

NOVEL DIMERISATION OF BICYCLO[3.3.0]OCT-2-EN-3-ONE

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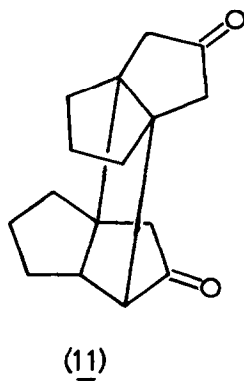
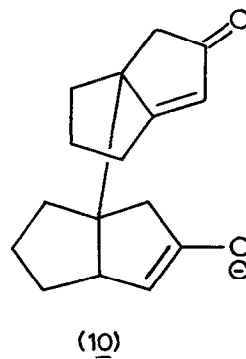
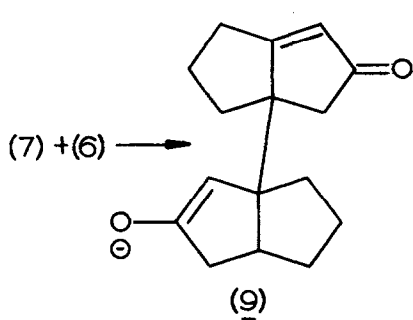
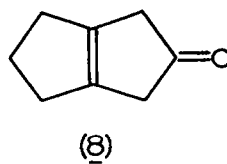
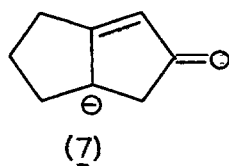
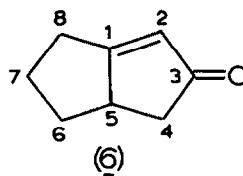
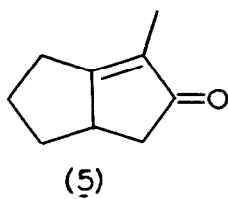
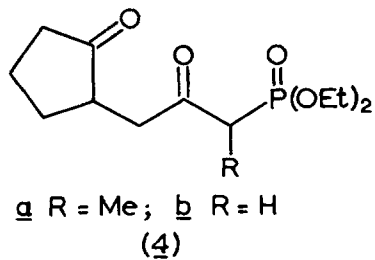
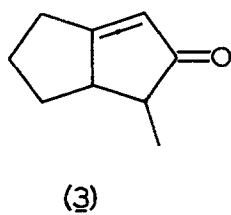
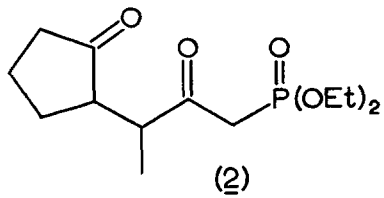
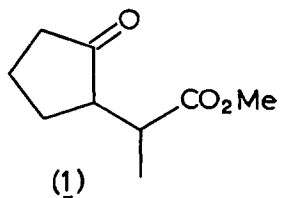
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Summary Application of the intramolecular Wadsworth-Emmons reaction to bicyclo[3.3.0]oct-2-en-3-ones results in the formation of a novel dimer (11) of the parent member (6) whose structure has been determined by X-ray crystallography.

The recognition of a wide range of biologically active natural terpenes showing structures based on the linear fusion of two or more cyclopentane rings e.g. hirsutic acid,¹ pentalenolactone,² quadrone³ has resulted in the development of a number of methods for cyclopentane annulation during the past decade.^{4,5} In connection with synthetic studies in this area, we required a general route to bicyclo[3.3.0]oct-2-en-3-ones which were devoid of substituents at C-2 and C-5. To our knowledge this type of substituted bicyclo-octenone has not previously been made. In this paper, we describe the application of the intramolecular Wadsworth-Emmons reaction⁶ to bicyclo[3.3.0]oct-2-en-3-ones, which has resulted in the isolation of a novel dimer (11) of the parent member (6).⁷

