1H, H-4), 7.34 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-3), 7.28 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-2), 3.02 (q, ^3J(H,H) = 7.0 Hz, 1H, H-8), 2.84 (s, 3H, 10-CH_3), 2.80 (m, 2H, H-11), 2.56 (s, 3H, 6-CH_3), 2.56 (m, 2H, H-11a), 1.78 (m, 4H, H-12/12a), 1.18 (d, ^3J(H,H) = 7.0 Hz, 3H, 8-CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 146.7 (s, C-6), 134.1 (s, C-10a), 130.3 (s, C-4a), 125.2 (d, C-2), 122.1 (d, C-3), 119.9 (d, C-1), 119.5 (s, C-9a), 117.7 (s, 7-CN), 116.0 (s, 9-CN), 112.9 (d, C-4), 107.8 (s, C-10), 92.1 (s, C-7), 63.4 (s, C-9), 48.8 (t, C-11/11a), 38.6 (d, C-8), 23.5 (t, C-12/12a), 20.2 (q, 6-CH_3), 16.0 (q, 8-CH_3), 9.0 (q, 10-CH_3); IR (ATR): $\tilde{\nu}$ = 2961 (m), 2241 (m), 1450 (vs), 1322 (s), 1286 (s), 742 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 210, 250, 340; MS (70 eV, EI): *m/z* (%): 330 (36) [M^+], 261 (100) [$M^+ - C_4H_7N$], 246 (72), 245 (76), 244 (80), 231 (18), 192 (10); HRMS calcd for $C_{21}H_{22}N_4$ 330.1844, found 330.1844.

9-(1-Pyrrolidino)-7-cyano-6,8,10-trimethylpyrido[1,2-*a*]indole (5): Yellow solid; m.p. = 192 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.14 (d, ^3J(H,H) = 7.5 Hz, 1H, H-4), 7.76 (d, ^3J(H,H) = 7.5 Hz, 1H, H-1), 7.43 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-2), 7.28 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-3), 3.26 (m, 4H, H-11/11a), 3.18 (s, 3H, 6-CH_3), 2.62 (s, 3H, 10-CH_3), 2.30 (s, 3H, 8-CH_3), 2.07 (m, 4H, H-12/12a); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 144.8 (s, C-6), 135.2 (s, C-9), 134.3 (s, C-9a), 132.4 (s, C-10a), 131.3 (s, C-4a), 125.9 (s, C-8), 123.2 (d, C-2), 120.7 (d, C-3), 118.6 (d, C-1), 118.5 (s, 7-CN), 115.2 (d, C-4), 103.2 (s, C-10), 96.5 (s, C-7), 51.4 (t, C-11/11a), 26.4 (t, C-12/12a), 21.4 (q, 6-CH_3), 15.5 (q, 8-CH_3), 8.9 (q, 10-CH_3); IR (CCl_4): $\tilde{\nu}$ = 2823 (w), 2214 (s) 1418 (vs), 1360

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(s), 1221 (vs), 1152 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 210, 230, 240, 270, 335 (sh), 340, 355; MS (70 eV, EI): *m/z* (%): 303 (100) [M^+], 275 (36), 260 (40), 234 (92), 233 (88), 219 (12), 130 (10), 57 (12); HRMS calcd for $C_{20}H_{21}N_3$ 303.1735, found 303.1735.

