Base-catalyzed Aldol Reaction of 3,3,5,5-Tetramethylcyclopentane-1,2-dione with Benzyl Methyl Ketone: Formation and the Crystal and Molecular Structures of a Vinyl Alcohol and a Bicyclo[3.3.0]octenone Derivative

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The base-catalyzed aldol reaction of 3,3,5,5-tetramethylcyclopentane-1,2-dione with benzyl methyl ketone yields two 1:1 adducts, for which crystal and molecular structures have been determined by single-crystal diffraction techniques: 2-(2-hydroxy-3-phenyl-2-propen-1-ylidene)-3,3,5,5-tetramethylcyclopentanone crystallizes in the triclinic space group $P\bar{1}$; 1-hydroxy-6,6,8,8-tetramethyl-2-phenylbicyclo[3.3.0]oct-4-en-3-one is orthorhombic with the space group $P2_12_12_1$. The vinyl alcohol derivative contains three crystallographically independent molecules in which the hydroxyl group is linked to the carbonyl oxygen through a strong intramolecular hydrogen bond (O⋯O=2.55−2.58 Å), which persists in solution.

Aldol reactions[1] of enolizable 1,2-dicarbonyl compounds have attracted considerable attention; for example, reactions of dimethyl-β-ketoglutarate with various α-diketones have been shown to furnish 1:2 adducts (two β-ketoglutarate molecules),[2-5] providing thereby a route to certain bi- and tricyclic compounds through a sequence of aldolizations and Michael additions. To date, however, only a few aldol reactions of non-enolizable 1,2-dicarbonyl compounds have been reported, and rather than 1:2 adducts these reactions have yielded only 1:1 adducts.[6-7] Exceptionally, we found the base-catalyzed reaction of 3,3,5,5-tetramethylcyclopentane-1,2-dione (*1*) with acetone or ethyl methyl ketone to produce 1:2 aldol-type adducts: the 1-oxaspiro[4.4]-nonane derivatives (two molecules of *1*)[8-9] *2a* and *2b* (Scheme 1). To establish the generality,

Scheme 1.

2a R=H
2b R=CH₃
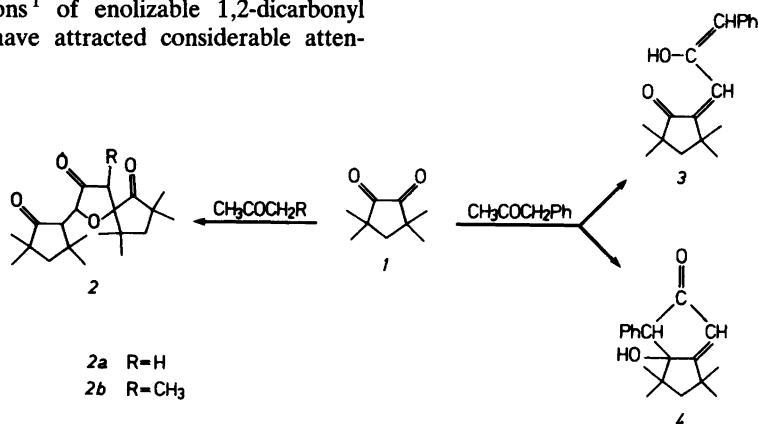
we went on to study the aldol reaction of *1* with benzyl methyl ketone. Two 1:1 adducts, *3* and *4*, were found, formed by the reaction of one and both carbonyl groups, respectively, in a normal aldol reaction. The pair of compounds constitutes an example of ring-chain tautomerism.[10] The reaction is in contrast to that of camphorquinone with dimethyl-*β*-ketoglutarate, where the product is a 1:1 adduct but a ring structure is formed *via* hemi-acetal formation.[7]

