85. The *Diels-Alder* Chemoselectivity of 3,4,6,7-Tetramethylidenebicyclo[3.2.1]octane-2-*exo*,8-*syn*-diyl Derivatives

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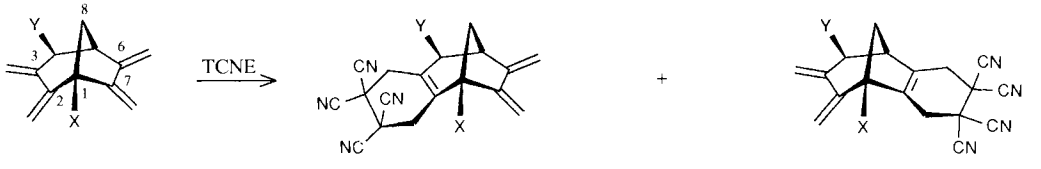
Strong dienophiles prefer to add onto the diene moiety attached at C(2),C(3) of 2,3,6,7-tetramethylidenebicyclo[3.2.1]octane ((±)-**1**; see *Scheme 1*), whereas in the case of 3,4,6,7-tetramethylidenebicyclo[3.2.1]octane-2-*exo*,8-*syn*-diyl derivatives, the diene moiety at C(6),C(7) reacts faster than that at C(3),C(4), as long the bulk of the 8-*syn*-substituent is large enough (see *Schemes 2* and *3*).

Introduction. – Kinetic measurements showed that ethylenetetracarbonitrile (= tetracyanoethylene; TCNE) adds to (±)-2,3,6,7-tetramethylidenebicyclo[3.2.1]octane *ca.* 300 times more rapidly onto the diene moiety at C(2),C(3) giving mono-adduct **2** than onto the diene moiety at C(6),C(7), giving mono-adduct **3** (*Scheme 1*) [1]. This chemoselectivity suggested that substituted derivatives of (±)-**1** could become interesting synthetic intermediates in a doubly convergent approach to the total synthesis of naphthocyclinones (see *e.g.* **10**) [2] and derivatives, an approach in which two different dienophiles

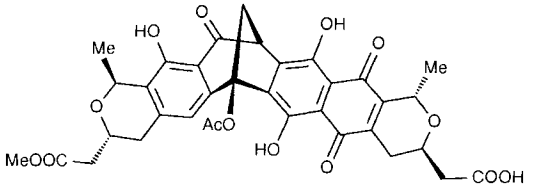
Scheme 1



(±)-**1** X = Y = H
(+)-**4** X = MeO, Y = OH[2])
(+)-**7** X = MeO, Y = (*t*-Bu)Me_2SiO[2])

2 X = Y = H (*ca.* 300:1)
5 X = MeO, Y = OH (*ca.* 1:1)
8 X = MeO, Y = (*t*-Bu)Me_2SiO (*ca.* 1:1)

3 X = Y = H
6 X = MeO, Y = OH
9 X = MeO, Y = (*t*-Bu)Me_2SiO



10 naphthocyclinone *β*

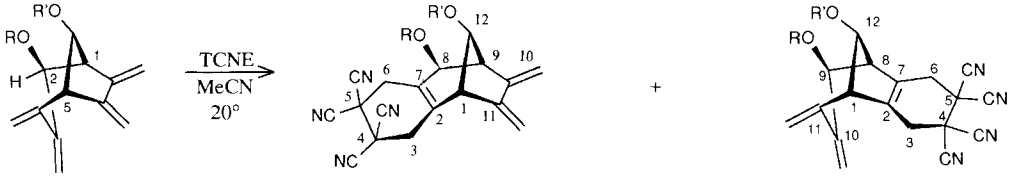
[1]) Present address: *Orgamol SA*, CH-1902 Evionnaz (VS).
[2]) Arbitrary numbering.

would be added sequentially to the exocyclic tetraenes, in analogy with a principle developed for our total syntheses of anthracyclinones [3]. With that goal in mind, we prepared the optically pure tetraenes (+)-**4** and (+)-**7** and found [4] that their chemoselectivity toward most dienophiles is inexistent, *i.e.*, both their diene moieties at the three-membered branch and at the two-membered branch of the main ring add with similar reactivities. With 1 equiv. of TCNE, *e.g.*, 1:1 mixtures of the corresponding mono-adducts **5**/**6** and **8**/**9**, respectively, were obtained (degassed benzene, 20°) together with the corresponding bis-adducts [4].

Recently, we presented an efficient synthesis of (±)-3,4,6,7-tetramethylidenebicyclo[3.2.1]octane-2-*exo*,8-*syn*-diol (**11**) [5]. We report here on the *Diels-Alder* reactivity of **11** and of its derivatives **12**–**15**. We shall show that their chemoselectivity toward strong dienophiles depends on the nature of the diol-protecting groups. Thus, judicious substitution at C(4) and C(8) in (±)-**1** allows one to change the preference of a strong dienophile for the diene moiety grafted at the three-membered branch of the main ring to that for the diene moiety attached at the two-membered branch.

Results. – The tetraenediol **11** [5] was selectively mono-acetylated to **12** (60%) on treatment with AcCl/pyridine (see *Scheme 2*). Treatment of **11** with NaH/DMF (−4°)

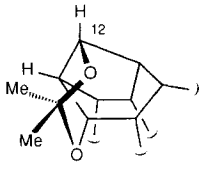
Scheme 2. *Chemoselectivity of the TCNE Cycloadditions*



1 R = R′ = H
2 R = Ac, R′ = H
3 R = R′ = Me
4 R, R′ = Me_2C
5 R = Ac, R′ = (*t*-Bu)Me_2Si

16 R = R′ = H (1:1.2)
18 R = Ac, R′ = H (1:1)
20 R = R′ = Me (3:2)
22 R, R′ = Me_2C (1:7[a])
24 R = Ac, R′ = (*t*-Bu)Me_2Si (1:5[b])

17 R = R′ = H
19 R = Ac, R′ = H
21 R = R′ = Me
23 R, R′ = Me_2C
25 R = Ac, R′ = (*t*-Bu)Me_2Si



i

[a]) In benzene, 1:3. [b]) In benzene, 1:20.

followed by reaction with MeI furnished the corresponding dimethyl ether **13** (66%). The corresponding acetonide **14** (40%, after recrystallization) was obtained on stirring **11** with 2,2-dimethoxypropane in anhydrous DMF in the presence of a catalytical amount of TsOH. Treatment of mono-acetate **12** with (*t*-Bu)Me_2SiOTf, and 2,6-dimethylpyridine in CH_2Cl_2 (20°) led to the corresponding silyl ether **15** (61%). Except for acetonide **14** which could be isolated as a crystalline product, the other compounds **11**–**13** and **15** were readily polymerizable and had to be stored as dilute solutions at low temperature.

The structures of tetraenes **11**–**15** were confirmed by their spectral data. The signal attributions in the ^{1}H-NMR spectra were based on double-irradiation experiments, including nuclear *Overhauser* effect (NOE) measurements. Furthermore, typical *W*-type ^4J(H,H) coupling constants of 1.0–1.8 Hz were observed between H–C(2) and H–C(8); vicinal coupling constants ^3J of 4.5–5.0 Hz were measured between H–C(8) and the bridgehead protons H–C(1) and H–C(5). The signals of the CH_2=C(3) groups were recognized by their NOE with H–C(2).

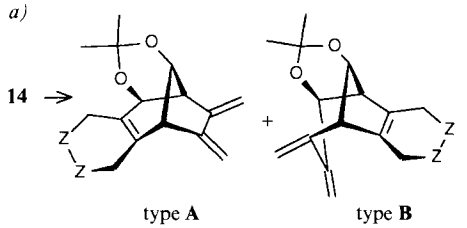
In the presence of 1 equiv. of TCNE in MeCN (20°), the tetraenediol **11** gave a 1:1.2 mixture of the corresponding mono-adducts **16**/**17** which could be separated and isolated by flash chromatography (silica gel) in 20 and 29% yield, respectively (*Scheme 2*). With the mono-acetate **12**, a 1:1 mixture of adducts **18**/**19** was formed. The latter were rapidly polymerized and could not be separated and isolated by chromatography. The dimethyl ether **13** added to 1 equiv. of TCNE giving a 3:2 mixture of the corresponding mono-adducts **20**/**21** which could be separated and isolated by flash chromatography in 30 and 12% yield, respectively.