9-(Dimethylamino)-7-cyano-6-ethyl-8,10-dimethylpyrido[1,2-*a*]indole (6): 3-Ethyl-2-[2-(3-methyl)indolyl]acrylonitrile **1b** (9 mg, 0.046 mmol) and 3-dimethylamino-2-pentenenitrile (22 mg, 0.32 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 15 mL) were electrolyzed at 460 mV (current consumption = 10 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:1) afforded 3 mg of **6** (22%). Yellow solid; m.p. = 230 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.98 (d, ^3J(H,H) = 7.5 Hz, 1H, H-4), 7.80 (d, ^3J(H,H) = 7.5 Hz, 1H, H-1), 7.43 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-2), 7.30 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-3), 3.58 (q, ^3J(H,H) = 7.0 Hz, 2H, H-11), 2.86 (s, 6H, 9-N(CH_3)$_2$), 2.66 (s, 3H, 10-CH_3), 2.36 (s, 3H, 8-CH_3), 1.57 (t, ^3J(H,H) = 7.0 Hz, H-12); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 149.8 (s, C-6), 136.6 (s, C-9), 136.4 (s, C-9a), 132.5 (s, C-10a), 130.1 (s, C-4a), 124.8 (s, C-8), 123.2 (d, C-2), 121.2 (d, C-3), 118.8 (d, C-1), 118.5 (s, 7-CN), 115.0 (d, C-4), 103.6 (s, C-10), 96.5 (s, C-7), 42.4 (q, 2C, 9-N(CH_3)$_2$), 27.0 (t, C-11), 15.8 (q, 8-CH_3), 11.9 (q, C-12), 9.2 (q, 10-CH_3); IR (CCl_4): $\tilde{\nu}$ = 2960 (s), 2927 (vs), 2213 (s), 1596 (s), 1448 (vs), 1268 (s), 1132 (s), 1074 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 210, 230, 270, 330, (sh), 340, 360; MS (70 eV, EI): *m/z* (%): 292 (10) [M^+ + H], 291 (42) [M^+], 181 (30), 163 (80), 149 (100), 73 (52), 57 (74), 55 (68); HRMS calcd for $C_{19}H_{21}N_3$: 291.1735, found 291.1735.

3-(Dimethylamino)-1,2-dicyano-3-ethyl-1a,9-dimethyl-1,2-dihydro-3*H*-cyclopropapyrrolo[1,2-*a*]indole (7): 3-Ethyl-2-[2-(3-methyl)indolyl]acrylonitrile **1b** (9 mg, 0.046 mmol) and 3-dimethylamino-2-pentenenitrile (30 mg, 0.24 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 30 mL) were electrolyzed for 200 min at 460 mV (current consumption = 46 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:3) afforded 5 mg of **7** (34%). Pale yellow solid; m.p. = 211 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, ^3J(H,H) = 8.0 Hz, 1H, H-8), 7.36 (d, ^3J(H,H) = 8.0 Hz, 1H, H-5), 7.15 (dd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 8.0 Hz, 1H, H-6), 7.11 (dd, 1H, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 8.0 Hz, 1H, H-7), 2.99 (dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-10), 2.38 (s, 6H, 3-N(CH_3)$_2$), 2.36 (s, 3H, 9-CH_3), 1.82 (dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-10a), 1.79 (q, ^3J(H,H) = 6.5 Hz, 1H, H-1a), 1.68 (d, ^3J(H,H) = 6.5 Hz, 3H, 1a-CH_3), 1.35 (t, ^3J(H,H) = 7.5 Hz, 3H, H-11); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 133.4 (s, C-4a), 133.0 (s, C-8a), 132.5 (s, C-9a), 122.4 (d, C-7), 120.2 (d, C-6), 119.7 (d, C-8), 114.6 (s, 1-CN), 113.5 (s, 2-CN), 112.1 (d, C-5), 103.6 (s, C-9), 86.3 (s, C-3), 43.9 (s, C-2), 39.0 (q, 2C, 3-N(CH_3)$_2$), 34.7 (d, C-1a), 28.3 (s, C-1), 28.0 (t, C-10), 12.4 (q, 1a-CH_3), 9.2 (q, C-11), 7.9 (q, 9-CH_3); IR (KBr): $\tilde{\nu}$ = 2923 (m), 2244 (w, CN), 1450 (vs), 1323 (s), 1286 (s), 1247 (s), 1014 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 210, 225, 285; MS (70 eV, EI): *m/z* (%): 318 (95) [M^+], 303 (26) [$M^+ - CH_3$], 274 (100) [$M^+ - N(CH_3)_2$], 259 (50), 244 (24), 84 (30), 69 (38), 57 (64), 55 (63); HMRS calcd for $C_{20}H_{22}N_4$ 318.1844, found 318.1844.

3-(1-Pyrrolidino)-1,2-dicyano-1a,3,9-trimethyl-1,2-dihydro-3*H*-cyclopropapyrrolo[1,2-*a*]indole (8a/b): 3-Ethyl-2-[2-(3-methyl)indolyl]acrylonitrile **1c** (43 mg, 0.22 mmol) and 3-dimethylamino-2-pentenenitrile (52 mg, 0.42 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 50 mL) were electrolyzed for 135 min at 470 mV (current consumption = 118 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:8) afforded 10 mg of a less polar diastereomer **8a** (*cis* arrangement of the cyclopropane ring system and dimethylamino group) (14%) and 3 mg of a more polar diastereomer **8b** (*trans* arrangement) (4%) to give a total yield of 18%.

