An Approach to the Synthesis of Fujenoic Acid

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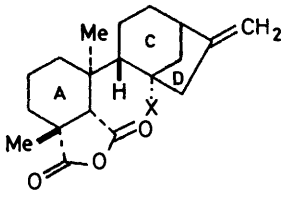
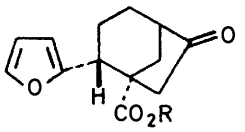
In experiments directed towards the total synthesis of fujenoic acid (1), the 2-(2-furyl)-6-oxobicyclo[3.2.1]octane-1-carboxylate (3b) was prepared as a key intermediate. The furyl group was designed to be transformed into ring A of fujenoic acid. In investigations of the transformation route, model compounds {the stereoisomeric dimethyl 1-methyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylates (4), (5), and (12)} were examined, and it was found that diester (12) could be effectively converted into dimethyl 1,3-dimethyl-6-oxocyclohex-3-ene-1,2-dicarboxylate (18), which corresponds to ring A of fujenoic acid. The key intermediate (3b) was obtained by a Dieckmann condensation of dimethyl 6-(2-furyl)-1-methoxycarbonylmethylcyclohexane-1,3-dicarboxylate (23).

FROM extracts of culture filtrates of *Gibberella fujikuroi*, Cross and his co-workers isolated fujenoic acid and fujenal and characterized [1] these two metabolites as the tricarbocyclic diterpenes (1) and (2), possessing a B-secokaurane skeleton. Structures (1) and (2) can each be regarded



(1) X = CO_2H
(2) X = CHO



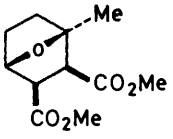
(3) a; R = H
b; R = Me

as composed of two parts, *i.e.* ring A and rings C and D. We have prepared the furyl compound (3) as a key intermediate in an attempt to synthesise these diterpenoids. We hoped that a functionalized ring A might be derived from the furyl group by Diels–Alder reaction with a suitably substituted dienophile.

Model Experiments for Ring A Construction.—We have previously reported [2] a preliminary model experiment for the construction of ring A of fujenoic acid, using the 7-oxabicyclo[2.2.1]heptane derivatives (4) and (5), and have demonstrated that the ether linkage is easily cleaved by boron trifluoride–ether in acetic anhydride, giving the corresponding acetates (6) and (7) in 40 and 70% yields, respectively. The model compound (4) was obtainable from methylfuran by a Diels–Alder reaction with maleic anhydride, followed by hydrogenation and esterification.

In order to find conditions for introducing a methyl group at C-4 (kaurane numbering) we have performed further model experiments. Our first attempts at direct methylation at C-4 of structure (4) with methyl iodide were unsuccessful under basic conditions [$LiNPr^i_2$ or $LiN(Pr^i)C_6H_{11}$]: epimerization at C-4 took place easily without formation of any methylated product. We therefore attempted to obtain the oxo-ester (8) from the acetate (6), the latter being obtainable quantitatively by treatment of the adduct (4) with acetic toluene-*p*-sulphonic anhydride.[3]

Several attempts to hydrolyse the acetate group of (6) were, however, unsuccessful. For example, treatment with various kinds of base resulted in elimination of



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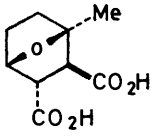

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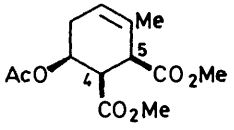
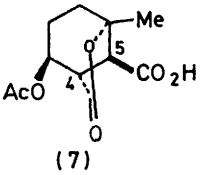


(6)



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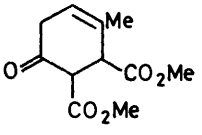

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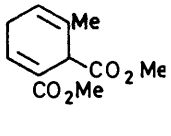

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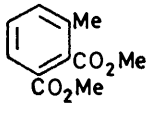

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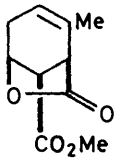


(11)

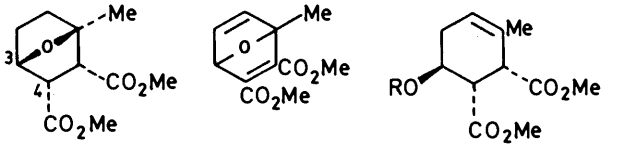
.acetic acid to give a mixture of diesters (9) and (10). On the other hand, the lactone (11) was formed quantita-

[1] (*a*) B. E. Cross, R. H. B. Galt, J. R. Hanson, P. J. Curtis, J. F. Grove, and A. Morrison, *J. Chem. Soc.*, 1963, 2937. (*b*) B. E. Cross, R. H. B. Galt, and J. R. Hanson, *ibid.*, p. 5052.