DISCUSSION

In base-catalyzed aldol reactions of simple methyl ketones the formation of a product with the double bond at the original methyl carbon is usual.[11] Noyce and Reed[12] have attributed this formation to the ready dehydration of the ketols formed by methyl carbon reaction. The formation of the vinyl alcohol *3* and the bicyclo[3.3.0]octenone derivative *4* in the reaction of benzyl methyl ketone with *1* thus follows the usual route. It seems likely that the ketol formed by the methyl carbon reaction rapidly dehydrates to give the anion of *3*, which either abstracts a proton to produce *3* or undergoes internal aldol reaction to form *4*. Cyclopentenone ketols of type *4* do not dehydrate at room temperature to stable cyclopentadienones.[6-7,13-15]

Previously, we have shown that acetone and ethyl methyl ketone, when allowed to react with *1* in alkaline medium, provide 1:2 adducts of type *2*.[8-9] The formation of these adducts can be explained through the sequence presented in Scheme 2. The ketol first formed by methyl carbon reaction is assumed to give the condensa-

tion product *5*, which, instead of undergoing internal aldol reaction to produce *6*, reacts with a second molecule of *1* to form the 1:2 adduct *7*. The adduct *7* does not then produce the condensation product *8*, but undergoes intramolecular Michael-type addition to form the final product *2*.

In principle, the 1:1 adducts formed in the reaction of *1* with benzyl methyl ketone could lead to the formation of 1:2 adducts either through reaction with a second carbonyl component or with a second methylene component. Relative to the formation of 1:2 adducts in the reaction of *1* with acetone or ethyl methyl ketone, two differences exist as possible explanations for the inability of *5* (Scheme 2, R=Ph) to react with *1*: a steric hindrance and the stabilization provided by the phenyl group. The latter explanation is preferred in that the reagent resembles dimethyl-*β*-ketoglutarate, which does not form 1:2 adducts with two carbonyl components.[2-5,7] The formation of adducts with only one methylene component might be due to the bulky methyl groups in accordance with the explanation given for the same behaviour in the reaction of camphorquinone with dimethyl-*β*-ketoglutarate.[7]

Molecular structure of 3. The asymmetric unit of the structure contains three crystallographically independent molecules; according to the ±2σ criterion, except for one angle value there are no significant differences in equivalent bond parameters and only negligible differences in the geometry of the three independent molecules.

Atomic coordinates for the non-hydrogen atoms, bond angles and deviations of atoms from best least-squares planes are listed in Tables 1−3.
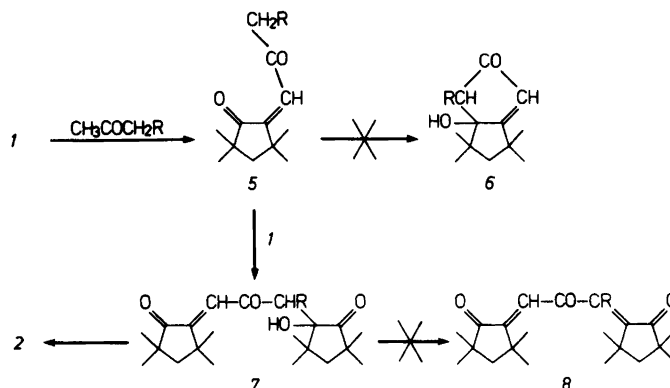
Scheme 2.

Table 1. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of the three independent molecules of 3, with standard deviations in parentheses.

