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Hetero Diels-Alder Reactions of 4,5-Dicyanopyridazine with Alkenes

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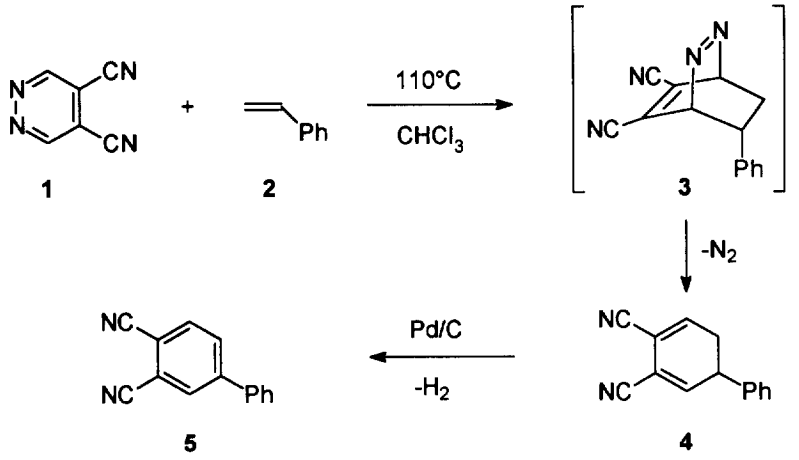
Abstract: The behaviour of the title compound **1** with some linear and cyclic olefins has been investigated. Except for the reaction with diphenylcyclopropenone **22**, affording **24** and **26** through cyclization processes of the primary Michael adduct **23**, a remarkable reactivity as azadiene was observed. The structures of the resulting dicyanocyclohexa-1,3-dienes, aromatic phthalonitriles, and polycyclic bis-adducts were established on the basis of spectral data. © 1997 Elsevier Science Ltd.

Whereas the synthetic utility of 1,2,4-triazines and 1,2,4,5-tetrazines as azadienes in [4+2] cycloadditions with a variety of dienophiles has been properly emphasized over the past decades,[1] the pyridazine system appeared much more disregarded,[2] probably due to misleading evaluations of its properties in the same context. After recent results from our laboratory clearly indicated that the dicyanoderivative **1** can enter as a 4π electron component into hetero Diels-Alder reactions,[3] and a preliminary screening fully confirmed for **1** a remarkable reactivity with unactivated dienophiles,[4] we undertook a systematic investigation of its behaviour towards different alkene counterparts.

RESULTS AND DISCUSSION

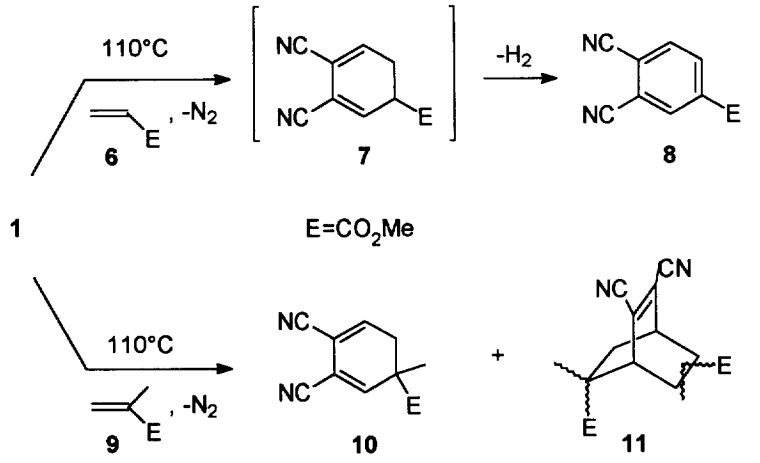
When compound **1** was heated with an excess of styrene **2** in chloroform at 110°C in the presence of 10% Pd/C,[5] 3,4-dicyanobiphenyl **5** was isolated in 38% yield. Although the labile cyclohexadiene **4**, coming from the primary adduct **3** by loss of nitrogen (Scheme 1),[6] could be obtained as the predominant reaction product (TLC,

^{1}H NMR) with 1 equivalent of **2** at 70°C, attempts to achieve its isolation by fractional sublimation or flash chromatography on deactivated (MeOH) silica gel, failed.



