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Domino Reactions of 4,5-Dicyanopyridazine with Dihydroheterocycles: Synthetic and Mechanistic Features

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Abstract: The title pyridazine **1** was found to react with both 2,3-dihydrofuran (**2**) and 3,4-dihydro-2*H*-pyran (**9**) to give the tetracyclic skeletons **5**−**8** and the phthalonitrile **12** through the intermediates **4** and **10**, respectively. A more complex mechanism was ascertained for the reaction of **1** with the pyrroline **14** which, under suitable conditions, afforded the bicyclic derivative **19** as the predominant product; selective elaborations of this species into the 5,6-dicyanoindoles **22** and **23** are reported.

Despite the scarce consideration enjoyed by monocyclic 1,2-diazines in the realm of polyazine azadienes as potential 4π electron components for intermolecular Hetero Diels−Alder (HDA) reactions,[1] a systematic investigation from our laboratory clearly demonstrated that 4,5-dicyanopyridazine (DCP) (**1**) readily functions as a more reactive counterpart with respect to the corresponding di- and tetraesters in [4+2] cycloadditions with a variety of dienophiles.[2] In particular, it reacted as a *masked or latent bis-diene* with different bis-dienophiles, providing a new excellent entry into carbo- and heterocage systems.[3]The same synthon has also been exploited both for the synthesis of dicyanocyclohexa-1,3-dienes[4] and as a straightforward complementary route to phthalonitriles.[5] In this context, we wish now to report new results on the reactivity of **1** toward a few dihydroheterocycles containing electron-rich 2π moieties.

When DCP was allowed to react with a large excess of 2,3-dihydrofuran (DHF) (**2**) (molar ratio 1:10) in chloroform at 70 °C, we isolated the diastereomeric couples of the tetracyclic derivatives **5**, **6** and **7**, **8** in 88% and 6% yields as 3:1 and 1.5:1 regioisomeric mixtures, respectively. The inverse electron-demand HDA reaction of **1** on the cyclic enol ether **2** leads to the labile adduct **3**,[6] which gives rise to a retro Diels−Alder (DA) loss of nitrogen; the resulting compound **4** was then converted by further cycloadditions with **2** into the final products, whose formation can be regarded on the whole as the outcome of three-step pericyclic homodomino processes (Scheme 1).[7] Although **4** could not be isolated, it was easily identified by spectral monitoring of the reaction course of **1** with a stoichiometric amount of DHF under the same conditions. After 30 h, the ^{1}H NMR spectrum clearly shows, together with the signals of **1** and **5**−**8**, two doublets at δ 6.87 and 6.70 for the diene protons and a doublet of doublets at δ 4.68 attributable to H-6; the resonances of the corresponding tertiary carbons were recognized in the ^{13}C NMR pattern at δ 146.5, 140.7, and 71.1, respectively.

On going from **2** to the less reactive 3,4-dihydro-2*H*-pyran (DHP) (**9**), the complete disappearance of DCP was observed only after a week at 110 °C in anhydrous toluene with an excess of the reagent (molar ratio 1:10) to give phthalonitrile **12** in 68% yield; the intermediate **10** now prefers to aromatize by ring-opening affording **12** through alcohol **11** (Scheme 2).

A more intriguing picture was observed for the behavior of **1** toward pyrroline **14**. Treatment of DCP at room temperature with 1 equiv of **14**, generated in situ from salt **13** and potassium *tert*-butoxide (molar ratio 1:1.5) in anhydrous tetrahydrofuran (THF), gave rise to a vigorous exothermic reaction leading in a few minutes to the total disappearance of the starting material; chromatographic workup of the resulting reaction mixture afforded the inseparable indolines **20** and **21** in 27% and 13% yields, respectively (Table 1, entry 1). Oxidation of this couple with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene afforded almost quantitatively the corresponding indoles **22** and **23** but, again, they could not be resolved chromatographically.