In the case of acetonide **14**, the addition of 1 equiv. of TCNE in MeCN occurred with the opposite chemoselectivity than in the case of **13**. In MeCN, a 1:7 mixture of the mono-adducts **22**/**23** was formed. Column chromatography allowed one to isolate **22** and **23** in 13 and 82% yield, respectively. In benzene, however, the chemoselectivity was lowered to 1:3, but still in favour of a cycloaddition involving the diene moiety grafted onto C(6),C(7). Interesting was also the observation that silyl ether **15** added to TCNE with the same type of chemoselectivity than acetonide **14**, giving a 1:20 mixture of the corresponding adducts **24**/**25** when the reaction was run in benzene. In MeCN, and unexpectedly, the chemoselectivity dropped to 1:5 (1 equiv. of TCNE, MeCN, 20°); mono-adducts **24** and **25** were isolated by column chromatography (silica gel) in 16 and 72% yield, respectively.

In order to test whether the relatively good chemoselectivity observed for the *Diels-Alder* addition of tetraenes **14** and **15** to TCNE would be preserved in the case of the

Scheme 3. *Chemoselectivity of the* Diels-Alder *Additions of* **14** *and* **15** *to Various Dienophiles* Z=Z (1 equiv.) *in MeCN* (20°)

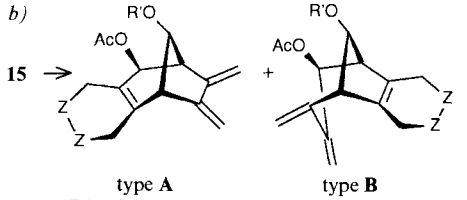
a)



type **A** type **B**

Z=Z	[A]/[B][a])
maleic anhydride	1:10[b])
MeOOCC=CCOOMe	1:1.5
1,4-benzoquinone	1:3[b])
phenyltriazoledione	1:2.5

b)



type **A** type **B**
R′ = (*t*-Bu)Me$_2$Si R′ = (*t*-Bu)Me$_2$Si

Z=Z	[A]/[B][a])
maleic anhydride	1:6[b])
MeOOCC=CCOOMe	1:3
1,4-benzoquinone	1:5[b])
phenyltriazoledione	1:8
1,2-didehydrobenzene	1:4

[a]) As determined by ^{1}H-NMR of the crude reaction mixtures. [b]) Mixture of *Alder*- and *anti-Alder*-stereoisomers.

cycloadditions to other dienophiles, we allowed tetraenes **14** (*Scheme 3a*) and **15** (*Scheme 3b*) to react with 1 equiv. of dienophiles such as maleic anhydride, dimethyl acetylenedicarboxylate, 1,4-benzoquinone, 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (and, in the case of **15**, also with didehydrobenzene generated by thermal decomposition of 2-diazoniobenzoate [6]). For all these cycloadditions, the diene moiety at C(6),C(7) of the tetraene was preferred (giving adducts of type **B**) to the diene moiety at C(3),C(4) (giving adducts of type **A**), as for the reactions with TCNE, the lowest chemoselectivity being observed with dimethyl acetylenedicarboxylate.

The structures of the pure mono-adducts **16**, **17**, and **20**–**25** were given by their elemental analyses and their spectral data. The UV absorption spectra of the mono-adducts **16**, **20**, **22**, and **24** showed typical absorption (λ_{max} *ca.* 236 nm, ε = 5000–7000) for the s-*cis*-butadiene moiety at C(10),C(11) adopting a nearly planar conformation (1,2-dimethylidenecyclopentane system) [7c]. This band was not visible in the UV absorption spectra of the isomeric adducts **17**, **21**, **23**, and **25** as their diene moiety at C(10),C(11) adopt a non-planar conformation (1,2-dimethylidenecyclohexane system). In the cases of **18**, **19**, and mono-adducts of type **A** and **B** (*Scheme 3*), the structures were deduced form the ^{1}H-NMR spectra of the crude reaction mixture and by comparison with those of the pure adducts **16**, **17**, and **20**–**25**. Double-irradiation experiments including NOE measurements allowed one to assign all signals in their ^{1}H-NMR spectra. In the case of mono-adducts of type **A**, NOE's were measured between the bridgehead proton H–C(9) and the proton H–C(8), and with one of the protons of CH_2=C(10); furthermore, NOE's between H–C(8) and CH_2(6) were observed. In the case of mono-adducts of type **B**, NOE's between H–C(9) and CH_2=C(10) and between H–C(12) and CH_2C(3), CH_2(6) were detected. The ^{1}H-NMR signals of CH_2=C(3) and CH_2=C(4) of the tetraenes **11**–**15** and those of CH_2=C(10) and CH_2=C(11) of the mono-adducts of type **B** (*e.g.* **17**, **19**, **21**, **23**, and **25**), showed geminal coupling constant ^2J = 1–1.5 Hz. The geminal coupling constants of the protons CH_2=C(6) and CH_2=C(7) of **11**–**15** and of CH_2=C(10) and CH_2=C(11) of the corresponding mono-adducts of type **A** (*e.g.* **16**, **18**, **20**, **22**, and **24**) were < 1 Hz. With adducts **22** and **23**, NOE's between one of the Me groups of the acetonide moiety and the bridgehead H–C(9) in **22** and H–C(8) in **23** were measured. This suggested that the six-membered ring of the acetonide group in these systems can adopt a boat conformation (see **i** in *Scheme 2*); this latter conformation may or may not be in equilibrium with a chair conformation.

Discussion. – Substitution of the bicyclic skeleton of the parent tetraene (±)-**1** with oxy substituents is expected to induce a retarding effect on its *Diels-Alder* additions due to an electronic factor (inductive effect [7]) and possibly to a steric factor (steric hindrance). Substitution at C(4) is expected to retard the cycloadditions of the diene moiety attached at C(2),C(3) more than that at C(6),C(7), in agreement with the observed decrease of chemoselectivity between the TCNE additions to (±)-**1** and those to (+)-**4** and (+)-**7** [4] on one hand (*Scheme 1*) and between (±)-**1** and **11**–**13** on the other hand (*Scheme 2*). The fact that similar chemoselectivities were observed for the cycloadditions of (+)-**4** and (+)-**7** can be explained either in terms of an *endo*-face selectivity for the dienophile addition onto the diene moiety at C(2),C(3)[2]) which makes the reaction insensitive to the change in bulk between the 4-*exo*-hydroxy (in (+)-**4**) and 4-*exo*-(*tert*-butyl)dimethylsilyloxy groups (in (+)-**7**) or in terms of a (*t*-Bu)Me_2SiO group that can turn away from the path of the dienophile attack onto the *exo*-face of the diene moiety attached at C(2), C(3)[2]). The latter hypothesis cannot be ruled out by *Dreiding* models. The removal of the 1-methoxy group in (+)-**4** and (+)-**7** and introduction of a hydroxy, alkoxy, or silyloxy groups at the *syn*-position of C(8) (see **11**–**15**) should not affect differentially the electronic properties of the two diene moieties, to a first approximation. Thus, one expects that the bulk of the 8-*syn*-substituents in **11**–**15** should retard the dienophile attack onto the *exo*-face of the diene unit at C(3), C(4) (systematic numbering; see *Scheme 2*) and thus favour the *Diels-Alder* reaction of the diene moiety at C(6),C(7), leading to mono-adducts of type **B**, in agreement with our results (*Schemes 2* and *3*). Indeed, the larger the

8-*syn*-substituent is the better is the chemoselectivity in favour of mono-adducts of type **B**, *i.e.* the reverse chemoselectivity than that observed in the *Diels-Alder* additions of the parent tetraene (±)-**1**. If the latter interpretation should be correct, it implies that addition to the *endo*-face of the diene moiety at C(3),C(4) is 'intrinsically' retarded, a hypothesis that could be tested by stereoselective mono-deuteration of one of two methylidene groups at C(3) or/and C(4) and analysis of the diastereoselectivity on formation of deuterated *Diels-Alder* mono-adducts [8]. The smaller chemoselectivities of the cycloaddition of the 'linear' dienophile dimethyl acetylenedicarboxylate compared with those observed with the bulkier dienophiles toward **14** (*Schemes 2* and *3a*) and **15** (*Schemes 2* and *3b*) can be interpreted in terms of competitive *endo- vs. exo*-mode of cycloadditions, the latter being less retarded for small dienophiles than for bulkier ones.