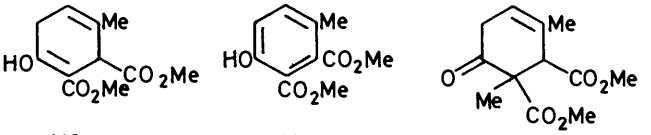
[2] Y. Kitahara, T. Kato, N. Ototani, A. Inoue, and H. Izumi, *J. Chem. Soc.* (*C*), 1968, 2508.

[3] Y. Mazur and M. H. Karger, *J. Org. Chem.*, 1971, **36**, 540.

tively from (6) under acidic conditions. Since lactonization was apparently favoured by the *cis*-relationship of the C-5 methoxycarbonyl group with the acetate group, the isomeric diester acetate (14) was then prepared and submitted to hydrolysis in the hope of avoiding lactonization. The Diels–Alder adduct



(12) (13) (14) R = Ac (15) R = H



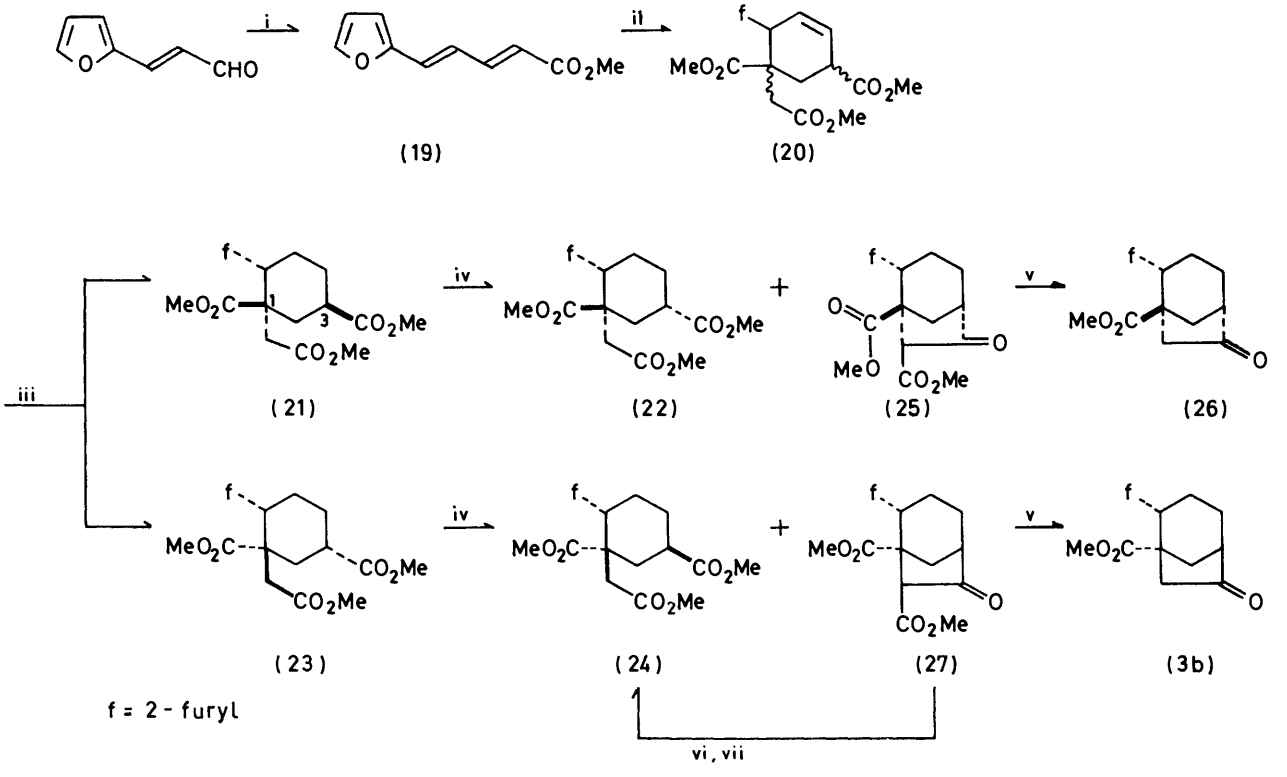
(16) (17) (18)

(13), obtained quantitatively by the reaction of methylfuran with dimethyl acetylenedicarboxylate, and the long-range W-type coupling (1.5 Hz) between the C-4 proton and one of the C-2 protons indicate the assigned stereo-structure (12).

