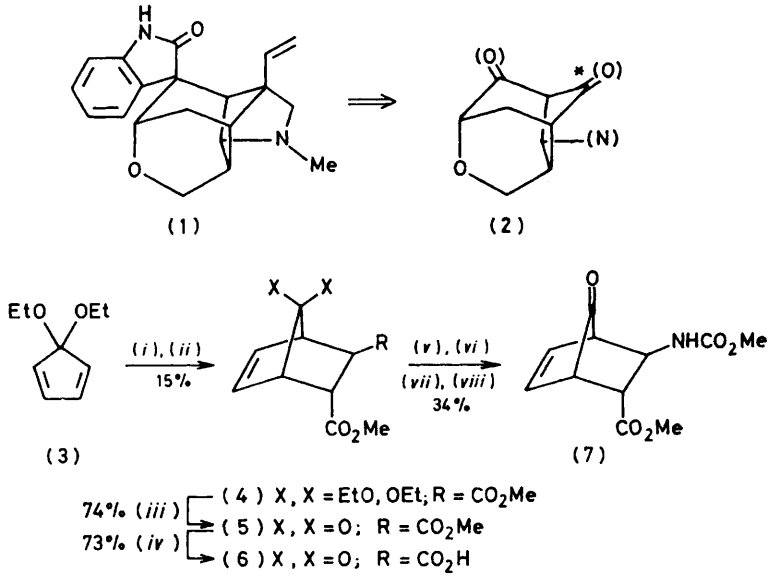
Synthetic Studies with 7-Functionalised Norbornenes, and their Synthesis by a Silicon-Controlled Carbocation Rearrangement †

By **Ian Fleming** * and **Joseph P. Michael**, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

As part of a projected synthesis of gelsemine (1), the synthesis of dimethyl 7-oxobicyclo[2.2.1]hept-5-ene-2-*endo*,3-*exo*-dicarboxylate (5) is described. The route involves the silicon-controlled rearrangement of 5-*exo*-bromo-3-*exo*-methoxycarbonyl-7-*anti*-trimethylsilylbicyclo[2.2.1]heptane-2,6-carbolactone (9), catalysed by silver ions in methanol, to give dimethyl 7-*syn*-hydroxybicyclo[2.2.1]hept-5-ene-2-*endo*,3-*exo*-dicarboxylate (11). Some related reactions show that a 7-trimethylsilyl group in a norbornene can be used to synthesise other 7-functionalised norbornenes. Thus the epoxide (13) of methyl 7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (12) rearranges on treatment with boron trifluoride–ether to give methyl 7-*anti*-hydroxybicylo-[2.2.1]hept-5-ene-2-*exo*-carboxylate (14), and treatment of (12) with bromine gives mainly the rearranged bromide, methyl 7-*anti*-bromobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate (16). Some limitations in this approach to 7-functionalised norbornenes are also described.

We plan to synthesise gelsemine (1) by way of a bicyclo-[3.2.1]octane derivative of the general form (2). In one approach to such a compound, we have been working with norbornenes such as the ketone (7), in which the C=C double bond will be used to expand the ring system of the bicyclo[2.2.1]heptene to a bicyclo[3.2.1]octane derivative. In this strategy, it is essential that we have advantage that we could use the 7-keto-group to differentiate between the two methoxycarbonyl groups, a major task, which we had to face at some stage. Thus one equivalent of alkali selectively hydrolysed the *exo*-methoxycarbonyl group to give the acid (6), presumably because the hydroxide ion initially attacked the ketone group to give an oxy-anion which can participate in the hydrolysis of the nearby ester group. Curtius degrad-



SCHEME 1 [2] (*i*) *trans*-ClCOCH=CHCOCl, room temperature, 17 h; (*ii*) NaOMe, MeOH, 5 °C, 1 h; (*iii*) $AlCl_3$, Et_2O, reflux, 30 min; (*iv*) NaOH, H_2O, 25 °C, 30 min; (*v*) $(COCl)_2$, CH_2Cl_2, 25 °C, 17 h; (*vi*) NaN_3, DMF, 5 °C, 20 min; (*vii*) C_6H_6, reflux, 30 min; (*viii*) MeOH, reflux, 30 min

RESULTS AND DISCUSSION

Our first route, a conventional one (Scheme 1), used the known 7,7-diethoxycyclopentadiene (3), and gave us a 7-oxonorbornene (5). This intermediate had the

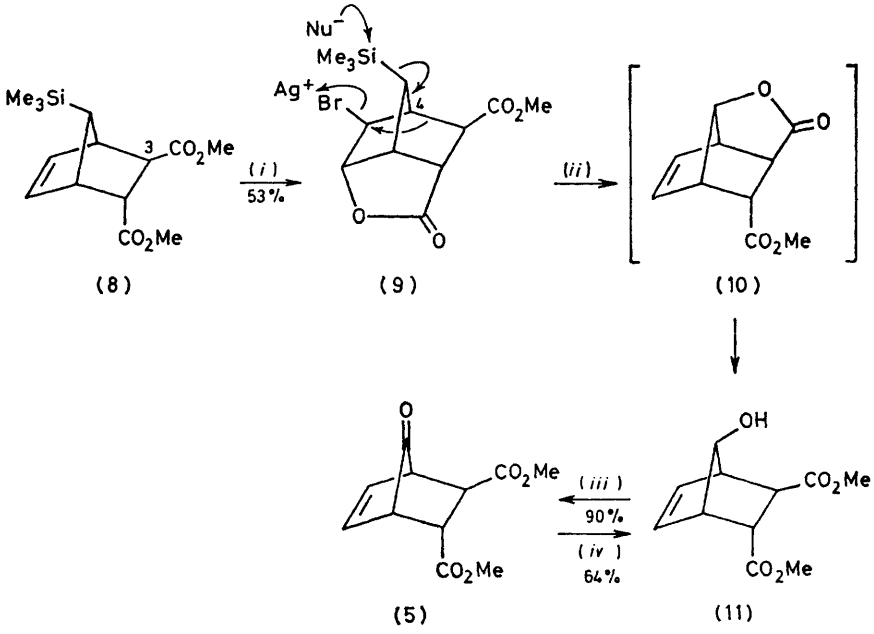
a functional group at the 7-position in the norbornene, in order that we can have, eventually, a functional group at the corresponding position (starred) in (2). We have, therefore, been working on various ways in which 7-functionalised norbornenes can be synthesised. We describe here some of our work, and, in particular, that part of it in which we used a silicon-controlled carbo-

† There are no reprints of this paper.

ation of the acid to give the urethane (7) completed our first objective.[2]

However, to make the diethoxycyclopentadiene (3) on a large scale was troublesome and time-consuming, and the yield in the Diels–Alder reaction was not good. We therefore sought a better synthesis of the ketone (5), and found it in the silicon-controlled carbo-cation rearrangement in Scheme 2. Dimethyl fumarate, like other reactive dienophiles,[3,4] captured the most abundant

Having been successful in our main aim, we examined a few other systems to see if this was a general approach to 7-functionalised norbornenes. Methyl acrylate, like other less-reactive dienophiles,[3] reacts with trimethylsilylcyclopentadiene to give a mixture of 5- and 6-silylated norbornene carboxylic esters with little regioselectivity.[6] Lewis-acid catalysis, however, raised the reactivity of the ester, and the major product was the 7-silylated norbornene (12). The epoxide (13) of this



