

Photochemical Behaviour of Bicyclo[5.3.1]undec-1(10)-en-9-one

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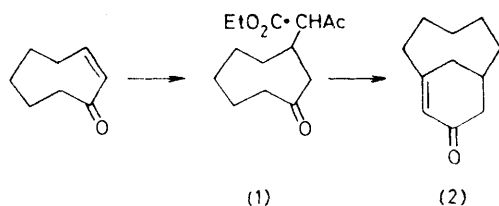
Bicyclo[5.3.1]undec-1(10)-en-9-one undergoes photodeconjugation to give bicyclo[5.3.1]undec-1(2)-en-9-one, which, in turn is transformed into the corresponding methylenebicyclo[4.2.2]decanone. The non-volatile fraction of the photolysate is shown to be a mixture of cyclobutane-type dimeric derivatives.

WE have previously reported the photochemical behaviour of bicyclo[9.3.1]pentadec-1(14)-en-13-one¹ and of bicyclo[6.3.1]dodec-1(11)-en-10-one.² For both ketones the photochemical behaviour depends on the presence of the polymethylene bridge.

We now report the photochemistry of bicyclo[5.3.1]undec-1(10)-en-9-one (2) and show that in this case the polymethylene bridge is not directly involved in the photochemical behaviour, the main products being cyclobutane-type dimers.

The title compound (2) was prepared from cyclo-oct-2-enone,³ in 57% overall yield.

The enone (2) was irradiated in benzene solution ($2.07 \times 10^{-2}M$) with a high-pressure Hg lamp through Pyrex. After irradiation for 12 h, g.l.c. analysis † of the volatile fraction (24.4%, see Experimental section) shows the presence of three products: unchanged (2)



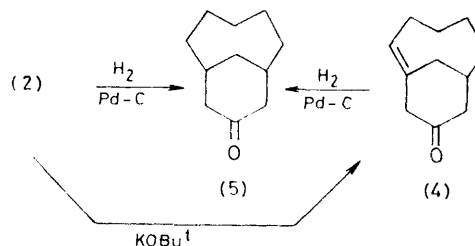
47%, (3) 21%, and (4) 32%. A study of product distribution *vs.* extent of irradiation established that the ratio (3):(4) increases as a function of time: this suggests that (3) arises from (4). The two photoproducts (3) and (4) were isolated by silica-gel column chromatography and by preparative g.l.c.‡ For both compounds (3) and (4) elemental analysis and mass spectroscopy indicate a composition, $C_{11}H_{16}O$, isomeric with the starting material. The n.m.r. spectrum of (4) shows the presence of an olefinic proton (1 H, t, $J = 7.5$ Hz, at δ 5.5) and the i.r. spectrum the carbonyl absorption at 1715 cm^{-1} . On this basis we assigned to (4) the structure of bicyclo[5.3.1]undec-1(2)-en-9-one. Catalytic hydrogenation of (4) and (2) affords the same dihydro-derivative (5). We also obtained (4) from (2) by deconjugation with $KOBu^t$.

The photodeconjugation of substituted cyclohex-3-enones is a well known process.^{4,5}

† Glass column, 2 m \times 3 mm, QF-1 5% on silanized Chromosorb W, 100–120 mesh, N_2 40 ml min^{-1} , 160 °C.

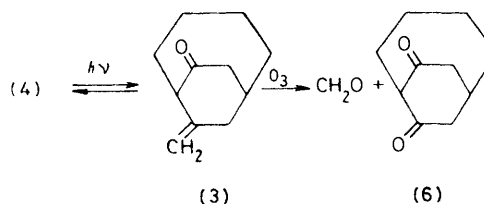
The n.m.r. spectrum of (3) shows the presence of an exocyclic methylene group (2 H, m, at δ 4.95 and 4.85) and the i.r. spectrum the carbonyl absorption at 1710 cm^{-1} . Ozonization of (3) afforded a diketone (6) with loss of formaldehyde.