Scheme 1

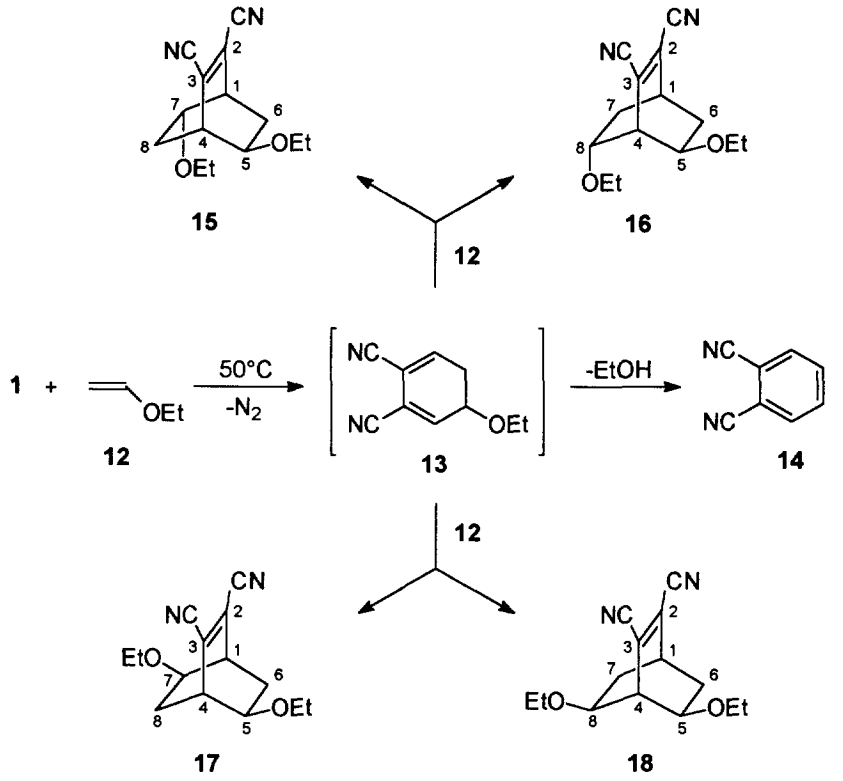
Treatment of **1** with methyl acrylate **6** at 110°C afforded the aromatic ester **8** in 58% yield through the unstable intermediate **7**, but replacement of the above dienophile with the corresponding methacrylate **9** enabled us to obtain the diene **10** in 64% yield, together with minor amounts of bis-adducts **11** (Scheme 2).



Scheme 2

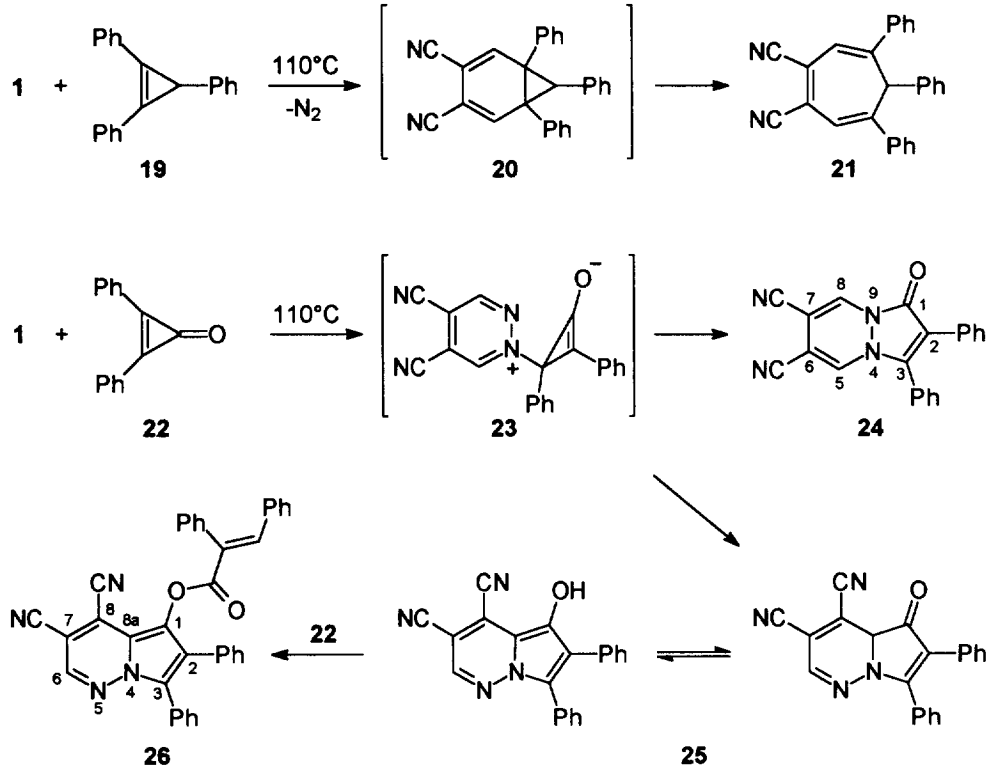
Although the dicyanopyridazine **1** reacted slowly with the activated enol ether **12** even at 50°C, compound **13** escaped from isolation since it was converted into **14** by loss of ethanol and, to a greater extent, into the

