Unusual Stereoselectivity in the Diels–Alder Addition of Cyclopentadiene with the Bicyclo[2.2.2]octene Nucleus

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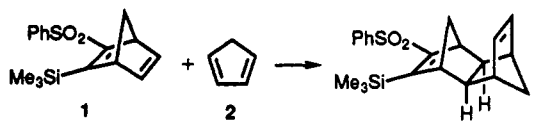
Cyclopentadiene adds to the substituted and electronically activated double bond of bicyclo[2.2.2]-octa-2,5-diene-2,3-dicarboxylic anhydride with pronounced *endo* selectivity. Only two of the four possible stereoisomers were formed. The stereochemical course of the reaction was determined by X-ray crystallography and by a combination of chemical and spectroscopic techniques.

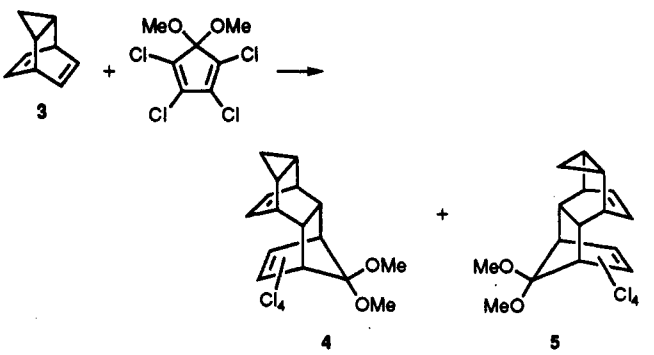
Introduction

For several years now, we have been interested in the stereoselectivities associated with strained bridged bicyclic molecules.[1–5] We discovered unexpected regio- and stereospecificity in the Diels–Alder cycloaddition of norbornadiene 1 with cyclopentadiene (2).[1] This prompted us to examine the much less studied Diels–Alder additions to the bicyclo[2.2.2]octene nucleus. It is well known that Diels–Alder additions to the bicyclo[2.2.1]heptenyl (norbornenyl) nucleus occur selectively at the *exo* face.[1,6–11] However, very little is known about Diels–Alder reactions between bicyclo[2.2.2]octenyl dienophiles and dienes.[11] The principal reasons for this dearth of information are the relatively low dienophilicity of the bicyclo[2.2.2]octenyl systems and the extremely facile retro-Diels–Alder reaction of bicyclo[2.2.2]octadienes.[11,12] Huisgen *et al.*[12] showed that the rate of a Diels–Alder cycloaddition to bicyclo-[2.2.2]octene is 2 orders of magnitude slower than the corresponding reaction with norbornene.



1 2 93% isolated yield

Grimme and Warner *et al.* carried out the Diels–Alder reaction between homobarrelene (3) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene to give the adducts 4 and 5.[13]



3 4 5

Clearly, in the case of 3, the normal retro-Diels–Alder fragmentation of the bicyclo[2.2.2]octadiene nucleus is disfavored as the highly strained cyclopropene would be produced in addition to benzene. We felt that the steric and electronic perturbations of the cyclopropyl group could easily alter the preferred stereoselectivity of the bicyclo-[2.2.2]octadiene nucleus, consequently 3 may not be representative of this nucleus.

Analogy with the norbornenyl systems[6–11] leads to the expectation of dominant *exo* Diels–Alder attack on bicyclo-[2.2.2]octadienyl dienophiles. However, it is well established, in contrast to norbornyl systems, that electrophilic attack of bicyclo[2.2.2]octa-2,5-diene (6) is initiated on the *endo* face![14] Similarly, additions of both a carbene[15] and a ketene[16] to 6 occur predominantly or exclusively from the *endo* face.