	Molecule (I)			Molecule (II)			Molecule (III)		
	x	y	z	x	y	z	x	y	z
O(1)	5886(8)	3773(5)	5079(3)	713(7)	-1243(4)	2582(3)	2503(7)	-3130(4)	9205(3)
O(2)	5189(7)	4140(4)	3724(3)	1146(6)	186(4)	3745(3)	2893(6)	-1366(4)	9041(3)
C(1)	6216(9)	2957(7)	4969(5)	1171(8)	-887(6)	2094(5)	1692(9)	-3558(6)	8609(5)
C(2)	6757(10)	2466(7)	5635(5)	1167(8)	-1489(6)	1308(4)	1147(8)	-4642(5)	8481(4)
C(3)	6887(14)	1471(8)	5218(5)	1520(11)	-715(7)	855(5)	359(12)	-4868(7)	7669(6)
C(4)	6745(8)	1393(6)	4374(4)	2202(8)	247(5)	1406(4)	176(8)	-3967(6)	7337(4)
C(5)	6227(7)	2341(5)	4226(4)	1793(7)	128(5)	2157(4)	1106(7)	-3150(5)	7951(4)
C(6)	8085(13)	3026(9)	6095(7)	2226(11)	-2161(8)	1413(8)	274(11)	-4780(7)	9055(7)
C(7)	5694(12)	2405(8)	6122(6)	-235(10)	-2090(7)	947(5)	2330(10)	-5219(6)	8603(6)
C(8)	8085(10)	1316(7)	4146(6)	1629(10)	1090(7)	1102(5)	-1291(10)	-3818(7)	7215(7)
C(9)	5742(12)	5107(7)	3936(7)	3730(9)	413(7)	1501(5)	578(12)	-4057(8)	6583(6)
C(10)	5872(7)	2525(5)	3515(4)	2062(7)	877(5)	2772(4)	1291(7)	-2219(5)	7862(4)
C(11)	5371(8)	3356(5)	3240(5)	1785(8)	953(6)	3536(4)	2120(8)	-1341(5)	8353(4)
C(12)	5100(8)	3307(5)	2481(5)	2190(8)	1822(6)	4032(4)	2122(8)	-498(6)	8094(4)
C(13)	4584(8)	4022(5)	2035(4)	2042(8)	2104(6)	4824(4)	2880(8)	466(5)	8468(4)
C(14)	4488(8)	4975(6)	2364(4)	1582(9)	1459(6)	5257(5)	3595(9)	721(6)	9234(5)
C(15)	3988(9)	5600(6)	1902(6)	1472(10)	1806(9)	6005(5)	4299(9)	1651(7)	9535(5)
C(16)	3577(10)	5291(7)	1116(6)	1836(13)	2778(11)	6325(6)	4308(10)	2342(7)	9100(7)
C(17)	3666(10)	4352(7)	786(5)	2329(11)	3421(8)	5922(7)	3636(11)	2117(7)	8346(7)
C(18)	4163(9)	3722(6)	1243(5)	2408(9)	3089(6)	5169(5)	2920(9)	1184(6)	8024(5)

Table 2. Mean values of the bond angles (°) of the three independent molecules of *3*. The e.s.d.'s of the individual angles range from 0.6 to 1.1°.

O(1)−C(1)−C(2)	121.8	C(1)−C(5)−C(4)	109.1
O(1)−C(1)−C(5)	127.5	C(1)−C(5)−C(10)	128.7
C(2)−C(1)−C(5)	110.7	C(4)−C(5)−C(10)	122.2
C(1)−C(2)−C(3)	102.6	C(5)−C(10)−C(11)	132.2
C(1)−C(2)−C(6)	108.7	O(2)−C(11)−C(10)	121.2
C(1)−C(2)−C(7)	110.1	O(2)−C(11)−C(12)	120.9
C(3)−C(2)−C(6)	113.8	C(10)−C(11)−C(12)	117.9
C(3)−C(2)−C(7)	111.7	C(11)−C(12)−C(13)	129.4
C(6)−C(2)−C(7)	109.7	C(12)−C(13)−C(14)	124.4
C(2)−C(3)−C(4)	112.2	C(12)−C(13)−C(18)	117.6
C(3)−C(4)−C(5)	103.4	C(14)−C(13)−C(18)	118.0
C(3)−C(4)−C(8)	110.3	C(13)−C(14)−C(15)	120.2
C(3)−C(4)−C(9)	111.6	C(14)−C(15)−C(16)	120.7
C(5)−C(4)−C(8)	111.6	C(15)−C(16)−C(17)	120.2
C(5)−C(4)−C(9)	111.9	C(16)−C(17)−C(18)	119.8
C(8)−C(4)−C(9)	108.0	C(13)−C(18)−C(17)	121.0

Table 3. Deviations (Å) of atoms from the best least-squares planes in *3*.

