Mechanism of the Boron Trifluoride-catalysed Cyclisation of Some Cyclo-octenylidene Derivatives

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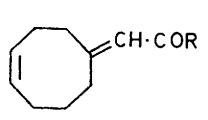
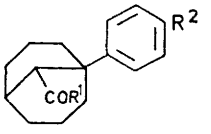
The conversion of ethyl cyclo-oct-4-enylideneacetate (1) into ethyl 1-phenylbicyclo[3.3.1]nonane-9-carboxylate (2) and the corresponding acid (3) by boron trifluoride–ether complex in benzene has been investigated, and a mechanism is suggested. Ethyl (1-phenylcyclo-oct-4-enyl)acetate (11) and ethyl 5-phenylcyclo-octylideneacetate (10) have been synthesised; examination of their separate reactions with boron trifluoride–ether in benzene shows that neither is an intermediate in the conversion.

HEATING the cyclo-octenylidene ester (1) with boron trifluoride–ether complex in benzene (1 : 1) for 17 h gives a mixture of the bicyclic ester (2) (30%) and the



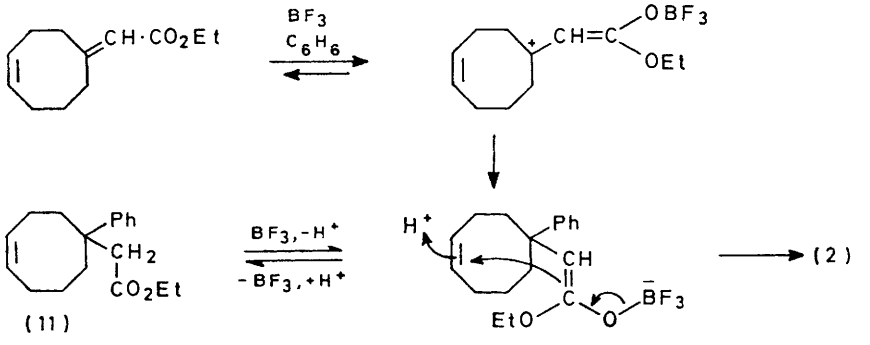
(1) R = OEt
(4) R = Me



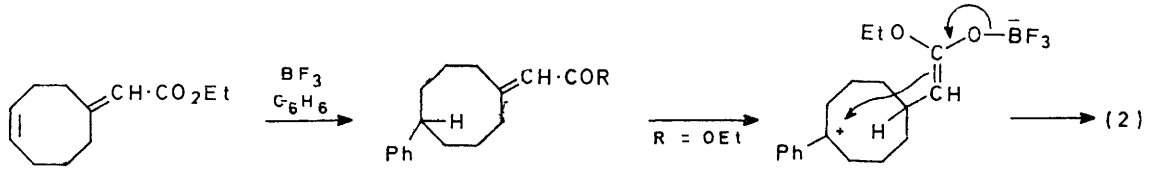
(2) R^1 = OEt, R^2 = H
(3) R^1 = OH, R^2 = H
(5) R^1 = Me, R^2 = H
(8) R^1 = OEt, R^2 = Me
(9) R^1 = OH, R^2 = Me

corresponding acid (3) (19%). The αβ-unsaturated ketone (4) also undergoes cyclisation under these conditions, to give the ketone (5).[1]

three mechanisms worthy of consideration (Schemes 1—3). A good analogy for the mechanism outlined in Scheme 2, which involves arylation of the cyclo-octene double bond[2] followed by 1,5-transannular hydride migration and cyclisation, is the conversion (6) → (7) by boron trifluoride–ether complex in benzene (Scheme 4);[3] this, together with the known propensity of medium-sized-ring compounds to undergo intramolecular hydride shifts,[4] makes this route plausible. All these mechanisms involve electrophilic attack on benzene, for which some evidence is available; the analogous bicyclo[3.3.1]nonanes (8) and (9) were obtained when toluene was substituted for benzene in the reaction, whereas no product was isolated when nitrobenzene was used as the solvent. Although reliable rate data were difficult to obtain, it did not appear that the reaction in toluene proceeded significantly faster (at the same



SCHEME 1



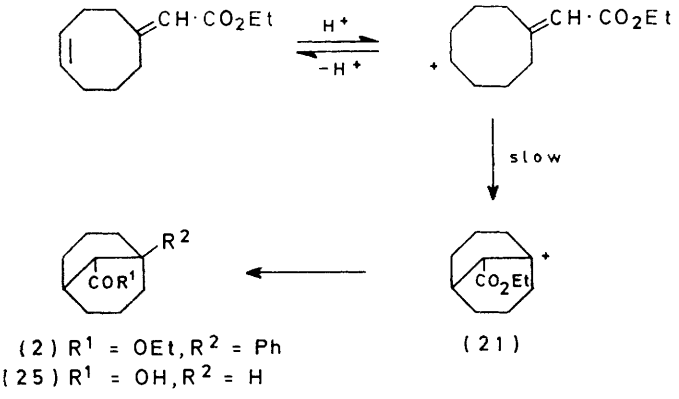
SCHEME 2

We report here some experiments carried out in an attempt to uncover the mechanism of this unusual transformation. There appeared at the outset to be temperature) than that in benzene, suggesting that the electrophilic substitution is not the rate-determining step.