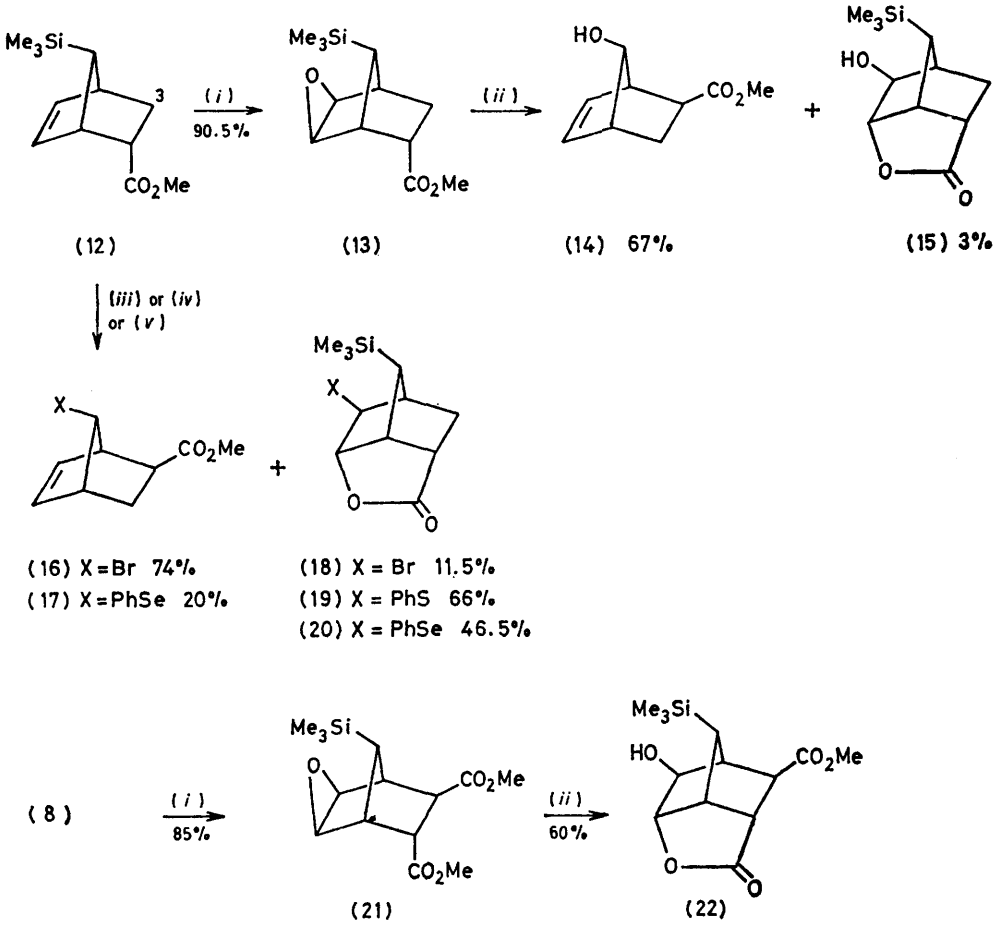
SCHEME 2 (*i*) Br_2; (*ii*), $AgNO_3$, MeOH; (*iii*) $(CF_3CO)_2O$, DMSO; (*iv*) $NaBH_4$

isomer of trimethylsilylcyclopentadiene. Bromination of the adduct (8) gave the bromolactone (9), and silver-ion-catalysed rearrangement (9, arrows) gave, presumably, the lactone (10), but this intermediate opened [(10) ⟶ (11)] in the (by now) acidic methanol used as a solvent. The overall yield from fumarate was 47% when intermediates were not isolated. The poor step (53%) was the bromolactonisation, but the key rearrangement step was very clean, giving a 98% yield of crystalline product. The trimethylsilyl group was needed; without it the starting material was the only compound which could be isolated, even after twice the time that it took for the silyl derivative to rearrange, and there was no sign of the product (11). The rearrangement was encouraged by the silyl group, because the Si–C bond stabilises the partial (or full) positive charge developing on C-4, and the outcome is controlled by the ready loss of the silyl group. A related reaction in the tin series has been reported by Hartmann and Traylor.[5] The alcohol (11) could be oxidised to the ketone (5), completing our less conventional, yet more convenient, synthesis of this compound, and the alcohol (11) was re-formed by reduction of the ketone (5), thus confirming the stereochemistry shown for this group.

adduct rearranged on treatment with boron trifluoride–ether to give the 7-hydroxynorbornene (14) (67%), together with a small amount of the unrearranged lactone (15) (3%). A closely similar reaction with bromine [(12) ⟶ (16)] shows that it is also possible to place a bromine atom at C-7 using the silicon-induced rearrangement. In contrast to the reaction of (8) with bromine, bromolactonisation [(12) ⟶ (18)] is only a minor pathway. Similarly, the epoxide (21) did not rearrange with boron trifluoride–ether but gave the lactone (22). Presumably, the presence of the second methoxycarbonyl group in (8) and (21) slows down the migration of the atom to which it is attached, thus allowing the lactonisations, already visible with (12), to take place instead.

However, it must be added that silicon-controlled rearrangement is not always a solution to the problem of placing a functional group on C-7 of a norbornene. We reported earlier[7] that, although the sodium salt of the carboxylic acid corresponding to the ester (12) underwent rearrangement on treatment with bromine, the product was unstable to the reaction conditions and went on to a tricyclic dibromide. Even less straightforward, phenylsulphenyl chloride reacted with the ester (12) to

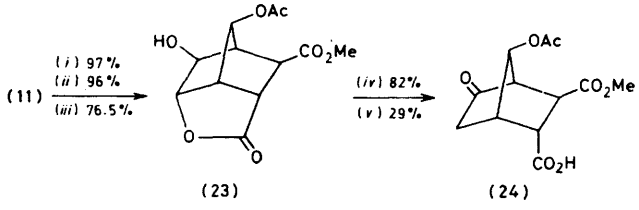
give unrearranged lactone (19) (66%) as the major product, and the rearranged product (22%) had reacted further with the sulphenyl chloride. Phenylselenenyl bromide was little better, giving selenolactonisation [8] [(12) ⟶ (20)] as the major reaction (46.5%) and a little of the simply rearranged product (17) (20%). Finally, we have, so far, been unable to get any useful



SCHEME 3 Reagents: (*i*) CF_3CO_3H; (*ii*) BF_3–OEt_2; (*iii*)Br_2; (*iv*) PhSCl; (*v*) PhSeBr

results from the reaction of (12) with carbon electrophiles.

We showed in Scheme 1 that it is possible to differenti-



SCHEME 4 (*i*) Ac_2O, Py; (*ii*) CF_3CO_3H; (*iii*) BF_3–OEt_2; (*iv*) RuO_4; (*v*) Zn, AcOH

ate the methoxycarbonyl groups at an early stage. Having now made the alcohol (11), we have been able to use another model sequence, which differentiates the methoxycarbonyl groups (Scheme 4), and simultaneously establishes a ketone group in (24) as a site for the ring-expansion.

