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The Structure of the Scarlet Compounds Obtained From the Acylation of Pyridazinylhydrazones

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Über die Struktur der roten Acylierungsprodukte von Pyridazinylhydrazonen

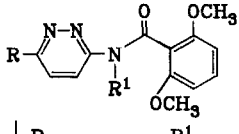
Bei der Acylierung von Pyridazinylhydrazonen (**3**) mit Säurechloriden oder Anhydriden in Benzol entstehen scharlachrote Triazolo[4,3-*b*]pyridazine (**4**), deren Struktur durch Röntgenstrahlbeugungsanalyse gesichert wird.

The herbicidal activity of the 2,6-dimethoxybenzamides **1** of 3-amino-6-*t*-alkyl-substituted pyridazines was reported in 1983[1]. In a structure-activity relationship study, the pyridazinylhydrazone **3a** was benzoylated with 2,6-dimethoxybenzoyl chloride. In THF with NaH the colorless amide **2a** obtained was always accompanied by traces of a scarlet component **4a** with higher R_f value. The formation of the latter could be optimized by refluxing equimolar amounts of **3a** with 2,6-dimethoxybenzoyl chloride in benzene for 4 h (Scheme 1).

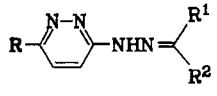
Combustion analysis indicated that **4a** had the same empirical formula $C_{20}H_{26}N_4O_3$ as **2a**. The structure of compounds **2** was assigned on chemical shift differences between the 4-H of pyridazines **2** *vs* **3** (see Exp. Part) and the ready hydrolysis (2 N HCl, 25°C/24 h or 50°C/4 h) of compounds **2** to their free amino analogues. The amino compounds were transformed to starting materials by gentle heating with acetone. The scarlet amide **4a** remained unchanged under these conditions.

Further experiments showed that pyridazinylhydrazones **3** reacted generally with acyl chlorides and acid anhydrides in anhydrous benzene at elevated temperatures to give scarlet, crystalline compounds as major or sole products in moderate to good yields.

Scheme 1

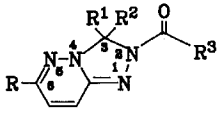


	R	R^1
1a	$(CH_3)_3C$	H
b	$CH_3C(C_2H_5)_2$	H
2a	$(CH_3)_3C$	$N{=}C(CH_3)_2$
c	$CH_3C(C_2H_5)_2$	NH_2

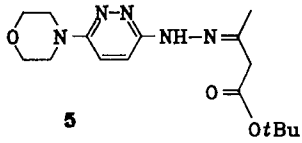


	R	R^1	R^2
3a	$(CH_3)_3C$	CH_3	CH_3
b	$(CH_3)_3C$	CH_3	$CH_2CO_2C(CH_3)_3$
c	$CH_3C(C_2H_5)_2$	CH_3	CH_3
d	Cl	CH_3	CH_3

0009–2940/85/1212–5009 $ 02.50/0



	R	R^1	R^2	R^3
4a	$(CH_3)_3C$	CH_3	CH_3	$2,6-(CH_3O)_2C_6H_3$
b	$(CH_3)_3C$	CH_3	CH_3	$CH_2C(CH_3)_3$
c	$(CH_3)_3C$	CH_3	CH_3	$CH(CH_3)(C_3H_7)$
d	Cl	CH_3	CH_3	$CH_2C(CH_3)_3$
e	Cl	CH_3	CH_3	CH_2Cl
f	$(CH_3)_3C$	CH_3	CH_3	CCl_3
g	$(CH_3)_3C$	CH_3	CH_3	$N(CH_3)_2$
h	$(CH_3)_3C$	CH_3	CH_3	$3-CF_3C_6H_4$
i	$(CH_3)_3C$	CH_3	CH_3	OC_2H_5
j	$(CH_3)_3C$	CH_3	$CH_2CO_2C(CH_3)_3$	OC_2H_5



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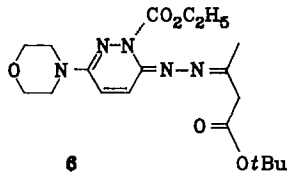

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An *X*-ray crystal structure analysis of a typical „scarlet amide" **4b** indicates in an unequivocal manner that compound **4b** is a triazolo[4,3-*b*]pyridazine with the position of the acyl group at N-2 (see ORTEP plot, Fig. 1).