The solvent effect on the *Diels-Alder* chemoselectivity of **14** and **15** (*Scheme 2*) is noteworthy but cannot be explained at this moment.

Conclusion. – While the *Diels-Alder* additions of 2,3,6,7-tetramethylidenebicyclo-[3.2.1]octane ((±)-**1**) prefer the diene moiety attached at the three-membered branch of the main ring rather than that at the two-membered branch, *exo*-substitution at C(2) and *syn*-substitution at C(8) (numbering according to *Scheme 2*) can reverse this chemoselectivity as long as the bulk of the 8-*syn*-substituent is large enough. This property should make the 3,4,6,7-tetramethylidenebicyclo[3.2.1]octane-2-*exo*,8-*syn*-diyl derivatives useful synthetic intermediates in a doubly convergent approach to the synthesis of annulated polycyclic systems that are analogues of the naphthocyclinones.

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Experimental Part

General. See [9]. FC = flash chromatography.

*(1*RS,*2*SR,*5*RS,*8*SR*)-8-Hydroxy-3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-yl Acetate* (**12**). A mixture of **11** (132 mg, 0.69 mmol), anh. pyridine (3 ml), and AcCl (1 equiv.) was stirred at 20° for 0.5 h (TLC control; SiO_2, Et_2O/light petroleum ether 1:1). H_2O (30 ml) and Et_2O (30 ml) were added. The aq. phase was extracted with Et_2O (30 ml, 3 times), the combined org. extract washed successively with aq. 1N HCl (30 ml, twice) and sat. aq. $NaHCO_3$ soln. (30 ml), dried ($MgSO_4$), and concentrated *in vacuo* to *ca.* 10 ml. The soln. of **12** was stored at −20° or used directly in the next reactions. Evaporation of an aliquot to dryness allowed one to evaluate the yield to *ca.* 60% (polymeric material). Spectral data: see [5].

*(1*RS,*2*SR,*5*RS,*8*SR*)-2,8-Dimethoxy-3,4,6,7-tetramethylidenebicyclo[3.2.1]octane* (**13**). A suspension of 80% NaH in oil (505 mg, 10 equiv.) was washed 3 times with anh. pentane (25 ml) and then suspended in anh. DMF (25 ml). After cooling to −4°, **11** [5] (400 mg, 2.1 mmol) in anh. DMF (8 ml) was added dropwise under N_2 and stirring. After 10 min at −4°, MeI (1.3 ml, 10 equiv.) was added (TLC control (silica gel, CH_2Cl_2/Et_2O 3:1)) and after *ca.* 1 h stirring, the mixture was poured onto a vigourously stirred mixture of brine (50 ml) and pentane (50 ml). The aq. phase was extracted with pentane (50 ml, 3 times) and the combined org. phase washed with H_2O (50 ml), dried ($MgSO_4$), and concentrated to *ca.* 10 ml *in vacuo*. This soln. of **13** was stored at −20° or used directly in the next reactions. Evaporation of an aliquot to dryness allowed one to evaluate the yield to *ca.* 66% (polymeric material). UV (MeCN): 242 (sh, *ca.* 10000), 262 (sh, *ca.* 4900). UV (isooctane): 240 (*ca.* 9700), 261 (sh, *ca.* 4300). IR ($CHCl_3$): 3080, 3000, 2950, 2925, 2870, 2825, 1800, 1730, 1635, 1465, 1450, 1420, 1375, 1340, 1315, 1270, 1120, 1095, 1080, 1030, 1010, 980, 935, 925, 895, 860, 840. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.43 (*d*, ^2J = 1.8, 1 H), 5.41 (br. *s*, 1 H), 5.33 (br. *s*, 1 H), 5.13 (*d*, ^2J = 1.4, 1 H), 5.0 (br. *s*, 1 H), 4.93 (br. *s*, 2 H), 4.81 (*d*, ^2J = 1.4, 1 H, 8 olef. H); 3.69 (*ddd*, ^3J = 4.8, 4.7, ^4J = 1.0, H_{anti}–C(8)); 3.60 (br. *d*, ^3J = 3.0, H_{endo}–C(2)); 3.40 (*m*, H–C(5)); 3.37, 3.30 (2*s*, 2 MeO); 3.20 (*m*, H–C(1)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 145.9 (*s*, 2 C), 144.2 (*s*), 141.1 (*s*, C(3), C(4), C(6), C(7));

118.1 (*td*, ^1J(C,H) = 160, ^3J(C,H) = 3, CH_2=C(3)); 109.3 (*td*, ^1J(C,H) = 158, ^3J(C,H) = 4), 107.0 (*t*, ^1J(C,H) = 158), 105.8 (*t*, ^1J(C,H) = 159, CH_2=C(4), CH_2=C(6), CH_2=C(7)); 85.6, 81.3 (2*d*, ^1J(C,H) = 146, C(2), C(8)); 57.1, 56.6 (2*q*, ^1J(C,H) = 140, 2 MeO); 53.7 (*d*, ^1J(C,H) = 140), 47.5 (*d*, ^1J(C,H) = 145, C(1), C(5)). MS (70 eV): 218 (13, $M^{+\cdot}$), 217 (2, $[M-1]^+$), 203 (13), 187 (12), 186 (22), 173 (12), 171 (57), 157 (10), 155 (28), 154 (23), 153 (17), 143 (31), 142 (19), 141 (39), 131 (10), 129 (53), 128 (100), 127 (16), 117 (18), 116 (16), 115 (61), 105 (13), 91 (46), 77 (22), 75 (64), 65 (15), 53 (11), 51 (14).

