Polyfunctionalized Cage Compounds by Pericyclic Domino Processes of 4,5-Dicyanopyridazine with Dienes: Applications and Limits

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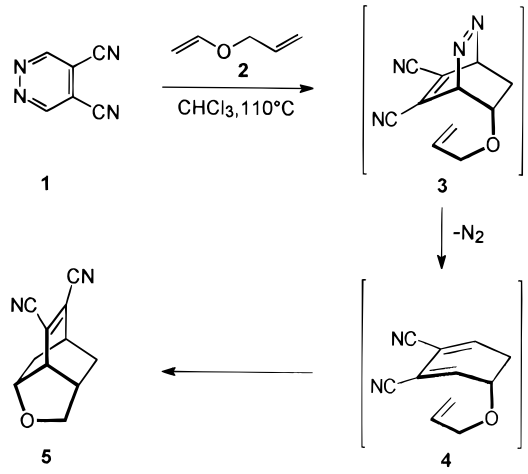
The title compound **1** was found to behave as an attractive *masked bis-diene* to give 4-oxatricyclo-[4.3.1.$0^{3,7}$]dec-8-ene, 5-aza- and 5-silatricyclo[5.3.1.$0^{3,8}$]undec-9-ene, tricyclo[3.2.1.$0^{2,7}$]oct-3-ene, and tricyclo[5.3.1.$0^{3,8}$]undec-9-ene derivatives through purely pericyclic, three-step homodomino processes with diverse bis-dienophiles; whereas the reaction with myrcene (**21**) was characterized by a complete sitoselectivity affording compound **25**, treatment of **1** with (*R*)-(−)-β-citronellene (**26a**) gave a 3:1 mixture of the homochiral diastereomers **30a** and **31a**. Some limits of this methodology, mainly arising from competitive side reactions upon the key cyclohexa-1,3-diene intermediates, are emphasized. The structures of the new compounds were established on the basis of spectral data.

Although 1,2-diazines have been scarcely employed as heterodienes in inverse-electron-demand [4 + 2] cycloadditions,[1] probably due to some discouraging results,[2] a systematic investigation undertaken by our group clearly demonstrated that 4,5-dicyanopyridazine (DCP) (**1**) exhibits a remarkable reactivity toward several 2π electron counterparts.[3] Particularly, after DCP was shown to react under relatively mild conditions with 2,3-dimethylbuta-1,3-diene to give a tricyclo[3.2.1.$0^{2,7}$]oct-3-ene skeleton through a pericyclic domino process,[4] it has been more recently exploited in similar reactions with diverse bis-dienophiles for a direct access to carbo- and hetero-cage derivatives.[5] In this context, we wish now to report new results on the possibility of expanding the scope of this attractive strategy for the synthesis of title compounds.

Results and Discussion

Treatment of **1** with an excess of allyl vinyl ether (**2**) in chloroform at 110 °C for 24 h afforded nearly quantitatively 8,9-dicyano-4-oxatricyclo[4.3.1.$0^{3,7}$]dec-8-ene (**5**) by a three-step homodomino reaction: the labile primary adduct, coming from an intermolecular [4 + 2] cycloaddition of DCP upon the most activated double bond of **2**, evolved into the final product by loss of nitrogen followed by an intramolecular Diels−Alder reaction of the resulting cyclohexadiene **4**, strongly assisted by entropic acceleration (Scheme 1). Noteworthy, no trapping was observed for **4** by the large excess of the reagent.

Scheme 1



The same substrate reacted more slowly with vinyl methacrylate (**6**) to give the desired tricyclic lactone **8** in 56% yield; however, phthalonitrile (**9**) (39%) was also obtained in this case through a competitive elimination of methacrylic acid from the likely common intermediate **7** (Scheme 2). Even longer reaction times were required with vinyl cinnamate (**10**) (Experimental Section), and compound **11** was isolated as a pure product in 34% yield by careful resolution of the complex reaction mixture.

Unfortunately, repeated attempts to form in an analogous fashion 5-oxatricyclo[5.3.1.$0^{3,8}$]undec-9-en-4-ones were unsuccessful. Whereas reactions of **1** with allyl methacrylate, allyl cinnamate, and allyl crotonate led to untractable materials, treatment of DCP with **12** gave the ester **14** in 40% yield as a result of a preferential aromatization of the intermediate **13**; according to a previous result,[5] this conversion probably involves a hydrogen transfer from the latter to the starting dicyanopyridazine **1**.

On the contrary, when **12** was replaced with the amide **15**, the tricyclic δ-lactam **17** was obtained in 37% yield through the open-chain compound **16** (Scheme 3).[6]

(1) (a) Boger, D. L.; Weinreb, S. N. *Hetero Diels−Alder Methodology in Organic Synthesis*; Academic Press: New York, 1987; p 313. (b) Coates, W. J. In *Comprehensive Heterocyclic Chemistry II*; Boulton, A. J., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 6, p 30.

(2) (a) Maggiora, L.; Mertes, M. P. *J. Org. Chem.* **1986**, *51*, 950. (b) Benson, S. C.; Gross, J. L.; Snyder, J. K. *J. Org. Chem.* **1990**, *55*, 3257.

