Tetrahedron Vol. 37, No. 25, pp. 4503 to 4508, 1981
Printed in Great Britain.

0040-4020/81/254503-06$02.00/0
Pergamon Press Ltd.

APPLICATION OF THE INTRAMOLECULAR WADSWORTH–EMMONS REACTION TO BICYCLO[3.3.0]OCT - $\Delta^{1,2}$ - EN - 3 - ONES. SYNTHESIS AND X-RAY STRUCTURE OF A NOVEL DIMER OF THE PARENT MEMBER

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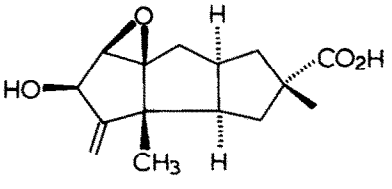
(*Received in U.S.A.* 1 *April* 1981)

Abstract—The cyclisation of β,ϵ-diketophosphonates is shown to provide an expeditious route to bicyclo[3.3.0]oct - $\Delta^{1,2}$ - en - 3 - ones, which lack substituents at C-2 and C-5. Application of the method to the parent member **12** results in the formation of a novel dimer **16** whose structure has been determined by X-ray crystallography. The dimer is thought to derive from **12** by a double Michael addition sequence involving the allyl anion **13** and the enolate **15**.

Biologically active terpenes showing structures based on the linear fusion of two or more cyclopentane rings (e.g. hirsutic acid **1**,[1] coriolin **2**,[2] pentalenolactone **3**,[3] and quadrone **4**[4]) are a rapidly expanding group of natural products.[5] The combination of novel structure and interesting biological properties has attracted the attention of many synthetic chemists to this class of compound, and a number of total syntheses have been recorded.[5,6]

Our interest in the preparation of substituted bicyclo[3.3.0] oct - $\Delta^{1,2}$ - en - 3 - ones for synthetic work in this area, has led us to investigate the application of the intramolecular Wadsworth–Emmons reaction, using β,ϵ-diketophosphonates, as a route to these compounds.[7,8] The use of β,ζ-diketophosphonates to synthesise cyclohex - 2 - enones was reported by Grieco and Pogonowski in 1973,[9] and first Heathcock[10a] and then Piers[10b] and their respective collaborators later demonstrated the potential of β,ϵ-diketophosphonates in cyclopentane annulations leading to hydrindenones.[11] β,ϵ-Diketophosphonates have not previously been used to synthesise bicyclo[3.3.0]oct - $\Delta^{1,2}$ - en - 3 - ones, and at the outset of these investigations the parent member **12** was unknown.

We first examined the synthesis of the bicyclo-octenone **8** from the diketo-phosphonate **7**. Protection of the ketoester **5** as the dioxolan followed by reaction with lithium diethylmethylphosphonate and hydrolysis of the intermediate dioxolan-phosphonate **6** led to the diketo-phosphonate **7** in 75% overall yield. Treatment of **7** with sodium hydride (1 equivalent) in dimethoxyethane at 60° then led (70%) to the bicyclo-octenone **8** uncontaminated with the positional isomer **10**. The synthesis of **8** by the route outlined can be commended not only because of the high overall yields, but also because it results in no isomerisation of the double bond to the more substituted position [i.e. to **10**], a feature encountered in most conventional aldol condensation approaches to these compounds.[12–14] Interestingly, brief treatment of the bicyclo-octenone **8** with 5% ethanolic potassium hydroxide at room temperature resulted in complete conversion to the



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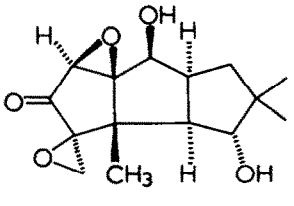

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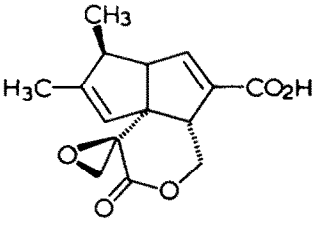

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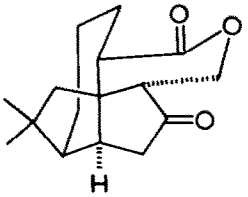


(4)

isomeric cyclopentenone **10** within 12 min (glc monitoring). The structure of **10** was confirmed by an independant synthesis using a similar Wadsworth–Emmons reaction with the diketo-phosphonate **9**.

