usual manner.[19] Analyses were identical with those described above.

10-Methyl-1-tridecene (7, *R* and *S*). The carbinol 6 (*R* or *S*; 4.23 g, 19.95 mmol) was added at one time to a cooled (0–5 °C) solution of PPh_3Br_2 (from 6.3 g, 24 mmol, of PPh_3 and 3.85 g, 24 mmol, of Br_2) in CH_2Cl_2 (40 mL). The resulting mixture was allowed to stir without external cooling for 2 h. Methanol (1 mL) was added to discharge the excess PPh_3Br_2, and the solvent was stripped. The residue was triturated with hexane and filtered. The filtrate was concentrated, and the oily residue was then filtered through silica gel (10 g) with pentane (100 mL). Removal of the solvent gave the crude alkyl bromide (>95% GLC pure) quantitatively. Foaming prevented distillation: IR 3080, 990, 910 cm^{-1} ($CH{=}CH_2$); NMR δ 0.89 (brt, 3 H, CH_3CH_2), 2.05 (m, 2 H, $CH_2C{=}$), 3.43 (d, 2 H, J = 6.9, $CHCH_2Br$), 4.9 and 5.8 (m, 3 H, $CH{=}CH_2$); CIMS, m/e 195 (P + 1 - Br). The crude bromide (4.9 g, 17.8 mmol) was treated with commercial $LiEt_3BH$ (38 mL of a 0.95 M solution) in THF (20 mL) of 0–5 °C for 0.5 h and then without external cooling for another 1.5 h to ensure completion. The mixture was worked up oxidatively with 3 N NaOH (14 mL) and 30% H_2O_2 (14 mL) in the usual way.[13] Extraction with pentane, drying ($MgSO_4$), and concentrating provided a mixture (ca. 4:1) of the alkene 7 and an alcohol, 10-methyl-1-tridecanol. These were separated by chromatography on silica gel (10 g), the alkene eluting with pentene (foaming again rpevented distillation): 2.75 g (70% yield from **6b**); IR 3080, 990, 910 cm^{-1} ($CH{=}CH_2$); NMR δ 0.87 and 0.88 (overlapped d and t, 3 H each, CH_3CH_2 and CH_3CH), 2.04 (m, 2 H, $CH_2C{=}$), 4.9 and 5.8 (m, 3 H, $CH{=}CH_2$), CIMS, m/e 197 (P + 1). Elution with 1:1 EtOAc/hexane gave the alcohol byproduct (identical with a sample prepared by hydroborating–oxidizing racemic 7 (1.05 g, 20%): bp 98–100 °C (0.1 mm); IR 3640 cm^{-1}; NMR δ 0.85 (d, 3 H, J = 7 Hz, CH_3CH), 0.88 (t, 3 H, J = 7 Hz, CH_3CH_2), 3.64 (t, 2 H, J = 6.8 Hz, CH_2CH_2OH); CIMS, m/e 214 (P + 1), 197 (P + 1 - 18).

10-Methyl-2-tridecanol (8, *R* and *S*). The alkene 7 (*R* or *S*, 0.97 g, 4.95 mmol) in THF (9 mL) was added dropwise to a stirred, cooled (0–5 °C) solution of $Hg(OAc)_2$ (1.84 g, 5.4 mmol) in H_2O (9 mL). The resulting mixture was stirred for 1.5 h beyond discharge of its yellow color. To the mixture was added 3.0 N NaOH (17 mL) and then]7 mL of 3.0 N NaOH that was 1.0 N in $NaBH_4$, the latter with ice cooling of the reaction mixture. The final mixture was stirred another 15 min without cooling, diluted with brine, and extracted with hexane. The extract was dried ($MgSO_4$) and concentrated. The residue was distilled to give product: 1.0 g (95%); bp 63–65 °C (0.04 mm); IR 3640 cm^{-1}; NMR δ 3.78 (m, 1 H, CHOH); CIMS, m/e 197 (P + 1 - 18). These alcohols (*R*)- and (*S*)-8 were identical with those prepared by an independent route.[5]

10-Methyl-2-tridecanone (1, *R* and *S*). The alcohol 8 (*R* or *S*; 0.45 g, 2.1 mmol) was dissolved in 5 mL of ether to which was added a solution of $Na_2Cr_2O_7$ (0.4 g, 1.3 mmol) and H_2SO_4 (0.3 mL, 5.0 mmol) in 2 mL or H_2O. The resulting mixture was stirred for 2 h and then worked up in the usual manner. The ketone was distilled bulb-to-bulb to give (*R*)-1 (and (*S*)-1): 0.35 g (78%): bath temperature 180 °C (30 mm); $[\alpha]^{24}_D$ for (*R*)-1 -1.71° (*c* 9.35, $CHCl_3$); IR 1720 cm^{-1}; NMR δ 2.13 (s, 3 H, $CH_3C{=}O$), 2.42 (t, 2 H, J = 7 Hz, $CH_2CH_2C{=}O$); CIMS, m/e 213 (P + 1).