*(1*RS,*2*SR,*5*RS,*8*SR*)-2,8-(Isopropylidenedioxy)-3,4,6,7-tetramethylidenebicyclo[3.2.1]octane* (**14**). A mixture of **11** (300 mg, 1.58 mmol), anh. DMF (7.5 ml), 2,2-dimethoxypropane (0.6 ml, 3 equiv.), and 0.6% soln. of TsOH in DMF (5 ml) was stirred at 20° under Ar for 12 h. The mixture was then poured onto a vigourously stirred mixture of brine (100 ml) and pentane (50 ml). The aq. phase was extracted with pentane (50 ml, twice), the combined org. phase washed with H_2O (50 ml, twice), dried ($MgSO_4$), and evaporated, and the residue purified by FC (silica gel, light petroleum/CH_2Cl_2/Et_2O 10:9:1, R_f 0.6): 148 mg (40%). Colourless crystals. M.p. 103–106°. UV (MeCN): 235 (9600). UV (isooctane): 235 (9900). IR (KBr): 3095, 3005, 2975, 2950, 2920, 1830, 1800, 1640, 1620, 1460, 1435, 1385, 1375, 1355, 1340, 1295, 1280, 1250, 1225, 1210, 1200, 1185, 1165, 1110, 1090, 1025, 990, 965, 930, 915, 895, 865, 840, 820, 780, 740, 665. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.47 (br. *s*, 1 H), 5.40 (*d*, ^2J = 1.4, 1 H), 5.37 (*s*, 1 H), 5.20 (*d*, ^2J = 1.2, 1 H), 5.05 (*s*, 1 H), 5.03 (*d*, ^2J = 1.4, 1 H), 5.02 (*s*, 1 H), 4.84 (*d*, ^2J = 1.2, 1 H, 8 olef. H); 4.45 (*ddd*, ^3J = 5.5, 5.4, ^4J = 1.8, H_{anti}–C(8)); 4.36 (*dd*, ^3J = 5.0, ^4J = 1.8, H_{endo}–C(2)); 3.50, 3.48 (2*m*, H–C(1), H–C(5)); 1.54, 1.33 (2*s*, Me_2C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 146.7 (*s*), 145.7 (*s*), 144.3 (*s*, 2 C, C(3), C(4), C(6), C(7)); 116.5, 109.4 (2*td*, ^1J(C,H) = 158, ^3J(C,H) = 4), 108.0, 106.5 (2*t*, ^1J(C,H) = 158, CH_2=C(3), CH_2=C(4), CH_2=C(6), CH_2=C(7)); 97.7 (*s*, $(Me)_2C$); 77.6 (*d*, ^1J(C,H) = 150), 71.3 (*d*, ^1J(C,H) = 156, C(2), C(8)); 57.4 (*d*, ^1J(C,H) = 142), 43.5 (*d*, ^1J(C,H) = 141, C(1), C(5)); 31.1 (*q*, ^1J(C,H) = 127), 29.4 (*q*, ^1J(C,H) = 125, $(Me)_2$C). MS (70 eV): 231 (2, $[M+1]^+$), 230 (10, $M^{+\cdot}$), 215 (15), 172 (49), 171 (13), 157 (22), 155 (10), 144 (22), 143 (33), 141 (35), 129 (100), 128 (99), 127 (27), 116 (11), 115 (43), 103 (10), 91 (43), 77 (10), 65 (15). Anal. calc. for $C_{15}H_{18}O_2$ (230.3): C 78.23, H 7.88; found: C 78.26, H 7.79.

*(1*RS,*2*RS,*5*SR,*8*RS*)-8-[(*tert*-Butyl)dimethylsilyloxy]-3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-yl Acetate* (**15**). A mixture of **12** (50 mg, 0.21 mmol), CH_2Cl_2 (2 ml), 2,6-dimethylpyridine (64 µl, 3 equiv.), and (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate (73 µl, 1.5 equiv.) was stirred at 20° for 16 h (TLC control (silica gel, CH_2Cl_2/Et_2O 9:1): R_f (**15**) 0.85). The mixture was poured onto a vigourously stirred mixture of brine (10 ml) and CH_2Cl_2 (3 ml), the aq. phase extracted with CH_2Cl_2 (5 ml, twice), and the combined org. phase concentrated *in vacuo* to *ca.* 3 ml and purified by FC (silica gel, CH_2Cl_2/Et_2O 10:1, R_f 0.4): 53.6 mg (61%) of a colourless oil that polymerized quickly. A dil. soln. of **15** in CH_2Cl_2 was stored at –20° or used directly in the following steps. UV (MeCN): 251 (8400), 267 (sh, 3200). UV (isooctane): 249 (10600), 262 (sh, 6000). IR ($CHCl_3$): 3085, 2955, 2930, 2860, 1800, 1720, 1640, 1470, 1425, 1405, 1370, 1250, 1135, 1075, 1050, 1020, 985, 965, 900, 865, 840. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.55 (*d*, ^2J = 1, 1 H), 5.49 (*s*, 1 H), 5.38 (*s*, 1 H), 5.20 (*d*, ^2J = 1, 1 H), 5.15 (*m*, 2 H), 4.97 (*s*, 1 H), 4.78 (*d*, ^2J = 1, 1 H, 8 olef. H); 5.35 (*d*, ^3J = 3, H_{endo}–C(2)); 4.17 (*ddd*, ^3J = 5.0, 4.9, ^4J = 1, H_{anti}–C(8)); 3.20 (br. *d*, ^3J = 5, H–C(5)); 2.98 (*m*, H–C(1)); 2.05 (*s*, AcO); 0.90 (*s*, *t*-Bu); 0.08, 0.06 (2*s*, Me_2Si). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 170.7 (*s*); 146.2, 145.6, 143.9, 141.4 (4*s*, C(3), C(4), C(6), C(7)); 118.9 (*td*, ^1J(C,H) = 158, ^3J(C,H) = 3), 109.5 (*td*, ^1J(C,H) = 158, ^3J(C,H) = 5), 107.9, 105.9 (2*t*, ^1J(C,H) = 158, CH_2=C(3), CH_2=C(4), CH_2=C(6), CH_2=C(7)); 76.1 (*d*, ^1J(C,H) = 159), 72.6 (*d*, ^1J(C,H) = 147, C(2), C(8)); 56.4 (*d*, ^1J(C,H) = 142), 49.8 (*d*, ^1J(C,H) = 143, C(1), C(5)); 25.6 (*q*, ^1J(C,H) = 129, Ac); 17.9 (*s*, $(Me)_3C$Si); –4.9, –5.0 (2*q*, ^1J(C,H) = 118, $(Me)_2$Si). CI-MS (NH_3): 347 (0.8, $[M+1]^+$), 290 (2), 289 (9), 287 (4), 229 (2), 156 (3), 155 (11), 153 (1), 147 (2), 143 (1), 141 (2), 129 (2), 128 (4), 127 (1), 119 (3), 118 (9), 117 (100), 75 (20), 73 (12).

Cycloaddition of TCNE to **11**. A mixture of **11** (180 mg, 0.946 mmol) and TCNE (122 mg, 0.946 mmol) in anh. MeCN (10 ml) was stirred at 20° for 1 h (TLC control (silica gel, CH_2Cl_2/Et_2O 3:1)). Then, TCNE (28 mg) was added and the mixture stirred for 15 min (complete disappearance of **11**). ^{1}H-NMR of the crude mixture: **16**/**17** 1:1.2. Column chromatography (*Lobar B*, *Lichroprep Si 60*, 40–63 µm, CH_2Cl_2/Et_2O 3:1) gave first 59 mg (20%) of **16** and then 87 mg (29%) of **17**.

*Data of (1*RS,*8*SR,*9*RS,*12*SR*)-8-*exo,*12-*syn*-Dihydroxy-10,11-dimethylidenetricyclo[7.2.1.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**16**): White solid. M.p. 190° (dec.). UV (MeCN): 204 (8000), 236 (6000). IR (KBr): 3350, 2950, 2330, 2250, 1710, 1650, 1625, 1430, 1375, 1315, 1265, 1240, 1220, 1180, 1130, 1070, 1030, 1015, 990, 955, 935, 905, 895, 860, 830. ^{1}H-NMR (250 MHz, CD_3CN): 5.55 (*d*, ^2J = 0.7, 1 H), 5.28 (br. *s*, 1 H), 5.23 (br. *s*, 1 H), 4.98 (br. *s*, 1 H, CH_2=C(10), CH_2=C(11)); 4.28 (br. *dd*, ^3J = 5, 4.9, H_{anti}–C(12)); 4.02 (*m*, H_{endo}–C(8), OH); 3.67 (*m*, 1 H, OH); 3.57 (*m*, 1 H), 3.32–3.13 (*m*, 2 H), 3.00 (*m*, 1 H, CH_2(3), CH_2(6)); 3.07 (*m*, H–C(9)); 2.91 (*d*, ^3J = 5, H–C(1)). ^{13}C-NMR (50.3 MHz, CD_3CN): 146.8, 145.5 (2*s*, C(10), C(11)); 127.6, 125.3 (2*s*, C(2), C(7)); 112.6, 111.8, 111.7 (3*s*, 4 CN); 110.0 (*t*, ^1J(C,H) = 159), 104.2 (*t*, ^1J(C,H) = 160, CH_2=C(10), CH_2=C(11)); 73.7 (*d*, ^1J(C,H) = 149), 71.9 (*d*, ^1J(C,H) = 152, C(8), C(12)); 52.5 (*d*, ^1J(C,H) = 141), 50.7 (*d*, ^1J(C,H) = 150, C(1), C(9));

39.6 (*s*, C(4), C(5)); 35.2, 33.3 (2*t*, ^1J(C,H) = 140, C(3), C(6)). CI-MS (NH_3): 336 (0.8, $[M + 18]^+$), 318 (2, $M^{+\cdot}$), 317 (11), 300 (10), 273 (24), 272 (100), 271 (33), 205 (13), 193 (11), 190 (11), 178 (15), 171 (11), 154 (11), 152 (10), 144 (57), 141 (18), 130 (12), 128 (31), 126 (19), 115 (24). Anal. calc. for $C_{18}H_{14}N_4O_2$ (318.3): C 67.92, H 4.43; found: C 64.03, H 5.12.