Against this background we reasoned that with a reactive diene and with suitable substitution of the dienophile, the stereoselectivity of the bicyclo[2.2.2]octadiene nucleus in Diels–Alder chemistry could be effectively probed. The anhydride 7 appeared to be an ideal dienophile. The stereochemical results for the addition of cyclopentadiene to each of norbornadiene (8)[7] and anhydride 9[8] are essentially the same. Thus we anticipated that 7 would

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(1) Williams, R. V.; Sung, C.-L. A. *J. Chem. Soc., Chem. Commun.* **1987**, 590.
(2) Ji, X.; van der Helm, D.; Williams, R. V.; Ebey, W. J. *Acta Crystallogr.* **1989**, *B45*, 93.
(3) Williams, R. V.; Lin, X. *J. Chem. Soc., Chem. Commun.* **1989**, 1872.
(4) Williams, R. V.; Kelley, G. W.; Loebel, J.; van der Helm, D.; Page, P. C. B. *J. Org. Chem.* **1990**, *55*, 3840.
(5) Williams, R. V.; Chauhan, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1672.
(6) Soloway, S. B. *J. Am. Chem. Soc.* **1952**, *74*, 1027.
(7) Stille, J. K.; Frey, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4273.
(8) Edman, J. R.; Simmons, H. E. *J. Org. Chem.* **1968**, *33*, 3808.
(9) Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383. Bartlett, P. D.; Combs, G. L., Jr.; Le, A.-X. T.; Watson, W. H.; Galloy, J.; Kimura, M. *J. Am. Chem. Soc.* **1982**, *104*, 3131.
(10) De Lucchi, O.; Licini, G.; Pasquato, L. *J. Chem. Soc., Chem. Commun.* **1985**, 418.
(11) De Lucchi, O.; Piccolrovazzi, N.; Licini, G.; Modena, G.; Valle, G. *Gazz. Chim. Ital.* **1987**, *117*, 401.
(12) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951.
(13) Bertsch, A.; Grimme, W.; Reinhardt, G.; Rose, H.; Warner, P. M. *J. Am. Chem. Soc.* **1988**, *110*, 5112.
(14) Berson, J. A. In *Molecular Rearrangements*; de Mayo, P., Ed.; J. Wiley: New York, 1963; Vol. 1, page 216.
(15) Jefford, C. W.; Delay, A.; Wallace, T. W.; Burger, U. *Helv. Chim. Acta* **1976**, *59*, 2355.
(16) Erden, I.; de Meijere, A. *Tetrahedron Lett.* **1983**, *31*, 3811.

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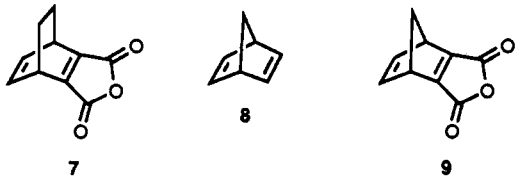
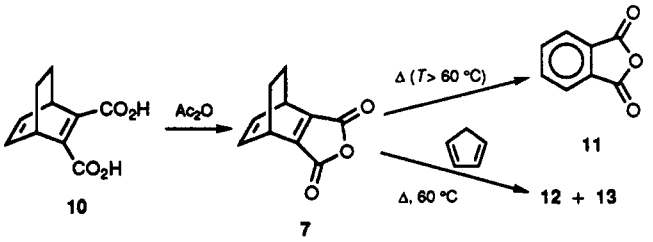
allow a reasonable elucidation of the preferred stereoselectivity of the bicyclo[2.2.2]octadiene nucleus in Diels–Alder additions.



Discussion and Results

The anhydride **7** is easily prepared by acetic anhydride treatment of the known diacid **10**[17] (which we made by the improved procedure of the cycloaddition of acetylene dicarboxylic acid to 1,3-cyclohexadiene). Low-temperature Diels–Alder reaction between **7** and cyclopentadiene (**2**) is rather sluggish. However, upon heating to reaction temperatures greater than 100 °C the retro-Diels–Alder reaction of **7** to give phthalic anhydride (**11**) dominated. The cleavage of **7** to **11** was most conveniently monitored by ^{1}H NMR spectroscopy. After 1 h at 110 °C, complete conversion to **11** resulted. There was no detectable yield of **11** on heating **7** to 60 °C for 1 h; at intermediate temperatures (80–110 °C) varying degrees of decomposition were observed. Prolonged heating of **7** at 60 °C resulted in barely detectable retro-Diels–Alder fragmentation.