Irradiation of a benzene solution of (4) ($4.17 \times 10^{-2}M$,



20 h) afforded an apparent photostationary state of (3) (76%) and (4) (24%). The presence of oxygen does not affect this reaction, but in acetone the formation of (3) from (4) was completely prevented. These facts suggest that a singlet excited state of (4) is involved in the formation of (3). Moreover the assigned structure (3) is also in line with the well known photochemical behaviour of β,γ -unsaturated ketones.⁶

T.l.c. analysis § of the non-volatile fraction (75.6%) shows the presence of four products: (7)–(10), obtained in a pure state by silica gel column chromatography.



For each of them elemental analysis and mass spectroscopy indicate a composition $C_{22}H_{32}O_2$, strongly suggesting a cyclobutane-type dimeric structure. In the n.m.r. spectrum of (7) and (10) a singlet due to two hydrogens, respectively at δ 2.43 and 2.79, is present, in agreement with the dimers obtained from 3-methylcyclohexen-2-one.⁷

‡ Glass column, 2 m \times 6 mm, QF-1 5% on silanized Chromosorb W, 60–80 mesh, N_2 140 ml min^{-1} , 170 °C.

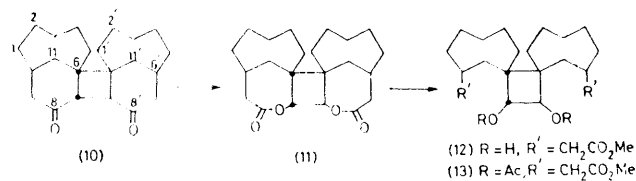
§ Eluant Et_2O -*n*-hexane (1:1 v/v).

Corey *et al.*⁸ have demonstrated that both *cis*- and *trans*-ring junctions between six- and four-membered rings may be obtained in a photochemical reaction. They have also shown that a *trans*-junction adjacent to a carbonyl group is less stable than a *cis*-junction, and that on treatment with dilute alkali such *trans*-joined compounds isomerize to the more stable *cis*-isomers.

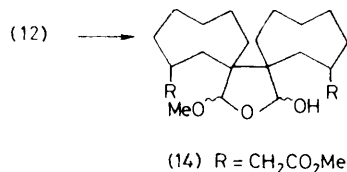
Compounds (7) and (10) were completely stable to alkaline treatment; it is therefore clear that in both compounds ring junctions are *cis*.

Dipole-moment measurements allow a distinction between head-to-head (h-h) and head-to-tail (h-t) dimers⁹ and afforded a value of 1.29D for (7) and of 5.46D for (10). Therefore (7) must be a h-t and (10) a h-h dimer. It is also known¹⁰ that the ratio h-h/h-t for enone dimers increases with solvent polarity. The ratio (10):(7), which is *ca.* 1:1 in benzene, becomes *ca.* 3:1 in MeOH.

The structure head-to-head *cis-anti-cis* was assigned to (10) based on the above data and the chemical behaviour. Bayer-Villiger oxidation of (10) afforded a dilactone (11) from which a dihydroxy-diester (12) was obtained by reaction with acidic MeOH.



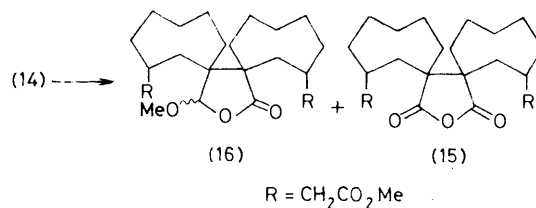
The dilactone (11) showed a band in its i.r. spectrum at 1740 cm⁻¹ (lactone C=O) and its n.m.r. spectrum included a singlet at δ 4.16 (cyclobutyl protons). The mass spectrum agrees with the proposed structure. In the dihydroxy-diester (12) the presence of two OH groups was inferred from spectroscopic data and confirmed by formation of the corresponding diacetate (13). The dihydroxy-diester (12) was oxidized by lead tetraacetate, in MeOH and in the presence of CCl₃CO₂H, giving (14), obtained in a pure state by silica-gel column chromatography. This product showed in its n.m.r. spectrum four singlets: at δ 3.26 (3 H, OCH₃), 3.6 (6 H, CO₂CH₃), 4.5 (1 H, OCHOCH₃), and 5 (1 H, OCHOH). Treatment of (14) with dilute H₂SO₄ in tetrahydrofuran afforded a mixture of at least two products



whose n.m.r. spectrum lacked signals at δ 3.26, 4.5 and 5, and showed two singlets at δ 9.7 and 5.33. Although the products were not isolated, we suppose they represent the parent aldehyde of (14) and the cyclic form of the corresponding hydrate.

