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Study of the Formation and Thermal Decomposition of an Azo-Bridged Tricyclic Ring System

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Dedicated to Prof. Douglas Lloyd on the occasion of his 85th birthday

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1-Amino-2-methyl-1,3-pentadienes were treated with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate to give diazatricyclo[2.2.2.0]octenes and dimethyl 4-methylpyridazine-3,6-dicarboxylate, the product distribution being largely dependent on the nature of the amino substituent. Under similar conditions the analogous 1-morpholino-1,3-butadiene afforded dimethyl pyridazine-3,6-dicarboxylate as the major product. The tricyclic products underwent selective thermal decomposition to give dimethyl 4-methylpyridazine-3,6-dicarboxylate in excellent yield. The proposed mechanism of the formation as well as of the decomposition was supported by quantum chemical calculations and experimental evidence.

Introduction

1,2,4,5-Tetrazines have received considerable attention in fields as diverse as natural product synthesis,[1] plant protection[2] or the synthesis of liquid crystals.[3] The inherent reactivity of the six-membered ring system also makes tetrazines useful reagents for the preparation of other heterocycles such as pyridazines[4] and pyrroles.[5] Probably the most characteristic transformation of tetrazines is their participation in "inverse electron-demand" Diels–Alder reactions with electron-rich olefins,[6] where minor steric differences may lead to a dramatic change in the regioselectivity of the cycloaddition. 4-Amino-1-hetaryl-1,3-butadienes (**1**, R′ = azolyl or azinyl, R′′ = H), for example, were found to react with dimethyl tetrazine-3,6-dicarboxylate (**2**) selectively at the double bond next to the amine moiety to give (hetarylvinyl)pyridazines **3** in moderate to good yields (Scheme 1).[7,8] The analogous 2-methyl-dienamines (**1**, R′′ = CH_3), on the other hand, reacted with two equivalents of tetrazine **2**, through the probable formation of intermediate **4**, and the pyridazine derivatives **5** and **6** were formed in equimolar amounts.[9] Intriguingly, when a 1-amino-2-methyl-1,3-pentadiene (**1**, R′ = R′′ = CH_3) was treated with the tetrazine diester **2** the azo-bridged tricycle **7** was obtained in good yield[10] and with excellent diastereoselectivity. The structure of the product, which was confirmed by X-ray analysis, suggests that the reaction proceeds via a domino "inverse electron-demand" Diels–Alder reaction.[11] The first reaction takes place at the sterically less hindered disubstituted double bond[12] as before, giving **4**, and this then undergoes another intramolecular "inverse electron-demand" Diels–Alder reaction, or alternatively reacts with another molecule of **2**, as previously reported for 1-amino-4-hetaryl-2-methyl-1,3-butadienes.[8]

Results and Discussion

The unique structure of the ring system **7**, and its potential use as a precursor in the synthesis of cage compounds,[13] prompted us to study the scope and limitations of the reaction leading to its formation. A series of amino-substituted 2-methyl-1,3-pentadienes (**8a**–**d**) was prepared in moderate to good yield from 2-methyl-2-pentenal and the appropriate secondary amine in the presence of a mineral clay using microwave irradiation.[14] The dienamines

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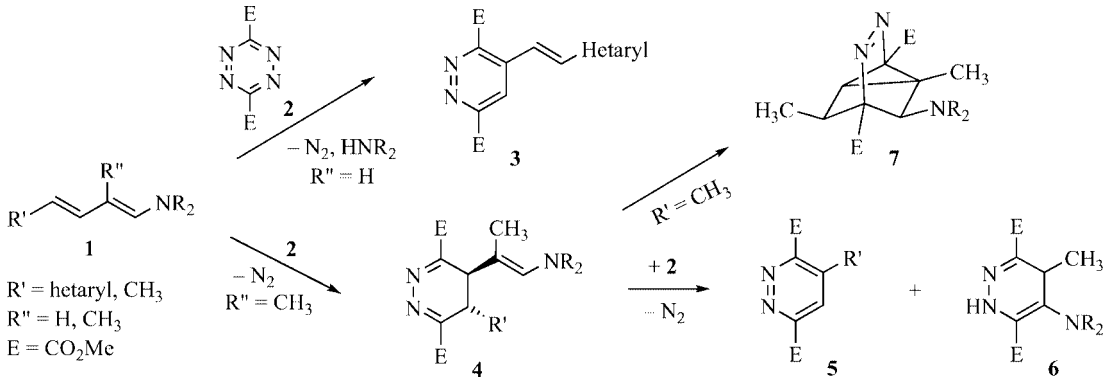


