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Differences in Rates of Diels–Alder Reactions as Experimental Indicators of Synchronous or Asynchronous Transition States

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Abstract: Assessment of the relative rates of the Diels–Alder reactions of the unsymmetrical diene 2-(trimethylsilyloxy)-1,3-cyclohexadiene (**1**) and its 6,6- and 5,5-dimethyl analogs **2** and **3** indicated that with symmetrical, ethylenic dienophiles (*para*-benzoquinone, maleic anhydride and *N*-phenylmaleimide) the Diels–Alder reaction is almost synchronous, but with tetracyanoethylene and with diethyl acetylenedicarboxylate the addition is sufficiently asynchronous as to lead to different rates of reaction with dimethyl-dienes **2** and **3**.

Keywords: Diels–Alder reactions; steric and strain effects

INTRODUCTION

The Diels–Alder reaction has been the subject of considerable debate about the details of its mechanism.[1] Substituted and deuterated[2] addends retain their relative configurations during the reaction, which is consistent with a concerted mechanism in which both new σ-bonds are forming at the transition state, without the intermediacy of biradical or zwitterionic species. The concerted pathway is in agreement with linear free energy relationships[3] and measurements of kinetic isotope effects (KIE's) with symmetrical dienes,[4] 2-methylfuran,[5] and isoprene.[6,7] An unsymmetrical diene cannot undergo an completely synchronous reaction, with incipient σ-σ-bonds of exactly the same length at the transition state, and this asynchronicity has been detected in the KIE's.[5-7] Computational work has shown that the transition state is generally symmetrical with symmetrical addends,[8-10] although it was reported that the Diels–Alder reaction of cyclopentadiene and acetylenedicarboxylic acid has a very unsymmetrical transition state.[10] The lengths of the incipient σ-bonds can be quite different with an unsymmetrical addend,[7,9,11] with the shorter bond being the one predicted using a simple FMO analysis.[9,12] It has been argued that changes in regioselectivity between thermal Diels–Alder reactions and those catalyzed by Lewis acids are a manifestation of a less synchronous, even ionic, reaction,[13] but what has not been reported is whether reaction rates can be correlated with the degree of synchronicity in thermal Diels–Alder reactions.

RESULTS AND DISCUSSION

The KIE data indicate significant differences in the extent of σ-bond-formation at the two termini of methyl-substituted dienes at the transition state with symmetrical dienophiles.[5,6d] It is reasonable to assume that any reaction with the oxygen-substituted diene **1** should also be asynchronous, i.e., the new σ-bond at C-1 of

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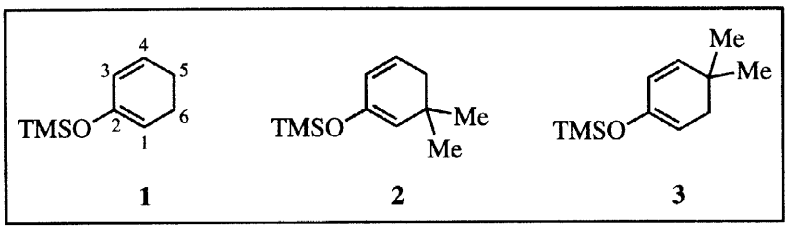
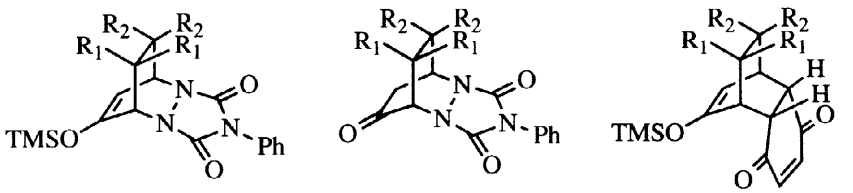
the diene should be shorter than the one at C-4 at the transition state. Introduction of a sterically hindering group near C-1 would therefore be expected to have a different, probably more adverse, effect than would the same steric hindrance near C-4. Thus, we postulated that an asynchronous mechanism could result in the Diels–Alder reaction of diene **2** being significantly slower than the reaction of diene **3**.



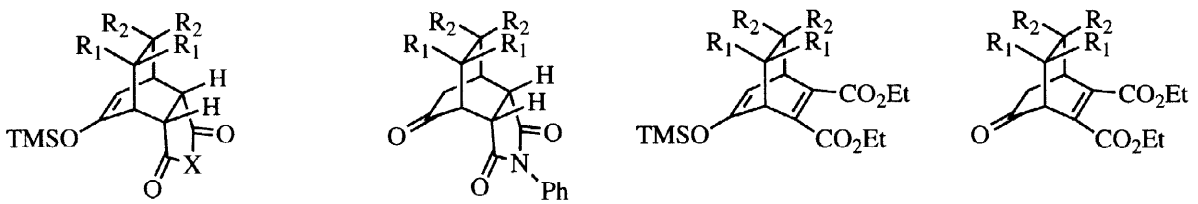
1 **2** **3**



4a R_1 = H, R_2 = H
5a R_1 = Me, R_2 = H
6a R_1 = H, R_2 = Me

4b R_1 = H, R_2 = H
5b R_1 = Me, R_2 = H
6b R_1 = H, R_2 = Me

7 R_1 = H, R_2 = H
8 R_1 = Me, R_2 = H
9 R_1 = H, R_2 = Me

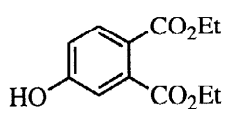


10 X = O, R_1 = H, R_2 = H
11 X = O, R_1 = Me, R_2 = H
12 X = O, R_1 = H, R_2 = Me
13a X = N-Ph, R_1 = H, R_2 = H
14a X = N-Ph, R_1 = Me, R_2 = H
15a X = N-Ph, R_1 = H, R_2 = Me

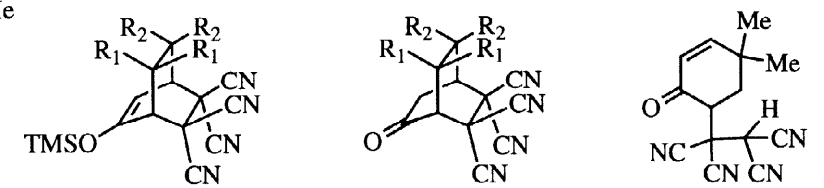
13b R_1 = H, R_2 = H
14b R_1 = Me, R_2 = H
15b R_1 = H, R_2 = Me

