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4-(1-HYDROPEROXY-1-METHYLETHYL)-1,3-CYCLOPENTADIENYL METHYL KETONE: ITS FORMATION FROM α-TERPINEOL AND BEHAVIOUR AS A DIMETHYLFULVENE EPOXIDE.[1†]

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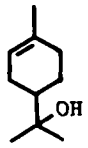
Ozonolysis of α-terpineol (1) then steam distillation in presence of acid gives the known 4-isopropylidenecyclopentenyl methyl ketone (4). This is oxidized in air to 4-(1-hydroperoxy-1-methylethyl)-1,3-cyclopentadienyl methyl ketone (10), a compound frequently reacting as if it were one of the elusive dimethylfulvene epoxides. It is converted by silica gel to two dimers (12, 13) of 2-acetyl-6,6-dimethylfulvene epoxide (19). Catalytic reduction of the dimers occurs mostly by *exo* addition of hydrogen to the conjugated double bond, and thermolysis of the dimers yields 4-acetyl-6,6-dimethylcyclohexa-2,4-dienone (20). With triphenylphosphine the hydroperoxide (10) yields two [6 + 4] dimers of 2-acetyl-6,6-dimethylfulvene (26). This is the first reported isolation of [6 + 4]dimers of a fulvene. The hydroperoxide (10) adds diazomethane to give an unstable pyrazoline (28); this pyrazoline loses nitrogen to yield a single isomer c. 5-acetyl-3',3'-dimethylbicyclo[3.1.0]hex-3-ene-2-spiro-2'-oxirane (29). Catalytic hydrogenation of the latter involves ring opening of the epoxide.

Introduction. Ozonolysis of α-terpineol (1)§ has been reported[2,3] to yield the cyclic hemiacetals (2), chromic oxidation of which gives the corresponding lactone (3, homoterpenyl methyl ketone, also obtained from α-terpineol by permanganate oxidation followed by chromic acid[4]). The first of these reports[2] was not followed by a full paper, and the second[3] quotes ^{1}H-NMR data for 2 and 3 which are at considerable variance with our figures (see experimental). The conversion of the hemiacetals to 4-isopropylidene-1-cyclopentenyl methyl ketone (4) by steam distillation with phosphoric acid was mentioned,[2] together with the catalytic reduction of 4. In this paper we describe fully the ozonolysis of α-terpineol, and the curious product from air oxidation of the ketone (4).



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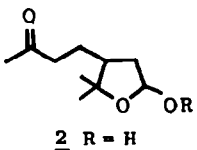

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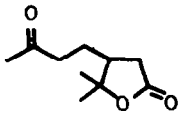
7 R = CH_3



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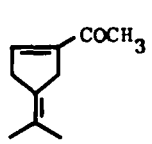

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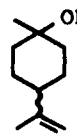

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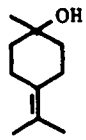

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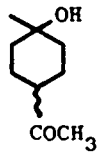

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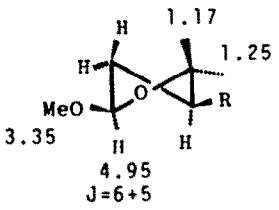
† This paper is dedicated to Professor Ralph Raphael on the occasion of his 65th birthday. It forms part of the subject of a lecture for which Professor Raphael suggested the title: "Monoterpenes are not Monotonous".

§ The chirality of the starting material is not considered in this paper.



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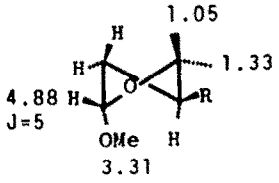

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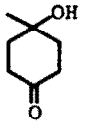

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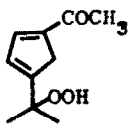

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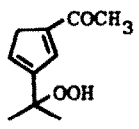