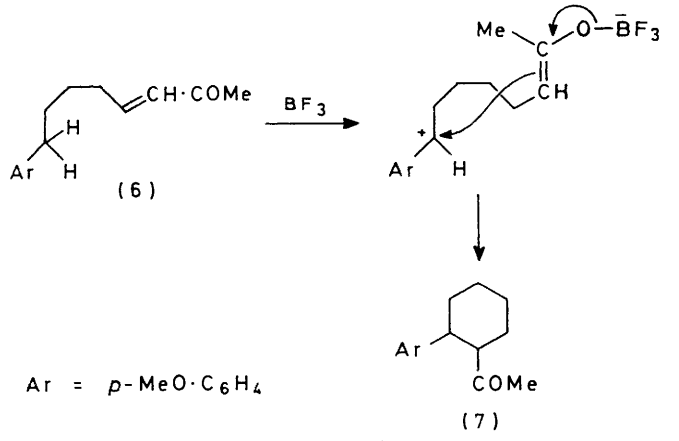
Scheme 3 differs from Schemes 1 and 2 in having no intermediates which could reasonably be expected to be

[1] R. S. Atkinson and R. H. Green, *J.C.S. Perkin I*, 1975, 340.
[2] F. E. Condon, *J. Amer. Chem. Soc.*, 1948, **70**, 2265.
[3] R. S. Atkinson and R. H. Green, *J.C.S. Perkin I*, 1974, 394.
[4] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.*, 1966, **20**, 119.

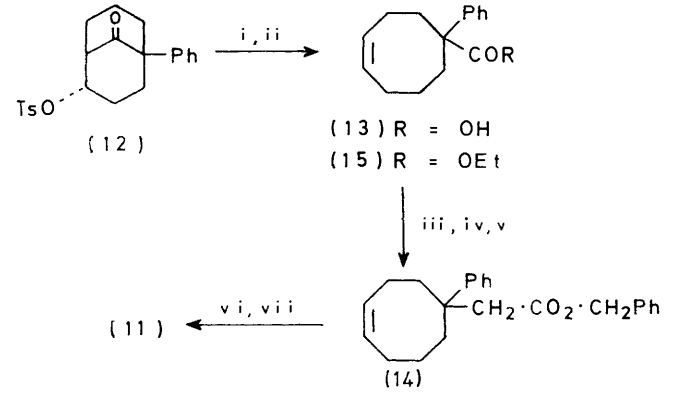
isolable. Thus the ester (10) (Scheme 2) or (11) (Scheme 1) could be present in the reaction mixture although its concentration might be small. However,



SCHEME 3



SCHEME 4



SCHEME 5 Reagents: i, NaOEt; ii, NaOH; iii, $SOCl_2$; iv, CH_2N_2; v, heat, $PhCH_2OH$; vi, NaOH; vii, HCl–EtOH

no intermediates were isolated by working up the reaction mixture after a shorter reflux period, when some starting material still remained. To test for the intermediacy of (10) or (11), therefore, we synthesised them by independent routes and subjected them to the conditions for the conversion (1) ⟶ (2).

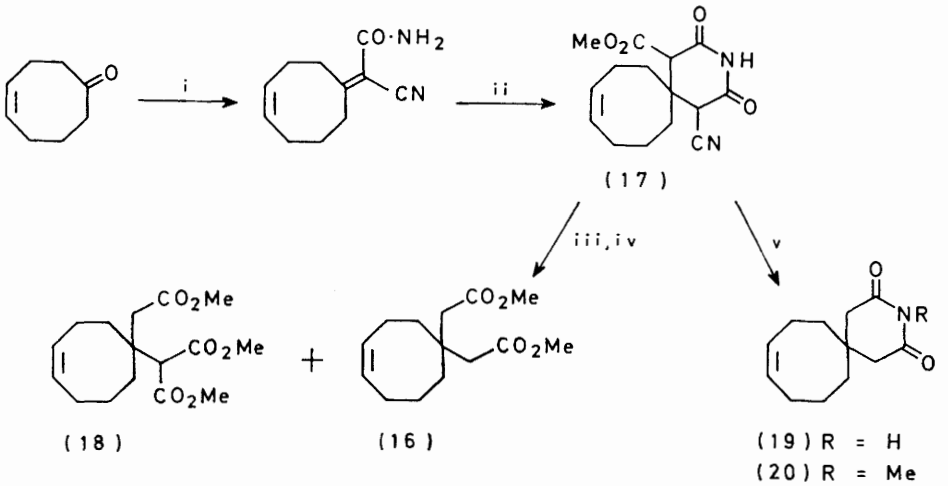
The ester (11) was synthesised from the *endo*-tosylate (12) [an intermediate in the synthesis of a degradation product of (2)] [1] by the route indicated in Scheme 5. Fragmentation of the oxo-tosylate (12) [5] gave a crystalline acid (13) after hydrolysis. Arndt–Eistert homologation of (13) with thermal decomposition of the intermediate diazoketone in benzyl alcohol–collidine [6] gave the benzyl ester (14) in poor yield. The major product after hydrolysis was the starting acid (13). The mixture of acids was converted into the corresponding ethyl esters (11) and (15). These were difficult to separate chromatographically, and advantage was taken of the more hindered nature of the ester function in (15). Thus two selective hydrolysis–re-esterification cycles with removal of unhydrolysed esters gave, after chromatography, a pure sample of the ethyl ester (11) with its distinctive two-proton n.m.r. singlet at δ 2.50.