(3) (a) Nesi, R.; Giomi, D.; Turchi, S.; Falai, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2201. (b) Turchi, S.; Giomi, D.; Capaccioli, C.; Nesi, R. *Tetrahedron* **1997**, *53*, 11711. (c) Turchi, S.; Nesi, R.; Giomi, D. *Tetrahedron* **1998**, *54*, 1809. (d) Nesi, R.; Turchi, S.; Giomi, D.; Corsi, C. *Tetrahedron* **1998**, *54*, 10851.

(4) Nesi, R.; Giomi, D.; Turchi, S.; Paoli, P. *Tetrahedron* **1994**, *50*, 9189.

(5) Giomi, D.; Nesi, R.; Turchi, S.; Coppini, R. *J. Org. Chem.* **1996**, *61*, 6028.

10.1021/jo991191v CCC: $19.00
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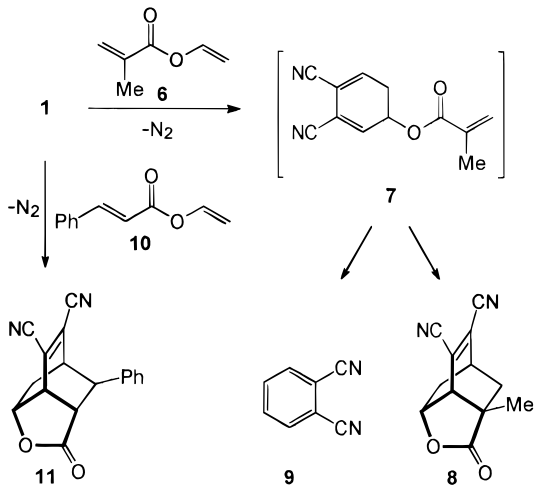
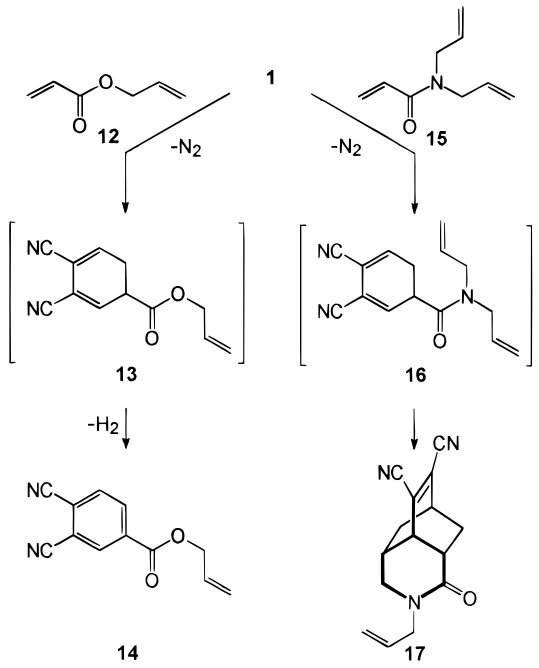
Scheme 2



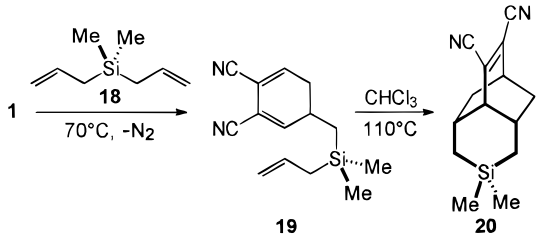
Scheme 3



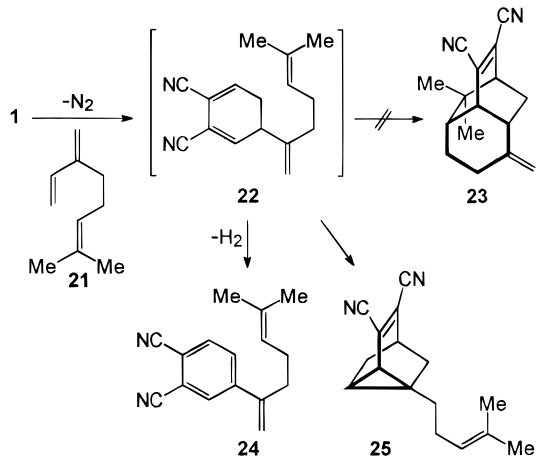
Efforts to carry out a direct domino conversion of DCP and diallyldimethylsilane (**18**) into the cage system **20** at 110 °C caused both decomposition and isomerization processes of the silylated reagent, and the complex reaction mixtures contained only small amounts of the desired product (^{1}H NMR). On the other hand, although the cyclohexadiene derivative **19** was easily isolated in 66% yield under milder conditions, its subsequent cycloaddition into **20**, strongly hampered by the encumbering methyl groups, was achieved in only 32% yield by prolonged heating at the original temperature (Scheme 4).

