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Inverse-Electron-Demand *Diels-Alder* Reactions of Condensed Pyridazines VI [1, 2]: Ring Transformations of Pyrido[2,3-*d*]pyridazine into *g*-Fused Quinolines

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Summary. A series of *g*-annelated quinolines was synthesized, employing pyrido[2,3-*d*]pyridazine as an azadiene in inverse-electron-demand *Diels-Alder* reactions with electron-rich dienophiles (enamines and a ketene-N,S-acetal). In cases where isomer mixtures were obtained, NOE difference spectroscopy was used for structural assignment.

Keywords. Pyrido[2,3-*d*]pyridazine; *g*-Annelated quinolines; Inverse-electron-demand *Diels-Alder* reactions; [4 + 2] Cycloaddition reactions.

***Diels-Alder*-Reaktionen mit inversem Elektronenbedarf an kondensierten Pyridazinen, 6. Mitt. [1, 2]: Ringtransformationen von Pyrido[2,3-*d*]pyridazin in *g*-anellierte Chinoline**

Zusammenfassung. Die Darstellung einer Reihe *g*-anellierter Chinoline wird beschrieben. Dabei wurde Pyrido[2,3-*d*]pyridazin als Azadien in *Diels-Alder*-Reaktionen mit inversem Elektronenbedarf unter Verwendung elektronenreicher Dienophile (Enamine und ein Keten-N,S-Acetal) eingesetzt. In jenen Fällen, wo Isomerengemische erhalten wurden, erfolgte die jeweilige Strukturzuordnung mittels NOE-Differenzspektroskopie.

Introduction

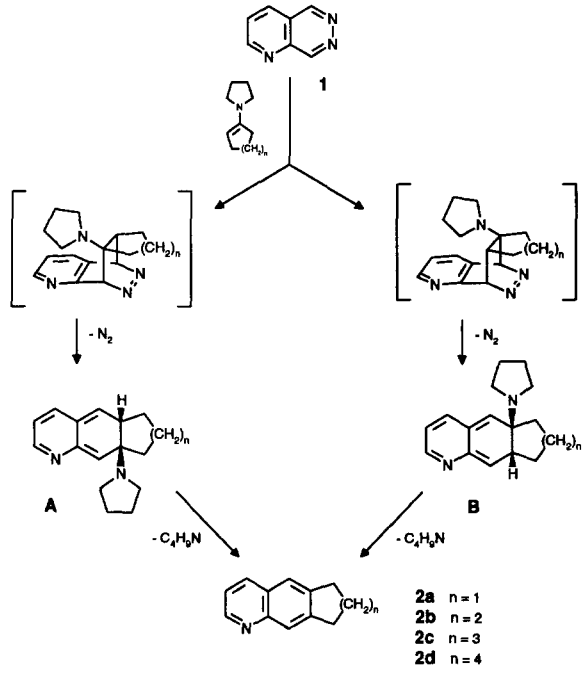
Ring transformations of π-electron-deficient N-heteroaromatics into a wide array of heterocyclic as well as carbocyclic systems, employing the inverse-electron-demand *Diels-Alder* methodology, have been proven to be of considerable synthetic value [4]. Among other azines, pyridazine derivatives were successfully employed as azadienes, either in *inter*molecular reactions with electron-rich dienophiles or – if the dienophilic unit is attached to the heterocycle by a spacer chain – in *intra*-molecular [4 + 2] cycloaddition reactions [4]. Whereas in the latter case even unactivated dienophiles (like olefins) and/or unactivated azadienes (bearing no electron-withdrawing groups) were found to undergo such thermally induced