Whereas **20** can be regarded as the result of a [4+2] cycloaddition of **1** on the extremely reactive thioketene aminal **14**, followed by elimination of nitrogen and methanethiol from **17**[6] and **18**, the concomitant formation of **21** appeared less straightforward. According to the firmly established mechanistic pattern of the reactions of **1** with enamines,[5b] it could be tentatively accounted for on the basis of a more complex, four-step domino process involving the highly conjugated dienamine **19** as the additional key intermediate; this species, arising from a [1,5] sigmatropic rearrangement of **18**, can then evolve into the final products **20** and **21** by loss of MeSH and H_2 fragments, respectively (Scheme 3).

To substantiate this hypothesis and with the aim of exploiting its synthetic potentialities, we decided to carry out the above reaction under milder conditions. Operating at 0 °C for 1 h (Table 1, entry 2), we isolated, along with **20** and **21**, the desired compound **19** in 8% yield and the pyrrolinyl-pyridazine **16** (9%) coming from a

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(2) For similar effects of CN groups on carbo- and aza-dienes, see: (a) Cobb, R. L.; Vives, V. C.; Mahan, J. E. *J. Org. Chem.* **1978**, *43*, 931−936. (b) Sisti, N. J.; Motorina, I. A.; Tran Huu Dau, M.-E.; Riche, C.; Fowler, F. W.; Grierson, D. S. *J. Org. Chem.* **1996**, *61*, 3715−3728.

(3) (a) Nesi, R.; Giomi, D.; Turchi, S.; Paoli, P. *Tetrahedron* **1994**, *50*, 9189−9194. (b) Giomi, D.; Nesi, R.; Turchi, S.; Coppini, R. *J. Org. Chem.* **1996**, *61*, 6028−6030. (c) Giomi, D.; Nesi, R.; Turchi, S.; Mura, E. *J. Org. Chem.* **2000**, *65*, 360−364.

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(6) The stereochemistry is portrayed arbitrarily.

(7) For a proper definition and classification of domino reactions, see: Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115−136.

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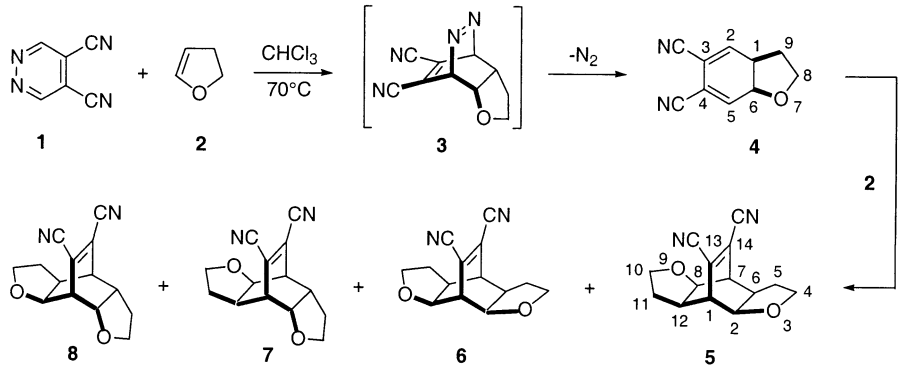
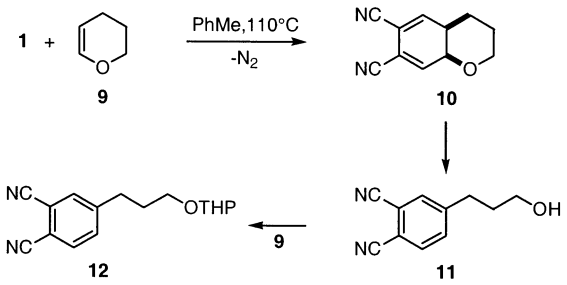
SCHEME 1