Scheme 1. Alternative reactions of dienamines with the tetrazine diester **2**.

8a–**d** were added to the tetrazine diester **2** in acetonitrile at room temperature and a fast reaction took place, evidenced by the evolution of nitrogen gas. Analysis of the reaction mixtures revealed the concomitant formation of two major new products in different ratios, which were identified as the expected tricycles **7a**–**d** along with the pyridazine derivative **9** (Scheme 2). The ratios of the components (**7**:**9**) were determined by a high-resolution NMR spectroscopic investigation of the crude reaction mixtures (Table 1). The highest proportion of the tricycles **7a**–**d** in the reaction mixture was obtained by the slow addition of a dilute solution of **2** in acetonitrile to a solution of the appropriate dienamine **6a**–**d**. Fast or reverse addition, on the other hand, led to an increase in the proportion of **9** (Table 1). It appears that the higher the delocalisation ability of the lone pair on the nitrogen atom,[15] the higher the proportion of product **9** in the mixture.

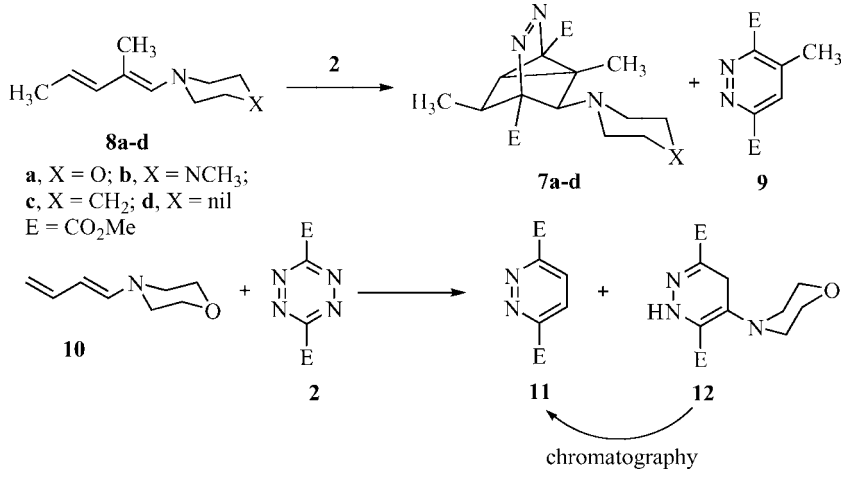
The tricyclic products **7a** and **7b** were isolated from crystallisation, while the lower proportion of **7c** and **7d** in the corresponding reaction mixtures made it impossible to obtain them in the pure form. Attempts to separate the products using column chromatography were also in vain, as the tricycles **7c**,**d** partly decomposed under the applied conditions to give **9** and other byproducts. When 1-morpholino-1,3-butadiene (**10**) was treated with the tetrazine diester **2**,

Table 1. Product distribution (%) of the reaction of dienamines **6a**–**d** with the tetrazine diester **2** (determined by NMR spectroscopy).