* Dedicated with best wishes to Prof. Dr. F. Sauter on the occasion of his 65th birthday

cyclization processes due to the entropic assistance provided by linkage of the reactants, an intermolecular cycloaddition reaction between a pyridazine derivative and a dienophile usually requires some activation of both components. Thus, electron-rich dienophiles (like enamines, enol ethers, ynamines, ketene acetals, *etc.*) are employed, and the introduction of electron-withdrawing substituents into the azine nucleus leads to a sufficiently low LUMO energy of the azadiene. Another possibility to achieve the latter effect is the annelation of a second (hetero)aromatic ring to the 1,2-diazine unit, as demonstrated previously for 1,2-diazines fused to five-membered [1, 5, 6] and six-membered [7–10] heterocycles. Even with unsubstituted phthalazine, thermally induced [4 + 2] cycloaddition reactions with enamine-type dienophiles have been reported [11, 12]. In continuation of our recent studies, we here report on the utilization of the unsubstituted triazanaphthalene, pyrido[2,3-*d*]pyridazine, as an azadiene in $LUMO_{diene}$-controlled *Diels-Alder* reactions.

Results and Discussion

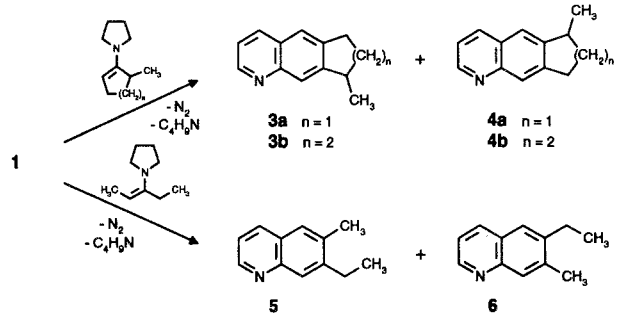
In a first series of experiments, pyrido[2,3-*d*]pyridazine (**1**) (conveniently prepared from quinolinic acid according to Ref. [13]) was reacted with enamines derived from five-, six-, seven-, and eight-membered cyclic ketones in refluxing 1,4-dioxane to give *g*-annelated quinolines of type **2** in reasonable yields (31–67%). Expectedly, marked differences in the times required for complete consumption of the starting material were observed (tlc monitoring), depending on the ring size of the employed dienophile: similar to earlier findings [7, 8], 1-pyrrolidino-1-cyclohexene ($n = 2$; cf. Scheme 1) proved to be considerably less reactive (7 days of refluxing required) than



Scheme 1

the other enamines ($n = 1$: 20 hours; $n = 3$: 2 hours; $n = 4$: 96 hours). The ^{1}H NMR spectrum of the crude product obtained from **1** and 1-pyrrolidino-1-cyclopentene indicated that in this case – in contrast to the six-, seven-, and eight-membered analogs – substantial amounts of dihydroquinoline intermediates (still bearing the pyrrolidine moiety) of type **A**/**B** were present in the mixture. Thus, the material was refluxed in toluene/trifluoroacetic acid (in analogy to similar conversions reported previously [7, 8]) to give the aromatic quinoline derivative **2a** in 43% overall yield.

In order to gain insight into the regiochemistry of the inverse-electron-demand *Diels-Alder* reaction of the triazanaphthalene **1** with enamine-type dienophiles, **1** was also reacted with enamines which do not lead to a single aromatic product (like compounds **2**) after cycloaddition/cycloreversion and subsequent amine elimination. Thus, the methyl-substituted cycloalkanone enamines, 6-methyl-1-pyrrolidino-1-cyclohexene and 5-methyl-1-pyrrolidino-1-cyclopentene, as well as the acyclic enamine, 3-pyrrolidino-2-pentene, were employed as reagents. Again, significant reactivity differences were observed with the enamines used in these ring transformations (reaction times ranging from 20 hours at 101 °C to 4 days at 180 °C, see Experimental); expectedly, the six-membered cyclic enamine reacted slower than its desmethyl analog (see above) and gave the lowest yields. In all cases, the ^{1}H NMR spectra of the crude products indeed indicated the presence of two isomeric quinoline derivatives (one of them clearly dominating).