1. Plane through C(1), C(2), C(4), and C(5)

	C(1)	C(2)	C(4)	C(5)	C(3)
Molecule (I)	−0.01	0.01	−0.01	0.01	−0.17
Molecule (II)	−0.01	0.01	0.00	0.01	−0.30
Molecule (III)	−0.01	0.01	−0.01	0.01	−0.14

2. Plane through O(1), C(1), C(5), C(10), C(11), and O(2)

	O(1)	C(1)	C(5)	C(10)	C(11)	O(2)	C(2)	C(3)
Molecule (I)	0.00	−0.01	0.00	0.00	0.00	0.00	0.05	−0.12
Molecule (II)	0.00	0.01	−0.02	0.01	0.01	−0.02	0.06	−0.26
Molecule (III)	0.00	0.01	−0.01	0.00	0.01	−0.01	0.05	−0.12

	C(4)	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
	0.01	0.00	−0.01	0.19	0.16	−0.07	−0.27	−0.25
	−0.02	0.04	0.05	0.19	0.18	0.05	−0.06	−0.08
	−0.02	−0.01	−0.04	0.16	0.10	−0.15	−0.37	−0.31

3. Plane through C(13), C(14), C(15), C(16), C(17), and C(18)

	C13)	C(14)	C(15)	C(16)	C(17)	C(18)
Molecule (I)	0.00	0.00	0.00	0.00	0.00	0.00
Molecule (II)	0.00	0.01	0.00	−0.01	0.02	−0.01
Molecule (III)	−0.01	0.00	0.01	−0.01	0.00	0.00

The numbering system of *3* and the mean values of the lengths of selected bonds of the three independent molecules are shown in Fig. 1. The shortening of the C−C single bonds between two sp^2-hybridized carbon atoms agrees with published values.[16] Likewise, the significant shorten-ing of the C−O bond is similar to that found for $C(sp^2)$−O bonds.[17]

Although the bond lengths of *3* are as would be expected, some features of the structure in the solid state and in solution deserve comment. The short interatomic distance between O(1) and
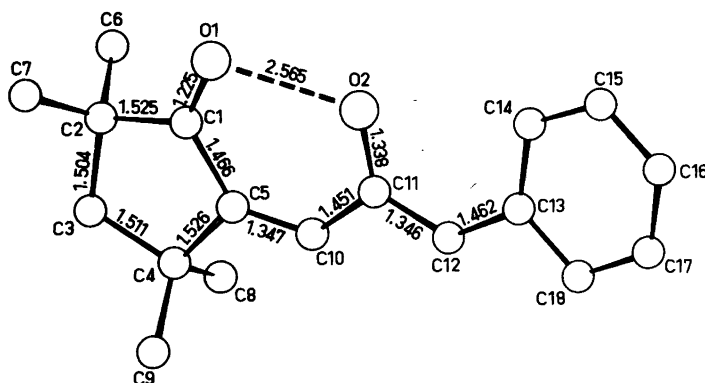
Fig. 1. View of a molecule of *3* and the mean values of the lengths of selected bonds of the three independent molecules; the broken line denotes an intramolecular hydrogen bond. Hydrogen atoms have been omitted for clarity. The e.s.d.'s of the individual bond lengths range from 0.008 to 0.019.