We next turned our attention to the synthesis of the parent bicyclo[3.3.0]oct - $\Delta^{1,2}$ - en - 3 - one **12** from the diketo-phosphonate **11**. To our surprise, treatment of **11** with sodium hydride in dimethoxyethane at 60° led only to a tarry mass, whereas at room temperature using two equivalents of sodium hydride, a crystalline dimer ($C_{16}H_{20}O_2$) m.p. 88–89° was obtained instead, in 52% yield. In only one experiment were we able to isolate by chromatography a small amount of the monomer **12** from this condensation.

We first thought that the dimer $C_{16}H_{20}O_2$ was produced from **12** by straightforward [2+2] cycloaddition brought about by the strain in the bridgehead double bond in the latter. Spectral data on the dimer however were not compatible with a cyclobutane structure, and accordingly the structure of the dimer was investigated by X-ray analysis.

The crystallographic study revealed that the dimer is based on a novel dimerisation across the C-2, C-5 and the C-1, C-5 carbon atoms of the monomer (i.e. **12**→**16**). Dimerisation has therefore generated a further cyclopentane ring in the structure with the formation of the C-1, C-15 and C-5, C-12 bonds (see Fig. 1). The final fractional atomic co-ordinates for the non-hydrogen atoms, together with their estimated standard deviations are listed in Table 1. Those for the hydrogen atoms are given in Table 2. The Fig. 1 shows a perspective view of the molecule, and gives the numbering scheme used. Tables 3 and 4 give the bond lengths and bond angles together with their estimated standard deviations. The internal torsion angles around each of the five rings in the structure are displayed in Table 5.

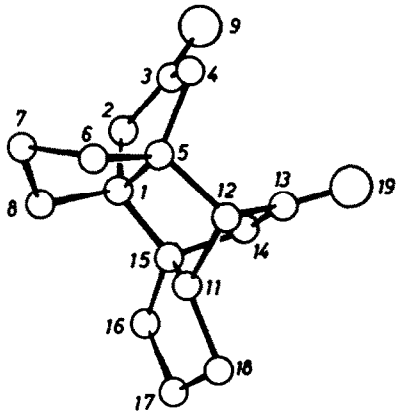
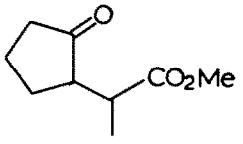


Fig. 1.



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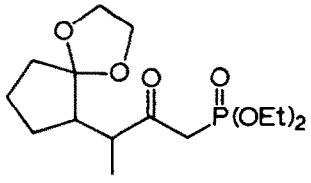

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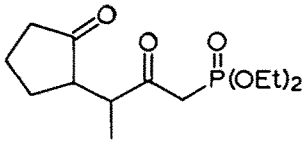

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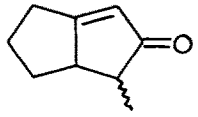

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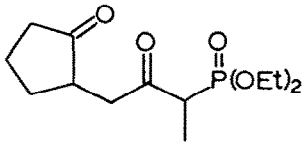

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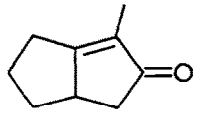

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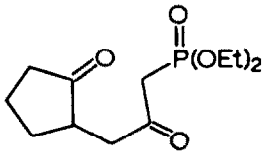

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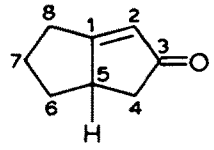

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The strained nature of the bridged cyclopentane dimer is revealed in the molecular geometry displayed in Tables 3–5. Three of the carbon–carbon bonds are significantly longer than usual. Two of these [C(1)–C(5) and C(5)–C(12)] are predictably part of the central cyclopentane ring formed on dimerisation, but the third [C(16)–C(17)] is somewhat removed from the bridged ring system. Apart from the carbon–carbon bonds shortened by neighbouring carbonyl groups, as expected, there are in addition two significantly short bonds remote from the bridged ring at C(6)–C(7) and C(17)–C(18).