bicyclic systems **15-18** by further cycloadditions with **12** (Scheme 3); careful chromatographic workup of the complex reaction mixture allowed us to isolate, in addition to **14** (12%), two fractions which were identified as 1:1 and 4:1 mixtures of the isomers **15** and **16** (65%), and **17** and **18** (15%), respectively.



Scheme 3

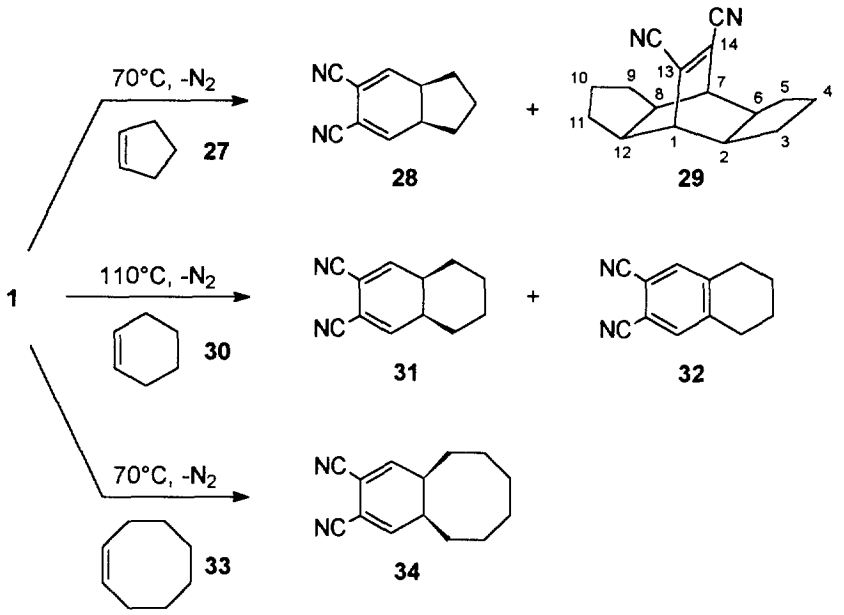
Compound **1** reacted easily at 110°C with 1,2,3-triphenylcyclopropene **19** to give 3,4-dicyano-1,6,7-triphenylcyclohepta-1,3,5-triene **21** in 77% yield, through a [4+2] cycloaddition followed by ring-enlargement of **20**. Nevertheless, like pyridazine,[7] it prefers to behave as a nucleophile with the strongly electrophilic cyclopropenone **22**, affording a mixture of the bicyclic derivatives **24** and **26** by a competing electrocyclization of the proposed betaine intermediate **23** (Scheme 4).



Scheme 4

Finally, the possibility of exploiting **1** as a synthon in hetero Diels-Alder reactions with other cycloalkenes for a direct entry into condensed dicyanocyclohexadiene systems, was found to be partially influenced by the ring size of the dienophile (Scheme 5).