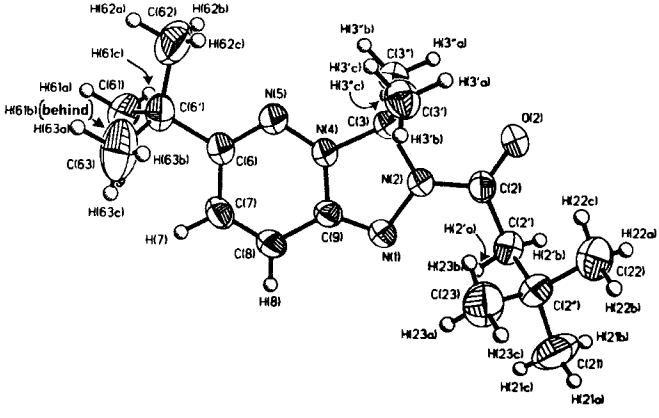

Fig. 1. ORTEP plot of compound **4b**

Discussion

The triazolo[4,3-*b*]pyridazine nucleus was first obtained by *Bülow* in 1909[2]. Interest in this ring system remained dormant until the 1950's, after which a number of syntheses were reported[3].

In recent years, following the commercialization of the antihypertensive drug Hydralazine[4], substantial research has been done on the chemistry of phthalazine and pyridazinylhydrazine derivatives[5]. In particular, the bicyclic compounds derived from ring-closure reactions of 3-hydrazinopyridazines have been documented by several group of researchers[6–8].

In none of the references were we able to find a cyclization of the nature we describe in this paper. However, we noted an observation by *Matyus* et al.[8] in which they treated a pyridazinylhydrazone **5** with ethyl pyrocarbonate in benzene to give, at elevated temperatures, a compound **6** that crystallized in *red needles* for which they proposed an *endo*-acyl structure.

This result was surprising to us in view of our findings that in all of the cases we had studied with acyl chlorides and pyridazinylhydrazones we obtained compounds that we had unequivocally characterized as triazolo[4,3-*b*]pyridazines via *X*-ray structure analysis. Of course, a characterization by proton magnetic resonance or ^{13}C NMR alone, while consistent with a structure such as **6**, cannot be unambiguous. Therefore, we probed the reaction of pyridazinylhydrazones **3a** and **b** with ethyl chloroformate and/or diethyl pyrocarbonate in an attempt to support or refute the „*endo*-acyl" structures analogous to **6**.

Treatment of 3-(1,1-dimethylethyl)-6-hydrazinopyridazine[1] with acetone or *tert*-butylacetoacetate, afforded **3a** and **b**, respectively. Compound **3b** existed in *E*- and *Z*-isomers, but upon crystallization from hexane gave pure (*E*)-**2b** with m.p. 102–106°C.

When **3a** was heated with ethyl chloroformate in benzene for 13 h, it afforded compound **4i** in 70% yield. Treatment of **3a** with ethyl pyrocarbonate in benzene and heating to reflux for 4 h afforded the same compound **4i** in a higher state of purity. Identity was also established by superimposable IR and NMR spectra. Finally, an *X*-ray crystal structure analysis established that **4i** is indeed a triazolo[4,3-*b*]pyridazine and not the „*endo*-acylated" compound. By analogy, treatment of **3b** with ethyl chloroformate gives **4j** in 50% recrystallized yield.