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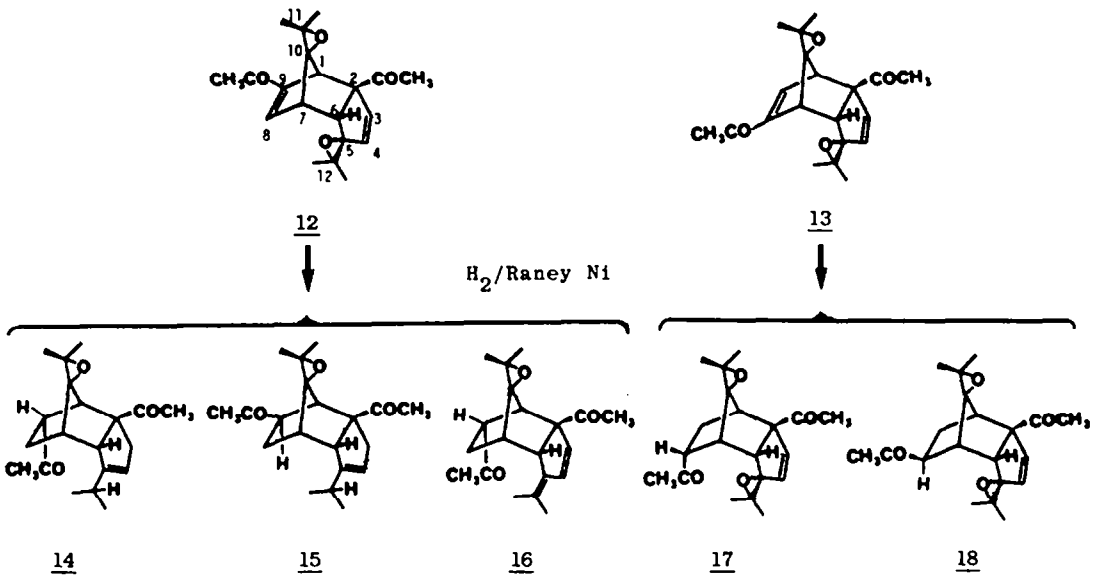
Ozonolysis of α-terpineol; formation of 4-(1-hydroperoxy-1-methylethyl)-1,3-cyclopentadienyl methyl ketone. Commercial terpineol, as used here, contains up to about 10% of the β-terpineols (5) and γ-terpineol (6). Ozonolysis of this material in methanol gave the cyclic acetals (7) as the main products, together with small amounts of the ketones (8, 9) from the β- and γ-terpineol impurities. The two isomers of 7 (*cis:trans* = 35:65) could not be separated under any conditions tried, except on capillary gas chromatography (GC). The ^{1}H-NMR spectral data shown on the formulae (7a, 7b) shows how the stereochemical attributions were made based on the coupling constants of the protons on the acetal carbon atoms. We also prepared the hemiacetals 2 [2] by ozonolysis of α-terpineol in caprylic acid,[5] and noted that the *cis:trans* ratio was the same as in 7.

The hemiacetals (2) are extensively decomposed on GC. Injection of a sample containing none of the lactone (3) (determined by ^{1}H-NMR spectrometry) results in a large number of peaks from lighter substances, while 66% of the product eluted is the lactone (3). Only about 10% of the hemiacetal (2) emerged unscathed.

Steam distillation of either the hemiacetals (2) or the acetals (7) in the presence of phosphoric acid[2] gave the crystalline isopropylidenecyclopentenyl methyl ketone (4, m.p. 47-48°*), once thought to occur in *Eucalyptus globulus*;[6] Wolinsky later showed this tree to contain the isopropenyl isomer.[7] On allowing the pale yellow crystals of the ketone (4) to stand in air, the colour darkened, and crystals of the hydroperoxide (10, m.p. 82-84°) were obtained after three days. The NMR and IR spectra of 10 clearly indicated an unsaturated ketone (ν_{max} 1645 cm^{-1}) and an AB vinyl proton system (7.29 and 6.51 ppm, J=2 Hz). The alternative formulation (11) we considered to be excluded by the fact that the signal at 7.29 ppm had only a further long-range coupling (J=1 Hz), whereas 11 should have a higher coupling between the methylene group and one vinyl proton than between the two vinyl protons. The peroxide index of 10 was about 72,000, and differential thermal calorimetry showed the substance to be unstable above about 40°, liberating 6.24×10^5 J/kg. The mass spectrum (MS) of 10 (apparently undecomposed after passage through the GC-MS system!) exhibited the fragment of highest molecular weight at *m/z* 160 ($M^+ - H_2O$), and a small fragment at *m/z* 146 ($M^+ - O_2$) was also visible.