EXPERIMENTAL

Dimethyl 7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-exo-*dicarboxylate* (8) (*Experiment by Dr. R. L. Snowden*).—Trimethylsilylcyclopentadiene [9] (3.73 g, 26 mmol) and dimethyl fumarate (3.60 g, 25 mmol) in benzene (30 ml) were kept at room temperature for 20 h and the solvent evaporated *in vacuo* to give the *trimethylsilyl diester* (8) (5.60 g, 79%) as needles, m.p. 64—66 °C (from hexane) (Found: C, 59.6; H, 7.95. $C_{14}H_{22}O_4Si$ requires C, 59.6; H, 7.8%), R_F (Et_2O) 0.63; $\nu_{max.}$ (CCl_4) 1 742 cm^{-1} (C=O); δ($CDCl_3$) 6.17 (1 H, dd, *J* 6 and 4 Hz, H-5), 5.95 (1 H, dd, *J* 6 and 4 Hz, H-6), 3.70 (3 H, s, CO_2Me), 3.62 (3 H, s, CO_2Me), 3.36 (1 H, dd, *J* 4 and 4 Hz, H-2-*exo*), 3.32 (1 H, m, H-1), 3.16 (1 H, m, H-4), 2.70 (1 H, d, *J* 4 Hz, H-3-*endo*), 1.27 (1 H, s, H-7), and −0.90 (9 H, s, $SiMe_3$); *m/z* 282 (M^+, 5%), and 217 (100). Assignment of H-5 and H-6 was on the basis of a double-resonance experiment.

5-exo-*Bromo*-3-exo-*methoxycarbonyl*-7-anti-*trimethylsilyl*-*bicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (9).—A solution of bromine (2.7 ml, 8.48 g, 53.0 mmol) in chloroform (25 ml) was added dropwise at room temperature over 1.5 h to a

stirred solution of the trimethylsilyl diester (8) (13.50 g, 47.8 mmol) in chloroform (100 ml). The mixture was kept for 4 h, then shaken with sodium thiosulphate solution and worked up in the usual way to give a semi-crystalline oil consisting of a mixture of the desired bromolactone (9) and the by-products of the reaction. The bromolactone could be isolated as prisms (9.0 g, 53%) from benzene–light petroleum (b.p. 60—80 °C). A sample, recrystallised from acetonitrile, had m.p. 161.5—162.5 °C (Found: C, 44.9; H, 5.55. $C_{13}H_{19}BrO_4Si$ requires C, 45.0; H, 5.5%), R_F (Et_2O) 0.62; $\nu_{max.}$ ($CHCl_3$) 1 785 (lactone), 1 734 (ester), 1 250 ($SiMe_3$) and 840 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 4.94 (1 H, d, *J* 5 Hz, H-6), 3.78 (1 H, d, *J* 2 Hz, H-5), 3.74 (3 H, s, CO_2-Me), 3.28 (1 H, m, H-1), 3.05 (2 H, m, H-2 and H-4), 2.81 (1 H, d, *J* 2 Hz, H-3), 1.35 (1 H, s, H-7), and 0.20 (9 H, s, $SiMe_3$); *m/z* 333 (55%, $^{81}M^+$ — Me), 331 (56, $^{79}M^+$ — Me), 305 (25, $^{81}M^+$ — MeO), 303 (24, $^{79}M^+$ — MeO), 267 (90, M^+ — Br), 150 (70), 149 (63), 139 (100), 137 (100), 135 (66), and 91 (70).

Dimethyl 7-syn-*hydroxybicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-exo-*dicarboxylate* (11).—The bromolactone (9) (2.05 g, 5.91 mmol) and silver nitrate (5.0 g, 29.3 mmol) were refluxed in methanol (100 ml) for 8 h in the dark with vigorous mechanical stirring. The reaction mixture was filtered through Celite to remove the precipitated silver bromide; the filtrate was concentrated *in vacuo* to about 25 ml and was poured into water (100 ml). The aqueous solution was extracted with chloroform (3 × 30 ml). The combined extracts were washed with saturated brine solution, dried ($MgSO_4$), and evaporated *in vacuo* to give the *hydroxy-diester* (11) (1.31 g, 98%) as needles, m.p. 77.5—78.5 °C [from ether–light petroleum (b.p. 60—80 °C)] (Found: C, 58.7; H, 6.3. $C_{11}H_{14}O_5$ requires C, 58.4; H, 6.25%), R_F (Et_2O) 0.50; $\nu_{max.}$ ($CHCl_3$) 3 600 and 3 550—3 250 (br, OH), 1 725 cm^{-1} (br, C=O); δ($CDCl_3$) 6.21 (1 H, m, H-5), 5.93 (1 H, m, H-6), 3.73, 3.63 and 3.60 (8 H, superimposed s, s, and m, H-7, H-2-*exo*, and CO_2Me), 3.42 (s, OH, exchanges with D_2O), 3.08 (2 H, m, H-1 and H-4), 2.79 (1 H, d, *J* 5 Hz, H-3-*endo*); *m/z* 195 (46%, M^+ — MeO), 194 (61, M^+ — MeOH), 137 (38), 107 (61), 85 (69), and 83 (100). The alcohol was further characterized as its *acetate* (pyridine–acetic anhydride, room temperature, 66 h, 97%), b.p. 110—115 °C/0.01 mmHg, m.p. 66—69 °C (from benzene) (Found: C, 58.0; H, 6.05. $C_{13}H_{16}O_6$ requires C, 58.2; H, 6.0%), R_F (Et_2O) 0.65; $\nu_{max.}$ ($CHCl_3$) 1 730 (C=O); δ($CDCl_3$) 6.25 (1 H, ddd, *J* 1, 4, and 6 Hz, H-5), 5.98 (1 H, ddd, *J* 1, 4, and 6 Hz, H-6), 4.48 (1 H, br s, H-7), 3.71, 3.68, and 3.66 (7 H, s, s, and m, 2 × CO_2Me and H-2′-*exo*), 3.39 (1 H, m, H-1), 3.22 (1 H, m, H-4), 2.85 (1 H, d, *J* 5 Hz, H-3-*endo*), and 1.92 (3 H, s, OAc); *m/z* 268 (7%, M^+), 237 (18, M^+ — MeO), 226 (34, M^+ — CH_2CO), 209 (26, M^+ — CO_2Me), 194 (91), 154 (100), 149 (58), 113 (83), and 107 (63). Assignment of H-5 and H-6 was by analogy with (8) above.

Combined Procedure for Large-scale Preparation of the Hydroxy-diester (11) *without Recrystallization of the Intermediates*.—Dimethyl fumarate (3.68 g, 25.6 mmol) and trimethylsilylcyclopentadiene [9] (4.20 g, 30.4 mmol) were kept in dichloromethane (70 ml) at room temperature for 24 h. The solvent was removed *in vacuo*, the residue dissolved in light petroleum (b.p. 60—80 °C) and filtered through silica gel (150 g, slurried with light petroleum). Elution with light petroleum (500 ml) removed non-polar impurities. The ester (8) was then eluted with light petroleum–ethyl acetate (2 : 1 v/v, 500 ml) and obtained as a pale yellow crystalline mass (7.20 g, quantitative), m.p. 59—63 °C. Bromine (1.50 ml, 4.71 g, 29.4 mmol) in methanol (40 ml) was added dropwise at 0 °C over 1 h with vigorous stirring to this ester in methanol (100 ml), in which sodium hydrogencarbonate (2.20 g, 26.2 mmol) was suspended. Stirring was continued for 4 h at room temperature, the solution was concentrated *in vacuo* (to about 50 ml), and then poured into dilute sodium thiosulphate solution (300 ml). The aqueous solution was extracted with dichloromethane (5 × 60 ml), and the combined extracts were washed with brine (2 × 100 ml), dried ($MgSO_4$), and evaporated *in vacuo* to a semi-crystalline oil (8.59 g). This oil and silver nitrate (10.50 g, 61.5 mmol) were refluxed with vigorous mechanical stirring in methanol (150 ml) for 10 h in the dark. The solution was filtered through Celite, concentrated *in vacuo* to *ca.* 50 ml, and poured into water (300 ml). The aqueous solution was extracted with dichloromethane (4 × 40 ml), and the combined extracts were washed with brine (100 ml), dried ($MgSO_4$), and evaporated *in vacuo* to a gum (aboug 6 g). This gum was chromatographed on silica gel (130 g, slurried with 4 : 1 v/v light petroleum–ether), eluting successively with 4 : 1, 3 : 2, and 2 : 3 light petroleum–ether. The *hydroxy-diester* (11) was obtained as a cream-coloured crystalline mass (2.73 g, 47% based on dimethyl fumarate), m.p. 70—73 °C. This product could be used without further purification in subsequent reactions.