16a R_1 = H, R_2 = H
17a R_1 = Me, R_2 = H
18a R_1 = H, R_2 = Me

16b R_1 = H, R_2 = H
17b R_1 = Me, R_2 = H
18b R_1 = H, R_2 = Me



19



20 R_1 = H, R_2 = H
21a R_1 = Me, R_2 = H
22a R_1 = H, R_2 = Me

21b R_1 = Me, R_2 = H
22b R_1 = H, R_2 = Me

23

In order to assess only the effect of the nonsymmetry in the diene, six symmetrical dienophiles were employed. 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD), *para*-benzoquinone (PBQ), maleic anhydride (MA), *N*-phenylmaleimide (NPM), and diethyl acetylenedicarboxylate (DAD) underwent Diels–Alder reactions with dienes **1**, **2**, and **3** in benzene solution to give adducts (**4a–18a**) essentially quantitatively, although overheating adducts derived from DAD led to production of the phthalate **19** by a *retro*-Diels–Alder process. Tetracyanoethylene (TCNE) reacted with all three dienes very quickly to give adducts **20–22a**, but TCNE with **3** also gave some of the product **23**. (Two mechanisms have been identified to account for the formation of related com-

pounds with TCNE.[14]) Purification and characterization of the adducts were hampered by the fragility of the silyl enol ether functions (especially with **16a–18a**) and the possibility of reversibility of the Diels–Alder reactions and decomposition of the adducts, particularly with TCNE,[15] so in many instances characterization was more complete for the hydrolysis products (**4b–22b**).

The relative rates of the Diels–Alder reactions of dienes **1**, **2**, and **3** were estimated with the six dienophiles in a series of competitive reactions involving pairs of dienes. Rates of reaction, relative to the rate with diene **1**, are given in Table 1. AM1[16] calculations (Table 2) with the dienes **1**, **2**, and **3** show that attachment of *gem*-dimethyl groups onto diene **1** affects both the energy of the diene HOMO as well was the coefficients at C-1 and C-4. However, every dienophile reacted more quickly with **1** than with **2** or **3**, although the differences in rate were small with PTAD, which has been shown to be the least sterically-demanding dienophile of the six.[17] The data in Table 1 confirms that the rate-retarding effect of steric hindrance from the methyl groups of **2** and **3** is more important than any rate enhancement ascribable to differences in the diene HOMO.

Table 1. Rates of the reactions of dienes **2** and **3**, relative to the rate with diene **1** (rate = 1).

dienophile	diene **2**	diene **3**	reaction conditions
4-phenyl-1,2,-triazoline-3,5-dione (PTAD)	0.9	0.7	C_6H_6, rt, 30 min
para-benzoquinone (PBQ)	0.04	0.04	C_6H_6, reflux, 16 h
maleic anhydride (MA)	0.09	0.08	C_6H_6, reflux, 30 h
N-phenylmaleimide (NPM)	0.1	0.08	C_6H_6, reflux, 30 h
diethyl acetylenedicarboxylate (DAD)	0.4	0.05	C_6H_6, reflux, 48 h
tetracyanoethylene (TCNE)	0.02	0.1	CD_2Cl_2, rt, 10 min

Table 2. HOMO energies and coefficients for dienes **1–3** (AM1).

diene	HOMO energy (eV)	coefficient of HOMO at C-1	coefficient of HOMO at C-4
1	–8.726	–0.4826	+0.5092
2	–8.774	–0.4907	+0.5210
3	–8.779	–0.4941	+0.5172

The HOMO energies of **2** and **3** are the same (Table 2) and in the *exo* region of the *endo* Diels–Alder transition state with either **2** or **3**, PBQ, MA, and NPM must project a hydrogen toward a methyl group on the diene. Very similar rates of addition to **2** and **3** were observed with these dienophiles. This indicates that the steric hindrance encountered by the incoming dienophile is essentially the same with **2** and with **3**. Therefore, the Diels–Alder reactions with these dienophiles are not sufficiently asynchronous to allow the position of the *gem*-dimethyl groups to influence the reaction rate in a significant way.

Facial selectivity studies with TCNE have indicated that this very reactive dienophile is more sterically demanding than PBQ, MA, or NPM.[17] In contrast with these ethylenic dienophiles, the Diels–Alder addition of TCNE with **2** was slower than with **3**, even though a proportion of **3** was diverted to **23**. This finding is in accord with the original supposition for an asynchronous transition state. However, TCNE was the only dienophile of the six that behaved this way.

Acetylene should be sterically less demanding than the ethylenic dienophiles.[17] Therefore, it was not surprising that the reaction of DAD with **1** was only about twice as fast as with **2**. However, the reaction of

DAD with **1** was 25 times faster than with **3**. This might suggest an asynchronous transition state with the "lopsidedness" of the transition state being opposite to what would be predicted on the basis of FMO considerations. However, a better explanation can be based on *ab initio* computational work by Morokuma and coworkers.[10] They found that the transition state for the addition of acetylenedicarboxylic acid to cyclopentadiene is very lopsided, with incipient σ-bonds of 2.030 Å and 2.712 Å. The carboxylate group nearer the longer incipient σ-bond activates the reacting π-bond of the dienophile and so this carboxylate is roughly parallel-planar with the π-system of the diene. This carbonyl is also *endo* with respect to the diene's π-system. The carboxylate nearer the shorter incipient σ-bond is very far from parallel-planar with the π-system of the diene. A similar geometry in the transition states involving our dienes must situate the shorter incipient σ-bond at C-1 of the diene. This would mean than methyl groups at C-6 of the diene (i.e., diene **2**) would avoid steric hindrance with the incoming dienophile since the closer carboxylate moiety would not be close to parallel-planar with the π-system of the diene. On the other hand, even though the longer incipient σ-bond would be at C-4 with our dienes, the carboxylate moiety closer to C-4 would be approximately parallel-planar with the diene's π-system, and therefore a steric interaction with a methyl group at C-5 (i.e., diene **3**) would be unavoidable.

In conclusion, the results of Diels–Alder reactions with the unsymmetrical dienes **1–3** indicate a high level of synchronicity with symmetrical ethylenic dienophiles (PBQ, MA, and NPM), but additions with TCNE and DAD are much less synchronous.

EXPERIMENTAL

Melting points (mp) were determined on a Fisher-Johns apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Mattson FT instrument as thin films unless otherwise indicated. Nuclear magnetic resonance (NMR) spectra were obtained on a General Electric GE 300-NB instrument as $CDCl_3$ solutions. In some instances, the ^{13}C NMR chemical shift is followed in parentheses by the number of attached hydrogens, as determined by APT and/or heteronuclear correlation spectra. Mass spectral (MS) data were obtained with a V.G. Micromass 7070HS instrument or from a Hewlett-Packard 5970 mass selective detector (GC-MS).

