II listing fractional atomic coordinates and equivalent isotropic thermal parameters; (c) Table III listing anisotropic thermal parameters; (d) $^{13}C$ NMR spectrum of the dilactone **6a** (4 pages). Ordering information is given on any current masthead page.

## Synthesis and Diels–Alder Reactivity of 2,3,6,7-Tetrakis(methylene)bicyclo[3.2.1]octane

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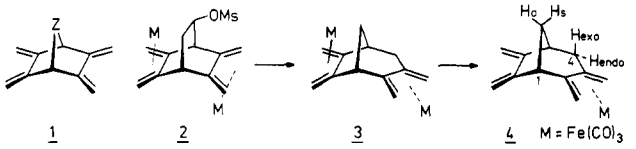
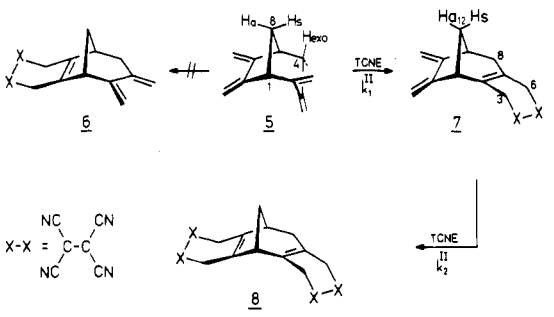
*Received November 18, 1985*

The tetraenes **1** (Z = O, $CH_2$, CH=CH, $(CH_3)_2C$=C) react with a dienophile ($k_1$) more rapidly than the corresponding monoadducts ($k_2$).[1] This principle (tandem Diels–Alder reactions) has been applied to the convergent synthesis of anthracyclinones.[2] We report here the synthesis of 2,3,6,7-tetrakis(methylene)bicyclo[3.2.1]octane (**5**), a new type of exocyclic double diene. We have found that the diene moiety at C(2),C(3) reacts more rapidly toward tetracyanoethylene (TCNE) than the diene moiety at C(6),C(7).




**1** **2** **3** **4**

The mesylate **2**, prepared from the corresponding alcohol (MsCl, pyridine, 20 °C, 30 min)[3] was reduced and rearranged[4] into **3** (73%) with $NaBH_4$ in $CF_3CH(OH)CF_3$ (20 °C, 8 min). On treatment of **3** with a 15-fold excess of trimethylamine oxide (acetone, 20 °C, 3 h) selective oxidation of the *exo*-$Fe(CO)_3$ moiety at C(6),C(7) was achieved, yielding **4** (88%, isolated).[5] On treating **3** with a 20-fold excess of $Fe(NO_3)_3$ in 1:1 $CH_2Cl_2$/EtOH (20 °C, 1.5 h), the tetraene **5** was obtained (72%). The relative configuration of the $Fe(CO)_3$ groups in **3** and **4** was given by X-ray crystallography on a derivative of **3**.[6] The structure of **3–5** and TCNE adducts **7** and **8** were deduced from their elemental analyses and spectral data. Unambiguous 360-MHz $^1H$ NMR signal assignments were based on NOE measurements. As expected, the H–H coupling constants suggested a chair conformation[7] for the C(1–5),C(8) ring in **5**, with a twisted diene moiety at C(2),C(3). A W $^4J$ coupling constant of 2.4 Hz was measured between H–C(4-endo) and H–C(8-anti). The latter coupling constant was only 1 Hz in the $^1H$ NMR spectrum of **4**. It was not visible in the case of **3**, in agreement with half-chair or envelope conformations for the C(1–5),C(8) rings in **3**




**6** **5** **7** **8**

and **4**. This is due to the rigidity of the diene–$Fe(CO)_3$ moieties that makes the C(1–4) centers to be coplanar or nearly coplanar.[6] The chair conformation of the C(1–5),C(8) ring in **5** was also indicated by the 2.5 Hz $^4J$ coupling constant observed for both the olefinic protons of the $H_2C$=C(3) group with H–C(4-exo) (copolanarity of these atoms). The 1,4-distance between the terminal carbon atoms of the diene at C(2),C(3) in **5** must be larger than that in the diene moiety at C(6),C(7). Accordingly,[8] the latter diene was predicted to react faster than the former in a Diels–Alder addition. Our kinetic data with TCNE (see Table I) contradict this prediction.