Dimethyl 7-*Oxobicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-exo-*dicarboxylate* (5).—The oxidation procedure used was that of Huang, Omura, and Swern.[10] A solution of trifluoroacetic anhydride (0.12 ml, 180 mg, 0.86 mmol) in dry dichloromethane (0.8 ml) was added dropwise to a solution of dimethyl sulphoxide (85 μl, 93 mg, 1.19 mmol) in dry dichloromethane (0.5 ml) cooled to −65 °C under nitrogen, and the resulting solution was stirred for 20 min. A solution of the hydroxy-diester (11) (113 mg, 0.5 mmol) in dichloromethane (0.8 ml) was added dropwise during 2 min by syringe. Stirring was continued for 15 min; the solution was warmed to room temperature over 10 min, and it was then left to stand at room temperature for a further 30 min. Triethylamine (0.2 ml, dried over Woelm alumina) was added; and after 20 min, the reaction mixture was poured into dilute hydrochloric acid and extracted with ether (10 ml) to give the *keto-diester* (5) (101 mg, 90%) as an unstable yellow oil, pure by n.m.r. and t.l.c., R_F (Et_2O) 0.45; $\nu_{max.}$ (CCl_4) 1 780 (ketone) and 1 730 cm^{-1} (ester C=O); δ($CDCl_3$) 6.66 (1 H, dd, *J* 6 and 4 Hz, H-5), 6.48 (1 H, dd, *J* 6 and 4 Hz, H-6), 3.73 (3 H, s, CO_2Me), 3.70 (3 H, s, CO_2Me), 3.54 (1 H, dd, *J* 4 and 4 Hz, H-2-*exo*), 3.34 (1 H, m, H-1), 3.21 (1 H, m, H-4), and 2.87 (1 H, d, *J* 4 Hz, H-3-*endo*) (Found: M^+, 224.067 5. $C_{11}H_{12}O_5$ requires *M*, 224.068 5); *m/z* 224 (0.5%, M^+), 209 (4, M^+ — Me), 193 (23, M^+ — MeO), 163 (22), 138 (25), 137 (93), 136 (42), 105 (100), 93 (75), and 91 (50). This unstable ketone was spectroscopically identical to that prepared by the route in Scheme 1.[2] Assignment of H-5 and H-6 was by analogy with (8) above.

5-exo-*Bromo*-3-exo-*methoxycarbonylbicyclo*[2.2.1]*heptane*-2,6-*carbolactone*.—Bromine (0.30 ml, 942 mg, 5.88 mmol) was added to dimethyl *trans*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (1.20 g, 5.71 mmol) in chloroform (15 ml) at room temperature. Aqueous work up gave the *bromolactone* (9; H for $SiMe_3$) (85%) as needles, m.p. 117.5—118.5 °C (from acetonitrile) (Found: C, 43.6; H, 3.95. $C_{10}H_{11}BrO_4$ requires C, 43.7; H, 4.0%), R_F (Et_2O) 0.67; $\nu_{max.}$ ($CHCl_3$) 1 795 and 1 780 (lactone) and 1 735 cm^{-1}

(ester); $\nu_{max.}$ (Nujol) 1 790, 1 775, and 1 740 cm^{-1}: $\delta(CDCl_3)$ 5.86 (1 H, d, J 4.4 Hz, H-6), 4.97 (1 H, d, J 2.3 Hz, H-5), 4.68 (3 H, s, CO_2Me), 4.2—3.9 (3 H, m, H-1, H-2, and H-3), 3.73 (1 H, s, H-4), 3.25 (1 H, d, J 12 Hz, H-7-*syn*), and 2.82 (1 H, d, J 12 Hz, H-7-*anti*); *m/z* 276 (10%, $^{81}M^+$), 274 (10%, $^{79}M^+$), 245 (46), 243 (44), 216 (39), 214 (39), 196 (78), and 195 (100). This compound, treated with silver nitrate (ten-fold excess) in boiling methanol under nitrogen, failed to produce the hydroxy-diester (11), as judged by t.l.c. After 24 h, only starting material was discernible; gradual decomposition to ill-defined products followed with longer periods of heating.

Reduction of the Keto-diester (5) *to the Hydroxy-diester* (11).—Sodium borohydride (10 mg, 0.26 mmol) was added to a stirred solution of the keto-diester (5) (83 mg, 0.37 mmol) in methanol (15 ml). After 1 h at room temperature, the solution was poured into dilute hydrochloric acid, worked up in the usual way, and purified by t.l.c. on silica gel eluting with benzene–ethyl acetate (2 : 1 v/v). The hydroxy-diester (11) (54 mg, 64%) was recrystallised from benzene–light petroleum (b.p. 60—80 °C) as needles, m.p. 78—79 °C, identical (mixed m.p., i.r., n.m.r., t.l.c.) with the hydroxy-diester prepared earlier.

Lewis-acid-catalysed Diels–Alder Reaction between Trimethylsilylcyclopentadiene and Methyl Acrylate.—Trimethylsilylcyclopentadiene [9] (3.57 g, 25.8 mmol) in dry ether (15 ml) was added dropwise over 10 min to a stirred, ice-cold solution of methyl acrylate (2.52 g, 29.5 mmol) and boron trifluoride–ether (3.6 ml, 4.16 g, 29.3 mmol) in dry ether (15 ml), and the mixture kept first at 0 °C for 1 h and then at room temperature for 42 h. An aqueous work-up and column chromatography on silica gel (Reeve Angel CT) eluting with 2 : 1 v/v light petroleum (b.p. 60—80 °C)–dichloromethane gave *methyl* 7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* (12) (2.85 g, 51%) as a pale yellow oil, b.p. 50 °C/0.01 mmHg (Found: C, 64.7; H, 8.8. $C_{12}H_{20}O_2Si$ requires C, 64.2; H, 9.0%), R_F (benzene) 0.39; $\nu_{max.}$ (neat liquid) 3 060 (=CH), 1 740 (C=O), 1 252 ($SiMe_3$), and 840 cm^{-1} ($SiMe_3$); $\nu_{max.}$ ($CHCl_3$) 1 725 (C=O), 1 252 ($SiMe_3$), and 842 cm^{-1} ($SiMe_3$); $\delta(CDCl_3)$ 6.08 (1 H, dd, J 2.5 and 6 Hz, H-5), 5.81 (1 H, dd, J 2.5 and 6 Hz, H-6) (H-5 and H-6 were assigned by a double-resonance experiment), 3.65 (3 H, s, CO_2Me), 3.29 (1 H, m, H-1), 3.08—2.81 (2 H, m, H-2 and H-4), 1.96 (1 H, ddd, J 3, 9 and 12 Hz, H-3-*exo*), 1.30 (1 H, dd, J 4.5 and 12 Hz, H-3-*endo*), 0.95 (1 H, s, H-7), and −0.05 (9 H, s, $SiMe_3$) (Found: M^+, 224.123 5. $C_{12}H_{20}O_2Si$ requires M, 224.123 3); *m/z* 224 (3%, M^+), 209 (21, M^+ − Me), 151 (25, M^+ − $SiMe_3$), 139 (20), 138 (100), 123 (42), and 122 (22); *methyl* 7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* (300 mg, 5.5%), as a pale yellow oil, R_F (benzene) 0.48; $\nu_{max.}$ ($CHCl_3$) 1 725 (C=O), 1 248 ($SiMe_3$), and 842 cm^{-1} ($SiMe_3$); $\delta(CDCl_3)$ 6.00 (2 H, m, H-5 and H-6), 3.68 (3 H, s, CO_2Me), 3.09 (1 H, m, H-1), 2.96 (1 H, m, H-4), 2.28 (1 H, dd, J 4.5 and 8.5 Hz, H-2), 1.91 (1 H, dt, J 4.5 and 11 Hz, H-3-*exo*), 1.39 (1 H, dd, J 8.5 and 11 Hz, H-3-*endo*), 1.17 (1 H, s, H-7), and −0.10 (9 H, s, $SiMe_3$) (Found: M^+, 224.123 8. $C_{12}H_{20}O_2Si$ requires M, 224.123 3); *m/z* 224 (1%, M^+), 210 (14), 209 (8), 138 (100), 123 (15), and 122 (18); and *methyl bicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* (469 mg, 12%) as a pale yellow oil, having identical t.l.c. behaviour, and i.r. and n.m.r. spectra [11] to that of an authentic sample.[12]