The bond angles in the dimer also show significant deviations from expected values. Although the bond angles at sp^3-hybridised carbon atoms within cyclopentane rings are usually somewhat smaller than the idealised value, many of the valence angles in this bridged cyclopentane dimer are very small. The two lowest values, with bond angles of less than 100°, both

Table 1. Fractional coordinates ($\times 10^4$) for the non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	4003(2)	1820(8)	4345(6)
C(2)	4266(3)	2938(12)	5303(7)
C(3)	4416(2)	4648(10)	4769(7)
C(4)	4381(3)	4410(11)	3507(7)
C(5)	4089(2)	2723(8)	3187(5)
C(6)	4339(2)	1232(11)	2588(7)
C(7)	4547(3)	39(11)	3544(8)
C(8)	4189(3)	−134(10)	4319(8)
O(9)	4547(2)	6001(7)	5303(6)
C(11)	3355(2)	1554(10)	2984(7)
C(12)	3613(2)	3132(9)	2525(7)
C(13)	3440(2)	4711(11)	3147(9)
C(14)	3356(3)	3999(13)	4299(10)
C(15)	3490(2)	1940(9)	4243(6)
C(16)	3203(3)	701(16)	4869(9)
C(17)	2772(3)	445(19)	3970(10)
C(18)	2843(2)	1359(16)	2867(11)
O(19)	3381(2)	6277(8)	2803(7)

Table 2. Fractional coordinates ($\times 10^3$) for the hydrogen atoms with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
H(2A)	446(3)	242(13)	580(8)
H(2B)	412(2)	313(10)	598(6)
H(4A)	459(5)	455(20)	265(13)
H(4B)	427(3)	538(13)	332(8)
H(6A)	451(3)	179(11)	196(5)
H(6B)	410(2)	58(9)	196(5)
H(7A)	479(2)	86(9)	395(5)
H(7B)	464(2)	−120(12)	328(7)
H(8A)	429(2)	−56(10)	508(7)
H(8B)	397(3)	−92(11)	391(6)
H(11)	347(2)	32(8)	279(4)
H(12)	359(2)	331(7)	173(4)
H(14A)	352(3)	442(12)	508(8)
H(14B)	317(8)	454(32)	432(20)
H(16A)	333(2)	−46(10)	507(5)
H(16B)	315(2)	105(11)	561(7)
H(17A)	265(5)	−100(25)	393(14)
H(17B)	261(5)	91(20)	470(12)
H(18A)	274(3)	280(16)	285(8)
H(18B)	276(2)	76(10)	211(6)

Table 3. Bond lengths (Å). All estimated standard deviations 0.01 Å

C(1)–(C(2)	1.52	C(7) – C(8)	1.52
C(1)–C(5)	1.57	C(11)–C(12)	1.53
C(1)–C(8)	1.54	C(11)–C(15)	1.51
C(1)–C(15)	1.54	C(11)–C(18)	1.54
C(2)–C(3)	1.50	C(12)–C(13)	1.50
C(3)–C(4)	1.49	C(13)–C(14)	1.51
C(3)–O(9)	1.21	C(13)–O(19)	1.22
C(4)–C(5)	1.53	C(14)–C(15)	1.56
C(5)–C(6)	1.55	C(15)–C(16)	1.52
C(5)–C(12)	1.57	C(16)–C(17)	1.57
C(6)–C(7)	1.49	C(17)–C(18)	1.50