SCHEME 2



competitive nucleophilic attack of **14** upon the strongly electrophilic C-4 carbon of **1**, followed by replacement of the thiomethyl group by CN^- in the resulting derivative **15**. This intermediate could not be obtained as a pure product, but it was easily recognized in the reaction mixture afforded by **1** and *isolated* **14** at −78 °C: whereas the ^{1}H NMR spectrum shows a singlet at δ 2.32 and two doublets at δ 8.71 and 9.71 for the SMe and pyridazine protons, the ^{13}C NMR pattern exhibits, together with the signals of the corresponding carbons at δ 17.5, 148.95, and 151.6, two diagnostic singlets at δ 150.5 and 104.4 for the pyrroline C(2′)−C(3′) double bond. Only a small increase of **19** was achieved under standard conditions at −78 °C (Table 1, entry 3), the substitution route being favored by lower temperatures. On the contrary, when only 1 equiv of *t*-BuOK was employed for the generation of **14** and the reaction was carried out at 0 °C, we succeeded in obtaining **19** in 51% yield together with minor amounts of **16** and **20** (Table 1, entry 4). Finally, the use of the *isolated* dienophile **14** under comparable conditions (Table 1, entry 5) allowed us to isolate **19** and **20** as pure products in 50% and 23% yields, respectively.

The isolation of **19** strongly supported the proposed mechanism, and its availability prompted us to perform selective elaborations. Whereas elimination of methanethiol, simply achieved by heating at 110 °C in ethyl acetate or treatment with *t*-BuOK at room temperature for 24 h, led to the dicyanoindoline **20** in 98% and 93% yields, oxidation with a stoichiometric amount of DDQ at room temperature afforded **21** in 60% yield. Both **20** and **21** were then converted into the corresponding indoles **22** and **23** in 97% yield by DDQ in refluxing benzene; the latter was also obtained in 75% overall yield from **19** by a one-pot procedure with 2.1 equiv of the same reagent.

All the spectral data of the new products **5**−**8**, **12**, **16**, **19**−**21**, and **23** (Experimental Section) are in agreement with the assigned structures, and only the most significant ones are discussed below. The stereo- and regiochemistry of compounds **5**−**8**, as well as their relative percentages in the isolated fractions, were determined on the basis of the following considerations:

(a) According to a C_2 and C_s symmetry of its components, coming from endo/anti approaches between **2** and **4**, the ^{13}C NMR spectrum of the largely predominant fraction shows seven resonances for **5** together with nine for **6**, the C-6, C-7, and C-8 carbons of the latter giving rise to a single signal at δ 43.4. On the contrary, 27 resonances are present in the pattern of the minor fraction, with an overlap at δ 77.8 for the C-2 carbons of the asymmetrical regioisomers **7** and **8** arising from endo/sin or exo/anti interactions of the same reagents.

(b) Whereas the ^{1}H NMR spectrum of **5** and **6** exhibit a multiplet at δ 4.07 and two triplets at δ 3.71 and 3.18 (relative intensities 8:1:1) for the endo protons vicinal to oxygen of the two isomers and H-1 and H-7 of the minor one, the pattern of the second couple is characterized by two well-resolved, diagnostic doublets of doublets at δ 4.41 and 4.31 and a triplet at δ 3.11 (relative intensities 1:1.5:1) attributable to the *exo*-H-2 protons of **8** and **7** and H-7 of the former, respectively.

(c) The lack of any ^{1}H NMR signal above δ 4.15 for the major fraction led us to discard less favorable diastereomers with endo tetrahydrofuran rings.

The presence of the fully conjugated N−C═C−C═C−C≡N moiety in **19** is well documented by its IR spectrum showing, together with a weak absorption at 2222 cm^{-1} for the 4-CN, a strong band at remarkably lower frequency (2175 cm^{-1}) for the second cyano substituent at position 3. Moreover, as a consequence of the push−pull electron drift, the diene CH group gives rise to notably shielded ^{1}H and ^{13}C NMR resonances at δ 4.69 and 83.2, respectively. Finally, the relative stereochemistry of **19**, suggested by a *supra* migration of the SMe group, was inferred from the comparison of the experimental $^3J_{1,2}$ coupling constant (10.0 Hz) with the theoretical values (12.1 and 4.3 Hz) obtained by molecular modeling calculations (Monte Carlo method in MacroModel) for rigid trans and cis configurations with dihedral angles of about 174° and 50°, respectively.