O(2) (ranging from 2.55 to 2.58 Å in the three independent molecules) indicates the presence of a strong intramolecular hydrogen bond in the solid state. The hydrogen bond confers stability on the enolic form, and spectral data show that the compound has the vinyl alcohol structure in solution as well. The ^{1}H NMR spectrum clearly shows the resonance signal of the enolic proton at δ 11.72 (*J* 1.7 Hz, allylic coupling through oxygen) and the effect of the hydrogen bond on the ^{13}C chemical shift of the carbonyl carbon (δ 216.7) is noticeable, when compared with other α,β-unsaturated cyclopentenones which generally resonate at δ 204-208.[18]

The other noteworthy close intramolecular contact is that between O(2) and C(14) (2.88–2.92 Å). It has been concluded, however, that C–H$\cdots$O bonds exist only where the C–H group is directly attached to a more electronegative atom.[19-20] The interaction between O(2) and C(14) therefore cannot be described as a hydrogen bond.

The intermolecular distances are of van der Waals type, the shortest distances between non-hydrogen atoms of the neighbouring molecules being 3.5 Å.

The three independent molecules adopt a flattened conformation in which all but the methyl carbon atoms are nearly in plane and the C(11)–C(12)–C(13)–C(14) torsion angles are 10.6(13), 8.5(14) and 10.6(14)° for molecules I, II and III, respectively. In all three molecules the conformation of the five-membered ring is an

envelope with C(3) displaced from the plane of the other atoms.

Molecular structure of 4. A view of the molecule of *4*, the numbering system and selected bond distances are shown in Fig. 2. Tables 4–6 present atomic coordinates for the non-hydrogen atoms, bond angles and deviations of atoms from least-squares planes. All bond lengths are as

Table 4. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of *4*.

	x	y	z
O(1)	1806(9)	3369(6)	5309(2)
O(2)	4087(8)	299(6)	4050(3)
C(1)	2046(11)	2884(9)	4803(3)
C(2)	2748(14)	3642(9)	4275(4)
C(3)	3018(12)	2730(8)	3835(3)
C(4)	3514(12)	2847(10)	3169(4)
C(5)	2795(15)	1344(13)	2908(4)
C(6)	1672(14)	627(9)	3404(4)
C(7)	2584(10)	1170(8)	3993(3)
C(8)	1550(12)	1311(9)	4598(4)
C(9)	5466(17)	2912(15)	3097(6)
C(10)	2702(21)	4183(14)	2868(5)
C(11)	-185(15)	1238(14)	3367(5)
C(12)	1602(17)	-1020(12)	3333(5)
C(13)	1778(12)	110(8)	5068(3)
C(14)	700(16)	-1075(12)	5050(5)
C(15)	752(21)	-2173(12)	5463(6)
C(16)	1986(20)	-2146(12)	5910(6)
C(17)	3160(18)	-984(13)	5930(5)
C(18)	3044(12)	130(10)	5505(4)

Table 5. Bond angles (°) in *4*.

O(1)–C(1)–C(2)	128.3(7)	C(11)–C(6)–C(12)	108.3(9)
O(1)–C(1)–C(8)	124.4(7)	O(2)–C(7)–C(3)	111.0(7)
C(2)–C(1)–C(8)	107.3(6)	O(2)–C(7)–C(6)	106.1(6)
C(1)–C(2)–C(3)	110.9(7)	O(2)–C(7)–C(8)	113.5(6)
C(2)–C(3)–C(4)	136.0(8)	C(3)–C(7)–C(6)	102.1(6)
C(2)–C(3)–C(7)	113.3(7)	C(3)–C(7)–C(8)	103.7(6)
C(4)–C(3)–C(7)	110.3(6)	C(6)–C(7)–C(8)	119.7(7)
C(3)–C(4)–C(5)	101.5(7)	C(1)–C(8)–C(7)	101.2(6)
C(3)–C(4)–C(9)	110.8(8)	C(1)–C(8)–C(13)	115.8(6)
C(3)–C(4)–C(10)	111.6(8)	C(7)–C(8)–C(13)	117.5(7)
C(5)–C(4)–C(9)	110.4(9)	C(8)–C(13)–C(14)	118.3(8)
C(5)–C(4)–C(10)	112.4(8)	C(8)–C(13)–C(18)	123.4(8)
C(9)–C(4)–C(10)	109.9(10)	C(14)–C(13)–C(18)	118.3(8)
C(4)–C(5)–C(6)	108.0(7)	C(13)–C(14)–C(15)	122.9(11)
C(5)–C(6)–C(7)	101.1(7)	C(14)–C(15)–C(16)	119.2(12)
C(5)–C(6)–C(11)	110.2(8)	C(15)–C(16)–C(17)	119.8(11)
C(5)–C(6)–C(12)	111.5(8)	C(16)–C(17)–C(18)	119.1(11)
C(7)–C(6)–C(11)	111.0(7)	C(13)–C(18)–C(17)	120.6(9)
C(7)–C(6)–C(12)	114.7(7)		