Table 4. Bond angles (°) with estimated standard deviations in parentheses

C(2)–C(1)–C(5)	106.7(5)	C(12)–C(11)–C(15)	97.2(5)
C(2)–C(1)–C(8)	110.9(6)	C(12)–C(11)–C(18)	126.3(7)
C(2)–C(1)–C(15)	116.3(6)	C(15)–C(11)–C(18)	103.7(7)
C(5)–C(1)–C(8)	105.4(5)	C(5)–C(12)–C(11)	99.2(5)
C(5)–C(1)–C(15)	101.3(5)	C(5)–C(12)–C(13)	105.1(6)
C(8)–C(1)–C(15)	114.8(5)	C(11)–C(12)–C(13)	100.1(7)
C(1)–C(2)–C(3)	107.0(6)	C(12)–C(13)–C(14)	106.8(7)
C(2)–C(3)–C(4)	109.9(6)	C(12)–C(13)–O(19)	127.1(11)
C(2)–C(3)–O(9)	124.0(8)	C(14)–C(13)–O(19)	126.0(9)
C(4)–C(3)–O(9)	126.2(8)	C(13)–C(14)–C(15)	102.6(7)
C(3)–C(4)–C(5)	107.4(6)	C(1)–C(15)–C(11)	101.4(5)
C(1)–C(5)–C(4)	106.5(5)	C(1)–C(15)–C(14)	108.3(6)
C(1)–C(5)–C(6)	104.6(5)	C(1)–C(15)–C(16)	124.6(6)
C(1)–C(5)–C(12)	105.1(5)	C(11)–C(15)–C(14)	100.6(7)
C(4)–C(5)–C(6)	112.1(6)	C(11)–C(15)–C(16)	105.8(6)
C(4)–C(5)–C(12)	115.3(5)	C(14)–C(15)–C(16)	112.6(7)
C(6)–C(5)–C(12)	112.2(5)	C(15)–C(16)–C(17)	102.7(8)
C(5)–C(6)–C(7)	104.2(6)	C(16)–C(17)–C(18)	109.0(8)
C(6)–C(7)–C(8)	104.0(6)	C(11)–C(18)–C(17)	103.1(8)
C(1)–C(8)–C(7)	103.3(6)		

occur at atoms that form part of the strained central cyclopentane ring [C(11) and C(12)]. Conversely there are also two very large exocyclic bond angles of approximately 125° in the same region [C(11) and C(15)].

The conformation of the five cyclopentane rings is described by their internal torsion angles in Table 5. Each ring is in the envelope conformation, with C(11) the out of plane atom in each of the three rings of which it is a member. The out of plane atoms in the other rings are C(7) and, surprisingly, the carbonyl C(3). However, the degree of twist of the flap of the envelope varies significantly in the different rings. In the central cyclopentane ring formed on dimerisation, and also the cyclopentanone ring with three atoms in common [C(11), C(12) and C(15)], the flap [C(11)] is 0.9 Å out of the respective planes containing the other members of each ring. In both of the cyclopentane rings unaltered from the monomer, the out-of plane atoms [respectively C(7) and C(11)] are only 0.6 Å out of plane. Finally, the remaining cyclopentanone ring is much flatter, with C(3) only 0.2 Å out of the plane of the other atoms. The bond angles in this ring are also noticeably larger than for the other rings.

Table 5. Selected Torsion angles in each of the 5-membered rings.