Treatment of **1** with cyclopentene **27** and cyclohexene **30** under different conditions gave **28** and **31** as the predominant products (Scheme 5), but a partial conversion into the bis-adduct **29** and the tetrahydronaphthalene **32**, respectively, could not be avoided; in contrast, we succeeded in obtaining the desired compound **34** in very good yields from the cleaner reaction of **1** with *cis*-cyclooctene **33**. The above dienes appear much more stable than **4**, probably due to the ring fusion with a cycloalkane moiety, and no difficulty was encountered in their workup.



Scheme 5

The structures of the new products[8] followed from analytical and spectral evidence (Experimental Section). Particularly, the ^{1}H- and ^{13}C NMR spectra of **10**, **28**, **31**, and **34** were characterized by resonances in the range δ 6.67-6.87 and δ 143.4-150.1, respectively, for the unsatured CH groups. The stereo- and regiochemistry of compounds **15-18**, as well as their relative percentages in the isolated fractions, were established on the basis of the following considerations:

(a) While the ^{13}C NMR spectrum of the mixture of the asymmetrical regioisomers **15** and **16**, arising from *endo*/*syn* approaches between **1** and **12**, showed twenty-five resonances,[9] the ^{1}H NMR pattern was characterized by two doublets of triplets of comparable intensities at δ 3.80 and 4.12 for the *exo* H-7 and H-8 protons of **15** and **16**, respectively,[10] coupled with the vicinal bridge and methylene hydrogens.

(b) According to a C_2 and C_s symmetry of the isomers **17** and **18**, coming from *endo*/*anti* interactions of the same reagents, seven resonances were easily identified in the ^{13}C NMR spectrum of the second fraction for the predominant component, together with some of those expected for the minor one. The lack of any ^{1}H NMR absorption above δ 3.70 led us to discard less favourable structures with *endo* ethoxy groups.

The ^{1}H NMR values of the ring protons between δ 8.03 and 8.56 agree well with the proposed skeletons **24** and **26**, containing a 1,2-dihydropyridazine and an aromatic azaindolizine system, respectively; moreover, a

remarkable shielding (δ 91.2 and 93.35) was observed for the C-6 and C-7 quaternary carbons of the former compound due to the electron drift in the N≡C–C=C–N< conjugated moieties.

Lastly, the *exo-exo* stereochemistry of the tetracyclic derivative **29** with a C_{2v} symmetry was inferred from a complementary analysis of its ^{1}H- and ^{13}C NMR patterns: whereas the latter showed only six resonances, no appreciable coupling was detected in the former for the H-1 and H-7 protons which gave rise to a singlet at δ 3.03, strongly supporting an *endo* configuration for the adjacent hydrogen atoms.

In summary, the results presented here provide additional evidence for the synthetic potential of 4,5-dicyanopyridazine **1** which, by virtue of its peculiar reactivity, gains credit as a valuable member in the realm of heterocyclic azadienes.

EXPERIMENTAL SECTION

General Procedure. Melting points were taken on a Büchi 510 apparatus and are uncorrected. Unless otherwise stated, IR spectra were measured as KBr pellets with a Perkin-Elmer 881 spectrophotometer, while ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions with a Varian Gemini instrument operating at 200 MHz and 50 MHz, respectively: chemical shifts are expressed in ppm (δ) and coupling constants in Hertz (Hz). Elemental analyses were obtained with a Perkin-Elmer 240C Analyzer. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck, 230-400 mesh) were used for TLC and flash chromatographies, respectively; petroleum ether employed for crystallizations and chromatographic workup refers to the fractions of b.p. 30-50°C and 40-70°C, respectively.

Unless otherwise indicated, all the reactions of the dicyanopyridazine **1**[11] were carried out in a screw-capped tube (Pyrex N. 13) on 1 mmol scale in $CHCl_3$ (1 ml); the raw product, left by evaporation to dryness under reduced pressure, was subjected to flash chromatography. Analytical samples of liquid or semi-solid products were obtained by dissolution in ether, filtration, evaporation to dryness and prolonged evacuation at room temperature (10^{-2} mmHg). When the conversion of **1** was incomplete, the yields of the isolated compounds were determined on the basis of the recovered starting material.

