cm^{-1}. ^{1}H NMR: δ 3.01–3.28 (8 H, m, AA'BB', $-CH_2CH_2-$), 4.07 (4 H, d, J = 15 Hz, $-CH_2S-$), 4.66 (4 H, d, J = 15 Hz, $-CH_2S-$); MS m/e 400 [M$^+$]. Anal. Calcd for $C_{16}H_{16}O_4S_4$: C, 47.98; H, 4.03. Found: C, 48.23; H, 4.18.

[2$_4$](2,3,4,5)Thiophenophane (Superthiophenophane) (1). The pyrolysis of 250 mg (0.63 mmol) of **21** was carried out in a manner similar to that described in the literature,[12] at 470 °C (1.5–2 Torr) for 5 min. The product was extracted with CH_2Cl_2. The ash that was carried into the extract was removed by filtration. The solvent was evaporated from the filtrate, and the residue was subjected to column chromatography on silica gel (hexane/CH_2Cl_2 (4:1)). Concentration of the eluate and recrystallization of the residue afforded 5.0 mg (0.018 mmol, 3%) of **1** as colorless prisms (hexane), mp 229–231 °C. IR: ν 2920, 1455, 1232, 1067, 532, 450 cm^{-1}. ^{1}H NMR: δ 2.46–2.88 (8 H, m, AA'BB', $-CH_2CH_2-$), 2.91–3.30 (8 H, m, AA'BB', $-CH_2CH_2-$); ^{13}C NMR: δ 26.7, 30.1, 143.4, 145.8. UV ($CHCl_3$): λ_{max} (nm) (log ε) 269 (3.95), 243 (3.79, shoulder). HRMS m/e 272.0693 [M$^+$] (100), calcd 272.0693 for $C_{16}H_{16}S_2$, 244 (17), 136 (73). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.23; H, 5.93.

Acknowledgment. X-ray crystallographic analysis of **5** was carried out by Dr. Takehiko Yamato and Mr. Souichirou Nagayama of Saga University, to whom the authors are grateful.

Supplementary Material Available: Tables of positional parameters, their estimated standard deviations, refined temperature factor expressions, bond distances, and bond angles of X-ray crystallographic study of thiophenophanes **5** and **1** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reactions of Spiro[2.4]hept-4-ene Derivatives with Tetracyanoethylene. Extensive Rearrangements Involving the Aza-Cope Process[1]

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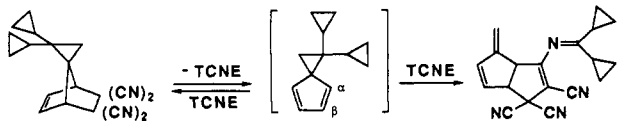
In CH_2Cl_2 or CH_3CN, 1,1-dicyclopropylspiro[2.4]hept-4-ene (**4a**) reacted readily with TCNE in a unique manner to give 4-[*N*-(dicyclopropylmethylene)amino]-6-methylenebicyclo[3.3.0]oct-3-ene-2,2,3-tricarbonitrile (**8a**), an imine after extensive rearrangements, and 3,3-dicyclopropylspiro[4.4]non-6-ene-1,1,2,2-tetracarbonitrile (**9a**), a [$_σ$2 + $_π$2] cycloadduct. In the reaction of 1-cyclopropyl-1-methyl derivative **4b**, 3-(1,1,2,2-tetracyanoethyl)-1-(2-cyclopropylallyl)cyclopentene (**10a**), formally a vinylogous homoene type adduct, was also produced in addition to **8b** and **9b**. The reaction of 1,1-dimethyl derivative **4c** produced **10b**, exclusively. The reaction of 1,1-dicyclopropylbenzo[*f*]spiro[2.4]hept-4-ene (**5a**) gave exclusively imine **11**, a benzoanalog of **8a**, whereas the reaction of saturated benzo derivatives **7** produced **15**, corresponding to **9**. The production of **8** (as well as **11**) and **10** might be depicted in a stepwise dipolar fashion, in which the first formed intermediate **17** will open its spiro-linked three-membered ring to give the second zwitterion **18**, which then either cyclizes to a nine-membered adduct **19** or undergoes a proton transfer to give **20**. **19** then undergoes aza-Cope rearrangement to afford **8**, and **20** ultimately tautomerizes to **10**. The parent spiroheptene **4d** gave merely a mixture of [$_π$2 + $_π$2] cycloadduct **14** and [$_σ$2 + $_π$2] cycloadduct **9c**. The formation of **8** and/or **10** is thus limited to occur in such vinylcyclopropanes that hold suitable pendant substituents which can provide greater stabilization to the zwitterionic intermediates. Even in the reaction of spiro[2.4]hepta-4,6-dienes with TCNE, 1,1-dicyclopropyl derivative **2a** produced a sizable amount of **3a**, corresponding to **8**, as well as **16a–16a'** in addition to the expected [$_π$4 + $_π$2] cycloadduct **1a**, whereas **2b–2c** produced simply the corresponding Diels–Alder adduct.

Introduction

In studying Diels–Alder reactions of spiro[2.4]hepta-4,6-diene derivatives, we have made the unexpected observation that Diels–Alder adduct **1a**, in which the spiro-linked cyclopropane is substituted by geminal cyclopropyl groups, undergoes isomerization at 50–80 °C to a bicyclic imine derivative **3a**.[2] Since this isomerization presumably



1a **2a** **3a**

proceeds via a retro-Diels–Alder reaction of **1a** followed by a reattack of tetracyanoethylene (TCNE) at the β position of spiroheptadiene **2a**,[2] we anticipated that the same type of transformation should occur with spiro[2.4]hept-4-enes **4**. In fact, the expected imine is formed readily in the reaction of *gem*-dicyclopropyl derivative **4a**, as well as in the reaction of its benzoanalog **5a**. In the

4a : $R^1 = R^2$ = c-Pr
4b : R^1 = c-Pr, R^2 = Me
4c : $R^1 = R^2$ = Me
4d : $R^1 = R^2$ = H

5a : R = c-Pr
5b : R = H

present paper, the results obtained in the reactions of **4a–d** and **5a–b**, as well as those of **2a–d**, are described, and the scope of the unique transformation to give the imine is presented.

Results and Discussion

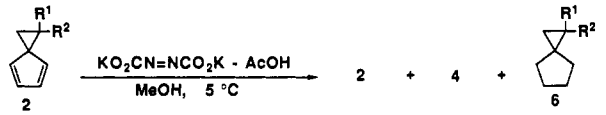
Preparation of the Substrates. 2a–c were prepared in the reaction of appropriately substituted fulvenes[3] with

(1) Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.
(2) Nishida, S.; Asanuma, N.; Tsuji, T.; Imai, T. *Chem. Lett.* **1991**, 495.