10-Methyl-1-dodecanol (9, *R* and *S*). The alcohol **6a** (*R* or *S*; 3.0 g, 15.1 mmol) was treated with PPh_3Br_2 in CH_2Cl_2 as described for **6b** above. The crude bromides (>95% GLC pure) gave equivalent spectral data and were employed directly for the hydroboration step. A solution of disiamylborane was prepared from 3-methyl-2-butene (3.85 mL, 36.2 mmol) and commercial BH_3·THF (18.1 mL of a 1.0 M solution) in the usual manner.[20] The bromoalkene [(*R*)- or (*S*)-2-ethyl-10-undecen-1-yl bromide, 15.1 mmol] was added dropwise as a solution in THF (5 mL), maintaining the mixture at 0–5 °C for 1 h. Then $LiEt_3BH$ (47.7 mL of a 0.95 M solution) was added at one time and the mixture allowed to stir overnight. The mixture was worked up oxidatively by sequentially adding 3.0 N NaOH (23 mL) and 30% H_2O_2 (23 mL). The mixture was kept at 40 °C for 0.5 h, diluted with H_2O, and extracted with hexane. The extract was dried ($MgSO_4$) and concentrated. The product was distilled through a Vigreaux column to give recovered alkene **6a** [0.25 g (9.1%); bp 50–52 °C (0.025 mm)] and (*R*)- or (*S*)-**9**: 1.73 g (57.7%); bp 84–86 °C (0.04 mm). The alcohols were identical with the racemic alcohol previously reported.[9]

10-Methyl-1-dodecanol Acetate (2, *R* and *S*). The alcohols **9** (*R* or *S*) were acetylated with Ac_2O in pyridine as previously described.[9] The product acetates were purified by passage through silica gel (20 g/1 g of acetate), eluting with 5% EtOAc/hexane. Bult-to-bulb distillation gave samples of (*R*)-**2** [$[\alpha]^{24}_D$ -5.57° (*c* 21.8, $CHCl_3$)] and **2*S*** [$[\alpha]^{24}_D$ +5.60° (*c* 21.8, $CHCl_3$)]. The previously reported rotation for this acetate prepared from commercial citronellol was 4.85°.[21] It is now clear that bioassays were reported based the basis of ca. 86.6 ee.[22]

Registry No. (*R*)-1, 82621-53-2; (*S*)-1, 82621-54-3; (*R*)-2, 71777-34-9; (*S*)-2, 71777-35-0; (±)-3a, 82621-55-4; (±)-3a acid chloride, 82621-56-5; (±)-3b, 82638-73-1; (±)-3b acid chloride, 82621-57-6; (*R**,*S**)-4a, 82621-58-7; (*R**,*R**)-4a, 82621-59-8; (*R**,*S**)-4b, 825638-74-2; (*R**,*R**)-4b, 82638-75-3; (*R**,*S**)-5a, 82621-60-1; (*R**,*R**)-5a, 82621-61-2; (*R**,*S**)-5b, 82621-62-3; (*R**,*R**)-5b, 82621-63-4; (*R*)-6a, 82621-64-5; (*S*)-6a, 82621-65-6; (*R*)-6b, 82621-66-7; (*S*)-6b, 82621-67-8; (*R*)-7, 82621-68-9; (*S*)-7, 82621-69-0; 8, 82621-70-3; (*R*)-9, 71777-32-7; (*S*)-9, 71777-33-8; (*S*)-α-methylbenzylamine, 2627-86-3; (*R*)-α-methylbenzylamine, 3886-69-9; ethylene oxide, 75-21-8; (*R*)-2-propyl-10-undecen-1-yl bromide, 82621-71-4; (*S*)-2-propyl-10-undecen-1-yl bromide, 82621-72-5; 10-methyl-1-tridecanol, 82621-73-6; (*R*)-2-ethyl-10-undecen-1-yl bromide, 82621-74-7; (*S*)-2-ethyl-10-undecen-1-yl bromide, 82621-74-7; disiamylborane, 1069-54-1; 10-undecenoic acid, 112-38-9.

