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(*E*,*E*)-1,2,3,4-Tetracyclopropylbuta-1,3-diene: Synthesis and Some of Its Properties[‡]

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Dedicated to Professor Dr. Philip J. Parsons on the occasion of his 60th birthday

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(*E*,*E*)-1,2,3,4-Tetracyclopropylbuta-1,3-diene (**3**) and (Z,Z)-1,4-diodo-1,2,3,4-tetracyclopropylbuta-1,3-diene (**4**) were prepared from dicyclopropylacetylene via an intermediate 2,3,4,5-tetracyclopropyltitanacyclopentadiene (**2**) in 91 and 77% yield, respectively. In the crystal, **3** adopts a conformation with an almost coplanar (ϕ = 163°) 1,3-diene core, with the inner vinylcyclopropane units in an orthogonal and the outer vinylcyclopropane moieties in an *s-trans* orientation. This diene, like 2,3-cyclopropylbuta-1,3-diene (**5**), undergoes facile concerted [4+2] cycloadditions at 130 °C with dimethyl acetylenedicarboxylate as well as *N*-phenylmaleimide and at 0 °C with *N*-phenyltriazolinedione. An X-ray crystal structure analysis of 2,3-dicyclopropylbuta-1,3-diene (**5**) also reveals a coplanar inner core with the vinylcyclopropane units in essentially orthogonal (ϕ_{av} = 89.3°) orientation. Differential scanning calorimetry (DSC) measurements indicate that **3** undergoes significant internal reorganization on going from the liquid to the crystalline phase, and a *gauche* conformer of **3** may well be favored over the *s-trans* conformer in the liquid.

Introduction

1,3-Butadiene is known to exist predominantly as an *s-trans* conformer (ψ = 180°)[2] with a very minor fraction in a *gauche* orientation (ϕ = 35°).[2h] In spite of this, 1,3-butadiene undergoes [4+2] cycloadditions (Diels–Alder reactions) with reasonable facility. Bulky substituents such as *tert*-butyl groups in the 2- and 3-position, however, force the 1,3-diene unit out of planarity.[3] Although the cyclopropyl group is considerably smaller than *tert*-butyl and even isopropyl substituents,[4] two cyclopropyl groups in the 2,3-positions might also influence the conformation of the buta-1,3-diene unit[5] and thus the facility of its undergoing a [4+2] cycloaddition. We therefore set out to investigate the structure of 2,3-dicyclopropylbuta-1,3-diene (**5**)[6] and the previously unknown (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) as well as the Diels–Alder reactivities of both.

Results and Discussion

Adopting the protocol of Sato et al.,[7] dicyclopropylacetylene (**1**)[8] was treated with isopropylmagnesium bromide in the presence of titanium tetraisopropoxide. Subsequent methanolysis of the intermediately formed titanacyclopentadiene **2** gave (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) as a single diastereomer in 90% yield (Scheme 1). Its configuration was established by an X-ray crystal-structure analysis (see Figure 1).[9] Addition of elemental iodine to a solution of the initially formed intermediate **2** furnished (*Z*,*Z*)-1,4-diiodo-1,2,3,4-tetracyclopropylbuta-1,3-diene (**4**) in 77% yield (Scheme 1).[10] The latter may be useful for various transition-metal-catalyzed cross-coupling reactions,[11] which would provide facile accesses to further 1,4-disubstituted 1,2,3,4-tetracyclopropylbuta-1,3-dienes.[12]

Crystal structure analysis revealed that the 1,3-diene unit in **3** is almost coplanar, with a dihedral angle ϕ = 163° in a close to *s-trans* (*ap*) conformation. Both of the outer ethenylcyclopropane moieties are also in an *s-trans* orienta-