0022-3263/92/1957-4658$03.00/0

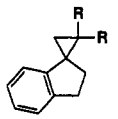
dimethylsulfonium methylide.[4,5] **2d** is a known compound.[6] **5a** was prepared in the reaction of 1,1-dicyclopropylethylene with 1-diazoindene.[7]

With regard to the partial reduction of **2** to **4**, it has been reported that the diimine reduction of a conjugated diene yields a 1,2-addition product.[8] In fact, we observed that strict 1,2-reduction of **2** occurred with diimine[9] to give a mixture of **2**, **4**, and saturated hydrocarbon **6**. Typical results are shown below.



a : $R^1 = R^2$ = c-Pr	33	37	31
b : R^1 = c-Pr, R^2 = Me	20	37[10]	43
c : $R^1 = R^2$ = Me	38	32	30
d : $R^1 = R^2$ = H	43	30	28

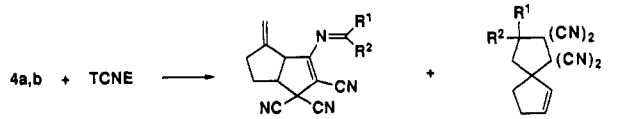
It was anticipated that the isolated double bond in **4** would be somewhat more reactive than the conjugated double bonds in **2**,[8a] and therefore the diimine reduction might not be a practical way to prepare **4**. Fortunately, however, diimine did not severely discriminate between **2** and **4**. The three components, **2**, **4**,[10] and **6**, were successfully separated by preparative GC. Hydrogenation of **5** to the corresponding indane **7** was straightforward.[11]

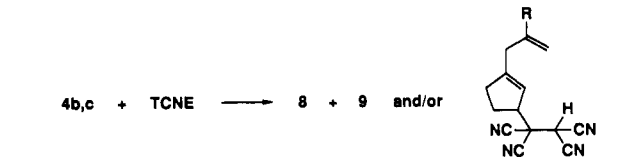


7a : R = c-Pr
7b : R = H

Reaction of 4a–c and 5 with TCNE. The reaction of **4a** with TCNE proceeded very rapidly at room temperature to produce a mixture of 4-[*N*-(dicyclopropylmethylene)amino]-6-methylenebicyclo[3.3.0]oct-3-ene-2,2,3-tricarbonitrile (**8a**) and 3,3-dicyclopropylspiro[4.4]-non-6-ene-1,1,2,2-tetracarbonitrile (**9a**).[12] In CH_2Cl_2 at room temperature, **8a** and **9a** were formed in 70 and 9% yield, respectively, whereas in CH_3CN they were produced in 72 and 19% yield.

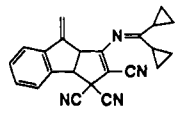
Similarly, the reaction of **4b**[10] yielded **8b**, **9b**,[10] and a new, formally vinylogous homoene type adduct **10a**.[13] The





yields of **8b**, **9b**, and **10a** were 28, <1, and 70% in CH_2Cl_2 and 48, 3, and 12% in CH_3CN, respectively. **10b** was produced as an overwhelmingly major product (exclusive by ^1H NMR)[13] in the reaction of **4c**.

The indene derivative **5a** produced exclusively **11** in its rapid reaction with TCNE. The reaction of **5b** was not clean and gave no isolable products.

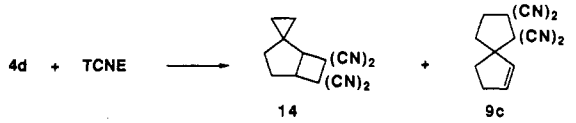


11

Structural Elucidation of 8 and 11. Structures of **8a**, **8b**, and **11** were deduced primarily on the basis of spectroscopic features as well as mechanistic considerations. The ^1H NMR and ^{13}C NMR spectra clearly indicate the presence of an *exo*-methylene group and four olefinic carbons, three of which are quaternary. The presence of an imine function in **8a** and **11** was proved by acid-catalyzed hydrolysis to give dicyclopropyl ketone and the corresponding enamine, **12** and **13**, respectively.

12 13

Reaction of Other Substrates. Parent **4d** reacted with TCNE at room temperature to produce a mixture of [$_\pi$2 + $_\pi$2] cycloadduct **14** and [$_\sigma$2 + $_\pi$2] cycloadduct **9c**.[12,14]



14 9c

Although the yields of the adducts were relatively low (**14** and **9c** being isolated in a 6 and 39% yield in CH_2Cl_2 and 20 and 24% in CH_3NO_2, respectively), there was no indication for the formation of the rearranged adduct corresponding to **8**. Spiroindan **7a** produced **15a** in a nearly quantitative yield. Although the corresponding spirofluorene derivative reacted rapidly with TCNE in CH_2Cl_2,[12] ca. 12 h was required for the total consumption of **7a** at

(3) (a) Crane, G.; Boord, C. E.; Henne, A. L. *J. Am. Chem. Soc.* **1945**, *67*, 1237. (b) Freiesleben, W. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 396. (c) Hanack, M.; Eggensperger, H. *Justus Liebigs Ann. Chem.* **1963**, *663*, 31. (d) Kerber, R. C.; Linde, H. G., Jr. *J. Org. Chem.* **1966**, *31*, 4321.

(4) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(5) Schröer, W.-D.; Friedrichsen, W. *Justus Liebigs Ann. Chem.* **1978**, 1648.

(6) Alder, K.; Ache, H.-J.; Flock, F. H. *Chem. Ber.* **1960**, *93*, 1888.

(7) Rewicki, D.; Tuchscherer, C. *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 44.

(8) (a) Siegel, S.; Foreman, M.; Fisher, R. P.; Johnson, S. E. *J. Org. Chem.* **1975**, *40*, 3599. Cf. also: (b) Garti, N.; Siegel, S. *Ibid.* **1976**, *41*, 3922. (c) Vidyarthi, S. K.; Willis, C.; Back, R. A.; McKitrick, M. *J. Am. Chem. Soc.* **1974**, *96*, 7647.

(9) (a) Corey, E. J.; Mock, W. L.; Pasto, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 2957. (b) van Tamelen, E. E.; Dewey, R. S.; Timmons, R. J. *Ibid.* **1961**, *83*, 3725. (c) Baird, W. C., Jr.; Franzus, B.; Surridge, J. H. *Ibid.* **1967**, *89*, 410.

(10) There were geometrical isomers (syn and anti) in **4b**, but we have been unsuccessful so far to separate them in pure form. Accordingly, a mixture of the isomers was used in the following experiments. The adduct **9b** was likewise a mixture of the geometrical isomers.

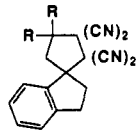
(11) Staley, S. W.; Fox, M. A.; Hirzel, T. K. *J. Am. Chem. Soc.* **1976**, *98*, 3910. As reported, catalytic hydrogenation of **5b** yielded a mixture of **6b** and ethylindan, whereas the reduction of **5a** gave no ring-cleaved product.

(12) (a) Nishida, S.; Murakami, M.; Oda, H.; Tsuji, T.; Mizuno, T.; Matsubara, M.; Kikai, N. *J. Org. Chem.* **1989**, *54*, 3859. (b) Nishida, S.; Murakami, M.; Mizuno, T.; Tsuji, T. *Ibid.* **1989**, *54*, 3868.

(13) Since this product stuck on a silica gel column, probably due to the presence of an acidic hydrogen, it was difficult to purify by chromatography. Fortunately, however, the reaction of **4c** produced only **10b** (^1H NMR). Accordingly, the product was rapidly passed through a short silica gel column to remove the colored material, and the resultant oil (obtained in 59% yield) was examined spectroscopically. The structure of **10a** was deduced by comparison of its ^1H NMR and ^{13}C NMR to those of **10b**. Since the reaction of **4c** was found to proceed more cleanly in dilute solution, it was carried out under more dilute conditions (×10).