Diastereomer 8a: pale yellow solid; m.p. = 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.49 (d, ^3J(H,H) = 7.5 Hz, 1H, H-8), 7.44 (d, ^3J(H,H) = 7.5 Hz, 1H, H-5), 7.18 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-6), 7.14 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-7), 2.64 (dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-12), 2.61 (s, 6H, 3-N(CH_3)$_2$), 2.44 (dd, ^3J(H,H) = 6.5 Hz, ^3J(H,H) = 8.5 Hz, 1H, H-1a), 2.36 (s, 3H, 9-CH_3), 2.29 (dq, 1H, ^2J(H,H) = 15.0 Hz, 7.5 Hz, 1H, H-12a), 2.08 (qdd, ^3J(H,H) = 6.5 Hz, ^3J(H,H) = 7.0 Hz, ^2J(H,H) = 14.0 Hz, 1H, H-10), 1.90 (qdd, 1H, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 8.5 Hz, 1H, H-10a), 1.32 (dd, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 7.0 Hz, 3H, H-11), 0.42 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 3H, H-13); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 132.9 (s, C-9a), 132.8 (s, C-4a), 131.2 (s, C-8a), 122.7 (d, C-7), 120.5 (d, C-6), 119.4 (d, C-8), 114.7 (s, 1-CN), 113.2 (s, 2-CN), 111.5 (d, C-5), 104.5 (s, C-9), 85.3 (s, C-3), 39.9 (s, 2C, 3-N(CH_3)$_2$), 38.8 (d, C-1a), 35.4 (s, C-2), 31.7 (t, C-12), 26.3 (s, C-1), 21.5 (t, C-10), 12.3 (q, C-13), 7.7 (q, C-11), 7.6 (q, 9-CH_3); IR (CCl_4): $\tilde{\nu}$ = 2976 (m), 2242(w), 1452 (vs), 1338 (s), 1036 (m) cm^{-1}); UV/Vis (MeOH): λ_{max} = 220, 280, 335 (sh); MS (70 eV, EI): *m/z* (%): 332 (66) [M^+], 288 (80), 259 (100), 199 (66), 184 (64), 129 (68), 73 (70), 57 (58); HRMS calcd for $C_{21}H_{24}N_4$ 332.2001, found 332.2001.

Diastereomer 8b: pale yellow solid; m.p. = 170 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, ^3J(H,H) = 7.5 Hz, 1H, H-8), 7.38 (d, ^3J(H,H) = 7.5 Hz, 1H, H-5), 7.12 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-6), 7.08 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-7), 2.98 (dd, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 15.0 Hz, 1H, H-12a), 2.38 (s, 6H, 3-N(CH_3)$_2$), 2.36 (s, 3H, 9-CH_3), 2.08 (qdd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 14.0 Hz, 1H, H-10), 1.92 (qdd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 14.0 Hz, 1H, H-10a), 1.83 (dd, ^3J(H,H) = 8.0 Hz, ^2J(H,H) = 15.0 Hz, 1H, H-12), 1.67 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-1a), 1.36 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 8.0 Hz, 3H, H-13), 1.25 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 3H, H-11); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 135.2 (s, C-4a), 133.0 (s, C-8a), 132.6 (s, C-9a), 122.3 (d, C-7), 119.9 (d, C-6), 119.4 (d, C-8), 114.6 (s, 1 or 2-CN), 113.2 (s, 1 or 2-CN), 111.9 (d, C-5), 103.7 (s, C-9), 86.3 (s, C-3), 43.2 (s, C-1 or 2), 41.9 (d, C-1a), 39.4 (q, 2C, 3-N(CH_3)$_2$), 28.2 (t, C-12), 27.5 (s, C-1 or 2), 21.7 (t, C-10), 12.1 (q, C-11), 9.1 (q, C-13), 7.9 (q, 9-CH_3); IR (ATR): $\tilde{\nu}$ = 2967 (s), 2241 (s), 1450 (vs), 1323 (s), 1247 (s), 996 (s), 741 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 225, 280, 330 (sh); MS (70 eV, EI): *m/z* (%): 332 (90) [M^+], 288 (96), 259 (100), 224 (20), 209 (22), 193 (20), 84 (16), 70 (16); HRMS calcd for $C_{21}H_{24}N_4$ 332.2001, found 332.2001.