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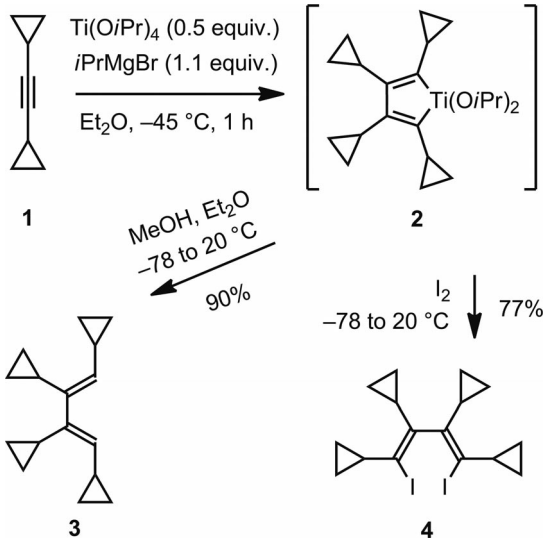


Scheme 1. Synthesis of (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) and (*Z*,*Z*)-1,2,3,4-tetracyclopropyl-1,4-diiodobuta-1,3-diene (**4**).

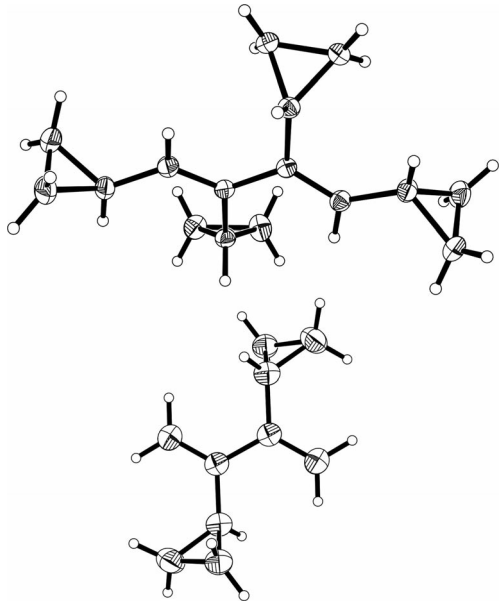


Figure 1. Molecular structures of (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**; top) and 2,3-dicyclopropylbuta-1,3-diene (**5**; bottom) in the crystals.[9]

tion,[13] while the two inner ethenylcyclopropane units adopt a virtually perpendicular *gauche* conformation with an average ϕ = 89.3° (Figure 1, upper part; ϕ is the torsion angle C=C–C···center of the opposite C–C bond in the cyclopropane ring). As far as the inner part is concerned, this is essentially the same conformation as that in 2,3-dicyclopropylbuta-1,3-diene (**5**) (Figure 1, lower part). The latter was prepared for comparison with **3** according to a known method[6a] but using an improved protocol for the preparation of the precursor, the 2,3-dicyclopropylbutane-2,3-diol.[6b] It should be noted that the observed single conformer of a molecule in the crystal is not necessarily the same as that in the liquid, in which an equilibrium of *s-trans* and a *gauche* conformer may exist.[2,14]

As in the cases of other molecules,[14] structures close to *s-trans* or *s-trans* conformations preferred in the crystals of **3** and **5** may be due to energetically favorable crystal packings (Figure 2), since differential scanning calorimetry (DSC) measurements indicate that the molecules undergo a significant internal reorientation on going from the liquid to the crystalline phase.