Methyl 5,6-exo-*Epoxy*-7-anti-*trimethylsilylbicyclo*[2.2.1]-*heptane*-2-endo-*carboxylate* (13).—Trifluoroacetic anhydride (0.45 ml, 675 mg, 3.63 mmol) was added dropwise during 2 min to a stirred solution of hydrogen peroxide (*ca.* 85%, 0.12 ml, *ca.* 2.9 mmol) in dry dichloromethane (2.5 ml) under nitrogen at 0 °C. Stirring was continued for 15 min, and the resulting solution added dropwise to a stirred, ice-cold solution of methyl 7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate (12) (231 mg, 1.03 mmol) in dry dichloromethane (15 ml) buffered with solid disodium hydrogenphosphate (2.14 g, 15.2 mmol) under nitrogen. After a further 30 min, the reaction mixture was poured into ether (30 ml) and worked up in the usual way to give the labile epoxide (13) (224 mg, 90.5%). The compound was used without further purification in the next reaction. Purification by t.l.c., eluting with light petroleum (b.p. 60—80 °C)–ethyl acetate (3 : 1 v/v) gave a sample of the *epoxide*, m.p. 35—37 °C (Found: C, 59.8; H, 8.5. $C_{12}H_{20}O_3Si$ requires C, 60.0; H, 8.4%), R_F (Et_2O) 0.45; $\nu_{max.}$ ($CHCl_3$) 1 725 (C=O), 1 252 and 838 cm^{-1} ($SiMe_3$); $\delta(CDCl_3)$ 3.68 (3 H, s, CO_2Me), 3.63 and 3.53 (2 H, 2 × t, J 4 Hz, H-5 and H-6), 2.85—2.53 (2 H, m, H-1 and H_2), 2.40 (1 H, m, H-4), 2.00 (1 H, dd, J 4 and 12 Hz, H-3a), 1.78 (1 H, dd, J 4 and 12 Hz, H-3b), 1.32 (1 H, s, H-7), and 0.05 (9 H, s, $SiMe_3$); *m/z* 240 (9%, M^+), 225 (24, M^+ − Me), 209 (16, M^+ − MeO), 181 (100, M^+ − CO_2Me), 180 (38), 165 (40), 154 (87), 146 (35), 139 (35), 107 (38), 99 (95), 91 (72), and 89 (67).

Methyl 7-anti-*hydroxybicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* (14).—Boron trifluoride–ether (0.12 ml, 140 mg, 1.0 mmol) was added at room temperature to a stirred solution of methyl 5,6-*exo*-epoxy-7-*anti*-trimethylsilylbicyclo[2.2.1]heptane-2-*endo*-carboxylate (13) (224 mg, 0.93 mmol) in dry ether (15 ml). After 1.5 h, the reaction mixture was worked up in the usual way and chromatographed on plates (SiO_2) eluting twice with light petroleum (b.p. 60—80 °C)–ethyl acetate (7 : 3 v/v) to give the *alcohol* (14) as an unstable oil (105 mg, 67%), R_F [light petroleum (b.p. 60—80 °C)–ethyl acetate 3 : 1 v/v] 0.20; $\nu_{max.}$ ($CHCl_3$) 1 705 cm^{-1} (C=O); $\delta(CDCl_3)$ 6.06 (2 H, dt, J 1.5 and 2.5 Hz, H-5 and H-6), 4.09 (1 H, s, OH, exchanges with D_2O), 3.73 (3 H, s, CO_2Me), 3.63 (1 H, m, H-7), 2.90 (1 H, dd?, J 1.5 and 3 Hz?, H-1), 2.78 (1 H, m, H-4), 2.38—2.10 (2 H, m, H-2-*endo* and H-3-*exo*), and 1.73—1.58 (1 H, m, H-3-*endo*) (Found: M^+, 168.079 1. $C_9H_{12}O_3$ requires 168.078 6); *m/z* 168 (M^+, 13%), 150 (14, M^+ − H_2O), 137 (49, M^+ − MeO), 136 (100), 109 (25, M^+ − CO_2Me), 108 (94), 107 (50), 92 (50), and 91 (99); and 5-exo-*hydroxy*-7-anti-*trimethylsilylbicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (15), as a solid (<5 mg, <3%), purified by sublimation at 110 °C/0.4 mmHg and recrystallisation from di-isopropyl ether, m.p. 141—144 °C (Found: C, 58.9; H, 7.9. $C_{11}H_{18}O_3Si$ requires C, 58.4; H, 8.0%), R_F [light petroleum (b.p. 60—80 °C)–ethyl acetate (3 : 1 v/v)] 0.11; $\nu_{max.}$ ($CHCl_3$) 1 779 (C=O), 1 255, and 840 cm^{-1} ($SiMe_3$) (Found: M^+ − 15, 211.0794. $C_{10}H_{15}O_3Si$ requires M, 211.0790); *m/z* 211 (12%, M^+ − Me), 135 (11), 111 (100), 108 (14), 107 (11), 91 (15), 85 (58), 83 (62), and 73 (66); the 1-*naphthylurethane derivative* of the alcohol (15) was obtained as needles, m.p. 125.5—126.5 °C (from benzene) (Found: C, 70.9; H, 5.75; N, 4.2. $C_{20}H_{19}NO_4$ requires C, 71.2; H, 5.7; N, 4.2%).