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Synthesis and Diels–Alder Reactivity of 7-Isopropylidene-2,3,5,6-tetramethylenebicyclo-[2.2.1]heptane (7,7-Dimethyl[2.2.1]hericene)[1]

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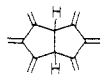
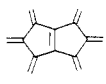
The 2,3,5,6-tetramethylenebicyclo[2.2.*n*]alkanes **1–5** and the 2,3,5,6,7,8-hexamethylenebicyclo[2.2.2]octane (**6**,[2,3] [2.2.2]hericene[1]) have interesting properties. Evidence for transannular interactions between the homoconjugated exocyclic *s-cis*-butadiene functions were found in the

(1) The shortened name [*l.m.n*]hericene is used for bicyclo[*l.m.n*]alkanes with $l + m + n$ methylidene groups,[2,3] after the latin name hericeus for hedgehog. We thank Professor H. Wyler for suggesting us this resemblance. Substituents at the bridgehead atoms are numbered 1 and $l + 2$, those at the exocyclic centers are numbered according to the positions of the connecting atoms, being part of the bicyclic skeleton. This nomenclature appears to us to be shorter than the bicyclo[*l.m.n*]-radialene nomenclature proposed by Hart et al.[4] Accordingly, the following compounds are named as shown. For the [*n*]radialene nomen-



[3.3.0]hericene



1,5-dehydro[3.3.0]hericene

clature, see: Weltin, E.; Gerson, F.; Murrel, J. N.; Heilbronner, E. *Helv. Chim. Acta* **1961**, *45*, 1400. Koeberich, G; Heinemann, H.; Zuendorf, W. *Tetrahedron* **1967**, *23*, 565 and references cited therein.

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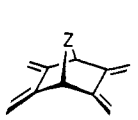
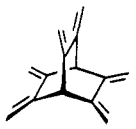
0022-3263/82/1947-3796$01.25/0

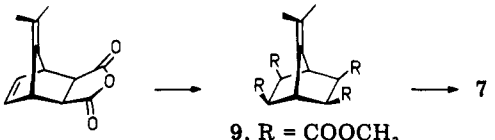


1, Z = O
2, Z = CH_2
3, Z = CH=CH
4, Z = CH_2CH_2
5, Z = OCH-CH
7, Z = $C=C(CH_3)_2$



6

UV[3,5-8] and photoelectron spectra.[2,9] The first equivalent of a strong dienophile adds to 1–3 and 5 more rapidly than the second equivalent, thus making these polyenes very attractive starting material for the preparation of polycyclic, polyfunctional systems by two successive Diels–Alder additions with different dienophiles. The ether tetraene 1 has been used to prepare various anthracycline derivatives.[10] We report now the synthesis and a few properties of 7-isopropylidene-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane (7).[11]



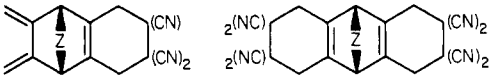
8

9, R = $COOCH_3$
10, R = CH_2OH
11, R = CH_2Cl

Under our conditions[5b,6b] (3–4 atm of CO, absolute MeOH, 4 molar equiv of $CuCl_2$, catalytical amount of Pd/C), the double carbomethoxylation[12] of the maleic anhydride adduct of 6,6-dimethylfulvene (8)[13] was selective at the endocyclic C(5,6) double bond and yielded the all-exo tetraester 9 (82%). Treatment with $LiAlH_4$ in THF gave the tetrol 10 (78%) which was transformed into the tetrachloride 11 (47%) upon reaction with $SOCl_2$ and pyridine. Quadruple elimination of HCl (*t*-BuOK, THF) furnished 7,7-dimethyl[2.2.1]hericene (7, 78%).

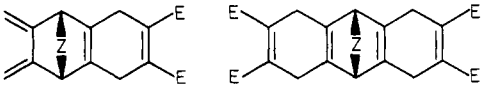
The structures of 9–11 and 7 were given by their spectral data, combustion analysis, mode of formation, and reactivity. The all-exo configuration of the substituents in 9–11 was confirmed by the absence of vicinal coupling between the bridgehead HC(1,4) and HC(2,3,5,6) protons.[14] Except for a small hyperchromic effect, the UV absorption spectrum of 7 [λ_{max} 235 nm (ϵ 18600)] was analogous to that of the tetraene 2 [λ_{max} 235 nm (ϵ 12500, isooctane)].[6] Contrary to the 7-isopropylidene-5,6-dimethylenebenzobicyclo[2.2.1]hept-2-ene reported recently,[15] 7 (as 1–6) did not absorb above 280 nm.

In the presence of 1 molar equiv of ethenetetracarbonitrile (tetracyanoethylene, TCNE), 7 yielded the monoadduct 12 that could be isolated pure. In the presence of



12, Z = $(CH_3)_2C=C$
16, Z = O
17, Z = CH_2

13



14 (E = $COOCH_3$) 15 (E = $COOCH_3$)

more than 2 molar equiv of TCNE the bis adduct 13 was formed. No other product could be detected. Similarly, 7 added to dimethyl acetylenedicarboxylate (DMAD) and gave the corresponding monoadduct 14 and bisadduct 15.