would be expected. The longest C–C bonds lie in the overcrowded region of the molecule; similar bond length extension has been observed in other molecules of comparable structure.[21-22] The strain in the bicyclo[3.3.0]octenone system is revealed by the bond angles: the geometry at C(7) and C(8) is distorted tetrahedron with valency angles ranging from 102.1 to 119.7 and 101.2 to 117.5°, respectively. The angle between the planes 1 and 2 (Table 6) is 10.9° and the torsion angle C(1)–C(8)–C(13)–C(18) is −32.2(12)°.

Table 6. Deviations (Å) of atoms from the best least-squares planes in *4*.

1. Plane through O(1), C(1), C(2), and C(8)

O(1)	C(1)	C(2)	C(8)	C(3)	C(7)
−0.01	0.02	−0.01	0.00	0.21	0.43

2. Plane through C(2), C(3), C(4), and C(7)

C(2)	C(3)	C(4)	C(7)	C(5)	C(6)
−0.02	0.04	−0.01	−0.01	−0.56	−0.98

3. Plane through C(13), C(14), C(15), C(16), C(17), and C(18)

C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
0.02	−0.02	0.00	0.01	−0.01	−0.01

The IR spectrum of *4* exhibits a sharp absorption band of the hydroxyl group at 3570 cm^{-1}, suggesting that weak intermolecular hydrogen bonds are present in solution. In the solid state, hydrogen bonding between the hydroxyl group and carbonyl oxygen, O(2)–H···O(1)[O(1) at ½+x, ½−y, 1−z]=2.847(9) Å, constitutes the major intermolecular attraction (Fig. 3). Other intermolecular contacts are of van der Waals type.

EXPERIMENTAL

Melting points were determined on an electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM PFT100 spectrometer. IR spectra were obtained on a Perkin-Elmer 125 spectrometer and UV spectra on a Shimadzu UV-200 spectrometer. High resolution mass spectra were taken on a JEOL JMS01 instrument.

The preparation of the starting compound is described in Ref. 23.

Aldol reaction of 1 with benzyl methyl ketone to yield the products 3 and 4. The diketone *1* (2.0 g, 0.013 mol) was dissolved in 0.2 M aqueous sodium hydroxide solution (500 ml) and benzyl methyl ketone (1.75 g, 0.013 mol) was added to the stirred solution at room temperature. Orange-yellow and white crystals, which formed within several hours, were separated by decanta-
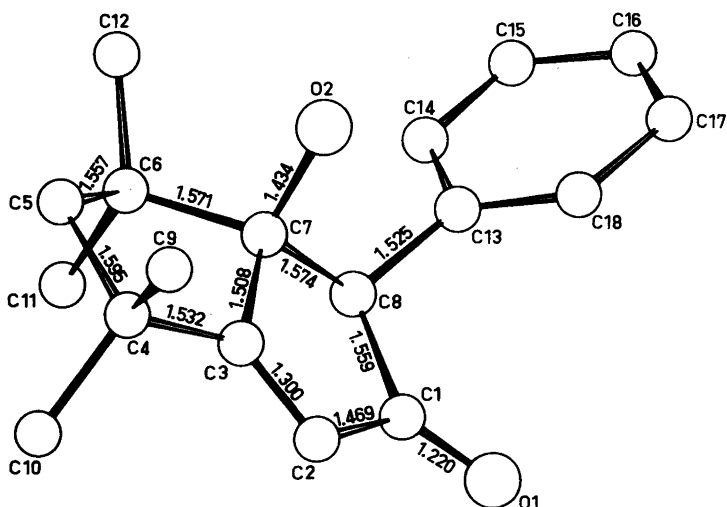
Fig. 2. View of a molecule of *4* with selected bond distances. Hydrogen atoms have been omitted for clarity. The e.s.d.'s of the bond lengths range from 0.009 to 0.021.