Treatment of (12) with acetic toluene-*p*-sulphonic anhydride afforded the dimethyl cyclohexenedicarboxylate (14) in quantitative yield. As expected in this case, the acetyl group of (14) was easily removed by methanolic hydrochloric acid to give the alcohol (15), in 90% yield. Oxidation of (15) with chromic oxide–pyridine complex and chromatography on silica afforded a mixture of enols (16) and (17), in 60 and 30% yield, respectively. The latter could be converted into the former in 40% yield by Birch reduction with lithium in liquid ammonia. The phenolic diester (17) was also obtained quantitatively when the adduct (13) was treated with sulphuric acid in dichloromethane.

The appearance of a one-proton signal at δ 12.42 in the ^{1}H n.m.r. spectrum of (16) revealed that it existed predominantly in the enol form. Introduction of a methyl group at C-4 was achieved with methyl iodide in the presence of potassium t-butoxide in t-butyl alcohol, giving compound (18) in 70% yield.

This model experiment implies that the furyl group of



(19) (20) (21) (22) (25) (26) (23) (24) (27) (3b)

f = 2-furyl

SCHEME Reagents: i, AcOMe–Na; ii, methyl itaconate, 160 °C; iii, H_2, Pd–C; iv, Bu^{t}OK; v, LiI–C_5H_5N; vi, KOH; vii, CH_2N_2

was catalytically reduced to give the *endo,cis*-diester (12). The stereochemistry of (12) was confirmed by its ^{1}H n.m.r. spectrum, in which the C-4 and C-3 proton signals appeared at δ 3.23 (ddd, $J_{4,5}$ 12, $J_{2,4}$ 1.5, $J_{3,4}$ 6 Hz) and 4.50 (t, $J_{3,4} = J_{2,3} = 6$ Hz), respectively. The 6 Hz coupling between the C-4 and C-3 protons

the intermediate (3) might be convertible into ring A of fujenoic acid although the stereochemistry at C-4 with respect to the C-5 methoxycarbonyl group remains undefined at this stage.

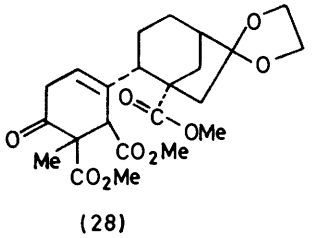
Synthesis of the Key Intermediate (3).—By application of a method analogous to that developed by Baker

and Goudie,[4] the intermediate (3) was synthesized as shown in the Scheme. Condensation of 3-(2-furyl)-acrylaldehyde with methyl acetate gave methyl 4-fur-furylidenecrotonate (19),[5] which was subjected to a Diels–Alder reaction with dimethyl itaconate to afford the adduct (20). The n.m.r. spectrum indicates that the adduct is a stereoisomeric mixture with respect to the furyl and neighbouring methoxycarbonyl groups. The mixture was catalytically reduced and separated by silica gel column chromatography to obtain two stereoisomeric triesters, (21) and (23), in 31 and 32% yield, respectively. The relative stereochemistry of the triesters was determined as follows. Treatment of the triester (23) with potassium t-butoxide in refluxing xylene resulted in a mixture of the bicyclic oxo-ester (27), the epimerized triester (24), and unchanged (23), which were isolated in 11, 19, and 8% yield, respectively. The epimerized triester (24) was formed selectively from the bicyclic oxo-ester (27) by fission of the five-membered ring with potassium hydroxide followed by esterification with diazomethane. These results show that the triester (23) has a *trans*-relationship between the C-1 CH_2CO_2Me and C-3 CO_2Me groups.

Similarly, the triester (21) was converted by potassium t-butoxide into a mixture of the bicyclic oxo-ester (25), unchanged (21), and the epimerized triester (22), which were isolated in 18, 11, and 5% yields, respectively.