*2-(Trimethylsilyloxy)-1,3-cyclohexadiene (**1**).*

To diisopropylamine (1.74 g, 17.2 mmol) in THF (55 mL) at 0 °C was added dropwise a 1.6 M solution of *n*-butyllithium (11.7 mL, 18.7 mmol). The solution was cooled to –78 °C, and a solution of 2-cyclohexen-1-one (1.50 g, 15.6 mmol) in THF (10 mL) was added dropwise. After 1 h, excess TMSCl was added and the mixture was kept at –78 °C for 1.5 h before warming to rt and stirring for a further 1 h. The THF was evaporated under vacuum, and the residue was taken up in anhydrous pentane (60 mL). A precipitate (LiCl) was removed by filtration. Evaporation of the pentane followed by vacuum distillation provided **1** as a colorless liquid (2.05 g, 78%): bp 35–37 °C / 3 mmHg; IR 3048, 3025 (w), 2957, 1649, 1594, 1401, 1251, 1198, 909 cm^{-1}; ^1H NMR δ 5.86 (1H, dt, J = 4.0, 9.7 Hz), 5.69 (1H, dq, J = 1.8, 9.9 Hz), 4.88 (1H, dt, J = 2.1, 4.0 Hz), 2.22–2.03 (4H, m), 0.19 (9H, s); ^{13}C NMR δ 148.0 (0), 128.9 (1), 126.3 (1), 102.4 (1), 22.6 (2), 21.7 (2), 0.2 (3C, 3); MS 169 (12, M^+ + 1), 168 (10, M^+), 167 (9), 151 (7), 147 (20), 145 (11), 86 (59), 75 (30), 73 (100), 68 (8), 67 (9), 58 (10).

*6,6-Dimethyl-2-(trimethylsilyloxy)-1,3-cyclohexadiene (**2**).*

Following the procedure for **1**, 5,5-dimethyl-2-cyclohexen-1-one (1.50 g, 12.1 mmol) gave **2** as a colorless liquid (1.89 g, 80%): bp 29–31 °C / 0.8 mmHg; IR 3047 (w), 3018 (w), 2958, 1649, 1592, 1401, 1252 (br), 846 (br) cm^{-1}; ^1H NMR δ 5.76 (1H, dt, J = 4.1, 10.0 Hz), 5.66 (1H, dq, J = 1.8, 9.9 Hz), 4.65 (1H, symmetrical m), 2.05 (2H, dd, J = 1.8, 4.1 Hz), 1.00 (6H, s), 0.18 (9H, s); ^{13}C NMR δ 146.5 (0), 127.5 (1), 125.1 (1), 114.8 (1), 38.0 (2), 31.8 (0), 28.7 (2C, 3), 0.1 (3C, 3); MS 197 (3, M^+ + 1), 196 (10, M^+), 182 (14), 181 (100), 165 (53), 105 (4), 91 (10), 82 (18), 75 (20), 73 (77).

5,5-Dimethyl-2-(trimethylsilyloxy)-1,3-cyclohexadiene (3).

Following the procedure for **1**, 4,4-dimethyl-2-cyclohexen-1-one (1.20 g, 9.66 mmol) gave **3** as a colorless liquid (1.45 g, 76%): bp 29–31 °C / 0.8 mmHg; IR 3041, 3017 (w), 2958, 1653, 1596, 1404, 1377, 1251, 1205, 897, 845 cm^{-1}; ^1H NMR δ 5.55 (2H, apparent d, J = 1.0 Hz), 4.79 (1H, tt, J = 1.4, 4.6 Hz), 2.12 (2H, d, J = 4.6 Hz), 1.01 (6H, s), 0.19 (9H, s); ^{13}C NMR δ 147.1 (0), 140.1 (1), 123.7 (1), 101.5 (1), 37.0 (2), 31.2 (0), 27.7 (2C, 3), 0.2 (3C, 3); MS 197 (3, M^+ + 1), 147 (7), 124 (24), 109 (10), 97 (9), 96 (100), 95 (12), 82 (64), 81 (48), 79 (14), 77 (9), 68 (22), 67 (44), 56 (10), 55 (20), 54 (9), 53 (38), 51 (13).

Competitive Diels–Alder reactions.

To a mixture of dienes was added dienophile in an amount stoichiometrically less than the less abundant diene. (Reaction conditions are shown in Table 1.) After the appropriate amount of time, the solvent was evaporated under vacuum. Ratios of adducts were estimated by careful integration of unoverlapped signals in the ^1H NMR spectra of these mixtures. In some instances, especially with adducts **16a–18a** that were very susceptible to hydrolysis, integration of the NMR spectra of deliberately hydrolyzed product mixtures served to corroborate the adduct ratios. The identity of the products was based on the ^1H NMR data given below for the individual adducts and their hydrolysis products. As a result of the initial experiments, the competitive reactions were repeated with blends of dienes that were calculated to give adduct ratios closer to 1:1 so that quantification by NMR integration would be more reliable. Heating some adduct mixtures and isolated adducts in benzene gave no sign of equilibration, except for adducts **20–22a**. These did not appear to equili-brate appreciably at room temperature, but they decomposed rapidly at more elevated temperatures.

Diene 1 with PTAD: 5,8-dihydro-6-(trimethylsilyloxy)-5,8-ethano-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H)-dione (4a).

Waxy solid; IR 1772 (m), 1716 (s), 1632 (m) cm^{-1}; ^1H NMR δ 7.45–7.26 (5H, m), 5.28 (1H, dd, J = 2,3, 6.4 Hz), 4.96 (1H, m), 4.73 (1H, apparent t, $J \approx$ 2.5 Hz), 2.23–2.11 (2H, m), 1.85–1.58 (2H, m), 0.22 (9H, s); ^{13}C NMR δ ^{13}C NMR δ 153.8 (2C), 131.5, 129.0, 128.1, 125.4, 100.5, 55.4, 51.9, 24.2, 22.4, –0.1; MS 343 (5, M^+), 275 (18), 250 (9), 177 (10), 168 (27), 167 (29), 166 (33), 151 (56), 119 (29), 75 (23), 73 (100); HRMS calcd for $C_{17}H_{21}N_3O_3Si$ 343.1351, found 343.1351. *Hydrolysis product: 5,7,8-trihydro-5,8-ethano-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H),6-trione (4b).* ^1H NMR (C_5D_5N, partial data) δ 4.84 (1H, narrow m), 4.80 (narrow m), 3.04 (1H, dt, J = 19.0, 3.0 Hz), 2.69 (1H, dd, J = 2.3, 19.0 Hz), 2.26 (1H, m), 2.14–1.94 (2H, m), 1.76 (1H, m); ^{13}C NMR (C_5D_5N) δ 199.7, 151.3, 150.8, 130.6, 127.2, 126.3, 124.1, 56.4, 48.9, 41.3, 21.8, 20.4.

Diene 2 with PTAD: 5,8-dihydro-10,10-dimethyl-6-(trimethylsilyloxy)-5,8-ethano-1H-[1,2,4]triazolo[1,2-a]-pyridazine-1,3(2H)-dione (5a).