	Slow addition		Inverse addition	
	7	**9**	**7**	**9**
a	>95	<5	75	25
b	75	25	55	45
c	50	50	40	60
d	15	85	>5	<95

TLC and NMR spectroscopic analysis of the crude reaction mixture revealed the formation of a major product **11** and a side product **12**, the latter being converted into **11** when chromatographic separation was attempted (Scheme 2). Again, slow addition of the tetrazine **2** to morpholinobutadiene **10** leads to a purer product. When two equivalents of tetrazine **2** were added to **10** the isolated amount of **11** was in excess of **10**, indicating the presence of the **12**→**11** transformation in solution. We were unable to find any evidence of the formation of a tricyclic product.[16,17]

Attention was now turned to the directed decomposition of these molecules. Irradiation of **7a** in different solvents led to the formation of mixtures that we were unable to separate and characterise. However, thermal decomposition experiments were more successful, not only in the prepara-



Scheme 2. The reactions of 1-aminobutadiene derivatives with the tetrazine diester **2**.

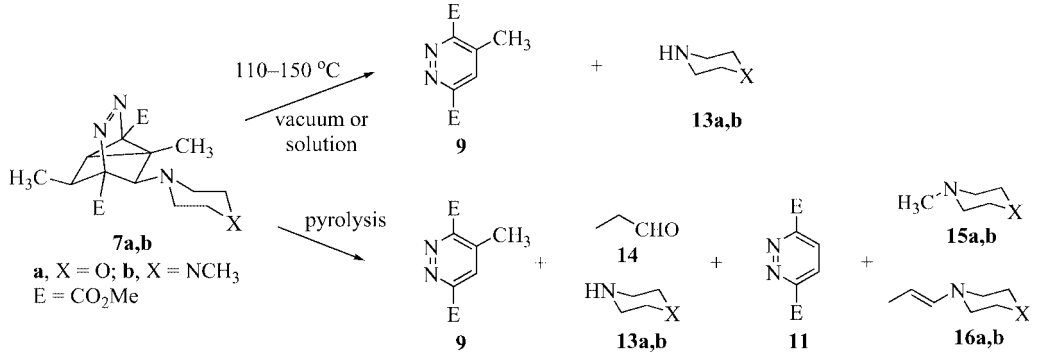
tive sense, but in that they also provided an insight into the so far unanswered details of the formation of **9**. Heating **7a** or **7b** in vacuo above its melting (decomposition) point leads to the formation of **9** in quantitative yield[18] (Scheme 3). By trapping the volatile side products we were also able to detect the formation of the appropriate amine (**13a**,**b**). Refluxing **7a** or **7b** for a prolonged time in toluene or xylene gave the same results. Removal of the volatiles gave only the pyridazine diester **9**, and the presence of the appropriate amine (**13a**,**b**) can also be detected in the gas phase by GC analysis. In order to achieve significant decomposition the temperature had to be above 100 °C, both in solution and in vacuo.

Examination of the thermal decomposition equation brought our attention to the fact that there is another fragment of the molecule that has not been accounted for. Formation of the pyridazine diester **9** and the amine **13** also implies the possible evolution of propyne. Samples of the tricycles **7a**,**b** were heated at 200, 250 and 300 °C, and the volatile components that formed were injected into a GC-MS apparatus using an argon stream. Analysis of the chromatograms unambiguously proved the presence of the appropriate secondary amine **13a**,**b** and a C_3 fragment, although not in the form of propyne but propanal (**14**). Dimethyl 4-methylpyridazine-3,6-dicarboxylate (**9**) was also identified in the pyrolysate along with varying minor amounts (up to 6%) of other products, such as dimethyl pyridazine-3,6-dicarboxylate (**11**), and the *N*-methyl (**15a**,**b**) and *N*-propenyl (**16a**,**b**) derivatives[19] of the appropriate amine (Scheme 3). The formation of propanal was rationalised by hydrolysis of the enamines **16a**,**b** under the analysis conditions.[20] Increasing the pyrolysis temperature apparently always leads to an increase in the proportion of side products. We assume that the initial step of the thermal decomposition of **7** is a retro-Diels–Alder reaction (Scheme 4) that leads either to **17** or **18**. Formation of the pyrolysis products stems from **18**, which is in a tautomeric equilibrium with **19**. This compound may be represented by two mesomeric forms, the neutral form A and the zwitterionic form B. In this latter form the rotation of the side chain around the single bond gives rise to **20**, which is capable of undergoing a [1,5] sigmatropic rearrangement to give either **21** (route a – hydrogen shift) or **22** (route b – methyl shift).