*Data of (1*RS,*8*RS,*9*SR,*12*SR*)-9-*exo,*12*-anti-*Dihydroxy-10,11-dimethylidenetricyclo[6.3.1.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**17**): White solid. M.p. 85° (dec.). UV (MeCN): 204 (7450). IR (KBr): 3400, 3090, 2940, 2260, 1710, 1635, 1425, 1335, 1290, 1245, 1230, 1185, 1150, 1080, 1010, 950, 915, 860, 835, 800, 765, 730. ^{1}H-NMR (250 MHz, CD_3CN): 5.47 (*d*, ^2J = 1.3, 1 H), 5.39 (*d*, ^2J = 1.5, 1 H), 5.07 (*d*, ^2J = 1.3, 1 H), 4.93 (*d*, ^2J = 1.5, 1 H, CH_2=C(10), CH_2=C(11)); 4.33 (br. *s*, ^3J = 5.0, 4.9, H_{syn}–C(12)); 4.26 (br. *d*, ^3J = 2.5, H_{endo}–C(9)); 3.36–3.03 (*m*, 5 H, H–C(1), CH_2(3), CH_2(6)); 2.77 (*m*, H–C(8)). ^{13}C-NMR (50.3 MHz, CD_3CN): 146.9, 142.5 (2*s*, C(10), C(11)); 135.2, 131.4, (2*s*, C(2), C(7)); 119.3, 113.0 (2*t*, ^1J(C,H) = 158, CH_2=C(10), CH_2=C(11)); 112.3, 112.2, 112.1, 112.0 (4*s*, 4 CN); 77.2 (*d*, ^1J(C,H) = 153), 71.8 (*d*, ^1J(C,H) = 148, C(9), C(12)); 55.1 (*d*, ^1J(C,H) = 142), 48.8 (*d*, ^1J(C,H) = 144, C(1), C(8)); 39.6, 39.5 (2*s*, C(4), C(5)); 32.2, 32.1 (2*t*, ^1J(C,H) = 140, C(3), C(6). CI-MS (NH_3): 318 (0.4, $M^{+\cdot}$), 301 (3), 300 (8), 285 (2), 274 (2), 273 (8), 272 (8), 271 (3), 245 (4), 219 (3), 205 (4), 182 (8), 172 (5), 170 (8), 168 (31), 166 (61), 164 (53), 154 (10), 131 (18), 129 (32), 110 (11), 106 (62), 105 (32), 98 (13), 97 (18), 96 (26), 94 (19), 92 (28), 91 (100). Anal. calc. for $C_{18}H_{14}N_4O_2$ (318.3): C 67.92, H 4.43; found: C 65.37, H 5.21.

Cycloaddition of TCNE to **12**. A soln. of **12** (20 ml, containing *ca.* 230 mg of **12**, *ca.* 1 mmol) was concentrated *in vacuo* to *ca.* 2 ml, and MeCN (20 ml) was added. The mixture was concentrated to 2 ml, and MeCN was added to 10 ml. TCNE (100 mg) was added portionwise (TLC control (silica gel, light petroleum ether/Et_2O/CH_2Cl_2 10:1:9)). After the complete disappearance of **12** (*ca.* 2 h), the mixture was analyzed by ^{1}H-NMR (**18**/**19** 1:1). ^{1}H-NMR (250 MHz, CD_3CN): 5.62, 5.58, 5.35, 5.30, 5.23, 5.19, 5.00, 4.94, 4.90 (10 H); 4.25, 4.12 (H–C(12)); 3.60–2.70 (bridgehead H's, CH_2's); 2.06, 2.00 (AcO).

Cycloaddition of TCNE to **13**. Same procedure as above, starting with 20 ml of a CH_2Cl_2 soln. of **13** containing *ca.* 218 mg (1 mmol). After the addition of 148 mg of TCNE and complete disappearance of **13** (TLC (light petroleum ether/CH_2Cl_2/Et_2O 10:10:2)), the ^{1}H-NMR showed a 3:2 mixture **20**/**21**. Separation by column chromatography (*Lobar B, Lichroprep Si 60*, 40–63 μm, light petroleum ether/CH_2Cl_2/Et_2O 5:5:1) gave first 103 mg (30%) of **20** and then 41 mg (12%) of **21**.

*Data of (1*RS,*8*SR,*9*RS,*12*SR*)-8-*exo,*12*-syn-*Dimethoxy-10,11-dimethylidenetricyclo[7.2.1.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**20**): White solid. M.p. 180° (dec.). UV (MeCN): 211 (9400), 227 (8700), 240 (8300), 246 (8000). UV (isooctane): 209 (9200), 228 (8000), 237 (8200), 243 (8000), 257 (3900). IR (KBr): 3460, 3090, 2990, 2960, 2930, 2890, 2830, 1630, 1460, 1435, 1370, 1350, 1310, 1310, 1245, 1225, 1190, 1120, 1095, 1075, 1010, 970, 950, 905, 830, 805. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.55 (*s*, 1 H, CH_2=C(10), *cis* to C(11)); 5.28 (*s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.18 (*s*, 1 H, CH_2=C(10), *trans* to C(11)); 4.93 (*s*, 1 H, CH_2=C(11), *trans* to C(10)); 3.80 (*dd*, ^3J = 5.5, 4.0, 1 H, H_{anti}–C(12)); 3.52 (*s*, MeO–C(12)); 3.51 (*m*, 1 H, CH_2(3) or CH_2(6)); 3.30 (*s*, MeO–C(8)); 3.28–2.60 (*m*, 6 H, H–C(1), H_{endo}–C(8), H–C(9), 3 H of CH_2(3) and CH_2(6)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 144.4, 144.1 (2*s*, C(10), C(11)); 126.4, 123.7 (2*s*, C(2), C(7)); 110.7, 110.6, 110.1, 110.0 (4*s*, 4 CN); 109.7, 104.2 (2*t*, ^1J(C,H) = 159, CH_2=C(10), CH_2=C(11)); 82.4, 78.0 (2*d*, ^1J(C,H) = 140, C(8), C(12)); 58.4 (*q*, ^1J(C,H) = 145), 57.1 (*q*, ^1J(C,H) = 142, 2 MeO); 49.4 (*d*, ^1J(C,H) = 141), 44.2 (*d*, ^1J(C,H) = 142, C(1), C(9)); 37.9 (*s*, C(4), C(5)); 35.2, 32.8 (2*t*, ^1J(C,H) = 138, C(3), C(6)). CI-MS (NH_3): 364 (17, $[M + 18]^+$), 347 (2, $[M + 1]^+$), 346 (1.4, $M^{+\cdot}$), 332 (4), 315 (10), 314 (15), 288 (6), 236 (6), 186 (30), 168 (13), 166 (29), 164 (24), 129 (12), 128 (11), 120 (13), 115 (11), 106 (42), 101 (20), 97 (14), 91 (61), 85 (20), 84 (16), 83 (19), 75 (100). Anal. calc. for $C_{20}H_{18}N_4O_2$ (346.4): C 69.35, H 5.24; found: C 68.03, H 5.34.