Viscous liquid; ^1H NMR δ 7.48–7.35 (5H, m), 5.15 (1H, dd, J = 2.3, 6.3 Hz), 4.86 (1H, m), 4.22 (1H, d, J = 2.3 Hz), 1.86 (1H, dd, J = 3.1, 12.8 Hz), 1.42 (1H, dd, J = 2.7, 12.8 Hz), 1.31 (3H, s), 1.07 (3H, s), 0.22 (9H, s); MS 371 (0.2, M^+), 195 (52), 181 (17), 179 (27), 119 (15), 91 (17), 75 (17), 73 (100), 45 (28). *Hydrolysis product: 5,7,8-trihydro-10,10-dimethyl-5,8-ethano-1H-[1,2,4]-triazolo[1,2-a]pyridazine-1,3(2H),6-trione (5b).* Cream-colored solid, mp 238–240 °C; IR (Nujol) 1774 (m), 1709 (s) cm^{-1}; ^1H NMR (C_5D_5N) δ 7.40–7.24 (5H, m), 4.89 (1H, m), 4.53 (1H, s), 3.01 (1H, dt, J = 19.2, 3.1 Hz), 2.67 (1H, dd, J = 2.2, 19.2 Hz), 1.87 (1H, ddd, J = 3.1, 3.7, 13.9 Hz), 1.61 (1H, dd, J = 2.1, 13.9 Hz), 1.15 (3H, s), 0.96 (3H, s); ^{13}C NMR (C_5D_5N) δ 201.6, 153.0 (2C), 132.6, 129.2, 128.3, 126.2, 67.3, 50.6, 41.8, 39.8, 33.5, 27.8, 27.7; MS 299 (32, M^+), 271 (30), 214 (82), 178 (13), 119 (100), 95 (26), 94 (24); HRMS calcd for $C_{16}H_{17}N_3O_3$ 299.1269, found 299.1269.

*Diene 3 with PTAD: 5,8-dihydro-9,9-dimethyl-6-(trimethylsilyloxy)-5,8-ethano-1H-[1,2,4]triazolo[1,2-a]-pyridazine-1,3(2H)-dione (**6a**).*

Colorless oil; ^{1}H NMR δ 7.50–7.35 (5H, m), 5.28 (1H, dd, *J* = 2.4, 6.4 Hz), 4.63 (1H, m), 4.42 (1H, d, *J* = 6.4 Hz), 1.89 (1H, dd, *J* = 3.3, 13.2 Hz), 1.56 (1H, dd, *J* = 2.7, 13.2 Hz), 1.32 (3H, s), 1.04 (3H, s), 0.22 (9H, s); MS 371 (3, M$^+$), 316 (10), 315 (43), 181 (15), 169 (10), 168 (66), 119 (27), 96 (15), 75 (16), 73 (100), 55 (12), 45 (28), 41 (22). *Hydrolysis product: 5,7,8-trihydro-9,9-dimethyl-5,8-ethano-1H-[1,2,4]triazolo[1,2-a]pyridazine-1,3(2H),6-trione (**6b**).* Colorless crystals, mp 181–183 °C; IR 1769 (m), 1740 (s), 1719 (s) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.59–7.36 (5H, m), 4.45 (1H, dd, *J* = 2.7, 3.8 Hz), 4.36 (1H, apparent t, *J* = 2.7 Hz), 2.96 (1H, dd, *J* = 2.4, 19.4 Hz), 2.78 (1H, dd, *J* = 3.0, 19.4 Hz), 2.21 (1H, dd, *J* = 3.8, 14.7 Hz), 2.00 (1H, dd, *J* = 2.7, 14.7 Hz), 1.34 (3H, s), 1.21 (3H, s); ^{13}C NMR (CD_3COCD_3) δ 202.1 (0), 153.9 (0), 152.6 (0), 133.1 (0), 129.5 (2C, 1), 128.6 (1), 126.7 (2C, 1), 60.6 (1), 59.3 (1), 40.1 (2), 39.4 (2), 34.0 (0), 29.3 (3), 27.6 (3); MS 299 (22, M$^+$), 271 (22), 214 (42), 119 (100), 95 (32), 94 (34), 91 (23), 69 (24), 55 (33), 41 (41); HRMS calcd for $C_{16}H_{17}N_3O_3$ 299.1269, found 299.1269.

Diene 1 with PBQ: (4aR,5R*,8R*,8aS*)-4a,5,8,8a-tetrahydro-6-(trimethylsilyloxy)-5,8-ethanonaphthalene-1,4-dione (**7**).*

Pale yellow solid, mp 96–97 °C; IR 1668 (s), 1633 (m) cm^{-1}; ^{1}H NMR δ 6.68 (1H, d, *J* = 10.5 Hz), 6.67 (1H, d, *J* = 10.5 Hz), 4.95 (1H, dd, *J* = 2.0, 7.0 Hz), 3.17 (1H, m), 3.00–2.94 (2H, m), 2.91 (1H, dd, *J* = 2.4, 8.9 Hz), 1.74–1.54 (3H, m), 1.42 (1H, m), 0.13 (9H, s); ^{13}C NMR δ 199.6 (0), 198.5 (0), 155.5 (0), 142.1 (1), 141.8 (1), 102.2 (1), 50.0 (1), 49.5 (1), 41.1 (1), 36.2 (1), 26.0 (2), 25.3 (2), 0.1 (3C, 3); MS 276 (2, M$^+$), 248 (2), 168 (97), 151 (28), 75 (43), 73 (100), 45 (36); HRMS calcd for $C_{15}H_{20}O_3Si$ 276.1181, found 276.1180.

Diene 2 with PBQ: (4aR,5S*,8R*,8aS*)-4a,5,8,8a-tetrahydro-10,10-dimethyl-6-(trimethylsilyloxy)-5,8-ethanonaphthalene-1,4-dione (**8**).*

Pale yellow oil; IR 1670 (s), 1634 (m) cm^{-1}; ^{1}H NMR δ 6.72 (1H, apparent s), 6.71 (1H, apparent s), 4.76 (1H, dd, *J* = 2.2, 6.9 Hz), 3.27 (1H, dd, *J* = 2.8, 9.0 Hz), 3.05 (1H, m), 2.86 (1H, dd, *J* = 2.2, 9.0 Hz), 2.53 (1H, dd, *J* = 2.2, 2.8 Hz), 1.42–1.23 (2H, m), 1.11 (3H, s), 0.94 (3H, s), 0.13 (9H, s); MS 304 (2, M$^+$), 276 (2), 248 (2), 196 (11), 181 (100), 166 (15), 165 (13), 151 (20), 73 (24); HRMS $C_{17}H_{24}O_3Si$ 304.1493, found 304.1496.