Formation, structure, and decomposition of acetyldimethylfulvene epoxide dimers. Thin-layer chromatography (TLC) of the hydroperoxide (10) results in two spots, and chromatography of 10 on silica gel enabled the substances responsible for these spots to be isolated in crystalline form. (The action of potassium carbonate on 10 was shown by NMR spectra to produce the same mixture.) The less polar isomer had structure 12, and the more polar isomer structure 13; these structures were established by X-ray crystallography.[1,8] The ^{1}H-NMR spectra of 12 and 13 (see table 1) were readily interpreted. In particular, the coupling constants of the bridgehead protons (H-1 and H-7) show that in 12 there are no protons on the carbon atoms adjacent to C-1, and one proton on each of the carbon atoms adjacent to C-7, while in compound 15, there is a proton on one carbon atom adjacent to both C-1 and C-7.

*The m.p. given in our preliminary publication[1] is incorrect.



Scheme 1. ^{1}H-NMR spectral data for compounds 12 - 18 are given in Table 1, and ^{13}C-NMR data in table 2.

Table 1. ^{1}H-NMR data for compounds 12 - 18. Chemical shifts in ppm with respect to Me_4Si. Coupling constants are given in brackets (Hz). d means doublet. Figures between the lines for *exo* and *endo* values refer to cases where there is only a single proton at the position. Compounds marked † had their proton couplings verified by homonuclear shift-correlated two-dimensional NMR.[9]

	12†	13†	14†	15	16	17†	18†
CH_3	1.25, 1.27	1.27, 1.28	1.03[d], 1.13[d]	1.07[d], 1.14[d]	1.37, 1.42	1.32, 1.38	1.14, 1.34
	1.31, 1.42	1.30, 1.43	1.37, 1.46	1.19, 1.31	1.78, 1.86	1.40, 1.43	1.44, 1.47
$COCH_3$	2.24, 2.29	2.26, 2.28	2.12, 2.24	2.18, 2.19	2.10, 2.14	2.12, 2.23	2.16, 2.18
1-H	3.66 (1.5)	3.43 (3.5, 1.5)	3.10 (3.5)		3.07 (4)	2.64 (5)	2.59 (4.5)
3-H	5.91 (5.5)	5.78 (5.5)	2.12, 2.17		5.41 (5)	5.84 (5.5)	5.83 (5.5)
4-H	5.51 (5.5)	5.63 (5.5)	5.27	5.35	6.45 (5)	5.64 (5.5)	6.00 (5.5)
6-H	2.71 (4.5, 1.5)	3.02 (4, 1.5)	3.73 (3)	3.79	3.80 (3)	3.30 (4.5)	3.38 (4.5)
7-H	3.65 (4.5, 3)	3.48 (4)	2.08 (4, 3)			2.28 (4.5, 4)	2.00 (4.5)
8-H_{ex}	7.11 (3)		1.51 (13, 11, 4)			2.78 (11, 7, 4)	3.06 (10, 6)
8-H_{en}			2.02 (13, 8)				
9-H_{ex}		6.79 (3.5)	2.75 (11, 8, 3.5)	2.68 (4)	2.61 (11, 8, 3.5)	1.58 (13, 11, 5)	2.21 (14, 6)
9-H_{en}						2.32 (13, 7)	1.50 (14, 9)

Over Raney nickel, the dimer 12 was hydrogenated rapidly, the main product (14) had the conjugated double bond reduced simultaneously with the isopropylidenecyclopentene epoxide system, with complete removal of the epoxide oxygen atom. A small amount of a slightly less polar compound was also isolated from this reduction, and we assign the *exo*-acetyl structure (15) to this substance. The assignment is based on the MS, which showed 15 to be isomeric with 14 ($C_{20}H_{28}O_3$) and the ^{1}H-NMR spectrum (incomplete because of impurities), where the signal attributed to 9-H was characteristic

Table 2. ^{13}C-NMR spectra of tricyclo[5.2.1.$0^{2,6}$]decanes. Additional CH_3 signals in Experimental.