tion and filtered from the reaction mixture after three days to give *3* (1.43 g, 41 % of theory) and *4* (0.55 g, 16 %). Recrystallization from aqueous propanol (1:1) afforded pure products and crystals suitable for X-ray analysis were obtained by slow evaporation of the same solution.

The vinyl alcohol derivative *3*, orange-yellow crystals, m.p. 80−81 °C. HRMS: mol. wt., obs. 270.1602, calc. for $C_{18}H_{22}O_2$ 270.1619. ^1H NMR (100 MHz, $CDCl_3$): δ 1.19 (6 H, s, CH_3), 1.26 (6 H, s, CH_3), 1.84 (2 H, s, CH_2), 5.70 (1 H, d, *J* 1.7 Hz, =CHPh), 6.25 (s, =CH), 7.23−7.83 (5 H,

aromatic multiplet), 11.72 (1 H, d, *J* 1.7 Hz, enolic proton). ^{13}C NMR (25.15 MHz, $CDCl_3$): δ 27.2 (2 CH_3), 32.2 (2 CH_3), 38.2 (quaternary C), 44.8 (quaternary C), 51.0 (CH_2), 117.4, 126.9, 128.2 (2 C), 129.4 (2 C), 136.5, 139.9, 143.2, 153.4 (olefinic and aromatic carbons), 216.7 (C=O). IR (10 % CCl_4): 2740 (enolic OH), 1665 (C=O), 1550 (C=C), 1085 cm^{-1} (C−O). UV [abs. ethanol (ε)]: 412 (19800) nm.

The bicyclo[3.3.0]octenone derivative *4*, white crystals, m.p. 153−154 °C. HRMS: mol. wt., obs. 270.1623, calc. for $C_{18}H_{22}O_2$ 270.1619. ^1H
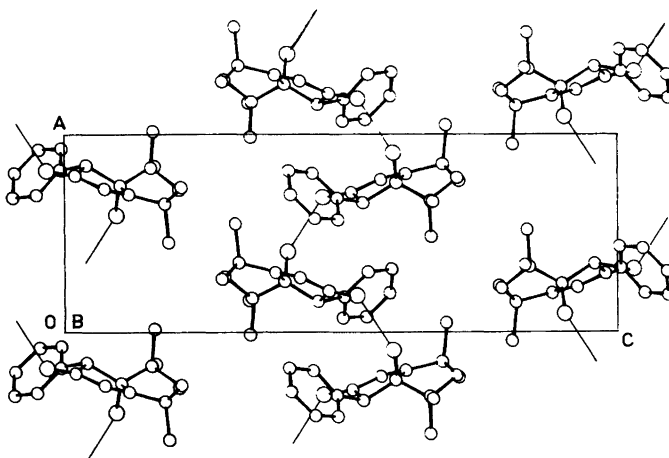

Fig. 3. The packing diagram of *4*; hydrogen bonds are shown by solid lines.