Similar steric effects also play a critical role in the reaction of **1** with myrcene (**21**) characterized by a total sitoselectivity. Thus, the intermediate **22**, coming from a primary interaction of DCP upon the terminal unsubstituted double bond of the terpene, afforded, together

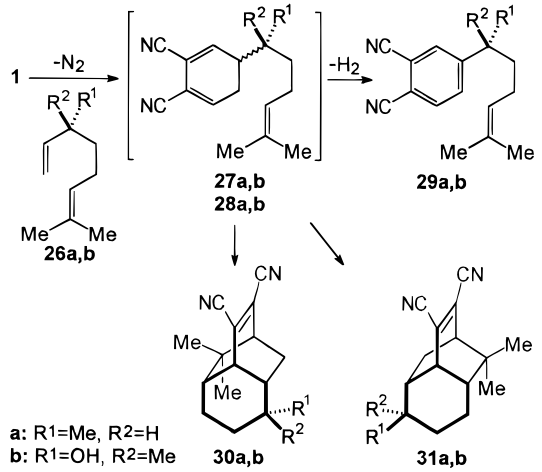
Scheme 4



Scheme 5



Scheme 6



with the corresponding aromatization product **24** (19%), the more strained tricyclooctene **25** (24%) rather than the cage derivative **23** by a preferential cycloaddition with the less hindered vicinal dienophilic moiety (Scheme 5).

Replacement of **21** with the homochiral terpenes **26a**,**b** caused a remarkable reduction of reactivity, and very complex reactions were observed under forcing conditions; nevertheless, whereas in the first case a 3:1 mixture of the diastereomeric tricycloundecenes **30a** and **31a** was obtained in 28% yield together with a minor amount of the aromatic product **29a**, in the second one we succeeded in isolating, in addition to **29b** (6%), the cage compounds **30b** and **31b** in 12% and 19% yields, respectively (Scheme 6).

Bearing in mind that the intramolecular cycloadditions of the diastereomers **27a**,**b** and **28a**,**b** must compete effectively both with aromatization processes and intermolecular Diels−Alder reactions of the same species with the excess of the bis-dienophiles **26a**,**b**, the clear-cut

(6) For the greater reactivity of the bis-allyl amide moiety with respect to the corresponding ester in intramolecular Diels−Alder reactions, see: Swarbrick, T. M.; Markó, I. E.; Kennard, L. *Tetrahedron Lett.* **1991**, *32*, 2549.

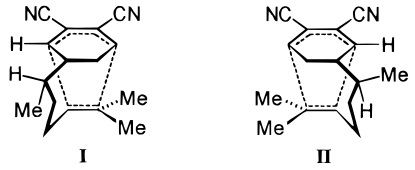
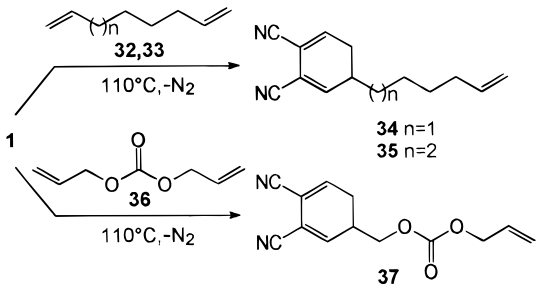


Figure 1.

Scheme 7



predominance of **30a** over **31a** can be tentatively accounted for by a different stabilization of the corresponding chairlike transition structures **I** and **II** (Figure 1), the latter being disfavored by a 1,3-diaxial methyl/hydrogen interaction.[7]

Repeated attempts to build up larger carbo- or heterocage skeletons with octa-1,7-diene (**32**), nona-1,8-diene (**33**), and diallyl carbonate (**36**) were completely unsuccessful, probably due to unfavorable entropic effects and repulsive nonbonding interactions. Moreover, although compounds **34**, **35**, and **37** were easily obtained in 50−52% yields from **1** and the above dienes (1 equiv, 110 °C) (Scheme 7), we did not succeed in isolating any phthalonitrile as a pure product from the complex reaction mixtures gained by heating the cyclohexadiene derivatives at higher temperature.

The structures of the new compounds **5**, **8**, **11**, **14**, **17**, **19**, **20**, **24**, **25**, **29**−**31a,b**, **34**, **35**, and **37** were determined on the basis of analytical and spectral evidence (Experimental Section). Whereas the ^{1}H NMR patterns of the 2,3-dicyanocyclohexa-1,3-dienes **19**, **34**, **35**, and **37** are characterized by a triplet and a doublet at δ 6.79−6.85 and 6.73−6.74 for the H-1 and H-4 protons, respectively, their ^{13}C coupled spectra exhibit two doublets at δ 143.5−150.9 for the corresponding alkenyl carbons. As for the benzoate **14**, the CH_2 resonance of the allyl moiety was detected as a doublet of triplets at δ 4.88.

The stereochemistry at C-10 for the γ-lactone **11**, determined by the *E* configuration of the cinnamate **10**, was confirmed by the lack of coupling between H-10 and the vicinal H-6 proton (θ = ca. 90°), which gives rise to a doublet ($J_{6,7}$ = 4.9 Hz) at δ 3.07 (Figure 2). The structure of **25** was firmly established on the basis of the ^{1}H and ^{13}C NMR resonances at δ 5.05 and 123.1, respectively, for the CH group of the terminal alkene moiety; furthermore, as previously reported for 3,4-dicyano-1,7-dimethyltricyclo[3.2.1.0^{2,7}]oct-3-ene,[4] a doublet (J = 12.4 Hz) was observed at δ 0.92 for the remarkably shielded endo protons at positions 6 and 8, together with a triplet (J = 4.8 Hz) at δ 3.0 for the bridgehead H-5. Finally, whereas the structures of the diastereomers **30a** and **31a** were