Scheme 2

Whereas the mixture (ratio 7:1, according to ^{1}H NMR) of 7-ethyl-6-methylquinoline (**5**) and its isomer (**6**) thus obtained could not be separated, NOE difference spectroscopy allowed an unequivocal discrimination between the two components: compound **5** was found to be the major isomer. On the other hand, with the mixtures of methylcycloalkene-annelated quinolines **3a**/**4a** (ratio 8:1) and **3b**/**4b** (ratio 2:1), we succeeded in isolation of the pure major component (**3a** and **3b**, respectively) by means of medium-pressure liquid chromatography (MPLC). Again, structural assignment for these compounds rests on NOE difference spectroscopy: saturation of the methyl resonance at 1.4 ppm leads to a marked NOE for the singulet of H-9 (in compound **3a**) or H-10 (in compound **3b**), respectively, at 7.85 ppm (compare Fig. 1).

Thus, it becomes evident that preferential attack of an enamine dienophile at the azadiene takes place in an orientation which leads (after expulsion of N_2 from an initially formed bridged cycloadduct) to an intermediate of type **A** (cf. Scheme 1),

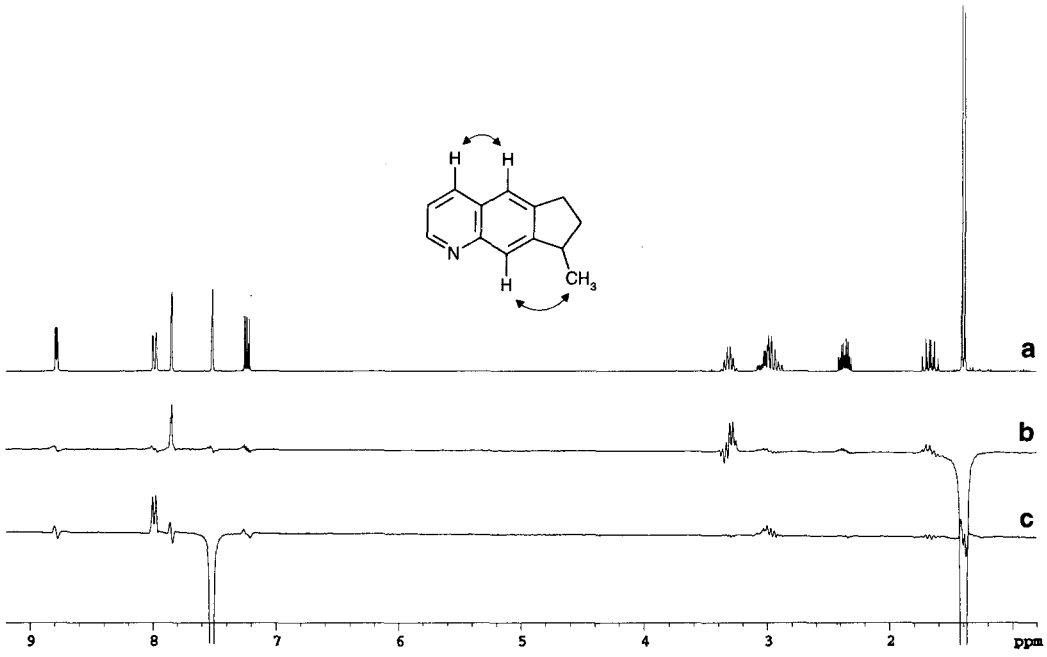
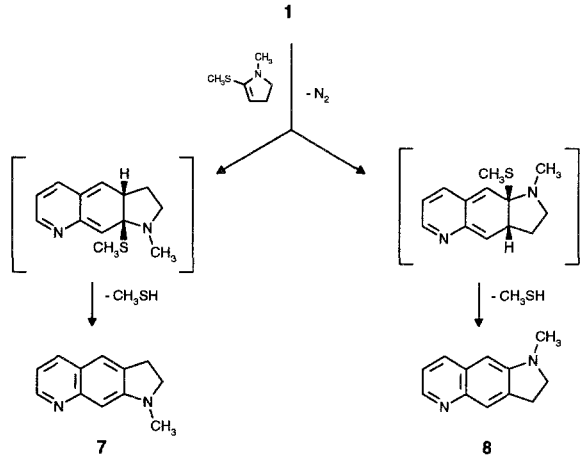