The unsaturated ester (10) was synthesised from the known [7] 5-phenylcyclo-octanone by a Reformatsky reaction with ethyl bromoacetate followed by dehydration of the intermediate hydroxy-ester with phosphoryl chloride in pyridine. Like the unsubstituted ethyl cyclo-octylideneacetate,[8] this ester, from n.m.r. evidence is a mixture of ester-conjugated and -unconjugated double-bond isomers (ratio *ca.* 1 : 2, respectively), whereas the ethyl cyclo-oct-4-enylideneacetate (1) contains only the exocyclic conjugated double bond isomer.

Exposure of the esters (10) and (11) separately to boron trifluoride–ether complex and benzene under the conditions necessary for cyclisation of (1) gave no trace of compound (2) or (3); hence the mechanisms in Schemes 1 and 2 can be rejected. Further support for this conclusion was obtained from attempted cyclisation of the diester (16) under the same conditions. If the mechanism in Scheme 1 were operative then there is no obvious reason why the phenyl group should not be replaceable by other groups, since it plays no obvious role in the reaction. The glutarate diester (16) was selected since it has two available $CH_2{\cdot}CO_2Et$ functions which would assist the cyclisation, and the bulk of this function would not be too dissimilar from that of the phenyl ring. This diester was synthesised by a modified Guareschi reaction [9,10] outlined in Scheme 6. Hydrolysis of the glutarimide (17) under acid conditions followed by esterification (diazomethane) gave two major products, which were separated by preparative g.l.c. The first-eluted component was the required diester (16). From its spectroscopic data, the other major product appeared to be the triester (18). A similar by-product in acidic hydrolysis of a substituted glutar-

[5] G. Stork and H. K. Landesmann, *J. Amer. Chem. Soc.*, 1956, **78**, 5128; G. L. Buchanan and G. W. McLay, *Tetrahedron*, 1966, **22**, 1521.
[6] A. L. Wilds and A. L. Meader, *J. Org. Chem.*, 1948, **13**, 763.
[7] N. L. Allinger, C. L. Neumann, and H. Sugiyama, *J. Org. Chem.*, 1971, **36**, 1360.
[8] J. Wolinsky and K. L. Ericson, *J. Org. Chem.*, 1965, **30**, 2208.
[9] R. S. Atkinson and A. S. Dreding, *Helv. Chim. Acta*, 1967, **50**, 23.
[10] S. M. McElvain and D. H. Clemens, *J. Amer. Chem. Soc.*, 1958, **80**, 3915.

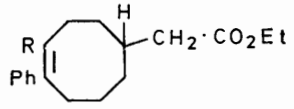
imide has been recorded.[10] Basic hydrolysis of (17) gave the simpler glutarimide (19), which yielded a crystalline *N*-methyl derivative (20). The diester (16) was unchanged under conditions which were successful in cyclising (1) to (2) and (3), which again militates against the mechanism in Scheme 1.



SCHEME 6 Reagents: i, $NC{\cdot}CH_2{\cdot}CO{\cdot}NH_2$–$H^+$; ii, $CH_2(CO_2Me)_2$–NaOMe; iii, H^+; iv, CH_2N_2; v, KOH–$(CH_2OH)_2$

The mechanism which does accommodate all that we know of the reaction at present is that given in Scheme 3. If the slow step in Scheme 3 is formation of the bridgehead carbocation (21), the rate of product formation will be unaffected by the reactivity of the aromatic substrate. It is lack of nucleophilicity of the ester double bond rather than difficulty in formation of the bridgehead carbocation which is likely to make this the slow step, since the bridgehead bicyclo[3.3.1]nonylium ion is not believed to be excessively strained.[11] A few examples of nucleophilic attack by ester-conjugated double bonds are known,[12] and electrophilic attack by the bridgehead bicyclo[3.3.1]nonylium ion occurs readily when the latter is generated by protonation of the bridgehead olefin.[13] The cyclisation of 1,5-dimethylenecyclo-octene to 1-bromo-5-bromomethylbicyclo[3.3.1]-nonane by bromine [14] is analogous to the present reaction.