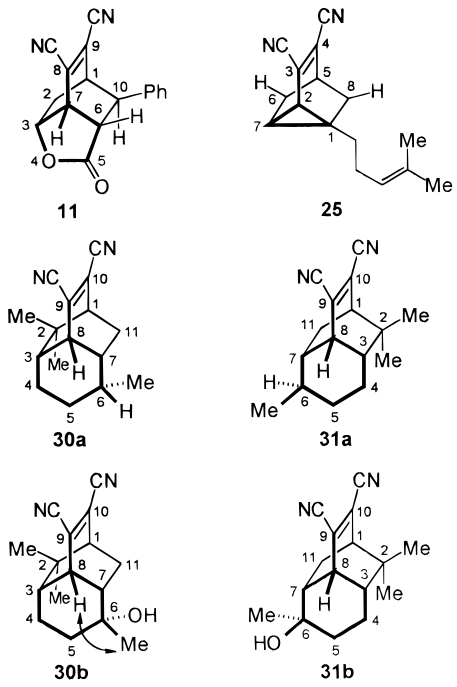


Figure 2.

attained, according to the spectral behavior of epimeric 6-methyltricyclo[5.3.1.0^{3,8}]undecanes,[8] in the light of the diagnostic downfield shift observed for the methyl group at position 6 on going from the endo (δ 0.88) to the exo configuration (δ 1.05), **30b** was distinguished from **31b** on the basis of a positive NOE effect detected for the former between the same substituent and H-8.

In conclusion, despite evident limits arising from a scarce reactivity toward a few counterparts or concomitant undesired evolution processes of the cyclohexadiene key intermediates, compound **1** can be rightly regarded as a versatile synthon in the realm of *masked or latent bis-dienes*[9] for elegant entries into diverse cage systems through purely pericyclic domino reactions.

Experimental Section

General Procedures. Melting points are uncorrected. IR spectra of solid and oily products were measured as KBr pellets and liquid films, respectively. Unless otherwise stated, ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 200 and 50 MHz, respectively. 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 chromatographic workup refers to the fractions of bp 40−70 °C. HPLC was performed with a RP18 5 μm column using CH_3CN/H_2O as eluent.

Thermal Reactions of 4,5-Dicyanopyridazine (1) with the Dienes 2, 6, 10, 12, 15, 18, 21, 26a,b, 32, 33, and 36: Synthesis of Compounds 5, 8, 11, 14, 17, 19, 24, 25, 29−31a,b, 34, 35, and 37. General Procedure. Unless otherwise indicated, a mixture of **1** (1 mmol) and the reagent in $CHCl_3$ (1 mL) was heated at 110 °C in a screw-capped tube (Pyrex no. 13), and the residue left by evaporation to dryness under reduced pressure was subjected to flash chromatography. When the conversion of **1** was incomplete, the yields of the isolated compounds were determined on the basis of the recovered starting material. Analytical samples of oily products were obtained by dissolution in dichloromethane, filtration,

(7) Impressive diastereospecificity was observed for intramolecular cycloadditions of cyclohexa-1,3-diene derivatives as a consequence of a more pronounced methyl/methyl overcrowding: Näf, F.; Decorzant, R.; Giersch, W.; Ohloff, G. *Helv. Chim. Acta* **1981**, *64*, 1387.

(8) Yamada, K.; Kyotani, Y.; Manabe, S.; Suanki, M. *Tetrahedron* **1979**, *35*, 293.

(9) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167.

evaporation to dryness, and prolonged evacuation at room temperature (10^{-2} Torr).

A. Treatment of **1** with allyl vinyl ether (**2**) (0.421 g, 0.55 mL, 5 mmol) for 24 h afforded 8,9-dicyano-4-oxatricyclo-[4.3.1.$0^{3,7}$]dec-8-ene (**5**) (0.184 g, 99%) that was crystallized from ether as ivory-colored needles: mp 117−118 °C; IR 2215, 1105 cm^{-1}; ^1H NMR δ 1.45−1.84 (m, 4H), 2.34−2.45 (m, 1H), 3.01 (m, 1H), 3.31 (t, J = 4.6 Hz, 1H), 3.78 (m, AB part of an ABX system, J = 8.1 and 3.7 Hz, 2H), 4.22 (t, J = 6.0 Hz, 1H); ^{13}C NMR δ 32.8 (d), 33.9 (t), 35.2 (d), 36.9 (t), 44.8 (d), 73.1 (d), 73.4 (t), 113.7 (s), 114.3 (s), 125.6 (s), 134.4 (s). Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.62; H, 5.41; N, 15.37.

B. The crude reaction product of **1** and vinyl methacrylate (**6**) (1.121 g, 1.20 mL, 10 mmol) (4 days) was mixed with sand and sublimed at 50 °C/18 Torr to give phthalonitrile (**9**) (0.050 g, 39%); the sand was then extracted with dichloromethane (2 × 15 mL) to yield (1*SR*,3*RS*,6*SR*,7*RS*)-8,9-dicyano-6-methyl-4-oxatricyclo[4.3.1.$0^{3,7}$]dec-8-en-5-one (**8**) (0.120 g, 56%) as an ivory-colored solid: mp 212−213 °C (from chloroform); IR 2220, 1783 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.03 (s, 3H), 1.24−1.38 (m, 1H), 1.56−1.83 (m, 2H), 2.06 (m, 1H), 3.26 (br s, 1H), 3.91 (d, J = 5.6 Hz, 1H), 4.72 (t, J = 5.6 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 19.6 (q), 31.0 (t), 35.2 (d), 35.6 (t), 41.7 (s), 47.85 (d), 73.7 (d), 114.4 (s), 115.05 (s), 124.0 (s), 135.5 (s), 179.3 (s). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.00; H, 4.63; N, 13.40.

