

Titration 11. The Titrigraph was coupled by its flexible drive shaft to a 0.5-ml syringe which delivered the titrant into the stirred sample.

Relative basicity studies were conducted in a similar manner, using 10- to 11-ml samples of 0.003 *M* solutions of 17 and various amines in acetonitrile; the temperature was 23°. The acetonitrile was purified by treatment with sulfuric acid and benzene (to azeotrope any water), and then distillation through a column of packed helices; the fraction of bp 82° was collected and used. Perchloric acid (0.1 *N*) in glacial acetic acid was prepared as described in the literature,^{22b} and was used as the titrant. Titrations were made on the instrument described above. Titration curves and calculations were made in a similar manner, except that values obtained were subtracted from 14 to give "p*K*_B" values.

Registry No.—1, 1278-02-0; 2, 12119-11-8; 3, 12427-83-7; 4, 12427-86-0; 5, 12427-84-8; 6, 12427-87-1; 7,

12427-73-5; 9, 12427-74-6; 11, 12427-80-4; 12, 12427-89-3; 13, 12427-77-9; 14, 12427-81-5; 15, 12427-88-2; 16, 12427-75-7; 17, 12427-76-8; 18, 12427-82-6; 19, 12427-85-9; 20, 12427-78-0; 21, 12427-79-1; 22, 12427-72-4.

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The Bis Adducts of Dimethyl Acetylenedicarboxylate and Certain Furans

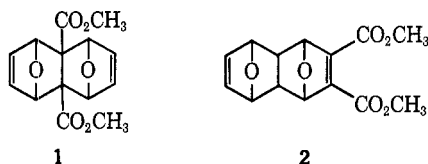
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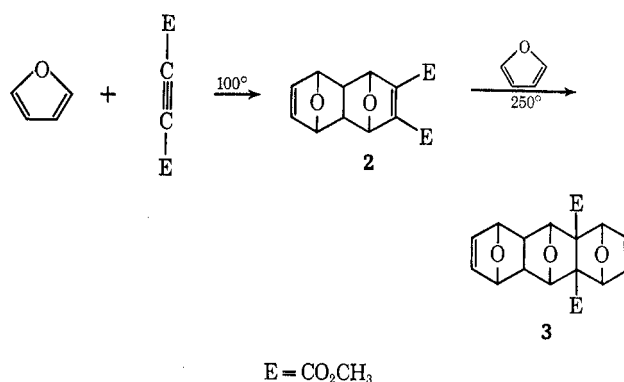
Received April 15, 1970

The structures of certain furan–dimethyl acetylenedicarboxylate bis-Diels–Alder adducts were determined by nmr spectroscopy. The reaction of furan with the acetylenic ester at room temperature led to the (exo–endo) bis adduct 4, whereas 2,5-dimethylfuran did not form a bis adduct. At 100° furan reacted with the acetylenic ester to give (exo–exo) bis adduct 7, (exo–endo) bis adduct 8, and tris adduct 9. Under similar conditions 2,5-dimethylfuran reacted with the acetylenic ester to give the (exo–endo) bis adduct 11. The parent cyclic ether 17 of 11 was prepared and shown to have the (exo–endo) configuration. Selective hydrogenation of 11 led to dihydro adduct 22. Acid treatment of 22 gave dimethyl 2,5-dimethylfuran-2,3-dicarboxylate and *p*-xylene while pyrolysis of 22 led to dimethyl 2,5-dimethylfuran-2,3-dicarboxylate, 2,5-dimethylfuran, and ethylene. The two (exo–endo) trimethyl bis adducts 19 and 21 were also prepared.

In 1931 Diels and Alder² isolated a furan–dimethyl acetylenedicarboxylate adduct with a mol ratio of 2:1. They suggested that adduct 1 was the product of this reaction; however they also noted that catalytic hydrogenation could be terminated after 1 equiv of hydrogen had reacted.



Later Diels and Olsen characterized 1 by forming its dilactone.³ This adduct was synthesized at relatively low temperature, whereas the previous adduct was prepared at elevated temperatures. This suggested that the first compound reported which was thought to be 1 may have been adduct 2. In the same paper they reported the isolation of the tris adduct, 3. Dimethyl acetylenedicarboxylate was allowed to react with excess furan for 17 hr at 100° and then allowed to react further at room temperature for 2 days. The isolation of 3 suggested that bis adduct 2 was formed at elevated temperatures, and then 2 reacted at room temperature to give 3.



At the time these adducts were prepared it was difficult to make stereochemical assignments. Due to the development of nmr spectroscopy the configurations of these and other adducts could be investigated.

Results

When furan was allowed to react with acetylenic ester at room temperature (exo–endo) adduct 4 was formed along with approximately 6% of (exo–exo) adduct 5.⁴ The nmr spectrum of 4 revealed that the less symmetrical (exo–endo) adduct was the major product because the chemical shifts of the two pairs of vinyl hydrogens were different. They appeared as apparent triplets at δ 6.6 and 6.4.⁵ The olefinic hydrogens of the symmet-

(1) (a) Taken from part of the Ph.D. Thesis of J. D. Slee, 1969. (b) To whom inquiries should be addressed.