Reaction of cyclopentadiene with **7** in benzene at 60 °C proceeded smoothly to give a mixture of two 1:1 adducts, **12** and **13** in 78% combined yield (**12**/**13**, 5:1). No other adducts were detected by means of NMR or thin-layer chromatographic analysis. It was immediately apparent from a cursory examination of the ^{1}H NMR spectra of **12** and **13** that, as anticipated, cycloaddition had occurred at the electronically activated double bond. However assignment of structure to compounds **12** and **13** was not trivial. Four products (**A**, **B**, **C**, or **D**) are possible for the cycloaddition of cyclopentadiene to the electronically activated double bond of **7** (Scheme I).

Detailed analysis of the spectroscopic data (including COSY and NOESY NMR) did not furnish an unambiguous assignment of structure. Good crystals of anhydride **12** were therefore subjected to X-ray structure determination. The bond distances and X-ray numbering system for **12** are shown in Figure 1. A stereo ORTEP drawing of the molecule is shown in Figure 2. The crystal structure clearly shows that the major product **12** has structure **C**.

In complete contrast with the norbornenyl series in which attack occurs predominantly from the *exo* face,[6-11] **12** results from *endo* attack by the cyclopentadiene. It should be noted that Diels–Alder cycloaddition to homobarrelane **3** also occurs from the *endo* face.[13]

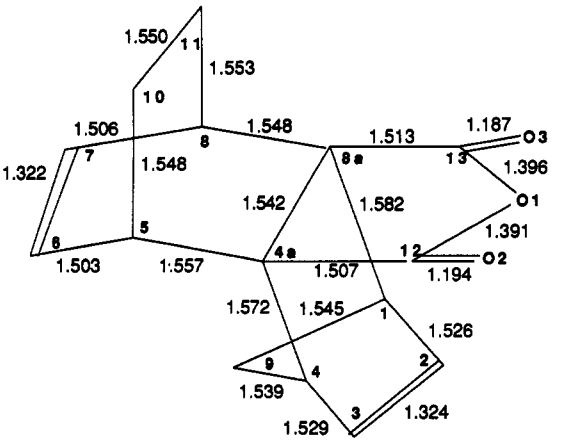
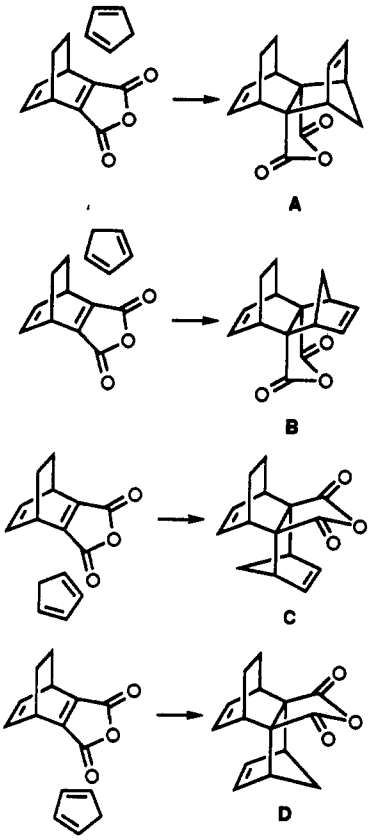


Figure 1. Chemical structure of **12** showing X-ray numbering scheme and bond distances. All e.s.d's are 0.002 Å.

Scheme I



Just as with the corresponding norbornenyl anhydride **9** adducts[9,18] only one of our adducts (**13**) undergoes base catalyzed hydrolysis to the corresponding diacid **14**. In fact, this proved to be the most convenient way to separate **12** from **13**. Assignment of structure to **14** proved to be no easier than the elucidation of the structure of **13**. However, in a key experiment with diacid **14** we were able to eliminate structure **D** from consideration for the structure of **13**. The diacid **14** was taken up into an aqueous basic solution to which iodine in aqueous potassium iodide was added. Rapid reaction ensued and although pure product could not be isolated, infrared spectrometry on the crude material clearly indicated the presence of a lactone. Mass spectral data also supported the suggested

(17) Prinzbach, H.; Eberbach, W.; Hagemann, H.; Philipposian, G. *Chem. Ber.* **1974**, *107*, 1957.