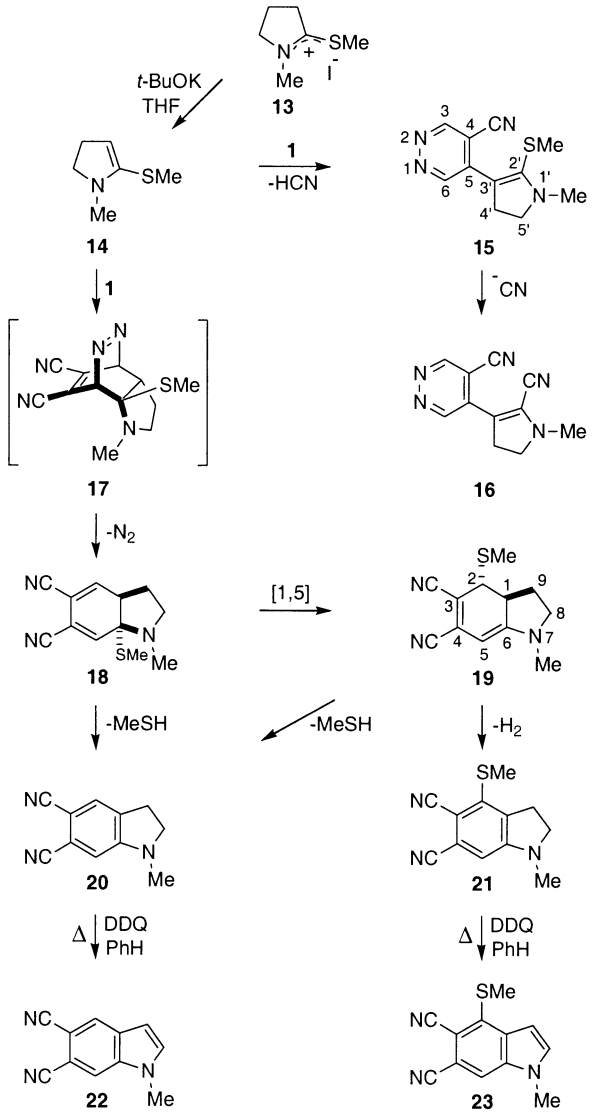
In summary, the results of this work emphasize a new facet of the cycloaddition chemistry of DCP with interesting mechanistic and synthetic implications. Particularly, the conversion of **1** and **14** into 5,6-dicyano-1-methylindole (**22**) in 70% overall yield through **19** and **20**

TABLE 1. Reactions of 1 with 14 in Anhydrous THF

	equiv					yield[a] (%)			
entry	**13**	*t*-BuOK	**14**	temp (°C)	time (min)	**16**	**19**	**20**[b]	**21**[b]
1[c]	1	1.5	(1)	rt	10			27	13
2[c]	1	1.5	(1)	0	60	9	8	14	14
3[c]	1	1.5	(1)	−78	60	42	12	11	5
4[c]	1	1	(1)	0	10	4	51	14	trace
5			1	0	30	2	50	23	

[a] Isolated yields. [b] The yields of the inseparable indolines **20** and **21** were determined by ^{1}H NMR analyses of the isolated fractions, through their relative molar ratios. [c] **14** was generated in situ from **13** and *t*-BuOK.

SCHEME 3



represents an excellent alternative to the direct benzoannelation of *N*-methylpyrrole with **1**, previously achieved in only 17% yield.[8]

Experimental Section[9]