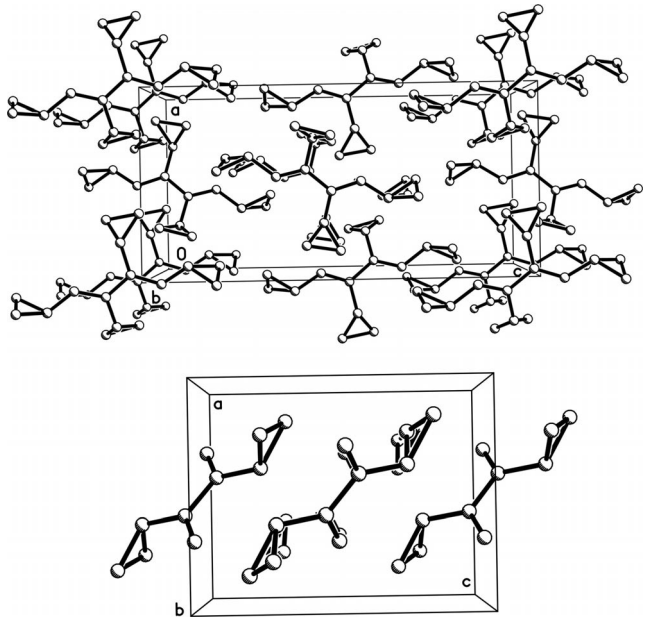


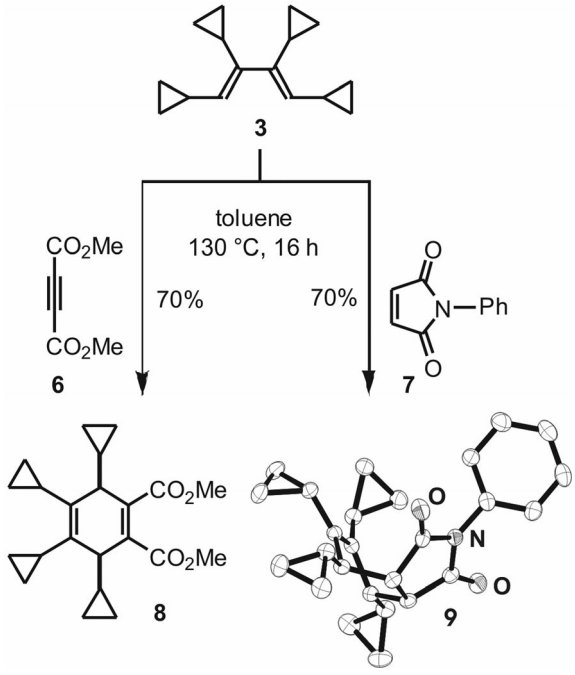
Figure 2. Fragments of the molecular packing of (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**; top) and 2,3-dicyclopropylbuta-1,3-diene (**5**; bottom) in the crystals.[9]

Upon slow cooling (10 K min^{-1}) of a sample of **3**, no crystallization occurs, but solidification into a glass takes place at –75 °C (see the Supporting Information). The glass transition is also visible at –71 °C upon re-warming, and crystallization becomes evident at –28 °C. The crystallization temperature varies slightly from one cycle to the next, e.g., in the third cycle it was –26 °C, but overall these events were well reproducible. In an isothermal experiment, the crystallization of **3** can be recorded as an exothermal event occurring at approximately –27 °C within about 20 min (see the Supporting Information). This behavior of severe supercooling and formation of a glass is somewhat unusual for a low molecular weight compound, but is well-known for polymers and is related to a slow crystallization.[15]

Although cyclopropyl groups are much less bulky than *tert*-butyl groups,[16] two of them at the inner carbon atoms of the butadiene derivative **3** apparently create enough congestion to slow down the conformational reorganization around –30 °C on going from the liquid to the crystalline state.

In spite of the overall steric congestion in (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**), it readily undergoes Diels–Alder reactions with dimethyl acetylenedicarboxylate

(DMAD; **6**) and *N*-phenylmaleimide (**7**), albeit only after extended heating (22 h) in toluene at 130 °C (Scheme 2). For comparison, butadiene[17a] and 2,3-dimethylbutadiene[17b,17c] react with DMAD at ambient temperature or at 70–80 °C, respectively. The products **8** and **9** were isolated in 70% yield each, and both were formed as single diastereomers, as indicated by their NMR spectra as well as by an X-ray crystal structure analysis of **9** (Scheme 2).[9]