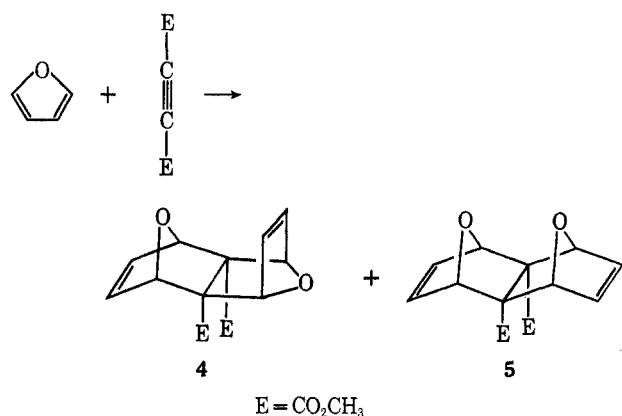
(2) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **490**, 143 (1931).

(3) O. Diels and S. Olsen, *J. Prakt. Chem.*, **156**, 284 (1940).

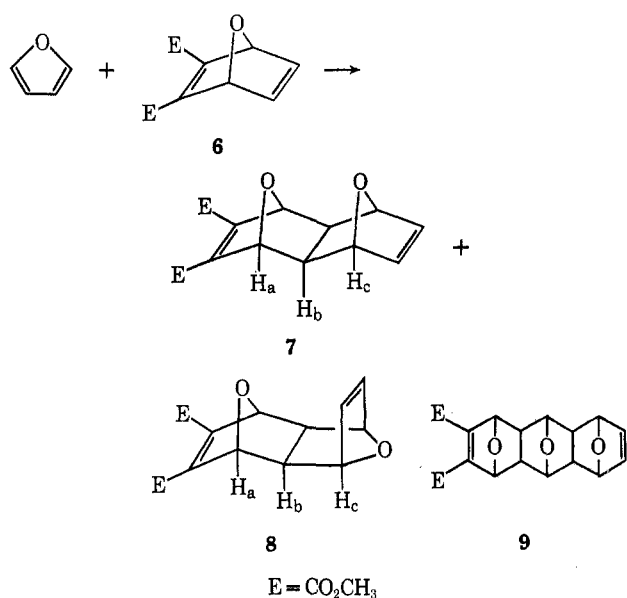
(4) J. Kallos and P. Deslongchamps, *Can. J. Chem.*, **44**, 1239 (1966).

(5) D. M. Grant and H. S. Gutowsky, *J. Chem. Phys.*, **34**, 699 (1961).

rical (exo-exo) and (endo-endo) structures, in contrast, would have identical chemical shifts.



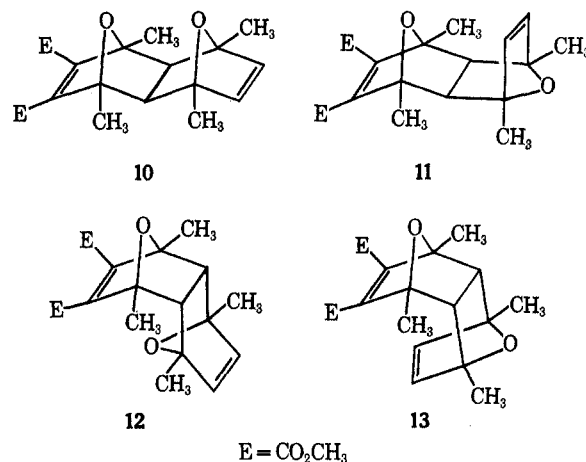
Reinvestigation of the reaction between excess furan and dimethyl acetylenedicarboxylate at 100° led to the isolation of three products.² Two bis adducts, 7 and 8, along with tris adduct 9 were formed by addition to the less substituted double bond of the 1:1 furan-acetylenic ester adduct 6. This is evident from the single, two proton resonance observed in the vinyl region of their nmr spectra.