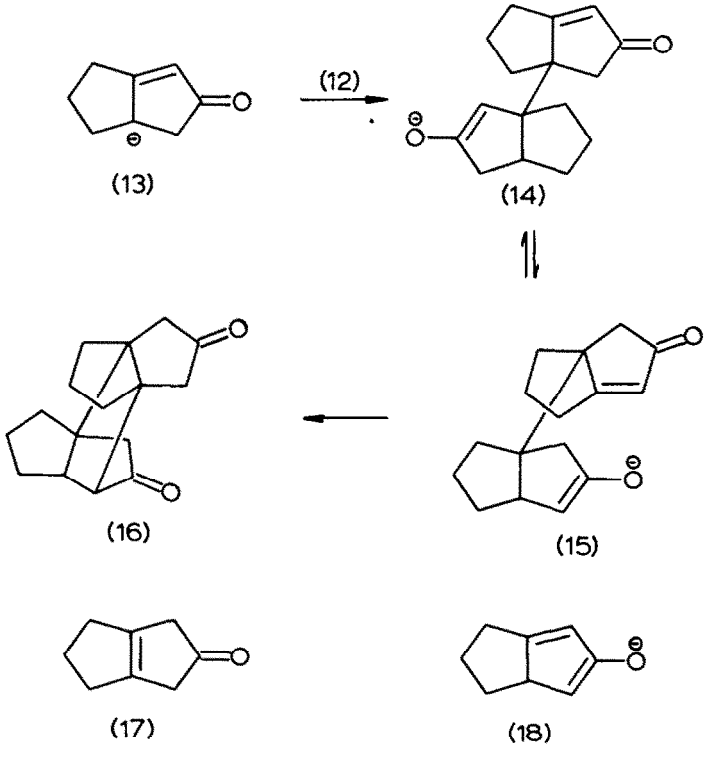
C(5)–C(1)–C(2)–C(3)	12
C(1)–C(2)–C(3)–C(4)	−17
C(2)–C(3)–C(4)–C(5)	15
C(3)–C(4)–C(5)–C(1)	−7
C(4)–C(5)–C(1)–C(2)	−3
C(8)–C(1)–C(5)–C(6)	−2
C(1)–C(5)–C(6)–C(7)	−24
C(5)–C(6)–C(7)–C(8)	41
C(6)–C(7)–C(8)–C(1)	−42
C(7)–C(8)–C(1)–C(5)	27
C(15)–C(11)–C(12)–C(13)	−53
C(11)–C(12)–C(13)–C(14)	33
C(12)–C(13)–C(14)–C(15)	−1
C(13)–C(14)–C(15)–C(11)	−33
C(14)–C(15)–C(11)–C(12)	53
C(18)–C(11)–C(15)–C(16)	40
C(11)–C(15)–C(16)–C(17)	−28
C(15)–C(16)–C(17)–C(18)	5
C(16)–C(17)–C(18)–C(11)	19
C(17)–C(18)–C(11)–C(15)	−36
C(15)–C(1)–C(5)–C(12)	−4
C(1)–C(5)–C(12)–C(11)	−31
C(5)–C(12)–C(11)–C(15)	54
C(12)–C(11)–C(15)–C(1)	−58
C(11)–C(15)–C(1)–C(5)	38

It seems likely that the dimer is derived from the monomer **12** by a two stage Michael addition sequence[15] involving the allyl anion **13** (to **14**), and the enolate **15** in a favoured 5 - *exo* - *Trig* process;[16] the stereoelectronic demands of such a sequence would also provide an explanation for the formation of the *syn*-rather than the *anti*-dione dimer. The dimerisation could also be formulated as a rare [4 + 2] cycloaddition involving the allyl anion **13** and the alkene **17** produced by isomerisation of **12**,[17] or alternatively as a [4 + 2] cycloaddition involving the enolate **18** and the alkene **17**. The isomerisation of **12** to **17** would not be entirely unexpected in view of the significant angle strain at the bridgehead in **12**[18] (see isomerisation of **8** to **10**) but we were unable to demonstrate the independent conversion of **12** to **16** using a range of base-catalysed conditions.

EXPERIMENTAL

Diethyl 2 - oxo - 3 - (2 - oxocyclopentyl)butyl phosphonate (**7**)

The diketophosphonate was prepared from methyl 2-(2-oxocyclopentyl) propionate is an analogous manner to that described



for the preparation of homologue **9** from ethyl 2-oxocyclopentylacetate.