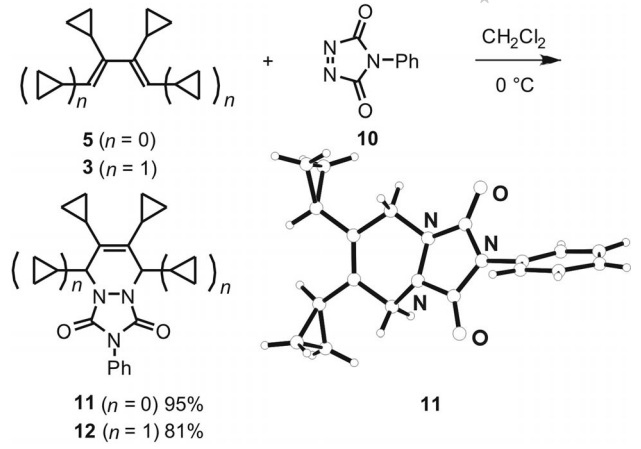


Scheme 2. Diels–Alder reactions of (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) with dimethyl acetylenedicarboxylate (**6**) as well as *N*-phenylmaleimide (**7**) and the crystal structure of the product **9**.[9]

On the other hand, the highly reactive dienophile *N*-phenyltriazolindione (**10**; PTAD),[18,19] instantaneously reacted with both 2,3-dicyclopropylbuta-1,3-diene (**5**) and (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) even at 0 °C (Scheme 3). The products **11** and **12** were isolated in 95 and 81% yield, respectively, and **12**, according to its NMR spectra, was obtained as a single diastereomer with the 3,6-cyclopropyl groups in *cis* orientation. This indicates a concerted [4+2] cycloaddition of **3** and **10** (PTAD)[18d] rather than a stepwise reaction via a zwitterionic intermediate.[18b] The latter reaction mode is well-known for PTAD, which can act as an oxidant.[19] However, the oxidation potential of (*E*,*E*)-1,2,3,4-tetracyclopropylbuta-1,3-diene (**3**) is apparently too high, so that it cannot transfer an electron to PTAD.[20]

Conclusions

(*E*,*E*)-1,2,3,4-Tetracyclopropylbuta-1,3-diene (**3**) as well as its 1,4-diiodo derivative **4** are easily accessible from dicyclopropylacetylene (**1**) by one-pot procedures. According to DSC measurements, a *gauche* conformer of **3** may well be favored over the *s-trans* conformer in the liquid, whereas a conformation with an almost coplanar (ϕ = 163°) 1,3-diene core is preferred in the crystal.



Scheme 3. [4+2] Cycloadditions of cyclopropyl-substituted butadienes **5** and **3** to *N*-phenyltriazolindione (**10**) and crystal structure of the product **11**.[9]

Experimental Section

General Remarks: All operations in anhydrous solvents were performed under argon in flame-dried glassware. Anhydrous diethyl ether, toluene, and THF were obtained by distillation from sodium benzophenone ketyl, anhydrous CH_2Cl_2 by distillation from calcium hydride, and methanol by distillation from magnesium methoxide. All other chemicals were used as commercially available. Organic extracts were dried with $MgSO_4$. NMR spectra were recorded with Bruker AM 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C NMR) or Bruker DPX 300 (300.13 MHz for ^{1}H and 75.54 MHz for ^{13}C NMR) instruments in $CDCl_3$ solutions, if not otherwise specified. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) measurements. Chemical shifts refer to δ_{TMS} = 0.00 ppm according to the chemical shifts of residual $CHCl_3$ signals. IR spectra were recorded with a Bruker IFS 66 FTIR on KBr pellets or oils between NaCl plates. Mass spectra were measured with a Finnigan MAT 95 (EI and HR-EI, at 70 eV, using preselected ion peak matching at $R >>$ 10000 to be within ±2 ppm of the exact masses) spectrometer. Melting points were determined with a Büchi 510 capillary melting point apparatus; values are uncorrected. TLC analyses were performed on precoated sheets (0.25 mm Sil G/UV$_{254}$; Macherey–Nagel). Silica gel grade 60 (230–400 mesh) (Merck) was used for column chromatography.