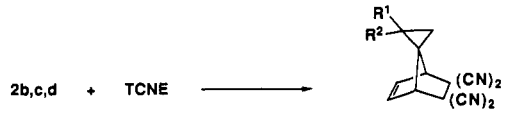
(14) Tsuji, T.; Nishida, S. *Acc. Chem. Res.* **1984**, *17*, 56.

room temperature. **7b** did not react with TCNE at room temperature. After 48 h at 100 °C in CH_2ClCH_2Cl, however, the consumption of **7b** reached 78%, and **15b** was isolated in a 80% yield. The saturated compound **6a** showed no indication of any reaction with TCNE after 2 weeks at 80 °C.



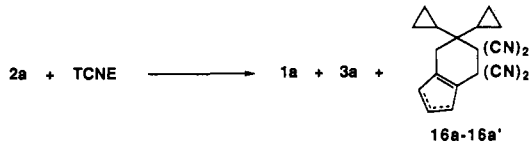
15a : R = c-Pr
15b : R = H

Reaction of 2 with TCNE. As a 1,3-cyclopentadiene, **2d** is known to undergo clean Diels–Alder reaction with TCNE.[15] The same is also true for **2b** and **2c** in our study.



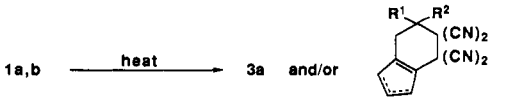
1b : R^1 = c-Pr, R^2 = Me
1c : $R^1 = R^2$ = Me
1d : $R^1 = R^2$ = H

However, **2a** produced not only **1a** (88% in CH_2Cl_2 and 74% in CH_3CN) but also **3a** (8% in CH_2Cl_2 and 20% in CH_3CN) and a mixture of 4,4-dicyclopropylbicyclo-[4.3.0]nona-1(6),7-diene-2,2,3,3-tetracarbonitrile (**16a**) and its 1(6),8-diene isomer (**16a'**; total yield of 2% in CH_2Cl_2 and 7% in CH_3CN).[2,16]



16a-16a'

Although control experiments indicated that **1a** isomerized to **3a** and **16a–16a'** at elevated temperature, the isomerization at room temperature was too slow to account for the observed results. The reaction of **2a** with TCNE was complete almost instantly at room temperature either in CH_2Cl_2 or CH_3CN and sizable amounts of **3a** (8–20%) and **16a–16a'** (2–7%) were produced. On the other hand, the isomerization of **1a** did not occur in CH_2Cl_2 at room temperature. In CH_3CN, **1a** did rearrange to **3a** but slowly (20% conversion after 24 h). Accordingly, it can be concluded that **3a** and **16a–16a'** were produced directly in the reaction of **2a** with TCNE. At 50 °C, nearly complete isomerization of **1a** occurred after 125 min in CH_3CN to give a 7:3 mixture of **3a** and **16a–16a'**. In $CHCl_3$, however, a mere 24% conversion occurred under similar conditions. Thus, the isomerization of **1a** proceeded more rapidly in a solvent of higher polarity, suggesting a dipolar process for the isomerization.

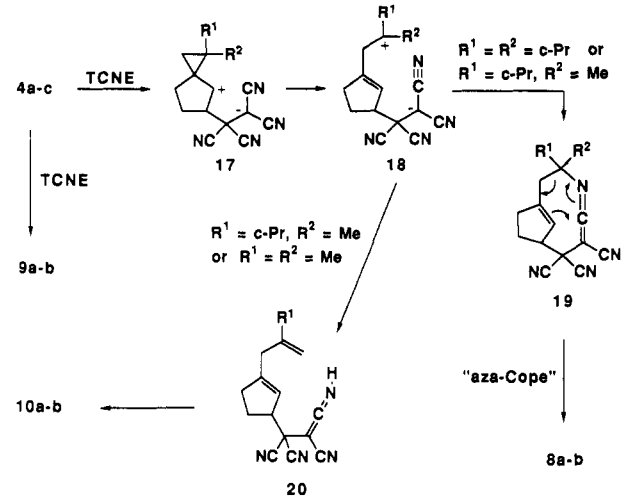


16a-16a' : $R^1 = R^2$ = c-Pr
16b-16b' : R^1 = c-Pr, R^2 = Me

Whereas *gem*-dicyclopropyl-substituted **1a** underwent ready isomerization, **1c** and **1d** did not show any sign of isomerization on being heated at 50–80 °C. **1b** however rearranged slowly in CH_3CN at 80 °C to **16b–16b'**.

(15) Murahashi, S.; Okumura, K.; Maeda, Y.; Sonoda, A.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2420.
(16) With regard to a probable pathway to produce **16**, see ref 2.

Scheme I



Unexpectedly, no indication for the formation of the corresponding imine was noted in this case.

Our proposal[2] that the isomerization of **1a** to **3a** might take a retro-Diels–Alder–reattack course has been primarily based on the fact that the TCNE derived moiety has to change its position from carbon α to carbon β to accomplish the transformation to **3a**. The retro-Diels–Alder reaction of **1**, particularly in CH_3CN, was indeed found to occur very readily, which was revealed by heating **1** in the presence of 1-methylspiro[2.4]hepta-4,6-diene (**2e**).[17,18] Thus, when **1a** is heated in a given solvent, **2a** and TCNE are reversibly produced in the reaction mixture and **3a** might be gradually accumulated. The present result obtained in the reaction of **4a**, in which the β position should be an active site, would be strong support for the proposed pathway.[2] In the isomerization of **1a**, attempts were made to trap the intermediates with methanol, but only isomerization to **3a** and **16a–16a'** were observed (^{1}H NMR).

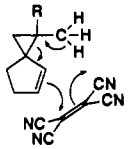
In the Diels–Alder reaction with TCNE, **2a** exhibited somewhat (ca. 2 times by following the peaks by ^{1}H NMR) higher reactivity than **2b–d**; the latter three showed nearly the same reactivity in either CH_3CN or CH_2Cl_2. The results are thus inconsistent with the possibility that reduced reactivity of **2a** (caused by steric hindrance) in the Diels–Alder process forces **2a** to take the unusual reaction route to produce **3a**.