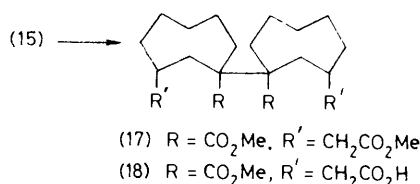
Chromic acid oxidation of (14) afforded a mixture of two products, (15) and (16).

The i.r. spectrum of (15) had bands at 1730 cm⁻¹ (ester C=O) and at 1770 and 1835 cm⁻¹, typical of a substituted succinic anhydride.¹¹ The i.r. spectrum of (16) showed no OH band while the carbonyl absorptions



were at 1730 and 1765 cm⁻¹. Its n.m.r. spectrum had four singlets at δ 3.4 (3 H, OCH₃), 3.63 and 3.66 (3 H each, CO₂CH₃), 4.7 (1 H, OCHOCH₃). Hydrolysis of the anhydride (15) with dilute methanolic KOH gave an acid, which was esterified with CH₂N₂ and purified by silica-gel column chromatography to give the tetramethyl ester (17). Alkaline hydrolysis of this ester afforded the diester-diacid (18).

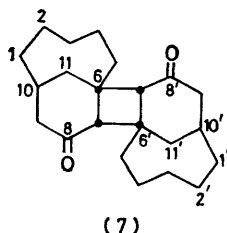
The above reactions establish a h-h orientation in the dimer (10). The dihydroxy-diester (12) does not react with sodium periodate in aqueous methanol, showing that the two OH groups in (12) must have a *trans*-relationship.¹² In the dimer (10) the stereochemical relationship of the two six-membered rings must be *anti* since the Baeyer-Villiger oxidation is known to proceed with retention of configuration¹³ and transesterification should not affect the stereochemistry of the molecule.



Qualitative experiments with Eu(fod)₃ as shift reagent (SR) supported the assigned stereochemistry for the ring junction of (10). For amounts of SR up to a 1:1 molar ratio only two sets of signals were strongly displaced downfield: these were assigned to the CH α to C=O (singlet) and to the diastereotopic protons of the CH₂ α to C=O (two doublets of doublets, $J_{vic} = 7.5$ and 3.6 Hz, $J_{gem} = 16.5$ Hz). Among them, the signal of CH was the most displaced one. No large shift for protons of the cyclo-octane loop was detected, and consideration of Dreiding molecular models indicate that they are placed on the opposite side of the molecule with respect to the carbonyl groups.

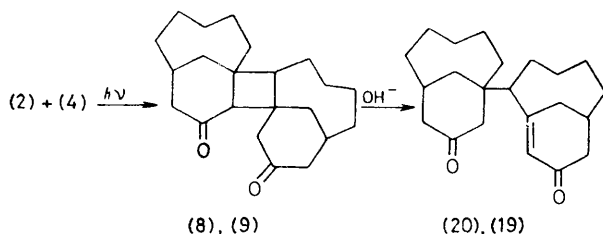
The *syn* h-t dimer structure was assigned to the compound (7) on the basis of the dipole moment value and of qualitative experiments with Eu(fod)₃. Compound (7) showed a more meaningful change on SR addition: the CH α to C=O were, as usual, the most affected, followed by the diastereotopic α -CH₂ groups. A third set of

signals was remarkably shifted downfield: from their multiplicity these signals (two doublets of doublets, $J_{vic} = 4.5$ and 3 Hz, $J_{gem} = 17$ Hz) were assigned to the diastereotopic protons of the CH_2 δ to $\text{C}=\text{O}$. To be so strongly affected by paramagnetic complexation at the carbonyl group, these protons must belong to a structure with a *syn* relationship of the two six-membered rings, in which one $\text{C}=\text{O}$ is found next to the $\delta\text{-CH}_2$ of the other cyclohexanone ring. In such a structure the cyclooctane loop is not too close to the site of complexation and hence its protons do not show any large shift. For an *anti* h-t structure, a CH_2 of the loop would have been found close in space to the complexed site, whereas the $\delta\text{-CH}_2$ of the other cyclohexanone ring would be distinctly far away from it.