Methyl 7-anti-*Bromobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* (16).—Bromine (71 μl, 223 mg, 1.39 mmol) was added to a stirred solution of the silyl compound (12) (280 mg, 1.25 mmol) in methanol (10 ml) at room temperature. After 1 h, the solvent was removed *in vacuo* and the resulting oil (*ca.* 370 mg) was separated by t.l.c. eluting with 3 : 1 v/v light petroleum (b.p. 60—80 °C)–ethyl acetate to give the *ester* (16) (212 mg, 74%) as a yellow oil, b.p. 100 °C/0.1

mmHg, R_F(benzene) 0.33; $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} (C=O); δ($CDCl_3$) 6.14 (2 H, m, H-5 and H-6), 4.29 (1 H, s, H-7), 3.72 (3 H, s, CO_2Me), 3.21 (1 H, m, H-1), 3.10 (1 H, m, H-4), 2.35 (1 H, dd, *J* 4 and 10 Hz, H-2-*endo*), 2.06 (1 H, ddd, *J* 4, 4, and 12 Hz, H-3-*exo*), and 1.52 (1 H, dd, *J* 10 and 12 Hz, H-3-*endo*) (Found: M^+, 229.993 8. $C_9H_{11}BrO_2$ requires *M*, 229.994 2); *m/z* 232 (3%, $^{81}M^+$), 230 (3, $^{79}M^+$), 151 (75, M^+ − Br), 146 (98), 144 (100), 139 (30), 137 (28), 92 (35), and 91 (99); 5-*exo*-bromo-7-*anti*-trimethylsilylbicyclo-[2.2.1]heptane-2,6-carbolactone (18) (42 mg, 11.5%) identical to the sample prepared earlier;[7] and *methyl* 5-endo,7-endo-*dibromotricyclo*[2.2.1^{2,6}]*heptane*-3-*carboxylate* (30 mg, 7.5%) (the methyl ester of the tricyclic acid described in ref. 7), R_F[light petroleum (b.p. 60—80 °C)–ethyl acetate (3 : 1 v/v)] 0.31; $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1} (C=O); δ($CDCl_3$) 4.27 (1 H, s, CHBr), 4.16 (1 H, s, CHBr), 3.74 (3 H, s, OMe), 2.83 (1 H, m, *J* small), 2.57 (1 H, t, *J* 2 Hz), 2.12 (2 H, d, *J* 5.5 Hz), and 1.72 (1 H, tt, *J* 1.5 and 5.5 Hz) (Found: M^+, 307.9042. $C_9H_{10}Br_2O_2$ requires *M*, 307.9048), *m/z* 312, 310, and 308 (≪1%, M^+), 231 (96, M^+ − Br), 229 (100, M^+ − Br), 199 (16), 197 (16), 149 (16), 125 (30), 122 (27), 118 (25), 93 (80), and 87 (32).

Reaction of Methyl 7-anti-*Trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* (12) *with Phenylsulphenyl Chloride*.—Phenylsulphenyl chloride (295 mg, 2.03 mmol) was added to the silyl compound (12) (380 mg, 1.695 mmol) in dry acetonitrile (10 ml) under nitrogen at room temperature. After 1 h, the solvent was removed *in vacuo* and the residue purified by t.l.c. eluting with dichloromethane–light petroleum (b.p. 60—80 °C) (2 : 1 v/v) to give an inseparable mixture of diastereoisomers of *methyl* 5-*chloro*-6,7-*bis*(*phenylthio*)*bicyclo*[2.2.1]*heptane*-2-*carboxylate* and *methyl* 6-*chloro*-5,7-*bis*(*phenylthio*)*bicyclo*[2.2.1]*heptane*-2-*carboxylate* as a viscous yellow oil (149 mg, 22%), which decomposed on attempted distillation at 160 °C/0.5 mmHg; R_F(CH_2Cl_2) 0.69; $\nu_{max.}$ ($CHCl_3$) 1 726 (ester) and 1 582 and 1 479 cm^{-1} (aromatic); δ($CDCl_3$) at least three singlets, at 3.70, 3.68, and 3.61, for CO_2Me (Found: M^+, 404.0679. $C_{21}H_{21}ClO_2S_2$ requires *M*, 404.0672); *m/z* 404 (75%, M^+ for major isotopes of S and Cl), 406 (33), 296 (32), 187 (28), 185 (31), 173 (38), 151 (46), 123 (52), 119 (39), 110 (100), and 109 (60); and 5-exo-*phenylthio*-7-anti-*trimethylsilylbicyclo*-[2.2.1]*heptane*-2,6-*carbolactone* (19) (354 mg, 66%), purified by sublimation at 130—135 °C/0.1 mmHg (328 mg, 61%). A sample was obtained as needles, m.p. 146—149 °C (from EtOAc) (Found: C, 64.2; H, 6.9. $C_{17}H_{22}O_2SSi$ requires C, 64.1; H, 6.95%), R_F (CH_2Cl_2) 0.53; $\nu_{max.}$ ($CHCl_3$) 1 773 (lactone), 1 583 and 1 480 (aromatic), 1 250 and 838 cm^{-1} ($SiMe_3$); δ(CD_2Cl_2) 7.34 (5 H, m, aromatic H), 4.65 (1 H, dd, *J* 1 and 5 Hz, H-6), 3.38 and 3.33 (2 H, m, H-5 and H-1), 2.67 (1 H, dd, *J* 1 and 3 Hz, H-4), 2.54 (1 H, m, H-2), 2.13 (1 H, ddd, *J* 3.5, 11, and 12 Hz, H-3-*exo*), 1.91 (1 H, ddd, *J* <1, 2, and 13 Hz, H-3-*endo*), 1.28 (1 H, s with incipient coupling, H-7), and 0.25 (9 H, s, $SiMe_3$); *m/z* 318 (22%, M^+), 304 (21), 303 (90, M^+ − 15), 167 (41), 129 (17), 110 (38), 109 (17), 91 (24), and 73 (100).

The Reaction of Methyl 7-anti-*Trimethylsilylbicyclo*[2.2.1]-*hept*-5-*ene*-2-endo-*carboxylate* (12) *with Phenylselenenyl Bromide*.—Bromine (23 μl, 72 mg, 0.45 mmol) was added to a stirred solution of diphenyl diselenide (140 mg, 0.45 mmol) in dry THF (2 ml) at room temperature. After 5 min, the red solution of phenylselenenyl bromide was added to a stirred, ice-cold solution of the silyl compound (12) (184 mg, 0.82 mmol) in dry nitromethane (15 ml) and the mixture kept at 0 °C for 1 h and at room temperature for 3 h. The product (370 mg) was purified by t.l.c., eluting with light petroleum (b.p. 60—80 °C)–ethyl acetate (7 : 3 v/v) to give: *methyl* 7-anti-*phenylselenenylbicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* (17) (252 mg, 20%), as a yellow oil, R_F (light petroleum (b.p. 60—80 °C)–ethyl acetate (3 : 1 v/v) 0.48; $\nu_{max.}$ ($CHCl_3$) 1 723 (C=O), 1 573 and 1 473 cm^{-1} (aromatic), δ($CDCl_3$) 7.5—7.4 (2 H, m, *o*-aromatic H), 7.3—7.15 (3 H, m, *m*- and *p*-aromatic H), 6.18 (2 H, m, H-5 and H-6), 3.69 (3 H, s, CO_2Me), 3.61 (1 H, m, H-7), 3.17 (1 H, m, H-4), 3.32 (1 H, m, H-1), 2.35 (1 H, dd, *J* 4.5 and 9.5 Hz, H-2), 2.04 (1 H, ddd, *J* 2.5, 4.5, and 11.5 Hz, H-3-*exo*), and 1.50 (1 H, dd, *J* 9.5 and 11.5 Hz, H-3-*endo*) (Found: M^+, 308.0317. $C_{15}H_{16}O_2Se$ requires *M*, 308.0315); *m/z* 308 (23%, M^+ for the major isotope of Se), 214 (25), 212 (25), 162 (33), 151 (45, M^+ − C_6H_5Se), 141 (58), 134 (29), 107 (67), 105 (38), and 91 (100); and 5-exo-*phenylselenenyl*-7-anti-*trimethylsilylbicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (20) (139 mg, 46.5%), as needles, m.p. 111—114 °C [from acetone–light petroleum (b.p. 60—80 °C)] (Found: C, 55.95; H, 6.0. $C_{17}H_{22}O_2SeSi$ requires C, 55.9; H, 6.1%), R_F (benzene) 0.19; $\nu_{max.}$ ($CHCl_3$) 1 770 (lactone), 1 575 and 1 474 (aromatic), 1 250 and 840 cm^{-1} ($SiMe_3$); δ(CD_2Cl_2) 7.65—7.45 (2 H, m, *o*-aromatic H), 7.45—7.3 (3 H, m, *m*- and *p*-aromatic H), 4.85 (1 H, dd, *J* 1 and 5 Hz, H-6), 3.35 (2 H, m, H-5 and H-1), 2.75 (1 H, br d, *J* *ca.* 3 Hz, H-4), 2.60 [1 H, m (16 lines?), H-2], 2.14 (1 H, ddd, *J* 3.5, 10 and 13 Hz, H-3-*exo*), 1.88 (1 H, dd, *J* 2 and 13 Hz, H-3-*endo*), 1.32 (1 H, s, H-7), and 0.30 (9 H, s, $SiMe_3$); *m/z* 366 (22%, M^+ for major isotope of Se), 353 (28), 352 (28), 351 (100, M^+ − Me), 349 (63), 215 (55), 213 (29), 146 (26), 144 (27), 137 (26), 145 (37), 135 (36), and 91 (72).