Closer examination of the reaction of the ester (10) with boron trifluoride–ether complex and benzene shows that no starting material remains after only $1\frac{1}{2}$ h under reflux, and if the reaction is then worked up two major products can be isolated. One is the crystalline acid (22) (24%) corresponding to the starting ester (10). Only signals for the αβ-unsaturated acid are visible in the n.m.r. spectrum of this acid. The other product is an ester, $\nu_{max.}$ 1 734 cm^{-1}, whose distinctive feature in the n.m.r. spectrum is a triplet at δ 5.80 (*J* 8 Hz). Integration of this triplet consistently gave a value less than one proton (*ca.* 0.8 H). Moreover, the mass spectrum shows that an impurity is present having a molecular weight of 300. Accurate mass measurement on this peak shows that the additional 28 mass units [in comparison with the starting ester (18)] are present as an ethyl group. Although we have not succeeded in separating this impurity, it appears that the major product is the ester (23) [M^+ 272 (intense peak)] and that impurity (24) has an additional ethyl group on the styrenoid double bond. The styrene chromophone is revealed in the u.v. [$\lambda_{max.}$ (EtOH) 248.5 nm (ε 9 000)].



(23) R = H
(24) R = Et

Thus it appears that the hydride shift does occur, but the benzylic cation loses a proton faster than it is trapped by the ester enolate. Presumably the ester (24) is the result of ethylation of the nucleophilic styrene double bond by boron trifluoride–ether complex.

On heating the ester (1) under reflux in boron trifluoride–ether complex alone or (better) in boron trifluoride–dioxan, and subsequent hydrolysis of the neutral fraction obtained, a crystalline acid was isolated which proved identical with an authentic sample of bicyclo[3.3.1]nonane-9-carboxylic acid (25) [15] kindly supplied by Professor H. O. House. Formation of this reduction product from the carbocation (21) presumably involves hydride ion donation from the ether solvent.

EXPERIMENTAL

G.l.c. analysis was performed with a Pye 104 chromatograph (flame ionisation detector). Boron trifluoride–diethyl ether complex was purified before use by the method of Zweifel and Brown.[16] The petroleum fraction used was

[11] W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, 1968, **33**, 1237.
[12] G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068; V. A. Kuzovkin, V. A. Smit, A. V. Semenovskii, and V. F. Kucherov, *Doklady Akad. Nauk S.S.S.R.*, 1973, **208**, 119.
[13] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, 1970, **92**, 948; J. R. Wiseman and W. A. Pletcher, *ibid.*, p. 956.
[14] K. H. Baggeley, W. H. Evans, S. H. Graham, D. A. Jonas, and D. H. Jones, *Tetrahedron*, 1968, **24**, 3445.
[15] H. O. House and T. H. Cronin, *J. Org. Chem.*, 1965, **30**, 1061.
[16] G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 28.

that boiling at 60—80 °C. B.p.s given refer to the bath temperature in bulb-tube distillations. For other general experimental procedures see ref. 1.

Ethyl (1-Phenylcyclo-oct-4-enyl)acetate (11).—*endo*-4-Hydroxy-1-phenylbicyclo[3.3.1]nonan-9-one (37 mg) was prepared and converted into the tosylate (12) as previously described.[1] The crude tosylate was heated under reflux for 20 min with sodium ethoxide (110 mg) in ethanol (5 ml). After cooling, acetic acid (2 drops) was added, the ethanol was evaporated off, and the residue was taken up with chloroform and water. Separation of the chloroform layer followed by drying and evaporation gave a product (33 mg) formulated as ethyl 1-phenylcyclo-oct-4-enecarboxylate, b.p. 160—165° at 0.2 mmHg, $\nu_{max.}$ 1 720s cm^{-1}, $\delta(CCl_4)$ 7.30 (m, 5 aromatic H), 5.75—5.20 (m, 4- and 5-H), 4.10 (q, *J* 7 Hz, $CH_2{\cdot}CH_3$), 2.9—1.4 (m, 10 aliphatic H), and 1.15 (t, *J* 7 Hz, $CH_2{\cdot}CH_3$).

The foregoing ester (30 mg) was heated under reflux for 46 h with sodium hydroxide solution (2N; 4 ml) and ethanol (0.5 ml). After cooling and extracting with ether, the aqueous layer was separated, acidified, and extracted with methylene chloride. The organic layer was washed with water, dried, and evaporated, and the residual solid crystallised from ethanol–water to yield *1-phenylcyclo-oct-4-enecarboxylic acid* (13) (11 mg, 41%), m.p. 121—122°, $\nu_{max.}$ 2 670w,br and 1 690s cm^{-1}, $\delta(CDCl_3)$ 11.55 (s, disappears on addition of D_2O, CO_2H), 7.30 (m, 5 aromatic H), 5.95—5.20 (m, 4- and 5-H), and 3.1—0.9 (m, 10 aliphatic H) (Found: C, 78.3; H, 7.8. $C_{15}H_{18}O_2$ requires C, 78.25; H, 7.9%).