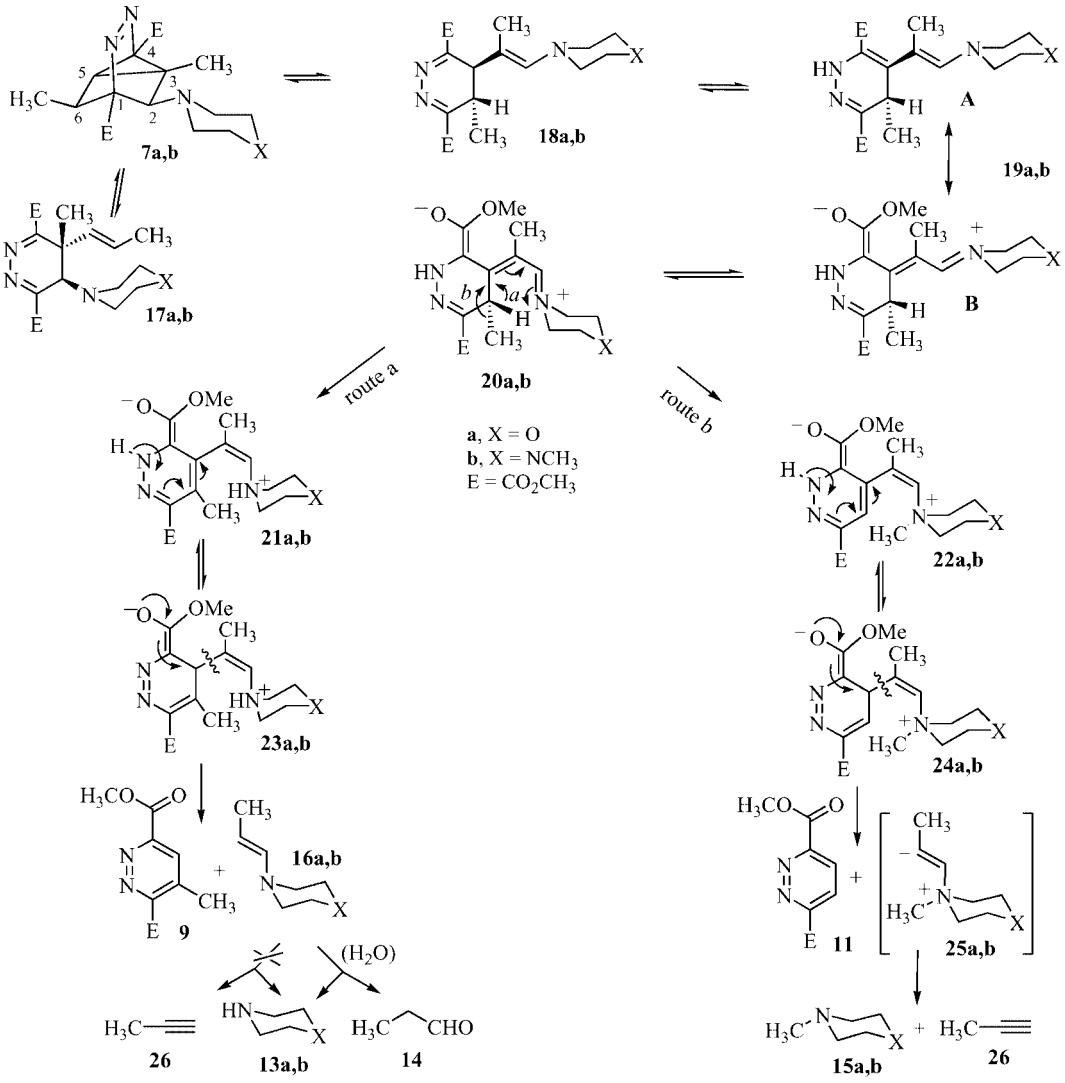
The analogous tautomeric equilibria of **21** and **22** give rise to **23** and **24**, respectively, followed by an elimination step that leads to the formation of the pyridazine diester derivatives and the enamines (**9** and **16** from **23**; or **11** and **25** from **24**). Compounds **25a** and **25b** are expected to afford the *N*-methylated amines **15a**,**b** and propyne (**26**) spontaneously by elimination, while the enamines **16a**,**b** might undergo elimination to furnish the amine **13a**,**b** and propyne (**26**), or in the presence of water **16a**,**b** might hydrolyse to the amine **13a**,**b** and propanal (**14**). The higher proportion of **9** and **13a**,**b** in the product (compared to **11** and **15a**,**b**) is in good accordance with the higher migratory aptitude of the hydrogen compared with the methyl group.