C. Chromatographic workup [toluene/ethyl acetate (20:3 v/v)] of the crude product from **1** and (*E*)-vinyl cinnamate (**10**) (0.871 g, 0.81 mL, 5 mmol) (9 days) afforded (1*RS*,3*RS*,6*SR*,-7*SR*,10*RS*)-8,9-dicyano-10-phenyl-4-oxatricyclo[4.3.1.$0^{3,7}$]dec-8-en-5-one (**11**) (R_f = 0.34, 0.095 g, 34%), as colorless crystals: mp 166.5−167 °C (from ether); IR 2227, 1778 cm^{-1}; ^1H NMR δ 1.80 (m, 1H), 2.20 (m, 1H), 3.07 (sbr d, J = 4.9 Hz, 1H), 3.50 (m, 1H), 3.59 (m, 1H), 4.07 (t, J = 4.9 Hz, 1H), 4.78 (dd, J = 7.5 and 4.9 Hz, 1H), 6.96−7.03 (m, 2H), 7.30−7.42 (m, 3H); ^{13}C NMR δ 33.25 (t), 43.15 (d), 43.3 (d), 43.8 (d), 45.6 (d), 74.3 (d), 113.0 (s), 113.5 (s), 123.9 (s), 126.9 (d), 128.15 (d), 129.3 (d), 133.9 (s), 138.7 (s), 175.65 (s). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.79; H, 4.48; N, 9.87.

D. Chromatographic resolution [petroleum ether/ethyl acetate (4:1 v/v)] of the residue coming from **1** and allyl acrylate (**12**) (0.561 g, 0.56 mL, 5 mmol) (48 h) gave allyl 3,4-dicyanobenzoate (**14**) (R_f = 0.43, 0.085 g, 40%) as ivory-colored crystals: mp 62−62.5 °C (from *n*-pentane/ether); IR 2235, 1726 cm^{-1}; ^1H NMR δ 4.88 (dt, J = 6.0 and 1.2 Hz, 2H), 5.33−5.49 (m, 2H), 5.93−6.13 (m, 1H), 7.93 (d, J = 8.1 Hz, 1H), 8.37−8.47 (m, 2H); ^{13}C NMR δ 67.1 (t), 114.6 (s), 114.7 (s), 116.5 (s), 119.4 (s), 120.0 (t), 131.0 (d), 133.8 (d), 133.9 (d), 134.3 (d), 134.8 (s), 162.8 (s). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.68; H, 3.80; N, 12.96.

E. Operating as above with ethyl acetate/petroleum ether (2:1 v/v) as eluent, the crude reaction product from **1** and *N*,*N*-diallyl acrylamide (**15**)[10] (0.166 g, 1.1 mmol) (6 days) yielded 5-allyl-9,10-dicyano-5-azatricyclo[5.3.1.$0^{3,8}$]undec-9-en-4-one (**17**) (R_f = 0.32, 0.094 g, 37%) that was crystallized from ethyl acetate as colorless needles: mp 180.5−181 °C; IR 2216, 1634 cm^{-1}; ^1H NMR δ 1.44 (ddd, J = 13.0, 5.1 and 2.6 Hz, 1H), 1.66−2.20 (m, 4H), 2.52−2.65 (m, 1H), 3.08 (quintet, J = 2.6 Hz, 1H), 3.14 (dd, J = 4.0 and 2.6 Hz, 1H), 3.35 (m, AB part of an ABX system, J = 12.7, 4.0, and 1.6 Hz, 2H), 3.80 (m, 1H), 4.18 (m, 1H), 5.14−5.29 (m, 2H), 5.63−5.83 (m, 1H); ^{13}C NMR δ 29.0 (t), 29.2 (d), 33.5 (t), 34.4 (d), 35.4 (d), 38.0 (d), 49.0 (t), 50.1 (t), 113.6 (s), 113.7 (s), 118.8 (t), 129.3 (s), 131.9 (d), 133.1 (s), 170.3 (s). Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.07; H, 5.99; N, 16.33.

F. Chromatographic workup [petroleum ether/ethyl acetate (8:1 v/v)] of the reaction product obtained from **1** and diallyldimethylsilane (**18**) (0.702 g, 0.91 mL, 5 mmol) at 70 °C for 6 days gave allyl[(2,3-dicyanocyclohexa-1,3-dien-5-yl)methyl]-dimethylsilane (**19**) (R_f = 0.35, 0.160 g, 66%), as a pale yellow oil: IR 2226 cm^{-1}; ^1H NMR δ 0.06 (s, 6H), 0.78 (m, 2H), 1.54 (d, J = 8.5 Hz, 2H), 2.27 (m, 1H), 2.50−2.77 (m, 2H), 4.82−4.90 (m, 2H), 5.73 (m, 1H), 6.73 (d, J = 4.4 Hz, 1H), 6.79 (t, J = 4.6 Hz, 1H); ^{13}C NMR δ −2.9 (q), 19.1 (t), 23.5 (t), 28.65 (d), 30.4 (t), 107.2 (s), 108.5 (s), 113.9 (t), 115.0 (s), 115.1 (s), 133.9 (d), 143.9 (d), 150.9 (d). Anal. Calcd for $C_{14}H_{18}N_2Si$: C, 69.38; H, 7.48; N, 11.56. Found: C, 69.04; H, 7.59; N, 11.22.