The second-order rate constants of the cycloaddition of TCNE to 7 (k_1) and to 12 (k_2) measured at various temperatures allowed the evaluation of the activation parameters which are reported in Table I together with those obtained for the additions of TCNE to the tetraenes 1 and 2 and to their monoadducts 16 an 17, respectively.[16]

The reactions were followed for at least 3 half-lives and were found to obey pseudo-first-order rate laws for the disappearance of the TCNE–toluene complex (λ_{max} 405 nm) when a 15–500-fold excess of the pentaene 7 or the tetraene 12 was used. There was no observable effect on the second-order rate constant due to changes of the initial concentration of the cycloaddents ([TCNE] = 1.0–4.0) × 10^{-4} M; ["diene"] = 3.5 × 10^{-3}–5 × 10^{-2} M) or due to changes in their initial concentration ratios.

As for the tetraenes 1 (k_1/k_2 = 375) and 2 (k_1/k_2 = 364), a relatively large rate ratio of k_1/k_2 = 250 was evaluated at 25 °C for the TCNE addition to 7 vs. 12 in toluene. Thus, the exchange of the $H_2C(7)$ bridge in 2 by a $(CH_3)_2C=C$ bridge (7) does not affect significantly the Diels–Alder properties of the 2,3,5,6-tetramethylenenorbornane systems. Several factors can be responsible of the observed effect ($k_1 \gg k_2$). As in the case of the cycloadditions of 1 and 2, it is not excluded that the change in $\Delta H^{\ddagger}$ might be due to a differential effect in the homoconjugative and hyperconjugative interactions between exocyclic dienes and endocyclic double bonds and/or to the nitrile inductive effect which would make the monoadduct 12 less reactive than 7 toward TCNE. A change in the exothermicities of the reaction 7 + TCNE → 12 vs. 12 + TCNE → 13 could also affect the $\Delta H^{\ddagger}$ term.

Experimental Section

General Methods: melting point (not corrected), Tottoli apparatus; UV spectra, Pye Unicam SP 1800 instrument [λ_{max}, nm (ϵ, mol^{-1} cm^{-1}), sh = shoulder]; IR spectra ($\bar{\nu}$, cm^{-1}), Beckman IR-4230 spectrometer; ^1H NMR spectra, Bruker WP 80 CW [δ(apparent multiplicity, apparent coupling constants $J_{H,H}$ in hertz, number of protons or tentative attributions); s = singlet, d =

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(11) To our knowledge, the [2.2.2]hericene 6 was the first case of a stable "permethylene"-substituted bicyclic system ever isolated, and 7 is the second example.

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(16) Preliminary kinetic data for the cycloadditions of DMAD to 7 and 14 gave $k_1 \simeq 179 \times 10^{-6}$ mol^{-1} s^{-1} and $k_2 \simeq 19 \times 10^{-6}$ mol^{-1} s^{-1}, respectively, at 38.9 °C in $CDCl_3$ ($k_1/k_2 \simeq 9.4$ by ^1H NMR). The additions of maleic anhydride were stereoselective; the structures of the corresponding mono- and bisadducts are under investigation.

Table I. Kinetic Data for Cycloadditions of 7 and 12 to TCNE in Toluene

"diene"	k^{II}, 10^4 mol^{-1} s^{-1} (statistical std dev,[a] temp of measurement ±0.1 K)					$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$10^4 k^{II}$ (298 K),[b] mol^{-1} s^{-1}
7 (k_1)	276 (±6, 281.7)	607 (±9, 293.6)	1140 (±20, 302.6)	2090 (±30, 312.3)	3048 (±100, 320.0)	11.3 ± 0.6	−25.6 ± 2.1	850 ± 40
12 (k_2)	42.2 (±1, 330.0)	68.8 (±1.5, 336.7)	159 (±5, 348.0)	223 (±3, 355.6)	338 (±8, 361.4)	14.8 ± 0.9	−24.6 ± 2.8	3.4 ± 0.7
1 (k_1)						14.8 ± 0.7	−26.4 ± 2.3	1.5 ± 0.04
16 (k_2)						17 ± 1.5	−30 ± 4	0.004 ± 0.0002
2 (k_1)						12.2 ± 0.5	−24.8 ± 1.6	255 ± 5
17 (k_2)						14.1 ± 1.0	−30.1 ± 3.4	0.7 ± 0.02

[a] For six to eight independent measurements with three or four differents solutions of the "dienes" and TCNE. [b] Interpolated or extrapolated.

doublet, t = triplet, q = quadruplet, m = multiplet, br = broad, δ(Me$_4$Si) 0.0]; ^{13}C NMR spectra, Bruker WP 60 spectrometer (15.08 MHz, spectrum width 3750 Hz, 4096 points FT mode) [δ(multiplicity, (considering also the long-range C–H coupling), $^1J_{C,H}$ in hertz)]; mass spectrum (MS), Hewlett-Packard HP 5980 A spectrometer [m/z (relative intensity)] in electron-ionization mode, 70 eV. Elemental analysis were performed by R. Ehrisman AG, Windisch, Switzerland, or by I. Beetz, Kronach, Germany.