Dicyclopropylacetylene[8] (1) and 2,3-Dicyclopropylbuta-1,3-diene[6] (5): Prepared according to previously published protocols. Data for **5**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43–0.48 (m, 4 H, *c*Pr-H), 0.65–0.72 (m, 4 H, *c*Pr-H), 1.45–1.56 (m, 2 H, *c*Pr-H), 4.91 (br. s, 2 H, =CH_2), 5.38 (br. s, 2 H, =CH_2) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT): δ = 6.0 (4 CH_2), 14.6 (2 CH), 109.9 (2 CH), 149.1 (2 C) ppm.

(*E*,*E*)-1,2,3,4-Tetracyclopropylbuta-1,3-diene (3): To a solution of dicyclopropylethyne (**1**; 1.0 g, 9.42 mmol) and Ti(O*i*Pr)$_4$ (2.67 g, 9.42 mmol) in anhydrous Et_2O (70 mL), kept at –78 °C, was added dropwise a solution of isopropylmagnesium bromide (1.41 M in Et_2O, 20.7 mmol, 14.7 mL), upon which the reaction mixture

turned yellow. After 1.5 h stirring at –50 to –40 °C, the black reaction mixture was cooled to –78 °C, and a mixture of anhydrous MeOH (5 mL) and anhydrous Et_2O (7 mL) was added dropwise. The mixture was warmed to ambient temperature and poured into 3 M aq. HCl (50 mL). The two phases were separated and the aqueous solution was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (30 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (55 g of silica gel; 3 × 20 cm column; pentane; R_f = 0.73) afforded **3** (906 mg, 90%) as a colorless oil, which solidified at low temperature to a glassy solid. IR (film): $\tilde{\nu}$ = 3080, 3003, 2868, 1457, 1428, 1387, 1292, 1174, 1097, 1044, 1018, 978, 965, 945, 891, 809, 736, 668, 600, 572, 518 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.22–0.50 (m, 8 H, *c*Pr-H), 0.57–0.87 (m, 8 H, *c*Pr-H), 1.51 (m_c, 2 H, *c*Pr-H), 1.77 (m_c, 2 H, *c*Pr-H), 4.75 (d, *J* = 9.5 Hz, 2 H, 1-H, 4-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 6.1 (4 CH_2), 7.2 (4 CH_2), 10.3 (2 CH), 11.0 (2 CH), 133.1 (2 CH), 139.2 (2 C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 214 (28) $[M]^+$, 199 (4) $[M - CH_3]^+$, 185 (18), 173 (22) $[M - C_3H_5]^+$, 157 (44), 143 (52), 129 (72), 117 (56), 105 (45), 91 (100), 79 (58), 67 (30), 55 (24), 41 (29) $[C_3H_5]^+$. $C_{16}H_{22}$ (214.35): calcd. C 89.65, H 10.35; found C 89.68, H 10.25. Its configuration was established by X-ray crystal structure analysis.[9]

(*Z*,*Z*)-1,2,3,4-Tetracyclopropyl-1,4-diiodobuta-1,3-diene (4): To a solution of dicyclopropylethyne (**1**; 1.0 g, 9.42 mmol) and $Ti(OiPr)_4$ (2.67 g, 9.42 mmol) in anhydrous Et_2O (70 mL), kept at –78 °C, was added dropwise a solution of isopropylmagnesium bromide (1.41 M in Et_2O, 20.7 mmol, 14.7 mL), upon which the reaction mixture became yellow. After 1.5 h stirring at –50 to –40 °C, the black reaction mixture was cooled to –78 °C, and iodine powder (7.19 g, 28.3 mmol) was added in one portion. The mixture was warmed to ambient temperature and poured into sat. aq. $Na_2S_2O_3$ (50 mL). The two phases were separated, and the aqueous solution was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with brine (30 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue (55 g of silica gel; 3 × 20 cm column; pentane; R_f = 0.45) afforded **4** (1.68 g, 77%) as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.58–0.80 (m, 8 H, *c*Pr-H), 0.80–1.08 (m, 8 H, *c*Pr-H), 1.68–1.95 (m, 4 H, *c*Pr-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 6.7 (2 CH_2), 7.5 (2 CH_2), 10.8 (2 CH_2), 11.0 (2 CH_2), 15.1 (2 CH), 19.2 (2 CH), 112.6 (2 C), 148.0 (2 C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 466 (36) $[M]^+$, 339 (100) $[M - I]^+$, 283 (6), 212 (11) $[M - 2\ I]^+$, 169 (28), 155 (42), 128 (40), 91 (34), 77 (25), 65 (12), 41 (16) $[C_3H_5]^+$. HRMS (EI): calcd. for $C_{16}H_{20}I_2$ $[M]^+$ 465.9654; found 465.9654.