Diene 3 with PBQ: (4aR,5R*,8R*,8aS*)-4a,5,8,8a-tetrahydro-9,9-dimethyl-6-(trimethylsilyloxy)-5,8-ethanonaphthalene-1,4-dione (**9**).*

Yellow wax; IR 1673 (s), 1636 (m) cm^{-1}; ^{1}H NMR δ 6.71 (1H, apparent s), 6.69 (1H, apparent s), 4.97 (1H, dd, *J* = 2.3, 6.9 Hz), 3.25 (1H, dd, *J* = 3.0, 9.0 Hz), 2.95 (1H, dd, *J* = 2.1, 9.0 Hz), 2.80 (1H, m), 2.72 (1H, dd, *J* = 3.0, 6.9 Hz), 1.48 (1H, dd, *J* = 2.7, 12.9 Hz), 1.41 (1H, dd, *J* = 3.3, 12.9 Hz), 1.10 (3H, s), 0.91 (3H, s), 0.13 (9H, s); ^{13}C NMR δ 200.4, 199.1, 154.2, 142.6, 141.4, 102.8, 48.1, 47.6, 46.1, 43.3, 42.0, 33.9, 30.8, 29.6, 0.1 (3C); MS 304 (1, M$^+$), 248 (16), 181 (16), 167 (16), 166 (100), 151 (55), 91 (13), 82 (86), 75 (20), 73 (51), 54 (18), 45 (22); HRMS $C_{17}H_{24}O_3Si$ 304.1493, found 304.1481.

Diene 1 with MA: (3aR,4R*,7R*,7aS*)-3a,4,7,7a-tetrahydro-5-(trimethylsilyloxy)-4,7-ethanoisobenzofuran-1,3-dione (**10**).*

Oil; IR 1868 (m), 1840 (m), 1780 (s), 1634 (s) cm^{-1}; ^{1}H NMR δ 5.00 (1H, dd, *J* = 2.2, 7.0 Hz), 3.18 (1H, m), 3.14 (1H, dd, *J* = 3.2, 8.7 Hz), 3.08 (1H, dd, *J* = 3.1, 8.7 Hz), 2.99 (1H, m), 1.66–1.38 (4H, m), 0.19 (9H, s); ^{13}C NMR δ 173.0 (0), 172.2 (0), 154.9 (0), 101.1 (1), 45.5 (1), 44.9 (1), 37.6 (1), 32.5 (1), 24.5 (2), 23.2 (2), –0.2 (3C, 3); MS 266 (7, M$^+$), 168 (100), 167 (14), 166 (20), 153 (21), 151 (37), 77 (19), 75 (40), 73 (77), 45 (39).

Diene 2 with MA: (3aR,4S*,7R*,7aS*)-3a,4,7,7a-tetrahydro-9,9-dimethyl-5-(trimethylsilyloxy)-4,7-ethano-isobenzofuran-1,3-dione (**11**).*

Waxy solid; IR 1863 (m), 1780 (s), 1634 (m) cm^{-1}; ^1H NMR δ 4.84 (1H, dd, *J* = 2.1, 6.9 Hz), 3.43 (1H, dd, *J* = 3.6, 8.7 Hz), 3.11 (1H, m), 3.01 (1H, dd, *J* = 3.3, 8.7 Hz), 2.52 (1H, dd, *J* = 2.1, 3.6 Hz), 1.30(1H, dd, *J* = 3.3, 12.9 Hz), 1.26 (1H, dd, *J* = 2.4, 12.9 Hz), 1.07 (3H, s), 0.99 (3H, s), 0.20 (9H, s); ^{13}C NMR δ 173.1, 172.8, 156.3, 97.5, 49.3, 44.6, 42.0, 40.9, 34.1, 33.4, 30.6, 28.4, –0.2; MS 294 (1, M^+), 279 (16), 251 (5), 238 (4), 196 (15), 181 (100), 166 (22), 165 (13), 151 (34), 75 (15), 73 (31).

Diene 3 with MA: (3aR,4R*,7R*,7aS*)-3a,4,7,7a-tetrahydro-8,8-dimethyl-5-(trimethylsilyloxy)-4,7-ethano-isobenzofuran-1,3-dione (**12**).*

Waxy solid; IR 1861 (m), 1780 (s), 1636 (m) cm^{-1}; ^1H NMR δ 5.03 (1H, dd, *J* = 2.2, 7.0 Hz), 3.45 (1H, dd, *J* = 3.5, 8.7 Hz), 3.08 (1H, dd, *J* = 3.1, 8.7 Hz), 2.91 (1H, m), 2.68 (1H, dd, *J* = 3.5 , 7.0 Hz), 1.45 (1H, dd, *J* = 3.4, 13.2 Hz), 1.33 (1H, dd, *J* = 2.5, 13.2 Hz), 1.08 (3H, s), 0.97 (3H, s), 0.20 (9H, s); ^{13}C NMR δ 173.6, 172.2, 153.5, 101.6, 43.9, 43.7, 42.9, 39.8, 39.6, 34.0, 30.6, 29.2, –0.1; MS 294 (3, M^+), 238 (34), 181 (13), 166 (96), 151 (100), 91 (21), 77 (16), 75 (32), 73 (71), 45 (33).

Diene 1 with NPM: (3aR,4R*,7R*,7aS*)-3a,4,7,7a-tetrahydro-2-phenyl-5-(trimethylsilyloxy)-4,7-ethanoiso-indole-1,3-dione (**13a**).*

