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Cycloaddition of 1,4-Dimethyl-2,3-dimethylene-hexahydropyrazine to Electron Deficient Alkenes

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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Abstract—The mechanism of cycloaddition of 1,4-dimethyl-2,3-dimethylenehexahydropyrazine to moderately and highly electrophilic alkenes is probed by stereochemical studies. Retention of configuration for the *E*/*Z*-isomeric alkenes fumaro- and maleonitrile and loss of stereospecificity for dimethyl dicyanofumarate and dimethyl dicyanomaleate show that the mechanism of cycloaddition (concerted or stepwise) depends on the gap between nucleophilic and electrophilic character of the reaction partners. The behavior of 1,4-dimethyl-2,3-dimethylenenehexahydropyrazine follows that of other amino-substituted dienes. © 2000 Published by Elsevier Science Ltd.

Introduction

Normal Diels–Alder reactions most easily occur between donor-substituted dienes and acceptor-substituted dienophiles. Frontier molecular orbital theory provides a simple explanation on the basis of a concerted bond formation.[1,2] Most of these cycloadditions indeed take place via a concerted pathway. However, FMO theory does not account for: (i) higher reactivity of unsymmetrically donor-substituted dienes as compared to the corresponding symmetrically substituted molecules; and (ii) for a change to stepwise reaction when diene and dienophile are strongly donor-, respectively, acceptor substituted. More advanced theoretical treatments like valence bond diagrams offer an easy rationalization of these phenomena.[3] Nowadays, it is common sense that (4+2)-cycloadditions which found a convincing, but not complete mechanistic description within the rules of conservation of orbital symmetry[4] may take place in a synchronous or stepwise manner depending on the nature and number of substituents on diene and dienophile.

In a series of experimental and theoretical investigations, we have studied the influence of one or several dialkylamino or alkoxy groups in the diene on reactivity and mechanism of cycloadditions to strongly acceptor-substituted dienophiles. It was shown by ab initio calculations that coulombic interactions are responsible for the increased reactivity of non-symmetrically substituted reaction partners due to charge separation in the transition states.[5] A change from concerted to stepwise ionic reaction was found when (*E*)-1-(dimethylamino)-1,3-butadiene reacts with dimethyl dicyanofumarate. The intermediate zwitterion could be detected spectroscopically by means of stopped-flow techniques.[6] 1,1-Bis(dimethylamino)-1,3-butadiene, being confined to an antiperiplanar conformation, gave a stable, isolable zwitterion with the same dienophile which decomposed on heating.[7,8] Zwitterions could be trapped in reactions of 1,1-dimethoxy-1,3-butadiene with highly electrophilic alkenes, too.[9] Symmetrically 1,4-bis(dimethylamino)-substituted 1,3-butadienes, either in open or in synperiplanar fixed structure, still provided another pathway of cycloaddition to highly electron-deficient alkenes, involving an initial electron transfer, followed by zwitterion- and cycloadduct formation.[10–13]

So far, we have examined mono-, 1,1-bis-, and 1,4-bis-(dimethylamino)-substituted dienes with respect to their cycloaddition behavior towards highly electrophilic alkenes. Here, we report on a study of the reactions of a 2,3-diamino-substituted diene with strong acceptor dienophiles. 1,4-Dimethyl-2,3-dimethylenehexahydropyrazine (**1**), the model diene, has been introduced as diene in cycloadditions by Ahlbrecht et al.[14] Reactions were reported for moderately activated dienophiles. It was concluded from the cycloaddition of **1** to diethyl maleate, which led to a mixture of stereoisomeric cycloadducts, that these cycloadditions are two-step in nature. As our experience had shown that, due to its easy base-catalyzed isomerization, dimethyl maleate is not a good candidate for stereochemical studies, we decided to test the stereospecificity of the

Keywords: (4+2)-cycloaddition; Diels–Alder reaction; reaction mechanism; stereospecificity.