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C=O	C=O	C-11	C-12
12	48.1	87.1	136.4	135.1	75.6[1]	44.7	47.8	143.9	145.3	62.9[2]	194.3	204.9	63.2[2]	75.5
13	45.2	88.6	136.6	135.6	75.7[1]	45.0	49.8	146.8	139.7	64.0	193.8	205.6	62.1	75.1[1]
14	50.9	83.8	37.2	122.2	149.5	56.5	44.2	20.2	39.4	63.2	207.1	208.5	62.0	29.0
17	45.1	83.7	135.8	135.0	74.2	44.9	49.9	40.9	21.3	62.5	206.5	205.3	61.8	73.0

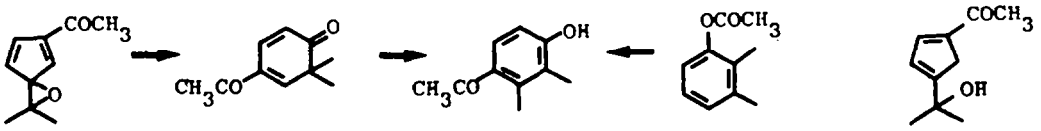
Subscripts refer to interchangeable attributions.

of an *endo* proton in a bicyclo[2.2.1]heptane adjacent to an *exo* carbonyl group.[10] In another hydrogenation, we stopped the reaction before it slowed down, and isolated a sample of 14 that was contaminated with ca. 15% of another compound which we believe to be the intermediate (16) between 12 and 14 because of the presence of additional signals to those of 14 in the ^{1}H-NMR spectrum. These signals corresponded to a diene, and there was also a signal of exactly the same fine structure as that of the proton on C-9 of compound 14, but shifted upfield to 2.61 ppm in the new compound. The GC-MS coupling showed in the GC trace the presence of a new peak of slightly longer retention time than 14 (on a SE 54 capillary column) which gave a fragment at *m/e* 316 ($C_{20}H_{26}O_3$).

Catalytic hydrogenation of the other dimer (13) was slower and only one equivalent of hydrogen was absorbed. The main product was the dihydro compound (17) together with a small amount of the 8-*exo*-acetyl isomer (18) with a slightly shorter retention time on TLC.

The ^{1}H-NMR spectra of the main products (14, 17) of the hydrogenation of the dimers (12, 13) present an unusual facet. That of 14 shows clearly that HC-1 is coupled with HC-9 (J=3.5 Hz) and that the latter is coupled to both protons at C-8. In bicyclo[2.2.1]heptanes coupling between two *exo* protons is greater than between two *endo* protons,[10] consequently the high coupling constant of HC-9 (11 Hz) shows the H_{exo} signal to be at 1.51 ppm, the lower coupling (8 Hz) leading to H_{endo} at C-8 at 2.02 ppm. This reasoning is supported by the coupling J_{8exo}-J_7 of 4 Hz (the *endo* proton at C-8 does not couple with the bridgehead HC-7) and we must conclude that H_{8exo}C-8 is at higher field than H_{8endo}C-8. Similar reasoning leads to the same conclusion for the protons on C-9 in 17. In both cases the anomalous behaviour is ascribed to restricted rotation of the acetyl group on C-9 (in 14) or C-8 (in 17) imposed by the proximity of the *endo* cyclopentene ring, and particularly by the *endo* epoxide group in 17. The deshielding cone of the acetyl carbonyl group is thus forced to adopt a position where it is directed towards the adjacent *endo* proton.

As compounds 12 and 13 are dimers of acetyldimethylfulvene epoxide (19), thermolysis should give dialkylcyclohexadienones,[11] a reaction used by Näf et al. in a synthesis of patchouli skeletons.[12] Indeed both dimers (12, 13) yield the same mixture on thermolysis at 270°, the major component of which was 4-acetyl-6,6-dimethylcyclohexa-2,4-dienone (20). The ^{1}H-NMR spectrum of the crude material showed signals corresponding to 4-hydroxy-2,3-dimethylacetophenone (21), confirmed by preparation of the latter by low temperature Fries rearrangement of 2,3-dimethylphenyl acetate (22).[13,14] Alder has described the high temperature rearrangement of 6,6-dimethylcyclohexa-2,4-dienone to 2,6-dimethylphenol;[11] in the present case migration of one of the *gem*-dimethyl groups takes place by a 1,2-shift.