3,4-Dicyanobiphenyl (5). 10% Pd/C (0.13 g) was added to a solution of **1** and styrene (**2**) (0.208 g, 0.229 ml, 2 mmol) and the mixture was heated at 110°C for 24 h, filtered, and evaporated to dryness; chromatographic workup (toluene) of the residue afforded compound **5** (R_f = 0.30, 0.078 g, 38%) that was crystallized from petroleum ether/ether as ivory-coloured needles, m.p. 156-157°C; IR ν 3071, 2946, 2233, 1595 cm^{-1}; ^{1}H NMR δ 7.48-7.63 (m, 5H), 7.85-8.10 (m, 3H); ^{13}C NMR δ 113.9 (s), 115.4 (s), 115.45 (s), 116.4 (s), 127.2 (d), 129.5

(d), 129.8 (d), 131.4 (d), 132.0 (d), 133.8 (d), 136.9 (s), 146.5 (s). Anal. Calcd. for $C_{14}H_8N_2$: C, 82.34; H, 3.95; N, 13.72. Found: C, 82.01; H, 3.92; N, 14.0.

Methyl 3,4-Dicyanobenzoate (8). The raw product from the reaction of **1** with methyl acrylate (**6**) (0.43 g, 0.45 ml, 5 mmol) under the above conditions was resolved into two fractions with petroleum ether/acetone (3:1 v/v) as eluent. The first band gave the ester **8** (R_f = 0.39, 0.104 g, 58%) as colourless crystals, m.p. 155-157°C (from AcOEt); IR ν 3108, 3083, 3055, 2238, 1721 cm^{-1}; ^1H NMR δ 4.0 (s, 3H), 7.93 (d, J = 8.1 Hz, 1H), 8.37 (dd, J = 8.1 and 1.6 Hz, 1H), 8.44 (d, J = 1.6 Hz, 1H); ^{13}C NMR δ 53.5 (q), 114.6 (s), 114.7 (s), 116.3 (s), 119.2 (s), 133.7 (d), 133.8 (d), 134.2 (d), 134.6 (s), 163.5 (s). Anal. Calcd. for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.45; H, 3.35; N, 15.13.

A small amount of unreacted **1** (R_f = 0.30, 0.005 g) was recovered from the second fraction.

Methyl 2,3-Dicyano-5-methylcyclohexa-1,3-diene-5-carboxylate (10). The residue obtained by treatment of **1** with methyl methacrylate (**9**) (0.501 g, 0.54 ml, 5 mmol) at 110°C for 4 days was resolved with petroleum ether/AcOEt (3:1 v/v) as eluent; after the first fraction (R_f = 0.48), containing a mixture of bis-adducts **11,** was discarded and the unreacted starting material (R_f = 0.33, 0.054 g) was recovered from the following one, the slowest moving band yielded the ester **10** as a pale yellow liquid (R_f = 0.25, 0.076 g, 64%); IR (liquid film) ν 3066, 2229, 1735, 1582 cm^{-1}; ^1H NMR δ 1.37 (s, 3H), 2.52 (dd, J = 19.5 and 5.3 Hz, 1H), 3.03 (dd, J = 19.5 and 4.2 Hz, 1H), 3.77 (s, 3H), 6.80-6.87 (m, 2H); ^{13}C NMR δ 23.5 (q), 32.1 (t), 42.2 (s), 53.2 (q), 108.0 (s), 108.1 (s), 112.3 (s), 114.5 (s), 143.45 (d), 146.3 (d), 172.9 (s). Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.02; H, 5.19; N, 13.63.