Conversion of methyl 2-(2-oxocyclopentyl)propionate **5**[19] into the corresponding dioxolan (89%), ν_{max} 1735 cm^{-1}, δ1.11 (m, $CHCH_3$), 1.4–1.8 (m, 6H), 2–2.6 (m, 2H), 3.5 (OMe), 3.7–3.9 (m, 4H) followed by reaction with diethylmethylphosphonate[20] led to the keto-phosphonate **6** (84%), ν_{max} 1720, 1260, 1050 cm^{-1}, $\delta(CDCl_3)$ 1.1–1.6(m, $2\times CH_2CH_3 + CH\cdot CH_3$), 1.5–2.5 (m, 8H), 3.0–3.4 (m, CH_2P), 3.8–4.0 (OCH_2CH_2O), 4.0–4.40 (m, CH_2CH_3). Removal of the dioxolan grouping then gave the diketophosphate (87%) as a colourless liquid, b.p. 165° at 0.1 mm Hg, ν_{max} 1735, 1710 cm^{-1}, $\delta(CDCl_3)$ 1.2–1.6 m ($2\times CHCH_3 + CHCH_3$), 1.5–2.3 (m, 8H), 3.1–3.4 (m, CH_2–P), 4.41–4.4 (m, CH_2CH_3).

4 - Methylbicyclo[3.3.0]*oct - $\Delta^{1,2}$ - en - 3 - one* (**8**)

The bicyclo-octenone was prepared from diethyl 2 - oxo - 3 - (2 - oxocyclopentyl)butyl phosphonate by the procedure outlined for the synthesis of the corresponding 2 - methylbicyclo - oct - $\Delta^{1,2}$ - en - 3 - one. The bicyclooct - $\Delta^{1,2}$ - en - 3 - one (70%) showed b.p. 97° at 15 mm Hg., λ_{max} (EtOH) 230 nm, ν_{max} (film) 1700, 1625 cm^{-1}, δ1.21 (d, J6.5, CHMe), 1.2 (m, 2H), 1.8–2.8 (m, 5H), 5.8 (:CH).[14] A solution of the enone (0.1 g) in 5% ethanolic potassium hydroxide (5 cm^3) was left at 25° for 0.3 hr, then acidified and extracted with ether. Evaporation of the ether left 2 - methyl - bicyclo[3.3.0]oct - $\Delta^{1,2}$ - en - 3 - one (85 mg, 85%) whose spectral data were identical with those of an authentic sample.

Ethyl 2 - oxocyclopentylacetate

Ethyl bromoacetate (38.3 cm^3) was added over 0.25 h to a stirred solution of 1 - pyrrolidinylcyclopentene[21] in benzene (150 cm^3) heated under reflux. The mixture was heated under reflux for a further 1 hr then cooled and evaporated *in vacuo*. The residue was dissolved in ethanol (100 cm^3) containing water (20 cm^3) and the resulting solution was heated under reflux for 2 hr, then evaporated to leave a red coloured oil. The oil was diluted with water (100 cm^3) and then extracted with ether (3 × 180 cm^3). The combined ether extracts were washed successively with 2M-hydrochloric acid (100 cm^3), 5% sodium hydrogen carbonate solution (100 cm^3) and water (30 cm^3), then dried and evaporated. Distillation of the residue gave the keto-ester (19.2 g, 38%)[22] as a colourless liquid, b.p. 120–30° at 7 mm Hg, ν_{max} (film) 1740, 1720 cm^{-1}, $\delta(CDCl_3)$ 1.21 (t, J8, CH_2CH_3), 1.5–2.8 (m, 9H), 4.1 (q, J8, CH_2CH_3).

Diethyl 1 - Methyl - 2 - oxo - 3 - (2 - oxocyclopentyl)propyl phosphonate **9**

A solution of ethyl 2-oxocyclopentylacetate (7.7 g) in ethylene glycol (3.23 g) and benzene (20 cm^3) containing p-toluenesulphonic acid (25 mg) was heated under reflux for 3 hr using a Dean and Stark separator. The solution was washed with 5% sodium hydrogen carbonate solution, then dried and evaporated to leave the corresponding dioxolan[22] (9 g, 92%) as an almost colourless liquid showing ν_{max} (film) 1735 cm^{-1}, $\delta(CDCl_3)$ 1.22 (t, J7, CH_2CH_3), 1.5–2.7 (m, 9H), 3.9 (OCH_2CH_2O), 4.12 (q, J7, CH_2CH_3). A sample distilled at 120–2° at 20 mm Hg with extensive decomposition.