Considering now the ^{13}C n.m.r. spectra of (10) and (7), a large difference in chemical shift is noted for C-5 and C-5' in (10) compared with the same carbons in compound (7). In fact the *anti* h-h configuration of (10) holds C-5 and C-5' in a γ -gauche relationship with C-11' and C-11 respectively in the other half of the molecule: hence the strong upfield compression shift. In the *syn* h-t configuration of (7), C-5 and C-5' have no steric compression and their resonance is found further downfield at *ca.* 45 p.p.m. In (10) C-11 and C-11' have a lower chemical shift than expected, partly due to the γ -gauche compression shift with C-5' and C-5 and partly because of the shielding effect of the anisotropic C-8 and C-8' carbonyl groups. In (7) C-11 and C-11' are found at almost the same field strength as in (10), probably because of a complex interplay of anisotropy effects of both carbonyl groups coupled with a γ -gauche position with respect to one of them.

Alkaline treatment of compounds (8) and (9) afforded in quantitative yields (20) and (19), respectively, through



the cyclobutane ring opening with formation of a $\beta\beta$ -disubstituted conjugated double bond. Since the relative positions of the two carbonyl groups in (8) and (9) must allow this *retro*-Michael type reaction, (8) and (9) should arise from a regiospecific photocycloaddition

reaction between (2) and (4). This hypothesis was verified by irradiating (2) in the presence of a large excess of (4). Under these conditions only (8) and (9) were formed. On this basis we assume the illustrated general structures for (8), (9) and the corresponding 'open' derivatives (20) and (19).

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. I.r. spectra were taken on a Perkin-Elmer 377 instrument. ^1H N.m.r. spectra were recorded in $[\text{2H}]$ chloroform solution with a Varian HA 100 or A 60-A spectrometer. Chemical shifts are given in δ from tetramethylsilane as internal standard and refer to the centre of the signal. The u.v. spectra were recorded for 96% ethanolic solutions on a Beckmann DB-GT spectrometer. The mass spectra were obtained with a Varian MAT 311-A mass spectrometer equipped with a combined FI, FD, and EI ion source. Dipole moments were measured with a WTW DM 01 dipole-meter for CCl_4 solutions. G.l.c. analyses were run on a Pye series 104 chromatograph. Column chromatography was performed on Merck Kieselgel 60, 0.063–0.200 mm. T.l.c. was carried out using Merck Kieselgel F₂₅₄. Magnesium sulphate was used as drying agent. Evaporation was carried out *in vacuo* (rotary evaporator). Irradiations were carried out with a 125-W HPK Phillips high-pressure Hg lamp. ^{13}C N.m.r. spectra were taken at 20.0 MHz on a CFT-20 Varian instrument (δ from SiMe_4 , CDCl_3 solutions). Tentative assignments: peaks are exchangeable within 1 p.p.m.

Immersion-well apparatus. This consists of a water-jacketed Pyrex well housing a 125-W lamp. The well fits into a cylindrical 400 or 200 ml reaction vessel equipped with an inlet for gas and an outlet for the removal of aliquot portions.

Irradiation. In a typical irradiation experiment, ketone was dissolved in the appropriate solvent and the solution placed in the reaction vessel, which was held in place around the immersion-well apparatus. Nitrogen was bubbled through the solution for 10 min before irradiation.