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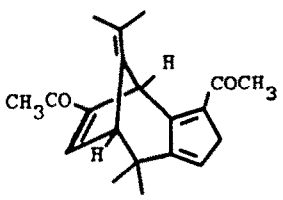

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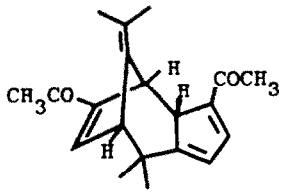

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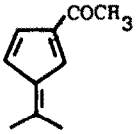

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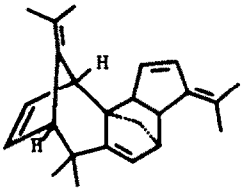

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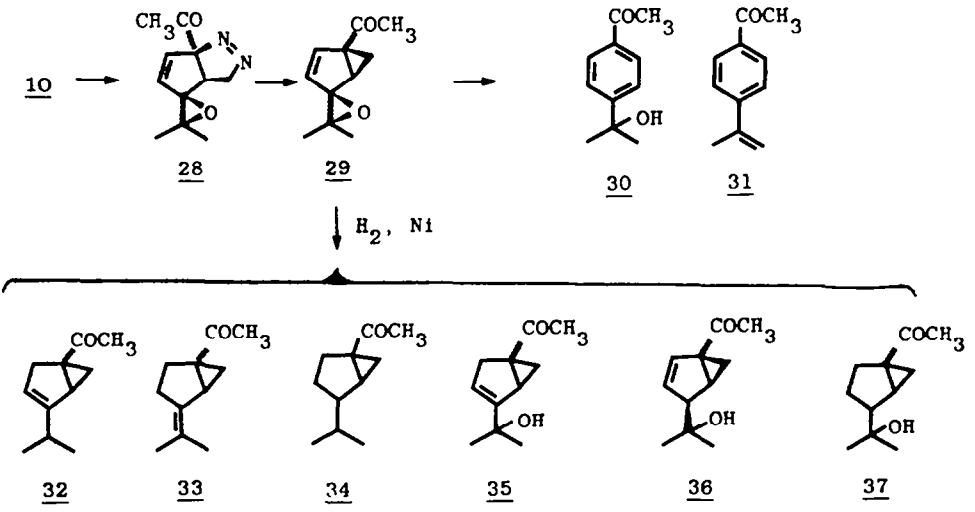
Reaction of the hydroperoxide (10) with triphenylphosphine. When the hydroperoxide (10) was mixed with triphenylphosphine in an NMR tube, the signals expected for the corresponding alcohol (23) appeared. These were close to, but not identical with those of the hydroperoxide. After attempting to purify the product from a larger scale reaction, we isolated by column chromatography two compounds to which we attribute structures 24 and 25. The former, slightly less polar, was obtained crystalline, but the latter was never obtained completely pure. Further chromatography on silica gel gave a less pure compound, and treatment of 25 with basic aluminium oxide in ether converted it practically quantitatively to 24. In both compounds, the presence of the group $CH_3COC{=}CH{-}CH$ was inferred by analogy with signals and couplings of the dimers 12 and 13. In 24 and 25 the other carbonyl group was also conjugated, but with a diene (by UV spectra, which are consistent with the predictions of the Woodward rules[15]). There are in each case two methyl groups on a double bond; the two remaining methyl groups are attached to a saturated carbon atom giving rise to the ^{13}C-NMR signal at 41.2 ppm (in 24) and 44.1 ppm (in 25). The mass spectrum of both isomers is identical, and corresponds to that of one molecule of 2-acetyl-6,6-dimethylfulvene (26, $C_{10}H_{12}O$). The simplest way of putting these facts together is by invoking a [6 + 4] dimerization of 26. A similar tricyclo[6.2.1.$0^{2,6}$]undecane structure was proposed by Neuenschwander et al.[16] as the first step in the trimerization of 6,6-dimethylfulvene to 27, and their NMR data for the *gem*-dimethyl group on the saturated carbon atom are close to ours. In our ^{13}C-NMR spectrum of 24, the only doublets are at 43.3 and 53.7 ppm. The ^{13}C-^{1}H-correlation spectrum[17] shows that these are associated with proton signals at, respectively, 5.16 and 3.20 ppm. We know that the latter is the saturated proton of the COC=CH-CH group (J 2.5 Hz), so the signal at 5.16 ppm must be attributed to a proton which is not only allylic to three double bonds, but also in the deshielding cone of two carbonyl groups! In the isomer 25, there are only two allylic double bonds to this proton, and the signal moves to 4.36 ppm, which may be compared to 3.61 ppm in 6,6-dimethylfulvene dimer[18] (two allylic bonds but no carbonyl group) and 3.66 ppm in the epoxide 12 (one allylic bond and at least one carbonyl group). It is also noteworthy that this proton is a sharp singlet in the case of 24, but is coupled (J 3.5 Hz) with the proton at 3.46 ppm in 25. (Further data for the support of these structures is in the experimental section.)