An equivalent of n-butyl lithium in hexane was added over 0.3 hr to a stirred solution of diethyl ethylphosphonate[23] (8.3 g) in dry tetrahydrofuran (100 cm^3) at −78° under nitrogen, and the resulting mixture was stirred at −78° for a further 0.25 h. The dioxolan (5.4 g), from above, was added, and the mixture was stirred at −78° for 1 hr, and then allowed to warm to room temperature over 1 hr, when it was diluted with 10% ammonium chloride solution (50 cm^3) and extracted with ether (2 × 50 cm^3). Evaporation of the combined and dried ether extracts and distillation of the residual diethyl ethylphosphonate left diethyl 1 - methyl - 2 - oxo - 3[2 - (1,3 - dioxolano)cyclopentyl]propyl phosphonate (78 g, 94%), ν_{max} (film) 1705, 1250, 1040 cm^{-1}, δ1.1–1.4 (m, 9H), 1.5–1.8 (m, 6H), 3.0–3.4 (m, CH_2-P), 3.84 (OCH_2CH_2O), 4.1 (m, CH_2CH_3) which was hydrolysed directly in the next stage.

A solution of the dioxolan phosphonate (6.5 g) in ethanol (65 cm^3) and 2M-hydrochloric acid (65 cm^3) was stirred at 25° for 2 hr. and then neutralised with solid potassium carbonate and extracted with ether (3 × 100 cm^3). The combined ether extracts were dried and then distilled to give the diketophosphonate (5.4 g, 95%) as a colourless liquid, b.p. 160° at 0.1 mm Hg, ν_{max} (film) 1735, 1705 cm^{-1}, $\delta(CDCl_3)$ 1.3–1.6 (m, $2\times CH_2CH_3$ + CHMe), 3.15–3.4 (m, CH_2–P), 4.1–4.4 (m, CH_2CH_3). (*m/e* 290.1297, $C_{13}H_{23}OP$ requires M 290.1283).

2 - Methylbicyclo[3.3.0]*oct - $\Delta^{1,2}$ - en - 3 - one* **10**

A solution of diethyl 1 - methyl - 2 - oxo - 3 - (2 - oxocyclopentyl)propyl phosphonate (5.4 g) in dimethoxyethane (25 cm^3) was added to a stirred suspension of sodium hydride (0.5 g) in dimethoxyethane (250 cm^3) at 0° under nitrogen. The mixture was stirred at 0° for 0.25 hr, then allowed to warm to room temperature over 1 hr, and heated at 60° for 3 hr. The cooled mixture was acidified with 2M-hydrochloric acid (10 cm^3), and the organic layer was then separated and washed with saturated sodium chloride solution. Evaporation of the dried organic phase and distillation of the residue gave the bicyclo octenone (2 g, 80%) as a colourless liquid b.p. 85° at 9 mm Hg (Lit.[12a] b.p. 107–8° at 14 mm Hg), λ_{max}(EtOH) 237 nm; ν_{max} 1705, 1665 cm^{-1}, $\delta(CDCl_3)$ 0.8–1.3 (m, 2H), 1.69 (:CMe), 1.8–2.2 (m, 4H), 2.3–2.6 (m, $COCH_2$), 2.7 (CH). The 2,4-dinitrophenylhydrazone derivative crystallised from ethyl acetate and had m.p. 187° (Lit[12a] m.p. 187°).

Diethyl 2 - oxo - 3 - (2 - oxocyclopentyl)propyl phosphonate (**11**)