In the presence of 1 molar equiv of TCNE, **5** gave the monoadduct **7** (93%); no trace of the isomeric product **6** or bisadduct **8** could be detected in the mother liquor of crystallization of **7**. The addition of a second equivalent of TCNE to **7** was a much slower reaction, giving **8** (93%, isolated). The second-order rate constants of reaction **5** + TCNE → **7** ($k_1^{II}$) and **7** + TCNE → **8** ($k_2^{II}$) measured at various temperatures allowed the evaluation of the activation parameters reported in the table. A rate ratio $k_1/k_2$ = 300 was obtained at 25 °C and appears to be mostly due to a difference in the activation entropy term. Further data with other dienophiles and/or solvents are required to substantiate this result. Tetraene **5** was about 100 times more reactive than **1** (Z = $CH_2$) toward TCNE.[1] Among the several possible interpretations for our kinetic results, we can invoke a possible larger steric hindrance to the approach of the dienophile to the diene moiety at C(6),C(7) than for the diene moiety at C(2),C(3) and a higher flexibility (fast chair/twist interconversion of the six-membered ring) of the latter than of the former diene moiety in **5**. In any event, our preliminary results show the new tetraene **5** to be a valuable synthetic intermediate for tandem Diels-Alder reactions. Monoadducts with the diene moiety at C(6),C(7) are available by using the semiprotected tetraene **4**. Substituted derivatives of **4** and **5** can be envisioned as starting material for the synthesis of naphthocyclinones.[10]

## Experimental Section

General Remarks, see ref 2.

***trans*-μ-[(1*RS*,2*RS*,4*SR*,5*SR*,6*RS*,7*RS*,8*SR*)-*C*,5,6,*C*-η:*C*,7,8,*C*-η-(5,6,7,8-Tetrakis(methylene)-2-bicyclo[2.2.2]octyl methanesulfonate)]bis(tricarbonyliron) (2).** Hydroboration of **1** (Z = CH=CH) followed by oxidative workup gave the corresponding alcohol **1** [Z = $CH_2CH(OH)$].[3] The latter (227 mg, 0.5 mmol) was dissolved in anhydrous pyridine (1 mL) and then cooled to 0 °C. After addition of methanesulfonyl chloride (74 mg, 0.6 mmol) the mixture was stirred at 20 °C for 30 min under $N_2$ atmosphere. $CH_2Cl_2$ (15 mL) was added and the mixture was

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(7) Martin, H.-D.; Heller, C.; Mayer, B.; Beckhaus, H.-D. *Chem. Ber.* **1980**, *113*, 2589 and references cited therein.

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(9) Kinetic measurements, see: Pilet, O.; Chollet, A.; Vogel, P. *Helv. Chim. Acta* **1979**, *62*, 2341.

(10) Krone, B.; Zeeck, A. *Liebigs Ann. Chem.* **1983**, 471. Egert, E.; Noltemeyer, M.; Sheldrick, G. M.; Saenger, W.; Brand, H.; Zeeck, A. *Ibid.* **1983**, 503.

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**Table I. Kinetic Data for the Cycloadditions of TCNE to 5 ($k_1^{II}$) and 7 ($k_2^{II}$) in Toluene[9]**

$k_1^{II}$[dm$^3$ mol$^{-1}$ s$^{-1}$] = 0.57 (263 K), 1.02 (273 K), 1.50 (283 K), 250 (293 K), 3.86 (303 K); $\Delta H_1^{\ddagger}$ = 6.9 ± 0.84 kcal/mol, $\Delta S_1^{\ddagger}$ = −33 ± 2 cal K$^{-1}$ mol$^{-1}$
$k_1^{II}$ = 3.1 at 298 K
$k_2^{II}$ = 0.0051 (283 K), 0.0074 (293 K), 0.0127 (303 K), 0.0194 (313 K), 0.0293 (323 K); $\Delta H_2^{\ddagger}$ = 7.5 ± 0.9 kcal/mol, $\Delta S_2^{\ddagger}$ = −42 ± 3 cal K$^{-1}$ mol$^{-1}$
$k_2^{II}$ = 0.01 at 298 K