Reaction of Compound 1 with Ethyl vinyl ether (12). A solution of **1** and **12** (0.722 g, 0.96 ml, 10 mmol) in $CHCl_3$ (2 ml) was stirred at 50°C for 7 days, and the raw product was resolved into three components with petroleum ether/AcOEt (5:2 v/v) as eluent. The fastest moving fractions gave a 1:1 mixture of (5*RS*, 7*SR*)-2,3-dicyano-5,7-diethoxybicyclo[2.2.2]oct-2-ene (**15**) and (5*RS*, 8*RS*)-2,3-dicyano-5,8-diethoxybicyclo[2.2.2]oct-2-ene (**16**) as a pale yellow oil (R_f = 0.69, 0.160 g, 65%); IR (liquid film) ν 2976, 2935, 2879, 2223 cm^{-1}; ^1H NMR δ 1.08-1.48 (m, 15H), 1.70-2.10 (m, 3H), 2.18 (ddd, J = 13.8, 8.1, and 2.6 Hz, 1H), 2.45 (ddd, J = 13.9, 8.1, and 2.6 Hz, 1H), 3. 01 (quintet, J = 3.0 Hz, 1H), 3.16 (q, J = 2.9 Hz, 1H), 3.22-3.62 (m, 12H), 3.80 (sbr dt, J = 8.0 and 3.0 Hz, 1H), 4.12 (dt, J = 8.1 and 2.8 Hz, 1H); ^{13}C NMR δ 15.15 (q), 15.2 (q), 27.5 (t), 28.65 (t), 31.6 (t), 34.6 (t), 35.5 (d), 39.0 (d), 39.75 (d), 44.0 (d), 63.8 (t), 63.95 (t), 64.4 (t), 64.8 (t), 71.0 (d), 73.0 (d),

73.1 (d), 76.0 (d), 113.9 (s), 114.3 (s), 114.4 (s), 127.2 (s), 129.1 (s), 130.55 (s), 132.6 (s). Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.57; H, 7.62; N, 10.95.

After phthalonitrile (**14**) (R_f = 0.45, 0.016 g, 12%) was isolated from the second band, the slowest running one afforded a 4:1 mixture of (5*RS*, 7*RS*)-2,3-dicyano-5,7-diethoxybicyclo[2.2.2]oct-2-ene (**17**) and (5*R*, 8*S*)-2,3-dicyano-5,8-diethoxybicyclo[2.2.2]oct-2-ene (**18**) as a waxy white product (R_f = 0.27, 0.036 g, 15%); IR ν 2979, 2876, 2220 cm^{-1}; ^1H NMR δ 1.08-1.22 (m), 1.34-1.48 (m), 1.78-1.96 (m), 3.25-3.70 (m); ^{13}C NMR δ: 15.2 (q), 30.4 (t), [34.2 (d)], 38.9 (d), [44.8 (d)], 64.2 (t), [73.4 (d)], 75.4 (d), 114.6 (s), 128.6 (s).[12] Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.14; H, 7.41; N, 10.97.

3,4-Dicyano-1,6,7-triphenylcyclohepta-1,3,5-triene (21). Chromatographic resolution [petroleum ether/AcOEt (3:1 v/v)] of the residue from the reaction of **1** with **19** (0.268 g, 1 mmol) at 110°C for 48 h, yielded compound **21** (R_f = 0.64, 0.22 g, 77%) that was crystallized from ether as yellow needles, m.p. 186°C; IR ν 3056, 3020, 2222, 1600, 1492 cm^{-1}; ^1H NMR δ 5.97 (br s, 1H), 6.99 (d, J = 1.5 Hz, 2H), 7.13-7.62 (m, 15H); ^{13}C NMR δ 50.4 (d), 116.7 (s), 119.4 (s), 122.7 (d), 126.2 (d), 127.5 (d), 127.95 (d), 128.2 (d), 129.2 (d), 130.3 (d), 137.2 (s), 139.7 (s), 145.1 (s). Anal. Calcd. for $C_{27}H_{18}N_2$: C, 87.54; H, 4.90; N, 7.56. Found: C, 87.26; H, 5.10; N, 7.30.

Some unreacted **1** (R_f = 0.33, 0.030 g) was recovered from the later fractions.