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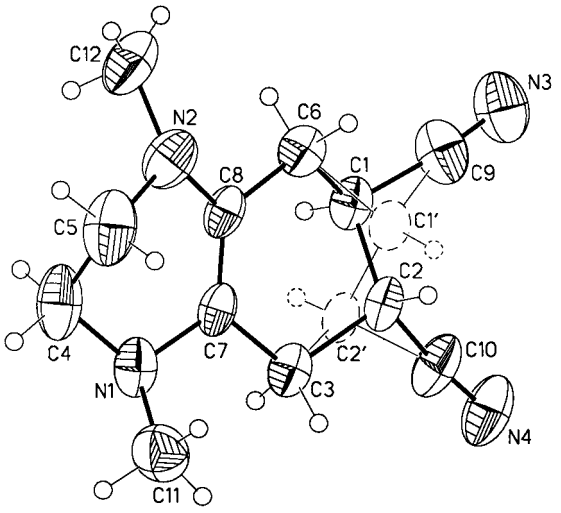


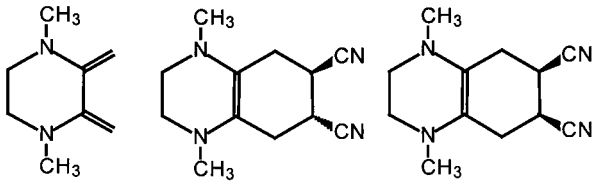
Figure 1. X-Ray structure of the cycloadduct **2** of 1,4-dimethyl-2,3-dimethylenehexahydropyrazine and fumaronitrile.

cycloaddition of **1** to moderately activated dienophiles such as fumaro- and maleonitrile before reporting on reactions of **1** with dimethyl dicyanofumarate, dimethyl dicyanomaleate, and tetracyanoethene.

Results and Discussion

(*E*/*Z*)-1,2-Dicyanoethene (fumaro- and maleonitrile). Ahlbrecht et al.[14] described cycloadditions of **1** to a number of dienophiles and isolated 55–90% of the corresponding cycloadducts. Two-step mechanisms via zwitterions were assumed because diethyl maleate did not add stereospecifically to **1**. Our experience with dialkylamino-substituted dienes had shown that dialkyl maleate easily isomerizes to the fumarate derivative under the influence of base.[8,12,13] Thus, the 'non-stereospecific' cycloaddition of diethyl maleate, normally a sign for a two-step mechanism, probably was the result of isomerization of diethyl maleate prior to addition. Fumaro- and maleonitrile are less prone to isomerization by base and have been used in our studies several times to demonstrate stereospecific cycloaddition of activated dienophiles to dialkylamino-substituted dienes.[12,13] Ahlbrecht et al. only reported the reaction of **1** with fumaronitrile, thus being not able to prove or disprove stereospecificity. Therefore, the cycloaddition of fumaronitrile was reinvestigated and complemented by the reaction of **1** with maleonitrile.

Equimolar solutions of **1** and fumaro- or maleonitrile, respectively, in THF (0.5 M) led to the cycloadducts in 48% (Lit.[14] 55%) (**2**) and 84% (**3**) isolated yield, respectively. The reactions were carried out at room temperature and in the absence of oxygen to avoid side reactions of the oxidation sensitive diene. Analysis of the crude reaction mixtures by ^{1}H NMR spectroscopy in the presence of a standard revealed 94 and 89% yield, respectively. The products cannot be easily distinguished by their ^{1}H NMR spectroscopic data because the spectra proved to be very similar, showing almost identical chemical shifts for corresponding protons. In particular, it was not possible to determine the relative position of the cyano groups in **2** and **3**.

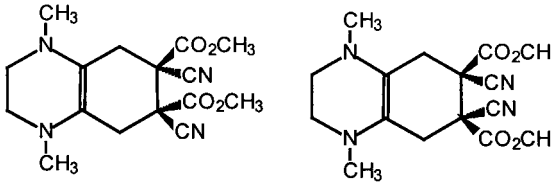


1 **2** **3**

The ^{1}H NMR spectrum of a 1:1 mixture of **2** and **3** revealed that the cycloadducts are not identical. *N*-Methyl signals appeared at δ=2.497 (**2**) and 2.504 ppm (**3**), and the *N*-methylene protons at δ=2.898 (**2**) and 2.903 ppm (**3**). Analysis of the crude reaction mixtures showed that within the limits of ^{1}H NMR sensitivity the cycloadducts are mutually not contaminated.