On a larger scale it was expedient to use a mixture of *endo*- and *exo*-alcohols, which necessitated purification of the intermediate ester by chromatography over Kieselgel. The yield of ester obtained was 63%.

Arndt–Eistert homologation of the acid (13). The acid (13) (700 mg) was dissolved in thionyl chloride (5 ml) and stirred vigorously for 4 h at room temperature in a stream of dry nitrogen. The excess of thionyl chloride was removed under reduced pressure, and the acid chloride remaining was dissolved in dry ether (10 ml) and added dropwise to a solution (80 ml; dried over powdered KOH) of an excess of diazomethane in ether. After 3 h at room temperature, the ether and diazomethane were removed under reduced pressure, and the residue was dissolved in ether and washed with sodium carbonate solution. The ethereal solution was dried and evaporated and the oil remaining decomposed immediately by adding dropwise to a boiling mixture of benzyl alcohol (10 ml) and collidine (10 ml) and heating under reflux for 8 min under nitrogen. After cooling, the solution was poured into hydrochloric acid (2N) and extracted with ether; the ether layer was separated, dried, and evaporated to give a red oil containing benzyl alcohol. This mixture was hydrolysed by heating under reflux with sodium hydroxide (2N) and ethanol for 35 min. Benzyl alcohol was removed by extracting with ether and the residual aqueous solution was acidified and extracted with chloroform. The chloroform extract was dried and evaporated to give an oil (263 mg). Esterification with ethanol containing hydrogen chloride in the usual way gave a mixture of ethyl esters, which was further enriched in the required homologated ester by re-hydrolysis for 15 min and re-esterification as above. The resulting mixture was distilled to give an oil (79 mg), b.p. 160—170° at 0.2 mmHg, which was a 1 : 1 mixture of the two ethyl esters (n.m.r.). Chromatography of this mixture on Kieselgel (benzene) gave the *ester* (11) (20 mg) as an oil, b.p. 165—175° at 0.2 mmHg; $\nu_{max.}$ 1 730s cm^{-1}; $\delta(CCl_4$; 100 MHz) 7.40—6.95 (m, 5 aromatic H), 5.8—5.1 (m, 4- and 5-H), 3.80 (q, *J* 7 Hz, $CH_2{\cdot}CH_3$), 2.6—1.0 (m, 12 aliphatic H, including s, δ 2.50, $CH_2{\cdot}CO_2Et$), and 0.95 (t, *J* 7 Hz, $CH_2{\cdot}CH_3$) (Found: M^+, 272.1770. $C_{18}H_{24}O_2$ requires *M*, 272.1776), *m/e* 272 (12%, M^+), 185 (22), 184 (26), 143 (23), 141 (20), 129 (50), 118 (37), 117 (53), 115 (51), 105 (43), 104 (35), 91 (100), 81 (47), and 77 (40).

Attempted Rearrangement of the Ester (11) *with Boron Trifluoride–Ether in Benzene.*—The ester (11) (16.4 mg) was dissolved in a mixture of boron trifluoride–ether (1 ml) and dry benzene (1 ml) and heated under reflux for 17 h. After cooling, the mixture was poured cautiously into sodium carbonate solution in a separating funnel and, after shaking cautiously at first and then vigorously, the benzene layer was separated, washed with water, dried, and evaporated. The residual oil (15.7 mg) was purified by passing through a silica column in benzene, and the oil (12 mg) eluted was examined by n.m.r. (100 MHz). Comparison with authentic ethyl 1-phenylbicyclo[3.3.1]nonane-9-carboxylate showed the latter to be totally absent. In particular, the peaks from the 9-proton and the ethyl ester were lacking.

Synthesis of Dimethyl Cyclo-oct-4-ene-1,1-diyldiacetate (16).—Cyclo-oct-4-enone (2 g) was heated under reflux with cyanoacetamide (1.8 g), ammonium acetate (1 g), acetic acid (2.1 g), and benzene (60 ml) for 16 h under a water separator. The mixture was then cooled, the solvents were removed under reduced pressure, and the pH was adjusted to 6 by addition of sodium carbonate with shaking. The chloroform layer was separated, the aqueous layer was extracted twice more with chloroform, and the combined chloroform extracts were dried and evaporated to yield an oil which crystallised from ethanol to give *2-cyano-2-(cyclo-oct-4-enylidene)acetamide* (1.8 g, 59%) as needles, m.p. 115.5—116°, $\nu_{max.}$ 3 450m, 3 335w, 3 270w, 3 140m, 2 215w, and 1 678s cm^{-1}; $\delta(CDCl_3)$ 6.34br (s, NH_2), 5.78 (m, 4- and 5-H), and 3.3—1.5 (m, 10 aliphatic H) (Found: C, 69.6; H, 7.5; N, 15.0. $C_{11}H_{14}N_2O$ requires C, 69.45; H, 7.4; N, 14.75%).