Ethyl 2-(3-Oxocyclo-octyl)acetoacetate (1).—To a mixture of cyclo-oct-2-en-one ³ (12.6 g) and ethyl acetoacetate (20 g) a solution of EtONa in EtOH [from Na (300 mg) and EtOH (5 ml)] was added. After 12 h at room temperature, the reaction mixture was diluted with Et_2O (200 ml), washed with H_2O (2×50 ml) and dried. *In vacuo* distillation of the residue remaining after solvent evaporation afforded (1), b.p. 145–147 °C at 1 mmHg (24 g, 93%), ν_{max} (film) 1740 and 1705 cm^{-1} ; δ 4.2 (2 H, q, $\text{CO}_2\text{CH}_2\text{Me}$), 3.54 [0.5 H, d, J 7 Hz, $-\text{CH}(\text{CO}_2\text{Et})\text{COMe}$], 3.48 [0.5 H, d, J 8 Hz, $\text{CH}(\text{CO}_2\text{Et})\text{COMe}$], 2.4 (4 H, m, CH_2COCH_2), 2.27 (3 H, s, COCH_3), and 1.28 (3 H, t, $\text{CO}_2\text{CH}_2\text{CH}_3$).

Bicyclo[5.3.1]undec-1(10)-en-9-one (2).—Ethyl 2-(3-oxocyclo-octyl)acetoacetate (1) (24 g) was added to a mixture of AcOH (140 ml), H_2O (80 ml), and H_2SO_4 (20 ml). The solution was heated under reflux for 5 h. After cooling, water (400 ml) was added to the mixture which was then extracted with *n*-pentane (3×100 ml). The organic layer was dried and the solvent evaporated. The residue was distilled *in vacuo* affording (2) (9.5 g, 61.3%), b.p. 104–106 °C at 0.7 mmHg, ν_{max} (film) 1665 cm^{-1} ; δ 5.88 (1 H, s, $=\text{CHCO}$); λ_{max} 243 (12 600) and 324 (60); λ_{max} (n-hexane) 233 (12 650); m/e 164 (M^+ , 41) and 82 (100).

Irradiation of Bicyclo[5.3.1]undec-1(10)-en-9-one (2) in

Benzene.—In a typical run the ketone (2) (1.2 g) was dissolved in benzene (350 ml) and irradiation carried out for 12 h. Solvent was then evaporated. The residue from four runs, distilled *in vacuo*, afforded 1.16 g of volatile fraction, b.p. 80–125 °C at 0.3–0.5 mmHg and 3.6 g of non-volatile fraction.

Volatile fraction. G.l.c.* showed three products: (2) (47%), (3) (21%), and (4) (32%). Silica-gel (50 g) column chromatography (eluant n-pentane to n-pentane-Et₂O, 10 : 1 v/v) afforded (2) (520 mg) and a mixture of (3) and (4) (550 mg). Preparative g.l.c.† of the (3)–(4) mixture afforded: (3) (150 mg) [b.p. 130–135 °C at 5 mmHg; ν_{\max} (film) 1 710 and 1 638 cm⁻¹; δ 4.95 and 4.85 (2 H, m, =CH₂), and 3.2 [1 H, m, COCH(C=)CH₂]; *m/e* 164 (*M*⁺) (85), 79 (100), and (4) (230 mg) [b.p. 94–98 °C at 3 mmHg; ν_{\max} (film) 1 715 and 1 670 cm⁻¹; λ_{\max} 290 (142), λ_{\max} (iso-octane) 288 (106), 297 (142), 306 (90), and 317 (46); δ 5.5 (1 H, t, *J* 7.5 Hz, C=CHCH₂), and 3.04 (4 H, m); *m/e* 164 (*M*⁺, 40) and 95 (100)].