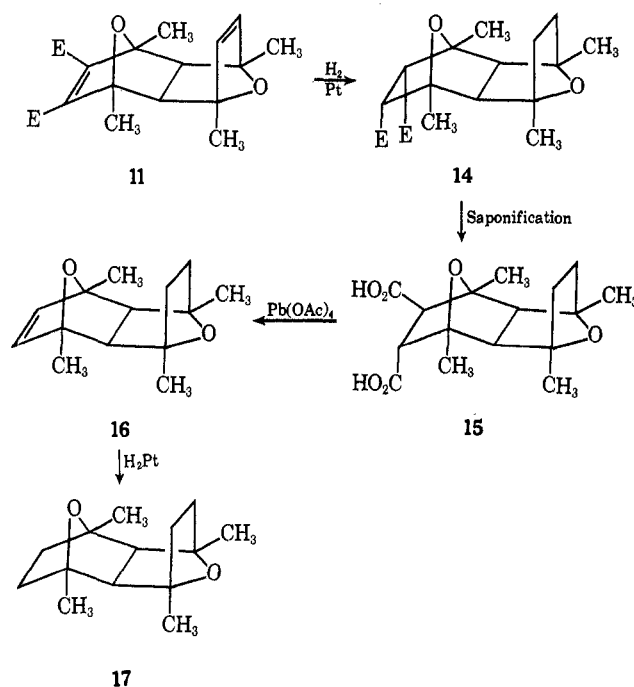
The dihedral angles between H_a and H_b as well as between H_b and H_c of (exo-exo) adduct 7 are approximately 90° thus giving rise to coupling constants $J_{ab} \cong 0$ Hz and $J_{bc} \cong 0$ Hz.⁶ The (exo-endo) adduct 8 has dihedral angles of approximately 90° between H_a and H_b, and 45° between H_b and H_c as indicated by the coupling constants $J_{ab} = 0$ Hz and $J_{bc} = 4.5$ Hz. The stereochemistry of the tris adduct was not determined.

When excess 2,5-dimethylfuran was allowed to react with dimethyl acetylenedicarboxylate only a 1:1 adduct formed. Apparently steric hindrance prevents a second mole of furan from adding to the initially formed mono adduct.⁷ However, the reaction of excess 2,5-dimethylfuran with the acetylenic ester at 100° gave rise to a single bis adduct. In this case addition of the second mole of 2,5-dimethylfuran occurred at the less substi-

tuted double bond. Four structural configurations are possible: (exo-exo) adduct 10, (exo-endo) adduct 11, (endo-exo) adduct 12, and (endo-endo) adduct 13.



Evidence indicating that (exo-endo) bis adduct 11 is the most likely configuration was obtained by preparation of its parent compound. Catalytic hydrogenation of 11 gave *cis* diester 14. Saponification led to *trans* diacid 15, which in turn was bisdecarboxylated with lead tetraacetate⁸ to olefin 16. Hydrogenation of 16 produced the parent compound 17.



The nmr spectrum of 17 demonstrated that it possessed two nonequivalent pairs of methyl groups. Only (exo-endo) adduct 11 and (endo-exo) adduct 12 could give rise to 17. Since endo addition to the initially formed 1:1 adduct is sterically unfavorable,⁹ (exo-endo) adduct 11 is the proposed structure for the bis adduct.

Supporting evidence for the (exo-endo) configuration was obtained by synthesizing trimethyl bis adduct 19. This adduct was prepared from monoadduct 18 and 2-methylfuran. The dihedral angle between H_a and H_b

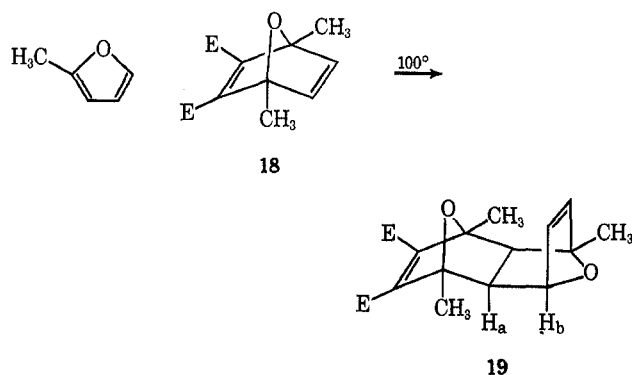
(6) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(7) K. Alder and K. H. Backendorf, *Justus Liebigs Ann. Chem.*, **535**, 101 (1938).

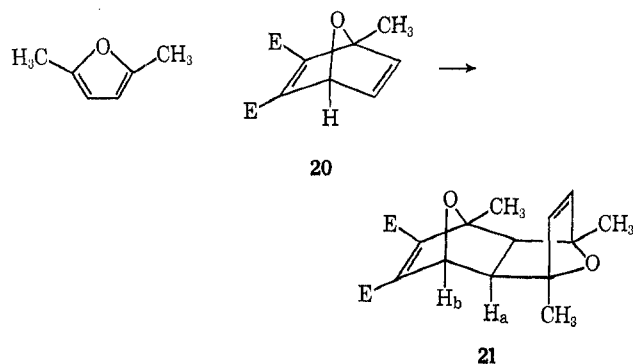
(8) J. Wolinsky and C. M. Dimarist, *J. Amer. Chem. Soc.*, **90**, 113 (1968).

(9) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

was estimated to be 45° because $J_{ab} = 5.2$ Hz. As in the tetramethyl bis adduct endo addition is unlikely due to steric hindrance. For these reasons adduct **19** has been assigned the (exo-endo) configuration.