Methyl 5-cyano-2,4-dioxo-3-azaspiro[5.7]tridec-9-ene-1-carboxylate (17). The foregoing cyanoacetamide (1.7 g) dissolved in dry methanol (8 ml) was added to sodium methoxide in dry methanol [from sodium (0.41 g) in methanol (13 ml)], followed by dimethyl malonate (2.35 g). After 63 h at room temperature, a white solid had separated which dissolved on neutralisation with hydrochloric acid. The solvent was evaporated off, the residue dissolved in chloroform and water, and the chloroform layer separated, dried, and evaporated to give a thick oil (1.8 g). Crystallisation from aqueous ethanol gave a solid, m.p. 135—137° (decomp.) (1.4 g, 54%) formulated as the glutarimide (17), $\nu_{max.}$ 3 190m, 1 750w, 1 725s, and 1 700s cm^{-1} (a satisfactory analysis was not obtained for this compound); *m/e* 290 (1%, M^+), 258 (15), 203 (18), 189 (15), 164 (63), 150 (25), 138 (17), 125 (40), 91 (30), 79 (41), 67 (61), and 44 (100).

Hydrolysis of the glutarimide (17). The glutarimide (3.6 g) was heated under reflux for 17 h with water (9 ml), concentrated hydrochloric acid (9 ml), and glacial acetic acid (30 ml). All the solvent was removed under reduced pressure, and the residual oil was heated under reflux for 50 h with sodium hydroxide solution (10N; 35 ml). Concentrated sulphuric acid (14 g) in water (40 ml) was then cautiously added, and the mixture heated under reflux for a further ½ h. After cooling, the solution was extracted

with ether; the extract was washed with water, dried, and evaporated. The oil obtained (3.2 g) was esterified with diazomethane and the resulting ester distilled to give an oil, b.p. 185—200° at 2 mmHg. G.l.c. of this oil (3% OV 17; oven temp. 250 °C; nitrogen flow rate 50 ml min^{-1}) showed three components in the ratio 16 : 20 : 1 (retention times 2, 4, and 3 min, respectively). A pure sample of the first-eluted component was collected by preparative g.l.c. (10% SE 30; oven temp. 235 °C; nitrogen flow rate 40 ml min^{-1}) and was shown to be the *diester* (16), b.p. 190—200° at 2 mmHg; $\nu_{max.}$ 1 735s cm^{-1}; δ(CCl_4) 5.9—5.35 (m, 4- and 5-H), 3.55 (s, 2 × OMe), 2.40 (s, 2 × CH_2·CO_2Et), and 2.30—1.95 and 1.70—1.35 (m, 10 aliphatic H) (Found: C, 65.95; H, 8.9. $C_{14}H_{22}O_4$ requires C, 66.1; H, 8.7%).

The second eluted major product was formulated as the triester (18), b.p. 190—200° at 2 mmHg, $\nu_{max.}$ 1 732s,br cm^{-1}; δ(CCl_4) 5.95—5.45 (m, 2 olefinic H), 3.67 (s, 2 × OCH_3), 3.58 (s, OCH_3), and 3.0—1.2 (m, 13 aliphatic H, including 2.73, s), *m/e* 312 (3%, M^+), 281 (30), 239 (40), 181 (50), and 180 (100).

Attempted Rearrangement of the Diester (16) *with Boron Trifluoride–Ether in Benzene.*—The diester (16) (20 mg) was heated under reflux in benzene (1 ml) and boron trifluoride–ether (1 ml) for 17 h. Work-up as described above gave only the diester (16).

3-*Azaspiro*[5.7]*tridec*-9-*ene*-2,4-*dione* (19).—The substituted glutarimide (17) (1 g) was heated under reflux in ethylene glycol (30 ml) with potassium hydroxide (1.5 g) for 1¼ h under nitrogen. The solution was poured into water, acidified to pH 6, and extracted with ether. Drying the ether layer and evaporation gave the *glutarimide* (19), which crystallised from ethanol as white flakes, m.p. 152—155°, $\nu_{max.}$ 3 210w, 3 085w, 1 730m, and 1 675s cm^{-1}; δ($CDCl_3$) 5.8—5.5 (m, 9- and 10-H), 2.55 (s, 2 × 1- and 2 × 5-H), and 2.6—1.9 and 1.85—1.35 (m, NH and 10 aliphatic H) (Found: C, 69.3; H, 8.2; N, 6.65. $C_{12}H_{17}NO_2$ requires C, 69.55; H, 8.25; N, 6.65%).