Tetramethyl 7-Isopropylidenebicyclo[2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetracarboxylate (9). 6,6-Dimethylfulvene–maleic anhydride adduct (8;[13] 15 g, 0.073 mol), dry $CuCl_2$ (49.4 g, 0.367 mol), 10% Pd/C (1.8 g, 1.75 mmol), and anhydrous methanol (250 mL) were placed under N_2 in a 1-L Pyrex flask (Parr apparatus). After careful degassing, the mixture was pressurized with CO (3 atm) and stirred for 48 h at 20 °C; the CO pressure was maintained at 2–4 atm. After removal of the solvent in vacuo, the residue was triturated with $CHCl_3$ (150 mL) and water saturated with $NaHCO_3$ (150 mL). The solid was removed by filtration (Celite). The organic layer was washed with saturated aqueous $NaHCO_3$ solution (3 × 40 mL) and dried ($MgSO_4$). After evaporation of the solvent, the crude tetraester 9 was obtained as a white solid that was recrystallized from ether: 22.2 g (82%); colorless crystals; mp 108–110 °C; UV (EtOH, 95%) 270 (160); IR (KBr) 2970, 1750, 1440, 1375, 1340, 1300, 1285, 1275, 1270, 1240, 1190, 1160, 1030, 930, 890, 850, 770; ^{1}H NMR ($CDCl_3$) 3.60 (s, 12 H, OCH_3); 3.30 (s, 2 H, HC(1.4)), 2.80 (s, 4 H, HC-(2,3,5,6)), 1.75 (s, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) 171.68 (s, CO), 133.07 (m, C(7)), 124.51 (m, C=C(7)), 51.47 (q, 148, OCH_3), 49.16 (dm, 137, C(2,3,5,6)), 42.67 (dd, 148, $^3J_{C,H}$ = 8, C(1,4)), 20.57 (q, 126, $(CH_3)_2C$=C(7)); MS, 368 (3, M^+), 337 (9), 308 (6), 276 (6), 249 (21), 248 (32), 149 (100). Anal. Calcd for $C_{18}H_{24}O_8$ (mol wt 368.39): C, 58.69; H, 6.57. Found: C, 58.66; H, 6.54.

7-Isopropylidenebicyclo[2.2.1]heptane-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetramethanol (10). To a vigourously stirred suspension of $LiAlH_4$ (4.64 g, 0.122 mol) in anhydrous THF (150 mL) maintained at 0 °C and under N_2 was added a solution of the tetraester 9 (15 g, 0.04 mol) in anhydrous THF (50 mL) dropwise. At the end of the addition, the mixture was allowed to warm to 20 °C and then was heated under reflux for 3.5 h. After the mixture cooled to 20 °C, water (16 mL) was added dropwise, and the mixture was heated under reflux for 1 h and immediately filtered through silica gel (80–100 g). The solid (SiO_2 + aluminum salts) was extracted with boiling ethanol (4 × 180 mL, boiling for 1 h each time). The extracts were filtered through silica gel also. After evaporation of the solvent, the crude tetrol 10 was recrystallized from methanol (15 mL), yielding 8 g (78%) of colorless crystals: mp 213–215 °C; UV (EtOH, 95%) 270 (20); IR (KBr) 3260 (br), 2920, 2860, 1520, 1480, 1450; ^{1}H NMR (CD_3OD) 4.72 (s, OH), 3.65–3.17 (m, CH_2OH), 2.45 (s, 2 H, HC(1.4)), 2.05 (m, 4 H, HC(2,3,5,6)), 1.67 (s 6H, CH_3); ^{13}C NMR (Me_2SO-d_6) 138.1 (m, C(7)), 119.0 (m, C=C(7), 60.6 (t, 139, CH_2OH), 46.8 (dm, 134, C(2,3,5,6)), 42.8 (dm, 142, C(1,4)), 20.76 (q, 126, $(CH_3)_2C$=C(7)); MS, 256 (5, M^+), 223 (40), 207 (5), 205 (4), 193 (4), 159 (29), 150 (29), 121 (55), 119 (57), 107 (53), 105 (60), 91 (100). Anal. Calcd for $C_{14}H_{24}O_4$ (mol wt 256.34): C, 65.60; H, 9.44. Found: C, 65.42; H, 9.33.