Reaction of the hydroperoxide (10) with diazomethane. Hydroperoxides generally react with diazomethane to give a methyl peroxide, although ether is a poor solvent for this reaction.[19] With our hydroperoxide (10), reaction with diazomethane is very rapid, and the initial product we characterized as the pyrazoline (28). This decomposed slowly on standing, and rapidly in boiling toluene[20] to give crystalline 5-acetyl-3',3'-dimethylbicyclo[3.1.0]hex-3-ene-2-spiro-2'-oxirane (29). The structure of the latter was established beyond doubt by NMR spectrometry (^{1}H and ^{13}C), and confirmed by two-dimensional (CCC2D) NMR spectroscopy[21] based on the INADEQUATE pulse sequence,[22] which confirmed the C-C connectivity. As expected, thermolysis of 29 gave mainly the acetophenone[23] (30), together with its dehydration product (31).[24] The stereochemistry of 29 could not be established with certainty, but we prefer an *endo* configuration for the epoxide ring (i.e. *trans* about the cyclopentene ring from the acetyl group) for the following reasons. This stereochemistry corresponds to addition of diazomethane from the less hindered side of 2-acetyl-6,6-dimethylfulvene epoxide (19) and the ^{13}C-NMR spectrum of the double bond and the epoxide carbon atoms is close to that of the dimers 12 and 13 which have similar stereochemistry. Hydrogenation of the oxirane (29)



over nickel, as in the case of the dimers (12, 13), does not result in reduction of the double bond as the first step. In one experiment, we isolated a small amount of material from which the epoxide oxygen atom had been eliminated (mostly 32, with 33 and 34). The main product from this experiment was the alcohol 35, formed by 1,4-addition of hydrogen to the vinyl epoxide system. In another experiment, we isolated the alcohol (35) as a mixture, only separable by capillary GC, with the isomeric alcohol (36). Although the latter was not obtained pure, its stereochemistry was quite clear from examination of the COSY ^{1}H-NMR-spectrum of the mixture with 35. The double bond of 36 is responsible for the AB part of an ABX system (5.58 and 6.24 ppm, J_{AB} 6 Hz, J_{AX}~1 Hz, J_{BX} 2.5 Hz). The X proton is at 3.21 ppm, and is further coupled with the proton at C-5 (at 2.16, $J_{4,5}$ 6 Hz) showing that these two protons are *cis*. The cyclopropane signals (AMX type) are at 1.21, 1.70, and 2.16 ppm, with J_{AM} 4 Hz, J_{AX} 5 Hz, and J_{MX} 8 Hz. The NMR spectra of 35 are in the experimental part. At first sight, the presence of this alcohol (36) seems to support the opposite stereochemistry for the initial epoxide (29), in that catalytic reduction over nickel is known to occur by hydrogenation from the epoxide side of the molecule.[25] The fact that the experiment was not reproducible, however, leads to some doubt as to the mechanism of formation of the alcohol (36). While a "roll-over" mechanism for catalytic reduction[26] seems excluded by the presence of substituents on the epoxide ring, conversion of the trisubstituted (35) to the disubstituted (36) double bond might occur on the catalyst. We therefore tried to convert 35 to 36 by stirring it with Raney nickel with insufficient hydrogen, but the only new compound we noted was the fully reduced alcohol (37). This evidence is inconclusive, although the considerable differences in the spectral data for the alcohol (36) from the epoxide (29) (especially the ^{13}C chemical shifts) do suggest that the two stereochemistries are different.