The diketophosphonate was prepared from ethyl 2-oxocyclopentenylacetate in a manner analogous to that described for the preparation of the homologue **9**. Acylation of diethylmethylphosphonate[20] with the dioxolan derived from ethyl 2-oxocyclopentylacetate led to diethyl 2 - oxo[2 - (1,3 - dioxolanocyclopentyl] propyl phosphonate (90%), ν_{max} (film) 1720, 1260, 1050 cm^{-1}, $\delta(CDCl_3)$ 1.26 (t, J8, CH_2CH_3), 1.6–2.7 (m, 9H), 3.13 (d, J22, CH_2P), 3.93 (OCH_2CH_2O), 4.2 m (CH_2CH_3), which on hydrolysis (EtOH–HCl) gave the diketophosphonate (74%) as a colourless liquid, b.p. 152–6° at 0.5 mm Hg, ν_{max} 1735, 1710 cm^{-1}, δ1.36 (t, J8, CH_2CH_3), 1.5–3.0 (m, 9H), 3.15 (d, J22, CH_2P), 4.0–4.4 (m, CH_2CH_3), (*m/e* 276.1140. $C_{12}H_{21}O_5P$ requires M 276.1126).

Bicyclo[3.3.0]*oct - $\Delta^{1,2}$ - en - 3 - one* **12** *and Dimer* (**16**)

A solution of diethyl 2 - oxo - (2 - oxocyclopentyl)propyl phosphonate (1.6 g) in dimethoxyethane (8 cm^3) was added over 5 min to a stirred suspension of sodium hydride (0.28 g) in dimethoxyethane (75 cm^3) at 0° under nitrogen. The mixture was allowed to warm to room temperature over 1.5 hr, then diluted with water (8 cm^3) and acidified with 2M-hydrochloric acid. The organic layer was separated, then washed with saturated salt solution (5 cm^3), dried and evaporated. Chromatography of the residue on silica gel G using 1:1 benzene-diethyl ether as eluant gave (i) the octenone (0.098 g., 14%), λ_{max} (EtOH) 231 nm., ν_{max} (film) 1700, 1615 cm^{-1}, δ1.0–1.4 (m, 2H), 1.8–2.4 (m, 4H), 2.4–2.9 (m, 3H), 5.91 (:CH), and (ii) the dimer (0.34 g., 52%) which crystallised from hexane as colourless needles, m.p. 88–9°, ν_{max} (KBr) 1735 cm^{-1}, δ1.0–2.7 (m), δ (carbon) 21.2, 24.3, 25.5, 28.7, 37.1, 40.9, 48.1, 49.6, 53.5, 54.9, 62.2, 63.5, 214.67, 218.2 ppm. (Found: C, 78.9; H, 8.4; *m/e* 244. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25% M 244).

Crystals of the dimer suitable for single crystal X-ray diffraction were obtained from hexane, and one of approximate dimensions 0.5 × 0.4 × 0.2 mm was mounted on a diffractomer. Accurate lattice parameters were obtained by least-squares refinement of 23 reflections measured on the diffractometer. Intensity data were collected with Mo-K_α radiation using an ω-2θ scan for $1° \leq \theta \leq 25°$. A total of 2281 reflections was measured of which 1190 had $I \geq 3\sigma(I)$ and were considered observed and used in the subsequent refinement. The data were corrected for Lorentz and polarisation factors, but no absorption corrections were applied. Crystallographic computations were performed using the Crystals system of programs. $C_{16}H_{20}O_2$, M = 244.3. Monoclinic a = 30.276(8), b = 7.297(2), c = 11.793(3) Å, β = 98.01(2)°, U = 2580 $Å^3$, D_c = 1.26 g cm^3, Z = 8, F(000) = 1056. Space group C2/c

from systematic absences and subsequent refinement. Mo-k_α radiation $\lambda = 0.71069$ Å, μ(Mok$_\alpha$) 0.88 cm^{-1}.

The structure was solved by direct methods using the MULTAN program. 180 reflections with E > 1.66 were used and the E map based on the best set of phases revealed the positions of all non-hydrogen atoms as the 18 highest peaks in the map. These positions were refined initially isotropically and subsequently anisotropically. A difference map revealed the positions of the hydrogen atoms which were then included in the refinement with isotropic vibrations. Refinement was terminated where maximum $\delta/\sigma = 0.1$ after a total of 17 cycles when the value of R was 0.094. Tables of observed and calculated structure factors and anisotropic temperature factors may be obtained from the authors.

Acknowledgement—We thank the S.R.C. for a studentship (to K.C.)

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