Non-volatile fraction. T.l.c.‡ showed four products: (7) (*R_F* 0.37), (8) (0.32), (9) (0.27), and (10) (0.20). Silica-gel (170 g) column chromatography (eluant n-hexane to Et₂O) afforded: (7) (780 mg), m.p. 140 °C from Et₂O; ν_{\max} (Nujol) 1 685 cm⁻¹; δ 2.43 (2 H, s); ¹³C n.m.r.: 28.1 (C-1, 1'), 21.1 (C-2, 2'), 24.5 (C-3, 3'), 18.6 (C-4, 4'), 45.4 (C-5, 5'), 38.6 (C-6, 6'), 60.8 (C-7, 7'), 210.0 (C-8, 8'), 46.0 (C-9, 9'), 30.5 (C-10, 10'), 28.1 (C-11, 11'); *m/e*: 328 (*M*⁺, 0.5) and 165 (100); (8) (650 mg), m.p. 133–134 °C from Et₂O–n-hexane; ν_{\max} (Nujol) 1 700 cm⁻¹; n.m.r. spectrum was inconclusive; *m/e* 328 (*M*⁺, 0.4), 164 (100); (9) (590 mg), m.p. 157–158 °C from CH₂Cl₂–Prⁱ₂O; ν_{\max} (Nujol) 1 690 cm⁻¹; δ 2.67 (1 H, s); *m/e* 328 (*M*⁺, 0.2), 164 (100); (10) (820 mg), m.p. 182–183 °C from CH₂Cl₂–Prⁱ₂O; ν_{\max} (Nujol) 1 700 and 1 685 cm⁻¹; δ 2.79 (2 H, s); ¹³C n.m.r.: 31.0 (C-1, 1'), 22.3 (C-2, 2'), 24.9 (C-3, 3'), 20.6 (C-4, 4'), 28.8 (C-5, 5'), 45.4 (C-6, 6'), 51.0 (C-7, 7'), 207.1 (C-8, 8'), 42.1 (C-9, 9'), 32.7 (C-10, 10'), 28.0 (C-11, 11'); *m/e* 328 (*M*⁺, 0.5) and 165 (100).

Bicyclo[5.3.1]undec-1(2)-en-9-one (4).—To a solution of bicyclo[5.3.1]undec-1(10)-en-9-one (2) (0.5 g) in anhydrous hexamethylphosphoric triamide (15 ml) under N₂, KOBu^t (1.7 g) was added. After 1 h at room temperature, the reaction mixture was diluted with 5% AcOH (100 ml) and extracted with n-pentane (2 × 50 ml). The organic layer was dried. After evaporation of the solvent the residue was distilled under reduced pressure to afford (4) (400 mg).

Bicyclo[5.3.1]undecan-9-one (5).—Bicyclo[5.3.1]undec-1(10)-en-9-one (2) (166 mg) was dissolved in AcOEt (30 ml) and 10% Pd-C catalyst (30 mg) added to the solution. Hydrogenation was then carried out at room temperature under atmospheric pressure until all the ketone (2) had disappeared, as shown by g.l.c. (*ca.* 30 min). Catalyst was then filtered off and solvent evaporated. Vacuum distillation afforded (5) (150 mg), b.p. 70–75 °C at 0.5 mmHg; ν_{\max} (film) 1 700 cm⁻¹. The same ketone (5) was obtained by an analogous reduction from the bicyclo[5.3.1]undec-1(2)-en-9-one (4).

Irradiation of Bicyclo[5.3.1]undec-1(2)-en-9-one (4).—The ketone (4) (685 mg) was dissolved in benzene (100 ml) and

irradiation carried out for 20 h. After solvent evaporation, the residue was distilled *in vacuo* giving 435 mg, b.p. 70–75 °C at 0.5 mmHg, mixture composition by g.l.c.: (4) (24%) and (3) (76%).

Bicyclo[4.2.2]decane-2,7-dione (6).—The photoketone (3) (0.4 g) was dissolved in CH₂Cl₂ (30 ml) and ozonized [10 l h⁻¹ O₂ with 7.5% O₃] at –20 °C. After flushing with N₂, the solvent was evaporated at room temperature, and to the residue water (10 ml) and Na₂SO₃ (1 g) were added. After 2 h at room temperature the reaction mixture was extracted with CH₂Cl₂ (2 × 20 ml). Evaporation of the dried solvent afforded, after crystallisation from Et₂O–n-pentane, pure (6) (210 mg), m.p. 176 °C; ν_{\max} (Nujol) 1 710 cm⁻¹; δ 3.17 (1 H, t, *J* 5 Hz), 2.65 (4 H, m); *m/e* 166 (*M*⁺, 40) and 95 (100).