In order to prove that the reactions occur with retention of alkene stereochemistry, an X-ray analysis was carried out for crystalline compound **2**. Fig. 1 displays an ORTEP plot of the fumaronitrile adduct. Although the cyclohexene unit is disordered it can be seen that the two cyano groups occupy equatorial positions, proving their *trans*-arrangement. By exclusion, it can be stated that cycloadduct **3** must have the *cis*-arrangement of the cyano groups. Thus, it can be concluded that **1** adds stereospecifically to the moderately activated dienophiles fumaro- and maleonitrile.

Dimethyl dicyanofumarate and dimethyl dicyanomaleate. The reaction of **1** with both dienophiles led to mixtures of cycloadducts **4** and **5**. Analysis of ^{1}H NMR spectra of the crude reaction mixtures indicated exclusive formation of these two 1:1 cycloadducts for each dienophile. Due to the structure of diene and dienophile, only two isomeric (4+2)-cycloadducts are possible (**4** and **5**). No indication was found that (2+2)-cycloadducts were formed. Quantitative ^{1}H NMR analysis in the presence of a standard revealed that dimethyl dicyanofumarate led to the mixture of isomers in 87% combined yield, while dimethyl dicyanomaleate gave 96% of the product mixture. The ratio of isomers did not depend on the nature of the dienophile or on temperature. It amounted to 35:65 favoring **5**.



4 **5**

When THF solutions of **1** and dimethyl dicyanofumarate were combined at room temperature the mixture immediately turned deep-red accompanied by slight warming. Within two hours, the color faded to light-red. When the reaction was carried out similarly at −60°C—due to the low solubility of the alkene at this temperature the solution is heterogeneous—the solution turned deep-blue on slowly

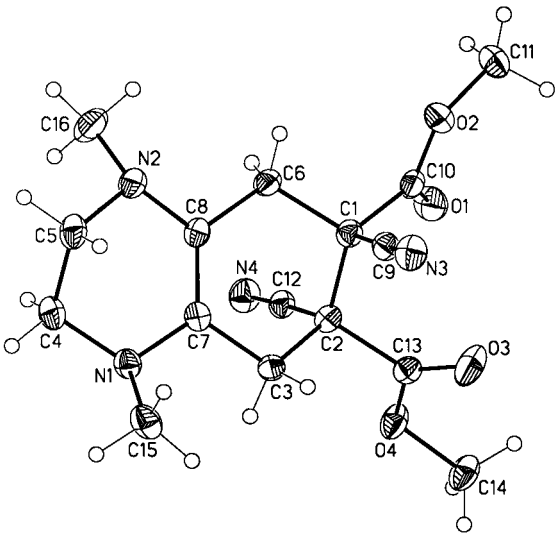


Figure 2. X-Ray structure of one of the stereoisomers of the cycloaddition of 1,4-dimethyl-2,3-dimethylenehexahydropyrazine to dimethyl dicyanofumarate (**4**).

adding the diene to the dienophile suspension. Only when warmed-up to room temperature or when the diene was added fast, the blue color could be avoided in favor of the light-red coloration observed above. This color phenomenon cannot be explained easily. It might be speculated that it indicates a charge transfer (CT) complex or the formation of a zwitterion. Previously in the reaction of 1,1-bis(dimethylamino)-1,3-butadiene with tetracyanoethene, a blue color observed at −40°C had been attributed to a zwitterion by means of ^{1}H and ^{13}C NMR spectroscopy.[7,8]

For further clarification of the mechanistic details, an experiment was carried out in which equimolar amounts of **1** and dimethyl dicyanofumarate were dissolved separately in d[8]THF and consecutively given into an NMR tube cooled to liquid-nitrogen temperature. This way, the components were captured in frozen solutions, one above the other. The procedure could not avoid the appearance of a blue colored interface between the two frozen compartments. When warmed to −80°C, the solid melted and was mixed immediately by shaking. The ^{1}H NMR spectrum recorded at −70°C three minutes after mixing only displayed signals of the cycloadducts, although the solution was colored deep-blue. Therefore, the blue color cannot be correlated with an intermediate of the cycloaddition process, but must be associated with a side reaction.