The half-height widths of the C-3 proton signals in the n.m.r. spectra of the four isomeric triesters indicated that these protons in the triesters (21) ($W_{\frac{1}{2}}$ 18 Hz) and (24) ($W_{\frac{1}{2}}$ 16 Hz) are axial, whereas those in the isomers (22) ($W_{\frac{1}{2}}$ 10 Hz) and (23) ($W_{\frac{1}{2}}$ 6 Hz) have the equatorial configuration. If we assume that the cyclohexane ring is in the chair conformation, and the furyl group is attached equatorially, the stereochemistry of these isomers is as depicted in the Scheme.

The Dieckmann condensation products (25) and (27), obtainable in 56 and 52% yield by an improved method were treated with lithium iodide in hot pyridine to give the corresponding demethoxycarbonylated products (26) and (3b) in good yields. The ^1H n.m.r spectra of (26) and (3b) in the presence of a shift reagent supported the assigned stereostructure.[6]



(28)

Although the sequential reactions shown in the Scheme are not stereoselective, the key intermediate (3b) could be thus synthesized in relatively few steps. By application of Diels–Alder reactions to the furan ring of (3b) and subsequent reactions, a demethylfujenoic acid derivative (28) has been synthesized.[7]

EXPERIMENTAL

M.p.s were measured with a Thomas-Hoover capillary apparatus. I.r. spectra were recorded with a Hitachi 215 grating spectrophotometer, n.m.r. spectra with a Varian T-60 or HA-100 instrument with deuteriochloroform or carbon tetrachloride as solvent and tetramethylsilane as internal standard, and mass spectra with a Hitachi RMU-6D spectrometer.

Dimethyl 1-Methyl-7-oxabicyclo[2.2.1]*heptane*-2-endo,3-endo-*dicarboxylate* (12).—A mixture of 2-methylfuran (8.2 g) and dimethyl acetylenedicarboxylate (14.2 g) was heated at 110 °C for 5 h in a sealed tube. The resulting adduct (13) (22.2 g) was, without purification, dissolved in methanol (200 ml) containing 5% palladium–carbon (1 g) and was shaken under hydrogen (uptake 3.6 l). Filtration, evaporation, and distillation of the residual oil gave the oily endo,-cis-*diester* (12) (14.6 g), b.p. 102—106 °C at 1 mmHg, δ (CCl_4) 1.46 (Me × 1), 1.63 (Me × 2), 2.77 (dd, *J* 12 and 2 Hz, 2-H), 3.23 (ddd, *J* 12, 6, and 1.5 Hz, 3-H), and 4.50 (t, *J* 6 Hz, 4-H) (Found: C, 57.4; H, 7.3. $C_{11}H_{16}O_5$ requires C, 57.9; H, 7.1%).

Cleavage of the 7-Oxabicyclo[2.2.1]*heptane Derivatives* (4) *and* (12).—To a stirred mixture of the *exo,cis*-diester (4) (5.0 g) and acetonitrile (20 ml) was added acetic toluene-*p*-sulphonic anhydride (5.0 g) and stirring was continued overnight at room temperature. The mixture was diluted with ether and the ethereal solution washed with aqueous sodium hydrogen carbonate and then water, and evaporated. The residue was passed through a short silica gel column to obtain the oily *dimethyl* c-6-*acetoxy*-3-*methylcyclohex*-3-*ene*-r-1,c-2-*dicarboxylate* (6) (5.8 g), *m/e* 270 (M^+), δ ($CDCl_3$) 1.88 (3 H, dd, *J* 3.7 and 2.0 Hz), 1.95, 3.68, and 3.73 (each 3 H, s), 2.94 (1 H, dd, *J* 6 and 2 Hz), 3.50br (1 H, d, *J* 6.0 Hz), and 5.50 (2 H, m) (Found: C, 57.3; H, 6.8. $C_{13}H_{18}O_6$ requires C, 57.8; H, 6.7%).

Similarly, the oily t-6-*acetoxy*-r-1,c-2-*dicarboxylate* (14) (1.60 g) was obtained [from the *endo,cis*-diester (12) (1.24 g)]; *m/e* 270 (M^+), δ (CCl_4) 1.72 (Me × 1), 3.68 (Me × 2), 1.93 (OAc), 2.87 (dd, *J* 11 and 6 Hz, 1-H), 3.36 (d, *J* 6 Hz, 2-H), and 5.40 (m, 4- and 5-H).