Conclusion

It appears that the treatment of pyridazinylhydrazones of acetone and other ketones with acyl chlorides, chloroformates, anhydrides, and carbamoyl chlorides affords novel triazolo[4,3-*b*]pyridazines **4** acylated at N-2 of the fused ring system. It is highly probable that the red derivatives reported by *Matyus* et al.[8,9] are members of this group of fused heterocycles and not the claimed „*endo*-acyl" derivatives **6**.

We thank Mr. *G. Babbitt* of the Lilly Research Laboratories for the IR and NMR spectra and Dr. *A. Kossoy* of the Lilly Research Laboratories for the microanalyses.

Experimental Part

IR spectra: Sargent-Welch Pye Unicam IR 3-200 spectrometer. – ^1H NMR spectra: Bruker WM-250 spectrometer, δ-scale, external reference tetramethylsilane. – Mass spectra: Hewlett-Packard HP-5985 B GC mass spectrometer. – Melting points: uncorrected.

Synthesis of Pyridazinylhydrazones

2-Propanone [6-(1,1-Dimethylethyl)-3-pyridazinyl]hydrazone (**3a**): A solution of 2.0 g (9.7 mmol) of 3-(1,1-dimethylethyl)-6-hydrazinopyridazine in 30 ml of acetone was gently warmed to reflux for 2.0 h. The reaction mixture was cooled to room temp. and the acetone was removed in vacuo on a rotary evaporator to afford a crystalline solid. This was recrystallized from 5.0 ml of petroleum ether (b.p. 30–60°C) to give pale yellow needles, m.p. 120–122°C, yield 1.75 g (70%). – ^1H NMR ($CDCl_3$): δ = 7.38 (m, 2H, pyridazine); 2.04, 1.96 (s, 6H, $=C(CH_3)_2$); 1.38 (s. 9H, *t*Bu).

$C_{11}H_{18}N_4$ (206.3) Calcd. C 64.05 H 8.80 N 27.16
Found C 63.83 H 8.53 N 26.91

1,1-Dimethylethyl (E)-3-[[6-(1,1-Dimethylethyl)-3-pyridazinyl]hydrazono]butanoate (**3b**): To a solution of 1.66 g (10 mmol) of 3-(1,1-dimethylethyl)-6-hydrazinopyridazine in 40 ml of anhydrous benzene (Linde 4 Å molecular sieves) was added 1.58 g (10 mmol) of *tert*-butyl acetoacetate. The reaction mixture was heated to reflux for 13 h. Water separated and was collected in a Dean-Stark trap. The reaction mixture was cooled and the benzene was removed in vacuo. A yellowish clear glass was produced (2.85 g, 93%) which was a mixture of (*E*)-**3b** and (*Z*)-(**3b**). Crystallization from hexane gave 1.1 g (36%) of pure (*E*)-**3b**, m.p. 102–106°C. – ^{1}H NMR ($CDCl_3$): δ = 8.28 (s, 1H, NH); 7.46, 7.43, 7.41, 7.37 (q, 4H, pyridazine); 3.28 (s, 2H, $N=CCH_2$); 2.01 (s, 3H, $N=CCH_3$); 1.48 (s, 9H, *t*BuO); 1.39 (s, 9H, *t*Bu). – MS: M^+ *m/z* = 306.

$C_{16}H_{26}N_4O_2$ (306.4) Calcd. C 62.72 H 8.55 N 18.28
Found C 62.93 H 8.36 N 18.38

Synthesis of Triazolo[4,3-b]pyridazines

2-(2,6-Dimethoxybenzoyl)-6-(1,1-dimethylethyl)-2,3-dihydro-3,3-dimethyl-1,2,4-triazolo-[4,3-b]pyridazine (**4a**): Orange needles, m.p. 88–90°C (hexane/benzene) in 24% yield. – MS: M^+ *m/z* = 370. – ^{1}H NMR ($CDCl_3$): δ = 7.20 (m, 2H, pyridazine); 6.63, 6.47 (3H, aromatic); 3.85 (s, 6H, OCH_3); 2.03 (s, 6H, $2CH_3$); 1.17 (s, 9H, $C(CH_3)_3$).