(18) Williams, R. V.; Sung, C.-L. A.; Kurtz, H.; Harris, T. M. *Tetrahedron Lett.* **1988**, *29*, 19.

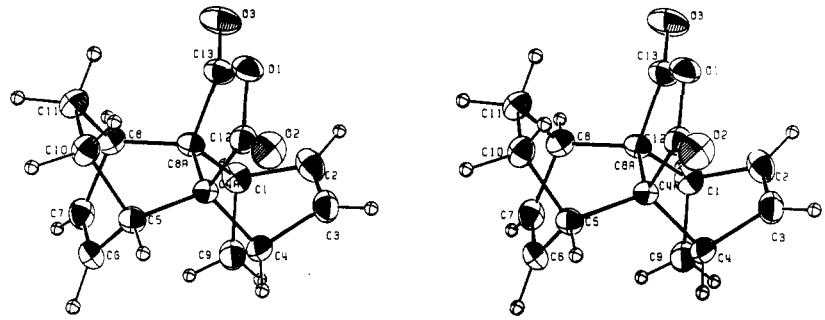
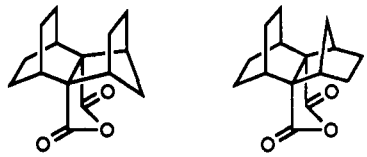


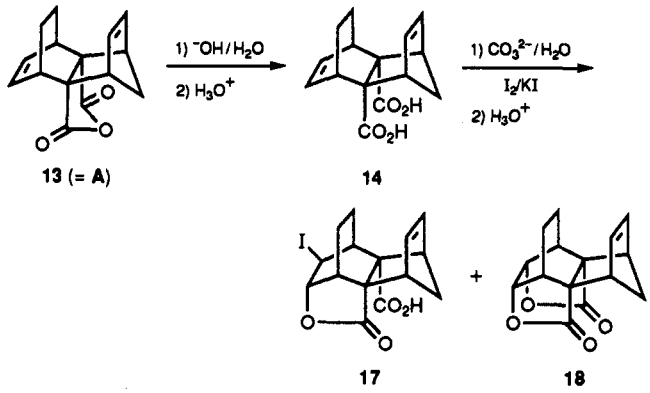
Figure 2. Stereo ORTEP plot of 12. (Thermal ellipsoid at 50% probability).

lactone formation. Of the remaining structures **A**, **B**, and **D**, only **A** and **B** are capable of forming a lactone under these conditions.[8,19] The choice between structures **A** or **B** was easily made from the results of catalytic hydrogenation of **12** and **13** individually and as a mixture of **12** and **13**. Structures **A** and **D** will give the same product (**15**) upon hydrogenation. Similarly structures **B** and **C** (= **12**) will both give **16** upon hydrogenation.



15 **16**

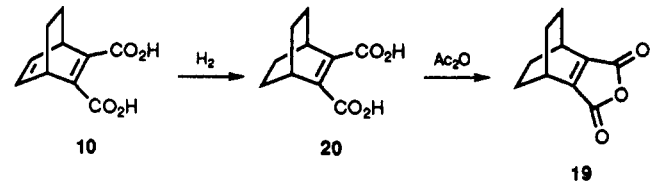
Hydrogenation of **12** and **13** resulted in two different compounds (easily seen from the "doubling" of peaks in the ^{13}C NMR spectrum from the hydrogenation of the mixed sample of **12** and **13**). Therefore, **13** must have structure **A**.



13 (= A) **14** **17** **18**

In an attempt to increase the efficiency of the cycloaddition process we examined the reactions of the partially hydrogenated anhydride **19**. **19** could not be prepared directly by partial hydrogenation of anhydride **7** but was easily accessed from diacid **10**. Partial hydrogenation of **10** gave the conjugated diacid **20**, which upon treatment with acetic anhydride yielded the desired **19**. It is of interest to note that in contrast to the "unstable" norbornadiene anhydride **8**[18] both bicyclo[2.2.2]octenyl anhydrides **7** and **19** are easily isolated, purified, and handled without any special precautions. They are stable to prolonged storage and do not show any particular sensitivity to atmospheric condition. Unfortunately **19** proved to be a very poor dienophile. In many attempted cycloadditions of **19** with cyclopentadiene, **19** was either recovered unchanged or under harsher conditions only intractable polymeric material was produced.