NMR (100 MHz, CDCl$_3$): δ 1.00 (3 H, s, CH$_3$), 1.12 (3 H, s, CH$_3$), 1.33 (3 H, s, CH)$_3$), 1.36 (3 H, s, CH$_3$), 1.50 (1 H, s, OH), 1.89 (2 H, center of AB quartet, J 13.0 Hz, CH$_2$), 3.85 (1 H, s, CHPh), 6.04 (1 H, s, =CH), 7.10–7.38 (5 H, aromatic multiplet). ^{13}C NMR (25.15 MHz, CDCl$_3$): δ 22.4 (CH$_3$), 26.3 (CH$_3$), 29.6 (CH$_3$), 31.0 (CH$_3$), 37.8 (quaternary C), 43.1 (quaternary C), 55.9 (CH$_2$), 58.7 (CHPh), 89.4 (C–O), 124.7 (=C-α), 127.4, 128.5 (2 C), 130.7 (2 C), 134.8 (aromatic carbons), 193.9 (=C-β), 208.8 (C=O). IR (10 % CCl$_4$): 3570 (OH), 1710 (C=O), 1637 cm^{-1} (C=C). UV [abs. ethanol (ε)]: 312 (66) nm.

Crystallography. (Correspondence concerning the X-ray analyses should be addresses to R.K.). Weissenberg photograps indicated triclinic symmetry for compound *3* and orthorhombic symmetry for *4*. Accurate lattice parameters for both compounds were obtained from least-squares refinement of 25 well-centered reflections using a Syntex $P2_1$ four-circle diffractometer.

Intensity data were collected on the same diffractometer in the interval $5°<2\theta<45°$ for *3* and $5°<2\theta<52°$ for *4*, using ω-scan technique and graphite-monochromatized MoKα-radiation. The intensity of the test reflections showed no systematic variation during the data collections. Of the measured reflections, 3214 having $F>4\sigma(F)$ and 1174 having $F>2\sigma(F)$, were considered as observed for *3* and *4*, respectively.

Crystal data for 3. C$_{18}$H$_{22}$O$_2$, FW=270.37, triclinic. Space group $P\bar{1}$ (No. 2), a=9.980(2), b=14.061(7), c=18.104(9) Å, α=100.19(4), β=101.06(3), γ=96.35(3)°, Z=6, V=2426 Å^3, D_{calc}=1.11 g cm^{-3}, λ=0.71069 Å.

Crystal data for 4. C$_{18}$H$_{22}$O$_2$, FW=270.37, orthorhombic, space group $P2_12_12_1$ (No. 19), a=7.888(6), b=9.145(5), c=22.161(15) Å, Z=4, V=1599 Å^3, D_{calc}=1.12 g cm^{-3}, λ=0.71069 Å.

Structure determination. The structures of *3* and *4* were solved by direct methods using the program MULTAN.[24] Initial E-maps revealed the positions of 59 non-hydrogen atoms of *3* and 14 non-hydrogen atoms of *4*, and the other non-hydrogen atoms were located from subsequent Fourier synthesis. After refinements of the positions of all non-hydrogen atoms the conventional R factors were 10.8 % for *3* and 12.3 % for *4*. For each molecule of *3* the hydrogen atoms bonded to O(2) were found from the Fourier map and the others were idealized at a distance of 1.0 Å from the bonded atoms. Because of the poor number of observed reflections the positional and thermal parameters (U=0.05 Å^2) for the hydrogen atoms of *3* were fixed in the final refinements. For compound *4* the hydrogen atoms were located in the Fourier map and the positional

parameters were refined in the final refinements, with fixed thermal parameters for H (U=0.05 Å^2).

The final R values were 8.1 % (R_w=7.7 %) for *3* and 8.4 % (R_w=7.7 %) for *4*. Unit weights and full-matrix least-squares technique were applied in the calculations using X-RAY SYSTEM programs.[25] Scattering factors for O and C were from Ref. 26 and those for H from Ref. 27. The final R values and the estimated standard deviations of bond parameters are relatively large, due at least partly to the poor number of statistically significant reflections.

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