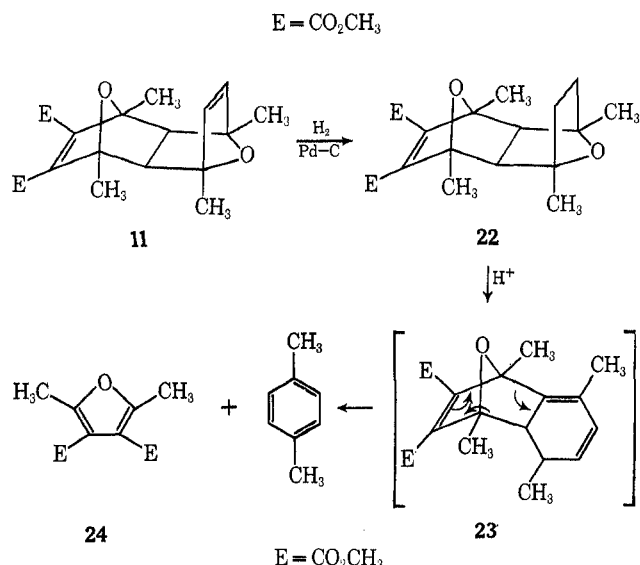
Synthesis of trimethyl bis adduct **21** from mono-adduct **20** and 2,5-dimethylfuran supports the postulate that exo addition to 7-oxabicyclo[2.2.1] systems are expected. Since $J_{ab} \cong 0$ Hz, the dihedral angle between H_a and H_b was estimated to be 90° . This result is consistent only with exo addition at the less substituted double bond of **21**. Adduct **21** most likely has the (exo-endo) configuration.



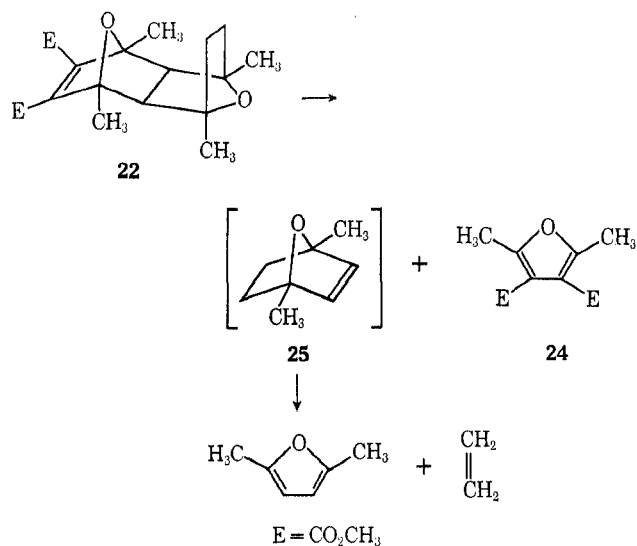
Taken together it is felt that the information presented concerning tetramethyl bis adduct **11**, trimethyl bis adduct **17**, and trimethyl bis adduct **21** is most consistent with the (exo-endo) configuration for this series of compounds.

Adduct **11** was selectively hydrogenated to its dihydro derivative **22**. Work of Alder and Rickert¹⁰ suggested that treatment of this compound with a strong acid such as trifluoroacetic acid would give rise to a naphthalene derivative by an acid-catalyzed elimination of 2 equiv of water. Instead, dimethyl 2,5-dimethylfuran-2,3-dicarboxylate **24** and *p*-xylene formed. Elimination of 1 equiv of water probably led to intermediate **23** which readily underwent a retrograde Diels-Alder reaction. Since no trace of **23** was observed in the nmr spectra at any time during the course of the reaction, the retrograde step was probably very facile.

Pyrolysis of **22** produced dimethyl 2,5-dimethylfuran-2,3-dicarboxylate **24**, 2,5-dimethylfuran, and ethylene.¹¹ A retro-Diels-Alder reaction led to **24** and



to intermediate **25**. The latter compound underwent further degradation to 2,5-dimethylfuran and ethylene.



Discussion

As in the earlier reports this series of reactions illustrates the temperature dependence of furan-dimethyl acetylenedicarboxylate bis adduct formation. At room temperature the kinetically controlled products were formed, whereas at elevated temperature products resulting from thermodynamic control were obtained. It is noteworthy that under kinetically controlled conditions the double bond substituted with carbomethoxy groups acted as a dienophile, whereas under thermodynamically controlled conditions equilibration led to addition at the less substituted double bond. This is not surprising since many furan Diels-Alder adducts are known to be thermally labile at relatively low temperatures.¹²

The formation of the (exo-endo) bis adduct **4** by the reaction of furan with dimethyl acetylenedicarboxylate at 25° is contrary to Alder's rule. The bulk of the methyl esters most likely caused this kinetically con-

(11) K. Alder and K. H. Backendorf, *Justus Liebigs Ann. Chem.*, **535**, 101 (1938).

(12) A. S. Onishchenko, "Diene Synthesis," Daniel Davey and Co., New York, N. Y., 1964, p 561.

(10) K. Alder and H. F. Rickert, *Chem. Ber.*, **70**, 1354 (1937).

trolled reaction to take a course which was not anticipated. In contrast, Kallos and Deslongchamps⁴ demonstrated that acetylenedicarboxylic acid reacted at room temperature to give the expected (exo-exo) adduct.