White solid, mp 141–142 °C; ^1H NMR δ 7.46–7.33 (3H, m), 7.27–7.21 (2H, m), 4.98 (1H, dd, *J* = 2.1, 7.0 Hz), 3.21 (1H, m), 3.03 (1H, m), 2.98 (1H, dd, *J* = 3.1, 8.2 Hz), 2.93 (1H, dd, *J* = 3.0, 8.2 Hz), 1.63 (3H, m), 1.47 (1H, m), 0.16 (9H, s); ^{13}C NMR δ 178.1 (0), 177.3 (0), 154.6 (0), 131.9 (0), 129.2 (0), 128.9 (2C, 1), 128.3 (1), 126.3 (2C, 1), 100.5 (1), 45.0 (1), 44.4 (1), 37.8 (1), 32.6 (1), 25.3 (2), 24.0 (2), 0.0 (3C, 3); MS 341 (14, M^+), 326 (5), 313 (8), 175 (25), 168 (100), 166 (26), 151 (32), 75 (26), 73 (69), 45 (16); HRMS calcd for $C_{19}H_{23}NO_3Si$ 341.1446, found 341.1433. *Hydrolysis product: (3aR*,4R*,7R*,7aS*)-3a,4,6,7,7a-pentahydro-2-phenyl-4,7-ethanoisoindole-1,3,5-trione (**13b**).* Colorless crystals, mp 225–226 °C; IR (Nujol) 1730 (shoulder), 1700 cm^{-1}; ^1H NMR δ 7.51–7.37 (3H, m), 7.20 (2H, m), 3.28 (1H, dd, *J* = 3.5, 9.6 Hz), 3.19 (1H, ddd, *J* = 1.3, 3.6, 9.6 Hz), 2.95 (1H, apparent q, *J* ≈ 3.1 Hz), 2.84 (1H, m), 2.33 (1H, ddd, *J* = 1.4, 2.7, 19.8 Hz), 2.27 (1H, broad d, *J* = 19.8 Hz), 1.99 (2H, m), 1.85 (2H, m); ^{13}C NMR δ 210.6 (0), 176.9 (0), 175.9 (0), 131.2 (0), 129.2 (2C, 1), 128.8 (1), 126.3 (2C, 1), 43.9 (1), 42.7 (1), 42.6 (1), 40.9 (2), 30.0 (1), 23.4 (2), 21.6 (2); MS 269 (100, M^+), 241 (15), 213 (26), 175 (19), 174 (13), 80 (85), 79 (59), 77 (36); HRMS calcd for $C_{15}H_{15}NO_3$ 269.1051, found 269.1051.

Diene 2 with NPM: (3aR,4S*,7R*,7aS*)-3a,4,7,7a-tetrahydro-9,9-dimethyl-2-phenyl-5-(trimethylsilyloxy)-4,7-ethanoisoindole-1,3-dione (**14a**).*

Colorless crystals, mp 153–154 °C; ^1H NMR δ 7.45–7.32 (3H, m), 7.22 (2H, br d, *J* ≈ 7.5 Hz), 4.82 (1H, dd, *J* = 1.9, 6.9 Hz), 3.32 (1H, dd, *J* = 3.4, 8.1 Hz), 3.13 (1H, apparent sextet, *J* = 3.1 Hz), 2.87 (1H, dd, *J* = 2.9, 8.1 Hz), 2.56 (1H, br t, *J* ≈ 2.5 Hz), 1.32 (2H, apparent d, *J* = 2.7 Hz), 1.11 (3H, s), 0.99 (3H, s), 0.16 (9H, s); ^{13}C NMR δ 178.2, 178.0, 155.9, 132.0, 128.9, 128.3, 126.3, 96.8, 49.3, 44.1, 41.8, 41.1, 34.2, 33.9, 30.8, 28.6, 0.0; MS 369 (6, M^+), 354 (5), 314 (18), 313 (71), 193 (30), 181 (28), 166 (100), 151 (82), 73 (42). *Hydrolysis product: (3aR*,4S*,7R*,7aS*)-3a,4,6,7,7a-pentahydro-9,9-dimethyl-2-phenyl-4,7-ethanoisoindole-1,3,5-trione (**14b**).* Colorless crystals, mp 245–246 °C; IR 1775 (w), 1710 (s) cm^{-1}; ^1H NMR δ 7.50-7.38 (3H, m), 7.19 (2H, distorted d, *J* = 7.0 Hz), 3.51 (1H, dd, *J* = 3.7, 9.5 Hz), 3.11 (1H, ddd, *J* = 1.3, 3.6, 9.5 Hz), 2.84 (1H, m), 2.60 (1H, d, *J* = 3.7 Hz), 2.25 (1H, broad d, *J* = 19.5 Hz), 2.18 (1H, apparent dt, *J* = 19.5, 2.6 Hz), 1.70 (1H, dd, *J* = 3.3, 13.9 Hz), 1.62 (1H, apparent dt, *J* = 13.9, 2.4 Hz), 1.20 (2H, s), 1.05 (3H, s); ^{13}C NMR δ 210.2 (0), 176.9 (0), 176.5 (0), 131.3 (0), 129.2 (2C, 1), 128.9 (1), 126.3 (2C, 1), 55.6 (1), 42.0 (1), 40.3 (2), 39.6 (1), 39.4 (2), 31.5 (3), 31.3 (0), 31.2 (1), 28.8 (3); MS 297 (100, M^+), 282 (10), 201 (18), 108 (30), 93 (41), 91 (23), 77 (25); HRMS calcd for $C_{18}H_{19}NO_3$

297.1364, found 297.1351.

Diene 3 with NPM: (3aR,4R*,7R*,7aS*)-3a,4,7,7a-tetrahydro-8,8-dimethyl-2-phenyl-5-(trimethylsilyloxy)-4,7-ethanoisoindole-1,3-dione (**15a**).*

Viscous oil; ^{1}H NMR δ 7.46–7.35 (3H, m), 7.23–7.20 (2H, m), 5.01 (1H, dd, *J* = 1.9, 7.0 Hz), 3.32 (1H, dd, *J* = 3.4, 8.1 Hz), 2.97–2.92 (2H, m), 2.72 (1H, dd, *J* = 3.4, 7.0 Hz), 1.46 (1H, dd, *J* = 3.2, 12.9 Hz), 1.39 (1H, dd, *J* = 2.2, 12.9 Hz), 1.12 (3H, s), 0.98 (3H, s), 0.17 (9H, s); ^{13}C NMR δ 178.8 (0), 177.4 (0), 153.2 (0), 134.1 (0), 128.9 (2C, 1), 128.3 (1), 126.4 (2C, 1), 101.1 (1), 44.0 (1), 43.1 (1), 42.2 (1), 40.5 (1), 40.0 (2), 34.5 (0), 30.9 (3), 29.3 (3), 0.1 (3C, 3); MS 369 (1, M$^+$), 313 (34), 193 (25), 181 (7), 166 (100), 151 (91), 91 (22), 77 (17), 75 (27), 73 (77), 45 (27). *Hydrolysis product: (3aR*,4R*,7R*,7aS*)-3a,4,6,7,7a-pentahydro-8,8-dimethyl-2-phenyl-4,7-ethanoisoindole-1,3,5-trione (**15b**).* Colorless crystals, mp 201–202 °C; IR 1711 cm^{-1}; ^{1}H NMR δ 7.48–7.34 (3H, m), 7.17 (2H, distorted d, *J* = 7.3 Hz), 3.50 (1H, ddd, *J* = 2.1, 3.5, 9.6 Hz), 3.21 (1H, dd, *J* = 3.3, 9.6 Hz), 2.86 (1H, apparent q, *J* ≈ 3.0 Hz), 2.60 (1H, apparent dt, *J* = 20.3, 2.3 Hz), 2.35 (1H, apparent q, *J* = 3.1 Hz), 2.08 (1H, dd, *J* = 2.6, 20.2 Hz), 1.73 (1H, dd, *J* = 3.0, 14.0 Hz), 1.70 (1H, dd, *J* = 3.0, 14.0 Hz), 1.18 (3H, s), 1.10 (3H, s); ^{13}C NMR δ 210 6 (0), 177.6 (0), 175.9 (0), 131.3 (0), 129.0 (2C, 1), 128.7 (1), 126.2 (2C, 1), 45.8 (1), 41.3 (1), 40.5 (1), 40.2 (1), 38.1 (2), 37.5 (2), 30.6 (0), 29.7 (3), 29.1 (3); MS 297 (100, M$^+$), 282 (19), 241 (21), 201 (15), 176 (17), 174 (11), 122 (17), 119 (18), 109 (16), 108 (24), 107 (18), 93 (48), 91 (48), 79 (20), 77 (39); HRMS calcd for $C_{18}H_{19}NO_3$ 297.1364, found 297.1366.