Fig. 1. 300 MHz ^{1}H NMR spectrum (trace **a**) and NOE difference spectra resulting from irradiation of CH_3 (trace **b**) and H-5 resonances (trace **c**) of compound **3a** ($CDCl_3$, 25 °C)

which means that the more electron-rich enamine carbon atom shows a higher affinity to the C-5 position of the azadiene than to C-8. Interestingly, this situation was found to be reversed when a cyclic ketene N,S-acetal (1-methyl-2-methylthio-2-pyrroline) was employed as a C=C dienophile. Here, after a reaction time of 3 days (dioxane, reflux temperature), a mixture of two isomeric dihydropyrroloquinolines was obtained in $> 80\%$ overall yield. Both isomers (ratio 1:1.7), which obviously result from loss of N_2 and subsequent elimination of methyl mercaptane from the initial cycloadducts, were obtained in pure form by MPLC. By means of NOE difference spectroscopy (using the N-methyl signal as well as the singulets of H-5 and H-9 as irradiation points), structure **8** was assigned to the major isomer and structure **7** to the minor component (see Scheme 3).

In conclusion, it could be demonstrated that – in spite of lacking electron-withdrawing (and thus activating) substituents – the triazanaphthalene **1** is able to undergo inverse-electron-demand *Diels-Alder* reactions with various electron-rich dienophiles. Compared to the low reactivity of pyridazine [11] (LUMO energy: -0.288 eV [14]), the annelation of a pyridine ring to the 1,2-diazine system (LUMO energy of the pyrido[2,3-*d*]pyridazine **1**: -1.215 eV [14]) results in a considerable decrease of the energy gap between the $HOMO_{dienophile}$ and the $LUMO_{diene}$ – an effect which obviously is sufficient for this type of [4 + 2] cycloaddition reaction to take place under reasonable conditions. The method described represents a simple synthetic pathway for the preparation of a series of *g*-annelated quinolines, in particular when enamines are used which give rise to the formation of a single quinoline derivative.



Scheme 3

Experimental

Melting points (uncorrected) were determined on a Kofler hot-stage microscope. Infrared spectra were recorded on a Perkin-Elmer 1605 FTIR instrument. ^{1}H NMR spectra were recorded on a Varian UNITY*plus* 300 (300 MHz) or a Bruker AC 80 (80 MHz) spectrometer (*TMS* as internal reference, δ in ppm). Mass spectra were obtained on a Hewlett-Packard 5890A/5970B-GC/MSD spectrometer, high-resolution mass spectra on a Finnigan MAT 8230 instrument (equipped with a data system SS300). Column chromatography was done on Merck Kieselgel 60, 0.063–0.200 mm, medium-pressure liquid chromatography (MPLC) was carried out on Merck LiChroprep Si 60, 0.040–0.063 mm (detection at 280 nm). Light petroleum refers to the fraction of b.p. 50–70 °C. Microanalyses were performed at the Institute of Physical Chemistry (Microanalytical Laboratory), University of Vienna.

7,8-Dihydro-6H-cyclopenta[g]quinoline [17] (**2a**)

A solution of 80 mg (0.6 mmol) **1** [13] and 330 mg (2.4 mmol) 1-pyrrolidino-1-cyclopentene [18] in 15 ml dry 1,4-dioxane was refluxed under argon for 20 h. The volatile components were removed *in vacuo* and the oily residue was dissolved in 20 ml toluene. After addition of 2 ml trifluoroacetic acid, the mixture was refluxed for 16 h, then it was evaporated. The residue was taken up in dichloromethane and was washed successively with aqueous sodium hydrogencarbonate solution and water. The organic layer was dried and evaporated and the residue was subjected to column chromatography (ethyl acetate). Recrystallization from light petroleum afforded 44 mg (43%) of almost colorless crystals. M.p. = 76–77 °C (Ref. [17]: m.p. = 79.5–81 °C); $C_{12}H_{11}N$ (169.23); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.78 (dd, J = 4.1 Hz, 1.5 Hz, 1 H, H-2), 8.01 (dd, J = 8.5 Hz, 1.5 Hz, 1 H, H-4), 7.88 (s, 1 H, H-9), 7.55 (s, 1 H, H-5), 7.25 (dd, J = 8.5 Hz, 4.1 Hz, 1 H, H-3), 3.25–2.90 (m, 4 H, Ar-CH_2), 2.40–1.90 (m, 2 H, CH_2).