General Procedure for the Diels–Alder Reactions of (*E*,*E*)-1,2,3,4-Tetracyclopropylbuta-1,3-diene (3) with Dienophiles 6 and 7 (GP1): Diene **3** and the respective dienophile were weighed into a thick-walled screw-capped Pyrex ampoule with a magnetic stirring bar. Anhydrous toluene was added, the ampoule was flushed with argon, sealed with the screw-cap and heated at 130 °C with magnetic stirring for 22 h. After cooling to ambient temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (pentane/Et_2O).

Dimethyl *cis*-3,4,5,6-Tetracyclopropylcyclohexa-1,4-diene-1,2-dicarboxylate (8): Column chromatography (110 g of silica gel; 3.5 × 35 cm column; pentane/Et_2O, 10:1; R_f = 0.30) of the residue obtained from diene **3** (1.00 g, 4.67 mmol) and DMAD **6** (663 mg, 4.67 mmol) in toluene (8 mL) according to GP1 furnished **8** (1.16 g, 70%) as a colorless amorphous solid; m.p. 65 °C. IR (KBr): $\tilde{\nu}$ = 3433, 3082, 3005, 2949, 2903, 2841, 1722, 1663, 1636, 1457, 1387, 1348, 1264, 1196, 1153, 1116, 1061, 1022, 972, 947, 916, 888, 862, 831, 795, 761, 747, 667, 561 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.25–0.60 (m, 14 H, *c*Pr-H), 0.52–0.71 (m, 2 H, *c*Pr-H), 0.75–0.91 (m, 2 H, *c*Pr-H), 1.63–1.72 (m, 2 H, *c*Pr-H), 2.45 (d, *J* = 8.1 Hz, 2 H, 3,6-H), 3.75 (s, 6 H, OMe) ppm. ^{13}C NMR (62.9 MHz, C_6D_6, DEPT): δ = 4.0 (2 CH_2), 4.6 (2 CH_2), 6.1 (2 CH_2), 7.2 (CH_2), 8.1 (CH_2), 10.3 (CH), 13.7 (CH), 17.8 (2 CH), 43.2 (2 C), 51.6 (CH_3), 52.7 (CH_3), 132.4 (C), 135.2 (C), 138.5 (C), 152.0 (C), 168.7 (2 C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 356 (97) $[M]^+$, 325 (36), 297 (63) $[M - C_2H_3O_2]$, 283 (100), 265 (72), 255 (42), 237 (84), 195 (39), 181 (37), 165 (44), 155 (39), 128 (32), 91 (22), 77 (11), 59 (24) $[C_2H_3O_2]^+$, 41 (41) $[C_3H_5]^+$. $C_{22}H_{28}O_4$ (356.47): calcd. C 74.13, H 7.92; found C 74.48, H 7.70.