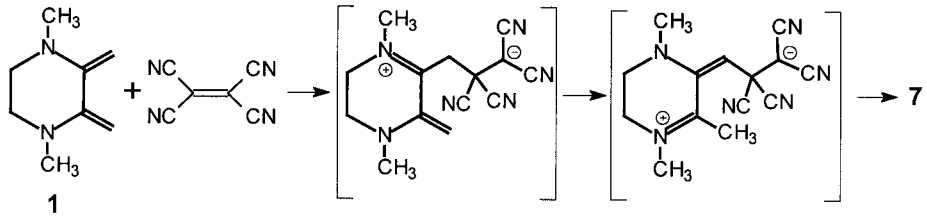
The assignment of NMR spectroscopic data with respect to the stereochemical relationship of the cyano groups in the cycloadducts proved to be impossible. However, the minor component of the two isomers crystallized and could be analyzed by X-ray crystallography. This compound displayed the stereochemistry of dimethyl dicyanofumarate, thus corresponding to **4**. Fig. 2 shows an ORTEP plot of the structure.

After stereochemical identification of the minor component by X-ray analysis, NMR data of both compounds could be assigned with the help of one- and two-dimensional NMR experiments (see Experimental).

The results support a two-step mechanism of cycloadduct formation, presumably via zwitterionic intermediates. The observation that dimethyl dicyanomaleate isomerizes in solution[12,13,15] in particular in the presence of base might be taken as an argument against this hypothesis. But at low temperature, isomerization is much slower than the rate of cycloadduct formation.[8] Formation of both **4** and **5** from both dienophiles also speaks against isomerization of dimethyl dicyanomaleate to the thermodynamically more stable dimethyl dicyanofumarate prior to cycloaddition. In case of a concerted reaction, the thermodynamically more stable dimethyl dicyanofumarate should have exclusively reacted to **4** and not to a mixture of **4** and **5**. The observation that the ratio of **4** to **5** is identical regardless which dienophile is used points to a thermodynamic equilibration of the intermediate prior to product formation.

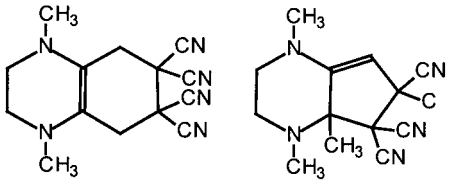
Attempts were made to trap a putative zwitterionic intermediate. This had been successful in the case of 1,1-bis-(dimethylamino)-1,3-butadiene[7,8] and 1,1-dimethoxy-1,3-butadiene[9] as dienes and dimethyl dicyanofumarate as dienophile using either methanol or picric acid as trapping agents. Such experiments might be difficult with **1** as it dimerizes under the influence of protons.[14] For this reason, the trapping experiments were carried out at low temperature in such a way that the dienophile which is only partly soluble at this temperature was suspended in methanol at −60°C. The diene, dissolved in cooled THF (−60°C), was added dropwise to the suspension of the dienophile. During this procedure, the dienophile dissolved completely. After removing the solvents at −30°C in vacuo, solid material was isolated which proved to be a mixture of **4** and **5** (^{1}H NMR analysis). Additional signals, which might be due to a trapped zwitterion, were present to such a low extent only that neither identification by isolation nor by spectroscopic means was possible. Interestingly, the ratio of **4** to **5** changed from 35:65 to 20:80 under these conditions. Trapping experiments with picric acid were also not successful. These results indicate that ring closure of the intermediate is faster than trapping probably due to the synperiplanar diene unit. A similar observation had been made for a bis(dimethylamino)-substituted bis(exomethylene)bicyclooctene where the diene unit is fixed in a synperiplanar conformation.[12,13]

Tetracyanoethene (TCNE). Tetracyanoethene is one of the most reactive dienophiles in Diels–Alder reactions. Since it does not carry a stereochemical label it cannot be used as mechanistic probe like *E*/*Z*-isomeric alkenes. On reacting equimolar amounts of this dienophile and **1** in THF at room temperature, the reaction mixture immediately turned dark-red and heated slightly. At −60°C, the solution became dark-purple under the same conditions. Removal of the solvent in both cases led to a dark-brown solid, which was 93% in (4+2)-cycloadduct **6** (quantitative NMR determination). A side product was present in 7% yield when the reaction was carried out at room temperature. At −60°C, **6** and the side product were formed in a ratio of 87:13. Purification of the crude reaction product proved to be difficult due to the thermal instability of **6**. Finally, pure material was obtained through repeated triturating with cold ethanol. This led to **6** as a slightly yellow solid in 70% yield. The side product was isolated after column chromatography of the