*Data of (1*RS,*8*RS,*9*SR,*12*SR*)-9-*exo,*12*-anti-*Dimethoxy-10,11-dimethylidenetricyclo[6.3.1.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**21**): White solid. M.p. 180° (dec.). UV (MeCN): 217 (8000). UV (isooctane): 208 (6800). IR (KBr): 3450, 3090, 2990, 2940, 2900, 2860, 2830, 1715, 1635, 1600, 1460, 1440, 1370, 1350, 1335, 1285, 1255, 1230, 1210, 1185, 1155, 1110, 1090, 1075, 1015, 1005, 975, 905, 865, 835, 795, 730, 650, 615. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.64 (br. *s*, 1 H, CH_2=C(10), *cis* to C(11)); 5.41 (br. *s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.11 (br. *s*, 1 H, CH_2=C(10), *trans* to C(11)); 4.94 (br. *s*, 1 H, CH_2=C(11), *trans* to C(10)); 3.93 (*ddd*, ^3J = 5.0, 4.9, ^4J = 1.0, H_{syn}–C(12)); 3.68 (br. *d*, ^3J = 2.0, H_{endo}–C(9)); 3.41 (*s*, MeO–C(12)); 3.36 (*s*, MeO–C(9)); 3.33–3.01 (*m*, 6 H, H–C(1), H–C(8), CH_2(3), CH_2(6)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 140.3 (*s*, C(10), C(11)); 134.5, 130.1 (2*s*, C(2), C(7)); 121.3 (*t*, ^1J(C,H) = 155), 112.5 (*t*, ^1J = (C,H) = 157, CH_2=C(10), CH_2=C(11)); 110.3 (*s*, 4 CN); 83.4 (*d*, ^1J(C,H) = 145), 78.8 (*d*, ^1J(C,H) = 144, C(9), C(12)); 57.6 (*q*, ^1J(C,H) = 142), 57.2 (*q*, ^1J(C,H) = 141, 2 MeO); 51.9 (*d*, ^1J(C,H) = 144), 46.2 (*d*, ^1J(C,H) = 147, C(1), C(8)); 37.9 (*s*, C(4), C(5)); 32.5, 32.2 (2*t*, ^1J(C,H) = 138, C(3), C(6)). MS (70 eV): 347 (9, $[M + 1]^+$), 346 (67, $M^{+\cdot}$), 313 (18), 299 (45), 222 (11), 196 (11), 187 (21), 186 (38), 185 (28), 180 (25), 178 (39), 177 (19), 176 (12), 173 (11), 172 (17), 171 (65), 159 (20), 158 (26), 157 (12), 156 (20), 155 (38),

154 (16), 153 (35), 149 (11), 145 (22), 144 (36), 143 (38), 141 (55), 140 (14), 134 (46), 130 (29), 129 (22), 128 (71), 127 (70), 119 (33), 115 (99), 75 (100). Anal. calc. for $C_{20}H_{18}N_4O_2$ (346.4): C 69.35, H 5.24; found: C 67.49, H 5.25.

Cycloaddition of TCNE to **14**. A mixture of **14** (127 ml, 0.55 mmol) and TCNE (70 mg, 0.55 mmol) in MeCN (10 ml) was stirred at 20° for 3 h (TLC control (light petroleum ether/CH_2Cl_2/Et_2O 5:5:1)). ^{1}H-NMR of the crude mixture: **22**/**23** 1:7. Separation by column chromatography (*Lobar B, Lichroprep Si 60*, 40–63 μm, light petroleum/CH_2Cl_2/Et_2O 5:5:1) gave first 25 mg (13%) of **22** and then 162 mg (82%) of **23**. The same reaction in benzene gave **22**/**23** 1:3.

*Data of (1*RS,*8*SR,*9*RS,*12*SR*)-8*-exo,*12*-syn-*(Isopropylidenedioxy)-10,11-dimethylidenetricyclo[7.2.1.0^{2,7}]-dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**22**): White solid. M.p. 124° (dec.). UV (MeCN): 218 (8900), 224 (9050), 236 (8700). UV (isooctane): 225 (4400), 235 (4300). IR (KBr): 2985, 2950, 2920, 1435, 1385, 1370, 1350, 1340, 1325, 1305, 1265, 1240, 1220, 1200, 1145, 1095, 1080, 1015, 1005, 985, 965, 905, 880, 845, 830, 810, 785, 740. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.57 (*s*, 1 H, CH_2=C(10), *cis* to C(11)); 5.36 (*s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.21 (*s*, 1 H, CH_2=C(10), *trans* to C(11)); 5.02 (*s*, 1 H, CH_2=C(11), *trans* to C(10)); 4.54 (br. *dd*, ^3J = 5.0, 4.9, H_{anti}–C(12)); 3.88 (br. *d*, ^3J = 4.0, H_{endo}–C(8)); 3.49 (*m*, 1 H, H–C(9)); 3.42 (*d*, ^2J = 18, 1 H), 3.15–2.90 (*m*, 4 H, CH_2(3), CH_2(6), H–C(1)); 1.52 (*s*, Me *cis* to C(9)); 1.36 (*s*, Me *trans* to C(9)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 143.3, 142.6 (2*s*, C(10), C(11)); 128.6, 123.8 (2*s*, C(2), C(7)); 111.1, 105.6 (2*t*, ^1J(C,H) = 158, CH_2=C(10), CH_2=C(11)); 110.7, 110.2, 109.8 (3*s*, 4 CN); 99.5 (*s*, Me_2C); 72.0 (*d*, ^1J(C,H) = 154), 71.2 (*d*, ^1J(C,H) = 158, C(8), C(12)); 53.6 (*d*, ^1J(C,H) = 146), 42.5 (*d*, ^1J(C,H) = 140, C(1), C(9)); 37.8 (*s*, C(4), C(5)); 34.6 (*t*, ^1J(C,H) = 138), 33.6 (*t*, ^1J(C,H) = 145, C(3), C(6)); 31.3 (*q*, ^1J(C,H) = 126), 29.2 (*q*, ^1J(C,H) = 128, Me_2C). CI-MS (NH_3): 359 (11, $[M + 1]^+$), 345 (2), 344 (31), 343 (100), 318 (2), 317 (2), 302 (3), 301 (11), 300 (9), 285 (9), 283 (12), 273 (15), 272 (66), 271 (20) 245 (4), 205 (10), 166 (13), 144 (16), 141 (12), 129 (21), 128 (25), 115 (23), 91 (43). Anal. calc. for $C_{21}H_{18}N_4O_2$ (358.4): C 70.38, H 5.06; found: C 68.09, H 5.15.

*Data of (1*RS,*8*RS,*9*SR,*12*SR*)-9*-exo,*12*-anti-*(Isopropylidenedioxy)-10,11-dimethylidenetricyclo-[6.3.1.0^{2,7}]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile* (**23**): White solid. M.p. 185° (dec.). UV (MeCN): 223 (8900). UV (isooctane): 225 (4300). IR (KBr): 3090, 2990, 2950, 2920, 1670, 1640, 1620, 1460, 1440, 1430, 1380, 1370, 1345, 1330, 1290, 1280, 1265, 1240, 1205, 1185, 1150, 1095, 1055, 1015, 965, 925, 910, 900, 885, 860, 840, 825, 815, 765, 735, 690, 670, 650. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.52 (br. *s*, 1 H, CH_2=C(10), *cis* to C(11)); 5.40 (br. *s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.18 (br. *s*, 1 H, CH_2=C(10), *trans* to C(11)); 4.90 (br. *s*, 1 H, CH_2=C(11), *trans* to C(10)); 4.62 (*ddd*, ^3J = 5.5, 5.4, ^4J = 1.6, H_{syn}–C(12)); 4.43 (*dd*, ^3J = 4.0, ^4J = 1.6, H_{endo}–C(9)); 3.24–3.01 (*m*, H–C(1), H–C(8), CH_2(3), CH_2(6)); 1.50 (*s*, Me *cis* to C(8)); 1.34 (*s*, Me *trans* to C(8)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 143.3, 141.0 (2*s*, C(10), C(11)); 134.5, 129.3 (*s*, C(2), C(7)); 120.2, 112.0 (2*t*, ^1J(C,H) = 159, CH_2=C(10), CH_2=C(11)); 110.4, 110.3, 110.1 (*s*, 4 CN); 98.7 (*s*, Me_2C); 73.5 (*d*, ^1J(C,H) = 160), 71.9 (*d*, ^1J(C,H) = 154, C(9), C(12)); 55.8 (*d*, ^1J(C,H) = 144), 42.8 (*d*, ^1J(C,H) = 142, C(1), C(8)); 38.0 (*s*, C(4), C(5)); 32.3 (*t*, ^1J(C,H) = 139), 32.0 (*t*, ^1J(C,H) = 138, C(3), C(6)); 30.8, 29.3 (2*q*, ^1J(C,H) = 125, Me_2C). CI-MS (NH_3): 359 (5, $[M + 1]^+$), 344 (2), 343 (13), 318 (2), 317 (5), 302 (2), 301 (15), 300 (21), 274 (5), 273 (18), 272 (71), 271 (20), 207 (9), 205 (9), 193 (10), 172 (11), 166 (13), 144 (25), 129 (23), 128 (21), 120 (22), 115 (20), 106 (39), 105 (69), 98 (20), 97 (43), 92 (21), 91 (100). Anal. calc. for $C_{21}H_{18}N_4O_2$ (358.4): C 70.38, H 5.06; found: C 70.29, H 5.07.