Reaction Pathways. The present reaction of **4** with TCNE to give **8** and **10** might be depicted in a way (Scheme I) similar to that proposed for the isomerization of **1a**.[2,16] Attack of TCNE at the β position in **4** will produce **17**, which undergoes cleavage of the spiro-linked three-membered ring to give **18**. Alternatively, direct formation of **18** from **4** and TCNE might also be a possibility. Cyclization of **18** at a nitrogen atom of the cyano group will yield **19**, which will suffer aza-Cope rearrangement to ultimately give **8**. The formation of **11** in the reaction of **5a** can be described in the same manner. We have previously encountered similar transformations in the reactions of *gem*-diaryl-substituted cyclopropylethylenes with TCNE,[19] although the reaction has been much slower

(17) Meyer, F.; Haynes, P.; McLean, S.; Harrison, A. G. *Can. J. Chem.* **1965**, *43*, 211. D'yachenko, A. I.; Menchikov, L. G.; Nefedov, O. M. *Izu. Akad. Nauk SSSR, Ser. Khim.* **1985**, 709.
(18) Since **1e** showed a distinctly different ^{1}H NMR pattern from **1a–d** as well as **3a**, **2e** was chosen as a trapping diene for TCNE to investigate the retro-Diels–Alder reactions of **1a–d**. Spiro[4.4]nona-1,3-diene was an inferior diene because it exhibited more than 300 times lower reactivity than **2**.
(19) Shimizu, N.; Fujioka, T.; Ishizuka, S.; Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1977**, *99*, 5972.

than in the present cases. With regard to the cyclization of the zwitterionic intermediate at the nitrogen atom of the cyano group (18 to 19), it should be mentioned that Huisgen[20] recently reported the formation of a 7-membered cycloadduct in the reaction of a thiocarbonyl ylide with 1,2-bis(trifluoromethyl)ethylene-1,2-dicarbonitrile.

When one of the substituents in 18 is methyl, the nitrogen atom will take up a proton intramolecularly[21] from the methyl group to give 20, which will tautomerize to 10. It is also conceivable that the hydrogen will transfer directly from the methyl to the carbanion in 18, but such a process appears to be less likely on the basis of molecular model considerations (an 11-membered vs a 9-membered cyclic process in a relatively rigid, crowded system). The formation of 10 might alternatively be described as "a concerted vinylogous homoene type process" (21), since the



21

adduct 8b, which is supposedly formed in a stepwise dipolar process, predominates in the solvent of higher polarity (48:12 in acetonitrile), whereas the formation of 10a predominates in the solvent of lower polarity (28:70 in CH_2Cl_2). However, we prefer at present to consider the reaction leading to 10 as a stepwise dipolar process, since the vinylogous homoene reaction appears to be unprecedented, and therefore claiming it as a concerted process will require further investigations.

In the reaction of *gem*-dicyclopropyl derivative 4a, no vinylogous homoene type product was produced. This may be attributed to the fact that the formation of a highly strained methylenecyclopropane moiety would impede such a process in the reaction with 4a.

Conclusion. The unique bicyclic imine formation is particularly important in the reactioin of *gem*-dicyclopropyl-substituted 4a and 5a. When the substituents are cyclopropyl and methyl (4b), a different reaction (the vinylogous homoene type reaction) to give 10a competes with the imine formation. When the pendant substituents are merely methyls as in 4c, the formation of 10b becomes exclusive. Parent spiroheptene 4d gave a mixture of [$_\pi$2 + $_\pi$2] cycloadduct and [$_\sigma$2 + $_\pi$2] cycloadduct with no indication for the formation of 8. The reactions to give 8 (as well as 11) and/or 10 will proceed most likely in stepwise fashion; thus the reaction pathways depend crucially on the nature of the pendant substituents in the starting substance. Even in the reaction of 2, the imine formation competes with the expected Diels–Alder reaction when the pendant substituents are cyclopropyls.

Experimental Section

General methods were the same as those described in the previous paper.[12a]

Spiro[2.4]heptadienes. The reaction of 6,6-dicyclopropylfulvene[3c] and 6-cyclopropyl-6-methylfulvene[3d] with dimethyloxosulfonium methylide[4,5] gave 2a (54% yield) and 2b (71% yield), respectively. 2a: bp 95–100 °C (3 Torr); IR 3080, 3010, 1620 cm^{-1}; UV λ_{max} (hexane) 235 nm (ϵ 7400); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.24–0.71 (m, 8 H), 1.11–1.40 (m, 2 H), 1.44 (s, 2 H), 6.50 (s, 4 H); MS *m/z* 172 (M$^+$, 94), 129 (100). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.71; H, 9.28. 2b: bp 77–79 °C (12 Torr); IR 3075, 3000, 2980, 2965, 2930, 2875, 1615 cm^{-1}; UV λ_{max} (hexane) 232 nm (ϵ 8300), 263 (ϵ 2400, sh); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.17–0.68 (m, 4 H), 1.08–1.29 (m, 1 H), 1.44 (s, 3 H), 1.48–1.65 (m, 2 H), 6.22–6.55 (m, 4 H); MS *m/z* 146 (M$^+$, 40), 131 (100). Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.41; H, 9.71. 2a was also prepared in the reaction of 5-diazo-1,3-cyclopentadiene with 1,1-dicyclopropylethylene (15% yield).[22,23] 2c[23b] and 2d[6] are known compounds.

Spiroindene 5 and Spiroindan 7. Thermal decomposition of 1-diazoindene[7] (5.6 g (39 mmol)) in 1,1-dicyclopropylethylene (21.6 g, 220 mmol) gave 5a (2.2 g, 9.9 mmol, 25% yield), which was hydrogenated with Adams catalyst to give 7a (78% yield).[11] 5a: mp 56–56.5 °C; UV λ_{max} (hexane) 232 nm (log ϵ 4.32), 245 (4.16, sh), 262 (3.91), 276 (3.73, sh), 289 (3.41), and 301 (3.35); IR (KBr disk) 3080, 3036, 3004 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.20–0.58 (m, 2 H), 0.58–0.85 (m, 6 H), 1.05–1.42 (m, 2 H), 1.45 (d, 1 H, *J* = 5.4 Hz), 1.59 (d, 1 H, *J* = 5.4 Hz), 6.72 (d, 1 H, *J* = 5.6 Hz), 6.87 (d, 1 H, *J* = 5.6 Hz), 7.05–7.35 (m, 2 H), 7.35–7.53 (m, 2 H). 7a: bp ca. 100 °C (0.005 Torr); UV λ_{max} (hexane) 203 nm (log ϵ 4.54), 231 (3.99), 267 (3.25), 274 (3.35), 282 (3.29); IR 3076, 3000, 2936, 2860 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.0–1.20 (m, 12 H), 2.11 (ddd, 1 H, *J* = 12.7, 9.7, 8.5 Hz), 2.57 (ddd, 1 H, *J* = 12.7, 7.5, 3.6 Hz), 2.90–3.10 (m, 2 H), 7.00–7.30 (m, 4 H); MS *m/z* 224 (M$^+$, 22), 195 (38), 181 (20), 167 (28), 130 (100). Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.99; H, 8.87. 5b and 7b are known compounds.[11,24]