washed with 1 N HCl (10 mL, 4 times) and then with $H_2O$ (10 mL, 3 times). After drying ($MgSO_4$), the solvent was evaporated in vacuo and the residue recrystallized from $CH_2Cl_2$/hexane, yielding 210 mg (79%), yellow crystals: IR ($CHCl_3$) 3030, 3000, 2050, 1995, 1975, 1450, 1365, 1340, 1170, 1145, 1020, 970, 925, 890; $^1$H NMR ($CDCl_3$) 5.41 (m, HC(2)), 3.90 (d, $J$ = 3 Hz, HC(1)), 3.51 (t, $J$ = 3 Hz, HC(4)), 3.07 (s, $CH_3$), 2.74 (m, HC(3) trans to C–O), 2.17 (m, HC(3) cis to C–O), 2.18, 2.10, 1.94, 1.88, 0.67, 0.63, 0.41, 0.33 (8 d, $J$ = 3 Hz); $^{13}$C NMR ($CDCl_3$) 111.8, 107.0, 105.1, 102.3 (4 s), 79.2 (d, 150, C(2)), 47.3 (d, 140, C(1)), 42.4 (d, 140, C(4)), 40.2, 38.2, 37.6 and 36.4 (4 t, 160), 39.5 (t, 137), C(3)), 38.5 (q, 139, $CH_3$); MS (70 eV), $m/e$ relative intensity 504 (9, $M^+$ − 28), 476 (31), 448 (12), 420 (3), 392 (6), 382 (7), 364 (46), 241 (43), 214 (20), 213 (100). Anal. Calcd for $C_{19}H_{16}O_9SFe_2$ (532.09): C, 42.89; H, 3.03. Found: C, 42.64; H, 3.00.

***trans*-μ-[(1*RS*,2*RS*,3*SR*,5*RS*,6*SR*,7*RS*)-*C*,2,3,*C*-η:*C*,6,7,*C*-η-(2,3,6,7-Tetrakis(methylene)bicyclo[3.2.1]octane)]bis(tricarbonyliron) (3).** $NaBH_4$ (55 mg, 1.4 mmol) was dissolved in $(CF_3)_2CHOH$ (2 mL). The mesylate **2** (20 mg, 0.040 mmol) was added and the mixture stirred at 20 °C for 8 min. After filtration on silica gel (1 g), the solvent was evaporated in vacuo and the residue purified by column chromatography on silica gel (1 g, hexane), yielding 12 mg (73%), yellow crystals after recrystallization from hexane: mp 98–99 °C; UV (isooctane) 285 (sh, 5900); IR (KBr) 2990, 2960, 2920, 2040, 1990, 1970, 1955, 1470, 1450, 1440, 1420, 1285, 1260, 1250, 1230, 1190, 1020, 1010, 950, 925, 890, 800, 730, 715; $^1$H NMR ($CDCl_3$) 3.17 (dd, $J$ = 17, 4.5, HC(4-exo)), 3.05 (d, $J$ = 4.5, HC(1)), 2.90 (t, $J$ = 4.5, HC(5)), 2.75 (dt, $J$ = 11, 4.5 HC(8-anti)), 2.70 (d, $J$ = 17, HC(4-endo)), 2.36 (d, $J$ = 11, HC(8-syn)), 2.07, 1.90, 1.89, 1.57, 0.58, 0.56, 0.54, 0.07 (8 d, $J$ = 3); $^{13}$C NMR ($CDCl_3$) 115.7, 109.0, 108.7, 101.5 (4 s), 43.3 (d, 146, C(1)), 41.3 (t, 134, C(4)), 39.2 (d, 146, C(5)), 41.1, 36.5, 35.9 and 35.4 (t, 161), 33.3 (t, 130, C(8)); MS (70 eV), $m/e$ (relative intensity) 438 (4), 410 (25), 408 (7), 382 (63), 380 (15), 354 (56), 352 (15), 326 (13), 298 (74), 296 (13), 270 (100), 268 (28), 244 (9), 242 (17), 240 (9), 214 (48), 212 (19), 210 (9). Anal. Calcd for $C_{18}H_{14}O_6Fe_2$ (438.00): C, 49.36; H, 3.22. Found: 49.40; H, 3.28.