***syn*-4,5,6,7-Tetracyclopropyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3-dione (9):** Column chromatography (110 g of silica gel; 3.5 × 35 cm column; pentane/Et_2O, 5:1; R_f = 0.31) of the residue obtained from diene **3** (1.00 g, 4.67 mmol) and *N*-phenylmaleimide (**7**) (815 mg, 4.71 mmol) in toluene (8 mL) according to GP1 furnished **9** (1.26 g, 70%) as a colorless amorphous solid; m.p. 152 °C. IR (KBr): $\tilde{\nu}$ = 3078, 3002, 2835, 1770, 1707, 1598, 1500, 1456, 1428, 1379, 1322, 1243, 1166, 1105, 1028, 909, 880, 869, 821, 754, 733, 703, 690, 624, 615, 583, 463 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.13 (m_c, 4 H, *c*Pr-H), 0.42 (m_c, 2 H, *c*Pr-H), 0.53 (m_c, 2 H, *c*Pr-H), 0.62–0.89 (m, 8 H, *c*Pr-H), 1.23 (d, *J* = 10.6, 3.7 Hz, 2 H, 4,7-H), 1.31–1.45 (m, 2 H, *c*Pr-H), 1.76 (m_c, 2 H, *c*Pr-H), 3.21 (dd, ^3J = 3.7, *J* = 1.9 Hz, 2 H, 3a,7a-H), 7.12–7.19 (m, 2 H, Ar-H), 7.29–7.37 (m, 1 H, Ar-H), 7.29–7.37 (m, 2 H, Ar-H_a) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ = 4.4 (2 CH_2), 8.1 (2 CH_2), 8.3 (2 CH_2), 8.7 (2 CH_2), 10.4 (2 CH), 12.5 (2 CH), 45.5 (2 CH), 48.2 (2 CH), 126.3 (2 CH), 128.3 (CH), 128.9 (2 CH), 131.9 (C), 138.9 (2 C), 177.3 (2 C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 387 (50) $[M]^+$, 358 (60), 344 (21), 330 (10), 316 (9), 302 (4), 268 (3), 228 (18), 212 (28) $[C_{16}H_{20}]^+$, 199 (38), 169 (45), 159 (82), 145 (90), 131 (100), 117 (93), 91 (79), 77 (36) $[C_6H_5]^+$, 67 (22), 41 (28) $[C_3H_5]^+$. $C_{26}H_{29}NO_2$ (387.53): calcd. C 80.59, H 7.54, N 3.61; found C 80.83, H 7.30, N 3.75. Its configuration was established by X-ray crystal structure analysis.[9]

General Procedure for [4+2] Cycloadditions of Cyclopropyl-Substituted Buta-1,3-dienes 3 and 5 to *N*-Phenyl-1,3,4-triazoline-2,5-dione (PTAD; 10) (GP2): A solution of PTAD (1 mmol) in anhydrous dichloromethane (10 mL) was added dropwise to a stirred solution of respective diene (1.1 mmol) in CH_2Cl_2 (10 mL) at 0 °C at such a rate that the reaction mixture decolorized before the addition of the next drop. After stirring for an additional 10 min, the reaction mixture was concentrated under reduced pressure. The product was purified as indicated below.

6,7-Dicyclopropyl-2-phenyl-5,8-dihydro-1*H*-[1,2,4]triazolo[1,2-*a*]-pyridazine-1,3(2*H*)-dione Hemihydrate (11·0.5H_2O): The residue, obtained from PTAD (**10**; 200.0 mg, 1.14 mmol) and 2,3-dicyclopropyl-1,3-butadiene (**5**; 169.0 mg, 1.26 mmol) according to GP2, was taken up with THF (5 mL), filtered through a 5-mm pad of silica gel and the solution was concentrated again. The oily residue solidified upon addition of hexane (2 mL). Slow evaporation of its solution in octane/CH_2Cl_2 at 4 °C was accompanied by absorption of atmospheric moisture and furnished the pure cycloadduct **11**·0.5H_2O (344.8 mg, 95%) as a hemihydrate in the form of long colorless needles. Upon heating, these needles "jump" at 60 °C, partially loose water at 92 °C, and melt at 102 °C, however, they immediately solidify again to form a new phase (also needles), which melt at 129–130 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.61 (m, 4 H, Cpr-H), 0.77–0.81 (m, 4 H, Cpr-H), 1.83–1.92 (m, 2 H, Cpr-H), 3.85 (s, 4 H, 2 CH_2), 7.33–7.39 (m, 1 H, Ar-H), 7.43–7.53 (m, 4 H, Ar-H) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 4.6