Scheme 1.

crude reaction mixture on silica with chloroform as eluant. Cycloadduct **6** was destroyed under these conditions, however, fractions could be obtained in which the side product was enriched. Adduct **6** was characterized by spectroscopic techniques and elemental analysis. Only small amounts of the side product could be isolated in pure form, but it was possible to characterize it as **7**.



6 **7**

The molecular mass of **7** corresponds to that of cycloadduct **6** as determined by high-resolution MS. According to the ^{1}H NMR spectrum, one olefinic proton (4.83 ppm, singlet) and three different methyl groups (2.76, 2.50, and 1.63 ppm) are present. DEPT spectra, inverse CH-COSY and inverse COLOC spectra established structure **7**. Diastereomeric cyclopentene derivatives of related structure were reported for products of the reaction of 2,3-dimorpholino-1,3-butadiene and β-nitrostyrene.[16] Their NMR spectroscopic properties are very similar to those of **7** and moreover, the structure of one of these diastereoisomers could be established by X-ray crystallography.[16] In both cases, the unexpected formation of cyclopentene derivatives can be explained by a two-step mechanism via zwitterionic intermediate involving rearrangement.

Although the formation of **6** does not allow mechanistic conclusions as to the concerted or non-concerted nature of the reaction, isolation of **7** is a strong hint for at least competing concerted and stepwise reaction. Scheme 1 presents a plausible mechanism which follows the suggested pathway for the formation of diastereomeric cyclopentene derivatives in the reaction of 2,3-dimorpholino-1,3-butadiene with β-nitrostyrene.[16] Thus, TCNE does not seem to behave different from dimethyl dicyanomaleate and dimethyl dicyanofumarate, in the sense that highly electrophilic dienophiles undergo two-step cycloaddition to **1**.

Conclusion

1,4-Dimethyl-2,3-dimethylene-1,4-hexahydropyrazine (**1**) adds to *E*/*Z*-isomeric fumaro- and maleonitrile in high yields in a stereospecific manner. The retention of stereochemistry points to a concerted reaction with this moderately activated pair of dienophiles. Highly electrophilic dienophiles dimethyl dicyanofumarate, dimethyl dicyanomaleate, and TCNE undergo two-step addition to **1** resulting in a non-stereospecific formation of (4+2)-cycloadducts for *E*/*Z*-isomeric alkenes. The identical ratio in which **4** and **5** are formed points to stereochemical equilibration of the zwitterionic intermediate. Zwitterions could not be trapped, neither by methanol nor by picric acid. Diene **1** behaves similarly to the other dialkylamino-substituted dienes studied previously.[6–13] TCNE represents an exception by leading in addition to the regular (4+2)-cycloadduct to a cyclopentene derivative in low yield which is typical for 2,3-diamino-1,3-butadienes being not rigid in a synperiplanar conformation.[16]

Experimental

General remarks

^{1}H and ^{13}C NMR spectra: Varian Gemini-200 and Bruker AMX-300. Internal standard TMS. High resolution MS: Fisons Instruments VG ProSpec 300 (70 eV). IR: Perkin–Elmer 1600 series FT-IR. All operations were carried out under argon 5.0 (purity 99.999%) which was further purified by passing it over an oxygen absorber (BASF R3-11) at 100°C, and consecutively through 50 cm long glass tubes filled with KOH, silica, and P_2O_5. Glassware was thoroughly dried in vacuo by heating with a heat gun. Solvents were dried and distilled under Ar. Quantitative ^{1}H NMR (200 MHz) determinations were performed with 1,4-dioxane as standard in benzene.

Materials

Fumaronitrile and TCNE were commercially available (Aldrich). 1,4-Dimethyl-2,3-dimethylenehexahydro-1,4-pyrazine,[14] maleonitrile,[17] dimethyl dicyanofumarate,[18] and dimethyl dicyanomaleate[15] were prepared according to literature procedures.