3-(Dimethylamino)-1,2-dicyano-9-ethoxyethyl-3-ethyl-1a-methyl-1,2-dihydro-3*H*-cyclopropapyrrolo[1,2-*a*]indole (9): 3-Ethyl-2-[2-(3-methyl)indolyl]acrylonitrile **1b** (15 mg, 0.059 mmol) and 3-dimethylamino-2-pentenenitrile (18 mg, 0.15 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 40 mL) were electrolyzed for 225 min at 460 mV (current consumption = 93 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:6) afforded 9 mg of 9 (41%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.55 (d, ^3J(H,H) = 7.5 Hz, 1H, H-8), 7.47 (d, ^3J(H,H) = 7.5 Hz, 1H, H-5), 7.17 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-6), 7.14 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-7), 3.69 (ddd, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 14.0 Hz, 1H, H-11), 3.60 (ddd, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 14.0 Hz, 1H, H-11a), 3.54 (m, 1H, H-12), 3.48 (m, 1H, H-12a), 3.08 (m, 2H, H-10/10a), 2.64 (dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-14), 2.60 (s, 6H, 3-N(CH_3)$_2$), 2.48 (q, ^3J(H,H) = 6.5 Hz, 1H, H-1a), 2.31 (dq, ^2J(H,H) = 15.0 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-14a), 1.67 (d, ^3J(H,H) = 6.5 Hz, 3H, 1a-CH_3), 1.20 (t, ^3J(H,H) = 7.0 Hz, 3H, H-13), 0.43 (t, ^3J(H,H) = 7.5 Hz, 3H, H-15); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 132.9 (s, C-4a), 132.4 (s, C-9a), 132.2 (s, C-8a), 122.8 (d, C-6), 120.7 (d, C-7), 119.7 (d, C-8), 114.7 (s, 1-CN), 113.4 (s, 2-CN), 111.7 (d, C-5), 106.3 (s, C-9), 85.7 (s, C-3), 70.1 (t, C-11), 66.2 (t, C-12), 40.1 (q, 2C, 3-N(CH_3)$_2$), 36.0 (s, C-2), 33.4 (d, C-1a), 31.9 (t, C-14), 27.4 (s, C-1), 24.2 (t, C-10), 15.3 (q, C-13), 12.2 (q, 1a-CH_3), 7.8 (q, C-15); IR (ATR): $\tilde{\nu}$ = 2925 (vs), 2855 (s), 2236 (w), 2202 (w), 1454 (vs), 1346 (s), 1109 (s) cm^{-1}; UV/Vis (MeOH): λ_{max} = 220, 275, 335 (sh); MS (70 eV, EI): *m/z* (%): 376 (50) [M^+], 322 (12) [$M^+ - N(CH_3)_2$], 318 (24), 317 (100) [$M^+ - C_3H_7O$], 286 (38), 272 (32), 149 (31), 73 (26), 69 (30), 57 (58), 55 (48); HRMS calcd for $C_{23}H_{28}N_4O$ 376.2263, found 376.2263.

2-{3-[Cyano-(1-methylpyrrolidin-2-ylidene)methyl]-3-methyl-3*H*-indol-2-yl}-3-phenylacrylonitrile (10): 3-Phenyl-2-[2-(3-methyl)indolyl]acrylonitrile **1d** (15 mg, 0.059 mmol) and 1-methyl-2-(cyanomethylene)pyrrolidine (14 mg, 0.11 mmol) in CH_3CN (+ 0.1 M $LiClO_4$, 60 mL) were electrolyzed for 170 min at 421 mV (current consumption = 62 C). Separation of the reaction mixture by flash chromatography (MTBE/PE, 1:1) and subsequently by preparative TLC (MTBE/MeOH, 40:1) afforded 9 mg (41%) of **10** as a yellow solid. M.p. = 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.16 (s, 1H, H-9), 8.12/8.13 (d, ^3J(H,H) = 8.0 Hz, 2H, H-11/11a), 7.74 (d, ^3J(H,H) = 7.5 Hz, 1H, H-7), 7.53 (m, 2H, H-12/12a), 7.53 (m, 1H, H-13), 7.38 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-6), 7.36 (d, ^3J(H,H) = 7.5 Hz, 1H, H-4), 7.30 (dd, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 7.5 Hz, 1H, H-5), 3.33 (s, 3H, H-19), 3.27 (m, 1H, H-18), 1.79 (ddd, ^3J(H,H) = 6.5 Hz, ^3J(H,H) = 9.0 Hz, ^2J(H,H) = 15.5 Hz, 1H, H-16), 1.68 (s, 3H, 3-CH_3), 1.54 (m, 1H, H-17), 1.21 (ddd, ^3J(H,H) = 6.0 Hz, ^3J(H,H) = 9.0 Hz, ^2J(H,H) = 15.5 Hz, 1H, H-16a); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 179.0 (s, C-2), 164.1 (s, C-15), 152.5 (s, C-7a), 149.0 (d,