This glutarimide (19) (500 mg) gave a crystalline *N*-methyl derivative (20) on stirring with sodium hydride (82 mg) in dimethylformamide (10 ml) for 30 min before adding methyl iodide (500 mg) and stirring overnight. Removal of the excess of methyl iodide under reduced pressure, saturation with water, and extraction with ether yielded a brown oil (after evaporation of the ether layer) which crystallised from ethanol to give the N-*methylglutarimide* (20) as fine needles (410 mg, 77%), m.p. 72—74°, $\nu_{max.}$ 1 720m and 1 670s cm^{-1}; δ($CDCl_3$) 5.9—5.25 (m, 9- and 10-H), 3.10 (s, NCH_3), 2.60 (s, 2 × 1- and 2 × 5-H), and 2.6—1.4 (m, 10 aliphatic H) (Found: C, 70.3; H, 8.55; N, 6.35. $C_{13}H_{19}NO_2$ requires C, 70.55; H, 8.65; N, 6.35%).

Ethyl 5-*Phenylcyclo-octylideneacetate* (10).—5-Phenylcyclo-octanone (1.1 g) [9] was dissolved in benzene (25 ml), and acid-washed zinc wool (1.04 g) and ethyl bromoacetate (0.8 g) were added. On heating under reflux for 10 min the zinc started to dissolve and more ketone (2.21 g) and bromo-ester (1.94 g) were added over the next 20 min. After heating under reflux for a further 2 h, the solution was cooled, transferred to a separating funnel, and shaken with ice-cold sulphuric acid (2N). The organic layer was separated, washed with water, dried, and evaporated and the residual liquid distilled to give a liquid formulated as ethyl (1-hydroxy-5-phenylcyclo-octyl)acetate, b.p. 140—160° at 0.3 mmHg. This hydroxy-ester was dehydrated by heating at 100 °C for 10 min in dry pyridine (10 ml) with phosphoryl chloride (0.55 g). After cooling, the mixture was poured into an excess of hydrochloric acid (2N) and extracted with benzene. The benzene layer was washed with sodium hydrogen carbonate solution and water, dried, and evaporated, and the residual oil was distilled to yield a product formulated as a mixture of αβ- (10) and βγ-unsaturated esters (ratio 1 : 2 respectively), b.p. 190—200° at 0.5 mmHg, $\nu_{max.}$ 1 734s, 1 711s, and 1 631m cm^{-1}; δ($CDCl_3$) 7.05br (s, 5 aromatic H), 5.73 (s, =CH·CO_2Et), 5.53 (t, *J* 8.5 Hz, C*H*=C·CO_2Et), 4.09 (q, *J* 7 Hz, CH_2·CH_3), 3.6—1.4 (m, aliphatic H including 2.99, s, CH_2·CO_2Et), and 1.25 (t, *J* 7 Hz, CH_2·CH_3). This compound was converted into the crystalline acid (22) by heating under reflux in an excess of sodium hydroxide solution (2N) containing 5% ethanol for 2 h. After acidification, the solution was extracted with methylene chloride and the organic layer was separated, dried, and evaporated. The residue crystallised from chloroform–light petroleum to yield 5-*phenylcyclo-octylideneacetic acid* (22) as white needles, m.p. 132—133°, $\nu_{max.}$ 2 600m,br, 1 686s, and 1 619s cm^{-1}; δ($CDCl_3$) 10.75br (s, CO_2H), 7.06 (m, 5 aromatic H), 5.79 (s, =C*H*CO_2H), 3.65—3.05 (m, 5-H), and 3.0—1.5 (m, 12 aliphatic H) (Found: C, 78.75; H, 8.35. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%).

Attempted Rearrangement of the Ester (10) *with Boron Trifluoride–Ether in Benzene.*—The ester (10) (0.59 g) was heated under reflux for 17 h with boron trifluoride–ether (25 ml) and benzene (25 ml) under nitrogen. The usual work-up gave an oil, the i.r. and n.m.r. spectra of which showed the absence of starting material. The oil was percolated through a short column of alumina in benzene–ethyl acetate (20 : 1) to remove boron trifluoride residues, and subsequently shown by g.l.c. to contain no ethyl 1-phenylbicyclo[3.3.1]nonane-9-carboxylate (1) by comparison with an authentic sample.

This experiment was repeated with a shorter reflux period (1½ h) and the reaction mixture was cautiously poured into ice-cold sodium hydroxide (2N). The aqueous layer was separated, acidified, and extracted with methylene chloride. After drying, the extract was evaporated and the residue crystallised from chloroform–light petroleum to yield 5-phenylcyclo-octylideneacetic acid (22) (24%), identical with a sample prepared by hydrolysis of the ester (10).