Various methods of increasing the reactivity of **7** were explored (Lewis acids including $AlCl_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$, and $LiClO_4$. The use of ultrasound was also examined). Only sonication appeared to be promising and we are currently undertaking further studies in this regard.



10 **20** **19**

In the case of the Diels–Alder addition of cyclopentadiene with **7** the factors controlling the π-facial selectivity must be closely balanced as some *exo* addition is observed along with the dominant *endo* addition. Presumably electronic and steric factors both play their part in determining not only this facial selectivity but also the *syn/anti* orientation of the etheno bridges. The picture that emerges is that, like the norbornenyl system, the bicyclo[2.2.2]octadienyl skeleton displays a distinct π-facial selectivity for attack by electrophiles,[14] chelotropic reactions,[15] [2 + 2] additions,[16] and (from this work) the Diels–Alder reaction. In contrast to the norbornenyl systems the favored direction of attack for the bicyclo[2.2.2]octadienyl systems is from the *endo* face. The relative importance of steric, hyperconjugative, homoconjugative, and torsional effects has yet to be elucidated. We are currently carrying out theoretical studies in an effort to discover the dominant factor(s) influencing the stereoselectivity.

Experimental Section

Infrared spectra were recorded on a DigiLab Qualimatic or Model FTS 15180, ^1H and ^{13}C NMR spectra on an IBM NR300 or NR200, and mass spectra on a VG7070 at 70 eV (EI) or using methane chemical ionization (CI). All reported mass spectra were recorded under 70 eV EI conditions except where noted. Melting points were determined in open capillaries or on a hot stage and are uncorrected. Microanalyses were performed by Desert Analytics. Petroleum ether refers to the fraction with a boiling range 35–60°C.

X-ray Structure Determination. Crystal data, intensity data, collection parameters, and refinement results are summarized in Table I. All X-ray measurements were made on an Enraf-Nonius CAD-4 diffractometer equipped with a liquid nitrogen low-temperature device. The cell parameters were obtained by a least square fit to $\pm 2\theta$ of 48 reflections measured at low temperature (163K) using Cu $K\alpha_1$. The space group was determined from systematic absences. Intensity data were

(19) Deslongchamps, P.; Kallos, J. *Can. J. Chem.* **1966**, *44*, 1239.

Table I. Experimental Crystallographic Data for 12

formula	$C_{15}H_{14}O_3$
MW	242.3
crystal size	0.15 × 0.18 × 0.28 mm
space group	*Pbca* (orthorhombic)
cell dimensions	
a	11.912(1) Å
b	15.993(1) Å
c	12.0954(5) Å
V	2304.3 Å^3
Z	8
D	1.396 g/cm^3
2θ range	0–150°
temperature	163 K
max scan time	60 s
scan angle	(0.8 + 0.2 tan θ)°
monitor reflection check	
orientation	3 (every 200 reflections)
intensity	3 (every 2 h of X-ray exposure)
max variation in intensities	5.4%
no. of unique data collected	2359
no. of obsd data with $I > 2\sigma(I)$	2074
R	0.046
R_w	0.058
S	2.20
max/min peak height	+0.22 e/Å^3
(Δ/σ)max	0.04

collected by applying the θ–2θ technique and corrected for Lorentz and polarization factors. The structure was determined by direct methods using the program SHELXS[20] and refined by a full-matrix least-squares routine, SHELX76,[21] in which the quantity $\Sigma\omega(kF_o - F_c)^2$ was minimized; $w = 1/\sigma_F^2$, σ_F was obtained from counting statistics. All hydrogen atoms were located from a difference Fourier map and refined isotropically, while all other atoms were refined anisotropically.[22]

Bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic Acid (10). A stirred solution of acetylene dicarboxylic acid[23] (10 g, 87.7 mmol) and 1,3-cyclohexadiene (7.71 g, 96.4 mmol) in dry THF (15 mL) was kept at 60 °C under nitrogen for 18 h. The THF was removed *in vacuo* and the resulting oily residue was triturated in petroleum ether (10 mL). The solid was separated and recrystallized from water to give the pure diacid **10** (15.47 g, 91%), mp 124–125°C (lit.[17] 123°C).

Bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic Anhydride (7). A stirred solution of the diacid **10** (1 g, 5.15 mmol) in acetic anhydride (7 g) was heated to 60 °C under nitrogen for 1 h. The solvent was removed *in vacuo* and the light brown residue was crystallized from petroleum ether to give colorless crystals of anhydride **7** (0.845 g, 93%): mp 100–101°C dec; ^{1}H NMR ($CDCl_3$) δ 6.42 (m, 2H, olefinic), 4.14 (m, 2H, bridgehead), 1.50 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) 167.09, 146.23, 133.38, 40.42, 24.20; IR (KBr) 2951, 1840, 1786, 1330, 1250, 1065, 879; MS, *m/z* (%) 149 (22.7), 148 (8.4), 104 (100), 76 (51.3), 63 (4.3). Anal. Calcd for $C_{10}H_8O_3$: C, 68.17; H, 4.58. Found: C, 68.17; H, 4.68.

Cycloaddition of Cyclopentadiene to Anhydride 7. A stirred solution of anhydride **7** (14 g, 79.5 mmol) and cyclopentadiene (52.5 g, 0.795 mol) in benzene (100 mL) was kept at 60°C under nitrogen for 1 week. Every 24 h cyclopentadiene (2.63 g) was added to the mixture. After 1 week the benzene, excess cyclopentadiene, and dicyclopentadiene were removed *in vacuo*. The residue was initially purified by filtration column chromatography (silica, petroleum ether to remove the hydrocarbons, and then ethyl acetate to elute the adducts **12** and **13**) to give a mixture of **12**/**13** (ratio 5:1) (15 g, 78%).

***anti*-Tetracyclo[6.2.2.1^{3,6}.0^{2,7}]trideca-4,9-diene-*endo*-2,7-dicarboxylic Anhydride (13).**[24] The mixture of **12** and **13** from above was further purified by very careful column chromatography (silica, petroleum ether/ethyl acetate 98:2). Eluting first was the minor anhydride **13** which was recrystallized from petroleum ether to give a pure sample of **13**, sublimes 98 °C; ^{1}H NMR ($CDCl_3$) δ 5.71 (m, 4H, olefinic), 3.15 (m, 2H, bridgehead), 2.95 (m, 2H, bridgehead), 1.70–1.10 (series of m, 6H, CH_2); ^{13}C NMR ($CDCl_3$) 177.0, 136.4, 130.5, 60.4, 50.8, 47.7, 33.8, 23.4; IR (KBr) 3100, 2900, 1850, 1783, 1770, 1481, 1471, 1358, 1332, 1307, 1250; MS, *m/z* (%) 215 (4.3), 214 (35.6), 178 (30.9), 169 (50.2), 141 (41.6), 115 (40.9), 105 (41.4), 92 (30.6), 66 (100). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.16; H, 5.73.

On further elution several mixed fractions were obtained followed by the pure major adduct ***anti*-tetracyclo-[6.2.2.1^{3,6}.0^{2,7}]-trideca-4,9-diene-*exo*-2,7-dicarboxylic anhydride (12),**[24] sublimes 108 °C (petroleum ether); ^{1}H NMR ($CDCl_3$) δ 6.30 (m, 4H, olefinic), 3.15–2.92 (m, 4H, bridgehead), 1.72–1.55 (m, 2H, CH_2), 1.34–1.23 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) 174.8, 139.6, 132.6, 62.2, 50.1, 48.9, 34.2, 22.8; IR (KBr) 2900, 2800, 1851, 1806, 1776, 1460, 1263; MS, *m/z* (%) 215 (12.5), 214 (100), 170 (37.6), 169 (34.5), 141 (15.7), 115 (25.0), 92 (18.8), 65 (15.7). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.28; H, 5.72.