Attempted Hydrolysis of the Acetate (6).—(*A*) A mixture of the acetate (6) (42 mg), dioxan (0.5 ml), water (0.5 ml), and sodium hydrogen carbonate (50 mg) was stirred at room temperature overnight. Extraction with ether afforded the diester (9) as the sole product. Reaction of the acetate (6) with sodium acetate in methanol at 60 °C also gave (9) as the sole product. *Dimethyl* 6-*methylcyclohexa*-2,5-*diene*-1,2-*dicarboxylate* (9) was an oil, *m/e* 210 (M^+), $\nu_{max.}$ (film) 1 732 and 1 714 cm^{-1}, δ (CCl_4) 1.79 (3 H, dd, *J* 2 and 3 Hz), 3.60 and 3.68 (each 3 H, s), 5.50 (m, 5-H), and 7.05 (t, *J* 4 Hz, 3-H).

(*B*) To a solution in methanol (10 ml) of the acetate (6) (117 mg) was added one drop of 12N-hydrochloric acid, and the mixture was stirred at room temperature for 5 days. Extraction with ether and work-up gave 2-*methoxycarbonyl*-6-*methylcyclohex*-5-*ene*-1,3-*carbolactone* (11) as the sole product, m.p. 79—80°, $\nu_{max.}$ (KBr) 1 773 and 1 748 cm^{-1}, δ (CCl_4) 1.85 (3 H, dd, *J* 2 and 3.9 Hz), 3.65 (3 H, s), 3.05 (d,

[4] A. J. Baker and A. C. Goudie, *Chem. Comm.*, 1971, 180.
[5] T. Shono, K. Mishina, and Y. Yahama, *Kogyo Kagaku Zasshi*, 1954, **57**, 769.
[6] T. Suzuki, Ph.D. Thesis, Tohoku University, 1975.
[7] T. Kato, T. Suzuki, N. Ototani, and Y. Kitahara, *Chem. Letters*, 1976, 887.

J 5 Hz, 1-H), 3.41 (t, *J* 5 Hz, 2-H), 4.86 (m, 3-H), and 5.32 (m, 5-H) (Found: C, 60.2; H, 6.9. $C_{10}H_{12}O_4$ requires C, 60.6; H, 7.1%).

Hydrolysis of the Acetate (14).—One drop of 12N-hydrochloric acid was added to a solution in methanol (10 ml) of the acetate (14) (300 mg). The mixture was kept for 3 days at room temperature, then poured into water and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated to give oily *alcohol* (15) (235 mg), *m/e* 228 (M^+), $\nu_{max.}$ (film) 3 600 and 1 736 cm^{-1}, δ (CCl_4) 1.73, 3.60, and 3.67 (each 3 H), 2.57 (dd, *J* 10 and 6 Hz, 1-H), 3.45 (d, *J* 6 Hz, 2-H), 4.32 (m, 6-H), and 5.43 (m, 4-H) (Found: C, 57.4; H, 7.3. $C_{11}H_{16}O_5$ requires C, 57.9; H, 7.1%).

The enol ester (16).—(A) *By oxidation of the alcohol* (15). To a mixture of the alcohol (15) (100 mg) and dichloromethane (10 ml) was added chromic oxide–pyridine complex (800 mg). The mixture was stirred at room temperature overnight, then passed through a short silica column to remove solids. The eluate was washed with aqueous hydrochloric acid and then water, dried ($MgSO_4$), and evaporated. The residual oil was passed through a silica column to give an oil (72 mg). The ^1H n.m.r. spectrum revealed that this was a 3 : 1 mixture of esters (16) and (17).