*Diene 1 with DAD: diethyl 5-(trimethylsilyloxy)bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**16a**).*

^{1}H NMR (partial data) δ 5.14 (1H, dd, *J* = 2.4, 6.7 Hz), 4.23 (2H, q, *J* = 7.2 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 3.83 (1H, m), 3.72 (1H, m), 1.30 (3H, t, *J* = 7.2 Hz), 1.29 (3H, t, *J* = 7.2 Hz). *Hydrolysis product: diethyl 2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (**16b**).* Pale yellow oil; IR 1729 (s), 1637 (w) cm^{-1}; ^{1}H NMR δ 4.27 (2H, q, *J* = 7.1 Hz), 4.25 (2H, q, *J* = 7.1 Hz), 3.63 (1H, dd, *J* = 2.5, 2.7 Hz), 3.43 (1H, quintet, *J* = 2.7 Hz), 2.16 (2H, narrow m), 2.04–1.66 (4H, m), 1.33 (3H, t, *J* = 7.1 Hz), 1.31 (3H, t, *J* = 7.1 Hz); ^{13}C NMR δ 208.8 (0), 165.6 (0), 164.2 (0), 143.1 (0), 134.2 (0), 61.4 (2C, 2), 49.4 (1), 38.8 (2), 34.7 (1), 23.9 (2), 22.6 (2), 13.9 (2C, 3); MS 266 (4, M$^+$), 221 (12), 192 (10), 179 (32), 178 (22), 151 (100), 150 (44), 149 (24), 123 (20), 105 (20), 79 (34), 77 (22); HRMS calcd for $C_{14}H_{18}O_5$ 266.1153, found 266.1157.

*Diene 2 with DAD: diethyl 8,8-dimethyl-5-(trimethylsilyloxy)bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**17a**).*

^{1}H NMR (partial data) δ 5.04 (1H, dd, *J* = 2.4, 6.6 Hz), 4.23 (2H, q, *J* = 6.9 Hz), 4.21 (2H, q, *J* = 7.2 Hz), 3.65 (1H apparent dt, *J* = 6.6, 2.7 Hz), 3.19 (1H, d, *J* = 2.4 Hz), 1.30 (3H, t, *J* = 6.9 Hz), 1.28 (3H, t, *J* = 7.2 Hz), 1.09 (3H, s), 0.98 (3H, s), 0.19 (9H, s). *Hydrolysis product: diethyl 7,7-dimethyl-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (**17b**).* Colorless oil; IR 1725 (s), 1635 (m) cm^{-1}; ^{1}H NMR δ 4.17 (2H, q, *J* = 7.1 Hz), 4.14 (2H, q, *J* = 7.1 Hz), 3.26 (1H, quintet, *J* = 2.8 Hz), 3.10 (1H, s), 2.07 (1H, dt, *J* = 18.6, 2.8 Hz), 1.96 (1H, dd, *J* = 2.3, 18.6 Hz), 1.56 (1H, dd, *J* = 2.7, 13.1 Hz), 1.47 (1H, dt, *J* = 13.1, 2.8 Hz), 1.23 (3H, t, *J* = 7.1 Hz), 1.20 (3H, t, *J* = 7.1 Hz), 1.02 (3H, s), 0.93 (3H, s); ^{13}C NMR δ 208.6 (0), 165.4 (0), 164.6 (0), 141.7 (0), 134.8 (0), 62.2 (1), 61.2 (2C, 2), 39.6 (2), 37.2 (2), 35.3 (0), 34.8 (1), 30.3 (3), 29.4 (3), 13.8 (2C, 3); MS 294 (36, M$^+$), 249 (27), 220 (51), 207 (58), 206 (54), 205 (23), 191 (27), 179 (94), 178 (100), 177 (23), 165 (40), 164 (27), 163 (52), 142 (32), 133 (50), 119 (33), 107 (55), 105 (34), 91 (51), 77 (32), 56 (37), 41 (97); HRMS calcd for $C_{16}H_{22}O_5$ 294.1466, found 294.1467.

*Diene 3 with DAD: diethyl 7,7-dimethyl-5-(trimethylsilyloxy)bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**18a**).*

^{1}H NMR (partial data) δ 5.17 (1H, dd, *J* = 2.4, 6.6 Hz), 4.22 (2H, d, *J* ≈ 7.5 Hz), 4.21 (2H, d, *J* ≈ 7.2 Hz), 3.53 (1H, apparent q, *J* ≈ 2.5 Hz), 3.27 (1H, d, *J* = 6.6 Hz), 1.291 (3H, t, *J* = 7.2 Hz), 1.288 (3H, t,

$J \approx 7.5$ Hz), 1.05 (3H, s), 1.00 (3H, s), 0.19 (9H, s). *Hydrolysis product: diethyl 8,8-dimethyl-2-oxobicyclo[2.2.2]oct-5-ene-5,6-dicarboxylate (**18b**).* Pale yellow oil; IR 1725 (s), 1635 (m) cm^{-1}; ^1H NMR δ 4.28 (2H, apparent q, J = 7.1, 1.7 Hz), 4.24 (2H, q, J = 7.2 Hz), 3.52 (1H, dd, J = 2.4, 3.4 Hz), 2.90 (1H, dd, J = 2.5, 3.0 Hz), 2.47 (1H, dd, J = 2.5, 19.0 Hz), 2.08 (1H, dd, J = 3.0, 19.0 Hz), 1.76 (1H, dd, J = 2.4, 13.5 Hz), 1.63 (1H, dd, J = 3.4, 13.5 Hz), 1.32 (3H, t, J = 7.1 Hz), 1.30 (3H, t, J = 7.2 Hz), 1.16 (3H, s), 1.07 (3H, s); ^{13}C NMR δ 208.5 (0), 165.7 (0), 164.0 (0), 144.9 (0), 132.3 (0), 61.0 (2), 60.9 (2), 50.5 (1), 46.6 (1), 38.3 (2), 34.9 (2), 33.8 (0), 31.0 (3), 27.8 (3), 13.6 (2C, 3); MS 294 (13, M^+), 251 (38), 249 (26), 207 (62), 206 (59), 205 (100), 191 (243), 179 (69), 178 (67), 177 (30), 163 (48), 133 (46), 119 (25), 107 (56), 105 (36), 91 (47), 77 (30), 41 (47); HRMS calcd for $C_{16}H_{22}O_5$ 294.1466, found 294.1458.