In the cases of the tetramethyl and trimethyl adducts the products arise from thermodynamic control. Equilibration at the elevated temperatures led to the thermodynamically most stable products. Models reveal that the (exo-exo) and the (endo-endo) configurations have particularly severe 1,3-dimethyl nonbonding interactions. Since endo attack on the bicyclic systems are unlikely due to additional steric factors, the (exo-endo) adduct in which the nonbonding 1,3 dimethyl interactions were somewhat less was favored. The products resulting from thermodynamic control were, therefore, a result of stringent steric requirements.

Experimental Section

(Exo-Endo) Bis Adduct 4.—Furan, 14.5 g (0.21 mol), and dimethyl acetylenedicarboxylate, 14.2 g (0.1 mol), were placed in a screw-capped test tube and allowed to react at room temperature for 5 weeks. The entire reaction mixture crystallized. An nmr of the material indicated that it was primarily (90%) the (exo-endo) isomer 4. The (exo-exo) isomer appeared to be present in approximately 6% (determined by the ratio of CO_2CH_3 resonances). Recrystallization (95% ethanol) gave adduct 4 as a white crystalline solid: mp 120–122°; ir (CHCl_3) 3000 (C–H), 2950 (C–H), 1735 (C=O), 1725 (C=O), 1430, and 1275 cm^{-1} ; nmr (CDCl_3) δ 3.71 (s, 6, $-\text{CO}_2\text{CH}_3$), 4.50 (d, 2, $J = 1$ Hz, bridgehead), 5.13 (d, 2, $J = 1$ Hz, bridgehead), 6.49 (t, 2, $J = 1$ Hz, $-\text{CH}=\text{CH}-$, AA' BB' system), and 6.62 ppm (t, 2, $J = 1$ Hz, $-\text{CH}=\text{CH}-$, AA' BB' system).
Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_6$: C, 60.43; H, 5.08. Found: C, 60.24; H, 5.12.

(Exo-Exo) Bis Adduct 7, (Exo-Endo) Bis Adduct 8, and Tris Adduct 9.—In a 75-ml glass pressure tube fitted with a Teflon-lined pressure cap was placed 22.7 g (0.32 mol) of furan and 14.2 g (0.1 mol) of dimethyl acetylenedicarboxylate. The tube was heated to 100° for 18 hr. After cooling the reaction mixture was treated with 100 ml of chloroform. The insoluble materials were removed by filtration and the chloroform solution was concentrated. Column chromatography (silicic acid, chloroform) of the concentrate led to three products.

The first compound from the column was (exo-endo) bis adduct 8: 7.5 g (35%); mp 120–122°; uv max (CH_3OH) 240 $\text{m}\mu$ (ϵ 4980); ir (CHCl_3) 2985 (C–H), 2945 (C–H), 1760 (C=O), 1720 (C=O), 1660 (C=C), and 1460 cm^{-1} (C=C); nmr (CDCl_3) δ 2.80 (d of d, 1, $J = 3$ and 1, $J = 1.6$ Hz, bridgehead protons between the dihydrofuran rings), 3.74 (s, 6, $-\text{CO}_2\text{CH}_3$), 4.70 (s, 2, bridgehead protons nearest the carbomethoxy groups), 4.78 (m, 2, bridgehead protons of the least substituted dihydrofuran ring), and 6.24 ppm (s, 2, $-\text{CH}=\text{CH}-$).
Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_6$: C, 60.43; H, 5.08. Found: C, 60.34; H, 5.06.

The second fraction contained 1.2 g (6%) of the white crystalline (exo-exo) bis adduct 7: mp 157–159°; uv max (CH_3OH) 237 $\text{m}\mu$ (ϵ 4840); ir (CHCl_3) 3020 (C–H), 300 (C–H), 2950 (C–H), 1725 (C=O), 1630 (C=C), 1430 (C=C), and 1265 cm^{-1} ; nmr (CDCl_3) δ 2.20 (s, 2, bridgehead protons between the dihydrofuran rings), 3.77 (s, 6, $-\text{CO}_2\text{CH}_3$), 4.88 (s, 2, bridgehead protons of the least substituted dihydrofuran ring), 5.09 (s, 2, bridgehead protons nearest the carbomethoxy groups), and 6.40 (s, 2, $-\text{CH}=\text{CH}-$).
Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_6$: C, 60.43; H, 5.08. Found: C, 60.34; H, 4.99.

The third fraction was eluted with a carbon tetrachloride-ethyl acetate (10:2) solution. Removal of the solvent gave 1.3 g (3.7%) of the white crystalline tris adduct 9: mp 213–215°; uv max (CH_3OH) 239 $\text{m}\mu$ (ϵ 4310); ir (CHCl_3) 2990 (C–H), 2950 (C–H), 1740 (C=O), 1715 (C=O), 1640 (C=C), and 1440 cm^{-1} ; nmr (CDCl_3) δ 2.65 (m, 4, bridgehead protons between rings), δ 3.80 (s, 6, $-\text{CO}_2\text{CH}_3$), 4.13 (m, 2, bridgehead protons on the least substituted dihydrofuran ring), 4.85 (m, 2, bridgehead protons on the tetrahydrofuran ring), 5.0 (s, 2, bridgehead protons on the tetrahydrofuran ring), 5.0 (s, 2, bridgehead protons nearest the carbomethoxy groups), and 6.27 ppm (s, 2, $-\text{CH}=\text{CH}-$).

Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_7$: C, 62.42; H, 5.19. Found: C, 62.22; H, 5.19.

(Exo-Endo) Bis Adduct 11.—A solution containing 11.1 g (0.078 mol) of adduct 18 and 25 g (0.26 mol) of 2,5-dimethylfuran was heated to 95° for 18 hr in a nitrogen atmosphere. Unreacted 2,5-dimethylfuran was removed by distillation at atmospheric pressure and adduct 18 was removed by vacuum distillation. The oily residue crystallized exothermically when treated with a small amount of pentane. Recrystallization from ether gave 2.6 g (10%) of the white crystalline adduct 11: mp 107–108°; uv max (CH_3OH) 233 $\text{m}\mu$ (ϵ 4950); ir (CHCl_3) 2975 (C–H), 2950 (C–H), 1715 (C=O), and 1630 cm^{-1} (C=C); nmr (CDCl_3) δ 6.24 (s, 2, $-\text{CH}=\text{CH}-$), 3.76 (s, 6, $-\text{CO}_2\text{CH}_3$), 2.72 (s, 2, bridgehead), 1.54 (s, 6, $-\text{CH}_3$), and 1.48 ppm (s, 6, $-\text{CH}_3$).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_6$: C, 64.64; H, 6.63. Found: C, 64.75; H, 6.50.

Reduced Diester 14.—A suspension of platinum oxide (50 mg) in 10 ml of 95% ethanol was saturated with hydrogen. A solution of 173 mg (0.518 mmol) of adduct 11 in 15 ml of 95% ethanol was then added. Exhaustive hydrogenation at atmospheric pressure required 23.9 ml (1.06 mmol) of hydrogen at STP corresponding to the reduction of two double bonds (theoretical 1.04 mmol). The platinum was removed by filtration through a fiber glass filter. Removal of solvent followed by recrystallization (pentane) gave 0.160 g (92%) of the reduced adduct 14: mp 154–156°; ir (CHCl_3) 2950 (C–H), and 1737 cm^{-1} (C=O); nmr ($\text{CF}_3\text{CO}_2\text{H}$) δ 3.82 (s, 6, $-\text{CO}_2\text{CH}_3$), 3.36 (s, 2, 2-CHCO_2-), 2.86 (s, 2, bridgehead), 2.4 (m, 2, 2-H of an A_2B_2 system), 1.72 (s, 7, 2- CH_3 plus 2-H of an A_2B_2 system), and 1.58 ppm (s, 7, 2-H plus 1-H of an A_2B_2 system).

Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_6$: C, 63.61; H, 7.69. Found: C, 63.89; H, 7.69.

Saponification of Diester 14.—Diester 14, 7.3 g (0.021 mol), dissolved in a solution containing 40 ml of water, 20 ml of methanol, and 4 g of sodium hydroxide was heated to 80° for 12 hr. The cooled solution was extracted once with 40 ml of ether and then it was acidified with concentrated hydrochloric acid to a pH of 2. The aqueous layer was placed in a liquid-liquid extractor and extracted with ether for 8 hr. After drying (MgSO_4) and filtration, removal of the solvent gave 5.6 g (80%) of diacid 15 as a white powder: mp 255–257° dec; ir (KBr) 3150 (O–H), 2950 (C–H), 1715 (C=O) 1390, 1210, and 810 cm^{-1} ; nmr (D_2O , Na_2CO_3 ; internal reference, sodium 2,2-dimethyl-2-silapentane-5-sulfonate) δ 2.91 (d, 1, $J = 6.3$ Hz, NaO C-CH-CH-CO Na , half of an AB quartet), 2.70 (d, 1, $J = 6.3$ Hz, $\text{NaO C-CH-CH-CO}_2\text{Na}$, half of an AB quartet), 2.20 (m, 4, bridgehead protons plus 2 protons from the AA'BB' system of the tetrahydrofuran ring), δ 1.61 (s, 3, $-\text{CH}_3$), and 1.40 ppm (s, 11, 3, $-\text{CH}_3$, plus 2-H from the AA'BB' tetrahydrofuran system).

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_8$: C, 61.99; H, 7.15. Found: C, 61.67; H, 7.07.