6,7,8,9-Tetrahydrobenzo[g]quinoline [19] (**2b**)

A solution of 80 mg (0.6 mmol) **1** [13] and 360 mg (2.4 mmol) 1-pyrrolidino-1-cyclohexene [18] in 15 ml dry 1,4-dioxane was refluxed under argon for 168 h. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate). Recrystallization from light petroleum gave 73 mg (67%) of almost colorless crystals. M.p. = 70–71 °C (Ref. [19]: m.p. = 71–72 °C); $C_{13}H_{13}N$ (183.26); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.78 (dd, J = 4.2 Hz, 1.7 Hz, 1 H,

H-2), 8.00 (dd, $J = 8.3$ Hz, 1.7 Hz, 1 H, H-4), 7.79 (s, 1 H, H-10), 7.46 (s, 1 H, H-5), 7.25 (dd, $J = 8.3$ Hz, 4.2 Hz, 1 H, H-3), 3.20–2.80 (m, 4 H, Ar-CH_2), 2.15–1.55 (m, 4 H, CH_2).

7,8,9,10-Tetrahydro-6H-cyclohepta[g]quinoline (**2c**)

A solution of 131 mg (1 mmol) **1** [13] and 660 mg (4 mmol) 1-pyrrolidino-1-cycloheptene [18] in 10 ml dry 1,4-dioxane was refluxed under argon for 2 h. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate). Recrystallization from light petroleum/*n*-pentane gave 97 mg (49%) of almost colorless crystals. M.p. = 70–71 °C; $C_{14}H_{15}N$ (197.28); calcd.: C 85.24, H 7.66, N 7.10; found: C 85.06, H 7.62, N 7.01; ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 8.78$ (dd, $J = 4.2$ Hz, 1.8 Hz, 1 H, H-2), 8.03 (dd, $J = 8.1$ Hz, 1.8 Hz, 1 H, H-4), 7.81 (s, 1 H, H-11), 7.51 (s, 1 H, H-5), 7.29 (dd, $J = 8.1$ Hz, 4.2 Hz, 1 H, H-3), 3.15–2.80 (m, 4 H, Ar-CH_2), 2.05–1.50 (m, 6 H, CH_2); EI-MS: m/z (%) = 197 (M^+, 100), 182 (43), 169 (26), 168 (46), 167 (32), 156 (24), 154 (25).

6,7,8,9,10,11-Hexahydrocycloocta[g]quinoline (**2d**)

A solution of 131 mg (1 mmol) **1** [13] and 717 mg (4 mmol) 1-pyrrolidino-1-cyclooctene [18] in 15 ml dry 1,4-dioxane was heated under argon to 110 °C for 96 h in a closed vessel. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate/ethanol, 19 + 1) to give 65 mg (31%) of an almost colorless, viscous oil. $C_{15}H_{17}N$ (211.31); calcd.: 211.1361; found: 211.1376 (HR-MS); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 8.76$ (dd, $J = 4.1$ Hz, 1.6 Hz, 1 H, H-2), 7.98 (dd, $J = 8.2$ Hz, 1.6 Hz, 1 H, H-4), 7.80 (s, 1 H, H-12), 7.45 (s, 1 H, H-5), 7.21 (dd, $J = 8.2$ Hz, 4.1 Hz, 1H, H-3), 3.10–2.70 (m, 4 H, Ar-CH_2), 2.05–1.10 (m, 8 H, CH_2); EI-MS: m/z (%) = 211 (M^+, 100), 182 (34), 168 (51), 167 (25), 156 (21), 154 (22).