Cycloaddition of TCNE to **15**. A soln. of **15** (*ca.* 200 mg, 0.6 mmol) in 20 ml of CH_2Cl_2 was concentrated *in vacuo* to *ca.* 2 ml, and MeCN (30 ml) was added. The soln. was concentrated *in vacuo* to *ca.* 2 ml, and MeCN (8 ml) was added. TCNE (100 mg, 0.7 mmol) was added portionwise until complete disappearance of **15** (TLC (light petroleum ether/CH_2Cl_2/Et_2O 10:9:1)). After 2 h at 20°, the ^{1}H-NMR of the crude showed a 1:5 mixture **24**/**25**. Separation by column chromatography (*Lobar B, Lichroprep Si 60*, 40–63 μm, light petroleum ether/CH_2Cl_2/Et_2O 10:9:1) gave first 43 mg (16%) of **24** and then 197 mg (72%) of **25**. The same reaction in benzene led to **24**/**25** 1:20.

*Data of (1*RS,*8*SR,*9*RS,*12*SR*)-12*-syn-*[(*tert*-*Butyl)dimethylsilyloxy]-4,4,5,5-tetracyano-10,11-dimethylidenetricyclo[7.2.1.0^{2,7}]dodec-2(7)-en-8*-exo-*yl Acetate* (**24**): White solid. M.p. 155° (dec.). UV (MeCN): 208 (9000), 228 (7000), 246 (6500). UV (isooctane): 208 (8600), 227 (sh, 6800), 230 (6600), 236 (7000), 243 (7100). IR (KBr): 3090, 2950, 2930, 2880, 2850, 2260, 1810, 1730, 1625, 1470, 1440, 1370, 1250, 1235, 1220, 1140, 1090, 1020, 970, 940, 905, 890, 855, 835, 775, 710, 665, 640, 615. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.59 (*d*, ^2J = 0.4, 1 H, CH_2=C(10), *cis* to C(11)); 5.34 (br. *s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.30 (*s*, 1 H, CH_2=C(11), *trans* to C(11)); 4.97 (*d*, ^3J = 0.8 H_{endo}–C(8)); 4.93 (*s*, 1 H, CH_2=C(11), *trans* to C(10)); 4.20 (*dd*, ^3J = 5.0, 4.4., H_{anti}–C(12)); 3.2–2.8 (*m*, CH_2(3), CH_2(6)); 3.01 (br. *d*, ^3J = 5.0, H–C(1)); 2.75 (br. *d*, ^3J = 4.4, H–C(9)); 2.14 (*s*, AcO); 0.89 (*s*, *t*-Bu); 0.06 (*s*, Me_2Si). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 170.7 (*s*, CO); 144.5, 143.0 (2*s*, C(10), C(11)); 129.1, 121.1 (*s*, C(2), C(7)); 111.1 (*t*, ^1J(C,H) = 160), 104.4 (*t*, ^1J(C,H) = 158, CH_2=C(10), CH_2=C(11)); 110.5, 110.4, 110.2, 110.0 (4*s*, 4 CN); 72.5, 69.7 (2*d*, ^1J(C,H) = 151, C(8), C(12)); 52.6 (*d*, ^1J(C,H) = 142), 49.2 (*d*, ^1J(C,H) = 145, C(1), C(9)); 37.7 (*s*, C(4), C(5)); 35.8 (*t*, ^1J(C,H) = 140), 32.9 (*t*, ^1J(C,H) = 138, C(3), C(6)); 25.5 (*q*, ^1J(C,H) = 125, Me_3CSi); 21.1 (*q*, ^1J(C,H) = 131, *Me*CO); 17.8 (*s*, Me_3CSi); –4.8, –4.2 (2*q*, ^1J(C,H) = 118, Me_2Si). MS (70 eV): 358 (5), 357 (8),

330 (1), 215 (1), 190 (1), 190 (1), 159 (2), 143 (1), 141 (1), 140 (1), 139 (1), 129 (2), 128 (3), 127 (4), 125 (1), 120 (1), 119 (5), 118 (9), 117 (100), 75 (30), 73 (13). CI-MS (NH_3): 417 (3, $[M-(t\text{-Bu})]^+$), 415 (2), 399 (1), 359 (2), 358 (10), 357 (16), 330 (3), 127 (10), 125 (11), 119 (21), 117 (100), 113 (11), 111 (16), 105 (24), 97 (24), 91 (36), 85 (53), 84 (29), 83 (29), 75 (30), 71 (63). Anal. calc. for $C_{26}H_{30}N_4O_3Si$ (474.6): C 65.80, H 6.37; found: C 65.02, H 6.24.

*Data of (1*RS,*8*SR,*9*SR,*12*SR*)-12*-anti-*[(*tert-*Butyl)dimethylsilyloxy]-4,4,5,5-tetracyano-10,11-dimethylidenetricyclo[6.3.1.0^{2,7}]dodec-2(7)-en-9-*exo-*yl Acetate* (**25**): White solid. M.p. 178° (dec.). UV (MeCN): 207 (8300), 241 (sh, 4200). UV (isooctane): 212 (6500), 243 (sh, 2900). IR (KBr): 2950, 2930, 2890, 2875, 1730, 1470, 1435, 1370, 1245, 1185, 1165, 1115, 1020, 985, 940, 885, 835, 800, 775, 670. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.67 (br. *s*, 1 H, CH_2=C(10), *cis* to C(11)); 5.41 (br. *s*, 1 H, CH_2=C(11), *cis* to C(10)); 5.29 (br. *s*, H_{endo}–C(9)); 5.21 (br. *s*, 1 H, CH_2=C(10), *trans* to C(11)); 4.81 (br. *s*, CH_2=C(11), *trans* to C(10)); 4.34 (*ddd*, ^3J = 5.0, 4.9, ^4J = 1.0, H_{syn}–C(12)); 3.22 (*m*, 2 H), 3.07 (*m*, 2 H, CH_2(3), CH_2(6)); 2.91 (*d*, ^3J(C,H) = 5,0, H–C(1)); 2.71 (br. *d*, ^3J = 4.9, H–C(8)); 2.06 (*s*, AcO); 0.88 (*s*, *t*-Bu); 0.08, 0.07 (2*s*, Me_2Si). ^{13}C-NMR (50.3 MHz, $CDCl_3$); 170.9 (*s*, CO); 140.6, 139.7 (*s*, C(10), C(11)); 134.7, 129.8 (2*s*, C(2), C(7)); 119.7 (*t*, ^1J(C,H) = 159), 111.7 (*t*, ^1J(C,H) = 158, CH_2=C(10), CH_2=C(11)); 110.4, 110.1 (*s*, 4 CN); 74.5 (*d*, ^1J(C,H) = 148), 66.4 (*d*, ^1J(C,H) = 150, C(9), C(12)); 54.1 (*d*, ^1J(C,H) = 141), 48.5 (*d*, ^1J(C,H) = 144, C(1), C(8)); 37.9 (*s*, C(4), C(5)); 32.0 (*t*, ^1J(C,H) = 138), 31.9 (*t*, ^1J(C,H) = 140, C(3), C(6)); 25.5 (*q*, ^1J(C,H) = 120, Me_2CSi); 21.3 (*q*, ^1J(C,H) = 115, MeCO); 17.8 (*s*, Me_3CSi); –4.9 (*q*, ^1J(C,H) = 119), –5.0 (*q*, ^1J(C,H) = 118, Me_2Si). CI-MS (NH_3): 492 (0.5, $[M+18]^+$), 475 (0.7, $[M+1]^+$), 418 (1), 417 (1.9), 415 (1.2), 359 (1.2), 358 (4), 357 (9), 141 (1.4), 119 (3.4), 118 (11), 117 (100), 75 (21), 73 (15). Anal. calc. for $C_{26}H_{30}N_4O_3Si$ (474.6): C 65.80, H 6.37; found: C 57.71, H 6.42.