(B) *By Birch reduction of the phenol ester* (17). To a solution of lithium (45 mg) in liquid ammonia (10 ml) was added the phenol ester (17) (224 mg) in dry tetrahydrofuran (2 ml) at solid carbon dioxide temperature. After 15 min, methanol (2 ml) was added and the solid CO_2–propan-2-ol bath was removed to allow the mixture to warm to room temperature. The mixture was diluted with water and neutral material was removed by shaking with ether. The aqueous layer was, after being acidified with hydrochloric acid, extracted with ether. The solution was washed with water, dried ($MgSO_4$), and evaporated to give a crude mixture, which was passed through a silica column to give *dimethyl* 3-*hydroxy*-6-*methylcyclohexa*-2,5-*diene*-1,2-*dicarboxylate* (16) (91 mg) as an oil, *m/e* 226 (M^+), $\nu_{max.}$ (film) 3 400, 1 737, 1 662, and 1 625 cm^{-1}, δ (CCl_4) 1.81, 3.73, and 3.80 (each 3 H), 3.99br (1 H, s, 1-H), 5.60 (1 H, m, 5-H), and 12.42 (1 H, s, OH) (Found: C, 58.7; H, 6.0. $C_{11}H_{14}O_4$ requires C, 58.4; H, 6.2%).

The Phenol Ester (17) *from the Adduct* (13).—To a stirred mixture of dichloromethane (200 ml) and the crude adduct (13), obtained by the reaction of 2-methylfuran (5.6 g) and dimethyl acetylenedicarboxylate (9.7 g), was added 36N-sulphuric acid (4 ml) with cooling in ice. After removal of the ice-bath, stirring was continued for 3 h and then the mixture was poured into water. The organic layer was washed with sodium hydroxide solution and the washings were acidified and extracted with ether. From the ethereal solution was obtained the phenol ester (17) (13.2 g), *m/e* 224 (M^+), $\nu_{max.}$ (KBr) 3 100, 1 732, 1 678, 1 598, 1 225, 841, and 800 cm^{-1}, δ ($CDCl_3$) 2.23 (Me × 1), 3.93 (Me × 2), 7.02 (1 H, d, *J* 9 Hz), 7.39 (1 H, d, *J* 9 Hz), and 10.87 (1 H, s).

Methylation of the Enol Ester (16).—To a solution in t-butyl alcohol (10 ml) of the enol ester (16) (219 mg) were added potassium t-butoxide (130 mg) and methyl iodide (0.2 ml). The mixture was stirred at 35 °C overnight, then diluted with ether, and the ethereal solution was washed with aqueous sodium hydroxide and then water, dried ($MgSO_4$), and evaporated to give the crude product (18) (205 mg). *Dimethyl* 2,6-*dimethyl*-3-*oxocyclohex*-5-*ene*-1,2-*dicarboxylate* (18) had m.p. 99—100 °C (from benzene), *m/e* 240 (M^+), $\nu_{max.}$ (KBr) 1 736 and 1 718 cm^{-1}, δ ($CDCl_3$) 1.50 (3 H, 2-Me), 1.90 (3 H, dd, *J* 1.0 and 3.0 Hz, 6-Me), 3.70 and 3.77 (Me × 2), 3.02 and 3.06 (each 1 H, t, *J* 6 Hz, 4-H_2), 3.27 (1 H, s, 1-H), and 5.69 (m, 5-H) (Found: C, 59.7; H, 6.6. $C_{12}H_{16}O_5$ requires C, 60.0; H, 6.7%).

Methyl 4-*Furfurylidenecrotonate* (19).—Small pieces of sodium (total 17 g) were gradually added with stirring to methyl acetate (400 ml) pre-cooled to −10 to −15 °C. Into this mixture was dropped 3-(2-furyl)acrylaldehyde (80 g) dissolved in anhydrous methyl acetate (100 ml), during 2 h, with the temperature of the mixture kept at −10 to −15 °C. The mixture was then stirred for an additional 8 h at the same temperature, kept in a refrigerator overnight, diluted with ether, neutralized with acetic acid, washed with water, dried ($MgSO_4$), evaporated, and distilled under reduced pressure to afford *methyl* 4-*furfurylidenecrotonate* (19) (43.4 g, 37%) as pale yellow crystals, b.p. 111 °C at 2 mmHg, m.p. 67—68° (Found: C, 67.8; H, 5.8. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.7%).