7-Isopropylidene-2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetrakis(chloromethyl)bicyclo[2.2.1]heptane (11). To a stirred mixture of anhydrous pyridine (9.87 g, 0.125 mol) and freshly distilled $SOCl_2$ (18.56 g, 0.156 mol) maintained at 0 °C under N_2 was added the tetrol 10 (8 g, 0.0312 mol) portionwise. At the end of the addition, the mixture became viscous; $SOCl_2$ (30.8 g, 0.259 mol) was added slowly. The mixture was allowed to warm to 20 °C. It was then stirred at 60 °C for 2.5 h. After the mixture was cooled to 20 °C, $CHCl_3$ (30 mL) was added. The excess of $SOCl_2$ was destroyed by dropwise addition of water (20 mL) under vigourous stirring, external cooling, and reflux. The organic layer was washed with water (2 × 10 mL), 2 N HCl (2 × 10 mL), saturated aqueous $NaHCO_3$ (2 × 10 mL), and water (2 × 10 mL) and dried ($MgSO_4$). After solvent evaporation, the crude tetrachloride 11 was obtained as a white powder (after washing with ether), pure enough for the next step. Recrystallization from $CHCl_3$ gave 4.8 g (47%) of colorless crystals: mp 116–116.5 °C; UV (EtOH, 95%) end absorption, ϵ_{230} 30; IR (KBr) 3010, 2970, 2940, 2880, 1450; ^{1}H NMR ($CDCl_3$) 3.55 (m, 4 H, H_2CCl), 3.25 (m, 4 H, H_2CCl), 2.90 (s, 2 H, HC(1,4)), 2.27 (m, 4 H, HC(2,3,5,6)), 1.72 (s, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) 134.22 (m, C(7)), 125.54 (m, C=C(7)), 47.40 (dm, 133, C(2,3,5,6)), 45.58 (dm, 144, C(1,4)), 43.58 (td, 150, $^3J_{C,H}$ = 3, CH_2Cl), 20.81 (qq, 126, $^3J_{C,H}$ = 4, $(CH_3)_2C$=C(7)); MS, 334 (2), 332 (7), 330 (13), 328 (11, M^+), 283 (31), 281 (94), 279 (100). Anal. Calcd for $C_{14}H_{20}Cl_4$ (mol wt 330.13): C, 50.94; H, 6.11; Cl, 42.96. Found: C, 50.88; H, 6.09; Cl, 43.03.

7,7-Dimethyl[2.2.1]hericene (7). Solid *t*-BuOK (8.1 g, 0.072 mol) was added in small portions (ca. 30 min) to a stirred solution of the tetrachloride 11 (2.5 g, 7.5 mmol) in anhydrous THF (50 mL) cooled to 0–10 °C. The mixture was stirred at 20 °C for 1 h and then was heated under reflux for 2.5 h. After the mixture was cooled to 20 °C, water (25 mL) was added until complete dissolution of KCl. The mixture was extracted with petroleum ether (4 × 50 mL). The organic extract was washed with water (3 × 50 mL) and dried ($MgSO_4$). After evaporation of the solvent, the crude pentaene 7 was crystallized from EtOAc: 1.1 g (78%); white crystals; mp 188–189 °C dec; UV (EtOH, 95%) 229 (sh, 19100), 235 (20800), 242 (sh, 19200), 257 (sh, 9200); UV (isooctane) 228 (sh, 17000), 235 (18600), 242 (sh, 16440), 255 (sh, 7000); IR (KBr) 3080, 3010, 2980, 2940, 2980, 2940, 2920, 1780, 1635, 1440, 1370, 1220, 1160, 1080, 880, 790, 770, 690; ^{1}H NMR ($CDCl_3$) 5.15 and 4.92 (s, 2 × 4 H, H_2C=C), 3.82 (s, 2 H, HC(1,4)), 1.65 (s, 6 H, $(CH_3)_2C$=C(7)); ^{13}C NMR ($CDCl_3$) 148.6 (m, C(2,3,5,6)), 137.5 (m, C(7)), 116.9 (m, C=C(7)), 100.7 (t, 159, CH_2=C(2,3,5,6)), 56.3 (dm, 144, C(1,4)), 20.0 (q, 126, $(CH_3)_2C$=C(7)); MS, 185 (8), 184 (37, M^+), 169 (100), 154 (37), 153 (34), 141 (32), 129 (25), 128 (36), 115 (50), 105 (9), 91 (42). Anal. Calcd for $C_{14}H_{16}$ (mol wt 184.28): C, 91.25; H, 8.75. Found: C, 91.21; H, 8.78.