Reaction of 1 with DHF (2). A mixture of **1** (0.0 65 g, 0.5 mmol) and **2** (0.351 g, 0.379 mL, 5.0 mmol) in chloroform (0.5 mL) was heated at 70 °C for 72 h in a screw-capped tube (Pyrex N. 13). The residue left by evaporation to dryness under reduced pressure was resolved into two components with ethyl acetate/petroleum ether (2:1 v/v) as eluent. The first band afforded a 1.5:1 mixture of (2*SR*,6*SR*,8*RS*,12*RS*)-13,14-dicyano-3,9-dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13-ene (**7**) and (2*SR*,6*SR*,8*SR*,-12*SR*)-13,14-dicyano-3,11-dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13-ene (**8**) as an ivory-colored solid (R_f 0.58, 0.007 g, 6%) that was crystallized from ether: IR 2213, 1073 cm^{-1}; ^{1}H NMR δ 1.70−2.25 (m), 2.34−2.56 (m), 2.71−2.87 (m), 2.91−3.07 (m), [3.11 (t, J = 3.2 Hz)], 3.31−3.49 (m), 3.68−3.93 (m), 3.98−4.13 (m), 4.31 (dd, J = 8.0 and 3.2 Hz), [4.41 (dd, J = 8.0 and 3.2 Hz)]; ^{13}C NMR δ 26.8, [27.2], 30.3, [31.1], 36.2, [36.85], 39.45, [40.7], [44.25], 44.3, 45.4, [45.8], [66.8], 66.95, [70.9], 71.1, [76.3], 76.8, 77.8, 114.2, [114.4], [114.45], 114.6, 128.5, [129.9], [132.7], 134.1.[10] Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.19; H, 5.83; N, 11.32.

The following band gave a 3:1 mixture of (2*RS*,6*RS*,8*RS*,-12*RS*)-13,14-dicyano-3,9-dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13-ene (**5**) and (2*RS*,6*RS*,8*SR*,12*SR*)-13,14-dicyano-3,11-dioxatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13-ene (**6**) as a white solid (R_f 0.35, 0.107 g, 88%) that was crystallized from ether/acetone: IR 2220, 1096, 1069 cm^{-1}; ^{1}H NMR δ 1.30−1.52 (m), 2.01−2.22 (m), 2.34−2.56 (m), [3.18 (t, J = 2.5 Hz)], 3.36−3.54 (m), [3.71 (t, J = 3.0 Hz)], 3.78−3.92 (m), 4.07 (m); ^{13}C NMR δ 30.1, [30.4], 39.6, [43.4], 44.9, [46.4], 68.3, [68.4], [77.9], 80.2, [114.8], 114.9, [115.0], [128.1], 129.2, [130.4].[10] Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.66; H, 6.08; N, 11.29.

1,2-Dicyano-4-[3-(tetrahydropyran-2-yloxy)propyl]benzene (12). Chromatographic workup [toluene/ethyl acetate (9:1 v/v)] of the residue coming from the reaction of **1** (0.065 g, 0.5 mmol) and **9** (0.421 g, 0.457 mL, 5.0 mmol) at 110 °C for 7 days in anhydrous toluene (0.5 mL) in the presence of a small amount of hydroquinone (0.006 g, 0.05 mmol) afforded phthalonitrile **12** (R_f 0.20, 0.092 g, 68%) as a pale yellow oil. An analytical sample was obtained by dissolution in ether, filtration, evaporation to dryness, and prolonged evacuation at 10^{-2} Torr: IR 2235 cm^{-1}; ^{1}H NMR δ 1.44−1.98 (m, 8H), 2.85 (t, J = 7.7 Hz, 2H), 3.35−3.56 (m, 2H), 3.69−3.90 (m, 2H), 4.53 (dd, J = 5.1 and 3.3 Hz, 1H), 7.56 (dd, J = 8.1 and 1.8 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 19.7, 25.35, 30.5, 30.6, 32.4, 62.65, 65.9, 99.1, 113.1, 115.5, 115.55, 115.7, 133.4, 133.45, 133.7, 148.9. Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.85; H, 6.82; N, 10.54.

Reactions of 1 with the Pyrroline 14: Synthesis of Compounds 16, 19, and 20. (A) A suspension of **13**[11] (0.129 g, 0.5 mmol) and *t*-BuOK (0.084 g, 0.75 mmol) in anhydrous THF (1 mL) was stirred at room temperature for 1 h; after the mixture was cooled at −78 °C, a solution of **1** (0.065 g, 0.5 mmol) in the same solvent (0.5 mL) was added and the mixture was set aside at the same temperature for 1 h. The residue left by evaporation to dryness was triturated with acetone and filtered; the solid recovered from the filtrate was resolved into three components with petroleum ether/ethyl acetate (1:1 v/v). While the first band afforded a 2:1 mixture of the indolines **20** and **21** (R_f 0.51, 0.016 g), the second one yielded (1*SR*,2*RS*)-3,4-dicyano-7-methyl-2-

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(9) General experimental information was given in: Giomi, D.; Turchi, S.; Danesi, A.; Faggi, C. *Tetrahedron* **2001**, *57*, 4237−4242.