The key to the course of the decomposition is the direction of the opening step. In the tricycle there are two similar six-membered rings that could break up in a retro "inverse electron-demand" Diels–Alder reaction to generate either **17a**,**b** or **18a**,**b**. The X-ray structure of **7a** shows[10] a strained structure with certain carbon–carbon bonds stretched beyond 158 pm. A comparison of the bond length data for the carbon–carbon bonds (Scheme 4) that might break up in the first step (158.9 pm for C1–C2 and 158.8 pm for C3–C4 versus 151.8 pm for C4–C5 and 158.1 pm for C6–C1) suggests that the formation of **18a**,**b** is energetically favoured over **17a**,**b**. Further support of this hypothesis comes from quantum chemical studies. The optimised structures for **7a–d**, **17a–d** and **18a–d** as well as the appropriate **7**–**17** and **7**–**18** transition state geometries were calculated on the DFT/6-31G level and their energies were refined in single point calculations using the 6-31G(d) set and the CPCM solvent model with settings corresponding to acetonitrile.[21] The results are summarised in Figure 1 and Table 2.

According to the calculations the formation of intermediates **18a–d** from **7a–d** is preferred both kinetically and thermodynamically. The differences in the calculated energies of the **17**–**18** pairs, as well as the **7**–**17** and **7**–**18** transition states is significant, favouring the latter compounds and reaction paths in all cases. The activation barrier of the preferred (and observed) **7**–**18** transformation shows a marked dependence on the electron-donating nature of the amine, illustrated by the significant 18 kJ/mol difference between the morpholine and pyrrolidine analogues. This finding supports an earlier mechanism suggestion[10] of a zwit-



Scheme 3. The thermal decomposition of **7a**,**b**.



Scheme 4. The proposed decomposition pathway of **7a**,**b** in the pyrolysis experiments.

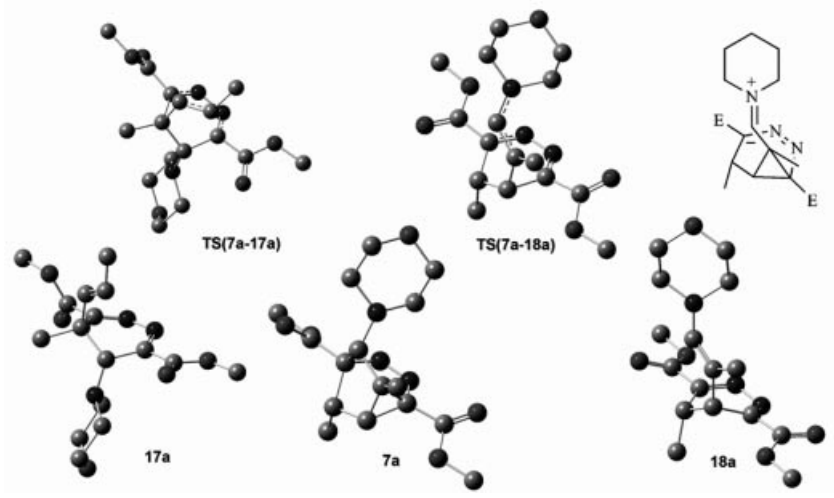


Figure 1. The calculated geometries of **7a**, **17a**, **18a**, and the TS(**7a**–**17a**) and TS(**7a**–**18a**) transition states and the zwitterionic representation of TS(**7a**–**18a**). The hydrogen atoms are omitted for clarity.