Hydrolysis of Anhydride 13. Aqueous potassium hydroxide (73 mg, 1.3 mmol in 0.5 mL H_2O) was added to a stirred solution of anhydride **13** (150 mg, 0.62 mmol) in ethanol (10 mL). The mixture was heated under reflux under nitrogen for 2 h. The solvents were removed *in vacuo*, the solid residue was dissolved in water (3 mL), concentrated HCl was added dropwise until the mixture became acidic, the precipitate of diacid **14** was extracted into dichloromethane (5 × 5 mL), and the extracts were washed with water (15 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The white solid was recrystallized from ether/petroleum ether to give pure diacid **14**: 123 mg (76%), mp 132–133 °C dec; ^{1}H NMR (DMSO-d_6) δ 12.2 (br s, 2H, OH), 5.63 (m, 4H, olefinic), 3.07 (m, 2H, bridgehead), 2.80 (m, 2H, bridgehead), 2.31–1.80 and 1.20–0.70 (m, 6H, CH_2); ^{13}C NMR (DMSO-d_6) 176.61, 138.18, 131.94, 57.42, 53.54, 49.68, 36.99, 23.49; IR (KBr) 3600–2400, 1693, 1465, 1399, 1334, 1260, 1161, 1103, 1054; MS, *m/z* (%) 214 (4.5), 169 (5.3), 141 (6.8), 115 (5.7), 105 (6.6), 104 (37.7), 92 (4.5), 76 (35.6), 66 (100); HRMS (CI, M + 1) calcd for $C_{15}H_{17}O_4$ 261.1127, found 261.1128.

Iodolactonization of Diacid 14. A solution of the diacid **14** (150 mg, 0.58 mmol), potassium carbonate (5 mL of 10% solution in H_2O), potassium iodide (1 g, 6 mmol), and iodine (0.5 g, 3.9 mmol) in water (3 mL) was warmed with swirling on a steam cone. After 30 min the cooled mixture was acidified (HCl) and extracted with ether (3 × 10 mL). The extracts were washed with water (20 mL), dried ($MgSO_4$), and evaporated *in vacuo* to give a mixture of the mono- and bis-lactones **17** and **18**. IR confirmed the formation of lactones, and mass spectrometry clearly supported this assignment, including the observation of molecular ions for both **17** and **18**. IR (KBr) 3500–2800, 2959, 2928, 1855, 1825, 1774, 1728, 1697, 1460, 1242, 1219, 1037, 1014, 945; MS (methane CI) 387 (M + 1, 17), 259 (M + 1, 18), for **17**, fragments at M – OH, M – COOH, M – I, M – I, OH, M – I, CO; for **18**, fragments at M – CO, M – COO.

Hydrogenation of Adduct 12. A solution of the major adduct **12** (500 mg, 2.1 mmol) in ethyl acetate (20 mL) was subjected to catalytic (5% Pd on C, 25 mg) hydrogenation at 40 psi on a Parr shaker for 12 h. The mixture was filtered through a Celite pad and the filtrate evaporated *in vacuo*. The resulting white solid

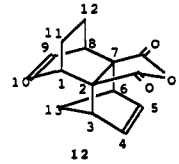
(20) Sheldrick, G. M. (1986). SHELXS Program for crystal structure determination. Institute fur Anorganische Chemie der Universitat, Tammannstrabe 4, D-3400 Gottingen, Federal Republic of Germany.

(21) Sheldrick, G. M. (1976). SHELX76. Program for Crystal Structure Determination. Univ. of Cambridge, England.

(22) The authors have deposited atomic coordinates for **12** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(23) Abbott, T. W.; Arnold, R. T.; Thompson, R. B. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 10.

(24) A note on nomenclature: *anti* refers to the relative orientation of the etheno bridges and *endo* and *exo* refer to the orientation of the anhydride moiety relative to the bicyclo[2.2.2]octene nucleus.