Reaction of 1 with Diphenylcyclopropenone (22). The raw product obtained from **1** and **22** (0.413 g, 2 mmol) at 110°C for 48 h was treated with acetone (20 ml) and filtered to give 1*H*-6,7-dicyano-2,3-diphenylpyrazolo[1,2-*a*]pyridazin-1-one (**24**) as a yellow solid (0.090 g), m.p.>300°C (from the same solvent); IR ν 3061, 2226, 2213, 1665, 1570 cm^{-1}; ^1H NMR (CF_3CO_2D) δ 7.28-7.79 (m, 10H), 8.18 (s, 1H), 8.56 (s, 1H); ^{13}C NMR (CF_3CO_2D) δ 91.2 (s), 93.35 (s), 113.1 (s), 113.4 (s), 116.4 (s), 127.9 (s), 130.8 (d), 131.25 (d), 131.3 (s, d), 131.4 (d), 132.0 (d), 132.6 (d), 133.9 (d), 134.4 (d), 144.1 (s), 157.8 (s). Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 74.99; H, 3.60; N, 16.66. Found: C, 74.69; H, 3.88; N, 16.38.

The filtrate was evaporated to dryness and the residue was subjected to flash chromatography with petroleum ether/AcOEt (5:2 v/v) as eluent; the fastest moving band afforded (7,8-dicyano-2,3-diphenylpyrrolo[1,2-*b*]pyridazin-1-yl)(*E*)-1,2-diphenylacrylate (**26**) (R_f = 0.67, 0.255 g, 47%) that was crystallized from acetone as purple red needles, m.p. 230-231°C; IR ν 3097, 3050, 2221, 1739, 1595, 1575 cm^{-1}; ^1H NMR δ 7.05-7.50 (m, 20H), 8.03 (s, 1H), 8.13 (s, 1H); ^{13}C NMR δ 96.3 (s), 111.3 (s), 114.0 (s), 114.2 (s), 114.4 (s), 125.2 (s), 126.4 (s), 127.3 (s), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 128.6 (d), 128.85 (d), 129.5 (s), 129.55 (d), 129.75 (d), 129.9 (d), 130.0 (d), 130.1 (s), 130.4 (d), 130.7 (s), 131.1 (d), 133.9 (s),

135.1 (s), 140.05 (d), 144.2 (d), 166.4 (s). Anal. Calcd. for $C_{36}H_{22}N_4O_2$: C, 79.69; H, 4.09; N, 10.33. Found: C, 79.38; H, 4.37; N, 10.19.

After elution of unreacted **22** in the following band (R_f = 0.17), the column was eluted with AcOEt to give a second crop of **24** (0.038 g, total yield 38%).

Cycloadditions of 1 with the Cycloalkenes 27, 30, and 33: Synthesis of Compounds 28, 29, 31, 32 and 34.

A. Chromatographic resolution [petroleum ether/AcOEt (3:1 v/v)] of the residue obtained from **1** and **27** (0.68 g, 0.878 ml, 10 mmol) at 70°C for 7 days, yielded (2*R*, 6*S*, 8*R*, 12*S*)-13,14-dicyanotetracyclo[5.5.2.0.^{2,6}0^{8,12}]tetradec-13-ene (**29**) (R_f = 0.65, 0.051 g, 28%) as a colourless solid, m.p. 131-132°C (from ether); IR ν 2956, 2863, 2217, 1538 cm^{-1}; ^{1}H NMR δ 0.92-1.08 (m, 4H), 1.19-1.40 (m, 2H), 1.53-1.69 (m, 2H), 1.80-1.96 (m, 4H), 2.20-2.38 (m, 4H), 3.03 (s, 2H); ^{13}C NMR δ 26.1 (t), 31.5 (t), 44.6 (d), 45.5 (d), 115.6 (s), 132.3 (s). Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.90; H, 7.83; N, 11.66.

The second band afforded 3,4-dicyanobicyclo[4.3.0]nona-2,4-diene (**28**) (R_f = 0.40, 0.072 g, 55%) that was crystallized from AcOEt as colourless needles, m.p. 253°C; IR ν 2973, 2940, 2869, 2223, 1628 cm^{-1}; ^{1}H NMR δ 1.40-1.58 (m, 4H), 2.10-2.28 (m, 2H), 2.84-2.93 (m, 2H), 6.70 (m, 2H); ^{13}C NMR δ 22.1 (t), 34.2 (t), 36.6 (d), 105.0 (s), 115.1 (s), 147.7 (d). Anal. Calcd. for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.43; H, 5.98; N, 16.19.