Diimine Reduction of 2. By following the procedure given in literature,[9c] 2 was reduced at <10 °C. The isolated hydrocarbon was composed of 2, 4, and 6 in ca. a 1:1:1 ratio, which were separated by preparative GC (PEG 20 M, 20% on Celite 545, 2 m, column temperature 70–160 °C). Attempts to increase the relative amount of 4 in the product mixture (changes in the reactant/reagent ratio, methods of generation of diimine, reaction temperature, and solvent) were unsuccessful. 4a: IR 3075, 3005, 2935, 2850, 1605 cm^{-1}, ^{1}H NMR (100 MHz, $CDCl_3$) δ −0.07 to 0.62 (m, 10 H), 0.75–0.96 (m, 2 H), 1.54–1.91 (m, 2 H), 2.11–2.56 (m, 2 H), 5.61–5.78 (m, 2 H, basically an AB quartet with additional couplings); MS *m/z* 174 (M$^+$, 14), 80 (100). Anal. Calcd for $C_{13}H_{18}$: C, 89.58; H, 10.41. Found: C, 89.51; H, 10.50. 4b (a ca. 1:1 mixture of geometrical isomers):[10] IR 3060, 2990, 2940, 2850, 1610 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ −0.03 to 0.51 (m, 5 H), 0.69–1.00 (m, 2 H), 1.09 and 1.12 (s, total of 3 H, two singlets in ca. 1:1), 1.59–1.95 (m, 2 H), 1.95–2.55 (m, 2 H), 5.41–5.79 (m, 2 H, AB system with additional couplings); MS *m/z* 148 (M$^+$, 31), 80 (100). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.10; H, 10.87. 4c: IR 3060, 2975, 2940, 2870, 1615 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.38 (d, 1 H, *J* = 4.2 Hz), 0.51 (d, 1 H, *J* = 4.2 Hz), 1.07 (s, 3 H), 1.10 (s, 3 H), 1.51–2.38 (m, 2 H), 2.38–2.56 (m, 2 H), 5.40–5.76 (m, 2 H, AB system with additional couplings); MS *m/z* 122 (M$^+$, 43), 107 (100).

Reaction of 4 with TCNE. Representative procedures: The reaction of 4a (174 mg, 1 mmol) with TCNE (128 mg, 1 mmol) in CH_2Cl_2 (total of 12 mL) was over almost instantly at room temperature. Evaporation of the solvent gave a solid (410 mg), which was recrystallized from a 1:1 mixture of hexane–ether to give 8a (183 mg). The mother liquor of the recrystallization was subjected to silica gel column chromatography (15 g with CH_2Cl_2 as eluant), which gave additional 8a (28 mg) and 9a (28 mg, 9%). The combined 8a (211 mg, 70%) was purified by recrystallization from hexane–ether. The same reaction in CH_3CN gave 8a and 9a in 72 and 19% yield, respectively. 8a: mp 121.6–122.0 °C dec; IR (KBr disk) 3090, 3015, 2965, 2930, 2870, 2245, 2210, 1670, 1570 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.88–1.43 (m, 10 H), 1.73–2.55 (m, 4 H), 3.43 (q, 1 H, *J* = 7.6 Hz), 3.95 (d, 1 H, *J* = 7.6 Hz), 4.89 (dd, 1 H, *J* = 2.0, 3.9 Hz), 5.09 (dd, 1 H, *J* = 2.0, 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 9.9 (m),[25] 14.4 (m),[25] 29.9 (t), 32.4 (t), 50.2 (d), 54.9 (d),

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81.6 (s), 111.1 (t), 112.1 (s), 112.6 (s), 114.4 (s), 145.0 (s), 172.0 (s), 181.7 (s); MS m/z 302 (M^+, 100), 79 (88), 78 (11). Anal. Calcd for $C_{19}H_{18}N_4$: C, 75.47; H, 6.00; N, 18.53. Found: C, 75.66; H, 6.02; N, 18.50. **9a**: mp 121.0–121.4 °C (hexane–ether); IR (KBr disk) 3095, 3055, 3025, 2970, 2935, 2870, 2245, 1615 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.46–0.50 (m, 1 H), 0.58–0.63 (m, 1 H), 0.73–0.85 (m, 6 H), 1.10 (tt, 1 H, J = 8.3, 5.4 Hz), 1.26 (tt, J = 8.3, 5.4 Hz), 1.68 (d, 1 H, J = 14.7 Hz), 1.75 (d, 1 H, J = 14.7 Hz), 2.19 (dt, 1 H, J = 13.7, 5.4 Hz), 2.48–2.56 (m, 1 H), 2.67–2.77 (m, 2 H), 5.93 (dt, 1 H, J = 5.9, 2.4 Hz), 6.24 (dt, 1 H, J = 5.9, 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 2.6 (m),[25] 3.1 (m),[25] 3.8 (m),[25] 17.2 (d), 19.2 (d), 32.2 (t), 36.5 (t), 42.8 (t), 54.2 (s), 55.6 (s), 56.3 (s), 65.5 (s), 110.8 (s), 111.0 (s), 130.6 (d), 138.9 (d); MS m/z 302 (M^+, 0.5), 41 (100). Anal. Calcd for $C_{19}H_{18}N_4$: C, 75.47; H, 6.00; N, 18.53. Found: C, 75.66; H, 5.98; N, 18.53.

The reaction of **4b**[10] and TCNE in CH_2Cl_2 gave **8b** (28%) and **10a** (ca. 70%, ^1H NMR). **8b**: oil; IR 3090, 3020, 2970, 2210, 1670, 1580 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99–1.09 (m, 4 H), 1.65–1.70 (m, 1 H), 1.88–1.94 (m, 1 H), 1.96 (s, 3 H), 2.25 (dtd, 1 H, J = 13.2, 7.8, 5.4 Hz), 2.42 (dddt, 1 H, J = 16.6, 9.3, 7.3, 2.0 Hz), 2.48–2.54 (m, 1 H), 3.43 (q, 1 H, J = 7.8 Hz), 3.96 (d, 1 H, J = 7.8 Hz), 4.90 (d, 1 H, J = 2.0 Hz), 5.09 (q, 1 H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2 (m),[25] 19.3 (d), 22.0 (q), 30.0 (t), 32.4 (t), 42.5 (s), 50.2 (d), 54.8 (d), 111.2 (t), 112.5 (s), 114.2 (s), 120.4 (s), 145.0 (s), 171.6 (s), 178.4 (s); MS m/z 276 (M^+, 93), 41 (100); HRMS calcd for $C_{17}H_{16}N_4$ 276.1375, found 276.1372. Since **10a** did not come out of the silica gel column,[13] its structure was deduced from the ^1H NMR and ^{13}C NMR spectra of the crude reaction mixture by comparing them with those of **10b** obtained in the following reaction. **10a**: ^1H NMR (500 MHz, CD_2Cl_2) δ 0.46–0.50 (m, 2 H), 0.68–0.71 (m, 2 H), 1.33 (m, 1 H), 2.06–2.09 (m, 1 H), 2.46–2.56 (m, 2 H), 2.66–2.69 (m, 1 H), 2.98 (m, 2 H, AA'), 3.68–3.70 (m, 1 H), 4.44 (s, 1 H), 4.75 (d, 1 H, J = 1.5 Hz), 4.78 (d, 1 H, J = 1.5 Hz), 5.51 (d, 1 H, J = 1.5 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 6.6 (t), 15.6 (d), 26.7 (t), 30.0 (t), 34.4 (d), 38.0 (t), 44.0 (s), 52.3 (d), 107.5 (s), 110.5 (s), 108.9 (t), 118.4 (d), 146.8 (s), 154.5 (s). In CH_3CN, **8b**, **10a**, and **9b** were produced in 48, 12, and 3% yield, respectively. **9b** (as a 57:43 mixture of geometrical isomers):[10] oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.42–0.49 (m, 1 H), 0.64 (septet, 1 H, J = 4.9 Hz), 0.74–0.83 (m, 2 H), 1.28–1.36 (m, 1 H), 1.37 and 1.42[26] (s, 3 H), 1.94–2.16 (m, 2 H; the minor isomer exhibited two doublets at 1.94 and 2.16 with J = 14.7 Hz), 2.15–2.22 (m, 1 H), 2.47–2.56 (m, 1 H), 2.65–2.79 (m, 2 H), 5.85 and 5.94[26] (dt, 1 H, J = 5.9, 2.0 Hz), 6.22–6.24 (m, 1 H); MS m/z 276 (M^+, 0.3), 80 (100). Anal. Calcd for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.28. Found: C, 73.75; H, 5.75; N, 20.54.