***trans*-6,7-Dicyano-1,4-dimethyl-1,2,3,4,5,6,7,8-octahydroquinoxaline (2).** Fumaronitrile (0.391 g, 5.00 mmol) and **1** (0.691 g, 5.00 mmol) were dissolved in 10.0 ml of dry and Ar saturated THF in Schlenk-vessels each. The diene solution was added dropwise (dropping funnel) to the dienophile solution at room temperature. After 3 d, the solvent was removed in vacuo (1.0 Pa) from the orange solution. The residue was partly solid, partly oily. Yield of the crude product: 94% (quant. ^{1}H NMR). The air sensitive product was crystallized from pentane/THF: yield 0.511 g (48%) (Lit.[14] 55%). Mp 107–108°C dec. (Lit.[14] 107–109°C dec.).

^{1}H NMR (200 MHz, $CDCl_3$): δ=3.18–3.06 (m, 2H, (C*H*(CN)), 2.90 (s, 4H, NCH_2), 2.78–2.42 (m, 4H, CH_2), 2.50 (s, 6H, NCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ=119.2 (*C*=*C*), 118.8 (*C*N), 48.2 (N*C*H_2), 40.2 (N*C*H_3), 28.8 ((*C*H(CN)), 28.3 (*C*H_2). Additional NMR experiments: CH-COSY, inverse COLOC. IR (KBr): ν=2966–2815 cm^{-1} (CH), 2242 (CN), 1636 (C=C). MS (70 eV): *m/z* (%): 216 (97) [M$^+$], 201 (100), 187 (6), 163 (7), 138 (22), 123 (28), 110 (10), 84 (8). HR-MS (70 eV): $C_{12}H_{16}N_4$: calcd 216.1375, found 216.1353. $C_{12}H_{16}N_4$ (216.3): calcd C 66.64, H 7.46, N 25.90; found C 66.29, H 7.37, N 26.05.

***cis*-6,7-Dicyano-1,4-dimethyl-1,2,3,4,5,6,7,8-octahydroquinoxaline (3):** Maleonitrile (0.391 g, 5.00 mmol) and **1** (0.691 g, 5.00 mmol) were dissolved in 10.0 ml of dry and Ar saturated THF in Schlenk-vessels each. The diene solution was added dropwise (dropping funnel) to the dienophile solution at room temperature. After 3 d, the solvent was removed in vacuo (1.0 Pa) from the orange solution. The product was obtained as red–brown oil. Distillation (Kugelrohr, bp 130–145°C/0.8 Pa) gave 0.873 g (84%) of an orange colored oil. Crude yield 89% (quant. ^{1}H NMR). The oil crystallized at −78°C and could then be recrystallized from pentane/THF: yield 0.744 g (73%) of orange colored crystals, mp 65–67°C dec. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.24–3.14 (m, 2H, *H*C(CN)), 2.90 (s, 4H, NCH_2), 2.68–2.52 (m, 4H, CH_2), 2.50 (s, 6H, NCH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ=119.2 (*C*=*C*), 118.4 (*C*N), 48.1 (N*C*H_2), 28.6 (H*C*(CN)), 28.0 (*C*H_2). IR (CCl_4): ν=2955–2807 cm^{-1} (CH), 2245 (CN), 1653 (C=C). MS (70 eV): *m/z* (%): 216 (100, M$^+$), 201 (90), 163 (11), 138 (36), 123 (33), 83 (19). HR-MS (70 eV): $C_{12}H_{16}N_4$: calcd 216.1375, found 216.1360. $C_{12}H_{16}N_4$ (216.3): calcd C 66.64, H 7.46, N 25.90, found C 66.87, H 7.96, N 25.46.