$C_{20}H_{26}N_4O_3$ (370.2) Calcd. C 64.84 H 7.07 N 15.12
Found C 65.12 H 6.85 N 14.92

6-(1,1-Dimethylethyl)-2-(3,3-dimethylbutanoyl)-2,3-dihydro-3,3-dimethyl-1,2,4-triazolo-[4,3-b]pyridazine (**4b**): To a solution of 2.06 g (10 mmol) of **3a** in 80.0 ml of anhydrous benzene (Linde 4 Å sieves) was added 1.4 ml (1.36 g, ca. 10 mmol) of 3,3-dimethylbutanoyl chloride. The reaction mixture was heated to reflux under nitrogen for 13 h and cooled. The deep-red solution was washed with saturated sodium hydrogen carbonate solution, and filtered through PS paper (Whatman). Removal of benzene in vacuo gave a scarlet crystalline solid **4b**. Recrystallization from hexane gave scarlet needles, m.p. 153–155°C, yield 1.65 g (54%). – ^{1}H NMR ($CDCl_3$) δ = 6.70 (s, 2H, 7- and 8-H); 2.50 (s, 2H, $-CH_2-$); 1.93 (s, 6H, $>C(CH_3)_2$); 1.22 (s, 9H, *t*Bu); 1.10 (s, 9H, *t*Bu).

$C_{17}H_{28}N_4O$ (304.4) Calcd. C 67.07 H 9.27 N 18.40 Found C 67.29 H 9.22 N 18.09

6-(1,1-Dimethylethyl)-2,3-dihydro-3,3-dimethyl-2-(2-methylpentanoyl)-1,2,4-triazolo[4,3-b]-pyridazine (**4c**): Scarlet cubes, m.p. 111–113°C (hexane/benzene) in 56% yield. – MS: M^+ *m/z* = 304. – ^{1}H NMR ($CDCl_3$): δ = 6.63 (m, 2H, pyridazine); 3.15 (m, 1H, CH); 1.83 (s, 6H, $2CH_3$); 1.17 (s, 9H, $C(CH_3)_3$), 1.6–0.6 (m, 7H, aliphatic).

$C_{17}H_{28}N_4O$ (304.4) Calcd. C 67.07 H 9.27 N 18.40 Found C 67.54 H 8.88 N 18.39

6-Chloro-2-(3,3-dimethylbutanoyl)-2,3-dihydro-3,3-dimethyl-1,2,4-triazolo[4,3-b]pyrid-azine (**4d**): Scarlet rods, m.p. 120–122°C (hexane), 43% yield. – MS: M^+ *m/z* = 282, 283. – ^{1}H NMR ($CDCl_3$): δ = 6.60 (q, 2H, pyridazine); 2.48 (s, 2H, $COCH_2$); 1.92 (s, 6H, $2CH_3$); 1.04 (s, 9H, $C(CH_3)_3$).

$C_{13}H_{19}ClN_4O$ (282.8) Calcd. C 55.22 H 6.77 N 19.81
Found C 55.44 H 6.72 N 20.07

6-Chloro-2-(chloroacetyl)-2,3-dihydro-3,3-dimethyl-1,2,4-triazolo[4,3-b]pyridazine (**4e**): Scarlet cubes, m.p. 157–159°C (hexane), in 10% yield. – MS: M^+ *m/z* = 260, 261. – ^{1}H NMR ([D_6]DMSO): δ = 7.10 (q, 2H, pyridazine); 4.40 (s, 2H, CH_2Cl); 1.80 (s, 6H, $2CH_3$).