**Tricarbonyl[(1*RS*,2*RS*,3*SR*,5*RS*)-*C*,2,3,*C*-η-(2,3,6,7-tetrakis(methylene)bicyclo[3.2.1]octane)]iron (4).** A mixture of **3** (150 mg, 0.34 mmol) and freshly sublimed trimethylamine oxide (400 mg, 5.33 mmol) in anhydrous acetone (38 mL) was stirred at 20 °C for 3 h. After removal of the precipitate by filtration, $H_2O$ (50 mL) was added and the mixture extracted with hexane (50 mL, 3 times). After drying ($MgSO_4$), the solvent was evaporated in vacuo and the residue purified by column chromatography on silica gel (3 g, $CH_2Cl_2$): yield 90 mg (88%); yellow oil (dried over $P_2O_5$ and paraffin); UV (EtOH 95%) 307 (sh, 1400) 218 (18 600); IR ($CH_2Cl_2$) 3085, 2960, 2900, 2890, 2880, 2840, 2040, 1980, 1790, 1630, 1470, 1455, 1420, 1330, 1195, 1130, 1115, 1040, 1020, 960, 895, 885, 850; $^1$H NMR ($CDCl_3$) 5.43, 5.13, 5.08 and 4.77 (4 s), 3.21 (d, $J$ = 4, C(1)), 3.15 (t, $J$ = 5, HC(5)), 3.9 (dd, $J$ = 16, 5, HC(4-exo)), 2.46 (d, $J$ = 16, HC(4-endo)), 2.06 (dddd, $J$ = 11, 5, 4.5, 1, HC(8-anti)), 2.02 (d, $J$ = 11, HC(8-syn)), 1.75, 1.39, 0.34 and 0.16 (4 d, $J$ = 3); $^{13}$C NMR ($CDCl_3$) 154.0, 151.4, 110.3 (3 s), 105.1 and 101.9 (2 t, 158), 99.8 (s), 46.3 (d, 142, C(1)), 40.7 (d, 142, C(5)), 39.8 (t, 158), 39.7 (t, 130, C(4)), 36.3 (t, 134, C(8)), 34.3 (t, 159); MS (70 eV), $m/e$ (relative intensity) 298 (1), 270 (5), 242 (36), 214 (100), 212 (18), 158 (16), 148 (19), 91 (17). Anal. Calcd for $C_{15}H_{14}O_3Fe$ (298.124): C, 60.43; H, 4.74. Found: C, 60.56, H, 4.85.

**2,3,6,7-Tetrakis(methylene)bicyclo[3.2.1]octane (5).** $Fe(NO_3)_3$ (800 mg, 1.98 mmol) was added portionwise to a stirred solution of complex **3** (50 mg, 0.11 mmol) in $CH_2Cl_2$ (0.1 mL) and EtOH (0.9 mL). After the end of the addition (90 min), the precipitate was filtered off on silica gel (1 g) and $H_2O$ (20 mL) was added. The mixture was extracted with hexane (50 mL, 3 times). After drying ($MgSO_4$) the extract, the solvent was evaporated in vacuo and the rsidue purified by column chromatography on silica gel (1 g, hexane), yielding 13 mg (72%), colorless oil: UV (EtOH 95%) 259 (sh, 5400), 249 (sh, 8350), 238 (9450), 224 (9600); UV (isooctane) 259 (sh, 5600), 246 (sh, 9200), 239 (9900), 223 (10 000); IR ($CH_2Cl_2$) 3080, 2960, 2900, 2880, 1790, 1630, 1620, 1460, 1420, 1380, 1190, 1125, 1110, 1040, 1020, 970, 895, 885, 845; $^1$H NMR ($CDCl_3$) 5.40, 5.35, 4.98 and 4.9 (4 s, $H_2C$=C(6) and $H_2C$=C(7)), 5.19 and 4.76 (2 br t, $J$ = 2.5, $H_2C$=C(3)), 4.94 and 4.69 (2 br d, $J$ = 2, $H_2C$=C(2)), 3.34 (d, $J$ = 5, HC(1)), 2.92 (ddd, $J$ = 5, 3, 2.6, HC(5)), 2.60 (ddt, $J$ = 14, 3, 2.5, HC(4-exo)), 2.37 (dt, $J$ = 14, 2.6, HC(4-endo)), 1.95 (dtd, $J$ = 11, 5, 2.6, HC(8-anti)), 1.70 (d, $J$ = 11, HC(8-syn)); $^{13}$C NMR ($CDCl_3$) 152.4, 150.8, 150.6 and 143.4 (4 s), 112.0, 104.6, 103.5 and 103.4 (4 t, 157), 52.1 (d, 144, C(1)), 42.7 (d, 142, C(5)), 42.0 (t, 130, C(4)), 37.6 (t, 134, C(8)); MS (70 eV); $m/e$ (relative intensity) 158 (71), 143 (67), 142 (29), 141 (25), 129 (79), 128 (93), 127 (31), 117 (43), 115 (64), 105 (32), 104 (31), 103 (28), 101 (23), 91 (100).