***trans*- and *cis*-6,7-Dicarbomethoxy-6,7-dicyano-1,4-dimethyl-1,2,3,4,5,6,7,8-octahydroquinoxaline (4 and 5).** (a) Dimethyl dicyanofumarate (0.971 g, 5.00 mmol) was suspended in 10 ml of dry and Ar saturated THF at room temperature. To this solution was given **1** (0.691 g, 5.00 mmol) dissolved in 10 ml of dry and Ar saturated THF through a dropping funnel. The initially deep-red colored solution turned transparent red. The solvent was removed in vacuo after 30 min leading to a dark-red solid, respectively a highly viscous oil. The ^{1}H NMR spectrum revealed the presence of two isomeric (4+2)-cycloadducts. Crude yield: 96% (quant. ^{1}H NMR), ratio of **4**:**5**=35:65. ^{1}H NMR (300 MHz, [D$_6$]benzene) crude product: δ=3.19 (s, 6H, OCH_3 (4)), 3.16–3.13 (m, 4H, CH_2, (5)), 3.12 (s, 6H, OCH_3 (5)), 3.06–2.84 (m, 4H, CH_2 (4), 2.55–2.40 (m, 4H, NCH_2 (4)), 2.41 (s, 4H, NCH_2 (5)), 2.05 (s, 6H, NCH_3 (4)), 2.02 (s, 6H, NCH_3 (5)). ^{13}C NMR (75 MHz, [D$_6$]benzene) crude product: (δ=166.86 (*C*=O (4)), 165.44 (*C*=O (5)), 118.96 (*C*=*C* (4)), 118.11 (*C*=*C* (5)), 117.02 (*C*N (5)), 115.83 (*C*N (4)), 53.66 (O*C*H$_3$ (5)), 53.64 (O*C*H$_3$ (4)), 47.73 (N*C*H$_2$ (4)), 47.66 (*C*(CN) (4)), 47.65 (N*C*H$_2$ (5)), 47.14 (*C*(CN) (5)), 39.75 (N*C*H$_3$ (4, 5), 34.59 (*C*H$_2$ (4)), 33.49 (*C*H$_2$ (5)). Additional NMR experiments: DEPT 90, DEPT 135, CH-COSY, inverse CH-COSY, inverse COLOC. MS (70 eV) of the crude product. *m/z* (%): 332 (100) [M$^+$], 317 (13), 273 (20), 258 (11), 214 (29), 199 (18), 175 (13), 138 (41), 123 (13).

Isolation of 4. Solid product was obtained after dissolving the crude material in pentane/THF and cooling the solution to −78°C. Recrystallization of this material from ethanol yielded creme colored needles. Isolated yield: 0.439 g (26% relative to the total yield, 74% relative to the total yield of **4** (determined by quant. ^{1}H NMR). Mp 152°C dec. ^{1}H NMR (300 MHz, [D$_6$] benzene): δ=3.19 (s, 6H, OCH_3), 3.06–2.84 (m, 4H, CH_2), 2.55–2.40 (m, 4H, NCH_2), 2.05 (s, 6H, NCH_3). ^{13}C NMR (75 MHz, [D$_6$]benzene): δ=166.86 (*C*=O), 118.96 (*C*=*C*), 115.83 (*C*N), 53.64 (O*C*H$_3$), 47.73 (N*C*H$_2$), 47.66 (*C*(CN)), 39.75 (N*C*H$_3$), 34.59 (*C*H$_2$). Additional NMR experiments: DEPT 90, DEPT 135, CH-COSY, inverse CH-COSY, inverse COLOC. IR (KBr): ν=2956–2791 cm^{-1} (CH), 2250 (CN), 1768/1751 (C=O), 1661/1640 (C=C). MS (70 eV): *m/z* (%): 332 (100) [M$^+$], 317 (15), 273 (20), 258 (6), 214 (18), 199 (15), 175 (8), 138 (45), 123 (11). HR-MS (70 eV): $C_{16}H_{20}N_4O_4$: calcd 332.1485, found 332.1488. $C_{16}H_{20}N_4O_4$ (332.4): calcd C 57.83, H 6.07, N 16.86, found C 57.82, H 6.19, N 16.97. (b) Dimethyl dicyanomaleate (0.971 g, 5.00 mmol) and **1** (0.691 g, 5.00 mmol) were dissolved in 10.0 ml of dry and Ar saturated THF in Schlenk-vessels each. The diene solution was added dropwise (dropping funnel) to the dienophile solution at room temperature. After 5 h, the solvent was removed in vacuo (1.0 Pa). The reaction was carried out in the dark. The products formed were identical to those of the reaction of **1** with dimethyl dicyanofumarate. Crude yield: 87% (quant. ^{1}H NMR), ratio **4**:**5**=35:65.