Table 2. Calculated relative heats of formation (kJ/mol) of compounds **7a**–**d**, **17a**–**d**, **18a**–**d** and transition states along the **7**–**17** and **7**–**18** path.

	17	TS(**7**–**17**)	**7**	TS(**7**–**18**)	**18**
a	48.27	141.39	0	83.58	9.30
b	49.03	142.57	0	80.50	11.12
c	49.52	144.04	0	75.80	10.21
d	38.84	135.78	0	65.56	7.39

terion-like transition state (Figure 1) with an iminium substructure. The lower activation barrier for the retro reaction in the presence of the more electron-donating amines might also account for the increased amount of **9** in the reaction of the dienamines **6c**,**d** with **2**. Not only is the intermediate of type **18** formed more easily from the tricycle **7** in these processes, its rearrangement to **9** or **11** is further facilitated by the increased electron-donating ability of the amine moiety through the stabilisation of the zwitterionic transition states.

Conclusions

In general, the reaction of electron-rich conjugated dienamines (**6a**–**d**, **10**) with tetrazines takes place at the sterically less hindered double bond of the diene chain. The fate of the initially-formed intermediate is largely influenced by the nature of the amine substituent. In certain cases we have been able to identify and/or isolate a product (**7a**–**d**) containing a strained azo-bridged tricyclic system that in some cases undergoes a selective retro "inverse electron-demand" Diels–Alder reaction on heating, leading through a cascade of tautomeric and sigmatropic shifts to the pyridazine derivative **9**. This explanation for the selectivity that is experienced is also supported by GC-MS identification of the minor products and quantum chemical modelling of the key reaction step.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AX 300 spectrometer at 300 and 75 MHz, respectively; chemical shifts (δ) are reported in ppm units by reference to Me_4Si and coupling constants (J) are reported in Hz. All Py-GC/MS measurements were carried out with a CDS Pyroprobe 2000 equipped with a platinum coil and quartz sample tube. The pyrolyser was coupled to a Hewlett–Packard 5985B GC/MS instrument. A sample (about 250 μg) was pyrolysed at 200–300 °C for 20 s. Helium carrier gas at a flow rate of 20 mL/min purged the pyrolysis chamber, which was kept at 120 °C. The separation of pyrolysis products was performed with a BP-10 fused-silica capillary column (25 m long, 0.2 mm I.D., 0.25 μm of 86% dimethyl/14% cyanopropylphenyl silicone phase, Chrompack), temperature programmed at 10 °C/min heating rate from 50 to 270 °C. The GC/MS interface was kept at 300 °C. The quadrupole mass spectrometer was operated in the EI mode at 70 eV. TLC was carried out on silica plates using UV detection and iodine as a developing agent. The preparation of **2**,[22] **6a**–**d**[10,23] and **10**[24] was reported earlier.

Reaction of Dienamines 6a–d and 10 with Dimethyl 1,2,4,5-Tetrazine-3,6-dicarboxylate (2)

General Procedure: The solution of **2** (0.198 g, 1 mmol) in acetonitrile (20 mL) was added dropwise from a glass capillary (ca. 3–4 hours) to the stirred solution of the dienamine (1 mmol) in acetonitrile (20 mL). The resulting solution was stirred for another hour and the solvent was evaporated under reduced pressure. The residue was recrystallised from ethyl acetate or chromatographed over silica gel using hexane/ethyl acetate mixtures as the eluent.

Tricycle 7a:[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.02 (s, 6 H), 3.58 (s, 1 H), 3.53–3.44 (m, 8 H), 2.63 (q, J = 6.9 Hz, 1 H), 2.58 (s, 1 H), 2.25 (s, 3 H), 1.33 (s, 3 H), 0.41 (d, J = 6.9 Hz, 3 H) ppm.