11-Isopropylidene-9,10-dimethylenetricyclo[6.2.1.0^{2,7}]undec-2(7)-ene-4,4,5,5-tetracarbonitrile (12). A mixture of the pentaene 7 (50 mg, 0.27 mmol) and TCNE (35 mg, 0.27 mmol) in $CHCl_3$ (2 mL) was stirred at 20 °C for 3 h. After the mixture was cooled to −20 °C, the monoadduct 12 was collected by filtration: Yield 78 mg (92%); colorless crystals; mp 244–245 °C dec; UV (EtOH, 95%) 225 (13800), 237 (sh, 12300), 242 (sh, 11400), 254 (sh, 8500); UV (dioxane 230 (5950), 239 (sh, 15000);

IR (KBr) 3100, 3020, 3000, 2960, 2930, 2860, 2260, 1640, 1435; ^{1}H NMR (CD_3COCD_3) 5.17 and 5.01 (s, 2 × 2 H, H_2C=C (9,10)), 3.98 (s, 2 H, HC(1,8)), 3.67 and 3.36 (d, 17, 2 × 2 H, H_2C(3,6)), 1.60 (s, 6 H, $(CH_3)_2C$=C(11)); ^{13}C NMR (CD_3CN) 147 (m, C(11)), 143.7 (m, C(9,10)), 137.2 (m, C(2.7)), 114.9 (m, C=C(11)), 112.5 (m, CN), 112.0 (m, CN), 102.6 (t, 159, CH_2=C(9,10)), 55.1 (dm, 152, C(1,8)), 40.2 (m, C(4,5)), 32.5 (t, 140, C(3,6)), 19.7 (qq, 126, $^3J_{C,H}$ = 4.5, $(CH_3)_2C$=C(11)); MS, 313 (20), 312 (12, M^+), 298 (34), 297 (100), 169 (98), 156 (30), 153 (30), 141 (28), 132 (94). Anal. Calcd for $C_{20}H_{16}N_4$ (mol wt 312.375): C, 76.90; H, 5.16; N, 17.94. Found: C, 77.37; H, 5.16; N, 17.88.

15-Isopropylidenetetracyclo[6.6.1.0^{2,7}.0^{9,14}]pentadeca-2(7),9(14)-diene-4,4,5,5,11,11,12,12-octacarbonitrile (13). A mixture of **7** (50 mg, 0.27 mmol) and TCNE (70 mg, 0.54 mmol) in acetone (2 mL) was stirred at 20 °C for 12 h. The bisadduct **13** was precipitated by addition of a few drops of pentane and cooling to −10 °C: yield 80 mg (67%); colorless crystals; mp 268–269 °C dec; UV (EtOH, 95%) final absorption (ϵ_{230} 5200); IR (KBr) 3030, 2990, 2950, 2930, 2880, 2860, 2260, 1615, 1440; ^{1}H NMR (CD_3COCD_3) 4.3 (s, 2 H, HC(1,8)), 3.75 (br s, 8 H, H_2C(3,6,10,13)), 1.50 (s, 6 H, $(CH_3)_2C$=C:15)); ^{13}C NMR (CD_3CN) 160 (m, C(15)), 143.1 (m, C(2,7,9,14)), 112.5 (m, CN), 112.1 (m, CN), 100.5 (m, C=C(15)), 55.8 (d, 152, C(1,8)), 40.1 (m, C-(4,5,11,12)), 33.8 (t, 140, C(3,6,10,13), 22.6 (qq, 126, $^3J_{C,H}$ = 4, $(CH_3)_2C$=C(15)); MS, 441 (14), 440 (28, M^+), 398 (6), 375 (49), 297 (66), 169 (47), 107 (42), 105 (56), 91 (47), 67 (100). Anal. Calcd for $C_{26}H_{16}N_8$ (mol wt 440.468): C, 70.90; N, 3.66; N, 25.44. Found: C, 70.63; H, 3.84; N, 25.28.

Dimethyl 11-Isopropylidene-9,10-dimethylenetricyclo-[6.2.1.0^{2,7}]undeca-2(7),4-diene-4,5-dicarboxylate (14). A mixture of **7** (0.22 g, 1.2 mmol), dimethyl acetylenedicarboxylate (0.171 g, 1.2 mmol), and toluene (5 mL) was heated in a Pyrex tube sealed under vacuum to 60 °C for 2 h. After solvent evaporation, the crude adduct **14** was purified on a silica gel column (hexane/EtOAc, 3:1) and recrystallized from hexane/EtOAc, yielding 0.305 g (78%) of colorless crystals: mp 112–113 °C; UV (dioxane) 238 (14 030), 244 (13 700), 255 (sh, 10 680); UV (CH_3CN) 237 (13 300), 244 (13 050), 253 (sh, 9850); IR (KBr) 3010, 2990, 2980, 1740, 1725, 1640, 1430, 1300, 1270, 1250, 1245, 1150, 890; ^{1}H NMR ($CDCl_3$) 5.05 and 4.88 (s, 2 × 2 H, H_2C=C(9,10)), 3.75 (s, 6 H), 3.6 (s, 2 H, HC(1,8)), 3.1 (m, 4 H, H_2C(3,6)), 1.6 (s, 6 H, $(CH_3)_2C$=C(11)); ^{13}C NMR (CD_3CN) 169.3 (m, CO), 149.1 (m, C(11)), 145.5 (m, C(9,10)), 138.3 (m, C(2,7)), 134.3 (m , C(4,5)), 112.3 (m, C=C(11)), 100.8 (t, 158, H_2C=C(9,10)), 54.8 (dm, 150, C(1,8)), 52.9 (q, 146, CH_3OOC), 27.5 (t, 130, C(3,6)), 19.7 (qq, 126, $^3J_{C,H}$ = 4, $(CH_3)_2C$=C(11)); MS, 327 (13), 326 (59, M^+), 309 (28), 294 (100), 279 (85), 267 (24), 251 (23), 242 (14), 235 (32), 227 (26), 208 (45), 193 (47), 178 (29), 165 (32), 156 (31), 149 (41), 141 (27), 115 (25). Anal. Calcd for $C_{20}H_{22}O_4$ (mol wt 326.39): C, 73.60; H, 6.79. Found: C, 73,67; H, 6.74.