The reaction of **4c** with TCNE in CH_2Cl_2 (under more dilute conditions, × 10) gave **10b** as the sole product, which was purified briefly by column chromatography.[13] **10b**: IR 3080, 2970, 2915, 2260, 1645 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.72 (s, 3 H), 2.00–2.06 (m, 1 H), 2.39–2.44 (m, 1 H), 2.44–2.51 (m, 1 H), 2.61–2.66 (m, 1 H), 2.87–2.94 (m, 2 H), 3.62–3.65 (m, 1 H), 4.37 (s, 1 H), 4.78 (d, 1 H, J = 1.5 Hz), 4.86 (d, 1 H, J = 1.5 Hz), 5.42 (d, 1 H, J = 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0 (q), 26.8 (t), 30.0 (d), 34.3 (t), 39.8 (t), 44.1 (s), 52.4 (d), 107.4 (s), 110.5 (s), 113.1 (t), 118.2 (d), 141.4 (s), 154.4 (s); MS m/z 250 (M^+, 2.5), 39 (100); HRMS calcd for $C_{15}H_{14}N_4$ 250.1219, found 250.1222.

The reaction of **4d** with TCNE in CH_2Cl_2 required 3 days at 25 °C. Concentration of the solution produced a white solid, which was briefly purified by silica gel column chromatography (12 g). Flash column chromatography (silica gel 5 g with hexane–CH_2Cl_2, 1:1) and recrystallization effected separation of **9c** (39%) and **14** (6%). **9c**: mp 119–119.5 °C (ethanol); IR 3020, 2955, 2945, 2250, 1620 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.15 (ddd, 1 H, J = 13.7, 8.3, 4.9 Hz), 2.26–2.32 (m, 1 H), 2.41 (dt, 1 H, J = 14.6, 8.3 Hz), 2.53–2.60 (m, 1 H), 2.64 (ddd, 1 H, J = 13.7, 8.3, 4.4 Hz), 2.69–2.76 (m, 1 H), 2.89 (m, 2 H), 5.84 (dt, 1 H, J = 5.9, 2.4 Hz), 6.26 (dt, 1 H, J = 5.9, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2 (t), 35.6 (t), 36.0 (t), 36.8 (t), 43.4 (s), 53.7 (s), 66.8 (s), 110.0 (s), 110.1 (s), 111.4 (s), 111.6 (s), 129.6 (d), 139.1 (d); MS m/z 222 (M^+, 7), 79 (100). Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 70.03; H, 4.53; N, 25.23. **14**: mp 163.5–164.5 °C (EtOH); IR 3010, 2965, 2945, 2880, 2250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.69 (t, 2 H, J = 7.8 Hz), 1.04 (dt, 1 H, J = 7.8, 5.9 Hz), 1.16 (dt, 1 H, J = 7.8, 5.9 Hz), 1.58 (dd, 1 H, J = 14.4, 7.6 Hz), 2.23 (dddd, 1 H, J = 14.7, 12.7, 7.3, 7.3 Hz), 2.29 (dd, 1 H, J = 14.9, 7.1 Hz), 2.61 (ddd, 1 H, J = 13.7, 13.2, 6.8 Hz), 3.05 (d, 1 H, J = 7.8 Hz), 3.81 (dd, 1 H, J = 7.8, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9 (t), 16.8 (t), 25.4 (s), 29.5 (t), 33.5 (t), 48.1 (d), 55.6 (d), 111.0 (s); MS m/z 222 (M^+, 0.7), 79 (100). The reaction in CH_3CN gave a dark tarry residue and the yields of **9c** (15%) and **14** (4%) were low. In CH_3NO_2, no deposition of the tarry residue was observed during the reaction and the yields of **9c** and **14** were 24 and 20%, respectively.

Reaction of 5a with TCNE. The reaction of **5a** (222 mg, 1.0 mmol) with TCNE (128 mg, 1.0 mmol) in CH_2Cl_2 (25 mL) was complete almost instantly at room temperature to give **11** (331 mg, 0.945 mmol, 95%): mp 155.5–156.5 °C dec; IR (KBr disk) 3100, 3010, 2240, 2210, 1645, 1580 cm^{-1}; UV (CH_3CN) λ_{max} 205 nm (log ϵ 4.49), 227 (4.26, sh), 245 (4.32, sh), 252 (4.35), 262 (4.23, sh), 279 (3.85, sh), 282 (3.79), 298 (3.64); ^1H NMR ($CDCl_3$, 100 MHz) δ 0.80–1.40 (m, 10 H), 4.40 (dt, 1 H, J = 7.6, 1.7 Hz), 4.55 (d, 1 H, J = 7.6 Hz), 5.11 (d, 1 H, J = 1.7 Hz), 5.66 (d, 1 H, J = 1.7 Hz), 7.32–7.75 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.0 (br t),[25] 14.3 (br q),[25] 44.0 (s), 53.2 (d), 54.8 (d), 83.2 (s), 107.9 (t), 111.6 (s), 112.2 (s), 114.6 (s), 121.0 (d), 127.2 (d), 129.7 (d), 130.0 (d), 138.4 (s), 139.4 (s), 143.1 (s), 171.0 (s), 182.5 (s); MS m/z 350 (M^+, 100). Anal. Calcd for $C_{23}H_{18}N_4$: C, 78.83; H, 5.18; N, 15.99. Found: C, 78.97; H, 5.11; N, 15.94.

Reaction of 7 with TCNE. The reaction of **7a** with TCNE in CH_2Cl_2 at room temperature for 12 h gave **15a** (88%): mp 231–232 °C; IR (KBr disk) 3085, 3010, 2945, 2245, 1635 cm^{-1}; UV λ_{max} (CH_3CN) 216 nm (log ϵ 3.97, sh), 262 (3.09, sh), 267 (3.21), 274 (3.23); ^1H NMR (100 MHz, $CDCl_3$) δ 0.40–1.20 (m, 9 H), 1.20–1.50 (m, 1 H), 1.79 (d, 1 H, J = 14.7 Hz), 2.25 (d, 1 H, J = 14.7 Hz), 2.20–2.60 (m, 1 H), 2.80–3.65 (m, 3 H), 7.25–7.70 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 2.0 (t), 3.2 (t), 3.7 (t), 4.0 (t), 16.1 (d), 19.4 (d), 30.8 (t), 40.0 (t), 44.2 (t), 54.1 (s), 54.8 (s), 57.1 (s), 63.2 (s), 110.7 (br s), 111.0 (s), 111.2 (s), 124.7 (d), 125.4 (d), 127.2 (d), 130.3 (d), 138.6 (s), 144.2 (s); MS m/z 352 (M^+, 3), 224 (44), 195 (58), 130 (100). Anal. Calcd for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90. Found: C, 78.51; H, 5.72; N, 15.80.