(4 CH_2), 11.6 (2 CH), 43.7 (2 CH_2), 125.4 (2 CH), 126.4 (CH), 128.1 (2 C), 129.1 (2 CH), 131.1 (C), 152.4 (2 C) ppm. (2 × **11**) × H_2O: $C_{36}H_{40}N_6O_5$ (636.74): calcd. C 67.91, H 6.33; found C 67.66, H 6.19. Its structure was confirmed by an X-ray crystal structure analysis.[9]

5,6,7,8-Tetracyclopropyl-2-phenyl-5,8-dihydro-1*H*-[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3(2*H*)-dione (12): Column chromatography (80 g of silica gel; 30 × 2.8 cm column; hexane/THF, 5:1; R_f = 0.33) of the residue obtained from PTAD (**10**; 175.2 mg, 1 mmol) and 1,2,3,4-tetracyclopropyl-1,3-butadiene (**3**; 235.8 mg, 1.1 mmol) afforded **12** (317.0 mg, 81%) as a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59–0.95 (m, 16 H, Cpr-H), 1.13–1.15 (m, 2 H, Cpr-H), 1.74–1.83 (m, 2 H, Cpr-H), 3.82 (d, J = 8.0 Hz, 2 H, 2 CH), 7.28–7.55 (m, 5 H, Ar-H) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 3.3 (2 CH_2), 4.9 (2 CH_2), 5.7 (2 CH_2), 7.6 (2 CH_2), 12.5 (2 CH), 16.9 (2 CH), 57.7 (2 CH), 125.2 (2 CH), 127.4 (CH), 128.7 (2 CH), 131.7 (C), 133.6 (2 C), 149.1 (2 C) ppm. $C_{24}H_{27}N_3O_2$ (389.49): calcd. C 74.01, H 6.99; found C 73.90, H 7.14.

Crystal Structure Determinations: Suitable crystals of compounds **9** and **11** were grown by slowly concentrating their diluted solutions; the crystals of hydrocarbons **3** and **5** were grown in situ in glass capillaries of 0.5 mm diameter. Single-crystal X-ray data were collected with a Bruker SMART CCD 6000 (for **3** and **5**) and a Stoe–Siemens–Huber IPDS-II (for **9**) diffractometer (graphite monochromator, Mo-K_α radiation), equipped with Cryostream (Oxford Cryosystems) low-temperature devices. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The H atoms in the structures of **3** and **5** were located in the difference Fourier map and refined isotropically; in the structure **9** they were placed in the calculated positions and refined in riding mode. The parameters of crystal data collections and structure refinements are presented in Table 1.[9]

Table 1. Crystal and data collection parameters for compounds **3**, **5**, and **9**.

	3	**5**	**9**
Empirical formula	$C_{16}H_{22}$	$C_{10}H_{14}$	$C_{26}H_{29}NO_2$
Molecular mass	214.34	134.21	387.50
Temperature [K]	120(2)	200(2)	133(2)
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1c$	$P2_12_12_1$
a [Å]	8.3232(2)	6.3375(8)	7.7020(6)
b [Å]	9.2129(2)	8.555(1)	15.2195(11)
c [Å]	16.9630(3)	8.147(1)	17.5981(16)
β [°]	90	90.06(3)	90
V [Å^3]	1300.74(5)	441.7(1)	2062.9(3)
Z	4	2	4
F(000)	472	148	832
D [gcm^{-3}]	1.094	1.009	1.248
μ [mm^{-1}]	0.061	0.056	0.078
Reflections collected	18008	3012	7185
Reflections independent	2182	1141	3533
R_{int}	0.0271	0.0414	0.0567
R_1 [$I \geq 2\sigma(I)$]	0.0316	0.0435	0.0401
wR_2(all data)	0.0909	0.1271	0.0957
Parameters refined	233	74	262
GOOF	1.128	1.020	1.046

Supporting Information (see footnote on the first page of this article): NMR spectra of all new compounds and DSC recordings for **3**.

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