Cycloaddition Reaction of Pyrido[2,3-d]pyridazine (**1**) *with 5-Methyl-1-pyrrolidino-1-cyclopentene*

A solution of 131 mg (1 mmol) **1** [13] and 604 mg (4 mmol) 5-methyl-1-pyrrolidino-1-cyclopentene [20] in 10 ml dry 1,4-dioxane was refluxed under argon for 72 h. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate/light petroleum, 1 + 1), followed by MPLC (ethyl acetate/light petroleum, 2 + 3). Evaporation of the first fraction gave 80 mg (44%) of pure *7,8-dihydro-8-methyl-6H-cyclopenta[g]quinoline* (**3a**) as a colorless oil. $C_{13}H_{13}N$ (183.25); calcd.: 183.1048; found: 183.1035 (HR-MS); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.79$ (dd, $J = 4.2$ Hz, 1.6 Hz, 1 H, H-2), 7.99 (dd, $J = 8.1$ Hz, 1.6 Hz, 1 H, H-4; shows NOE on irradiation at 7.52 ppm), 7.85 (s, 1 H, H-9; shows NOE on irradiation at 1.40 ppm), 7.52 (s, 1 H, H-5), 7.24 (dd, $J = 8.1$ Hz, 4.2 Hz, 1 H, H-3), 3.38–3.24 (m, 1 H, CH), 3.10–2.88 (m, 2 H, Ar-CH_2), 2.42–2.30 and 1.74–1.60 (m, 2 H, CH_2), 1.40 (d, $J = 6.9$ Hz, CH_3); EI-MS: m/z (%) = 183 (M^+, 49), 168 (100), 167 (39). The second fraction contained 30 mg (16%) of a mixture of **3a** and *7,8-dihydro-6-methyl-6H-cyclopenta[g]quinoline* (**4a**) as a colorless oil [21].

Cycloaddition Reaction of Pyrido[2,3-d]pyridazine (**1**) *with 6-Methyl-1-pyrrolidino-1-cyclohexene*

A solution of 400 mg (3.05 mmol) **1** [13] and 2.0 g (12.1 mmol) 6-methyl-1-pyrrolidino-1-cyclohexene [18] in 12 ml dry 1,4-dioxane was heated under argon to 180 °C for 96 h in an autoclave. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate/light petroleum, 1 + 1), followed by MPLC (ethyl acetate/light petroleum, 2 + 3). Evaporation of the first fraction gave 66 mg (11%) of *6,7,8,9-tetrahydro-9-methylbenzo[g]quinoline* (**3b**) as an almost colorless oil. $C_{14}H_{15}N$ (197.28); calcd.: 197.1204; found: 197.1197 (HR-MS); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 8.76$ (dd, $J = 4.2$ Hz, 1.6 Hz, 1 H, H-2), 7.96 (dd, $J = 8.3$ Hz, 1.6 Hz, 1 H, H-4), 7.92 (s, 1 H, H-10; shows NOE on irradiation at 1.39 ppm), 7.42 (s, 1 H, H-5), 7.22 (dd, $J = 8.3$ Hz, 4.2 Hz, 1 H, H-3), 3.25–2.75 (m, 3 H, Ar-CH_2, Ar-CH), 2.15–1.50 (m, 4 H, CH_2), 1.39 (d, $J = 6.9$ Hz, 3 H, CH_3); EI-MS:

m/z (%) = 197 (M^+, 66), 182 (100), 168 (24), 167 (40). The second fraction contained 57 mg of a mixture of **3b**, *6,7,8,9-tetrahydro-6-methylbenzo[g]quinoline* (**4b**), and an unidentified side product as a brownish oil [22].