$C_9H_{10}Cl_2N_4O$ (261.1) Calcd. C 41.40 H 3.86 N 21.46
Found C 42.16 H 3.68 N 21.83

6-(1,1-Dimethylethyl)-2,3-dihydro-3,3-dimethyl-2-(trichloroacetyl)-1,2,4-triazolo[4,3-b]-pyridazine (**4f**): Scarlet cubes, m.p. 227–229°C (hexane), in 31% yield. – MS: M^+ m/z = 351, 352. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.20 (q, 2H, pyridazine); 1.84 (s, 6H, 2 CH_3); 1.16 (s, 9H, $C(CH_3)_3$).

$C_{13}H_{17}Cl_3N_4O$ (351.7) Calcd. C 44.40 H 4.87 N 15.93
Found C 44.16 H 4.85 N 15.66

6-(1,1-Dimethylethyl)-2,3-dihydro-N,N,3,3-tetramethyl-1,2,4-triazolo[4,3-b]pyridazine-2-carboxamide (**4g**): Scarlet cubes, m.p. 118–120°C (hexane), in 22% yield. – MS: M^+ m/z = 277. – ^{1}H NMR ($CDCl_3$): δ = 6.67 (s, 2H, pyridazine); 2.98 (s, 6H, $N(CH_3)_2$); 1.88 (s, 6H, 2 CH_3); 1.21 (s, 9H, $C(CH_3)_3$).

$C_{14}H_{23}N_5O$ (277.4) Calcd. C 60.62 H 8.36 N 25.25 Found C 60.90 H 8.07 N 25.48

6-(1,1-Dimethylethyl)-2,3-dihydro-3,3-dimethyl-2-[3-(trifluoromethyl)benzoyl]-1,2,4-triazolo[4,3-b]pyridazine (**4h**): Scarlet plates, m.p. 113–115°C (hexane), in 20% yield. – MS: M^+ m/z = 378. – ^{1}H NMR ($CDCl_3$): δ = 6.74 (q, 2H, pyridazine); 7.48–8.2 (m, 4H, aromatic); 2.04 (s, 6H, 2 CH_3); 1.23 (s, 9H, $C(CH_3)_3$).

$C_{19}H_{21}F_3N_4O$ (378.4) Calcd. C 60.31 H 5.59 N 14.81
Found C 60.17 H 5.49 N 14.67

Ethyl 6-(1,1-Dimethylethyl)-2,3-dihydro-3,3-dimethyl-1,2,4-triazolo[4,3-b]pyridazine-2-carboxylate (**4i**)

Method A: To a solution of 2.06 g (10 mmol) of **3a** in 40.0 ml of anhydrous benzene (Linde 4 Å sieves) was added 1.08 g (10 mmol) of ethyl chloroformate. A red color was rapidly developed. The solution was heated with stirring to reflux for 13 h, then cooled and benzene was evaporated in vacuo to give a red crystalline solid. Recrystallization from ethyl acetate gave crystals, m.p. 150–152°C. The mother liquor was chromatographed over 250 g of Woelm 4530 dry-packed silica gel using CH_2Cl_2 as eluting solvent. The orange homogeneous fractions (TLC, E. Merck silica gel 60 F – 254/ethyl acetate, R_f = 0.4) were combined and the CH_2Cl_2 was removed in vacuo to give additional orange-red cubes of **4i**, m.p. 153–155°C. Total yield 1.96 g (70%). – MS: M^+ m/z = 278. – ^{1}H NMR ($CDCl_3$): δ = 6.71 (s, 2H, 7- and 8-H); 4.27 (q, 2H, $-CH_2-$); 1.86 (s, 6H, 2 CH_3); 1.36 (t, 3H, CH_3); 1.19 (s, 9H, *t*Bu). – IR (KBr): 1616 cm^{-1} (C=O).