Dimethyl 7-anti-*Trimethylsilyl*-5,6-exo-*epoxybicyclo*-[2.2.1]*heptane*-2-endo-3-exo-*dicarboxylate* (21) (*Experiment by Dr. R. L. Snowden*).—Trifluoroacetic anhydride (2 ml, 3 g, 14 mmol) was added dropwise to a stirred solution of hydrogen peroxide (0.24 ml, 85%, *ca.* 5.8 mmol) in dry dichloromethane (3 ml) under N_2 at 0 °C, and set aside for 15 min. This solution was added to a stirred mixture of the silyl compound (8) (1.27 g, 5 mmol) and anhydrous sodium carbonate (2.39 g, 22.5 mmol) in dry dichloromethane (5 ml) under N_2 at 25 °C and the mixture refluxed for 30 min, kept at 25 °C for 3 h, and then filtered through Celite. The product mixture was reacted again (using three-quarters of the above amounts, and following the same procedure) to give material containing a high proportion of epoxide. Purification by column chromatography [silica gel (150 g) made up in hexane; gradient elution using successive amounts (250 ml) of 0, 1, 2, 5, 10, 20, 40, and 60% Et_2O–hexane solutions, 50-ml fractions being collected] and recrystallisation from hexane gave the epoxide (21) as a white crystalline solid (860 mg, 85%), m.p. 83—86 °C, R_F (Et_2O) 0.57 (Found: C, 56.35; H, 7.5. $C_{14}H_{22}O_5Si$ requires C, 56.2; H, 7.4%); δ 3.68 (3 H, s, OMe) and 3.67 (3 H, s, OMe), 3.62 (2 H, m, H-4 and H-5), 3.14 (2 H, m, H-1 and H-4), 2.87 (1 H, m, H-2), 2.68 (1 H, m, H-3), 1.44 (1 H, s, H-7), and 0.02 (9 H, s, $SiMe_3$); $\nu_{max.}$ 1 735, 1 256, 1 198, and 1 180 cm^{-1}; *m/z* 298 (M^+, 17%) and 266 (100).

7-anti-*Trimethylsilyl*-5-exo-*hydroxy*-3-exo-*methoxy-carbonylbicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (22) (*Experiment by Dr. R. L. Snowden*).—Boron trifluoride–ether (1 ml, freshly distilled) was added to the epoxide (21) (800 mg) in ether (20 ml) at 25 °C under nitrogen and kept at 25 °C for 2 h. Aqueous work-up gave the *alcohol* (22) (460 mg, 60%), m.p. 149—151 °C, R_F (Et_2O) 0.4 (Found: C, 54.9;

H, 7.0. $C_{13}H_{20}O_5Si$ requires C, 54.9; H, 7.0%); δ 4.48 (1 H, dd, *J* 7 and 4 Hz, H-5), 4.07 (1 H, dd, *J* 7 and 4 Hz, H-6), 3.69 (3 H, s, OMe), 3.25 (2 H, m, H-1 and H-4), 3.08 and 2.82 (2 H, m, H-2 and H-3), 2.60 (1 H, s, OH), 1.12 (1 H, s, H-7), and 0.04 (9 H, s, $SiMe_3$); $\nu_{max.}$ (CCl_4) 3 500, 1 790, 1 745, and 1 260 cm^{-1}; *m/z* 284 (M^+, 3%) and 266 (100).

Dimethyl 6-syn-*Acetoxy*-5,6-exo-*epoxybicyclo*[2.2.1]*heptane*-2-endo,3-exo-*dicarboxylate*.—Trifluoroacetic anhydride (9.0 ml, 13.5 g, 64.3 mmol) was added dropwise during 2 min to a stirred solution of hydrogen peroxide (*ca.* 85%, 1.4 ml, *ca.* 34 mmol) in dry dichloromethane (20 ml) under nitrogen at 0 °C. Stirring was continued for 15 min. The resulting solution was then added over 5 min to an ice-cold, stirred solution of the acetate of (11) (5.70 g, 21.3 mmol) in dry dichloromethane (100 ml) buffered with solid disodium hydrogenphosphate (20 g, 141 mmol) under nitrogen. After a further 20 min, the mixture was poured into ether (150 ml). Aqueous work up gave the *epoxide* (5.83 g, 96% as a labile solid. A sample was obtained as needles, m.p. 96—96.5 °C (from C_6H_6) (Found: C, 55.2; H, 5.65. $C_{13}H_{16}O_7$ requires, C, 54.9; H, 5.65%), R_F (2:1 v/v benzene–ethyl acetate) 0.41; $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (C=O); δ($CDCl_3$) 4.71 (1 H, m, H-7), 3.73, 3.67 and 3.59 (7 H, s, s and m, 2 × CO_2Me and H-2-*exo*), 3.35 and 3.23 (3 H, dd and m, *J* 1.5 and 3 Hz, H-6, H-5, and H-3-*endo*), 3.02 and 2.98 (2 H m, H-1 and H-4), and 1.88 (3 H, s, OAc): *m/z* 253 (41%, M^+ — MeO), 225 (41, M^+ — CO_2Me), 211 (57), 197 (69), 165 (100), 137 (89), 105 (53).