C-9), 147.9 (s, C-3a), 132.8 (s, C-10), 132.3 (d, C-13), 130.8 (d, 2C, C-11/11a), 129.2 (d, 2C, C-12/12a), 128.3 (d, C-6), 127.6 (d, C-5), 122.4 (d, C-7), 121.9 (s, 14-CN), 121.3 (d, C-4), 116.5 (s, 8-CN), 105.6 (s, C-8), 67.3 (s, C-14), 56.8 (t, C-18), 36.1 (q, C-19), 30.2 (t, C-16), 27.7 (q, 3-CH_3), 19.9 (t, C-17); IR (ATR): $\tilde{\nu}$ = 2957 (s), 2927 (vs), 2856 (s), 2179 (m), 1580 (s), 1466 (m), 1373 (m), 1299 (m) cm^{-1}; UV/Vis (MeOH): λ_{max} = 210, 290, 350; MS (70 eV, EI): *m/z* (%): 378 (20), [M^+] 358 (12), 149 (28), 135 (20), 97 (22), 83 (30), 71 (38), 69 (50), 57 (94), 55 (100); HRMS calcd for $C_{25}H_{22}N_4$ 378.1844, found 378.1844.

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[1] For reviews see for example a) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, Berlin, **1987**; b) J. Mattay, *Angew. Chem.* **1987**, *99*, 849; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825.

[2] a) N. L. Bauld, *Tetrahedron* **1989**, *45*, 5307; b) B. Harirchian, N. L. Bauld, *J. Am. Chem. Soc.* **1989**, *111*, 1826.

[3] a) F. Müller, J. Mattay, *Chem. Rev.* **1993**, *93*, 99; b) J. Mattay, *Synthesis* **1989**, 233; c) M. Schmittel, H. V. Seggern, *Angew. Chem.* **1991**, *103*, 981; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 999; d) F. Müller, J. Mattay, *ibid.* **1992**, *104*, 207 and **1992**, *31*, 209.

[4] a) A. Gieseler, E. Steckhan, O. Wiest, *Synlett* **1990**, 275; b) A. Gieseler, E. Steckhan, O. Wiest, F. Knoch, *J. Org. Chem.* **1991**, *56*, 1405; O. Wiest, E. Steckhan, F. Grein, *ibid.* **1992**, *57*, 4034; O. Wiest, E. Steckhan, *Tetrahedron Lett.* **1993**, *34*, 6391.

[5] a) S. Blechert, R. Knier, H. Schroers, T. Wirth, *Synthesis* **1995**, 592; b) S. Blechert, *Liebigs Ann. Chem.* **1985**, 673; c) J. Wilkens, A. Kühling, S. Blechert, *Tetrahedron* **1987**, *43*, 3237.

[6] C. F. Gürtler, E. Steckhan, S. Blechert, *J. Org. Chem.* **1996**, *61*, 4136.

[7] O. Wiest, E. Steckhan, *Angew. Chem.* **1993**, *105*, 932; *Angew. Int. Ed. Engl.* **1993**, *32*, 901.

[8] C. F. Gürtler, E. Steckhan, S. Blechert, *Synlett* **1994**, 141.

[9] C. F. Gürtler, E. Steckhan, S. Blechert, *Angew. Chem.* **1995**, *107*, 2025; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1901.

[10] J. Mlcoch, E. Steckhan, *Tetrahedron Lett.* **1987**, *28*, 1081.

[11] T. Wirth, S. Blechert, *Synlett* **1994**, 717.

[12] J. Mlcoch, E. Steckhan, *Angew. Chem.* **1985**, 97, 429; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 412.

[13] This pathway is supported by calculations on a semiempirical level (AM1).

[14] For a review see for example: L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131.

0947-6539/97/0303-0452 $ 15.00+.25/0