Bisdecarboxylation of Diacid 15.—Into a 100-ml three-necked flask fitted with a mechanical stirrer, reflux condenser, and a gas inlet tube was placed 5.3 g (0.017 mol) of diacid 15 dissolved in 40 ml of dry pyridine. After saturation of the solution with oxygen, the gas inlet tube was removed and 11.4 g (0.256 mol) of lead tetraacetate (dried in a vacuum oven at 25°) was added directly to the solution. The flask containing the solution was then immersed in an oil bath preheated to 70°. After 5 min the stirred solution began to evolve carbon dioxide. As soon as the evolution of CO_2 ceased the reaction flask was cooled in an ice bath. The cooled solution was then treated with 50 ml of methylene chloride and extracted twice with 50 ml of 50% nitric acid (0°). The final traces of pyridine were removed by extraction with a 10% cadmium chloride solution followed by a final extraction with water. After drying the solution (MgSO_4), the methylene chloride was removed by careful distillation. The residue was treated with 15 ml of pentane and the insoluble material was removed by filtration. Removal of the pentane followed by sublimation (0.05 mm, 25°) of the oily residue gave 0.190 g (5.2%) of the white crystalline monoolefin 16: mp 60–63°; ir (CHCl_3) 2970 (C–H), 2935 (C–H), 1460 (C=C), 1380, 1310, 1250, 1145, and 850 cm^{-1} ; nmr (CCl_4) δ 2.17 (s, 1, 1-H of the A_2B_2 tetrahydrofuran system), 2.03 (s, 3, 2 bridgehead protons plus one proton from the A_2B_2 tetrahydrofuran system), 1.45 (s, 8, 2- CH_3 , plus 2-H of the A_2B_2 tetrahydrofuran system), and 1.28 ppm (s, 2, $-\text{CH}_3$).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.43; H, 9.16. Found: C, 76.29; H, 9.26.

Reduction of Monoolefin 16.—A suspension of platinum oxide (20 mg) in 15 ml of methanol was saturated with hydrogen. A solution of 0.101 g (0.45 mmol) of alkene 16 in 15 ml of methanol was then added through a rubber septum. After the uptake of hydrogen had ceased, the methanol solution was filtered through a glass fiber filter and the methanol was removed. The reduced diether 17, 0.090 g (90%), was purified by sublimation (0.05 mm, 25°): mp 54–55.5°; ir (CHCl₃) 2895 (C–H), 2885 (C–H), 2865 (C–H), 1460, 1380, 1140, 1080, and 850 cm⁻¹; nmr (CDCl₃) δ 2.24 (s, 1, 1 proton of an A₂B₂ tetrahydrofuran system), 2.09 (s, 3, 2 bridgehead protons plus 1-H from an A₂B₂ system), 1.51 (s, 5, -CH₂CH₂- plus 1-H of an A₂B₂ system, 1.46 (s, 7, 2-CH₃ plus 1-H of an A₂B₂ system), and 1.42 ppm (s, 6, 2-CH₃).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.74; H, 9.99. Found: C, 75.66; H, 9.81.

Diels-Alder Adduct of Diester 18 and 2-Methylfuran.—A solution of 16.8 g (0.071 mol) of adduct 18 and 24.8 g (0.3 mol) of 2-methylfuran was refluxed in a nitrogen atmosphere for 24 hr. The excess 2-methylfuran was removed by distillation at atmospheric pressure and unreacted 18 was removed by vacuum distillation, bp 82–84° (0.3 mm).

Column chromatography (silicic acid, CHCl₃) gave 3 g (13%) of a light yellow oil which crystallized after standing several days. Recrystallization from pentane gave adduct 19 as a white crystalline solid: mp 90–92°; ir (CHCl₃) 2960 and 2940 (C–H), 1715 (C=O), 1360 (C=C), 1435, 1385, and 1310 cm⁻¹; nmr (CDCl₃) δ 6.42 (d, 1, $J = 6.2$ Hz, RCH=CHR'); each signal is split further into a doublet $J = 1.8$ Hz), 6.24 (d, 1, $J = 6.2$ Hz, RCH=CHR), 4.64 (d, 1, $J = 5.2$ Hz bridgehead on the dihydrofuran ring; each signal is split further into a doublet $J = 3.8$ Hz), 3.76 (s, 6, -CO₂CH₃), 3.08 (d, 1, $J = 7.5$ Hz bridgehead; each signal split further into a doublet $J = 5.2$ Hz), 2.54 (d, 1, $J = 7.6$ Hz, bridgehead), 1.57 (s, 3, -CH₃), 1.48 (s, 3, -CH₃), and 1.46 ppm (s, 3, -CH₃).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.75; H, 6.29. Found: C, 63.87; H, 6.26.