The organic layer obtained after pouring the reaction mixture into base, which contained no starting ester (10) (n.m.r.), was purified by chromatography on Kieselgel [benzene–ethyl acetate (25 : 1)] and then by distillation to yield a product formulated as ethyl (5-phenylcyclo-oct-4-enyl)acetate (23) as a liquid (51%), b.p. 140—150° at 0.3 mmHg; $\nu_{max.}$ 1 734 cm^{-1}; δ(CCl_4) 7.25—6.75 (m, 5 aromatic H), 5.80 (t, *J* 8 Hz, 4-H), 3.96 (q, *J* 6 Hz, CH_2·CH_3), 3.0—1.2 (m, 13 aliphatic H), and 1.18 (t, *J* 6 Hz, CH_2·CH_3); $\lambda_{max.}$(EtOH) 248 nm (ε 9 000). The integration value of the n.m.r. triplet at δ 5.80 was *ca.* 30% less than required and the mass spectrum showed a small peak at *m/e* 300, with a more intense peak at *m/e* 272 (M^+) from (23). Accurate mass measurement on the peak at 300 (Found: 300.209 988. $C_{20}H_{28}O_2$ requires 300.208 919) indicates that the extra 28 mass units represent an additional ethyl group. Attempts to obtain a sample of the ester (23) free from the impurity were unsuccessful.

Reaction of Ethyl (*Cyclo-oct-4-enylidene*)*acetate* (1) *with Boron Trifluoride–Ether.*—The ester (1) (1 g) was heated under reflux for 17 h with boron trifluoride–ether (25 ml). After cooling, the mixture was poured cautiously into an

excess of sodium carbonate solution in a separating funnel, and after initially cautious, then vigorous shaking, extracted with ether. The ether layer was separated, dried, and evaporated to give an oil (0.92 g). Acidification of the basic aqueous layer and extraction with chloroform gave, after drying and removal of the chloroform, partly crystalline material (60 mg). The neutral oil (0.92 g) was hydrolysed by heating under reflux for 16 h with sodium hydroxide solution (50 ml; 2N) and sufficient ethanol to ensure a homogeneous solution. The cooled solution was extracted with ether and the aqueous layer acidified and extracted with chloroform; the chloroform layer was separated, dried, and evaporated to yield an oil (0.175 g) which, after combination with the acid partly crystalline fraction (60 mg) and distillation, b.p. 125—135° at 0.6 mmHg, gave an oil which slowly solidified. Crystallisation from chloroform–light petroleum gave white rhombs (123 mg, 14%), identical with a sample of ethyl bicyclo[3.3.1]-nonane-9-carboxylate kindly supplied by Professor H. O. House (m.p. and mixed m.p. 129—131°).

Repetition of the above experiment with a mixture of boron trifluoride–diethyl ether and dioxan (1 : 1) at 100 °C gave the same acid (178 mg, 21%).

Ethyl 1-p-*Tolylbicyclo*[3.3.1]*nonane-9-carboxylate* (8) *and* 1-p-*Tolylbicyclo*[3.3.1]*nonane-9-carboxylic Acid* (9).—To ethyl cyclo-oct-4-enylideneacetate (387 mg) in dry toluene (20 ml) was added boron trifluoride–ether complex (20 ml), and the solution was heated at 90 °C (bath temperature) for 17 h. The cooled mixture was then cautiously poured into sodium carbonate solution and shaken until carbon dioxide evolution had ceased. After separation of the organic layer, the aqueous layer was re-extracted with benzene and the combined organic extracts were washed with water and dried. Evaporation yielded an oil, which was purified by column chromatography (Kieselgel; benzene as eluant) to give an oil (176 mg), b.p. 165—170° at 0.2 mmHg. This slowly crystallised; recrystallisation from light petroleum gave the *ester* (8) (148 mg, 28%) as flakes, m.p. 53—55°, $\nu_{max.}$ 1 735s and 800s cm^{-1}; $\delta(CCl_4)$ 7.20, 7.05, 7.00, and 6.85 (4 aromatic H, AA'BB'), 3.85 (q, J 7 Hz, $CH_2{\cdot}CH_3$), 3.00br (s, 9-H), 2.8—1.35 (m, 16 aliphatic H with CH_3, s, at δ 2.25), and 1.00 (t, J 7 Hz, CH_2CH_3) (Found: C, 79.9; H, 9.15. $C_{19}H_{26}O_2$ requires C, 79.7; H, 9.15%).

The aqueous basic layer from extraction of the reaction mixture was acidified and extracted three times with chloroform. The combined extracts were washed with water, dried, and evaporated to give a white solid, which crystallised from chloroform–light petroleum to afford the *acid* (9) (110 mg, 21%), m.p. 196—198°, $\nu_{max.}$ 2 720w,br, 1 710s, and 805s cm^{-1}; $\delta(CDCl_3)$ 12.70br (s, CO_2H, disappears on addition of D_2O), 7.4, 7.25, 7.2, and 7.05 (4 aromatic H, AA'BB'), 3.15br (s, 9-H), and 2.65—1.45 (m, 16 aliphatic H including CH_3, s, at δ 2.30) (Found: C, 78.6; H, 8.45. $C_{17}H_{22}O_2$ requires C, 79.05; H, 8.6%).

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