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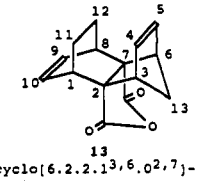
anti-tetracyclo[6.2.2.1^{3,6}.0^{2,7}]-trideca-4,9-diene-exo-2,7-dicarboxylic anhydride



13

anti-tetracyclo[6.2.2.1^{3,6}.0^{2,7}]-trideca-4,9-diene-endo-2,7-dicarboxylic anhydride

was purified by recrystallization (petroleum ether) to give **16**: 490 mg (96.4%), mp 229–230 °C; ^{1}H NMR ($CDCl_3$) δ 2.51 (m, 2H, bridgehead), 2.35 (dm, 1H, J =12 Hz, CH_2), 2.08 (m, 2H, bridgehead), 1.93–1.40 (m, 13H, CH_2); ^{13}C NMR ($CDCl_3$) 176.52, 60.39, 43.00, 40.32, 28.74, 27.41, 24.64, 22.19; IR (KBr) 2950, 1848, 1773, 1655, 1561, 1543, 1478, 1468, 1301, 1278, 1243, 1231; MS, m/z (%) 175 (6.4), 174 (44.6), 146 (100), 118 (89.1), 117 (23.1). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.36. Found: C, 73.08; H, 7.17.

Hydrogenation of Adduct 13. A solution of the minor adduct **13** (150 mg, 0.62 mmol) in ethyl acetate (10 mL) was subjected to catalytic (5% Pd on C, 50 mg) hydrogenation at 40 psi on a Parr shaker for 12 h. The mixture was filtered through a Celite pad and the filtrate evaporated *in vacuo*. The resulting white solid was purified by recrystallization (petroleum ether) to give **15**: 142 mg (92%), mp 257–258 °C; ^{1}H NMR ($CDCl_3$) δ 2.77 (m, 2H, bridgehead), 2.60–2.05 and 1.70–1.05 (m, 16H, remaining protons); ^{13}C NMR ($CDCl_3$) 178.04, 56.58, 46.17, 39.51, 28.59, 26.82, 24.52, 22.83; IR (KBr) 2954, 1858, 1767, 1654, 1501, 1489, 1226, 1206; MS, m/z (%) 174 (37.7), 146 (100), 118 (81.3), 91 (18.4). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.36. Found: C, 73.20; H, 7.17.

Partial Hydrogenation of Diacid 10. A solution of the diene **10** (8 g, 41.24 mmol) in ethyl acetate (25 mL) was subjected to catalytic (5% Pd on C, 160 mg) hydrogenation at 40 psi on a Parr shaker for 30 min. The mixture was filtered through a Celite pad and the filtrate evaporated *in vacuo*. The resulting white solid was purified by recrystallization (water) to give **bicyclo-[2.2.2]oct-2-ene-2,3-dicarboxylic acid (20)**, 7.8 g (96.5%), mp 153–154 °C; ^{1}H NMR ($CDCl_3$) δ 9.20 (br s, 2H, OH), 3.37 (m, 2H, bridgehead), 1.85–1.05 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$) 170.0, 144.0, 32.8, 24.9; IR (KBr) 3500, 3000, 1724, 1689, 1631, 1234; MS, m/z (%) 180 (18.9), 179 (100), 168 (11), 153 (19), 134 (10.2), 124 (27), 79 (30.4).

Bicyclo[2.2.2]oct-2-ene-2,3-dicarboxylic Anhydride (19). A stirred solution of diacid **20** (3 g, 15.31 mmol) in acetic anhydride (18.7 g) was kept at 100 °C under nitrogen for 1 h. The solvent was removed *in vacuo*, the resulting light-brown solid was recrystallized (petroleum ether) to give anhydride **17**, 2.4 g (88%), mp 152–153 °C; ^{1}H NMR ($CDCl_3$) δ 3.22 (m, 2H, bridgehead), 1.70 (m, 4H, CH_2), 1.25 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) 182.3, 152.7, 28.3, 25.4; IR (KBr) 2900, 1843, 1767; MS, m/z (%) 179 (3.7), 150 (100), 134 (83.4), 106 (69.7), 91 (47.6), 78 (64), 63 (11.4). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.43; H, 5.12. Found: C, 67.60; H, 5.71.

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