Diels-Alder Adduct of Diester 20 and 2,5-Dimethylfuran.—A solution containing 10.5 g (0.047 mol) of adduct 20, 9.0 g (0.094 mol) of 2,5-dimethylfuran, and 20 ml of toluene was heated to 96° for 18 hr in a nitrogen atmosphere. The toluene and unreacted 2,5-dimethylfuran were removed by distillation at atmospheric pressure and unreacted diester 20 was removed by vacuum distillation. Column chromatography (silicic acid, CHCl₃) of the residue gave a yellow oil which crystallized only after standing several days. Recrystallization (ether) gave 2 g, 13%, of adduct 21 as a white crystalline solid: mp 87–89°; ir (CHCl₃) 2580 and 2550 (C–H), 1715 (C=O), 1630 (C=C), 1430, and 1380 cm⁻¹; nmr (CDCl₃) δ 6.27 (d, 1, $J = 6$ Hz, R-CH=CH-R'), 6.18 (d, 1, $J = 6$ Hz R-CH=CH-R'), 4.58 (s, 1, bridgehead on furan ring) 3.81 (s, 3, -CO₂CH₃), 3.77 (s, 3, -CO₂CH₃), 2.65 (s, 2, bridgehead), 1.54 (s, 6, -CH₃), and 1.46 ppm (s, 3, -CH₃).

Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.75; H, 6.29. Found: C, 63.78; H, 6.24.

Selective Reduction of Adduct 11.—A suspension of 10 mg of 10% palladium on powdered charcoal in 10 ml of methanol was saturated with hydrogen and adduct 11, 0.973 g (2.41 mmol), dissolved in 15 ml of methanol was then introduced. The reduction

was stopped after 1 mol (2.93 mmol) of hydrogen had been consumed. Filtration of the reaction mixture through a glass fiber filter followed by removal of the solvent and recrystallization (hexane) gave 0.830 g (86%) of compound 22: mp 93–95°; ir (CHCl₃) 2960 and 2945 (C–H), 1710 (C=O), and 1635 cm⁻¹; nmr (CDCl₃) 3.80 (s, 6, -COOCH₃), 2.49 (s, 2, bridgehead) 2.21 (d, 2, $J = 7.2$ Hz, A₂B₂ system of furan ring), 1.65 (s, 8, 2-CH₃ plus 2 protons of an A₂B₂ system), and 1.43 ppm (s, 6, -CH₃).

Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.29; H, 7.14. Found: C, 64.44; H, 7.11.

Acid-Catalyzed Degradation of Monoolefin 22.—A solution containing 100 mg (0.30 mmol) of 22, two drops of trifluoroacetic anhydride and 0.3 ml of trifluoroacetic acid was placed in an nmr tube at room temperature. An nmr taken immediately after mixing was consistent with the starting material: nmr (CF₃CO₂H) δ 3.95 (s, 6, CO₂CH₃), 2.79 (s, 2, bridgehead), 2.32 (d, 1, $J = 5$ Hz, part of an A₂B₂ system of the tetrahydrofuran ring), 1.83 (s, 8, -CH₃ plus 2 protons of an A₂B₂ system), and 1.62 ppm (s, 6, -CH₃).

After 12 hr the solution had turned black and the nmr spectrum had changed to (CF₃CO₂H) δ 7.03 (s, 4, aromatic), 4.26 (s, 6, -CO₂CH₃), 2.65 (s, 6, -CH₃), and 2.24 ppm (s, 6, -CH₃).

Pyrolysis of Monoolefin 22. Procedure A.—In a 4-ml side-arm distilling flask was placed 0.800 g (3.39 mmol) of monoolefin 22. The compound was heated to 280° (sand bath) for 4 hr in a nitrogen atmosphere. 2,5-Dimethylfuran (110 mg, 36%) slowly distilled from the reaction mixture (ir was identical with that of a known sample). No attempt was made to trap the ethylene evolved during the pyrolysis.

When the sand bath temperature was increased to 350°, 244 mg (34%) of dimethyl 2,5-dimethylfuran-2,3-dicarboxylate (24) distilled from the reaction mixture: mp 58–61° (lit.⁵⁶ mp 58–61°); ir (CHCl₃) 3000 (C–H), 1750 (C=O), 1693 (C=C), 1445, 1320, and 1090 cm⁻¹; nmr (CDCl₃) δ 3.85 (s, 6, -COOCH₃) and 2.40 ppm (s, 6, -CH₃).

Procedure B.—A Pyrex tube, 1.5 cm in diameter, packed to a height of 22 cm with granular silicon carbide (10 mesh) was preheated in a vertical tube furnace to 380°. The tube was fitted with an addition funnel and a receiver consisting of a 100-ml three-necked flask fitted with a Dry Ice condenser. The collection flask was cooled in a Dry Ice-acetone bath. A slow stream of nitrogen was used as the carrier gas.

A solution of 0.952 g (2.85 mmol) of monoalkene 22 in 25 ml of benzene was slowly passed through the heated column. Removal of solvent (rotovaporator) from the material collected in the receiver gave 450 mg (75%), of dimethyl 2,5-dimethylfuran-dicarboxylate, mp 58–61° (lit.¹³ 58–61°).

Registry No.—4, 25860-27-9; 7, 25860-28-0; 8, 25860-29-1; 9, 25860-30-4; 11, 25860-31-5; 14, 25860-32-6; 15, 25860-33-7; 16, 25860-34-8; 17, 25860-35-9; 19, 25860-36-0; 21, 25860-37-1; 22, 25860-38-2.

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