Formation of the Dimethyl 6-(2-*Furyl*)-1-*methoxycarbonyl*-*methylcyclohexane*-1,3-*dicarboxylates* (21) *and* (23).—A mixture of methyl 4-furfurylidenecrotonate (19) (12.5 g) and dimethyl itaconate (11 g) was stirred at 160 °C under nitrogen for 24 h to give the Diels–Alder adduct (20) as a viscous oil. The adduct was, without purification, dissolved in methanol (200 ml) containing 5% palladium–charcoal (3 g) and shaken under hydrogen until 1.2 mol. equiv. of hydrogen had been absorbed. Filtration and evaporation left a pale yellow oil. This oil (13.3 g) was passed through a silica column in benzene–di-isopropyl ether (40 : 1). Elution with the same solvent afforded the oily *triester* (21) (4.1 g, 31%) (Found: C, 60.0; H, 6.2. $C_{17}H_{22}O_7$ requires C, 60.3; H, 6.6%) and then the *isomer* (23) (4.3 g, 32%) (Found: C, 60.1; H, 6.3%).

Dieckmann Condensations of the Triesters (21) *and* (23).—A mixture of the triester (21) (1.44 g), anhydrous benzene (35 ml), and dried potassium t-butoxide (610 mg) was refluxed for 2.5 h with stirring under nitrogen. After cooling, the mixture was poured into aqueous 10% acetic acid and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated, and the resulting oily material was dissolved in ether (10 ml) and kept at room temperature; *dimethyl* 2-(2-*furyl*)-6-*oxobicyclo*[3.2.1]*octane*-1,7-*dicarboxylate* (25) was deposited as crystals (728 mg, 56%), m.p. 127—128° (Found: C, 63.0; H, 5.9. $C_{16}H_{18}O_6$ requires C, 62.7; H, 5.9%).

A mixture of the isomeric triester (23) (1.314 g), anhydrous benzene (30 ml), and dried potassium t-butoxide (620 mg) was refluxed for 1 h with stirring under nitrogen. After cooling, the mixture was diluted with ether and passed through a short silica gel column in order to remove basic materials. Elution with ether afforded an oil (877 mg). Addition of a small amount of ether caused deposition of the isomeric *oxo-ester* (27) as crystals (618 mg, 52%), m.p. 121—122° (Found: C, 62.8; H, 5.7%).

Epimerization of the Triesters (21) *and* (23).—A mixture of the triester (21) (434 mg), anhydrous xylene (15 ml), and dried potassium t-butoxide (158 mg) was refluxed overnight under nitrogen, cooled, poured into 0.5N-sodium hydroxide, and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated, and the resulting oily mixture (210 mg) was passed through a silica (20 g) column. Elution with benzene–di-isopropyl ether (20 : 1) gave the triester (21) (52 mg), a mixture of (21) and the epimerized triester (22) (64 mg), and the epimerized triester (22) (22 mg). From the aqueous alkaline solution was obtained acidic material (192 mg) (after acidification with aq. HCl

and extraction with ether). Silica gel column chromatography afforded the Dieckmann product (25) (72 mg).

Epimerization of the Triester (23).—The triester (23) (537 mg) was treated with potassium t-butoxide (195 mg) under the same conditions as in the case of (21), and the neutral oil was chromatographed to give the epimerized triester (24) (117 mg), a mixture of (23) and (24) (22 mg), and the triester (23) (45 mg). From the acidic fraction was isolated the Dieckmann product (27) (68 mg).

Demethoxycarbonylation of the Dieckmann Product (27).—(*A*) A mixture of the Dieckmann product (27) (5.0 g), anhydrous pyridine (100 ml), and lithium iodide (3 g) was gently refluxed for 2 days under nitrogen. After cooling, the mixture was poured into ice–12N-hydrochloric acid and extracted with dichloromethane. The extract was washed (aq. HCl, aq. NaOH, and then water), dried ($MgSO_4$), and evaporated to leave *methyl* 2-(2-*furyl*)-6-*oxobicyclo*[3.2.1]-*octane*-1-*carboxylate* (3b) (3.94 g), m.p. 68—68.5° (Found: C, 68.0; H, 6.4. $C_{14}H_{16}O_4$ requires C, 67.6; H, 6.5%).

(*B*) A mixture of (27) (600 mg), anhydrous collidine (30 ml), and lithium iodide (1.84 g) was warmed at 140 °C for 4 h, then treated as in (*A*) to give the *oxo-acid* (3a) (360 mg) (from the aq. NaOH solution), m.p. 185—186° (Found: C, 66.4; H, 6.1. $C_{13}H_{14}O_4$ requires C, 66.7; H, 6.0%).

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