Cycloaddition of Maleic Anhydride to **14**. A mixture of **14** (47.4 mg, 0.2 mmol) and maleic anhydride (20.2 mg, 0.2 mmol) in MeCN (2 ml) was stirred at 20° for 24 h. The solvent was evaporated and the residue analyzed by ^{1}H-NMR: type **A**/type **B**/**14** 1:10:3. The diastereoisomeric ratio (*exo vs. endo*) of the two type of adducts was *ca.* 1:1. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.48–4.78 (olef. H's); 4.50–4.20, 3.68 (CH–O's); 3.50–2.20 (bridgehead H's, CH_2's); 1.52, 1.48, 1.30 (Me_2C).

Cycloaddition of Dimethyl Acetylenedicarboxylate to **14**. Same procedure as above using 25.8 µl of dimethyl acetylenedicarboxylate instead of maleic anhydride. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B**/**14** 1:1.5:1): 5.46–4.78 (olef. H's); 4.58–4.35, 3.88–3.80 (CH–O's); 3.74 (MeO); 3.50–2.55 (bridgehead H's, CH_2's); 1.52, 1.48, 1.47, 1.40, 1.39, 1.38 (Me_2C).

Cycloaddition of 1,4-Benzoquinone to **14**. Same procedure as above using 24.8 µm of 1,4-benzoquinone. After 4 d at 20°, the solvent was evaporated and the residue analyzed. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B**/**14** 1:3:2): 6.76, 6.65, 6.62, 6.60 (enedione H's); 5.45–4.75 (olef. H); 4.47–4.30, 3.78, 3.72, 3.48 (CH–O's C*H*–CH_2's); 3.34–1.90 (remaining bridgehead H's, CH_2's); 1.50–1.26 (Me_2C).

*Cycloaddition of 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione to* **14**. The 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (39.8 mg, 0,23 mmol) was added portionwise to a soln. of **14** (52.3 mg, 0.23 mmol) in MeCN (2 ml). Immediate decolourizing was observed. The solvent was evaporated and the residue analyzed. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B** 1:2.5): 7.50–7.32 (Ph); 5.48–4.88 (olef. H's); 4.62–3.97 (CH–O's, CH_2's); 1.52, 1.36 (Me_2C).

Cycloaddition of Maleic Anhydride to **15**. A soln. of **15** (5 ml) containing 54 mg (0.16 mmol) of **15** was concentrated *in vacuo* to *ca.* 1 ml, and MeCN (20 ml) was added. The solvent was evaporated to *ca.* 1 ml, and 1 ml of MeCN was added. Maleic anhydride (15.3 mg, 0.16 mmol) was added and the mixture stirred at 20° for 24 h. The solvent was evaporated. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B** 1:6; diastereoisomeric proportions *exo vs. endo ca.* 1:1): 5.49, 5.22, 5.15, 5.14, 4.97, 4.93, 4.85, 4.82, 4.78 (olef. H's, H–C(8) (**A**), H–C(9) (**B**)); 4.20, 4.00 (H–C(12)); 3.42, 3.37, 2.95–2.30 (bridgehead H's, CH_2's, C*H*–CH_2's); 2.08, 2.07, 2.03, 2.02 (AcO); 0.87–0.82 (*t*-Bu); 0.03–0.01 (Me_2Si).

Cycloaddition of Dimethyl Acetylenedicarboxylate to **15**. Same procedure as above using 1 equiv. of dimethyl acetylenedicarboxylate. ^{1}H-NMR (250 MHz, $CDCl_3$: 1:3:2 mixture of monoadducts of type **A**/type **B**/**15** 1:3:2): 5.60–4.70 (olef. H's, C*H*–OAc's); 4.30, 4,18, 4.13 (CH–OSi's); 3.87, 3.78 (COOMe); 3.45, 3.20–2.35 (bridgehead H's, CH_2's); 2.08, 2.05 (MeCO); 0.90–0.85 (*t*-Bu); 0.08–0.01 (Me_2Si).

Cycloaddition of 1,4-Benzoquinone to **15**. Same procedure as above, using 1 equiv. of 1,4-benzoquinone, and stirring at 20° for 4 d. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B** 1:5): 6.77, 6.64, 6.62, 6.60 (olef. H's α to CO); 5.48, 5.45, 5.23, 5.19, 5.18, 5.13, 4.88, 4.84, 4.79 (remaining olef. H's, C*H*–OAc's); 4.08 (CH–OSi's); 3.25, 3.15, 2.88, 2.72, 2.63, 2.28, 2.24 (bridgehead H's, CH_2's, C*H*–CH_2's); 2.07, 2.03 (MeCO); 0.86 (*t*-Bu); 0.0 (Me_2Si).

*Cycloaddition of 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione to* **15**. Same procedure as above using 1 equiv. of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B**/bis-adduct 1:8:7): 7.48, 7.35 (Ph); 5.64, 5.56, 5.37, 5.33, 5.24, 5.17, 5.08, 5.05, 4.92, 4,80 (olef. H's, C*H*–OAc's); 4.50, 4.40, 4.30–3.80

(CH–OSi's, CH_2's of cyclohexene moieties); 2.98, 2.77, 2.60 (bridghead H's); 2.10, 2.06 (Ac); 0.90 (*t*-Bu); 0.08 (Me_2Si).

Cycloaddition of Didehydrobenzyne to **15**. A CH_2Cl_2 soln. (5 ml) containing *ca.* 54 mg (0.16 mmol) of **15** was concentrated *in vacuo* to *ca.* 1 ml. $CHCl_3$ (20 ml) was added and the soln. concentrated to 1 ml. $CHCl_3$ (20 ml) was added and the soln. concentrated againt to *ca.* 1 ml *in vacuo* $CHCl_3$ (1 ml) was added and the soln. cooled to 0°. Anthranilic acid (64 mg, 0.48 mmol) and dimethoxyethane (1 ml) were added under stirring. Then, isopentyl nitrite (31 µl) was added slowly. After stirring at 0° for 15 min, the mixture was heated to 60° until the end of the gas evolution. The mixture was cooled to 20°, poured onto a sat. aq. $NaHCO_3$ soln. (5 ml), and extracted with CH_2Cl_2 (5 ml, 4 times), the combined org. extract dried ($MgSO_4$) and evaporated, and the residue analyzed. ^{1}H-NMR (250 MHz, $CDCl_3$; type **A**/type **B**/**15** 2:7:9): 7.13 (arom. H's); 5.58–4.78 (olef. H's, C*H*–OAc's); 4.45, 4.39, 4.20 (CH–OSi's); 3.60–2.55 (bridgehead H's, CH_2's of cyclohexadiene moietites); 2.15, 2.10, 2.08 (AcO); 0.97, 0.94, 0.88 (*t*-Bu); 0.10, 0.08 (Me_2Si).

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