Method B: To a solution of 0.70 g (3.4 mmol) of **3a** in 50 ml of anhydrous benzene (Linde 4 Å sieves) was added 0.6 ml (0.66 g, 4.0 mmol) of diethyl pyrocarbonate (Aldrich Chem. Co., Milwaukee, Wisconsin) under N_2. No color developed until heating was commenced. After heating to reflux with stirring for 2 h, TLC (Merck 60 F – 254, silica gel/ethyl acetate, R_f = 0.4) showed the reaction was completed. The benzene solvent was removed in vacuo to give a scarlet crystalline solid. Recrystallization from hexane gave scarlet cubes, m.p. 155–157°C. The IR and NMR spectra of this compound were superimposable with those obtained with method A. A mixture m.p. was undepressed. *X*-ray analysis confirmed the structure of **4i**.

$C_{14}H_{22}N_4O_2$ (278.4) Calcd. C 60.41 H 7.97 N 20.13
Found C 60.54 H 8.17 N 19.96

1,1-Dimethylethyl 6-(1,1-Dimethylethyl)-2-(ethoxycarbonyl)-2,3-dihydro-3-methyl-1,2,4-triazolo[4,3-b]pyridazine-3-acetate (**4j**): To a solution of 1.85 g of the (*E*)- and (*Z*)-mixture of **3b** (6.0 mmol) in 100 ml of anhydrous benzene (Linde 4 Å sieves) was added 0.70 g (6.5 mmol) of ethyl chloroformate. The solution was stirred and heated to reflux under N_2 for 13 h. Solvent was removed in vacuo to give a dark-red oil. The oil was chromatographed

over 250 g of Woelm 4530 dry-packed silica gel using 10% ethyl acetate/dichloromethane as eluting solvent. The homogeneous scarlet fractions were collected, combined and solvents removed in vacuo to give 1.15 g of an oil (50%) which crystallized under hexane, m.p. 98–100°C. – ^{1}H NMR ($CDCl_3$): δ = 6.72 (s, 2H, 7- and 8-H); 4.29 (q, 2H, $-CH_2-$); 3.52, 3.46, 2.95, 2.89 (AB quartet, J = 4.8 Hz, CH_2CO); 1.89 (s, 3H, CH_3); 1.35 (m, 12H, *t*Bu + CH_3); 1.20 (s, 9H, *t*Bu).

$C_{19}H_{30}N_4O_4$ (378.5) Calcd. C 60.30 H 7.99 N 14.80
Found C 60.08 H 7.74 N 14.88

Synthesis of Colorless Amides

2,6-Dimethoxybenzoic Acid, 1-[6-(1,1-Dimethylethyl)-3-pyridazinyl]-2-(1-methylethylidene)hydrazide (**2a**): To a suspension of 0.50 g of NaH 60% min. oil dispersion (10 mmol) in 20.0 ml of anhydrous THF (Linde 4 Å sieves) at 25°C was added dropwise a solution of 2.06 g (10 mmol) of **3a** in 20 ml of anhydrous THF. A gas was evolved and the temperature rose to 30°C. Gradually a precipitate of yellow sodium salt appeared. To this suspension at 40°C was added dropwise a filtered solution of 2.10 g (10 mmol) of 2,6-dimethoxybenzoyl chloride (DMBC). A clear amber solution resulted. No scarlet component was present according to TLC (E. Merck, silica gel 60 F – 254/ethyl acetate, R_f = 0.20). The benzene solution was diluted to 200 ml with additional benzene and washed with water, dried ($MgSO_4$), and filtered (animal carbon, Darco 60 G). Removal of the benzene from the filtrate in vacuo gave a crystalline solid. Recrystallization from ethyl acetate gave 2.8 g (76%) of **2a**, m.p. 163–164°C. – IR (Nujol): 1635, 1640 cm^{-1} (shoulder) (C=O). – ^{1}H NMR ([D_6]DMSO) (396 K): δ = 7.63 (s, 2H, pyridazine); 7.22 (t, 1H), 6.55 (d, 2H) (benzoyl protons); 3.70 (s, 6H, OCH_3); 2.04 (d, 6H, $N=C(CH_3)_2$); 1.35 (s, 9H, *t*Bu). – MS: M^+ m/z = 370.