Irradiation of Bicyclo[5.3.1]undec-1(10)-en-9-one (2) in the Presence of Bicyclo[5.3.1]undec-1(2)-en-9-one (4).—The ketones (2) (550 mg) and (4) (1.18 g) were dissolved in benzene (100 ml) and irradiation was carried out for 2.5 h. Silica-gel (50 g) column chromatography (eluant n-hexane to Et₂O) afforded (8) (430 mg) and (9) (445 mg).

Alkaline Isomerisation of the Dimers.—To the dimer (250 mg), dissolved in EtOH (15 ml), a solution of KOH in water (0.5 ml) [from KOH (1 g) and water (1.5 ml)] was added. After 30 min at 70 °C, the solvent was evaporated, water (15 ml) was added and the mixture extracted with CH₂Cl₂ (3 × 20 ml). Whereas (7) and (10) were stable under these conditions, (8) afforded (20) (210 mg) [m.p. 190 °C from CH₂Cl₂–Et₂O; ν_{\max} (Nujol) 1 710, 1 665, and 1 620 cm⁻¹; δ 5.96br (1 H, s); λ_{\max} 247 (12 000); *m/e* 329 (*M*⁺ + 1, 0.2) and 164 (100)] and (9) afforded (19) (195 mg) [m.p. 166 °C from CH₂Cl₂–Et₂O; ν_{\max} (Nujol) 1 715, 1 670, and 1 630 cm⁻¹; δ 5.83 (1 H, s); λ_{\max} 247 (12 000); *m/e* 329 (*M*⁺ + 1, 0.5) and 164 (100)].

Baeyer-Villiger Oxidation of the Dimer (10).—A solution of the dimer (10) (2.9 g) in CH₂Cl₂ (50 ml) was treated with 90% *m*-chloroperbenzoic acid (6.8 g) dissolved in CH₂Cl₂ (150 ml). The reaction mixture was allowed to stand at room temperature for 18 days. After evaporation of part of the solvent, water (50 ml), NaHCO₃ (3 g), and Na₂SO₃ (2.5 g) were added; the mixture was stirred for 24 h, and then extracted with CH₂Cl₂ (3 × 50 ml). The extract was dried and evaporated and the residue was purified by silica-gel (60 g) column chromatography (eluant n-hexane to Et₂O) affording (11) (2.85 g); m.p. 228–230 °C from CH₂Cl₂–Et₂O; ν_{\max} (Nujol) 1 740 cm⁻¹; δ 4.16 (2 H, s); *m/e* 360 (*M*⁺, 0.2) and 152 (100).

The Dihydroxy-diester (12).—A solution of the dilactone (11) (1.5 g) in MeOH (80 ml) was treated with three drops of H₂SO₄. After 1 h at 50 °C and 12 h at room temperature the solvent was evaporated, water (40 ml) was added and the mixture extracted with Et₂O (2 × 50 ml). The extract was dried and evaporated and the residue was purified by silica-gel (30 g) column chromatography (eluant Et₂O) affording (12) (1.47 g), m.p. 98–100 °C from Et₂O–n-hexane; ν_{\max} (Nujol) 3 400 and 1 730 cm⁻¹; δ 4br (2 H, s, OH), and 3.67 (8 H, s); *m/e* [F.I.] 424 (*M*⁺, 8), and 212 (100).

The Diacetoxy-diester (13).—A solution of the dihydroxy-diester (12) (220 mg) in dry pyridine (2 ml) was treated with acetic anhydride (1 ml). After 12 h at room temperature the solvent was evaporated, water (10 ml) was added and the mixture extracted with Et₂O (2 × 20 ml). The ethereal extract was washed successively with 1M HCl, H₂O, NaHCO₃ solution, and H₂O. Solvent evaporation

* Glass column, 2 m × 3 mm, QF-1 5% on silanized Chromosorb W, 100–120 mesh, N₂ 40 ml min⁻¹, 160 °C.