Tricycle 7b:[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (s, 3 H), 3.95 (s, 3 H), 3.54 (s, 1 H), 2.58 (q, J = 6.9 Hz, 1 H), 2.51 (s, 1 H), 2.32–2.18 (m, 8 H), 2.15 (s, 3 H), 1.25 (s, 3 H), 0.37 (d, J = 6.9 Hz, 3 H) ppm.

Tricycle 7c: ^{1}H NMR (300 MHz, $CDCl_3$, crude product): δ = 3.95 (s, 6 H), 3.52 (s, 1 H), 2.60–2.36 (m, 6 H), 2.10 (s, 3 H), 1.52–1.20 (m, 9 H), 0.35 (d, J = 6.9 Hz, 3 H) ppm.

Tricycle 7d: ^{1}H NMR (300 MHz, $CDCl_3$, crude product): δ = 3.94 (s, 6 H), 3.50 (s, 1 H), 2.67–2.30 (m, 6 H), 2.10 (s, 3 H), 1.62–1.40 (m, 7 H), 0.35 (d, J = 6.9 Hz, 3 H) ppm.

Dimethyl 5-Methylpyridazine-3,6-dicarboxylate (8):[25] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10 (s, 1 H), 4.08 (s, 3 H), 4.06 (s, 3 H), 2.63 (s, 3 H) ppm.

Dimethyl Pyridazine-3,6-dicarboxylate (10):[26] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 2 H), 4.07 (s, 6 H) ppm.

Pyrolysis of the Tricyclic Compounds 7a,b

In Solution: The tricyclic compound **7a** or **7b** (0,2 mmol) was heated in dry xylene (5 mL) at reflux for 6 h. The solvent was removed under reduced pressure to give dimethyl 4-methylpyridazine-3,6-dicarboxylate (**9**) in quantitative yield. The presence of the appropriate amine (**13a** or **13b**) in the gas phase could be detected by GC.

In Solid State: The tricyclic compound **7a** or **7b** (0,2 mmol) was placed at the bottom of a glass tube and half of the tube was inserted horizontally into a Kugelrohr oven, while the other half was cooled by dry ice. After evacuation of the tube (10^{-1} mbar) the oven was heated gradually (ca. 15 °C/min) to 150 °C. At around 120 °C the colour of the starting material turned yellow, a white solid started to condense in the heated part of the tube and a colourless liquid condensed at the parts cooled by dry ice. The heating and evacuation were stopped and the tube was cut into three pieces following the visible borders. The fractions were analysed by NMR spectroscopy. The colourless liquid consisted mostly of the appropriate amine **13a**,**b**, the white solid was identified as dimethyl 4-methylpyridazine-3,6-dicarboxylate (**9**), while the yellow solid showed signals belonging to compound **9** along with a minor component that was not identified.

Acknowledgments

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[17] We also tried to extend the process to other tetrazine derivatives such as 3,6-di(2′-pyridyl)tetrazine and 3,6-bis(trifluoromethyl)tetrazine, but the reactions led to complex mixtures without any apparent evidence of the formation of the appropriate tricycles.
[18] Flash vacuum pyrolysis of **7a** at various temperatures also gave **9** exclusively. Hamish McNab – unpublished results.
[19] The presence of **16a** was unambiguously proved by a comparison of the mass spectroscopic fragmentation patterns of independently prepared samples of *N*-propenylmorpholine and *N*-allylmorpholine. Signals arising from **16a** were also detected in the NMR spectra of the volatile fraction in the vacuum pyrolysis of **7a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.7 (d, J = 15.8 Hz, 1 H), 4.43 (dq, J = 15.8, 7.5 Hz, 1 H), 3.75 (t, J = 5.8 Hz, 4 H), 2.74 (t, J = 5.8 Hz, 4 H), 1.63 (d, J = 7.5 Hz, 3 H) ppm.
[20] Although the pyrolysed samples were of analytical purity, we were unable to avoid the presence of absorbed water in the pyrolysis-GC-MS apparatus, which might have led to the formation of the aldehyde.
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