G. Chromatographic resolution [petroleum ether/ethyl acetate (7:1 v/v)] of the residue coming from **1** and myrcene (**21**) (0.150 g, 0.19 mL, 1.1 mmol) (4 days) afforded, in order of decreasing mobility, 1,2-dicyano-4-(6′-methylhepta-1′,5′-dien-2′-yl)benzene (**24**) (R_f = 0.61, 0.039 g, 19%) as a yellow oil: IR 2234 cm^{-1}; ^1H NMR δ 1.52 (s, 3H), 1.66 (s, 3H), 2.12 (q, J = 7.5 Hz, 2H), 2.51 (t, J = 7.5 Hz, 2H), 5.07 (m, 1H), 5.33 (sbr s, 1H), 5.44 (sbr s, 1H), 7.72−7.80 (m, 3H); ^{13}C NMR δ 17.7 (q), 25.6 (q), 26.5 (t), 34.6 (t), 113.9 (s), 115.4 (s), 115.55 (s), 116.0 (s), 117.4 (t), 122.7 (d), 130.5 (d), 131.1 (d), 132.8 (s), 133.5 (d), 145.15 (s), 146.9 (s). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.04; H, 6.53; N, 12.09.

The second band gave 3,4-dicyano-1-(2′-methylpent-2′-en-5′-yl)tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**25**) (R_f = 0.49, 0.050 g, 24%) as a pale yellow oil: IR 2214 cm^{-1}; ^1H NMR δ 0.92 (d, J = 12.4 Hz, 2H), 1.50−1.77 (m, 10H), 1.89−2.11 (m, 4H), 3.0 (t, J = 4.8 Hz, 1H), 5.05 (m, 1H); ^{13}C NMR δ 17.7 (q), 24.1 (d), 25.7 (q), 26.2 (t), 27.3 (t), 27.6 (d), 30.6 (t), 31.5 (t), 31.6 (s), 36.6 (d), 114.8 (s), 115.1 (s), 122.5 (s), 123.1 (d), 123.7 (s), 132.5 (s). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.42; H, 7.38; N, 12.03.

Some unreacted DCP was recovered from the slowest moving fractions (R_f = 0.11, 0.017 g).

H. Operating as above with petroleum ether/ethyl acetate (12:1 v/v) as eluent, the crude product of **1** with (*R*)-(−)-β-citronellene (**26a**) (0.691 g, 0.91 mL, 5 mmol) (5 days) yielded a 3:1 mixture of (1*S*,3*S*,6*R*,7*R*,8*R*)-9,10-dicyano-2,2,6-trimethyltricyclo[5.3.1.$0^{3,8}$]undec-9-ene (**30a**) and (1*R*,3*R*,6*R*,7*S*,8*S*)-9,10-dicyano-2,2,6-trimethyltricyclo[5.3.1.$0^{3,8}$]undec-9-ene (**31a**) (R_f = 0.50, 0.058 g, 28%) as a white solid: ^1H NMR δ 0.85 (s), 0.88 (d, J = 6.6 Hz, 3H), [1.05 (d, J = 7.3 Hz)], 1.14 (s), [1.19 (s)], 1.20−2.0 (m), 2.47 (m), 2.58 (t, J = 2.5 Hz), [2.85 (m)]; ^{13}C NMR δ [18.2 (q)], 20.4 (q), 20.5 (t), [20.85 (t)], 21.4 (q), [21.8 (q)], [22.4 (t)], 25.5 (t), 25.6 (t), [26.1 (t)], [30.4 (d)], 33.0 (q), [33.2 (q)], 33.5 (d), [36.1 (d)], 36.2 (d), 37.1 (d), [37.7 (d)], 38.15 (s), [38.4 (s)], [39.3 (d)], 46.4 (d), 47.7 (d), [48.15 (d)], [113.7 (s)], 114.5 (s), [114.6 (s)], 114.9 (s), 131.05 (s), [131.1 (s)], 132.3 (s), [132.9 (s)].[11]

HPLC resolution of the above mixture yielded **30a** (0.015 g) as a white solid; an analytical sample, obtained by washing with the minimun amount of anhydrous ether, gradually wrinkled above 80 °C and melted at 93−94 °C: $[\alpha]^{22}_D$ = (+)-72.6° (*c* 0.5, $CHCl_3$); IR 2214 cm^{-1}; ^1H NMR δ 0.85 (s, 3H), 0.88 (d, J = 6.6 Hz, 3H), 1.14 (s, 3H), 1.20−1.82 (m, 9H), 2.47 (t, J = 2.8 Hz, 1H), 2,58 (t, J = 2.5 Hz, 1H). Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 79.68; H, 8.33; N, 11.85.