Tetramethyl 15-Isopropylidenetetracyclo[6.6.1.0^{2,7}.0^{9,14}]-pentadeca-2(7),4,9(14),11-tetraene-4,5,11,12-tetracarboxylate (15). A mixture of **7** (0.21 g, 1.14 mmol), dimethyl acetylenedicarboxylate (0.34 g, 2.4 mmol), and toluene (5 mL) was heated in a Pyrex tube sealed under vacuum to 60 °C for 24 h. After solvent evaporation, crude **15** was recrystallized from hexane/EtOAc (3:1), yielding 0.373 g (70%) of colorless crystals: mp 177–187 °C dec; UV (CH_3CN) final absorption (ϵ_{200} 23 100); IR (KBr) 3000, 2970, 2920, 2860, 2840, 1730, 1680, 1640, 1430, 1290, 1270, 1240, 1230, 1150, 1060; ^{1}H NMR ($CDCl_3$) 3.75 (s, 12 H), 3.65 (s, 2 H) 3.2 (m, 8 H), 1.45 (s, 6 H); ^{13}C NMR (CD_3CN) 169.5 (m, CO), 160.3 (m, C(15)), 143.9 (m, 2,7,9,14)), 134.5 (m, C(4,5,11,12)), 96.0 (m, C=C(15)), 54.6 (dd, 150, $^3J_{C,H}$ = 6, C(1,8)), 52.8 (q, 148, CH_3O), 29.8 (tm, 135, C(3,6,10,13)), 18.7 (qq 126, $^3J_{C,H}$ = 4, $(CH_3)_2C$=C(15)); MS, 469 (6), 468 (10, M^+), 466 (15), 450 (6), 435 (31), 407 (100), 377 (63), 348 (37), 318 (26), 215 (36), 202 (35), 59 (37). Anal. Calcd for $C_{26}H_{28}O_8$ (mol wt 468.505): C, 66.65; H, 6.02. Found: C, 66.76; H, 6.15.

For the kinetic measurements ref 17.

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Convenient Syntheses of 4,4-Dimethoxy Esters and Ketones[1]

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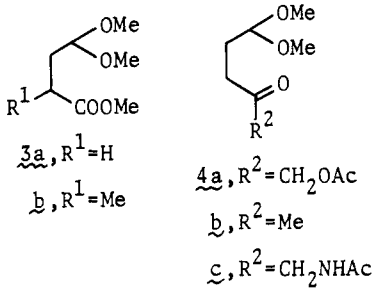
We have previously reported[2] a new synthetic method for the formation of unconventional nucleosides having oxacycloalkane substituents wherein [(trimethylsilyl)-oxy]alkanal dimethyl acetals (Me_3Si acetals, **1**) undergo a novel reaction with 2,4-bis[(trimethylsilyl)oxy]pyrimidines under Lewis acid catalyzed conditions (Scheme I). In connection with the above work, we required routes to 1,4-dicarbonyl compounds **3** and **4** which are key inter-



mediates for the preparation of the Me_3Si acetals.

The recent literature is replete with synthetic methods for formation of 1,4-dicarbonyl compounds since they are of extensive value for the syntheses of some natural products consisting of five-membered heterocycles such as pyrroles and furans as well as cyclopentenone ring systems.[3-10] We herein report a convenient synthesis of 4,4-dimethoxy esters **3** and ketones **4** based on electrochemical reactions of 2-substituted furans.

4,4-Dimethoxy Esters. It is well documented that the anodic oxidation of furans gives rise to the methoxylation at the 2- and 5-positions of the furan rings to provide the 2,5-dimethoxy-2,5-dihydrofurans.[11,12] Recently, Torii et al.[13] have developed a highly efficient procedure for either

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