Protection of the keto-ester (1) as the dioxolan, followed by reaction with lithium diethylmethylphosphonate (THF, -78° to 25°) and hydrolysis of the intermediate dioxolan-phosphonate (EtOH-2M HCl) led to the diketo-phosphonate (2) in 75% overall yield. Treatment of (2) with NaH (1 equivalent) in dimethoxyethane⁶ at 60° then led (70%) to the bicyclo-octenone (3) b.p. 95°/14 mm, ν_{\max} 1700, 1625 cm^{-1} , τ 4.2 (:CH), 8.78 d (J 6, CHCH₃) uncontaminated with the positional isomer (5). In a similar manner, treatment of the diketo-phosphonate (4a) with NaH gave 2-methylbicyclo[3.3.0]oct-2-en-3-one (5; 80%), b.p. 90-94°/15 mm, ν_{\max} 1705, 1665 cm^{-1} , τ 8.36 (:CMe), which was also produced when (3) was stirred in 5% ethanolic KOH at 25° for 12 mins (85%).

Surprisingly, treatment of the phosphonate (4b) with NaH in dimethoxyethane at 60° led to a tarry mass, whereas at 25° using two equivalents of NaH, a crystalline dimer (C₁₆H₂₀O₂), m.p. 88-89° (hexane), ν_{\max} 1735 cm^{-1} , of the anticipated bicyclo-octenone (6) was instead obtained in 52% yield. In only one experiment were we able to isolate a small amount of (6), ν_{\max} 231 nm,



ν_{\max} 1700, 1625 cm^{-1} , τ 4.18 (:CH) by chromatography.

Spectral data on the dimer obtained from (4b) were not compatible with a cyclobutane structure produced by simple $[\pi 2 + \pi 2]$ cycloaddition; accordingly the structure was investigated by X-ray analysis. The dimer crystallised in the monoclinic space group C2/c, with $a = 30.276(8)$, $b = 7.297(2)$, $c = 11.793(3)$, $\beta = 98.01(2)$ and $z = 8$. Intensity data were collected with Mo-K $_{\alpha}$ radiation using an automatic four-circle diffractometer, and 1190 reflections were considered observed. The structure was determined by direct methods using the Multan program, and refined by full-matrix least squares to a current R index of 9.4%. A general view of the resulting molecular structure is shown on the Figure, which reveals 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 (6).

It seems likely that the dimer is derived from (6) by a two stage Michael addition sequence⁸ involving the allyl anion (7) (to 9) and the enolate (10) in a favoured 5-exo-Trigonal process;⁹ 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) $[\pi 4 + \pi 2]$ cycloaddition¹⁰ involving the allyl anion (7) and the alkene (8) produced by isomerisation of (6). The isomerisation of (6) to (8) would not be entirely unexpected in view of the significant angle strain at the bridgehead in (6),¹¹ cf the isomerisation of (3) to (5), but this far we have been unable to demonstrate the conversion of (6) to (11) using a range of base-catalysed conditions.

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

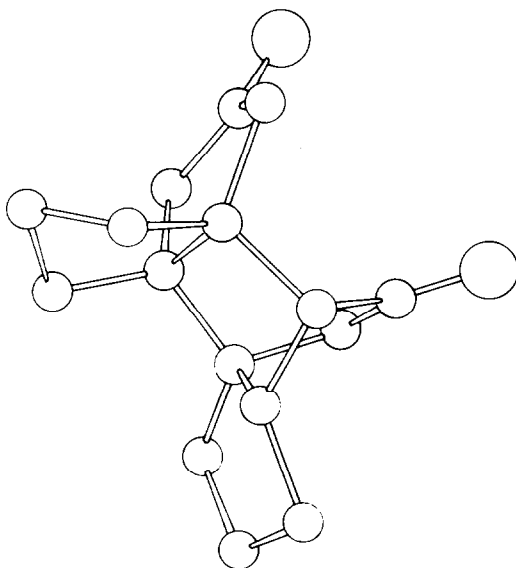


Figure. Computer drawing of the molecular structure of the dimer (11).

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