*Diethyl 4-hydroxyphthalate (**19**).*

Yellow oil; IR 3371 (broad), 1715 (s), 1604 (m) cm^{-1}; ^1H NMR δ 7.74 (1H, d, J = 8.6 Hz), 7.03 (1H, d, J = 2.5 Hz), 6.94 (1H, dd, J = 2.5, 8.6 Hz), 4.40–4.28 (4H, m), 1.37–1.31 (6H, m); ^{13}C NMR δ 169.3 (0), 167.0 (0), 159.7 (1), 135.7 (0), 131.7 (1), 121.0 (0), 117.0 (0), 115.1 (1), 62.0 (2), 61.4 (2), 13.9 (3), 13.8 (3); MS 238 (13, M^+), 193 (21), 166 (12), 165 (100), 137 (6), 121 (6), 120 (5), 81 (5), 63 (5); HRMS calcd for $C_{12}H_{14}O_5$ 238.0840, found 238.0846.

*Diene **1** with TCNE: 5,5,6,6-tetracyano-2-(trimethylsilyloxy)bicyclo[2.2.2]oct-2-ene (**20**).*

Pale pink solid, mp 122–124 °C (dec.); IR 2252 (w), 1642 (s) cm^{-1}; ^1H NMR δ 5.24 (1H, dd, J = 2.0, 7.3 Hz), 3.52 (1H, m), 3.24 (1H, m), 2.24–2.11 (2H, m), 1.87–1.61 (2H, m), 0.32 (9H, s); ^{13}C NMR δ 154.4, 112.1, 111.6, 111.2, 111.0, 99.8, 45.1, 44.2, 43.2, 41.0, 20.2, 19.0, –0.3; MS 296 (0.3, M^+), 281 (1), 168 (98), 153 (40), 75 (38), 73 (100), 45 (32).

*Diene **2** with TCNE: 5,5,6,6-tetracyano-7,7-dimethyl-2-(trimethylsilyloxy)bicyclo[2.2.2]oct-2-ene (**21a**).*

^1H NMR (partial) δ 5.04 (1H, dd, J = 1.9, 7.1 Hz), 3.47 (1H, ddd, J = 2.4, 3.6, 7.1 Hz), 1.27 (3H, s), 1.10 (3H, s), 0.30 (9H, s); MS 309 (2, M^+), 196 (9), 182 (17), 181 (100), 165 (11), 73 (31). *Hydrolysis product: 5,5,6,6-tetracyano-7,7-dimethylbicyclo[2.2.2]octan-2-one (**21b**).* Waxy solid; IR (Nujol) 2253 (w), 1747 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.18 (1H, m), 2.87 (1H, apparent dt, J = 20.4, 2.9 Hz), 2.84 (1H, s), 2.64 (1H, dd, J = 3.5, 20.4 Hz), 2.27 (1H, apparent dt, J = 15.4, 3.2 Hz), 1.82 (1H, dd, J = 3.1, 15.4 Hz), 1.54 (3H, s), 1.10 (3H, s); ^{13}C NMR (CD_2Cl_2) δ 199.8, 111.8, 111.3, 111.1, 110.9, 59.5, 41.3, 39.5, 38.7, 35.8, 33.3, 31.0, 29.3; MS 252 (3, M^+), 210 (4), 196 (10), 181 (100), 165 (46), 128 (28), 73 (30), 42 (58); HRMS calcd for $C_{14}H_{12}N_4O$ 252.1010, found 252.1007.

*Diene **3** with TCNE: 5,5,6,6-tetracyano-8,8-dimethyl-2-(trimethylsilyloxy)bicyclo[2.2.2]oct-2-ene (**22a**).*

^1H NMR (CD_2Cl_2) δ 5.36 (1H, dd, J = 2.0, 7.3 Hz), 3.21 (1H, m), 3.16 (1H, d, J = 7.3 Hz), 2.03 (1H, dd, J = 2.5, 14.7 Hz), 1.66 (1H, dd, J = 3.5, 14.7 Hz), 1.48 (3H, s), 1.06 (3H, s), 0.31 (9H, s); MS 309 (1, M^+), 196 (28), 181 (56), 165 (6), 75 (22), 73 (100), 56 (34), 45 (42). *Hydrolysis product: 5,5,6,6-tetracyano-8,8-dimethylbicyclo[2.2.2]octan-2-one (**22b**).* Data from crude mixture: ^1H NMR δ 3.07 (1H, dd, J =- 2.6, 3.7 Hz), 2.95 (1H, dd, J = 3.8, 21.0 Hz), 2.79 (1H, dd, J = 2.5, 21.0 Hz), 2.79 (1H, dd, J = 2.5, 3.8 Hz), 2.18 (1H, dd, J = 2.6, 15.8 Hz), 1.96 (1H, dd, J = 3.7, 15.8 Hz), 1.54 (3H, s), 1.15 (3H, s).

*4,4-Dimethyl-6 -(1,1,2,2-tetracyanoethyl)cyclohex-2-en-1-one (**23**).*

Colorless crystals, mp 136–140 °C (dec.); IR (Nujol) 1678 (s) cm^{-1}; ^1H NMR (CH_2Cl_2) δ 6.91 (1H, dd, J = 1.9, 10.0 Hz), 6.03 (1H, s), 5.98 (1H, d, J = 10.0 Hz), 3.33 (1H, dd, J = 4.6, 14.0 Hz), 2.34 (1H, ddd, J = 1.9, 4.6, 12.9 Hz), 2.21 (1H, dd, 12.9, 14.0 Hz), 1.33 (3H, s), 1.30 (3H, s); ^{13}C NMR (CH_2Cl_2) δ 194.0, 162.7, 125.5, 110.4, 109.7, 108.6, 108.0, 45.9, 42.1, 40.0, 35.0, 31.1, 30.0, 25.0; MS 252 (0.5, M^+), 226 (10), 225 (52), 210 (100), 198 (17), 183 (53), 182 (14), 155 (19), 128 (17), 96 (79), 81 (23), 67 (22), 53 (25), 41 (35); HRMS calcd for $C_{14}H_{12}N_4O$ 252.1010, found 252.0996; calcd for $C_{13}H_{11}N_3O$ (M^+–HCN) 225.0901, found 225.0897.

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