The reaction of **7b** with TCNE in 1,2-dichloroethane at 100 °C for 48 h (78% consumption) gave **15b** (80% yield based on the consumed amount of **7b**): mp 129–130 °C; IR (KBr disk) 3025, 2950, 2860, 2250 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.15–2.55 (m, 2 H), 2.60–3.60 (m, 6 H), 7.21–7.60 (m, 4 H).; ^{13}C NMR ($CDCl_3$) δ 30.4 (t), 37.3 (t), 37.8 (t), 39.4 (t), 44.7 (s), 53.8 (s), 64.5 (s), 110.2 (s), 111.2 (s), 111.7 (s), 124.7 (d), 125.4 (d), 127.4 (d), 130.3 (d), 138.4 (s), 144.4 (s); MS m/z 272 (M^+, 28), 155 (19), 144 (100). Anal. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.58. Found: C, 75.10; H, 4.35; N, 20.60.

Acid-Catalyzed Hydrolysis of 8a and 11. Ten drops of concd hydrochloric acid were added to a 2-propanol (20 mL)–benzene (10 mL) solution of **8a** (151 mg, 0.5 mmol), and the resultant mixture was stirred at room temperature for 10 h. The solution was then washed with 5% aqueous $NaHCO_3$, and the water layer was extracted with several portions of benzene. The benzene solutions were combined and dried over anhyd Na_2SO_4 and concentrated under reduced pressure to give a white solid (124 mg), to which ethanol was added to crystallize **12** (78 mg, 74%): mp 154.0–154.5 °C; IR (KBr disk) 3405, 3355, 3265, 3230, 2940, 2250, 1665, 1590 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.99–2.30 (m, 2 H), 2.43–2.60 (m, 2 H), 3.36 (q, 1 H, J = 7.2 Hz), 3.79 (d, 1 H, J = 7.2 Hz), 5.11–5.40 (m, 4 H; on the addition of D_2O, the signal separated into three groups at δ 5.14 (d, 1 H, J = 1.8 Hz), 5.21 (q, 1 H, J = 1.8 Hz), and 5.32 (br s, remaining NH_2)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.3 (t), 31.5 (t), 42.0 (s), 50.4 (d), 54.6 (d), 70.8 (s), 111.1 (t), 112.5 (s), 113.7 (s), 114.8 (s), 147.5 (s), 165.0 (s); MS m/z 210 (M^+, 91), 183 (100). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.55. Found: C, 68.73; H, 4.73; N, 26.52. From the evaporated solvent (benzene), the (2,4-dinitrophenyl)hydrazone of dicyclopropyl ketone (mp 196–197 °C, 52%) was obtained.

In a similar manner, **11** gave dicyclopropyl ketone (2,4-dinitrophenyl)hydrazone (54%) and **13** (75%): mp 192–194 °C dec; IR (KBr disk) 3435, 3345, 3270, 3230, 2245, 2205, 1660, 1600 cm^{-1};

(25) In the off-resonance ^{13}C NMR spectrum, this peak exhibited a complex shape partly due to overlapping of more than two peaks. This was frequently observed in the signals of pendant cyclopropyl group(s).

(26) A peak due to the minor isomer.

UV (95% EtOH) λ_{max} 205 nm (log ϵ 4.35), 217 (4.27, sh), 225 (4.15, sh), 252 (4.32), 262 (4.18, sh), 280 (3.81, sh), 288 (3.51, sh), 299 (3.21); ^{1}H NMR ($CDCl_3$, 100 MHz) δ 4.32 (dt, 1 H, J = 7.0, ca. 1 Hz), 4.46 (d, 1 H, J = 7.0 Hz), 5.31 (br s, 3 H, the addition of D_2O reduced the signal intensity to 1 H), 5.74 (s, 1 H), 7.35–7.80 (m, 4 H); MS m/z 258 (M^+, 100), 232 (32), 128 (43); HRMS calcd for $C_{16}H_{10}N_4$ 258.0905, found 258.0894. Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.41; H, 3.90; N, 21.69. Found: C, 73.95; H, 3.73; N, 21.58.

Reaction of 2 with TCNE. General procedures: Into a TCNE solution (0.1 M) was added an appropriate amount of the solution of **2** (0.5 M, 1:1 molar solution), and the reaction was allowed to proceed at room temperature. After removal of the solvent, the crude residue was checked by ^{1}H NMR spectroscopy. In the case of **2b–d**, the product was found to be exclusively the expected Diels–Alder adduct, **1b–d**.[15] In all cases, the adduct was a single stereoisomer assigned anti configuration, simply for stereochemical reasons. Competitive reactions revealed that **2a** was ca. 2 times more reactive than **2b–d** in either CH_2Cl_2 or CH_3CN.

1b: mp 120–121 °C dec; IR (KBr disk) 3150, 3090, 3065, 3000, 2980, 2945, 2920, 2870, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.07–1.01 (m, 7 H), 1.41 (s, 3 H), 3.64 (dd, 1 H, J = 1.7, 3.9 Hz), 3.83 (dd, 1 H, J = 1.8, 4.0 Hz), 6.82 (t, 2 H, J = 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.1 (m),[25] 3.8 (m),[25] 14.8 (d), 20.1 (t), 21.1 (q), 22.6 (s), 46.7 (s), 53.6 (s), 57.4 (d), 58.1 (d), 111.1 (s), 111.3 (s), 137.4 (d), 139.8 (d); MS m/z 274 (M^+, 0.4), 131 (100). Anal. Calcd for $C_{17}H_{14}N_4$: C, 74.43; H, 5.14; N, 20.42. Found: C, 74.47; H, 5.14; N, 20.44. **1c**: mp 175.5–179 °C dec; IR (KBr disk) 3150, 3085, 3005, 2980, 2965, 2930, 2885, 2240 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.11 (s, 2 H), 1.12 (s, 6 H), 3.63 (t, 2 H, J = 2.0 Hz), 6.81 (t, 2 H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0 (s), 22.4 (q), 24.8 (t), 46.9 (s), 53.5 (s), 58.0 (d), 111.1 (s), 111.3 (s), 138.7 (d); MS m/z 248 (M^+, 0.1), 105 (100). Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.49; H, 4.84; N, 22.51.