Cycloaddition Reaction of Pyrido[2,3-d]pyridazine (**1**) *with 3-Pyrrolidino-2-pentene*

A solution of 393 mg (3 mmol) **1** [13] and 1.67 g (12 mmol) 3-pyrrolidino-2-pentene [23] in 20 ml dry 1,4-dioxane was heated under argon to 110 °C for 20 h in a closed vessel. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate/ethanol, 19 + 1) to give 220 mg (43%) of a mixture (88:12, according to ^{1}H NMR) of *7-ethyl-6-methylquinoline* (**5**) *and 6-ethyl-7-methylquinoline* (**6**) as an almost colorless oil. $C_{12}H_{13}N$ (171.24); calcd.: 171.1048; found: 171.1054 (HR-MS); ^{1}H NMR (300 MHz, $CDCl_3$): δ (signals of **5**) = 8.78 (dd, J = 4.2 Hz, 1.6 Hz, 1 H, H-2), 7.95 (d, J = 8.1 Hz, 1 H, H-4), 7.88 (s, 1 H, H-8), 7.48 (s, 1 H, H-5; shows NOE on irradiation at 2.43 ppm), 7.23 (dd, J = 8.1 Hz, 4.2 Hz, 1 H, H-3), 2.78 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 2.43 (s, 3 H, CH_3), 1.33 (t, J = 7.5 Hz, 3 H, CH_2CH_3); δ (detectable signals of **6**) = 7.86 (s, 1 H, H-8), 2.72 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 2.47 (s, 3 H, CH_3), 1.29 (t, J = 7.5 Hz, 3 H, CH_2CH_3); EI-MS: *m/z* (%) = 171 (M^+, 70), 170 (32), 156 (100), 154 (20).

Cycloaddition Reaction of Pyrido[2,3-d]pyridazine (**1**) *with 1-Methyl-2-methylthio-2-pyrroline*

A solution of 262 mg (2 mmol) **1** [13] and 1034 mg (8 mmol) 1-methyl-2-methylthio-2-pyrroline [24] in 15 ml dry 1,4-dioxane was refluxed under argon for 72 h. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography (ethyl acetate/ethanol, 4 + 1), followed by MPLC (ethyl acetate/ethanol, 19 + 1). Evaporation of the first fraction gave 190 mg (52%) of *7,8-dihydro-6-methyl-6H-pyrrolo[2,3-g]quinoline* (**8**) as pale yellow crystals. M.p. = 92–93 °C (*n*-hexane); $C_{12}H_{12}N_2$ (184.24); calcd.: C 78.23, H 6.57, N 15.20; found: C 77.98, H 6.34, N 15.26; ^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.55 (dd, J = 4.2 Hz, 1.5 Hz, 1 H, H-2), 7.87 (dd, J = 8.2 Hz, 1.5 Hz, 1 H, H-4; shows NOE on irradiation at 6.45 ppm), 7.67 (s, 1 H, H-9), 7.19 (dd, J = 8.2 Hz, 4.2 Hz, 1 H, H-3), 6.45 (s, 1 H, H-5), 3.65–3.00 (m, 4 H, CH_2), 2.88 (s, 3 H, CH_3; shows NOE on irradiation at 6.45 ppm); EI-MS: *m/z* (%) = 184 (M^+, 80), 183 (100), 168 (27). Evaporation of the second fraction gave 110 mg (30%) of *7,8-dihydro-8-methyl-6H-pyrrolo[3,2-g]quinoline* (**7**) as a pale yellow wax-like solid. M.p. = 52–61 °C; $C_{12}H_{12}N_2$ (184.24); calcd.: 184.1000; found: 184.1004 (HR-MS); ^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.63 (dd, J = 4.4 Hz, 1.5 Hz, 1 H, H-2), 7.86 (dd, J = 8.0 Hz, 1.5 Hz, 1 H, H-4; shows NOE on irradiation at 7.35 ppm), 7.35 (s, 1 H, H-5), 7.04 (dd, J = 8.0 Hz, 4.4 Hz, 1 H, H-3), 6.80 (s, 1 H, H-9; shows NOE on irradiation at 2.91 ppm), 3.65–3.00 (m, 4 H, CH_2), 2.91 (s, 3 H, CH_3); EI-MS: *m/z* (%) = 184 (M^+, 75), 183 (100), 168 (28).

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[22] Only the signal of H-10 in the ^{1}H-NMR spectrum of compound **4b** is not overlapped by the corresponding signal of the isomer **3b** (80 MHz, $CDCl_3$): $\delta = 7.80$ (s, 1 H, H-10)
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