(10) The values in square brackets refer to the minor component.

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methylthio-7-azabicyclo[4.3.0]nona-3,5-diene (**19**) (R_f 0.29, 0.014 g, 12%) as yellow crystals: mp 127−128 °C (from ether); IR 2222, 2175 cm^{-1}; ^1H NMR δ 1.67−1.89 (m, 1H), 2.23 (s, 3H), 2.43−2.58 (m, 1H), 2.92 (s, 3H), 2.99−3.17 (m, 1H), 3.31 (d, A part of an ABMX system, J_{AB} = 16.9 Hz, 1H), 3.47−3.64 (m, 1H), 3.54 (dd, J = 10.0 and 1.0 Hz, 1H), 4.69 (sbr s, 1H); ^{13}C NMR δ 12.8, 29.5, 33.1, 45.2, 46.4, 54.0, 83.2, 100.65, 116.45, 118.0, 128.4, 159.1. Anal. Calcd for $C_{12}H_{13}N_3S$: C, 62.31; H, 5.66; N, 18.17. Found: C, 62.35; H, 5.39; N, 18.30.

The slowest moving fractions gave 4-cyano-5-(2-cyano-1-methyl-4,5-dihydropyrrol-3-yl)pyridazine (**16**) (R_f 0.18, 0.044 g, 42%), as red coral crystals: mp 129−130 °C (from ether); IR 2236, 2215 cm^{-1}; ^1H NMR δ 3.05 (s, 3H), 3.51 (m, 4H), 9.04 (d, J = 1.1 Hz, 1H), 9.70 (d, J = 1.1 Hz, 1H); ^{13}C NMR δ 30.7, 36.5, 53.9, 104.2, 111.5, 115.05, 116.0, 128.5, 133.6, 147.3, 151.6. Anal. Calcd for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N, 33.16. Found: C, 62.23; H, 4.11; N, 33.40.

(B) When the above reaction was carried out at 0 °C, chromatographic workup of the raw product afforded, together with a 1:1 mixture of **20** and **21** (0.029 g), compounds **19** (0.009 g, 8%) and **16** (0.010 g, 9%), identical with the species previously obtained.

(C) Operating as above at room temperature for 10 min, a 2:1 mixture of **20** and **21** (0.040 g) was isolated.

(D) When the generation of **14** was achieved from **13** with a stoichiometric amount of *t*-BuOK (0.056 g, 0.5 mmol) and the reaction with **1** was carried out at 0 °C for 10 min, compound **20** with a trace amount of **21** (0.013 g) was obtained along with the derivatives **19** (0.059 g, 51%) and **16** (0.004 g, 4%)

(E) A solution of **1** (0.065 g, 0.5 mmol) in anhydrous THF (2 mL) was added within 30 min under stirring in nitrogen atmosphere to a solution of the *isolated* pyrroline **14**[11] (0.065 g, 0.5 mmol) in the same solvent (1 mL) previously cooled at 0 °C. Operating as above, the raw product was resolved into three components. The fastest running band afforded 5,6-dicyano-1-methyl-2,3-dihydroindole (**20**) (R_f 0.51, 0.021 g, 23%) as a pale yellow solid which, after crystallization from ether, gradually darkened above 197 °C and melted at 208−209 °C: IR 2228, 2211 cm^{-1}; ^1H NMR δ 2.87 (s, 3H), 3.08 (t, J = 8.8 Hz, 2H), 3.64 (t, J = 8.8 Hz, 2H), 6.46 (s, 1H), 7.21 (sbr s, 1H); ^{13}C NMR δ 27.7, 33.55, 54.3, 101.4, 107.8, 116.3, 116.5, 117.3, 127.8, 135.0, 155.4. Anal. Calcd for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 71.85; H, 4.70; N, 23.05.