6,6,7,7-Tetracyano-1,4-dimethyl-1,2,3,4,5,6,7,8-octahydroquinoxaline (6). Tetracyanoethene (0.640 g, 5.00 mmol) and **1** (0.691 g (5.00 mmol)) were dissolved in 10.0 ml of dry and Ar saturated THF in Schlenk-vessels each. The diene solution was added dropwise (dropping funnel) to the dienophile solution at room temperature. The solution turned dark-red to brown. After 1 h, the solvent was removed in vacuo (1.0 Pa, respectively, 4.5×10^{-5} Pa). The dark-brown solid consisted of cycloadduct **6** and side product 6,6,7,7-tetracyano-1,4,7a-trimethyl-1,2,3,4,6,7a-hexahydro-7H-cyclopenta[b]pyrazine (**7**). Ratio of **6**:**7**= 93:7 at room temperature and 87:13 at −60°C. Yield of the crude product 93% (quant. ^{1}H NMR). The cycloadduct decomposes easily under elimination. The crude material was triturated first with benzene and then three times with cold ethanol. A light yellow powder was isolated which could not be crystallized. Isolated yield of **6** 0.948 g (70%), mp 133°C dec. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ=3.46 (s, 4H, NCH_2), 2.94 (s, 4H, CH_2), 2.60 (s, 6H, NCH_3). ^{13}C NMR (75 MHz, [D$_6$]acetone): δ=117.5 (*C*=*C*), 112.4 (*C*N), 48.3 (N*C*H_2), 40.2 (N*C*H_3), 40.0 (*C*(CN)$_2$), 33.2 (*C*H_2). Additional NMR experiments: DEPT 90, DEPT 135, CH-COSY. IR (KBr): ν=2963–2795 cm^{-1} (CH), 2255 (CN), 1555,1636 (C=C). MS (70 eV): *m/z* (%): 266 (56) [M$^+$], 251 (8), 206 (27), 182 (89), 165 (53), 138 (43), 129 (13), 123 (14), 105 (100), 77 (98). HR-MS (70 eV): $C_{14}H_{14}N_6$: calcd 266.1280, found 266.1262. $C_{14}H_{14}N_6$ (266.3): calcd C 63.14, H 5.30, N 31.56, found C 63.22, H 5.31, N 31.79.

6,6,7,7-Tetracyano-1,4,7a-trimethyl-1,2,3,4,6,7a-hexahydro-7H-cyclopenta-[b]pyrazine (7). The compound was isolated from fractions of the crude reaction mixture after

column chromatography on silica with trichloromethane as eluant. While **6** decomposed under these conditions, **7** could be isolated (0.031 g, 0.12 mmol). Mp 136°C dec. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ=4.83 (s, 1H,=C*H*), 3.19–2.87 (m, 4H, NCH_2), 2.76 (s, 3H,=C–NCH_3), 2.50 (s, 3H, (H_3C)C(NCH_3), 1.63 (s, 3H, CCH_3). ^{13}C NMR (75 MHz, [D$_6$]acetone): δ=158.5 (=*C*–N), 113.1/113.0/112.1/111.5 (*C*N), 85.2 (=*C*–H), 72.2 (*C*CH$_3$), 55.9 ((H_3C)C–*C*(CN)$_2$), 51.2 (=C–N(CH$_3$)*C*H$_2$), 48.2 ((H_3C)C–N(CH$_3$)*C*H$_2$), 46.6 (=C–*C*(CN)$_2$), 40.2 (=C-N*C*H$_3$), 38.6 ((H_3C)C–N*C*H$_3$), 12.2 (C*C*H$_3$). Additional NMR experiments: DEPT 90, DEPT 135, inverse CH-COSY, inverse COLOC. IR (KBr): ν=3097 cm^{-1} (=CH), 2962–2815 (CH), 2219/2204 (CN), 1634/1570 (C=C). MS (70 eV): *m/z*(%): 266 (100) [M$^+$], 251 (43), 237 (10), 224 (13), 212 (21), 202 (61), 187 (16), 174 (18), 160 (10), 125 (83). HR-MS (70 eV): $C_{14}H_{14}N_6$: calcd 266.1280, found 266.1270.

X-Ray structures. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publications. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CD2 1EZ, UK.

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