The second band gave 1,2-dicyano-4-[(6′*R*)-2′-methylhept-2′-en-6′-yl)]benzene (**29a**) (R_f = 0.37, 0.012 g, 6%) as a pale yellow oil: $[\alpha]^{24}_D$ = (−)100.0° (*c* 0.2, $CHCl_3$); IR 2234 cm^{-1}; ^1H NMR δ 1.26 (d, J = 7.0 Hz, 3H), 1.50 (s, 3H), 1.58−1.64 (m, 2H), 1.67 (s, 3H), 1.80−1.88 (m, 2H), 2.83 (sextet, J = 7.0 Hz, 1H), 5.02 (m, 1H), 7.51−7.75 (m, 3H); ^{13}C NMR δ 17.65 (q), 21.5 (q), 25.6 (q), 25.7 (t), 37.7 (t), 39.4 (d), 113.1 (s), 115.5 (s), 115.6 (s), 115.9 (s), 123.2 (d), 132.0 (d), 132.4 (d), 132.5 (s), 133.5 (d), 154.4 (s). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.30; H, 7.35; N, 12.06.

A small amount of **1** (0.020 g) was recovered by washing the column with ethyl acetate.

I. The reaction mixture of **1** with (*R*)-(−)-linalool (**26b**) (0.771 g, 0.89 mL, 5 mmol) (8 days) was resolved into three components with petroleum ether/ethyl acetate (2:1 v/v) as eluent. The faster running band afforded 1,2-dicyano-4-[(6′*R*)-6′-hydroxy-2′-methylhept-2′-en-6′-yl)]benzene (**29b**) (R_f = 0.60,

(10) Naito, T.; Honda, Y.; Miyata, O.; Ninomiya, I. *J. Chem. Soc., Perkin Trans. 1* **1995**, 19.

(11) The values in square brackets refer to the minor diastereomer.

0.016 g, 6%) as a yellow oil: $[\alpha]^{24}_D = (-)2.6°$ (*c* 0.2, $CHCl_3$); IR 3497, 2237 cm^{-1}; ^1H NMR δ 1.48 (sbr s, 3H), 1.55 (s, 3H), 1.64 (sbr s, 3H), 1.84−1.90 (m, 4H), 2.16 (sbr s, 1H), 5.04 (m, 1H), 7.78 (m, 2H), 7.93 (m, 1H); ^{13}C NMR δ 17.7 (q), 22.6 (q), 25.6 (q), 30.5 (t), 43.3 (t), 74.7 (s), 113.7 (s), 115.45 (s), 115.6 (s), 115.8 (s), 123.0 (d), 129.8 (d), 130.5 (d), 133.3 (d), 133.4 (s), 154.6 (s). Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.28; H, 6.99; N, 11.35.

The following band gave (1*R*,3*R*,6*R*,7*R*,8*R*)-9,10-dicyano-6-hydroxy-2,2,6-trimethyltricyclo[5.3.1.$0^{3,8}$]undec-9-ene (**31b**) (R_f = 0.40, 0.048 g, 19%) that, after crystallization from ether, gradually wrinkled above 165 °C and melted at 181−182 °C: $[\alpha]^{19}_D = (-)66.0°$ (*c* 0.45, $CHCl_3$); IR 2221 cm^{-1}; ^1H NMR δ 0.87 (s, 3H), 1.16 (s, 3H), 1.24 (s, 3H), 1.30−1.80 (m, 9H), 2.50 (m, 1H), 3.33 (m, 1H); ^{13}C NMR δ 21.6 (t), 21.9 (q), 24.2 (t), 30.1 (q), 30.9 (t), 33.05 (q), 36.9 (d), 38.2 (s), 40.2 (d), 41.85 (d), 48.1 (d), 71.45 (s), 114.5 (s), 114.8 (s), 131.2 (s), 132.8 (s). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.68; H, 7.62; N, 11.18.

The slowest moving fractions yielded (1*S*,3*S*,6*R*,7*S*,8*S*)-9,-10-dicyano-6-hydroxy-2,2,6-trimethyltricyclo[5.3.1.$0^{3,8}$]undec-9-ene (**30b**) (R_f = 0.20, 0.031 g, 12%), as a pale yellow oil: $[\alpha]^{22}_D = (+)67.0°$ (*c* 0.95, $CHCl_3$); IR 3473, 2223 cm^{-1}; ^1H NMR δ 0.87 (s, 3H), 1.0−2.10 (m, 8H), 1.19 (s, 3H), 1.24 (s, 1H), 1.35 (s, 3H), 2.51 (t, *J* = 2.7 Hz, 1H), 2.75 (t, *J* = 2.8 Hz, 1H); ^{13}C NMR δ 21.55 (q), 22.8 (t), 23.7 (t), 27.4 (q), 31.7 (t), 33.1 (q), 37.1 (d), 38.1 (s), 42.7 (d), 43.1 (d), 47.6 (d), 71.6 (s), 114.4 (s), 114.7 (s), 129.8 (s), 133.55 (s). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.86; N, 10.93. Found: C, 75.21; H, 7.98; N, 10.70.