**10,11-Bis(methylene)tricyclo[7.2.1.0$^{2,7}$]dodec-2(7)-ene-4,4,5,5-tetracarbonitrile (7).** A mixture of tetraene **5** (13 mg, 0.08 mmol) and TCNE (11 mg, 0.08 mmol) in anhydrous benzene (1 mL) was stirred at 20 °C for 20 min. The solvent was evaporated in vacuo and the residue recrystallized from $CH_2Cl_2$/hexane; yield 22 mg (93%), white solid, mp 167–170 °C dec: UV (EtOH 95%) 239 (7100); UV (isooctane) 244 (6400), 238 (6400), 226 (6000), 221 (6000); IR (KBr) 3090, 2990, 2960, 2910, 2890, 2830, 2250, 1620, 1460, 1440, 1425, 1260, 1235, 1200, 1175, 1130, 1100, 1085, 1020, 1010, 895, 885, 820; $^1$H NMR ($CDCl_3$) 5.45, 5.18, 5.12, 4.83 (4 s), 3.20–2.80 (m, $H_2C$(3) and $H_2C$(6)), 3.04 (m, HC(9)), 2.82 (dd, $J$ = 4, 1, HC(1)), 2.54 (m, HC(8-exo)), 2.02 (m, HC(8-endo)), 1.91 (dddd, $J$ = 11, 5, 4.5, 1, HC(12-anti)), 1.79 (d, $J$ = 11, HC(12-syn)); MS (70 eV), $m/e$ (relative intensity) 286 (100), 272 (42), 260 (26), 259 (30), 245 (22), 244 (32), 231 (24), 221 (25), 206 (51). Anal. Calcd for $C_{18}H_{14}N_4$ (286.337): C, 75.51; H, 4.93. Found: C, 75.51; H, 5.04.

**Tetracyclo[7.6.1.0$^{2,7}$.0$^{10,15}$]hexadeca-2(7),10(15)-diene-4,4,5,5,12,12,13,13-octacarbonitrile (8).** A mixture of **5** (15 mg, 0.09 mmol), TCNE 24 (mg, 0.19 mmol), and anhydrous benzene (1 mL) was stirred at 20 °C for 20 min. The solvent was evaporated in vacuo and the residue recrystallized from acetone, yield 37 mg (94%), white solid, mp >240 °C dec: UV (EtOH 95%) final abs. $\epsilon_{210}$ 7100; IR (KBr) 2990, 2950, 2890, 2830, 2820, 2260, 1710, 1650, 1440, 1310, 1290, 1245, 1230, 1140, 1130, 1100, 1050, 1005, 960, 840, 820; $^1$H NMR ($CD_3COCD_3$) 3.78–3.44 (m, 6 H), 3.29–3.02 (m, 2 H), 2.98 (t, $J$ = 5, HC(9)), 2.93 (d, $J$ = 5, HC(1)), 2.46 (m, HC(8)), 2.26 (m, HC(16)), 2.12 (m, HC(8)), 1.92 (d, $J$ = 16, HC(16)); MS (70 eV), $m/e$ (relative intensity) 414 (58), 388 (87), 360 (100), 334 (32), 308 (23), 286 (50), 271 (40), 250 (30). Anal. Calcd for $C_{24}H_{14}N_8$ (414.43): C, 69.56; H, 3.41. Found: C, 69.34; H, 3.49.

**Acknowledgment.** We thank the Swiss Science Foundation, the Herbette Foundation, Lausanne, and Hoffmann-La Roche & Co., AG, Basel, for generous financial support.

**Registry No.** 1 (Z = CH = CH), 62234-75-7; 1 (Z = $CH_2C$-H(OH), 87514-93-0; **2**, 102262-09-9; **3**, 102262-10-2; **4**, 102262-11-3; **5**, 102284-76-4; **7**, 102284-77-5; **8**, 102284-78-6.

## Tosylation of Alcohols

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*Received January 13, 1986*

The tosylation (sulfonylation) of alcohols is a common transformation which is often used to facilitate subsequent

0022-3263/86/1951-2386$01.50/0 