† Glass column, 2 m × 6 mm, QF-1 5% on silanized Chromosorb W, 60–80 mesh, N₂ 140 ml min⁻¹, 170 °C.

‡ Eluant Et₂O–n-hexane (1 : 1 v/v).

afforded (13) (160 mg), m.p. 90—91 °C from n-pentane; ν_{\max} (Nujol) 1 730 cm^{-1} ; δ 4.77 (2 H, s), 3.67 (6 H, s), and 2.06 (6 H, s); m/e [F.I.] 508 (M^+ , 16) and 43 (100).

Oxidation of the Dihydroxy-diester (12) with Lead Tetraacetate.—A solution of the diester (12) (1.3 g) in MeOH (30 ml) was treated with trichloroacetic acid (100 mg) and lead tetraacetate (2 g) at 5 °C. After 3 h at 5—10 °C the solvent was evaporated, water was added (50 ml) and the mixture extracted with Et_2O (3×50 ml). The extract was washed with water and dried. After removal of the solvent the residue was purified by silica gel (60 g) column chromatography (eluant n-hexane to n-hexane- Et_2O , 1 : 1 v/v) affording (14) (960 mg); non-distillable oil; ν_{\max} (film) 3 440 and 1 730 cm^{-1} ; δ 5 (1 H, s), 4.5 (1 H, s), 3.6 (6 H, s), 3.26 (3 H, s), and 2.25 (4 H, m).

Chromic Acid Oxidation of (14).—Jones reagent was added dropwise to a solution of (14) (750 mg) in acetone (40 ml) at 15 °C until a brown colour persisted for 5 min. Pr^iOH (2 ml) was added and then the solution was diluted with water (100 ml) and extracted with Et_2O (4×50 ml). The ethereal extract was washed twice with water and dried. After removal of the solvent the residue was separated by silica-gel (40 g) column chromatography (eluant n-hexane to n-hexane- Et_2O , 8 : 1 v/v) affording: (15) (250 mg) [non-distillable oil; ν_{\max} (film) 1 835, 1 770, and 1 730 cm^{-1} ; δ 3.67 (6 H, s)] and (16) (300 mg) [m.p. 96 °C from n-hexane; ν_{\max} (Nujol) 1 765 and 1 730 cm^{-1} ; δ 4.7 (1 H, s), 3.66 (3 H, s), 3.63 (3 H, s), and 3.4 (3 H, s); m/e 452 (M^+ , 5), 226 (100)].

The Tetramethyl Ester (17).—A solution of the diester anhydride (15) (250 mg) in MeOH (10 ml) was treated with KOH (1 g) and water (2 ml). After 24 h at room temperature the solvent was evaporated, water was added (15 ml), and the mixture acidified with 5 N HCl and extracted with CH_2Cl_2 (3×25 ml). The dried extract was esterified with an ethereal solution of CH_2N_2 . Removal of the solvent then afforded (17) (170 mg), m.p. 99 °C from n-hexane; ν_{\max} (Nujol) 1 720 cm^{-1} ; δ 3.72 (6 H, s), and 3.64 (6 H, s); m/e 482 (M^+ , 0.2), and 182 (100).

The Dimethyl Ester Dicarboxylic Acid (18).—A solution of the tetramethyl ester (17) (150 mg) in MeOH (15 ml) was treated with KOH (1 g) and water (1 ml). The solution

was heated under reflux for 3 h. After evaporation of the solvent, water (10 ml) was added, the solution acidified with 5N-HCl and extracted with CH_2Cl_2 (2×20 ml). Removal of the solvent afforded (18) (82 mg), m.p. 212 °C from acetone- Et_2O ; ν_{\max} (Nujol) 1 735 and 1 720 cm^{-1} ; δ 3.64 (6 H, s); m/e 228 (16), and 43 (100); [F.D.] m/e 455 ($M^+ + 1$).

Note added in proof: During publication of this work an independent synthesis of the bicyclo[5.3.1]undec-1(10)-en-9-one has been reported by Herbert O. House, Ronald F. Sieloff, Thomas V. Lee, and Marvin B. De Tar, *J. Org. Chem.*, 1980, 1800.

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