The following bands gave compounds **19** (0.058 g, 50%) and **16** (0.002 g, 2%).

Reactions of the Bicyclic Derivative 19. (A) A solution of **19** (0.023 g, 0.1 mmol) in ethyl acetate (1.5 mL) was heated at 110 °C for 24 h in a screw-capped tube (Pyrex N. 13). Removal of the solvent yielded the indoline **20** (0.018 g, 98%), identical with the product obtained above.

(B) A mixture of **19** (0.023 g, 0.1 mmol) and potassium *tert*-butoxyde (0.012 g, 0.11 mmol) in anhydrous THF (0.5 mL) was stirred at room temperature for 24 h. Chromatographic workup of the residue left by evaporation to dryness afforded compound **20** (0.017 g, 93%).

(C) A suspension of **19** (0.116 g, 0.5 mmol) and DDQ (0.125 g, 0.55 mmol) in anhydrous benzene (2.5 mL) was kept at room temperature under magnetic stirring for 24 h. Chromatographic resolution [petroleum ether/ethyl acetate (1:1 v/v)] of the brown solid left by evaporation to dryness gave 5,6-dicyano-1-methyl-4-methylthio-2,3-dihydroindole (**21**) (R_f 0.50, 0.069 g, 60%) as yellow needles: mp 148−149 °C (from ether); IR 2229, 2211 cm^{-1}; ^1H NMR δ 2.51 (s, 3H), 2.88 (s, 3H), 3.17 (t, J = 8.8 Hz, 2H), 3.67 (t, J = 8.8 Hz, 2H), 6.40 (s, 1H); ^{13}C NMR δ 18.2, 28.3, 33.6, 53.85, 105.5, 106.9, 116.3, 116.35, 118.3, 136.4, 138.65, 154.85. Anal. Calcd for $C_{12}H_{11}N_3S$: C, 62.86; H, 4.84; N, 18.33. Found: C, 62.71; H, 4.72; N, 18.05.

5,6-Dicyano-1-methyl-1*H*-indole (22). A mixture of **20** (0.092 g, 0.5 mmol) and DDQ (0.125 g, 0.55 mmol) in anhydrous benzene (2 mL) was refluxed with stirring for 12 h. Removal of the solvent left a residue that was subjected to flash chromatography with petroleum ether/ethyl acetate (1:1 v/v) as eluent to give compound **22** (R_f 0.42, 0.088 g, 97%) as an ivory-colored solid: mp 257 °C (after sublimation at 120−130 °C/10^{-2} Torr) (lit.[12] mp 257−258 °C).

5,6-Dicyano-1-methyl-4-methylthio-1*H*-indole (23). (A) Operating as above, reaction of **21** (0.115 g, 0.5 mmol) with DDQ (0.125 g, 0.55 mmol) gave compound **23** (R_f 0.41, 0.110 g, 97%) as ivory-colored needles: mp 199−200 °C (from ether); IR 2228, 2220 cm^{-1}; ^1H NMR δ 2.64 (s, 3H), 3.92 (s, 3H), 6.87 (dd, J = 3.3 and 0.8 Hz, 1H), 7.88 (d, J = 3.3 Hz, 1H), 8.35 (d, J = 0.8 Hz, 1H); ^{13}C NMR δ 18.5, 33.45, 102.7, 105.8, 107.1, 116.3, 117.3, 117.4, 132.0, 135.5, 135.6, 136.4. Anal. Calcd for $C_{12}H_9N_3S$: C, 63.41; H, 3.99; N, 18.49. Found: C, 63.53; H, 4.00; N, 18.65.

(B) A mixture of **19** (0.116 g, 0.5 mmol) and DDQ (0.238 g, 1.05 mmol) in anhydrous benzene (5 mL) was stirred at room temperature for 24 h and then refluxed for 12 h. Chromatographic workup of the raw product afforded the derivative **23** (R_f 0.41, 0.085 g, 75%), identical with the species previously described.

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