L. Chromatographic workup [petroleum ether/ethyl acetate (4:1 v/v)] of the reaction product of **1** and octa-1,7-diene (**32**) (0.121 g, 0.17 mL, 1.1 mmol) (4 days) afforded 2,3-dicyano-5-(hexen-6′-yl)cyclohexa-1,3-diene (**34**) (R_f = 0.41, 0.110 g, 52%) as a pale yellow oil: IR 2226 cm^{-1}; ^1H NMR δ 1.29−1.50 (m, 6H), 2.04 (q, *J* = 6.8 Hz, 2H), 2.21−2.34 (m, 1H), 2.46−2.64 (m, 2H), 4.92−5.04 (m, 2H), 5.66−5.87 (m, 1H), 6.74 (d, *J* = 3.7 Hz, 1H), 6.81 (t, *J* = 4.6 Hz, 1H); ^{13}C NMR δ 25.7 (t), 27.4 (t), 28.4 (t), 32.2 (d), 32.8 (t), 33.3 (t), 107.8 (s), 108.3 (s), 114.7 (t), 115.0 (s), 115.05 (s), 138.2 (d), 144.45 (d), 149.1 (d). Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 78.87; H, 7.49; N, 13.53.

M. Operating as above with petroleum ether/ethyl acetate (7:1 v/v) as eluent, the residue from the reaction of **1** with nona-1,8-diene (**33**) (0.137 g, 0.18 mL, 1.1 mmol) (5 days) yielded 2,3-dicyano-5-(hepten-7′-yl)cyclohexa-1,3-diene (**35**) (R_f = 0.20, 0.113 g, 50%) as a colorless liquid: IR 2227 cm^{-1}; ^1H NMR δ 1.20−1.50 (m, 8H), 2.04 (q, *J* = 6.8 Hz, 2H), 2.25−2.32 (m, 1H), 2.49−2.60 (m, 2H), 4.91−5.03 (m, 2H), 5.78 (m, 1H), 6.74 (d, *J* = 4.1 Hz, 1H), 6.81 (t, *J* = 4.6 Hz, 1H); ^{13}C NMR δ 26.25 (t), 27.6 (t), 28.6 (t), 28.8 (t), 32.3 (d), 33.05 (t), 33.5 (t), 108.1 (s), 108.6 (s), 114.5 (t), 114.95 (s), 115.0 (s), 138.6 (d), 144.2 (d), 149.05 (d). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.91; H, 7.85; N, 12.13.

N. Chromatographic purification [petroleum ether/ethyl acetate (2:1 v/v)] of the brown residue coming from **1** and diallyl carbonate (**36**) (0.156 g, 0.16 mL, 1.1 mmol) (5 days) gave allyl (2,3-dicyanocyclohexa-1,3-dien-5-yl)methyl carbonate (**37**) (R_f = 0.30, 0.127 g, 52%) as a yellow oil; IR 2229, 1746 cm^{-1}; ^1H NMR δ 2.34−2.70 (m, 2H), 2.90−3.09 (m, 1H), 4.17 (m, 2H), 4.64 (d, *J* = 5.9 Hz, 2H), 5.30 (sbr d, *J* = 10.3 Hz, 1H), 5.38 (sbr d, *J* = 16.5 Hz, 1H), 5.84−6.03 (m, 1H), 6.74 (d, *J* = 4.0 Hz, 1H), 6.85 (t, *J* = 4.6 Hz, 1H); ^{13}C NMR δ 24.5 (t), 32.5 (d), 67.2 (t), 68.95 (t), 108.75 (s), 110.1 (s), 114.5 (s), 114.6 (s), 119.5 (t), 131.0 (d), 143.5 (d), 143.8 (d), 154.5 (s). Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.93; H, 4.95; N, 11.47. Found: C, 63.61; H, 4.75; N, 11.70.

9,10-Dicyano-5,5-dimethyl-5-silatricyclo[5.3.1.$0^{3,8}$]undec-9-ene (20). A solution of compound **19** (0.071 g, 0.29 mmol) in $CHCl_3$ (0.5 mL) was heated at 110 °C in a sealed tube for 9 days, and the residue left by evaporation to dryness was subjected to flash chromatography with petroleum ether/ethyl acetate (15:1 v/v) as eluent to yield **20** (R_f = 0.48, 0.018 g, 32%) that was crystallized from ether as colorless needles: mp 146−147 °C; IR 2218 cm^{-1}; ^1H NMR δ 0.02 (s, 3H), 0.28 (s, 3H), 0.76−1.08 (m, 4H), 1.42 (ddd, *J* = 12.8, 5.5, and 2.2 Hz, 2H), 1.77 (m, 2H), 2.09−2.23 (m, 2H), 2.54 (t, *J* = 2.6 Hz, 1H), 2.95 (m, 1H); ^{13}C NMR δ 0.1 (q), 2.6 (q), 17.7 (t), 30.1 (d), 32.3 (t), 35.8 (d), 45.1 (d), 114.3 (s), 114.6 (s), 130.2 (s), 134.7 (s). Anal. Calcd for $C_{14}H_{18}N_2Si$: C, 69.38; H, 7.48; N, 11.56. Found: C, 69.05; H, 7.46; N, 11.25.

Some unreacted starting material (R_f = 0.12, 0.015 g) was recovered from the slower moving band.[12]

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JO991191V

(12) When a total conversion of **19** was attained under more forcing conditions, the desired compound **20** was isolated in much lower yield from the more complex reaction mixture.