$C_{20}H_{26}N_4O_3$ (370.3) Calcd. C 64.84 H 7.07 N 15.12
Found C 65.12 H 6.84 N 15.20

2,6-Dimethoxybenzoic Acid, 1-[6-(1-Ethyl-1-methylpropyl)-3-pyridazinyl]hydrazide (**2c**): To 5.0 g of **2b** was added 150 ml of 2 N HCl at 25°C, and the mixture was stirred for 12 h. The crystalline solid gradually went into solution. The pH of the clear solution was adjusted to 12 with dilute 2 N NaOH solution, and the reaction mixture was extracted with CH_2Cl_2. The CH_2Cl_2 solution was filtered through PS paper (Whatman) and solvent was removed in vacuo. The resulting semi-crystalline solid was recrystallized from ethyl acetate to give long, lustrous prisms, m.p. 142–145°C, yield 1.5 g (33%). – IR (Nujol): 3310, 3270, 3200 (NH); 1645 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 7.60–6.40 (m, 3H, aryl); 4.97 (s, broad, 2H, NH_2); 3.80 (s, 6H, OCH_3); 2.2–1.5 (m, 4H, aliphatic); 1.20 (s, 3H, CH_3); 0.75 (t, 6H, $2CH_3$ terminal). – MS: M^+ m/z = 358.

$C_{19}H_{26}N_4O_3$ (358.4) Calcd. C 63.67 H 7.31 N 15.63
Found C 63.40 H 7.04 N 15.41

3-(1,1-Dimethylethyl)-6-hydrazinopyridazine: To a solution of 17.9 g (0.10 mol) of 3-chloro-6-(1,1-dimethylethyl)pyridazine[1] in 250 ml of 2-propanol was added 50 ml of anhydrous hydrazine. The mixture was heated to reflux and monitored hourly by thin-layer chromatography (E. Merck silica gel 60 F – 254/ethyl acetate). The reaction was complete after 12 h. The solvent was removed in vacuo and the resulting semi-crystalline mass was dissolved in 800 ml of dichloromethane. The solution was washed with 500 ml of saturated sodium hydrogen carbonate solution. The organic layer was dried over anhydrous magnesium sulfate. Filtration with animal carbon (Darco 60 G) usind a medium porosity sintered-glass funnel gave an amber filtrate. Solvent was removed in vacuo to give a crystalline solid. Crude yield 17.6 g (100%). The crude material was suitable for further reactions. An

analytical sample was prepared by recrystallizing a 1.7 g batch from hexane/ethyl acetate to give 0.80 g (48% recovery) of a crystalline solid of m. p. 100–102 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.37, 7.25, 7.02, 6.91 (q, 2H, pyridazine); 4.2 (broad signal 3H, $NHNH_2$); 1.38 (s, 9H, *t*Bu). – IR (Nujol): 3270 (NH); 1615 cm^{-1} (=N– ⇌ –NH–).

$C_8H_{14}N_4$ (166.2) Calcd. C 57.78 H 8.49 N 33.71
Found C 58.09 H 8.48 N 33.94

X-Ray Structure Analysis of **4b**[10]

Compound **4b** exist as red-orange prisms in the space group $P2_1/C$, $Z = 4$, with unit cell dimensions $a = 9.924(3)$, $b = 18.443(6)$, $c = 11.173(3)$ Å, $B = 113.38° \pm 0.02°$. The calculated density is 1.077 g cm^{-3}. A total of 2905 reflections was measured on an automated four-circle diffractometer, using monochromatic copper radiation. The structure was solved by the direct methods routines of the SHELXTL program library and was refined by the least squares method to $R = 0.0601$, with anisotropic temperature factors for all atoms except hydrogen. Hydrogen atoms were included with isotropic temperature factors at calculated positions.

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[10] Further details and basic data concerning the *X*-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany) by specifying registry number CSD 51484, author, and the reference to this publication.

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