The unreacted **1** (R_f = 0.33, 0.030 g) was recovered from the following fractions.

B. The crude product from the reaction of **1** with **30** (0.82 g, 1.01 ml, 10 mmol) at 110°C for 4 days was resolved into three components with petroleum ether/ether (7:4 v/v) as eluent. The first band gave 2,3-dicyano-5,6,7,8-tetrahydronaphthalene (**32**) (R_f = 0.57, 0.024 g, 20%) as colourless crystals, m.p. 144-146°C (from ether); IR ν 3060, 3040, 2949, 2873, 2229, 1595 cm^{-1}; ^{1}H NMR δ 1.80-1.87 (m, 4H), 2.81-2.90 (m, 4H), 7.48 (s, 2H); ^{13}C NMR δ 21.9 (t), 29.3 (t), 112.2 (s), 115.7 (s), 134.2 (d), 144.0 (s). Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37. Found: C, 78.83; H, 5.69; N, 15.09.

The following band afforded 3,4-dicyanobicyclo[4.4.0]deca-2,4-diene (**31**) (R_f = 0.39, 0.062 g, 50%) that, after crystallization from AcOEt, gradually darkened above 260°C and melted at 275°C (dec.); IR ν 2947, 2238, 1591 cm^{-1}; ^{1}H NMR δ 1.38-1.60 (m, 8H), 2.53-2.68 (m, 2H), 6.75 (m, 2H); ^{13}C NMR δ 22.8 (t), 26.3 (t), 34.2 (d), 108.0 (s), 115.1 (s), 149.7 (d). Anal. Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20. Found: C, 77.98; H, 6.66; N, 15.02.

The unreacted **1** (R_f = 0.22, 0.044 g) was recovered from the slowest moving fractions.

C. Treatment of **1** with **33** (1.102 g, 1.30 ml, 10 mmol) at 70°C for 48 h afforded a crude product that was sublimed at 50-60°C, 10 mmHg, to yield the unreacted starting material (0.044 g); the residue was collected and washed with the minimun amount of *n*-pentane to give 10,11-dicyanobicyclo[6.4.0]dodeca-9,11-diene (**34**) (0.135 g, 96%) that was crystallized from AcOEt/cyclohexane as ivory-coloured crystals, m.p. 68-69°C; IR ν 3055, 2931, 2860, 2226, 1653 cm^{-1}; ^1H NMR δ 1.42-1.90 (m, 12H), 2.70-2.80 (m, 2H), 6.67 (m, 2H); ^{13}C NMR δ 26.2 (t), 26.3 (t), 36.0 (d), 107.2 (s), 115.1 (s), 150.1 (d). Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 78.98; H, 7.75; N, 13.02.

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5. Under these conditions, oxidation of **4** into **5** was favoured with respect to further cycloadditions with **2**.
6. The stereochemistry of **3** is portrayed arbitrarily.
7. Weidner, C. H.; Michaels, F. M.; Beltman, D. J.; Montgomery, C. J.; Wadsworth, D. H.; Briggs, B. T.; Picone, M. L. *J. Org. Chem.* **1991**, *56*, 5594-5598.
8. Only compound **5** has been reported previously; *e.g.*, see Thoma, P.; Habermann, W.; Kranz, J. Ger. Offen. 2,711,005/1978 (*Chem. Abstr.* **1979**, *90*, 7594) .
9. Apart from a few overlaps, almost identical intensities were observed for the corresponding resonances of the two structures.
10. The relative assignment of these signals was tentatively made on the basis of a slight broadening of the former, probably due to an additional ^4J coupling with the *exo* H-6 proton.
11. Di Stefano, L.; Castle, R. N. *J. Heterocycl. Chem.* **1968**, *5*, 53-59.
12. The values in square brackets refer to the most evident resonances of the minor component, that were exploited for a tentative evaluation of the relative amounts of the two isomers.

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