7-syn-*Acetoxy*-5-exo-*hydroxy*-3-exo-*methoxycarbonyl*-*bicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (23).—Boron trifluoride–ether (0.5 ml, 584 mg, 4.1 mmol) was added to a stirred solution of the epoxide (5.37 g, 18.9 mmol) in acetone (20 ml) at room temperature. An immediate yellow colour, rapidly darkening to brown, developed. After 2.5 h, the reaction mixture was worked up and chromatographed on silica gel (100 g, slurried with dichloromethane), eluting with dichloromethane (300 ml), dichloromethane–ether (1 : 1 v/v, 500 ml), and ether (500 ml). The *hydroxy-lactone* (23) was isolated as a solid (3.91 g, 76.5%), m.p. 102—106 °C, after trituration with ether–light petroleum (b.p. 60—80 °C). A sample was obtained as needles, m.p. 107—108 °C (from C_6H_6) (Found: C, 53.3; H, 5.3. $C_{12}H_{14}O_7$ requires C, 53.3; H, 5.2%), R_F (2 : 1 v/v benzene–acetone) 0.46; $\nu_{max.}$ ($CHCl_3$) 3 600 and 3 550—3 200 (br, OH), 1 788 (lactone), and 1 740 cm^{-1} (ester); δ($CDCl_3$) 5.33 (1 H, m, H-7), 4.49 (1 H, dt, *J* 1 and 4.5 Hz, H-6), 3.83 and 3.75 (4 H, s and s, H-5 and CO_2Me), 3.5—3.25 (2 H, m, H-2 and H-3), 3.18 (1 H, m, H-1), 2.87 (1 H, s, OH, exchanges with D_2O), 2.65 (1 H, m, H-4), and 1.94 (3 H, s, OAc); *m/z* 239 (6%, M^+ — MeO), 210 (47, M^+ — H — CO_2Me), 122 (43), 121 (34), 120 (95), 119 (100), 118 (77), and 117 (100).

7-syn-*Acetoxy*-3-exo-*methoxycarbonyl*-5-*oxobicyclo*[2.2.1]-*heptane*-2,6-*carbolactone*.—The hydroxy-lactone (23) (1.78 g, 6.57 mmol) was dissolved in dry, alcohol-free chloroform (15 ml). Sodium periodate (1.680 g, 7.84 mmol), hydrated ruthenium dioxide (50 mg), and water (2 ml) were added and the mixture stirred vigorously at room temperature for 17.5 h before being diluted with more chloroform (15 ml). Propan-2-ol (1 ml) was added to destroy any unreacted ruthenium tetraoxide and the mixture was drawn by suction through a short column (packed from the bottom) of Celite, charcoal, and magnesium sulphate, eluting with more chloroform (50 ml). The solvent was removed *in vacuo*. The resulting gum (*ca.* 2 g) was distilled twice, first at 190 °C/0.05 mmHg, and again at 160—170 °C/0.03 mmHg; the *keto-lactone* was obtained as a glass (1.448 g, 82%), R_F (benzene–acetone 2 : 1 v/v) 0.31; $\nu_{max.}$ ($CHCl_3$) 1 780 (br, lactone and ketone), 1 737 cm^{-1} (ester), δ([$^2H_6$]acetone) 5.27 (1 H, t, *J* 1.5 Hz, H-7), 4.70 (1 H, td?, *J* 1.5 and 5 Hz, H-6), 3.75 (3 H, s, CO_2Me), 3.45 (2 H, m, H-2 and H-3?), 3.25 (2 H, m, H-1 and H-4?), 1.97 (3 H, s, OAc) (Found: M^+, 268.058 6. $C_{12}H_{12}O_7$ requires *M*, 268.058 3); *m/z* 268 (11%, M^+), 240 (18), 210 (33), 208 (37), 180 (29), 157 (57), 151 (54), 127 (100), 125 (38), 122 (37), 115 (59), 95 (26), and 93 (38). The *dimethyl acetal* was prepared with hydrogen chloride gas in methanol and purifying the product by t.l.c., eluting with ether to give needles, m.p. 149—151 °C (from methanol) (Found: C, 53.3; H, 6.0. $C_{14}H_{18}O_8$ requires C, 53.5; H, 5.75%), R_F (Et_2O) 0.34; $\nu_{max.}$ ($CHCl_3$) 1 779 (lactone C=O) and 1 730 cm^{-1} (ester C=O); δ($CDCl_3$) 4.96 (1 H, t, *J* 1.7 Hz, H-7), 4.31 (1 H, dd, *J* 0.7 and 5 Hz, H-6), 3.70 (3 H, s, CO_2Me), 3.4—3.1 with 3.30, 3.24 and 3.10 (10 H, m with 2 × s and d, *J* 2.3 Hz, H-1, H-2, and H-4 with 2 × OMe and H-3), and 1.91 (3 H, s, OAc); *m/z* 314 (20%, M^+), 283 (14, M^+ — MeO), 271 (17, M^+ — OAc), 257 (25), 255 (28), 254 (28), 225 (26), 209 (41), 197 (100), 167 (33), 165 (28), 164 (33), 159 (49), 151 (98), and 135 (28). The keto-lactone is hygroscopic and it is more than probable that the ketone hydrate is formed. For this reason, it is essential to minimise the quantity of water used in the oxidation; the putative ketone hydrate is very soluble in water and can only be extracted from aqueous solution with great difficulty.

7-syn-*Acetoxy*-3-exo-*methoxycarbonyl*-5-*oxobicyclo*[2.2.1]-*heptane*-2-endo-*carboxylic acid* (24).—The keto-lactone (330 mg, 1.23 mmol) and activated zinc powder [13] (1.5 g, 23 mmol) were heated together under reflux in glacial acetic acid (20 ml) for 20 h. The mixture was cooled and filtered through Celite, washing the remaining solids thoroughly with acetic acid. The solvent was removed *in vacuo*. The residue was dissolved in ethyl acetate (25 ml) and worked up in the usual way to give the *keto-acid* (24) (97 mg, 29%) as needles, m.p. 138—140.5 °C (from C_6H_6) (Found: C, 53.2; H, 5.5. $C_{12}H_{14}O_7$ requires C, 53.3; H, 5.2%); $\nu_{max.}$ ($CHCl_3$) 3 600—2 400 (CO_2H), 1 738 (ester and ketone C=O), and 1 713 cm^{-1} (acid C=O); δ($CDCl_3$) 10.3—10.1 (1 H, br s, CO_2H), 5.00 (1 H, s, H-7), 3.82 and 3.70 (4 H, t and s, *J* 5 Hz, H-2 and CO_2Me), 3.32 (1 H, m, H-1 or H-4), 3.16 and 3.13 (2 H, d and m, *J* 5 Hz, H-3 and H-1 or H-4), 2.22 (2 H, m, H-6) and 1.97 (3 H, s, OAc); *m/z* 270 (7%, M^+), 239 (8, M^+ — MeO), 211 (10, M^+ — CO_2Me), 210 (23, M^+ — H — CO_2Me), 182 (68), 164 (41), 151 (39), 137 (28), 136 (63), 123 (34), 122 (31), 105 (28), 95 (30), 92 (37), and 91 (100). The *dimethyl ester* (diazomethane, ether, room temperature) was obtained as plates, m.p. 84—86 °C (from benzene–cyclohexane) (Found: C, 55.0; H, 5.85. $C_{13}H_{16}O_7$ requires C, 54.9; H, 5.65%), R_F (Et_2O) 0.53; $\nu_{max.}$ ($CHCl_3$) 1 765 (ketone) and 1 740 cm^{-1} (esters); δ($CDCl_3$) 5.03 (1 H, t, *J* 2 Hz, H-7), 3.82, 3.79 and 3.75 (7 H, m, and 2 × s, H-2 and 2 × CO_2Me), 3.36, 3.28, and 3.14 (3 H, t, d, and m, *J* 2 and 6 Hz, H-4, H-3, and H-1), 2.20 (2 H, d, *J* 2 Hz, H-6), and 2.03 (3 H, s, OAc); *m/z* 253 (37%, M^+ — MeO), 224 (21, M^+ — *H* — CO_2Me), 211 (25), 210 (27), 196 (58), 182 (37), 165 (33), 164 (100), 151 (43), 137 (42), 136 (43), and 91 (74).

We thank the S.R.C. for a fellowship (J. P. M.) and Dr. R. L. Snowden for the initial work on this project.

[0/1331 *Received*, 27*th August*, 1980]

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