The reaction of **2a** (172 mg, 1 mmol) with TCNE proceeded almost instantly to give three adducts. To the residue obtained by the evaporation of the solvent was added a mixture of $CHCl_3$–hexane to crystallize **1a**. After filtration, the mother liquor was subjected to silica gel chromatography to separate the components into a mixture of **1a–3a** and a mixture of **16a–16a′**. The yields of **1a**, **3a**, and **16a–16a′** were 88, 8, and 2% in CH_2Cl_2 and 74, 20, and 7% in CH_3CN, respectively (^{1}H NMR). Analytically pure samples of **3a** and **16a–16a′** were obtained in the isomerization of **1a** described below. **1a**: mp 118.5–120 °C; IR (KBr disk) 3090, 3020, 3000, 2250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12–0.17 (ddd, 2 H, J = 14.4, 9.8, 4.9 Hz), 0.18–0.23 (ddd, 2 H, J = 15.1, 9.8, 5.4 Hz), 0.40–0.45 (ddd, 2 H, J = 13.9, 9.8, 4.4 Hz), 0.57–0.62 (ddd, 2 H, J = 13.4, 8.8, 4.4 Hz), 0.75 (s, 2 H), 0.85 (ddd, 2 H, J = 13.2, 7.8, 5.4 Hz), 3.85 (t, 2 H, J = 1.95 Hz), 6.83 (t, 2 H, J = 1.95 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.4 (t), 3.3 (t), 14.1 (d), 15.6 (t), 26.9 (s), 46.6 (s), 53.9 (s), 57.3 (d), 111.1 (s), 111.3 (s), 138.5 (d); MS m/z 300 (M^+, 0.3), 91 (100). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.97; H, 5.32; N, 18.56.

Isomerization of 1. A solution of **1a** (41 mg, 0.14 mmol) in CH_3CN (5 mL) was heated at 80 °C under argon for 90 min to give **3a** (25 mg, 61%) and **16a–16a′** (10 mg, 24%). **3a**: oil; IR 3155, 3100, 3010, 2950, 2930, 2250, 2215, 1650, 1580 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87–1.33 (m, 10 H), 4.03 (d, 1 H, J = 6.6 Hz), 4.09 (dt, 1 H, J = 6.6, 2.2 Hz), 4.87 (s, 1 H), 5.10 (d, 1 H, J = 1.0 Hz), 6.16 (d, 1 H, J = 5.4 Hz), 6.32 (dd, 1 H, J = 5.4, 2.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.0 (m),[25] 43.2 (s), 52.9 (d), 55.1 (d), 81.7 (s), 111.9 (s), 112.4 (s), 114.4 (s), 110.5 (t), 133.3 (d), 137.3 (d), 147.1 (s), 171.5 (s), 182.5 (s); MS m/z 300 (M^+, 5.2), 78 (100); HRMS calcd for $C_{19}H_{16}N_4$ 300.1375, found 300.1390. **16a–16a′**: mp 154–155 °C (hexane–benzene); IR (KBr disk) 3105, 3025, 2910, 2885, 2250, 1630 cm^{-1}; UV λ_{max} (EtOH) 252.5 (ϵ 5100); ^{1}H NMR (500 MHz, C_6D_6) δ 0.27–0.30 (m, 8 H), 0.77–0.84 (m, 2 H), 1.52 and 1.49[26] (s, 2 H), 2.74 (quintet, 2 H, J = 1.5 Hz) and 2.26 (t, 2 H, J = 1.5 Hz),[26] 5.77 (dt, 1 H, J = 1.5, 5.4 Hz) and 6.00 (d, 1 H, J = 5.4 Hz),[26] 6.08 and 6.28[26] (dt, 1 H, J = 1.5, 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.6 (t), 2.8 (t), 15.5 (d), 26.0 (t), 26.7 (s), 35.8 (s),[26] 41.4 (t), 44.2 (s), 111.1 (s), 120.8 (s), 128.5 (d),[26] 132.5 (d), 135.4 (d),[26] 138.3 (d), 145.1 (s); MS m/z 300 (M^+, 10.3), 41 (100). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 76.16; H, 5.36; N, 18.43.

At room temperature, there were no ^{1}H NMR signals other than those of **1a** after 24 h in $CHCl_3$, but there were ca. 20% of the signals corresponding to **3a** in CD_3CN. At 50 °C in CH_3CN, the isomerization was complete after 125 min to give a mixture of **3a** and **16a–16a′** in a 7:3 ratio. Whereas, in $CHCl_3$ the consumption of **1a** was 24% after 125 min at 50 °C. Attempts were made to trap the intermediate with methanol by heating **1a** in CH_3CN in the presence of 5 equiv of CH_3OH, or running the reaction in neat CD_3OD, but only isomerization to **3a** and **16a–16a′** was observed (^{1}H NMR).

In a similar manner, **1b** (in CH_3CN at 80 °C for 90 min, 78% consumption) gave **16b–16b′** (51%, as a 3:1 mixture of isomers): mp 74–75 °C; IR (KBr disk) 3085, 3015, 2975, 2905, 2850, 2250, 1635 cm^{-1}; UV λ_{max} (EtOH) 253 nm (ϵ 5400); ^{1}H NMR, (500 MHz, C_6D_6) δ −0.06 to 0.03 (m, 1 H), 0.15–0.29 (m, 2 H), 0.34–0.41 (m, 1 H), 0.815 and 0.805[26] (s, 3 H), 0.84–0.93 (m, 1 H), 1.73 and 1.70[26] (s, 2 H), 2.68 (septet, 2 H, J = 1.5 Hz) and 2.22 (t, 2 H, J = 1.5 Hz),[26] 5.74 and 5.97[26] (dt, 1 H, J = 5.4, 1.5 Hz), 6.04 and 6.23[26] (dt, 1 H, J = 5.4, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.6 (t), 4.5 (t), 18.2 (d), 21.8 (q), 33.2 (t), 42.3 (t), 43.7 and 45.7[26] (s), 111.9 (s), 121.6 (s), 133.5 and 129.4[26] (d), 139.3 and 136.5[26] (d), 146.3 (s); MS m/z 274 (M^+, 4.3), 142 (100). Anal. Calcd for $C_{17}H_{14}N_4$: C, 74.43; H, 5.14; N, 20.42. Found: C, 74.32; H, 5.31; N, 20.24. No **3b** was produced in the isomerization of **1b** (^{1}H NMR).

Retro-Diels–Alder Reactions of 1a–d. A mixture of **1a** (20 mg, 0.07 mmol) and **2e** (71 mg, 0.67 mmol)[17,18] in CD_3CN was heated at 50 °C under argon. ^{1}H NMR analysis of the mixture revealed that the Diels–Alder adduct **1e** of the addendum was produced in 28% just after 1 min. The rearranged product **3a** started to appear after 10 min (ca. 4%). Prolonged heating of the mixture resulted in the gradual increase of the amount of **3a** in compensation for those of **1a** and **1e**. Thus, the amount of **1e** reached a maximum (78%) after 40 min and the ratio of **1a**:**1e**:**3a** was found to be 10:66:25 after 180 min. Similarly, the retro-Diels–Alder reactions of **1b–c** were found to occur readily in both CH_3CN and $CHCl_3$. **1e**: mp 181.4–184.0 °C dec; IR 3150, 3090, 3015, 2980, 2945, 2875, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.86–1.52 (m, 6 H), 3.42 (dd, 1 H, J = 2.0, 3.9 Hz), 3.60 (dd, 1 H, J = 2.0, 3.9 Hz), 6.79 (t, 2 H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1 (d), 15.1 (q), 19.0 (s), 46.7 (s), 48.9 (s), 56.8 (d), 59.9 (d), 111.1 (s), 138.4 (d), 138.6 (d); MS m/z 234 (M^+, 0.1), 91 (100). Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.94; H, 4.16; N, 23.93.

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