Conclusion. Formation of 4-isopropylidene-1-cyclopentenyl methyl ketone (4) from α-terpineol (1) by ozonolysis followed by acid-catalyzed ring closure has been confirmed. Oxidation of 4 by air occurs in the absence of light; this autoxidation gives the product one would expect with $^1O_2$ oxidation. The reaction is surprisingly clean, when one considers that polymerization occurs with air in the case of fulvene dimer.[27] The hydroperoxide (10) must have a relatively acidic proton on the ring, because very mild treatment causes it to behave as if it were a dimethylfulvene epoxide (19). Fulvene epoxides are known to dimerize, but the stereochemistry of the dimers has never been discussed. Since we obtain only one skeletal configuration of the rings (*syn* arrangement of the epoxides and an *endo* ring junction between the cyclopentene rings), we can safely assume that this is the same configuration that Alder obtained with 6,6-dimethylfulvene epoxide,[11] and by Näf et al. with a substituted fulvene epoxide.[12] The reduction of the hydroperoxide with triphenylphosphine leads to the so far unknown 2-acetyl-6,6-dimethylfulvene (26), which was isolated as two possible

dimers (24, 25). Although [6 + 4] cyclodimerization of fulvenes is theoretically possible,[28] it has only been observed as the presumed first step in the trimerization of 6,6-dimethylfulvene.[16] Otherwise, [6 + 4] cycloaddition occurs between fulvenes and electron-rich dienes.[29] The case we describe is the first example of a [6 + 4] dimerization of a fulvene where the dimers are isolated.

When we used diazomethane as a probe for proton reactivity, the hydroperoxide (10) again reacted exclusively and rapidly as if it were the acetylfulvene epoxide (19), thereby giving a novel access to the bicyclo[3.1.0]hexane system. It should be possible to extend these reactions to substituted derivatives of the cyclopentyl methyl ketone (4), and we therefore believe that a wide range of polycyclic systems has been made available by these results.

EXPERIMENTAL

Ozonolyses were carried out with either a Welsbach ozonizer giving ca. 4.42 g/m^3 O_3 with a current of air of 200 litres/h (for amounts of 10-20 g substrate), or a Brown-Boveri ozonizer yielding ca. 26.1 g/m^3 with an air throughput of 1000 litres/h. "Chromatography on silica gel" generally refers to medium pressure column chromatography using a Jobin-Yvon "Chromatospak" apparatus and Merck H (Type 60) silica gel. Unless otherwise stated, gas-liquid chromatography (GC) was done on a Carbowax column in a Carlo-Erba type 4200 chromatograph. IR spectra were measured in $CHCl_3$ on a Perkin-Elmer 125 spectrometer, and UV spectra in C_2H_5OH on a Kontron Uvikon-880 instrument. NMR spectra were measured in $CDCl_3$ on a Bruker WH-360 instrument (operating at 360 MHz for ^{1}H-NMR spectra and 22.63 MHz for ^{13}C-NMR spectra) using the Bruker Software Library DISN 85; chemical shifts are in ppm downfield from tetramethylsilane, and coupling constants (J) are in Hz. Mass spectra (MS) were obtained using a Finnegan 1020 quadrupole spectrometer coupled to a gas chromatograph containing a 30m glass capillary column packed with SE 54 stationary phase. Generally the most prominent values of *m/z* are quoted, with the relative abundance in brackets. Elemental analyses were carried out by Dr. H. Eder, Service de Microchimie, Institut de Chimie Pharmaceutique, University of Geneva.

4-(Tetrahydro-5-methoxy-2,2-dimethyl-3-furyl)-2-butanones (7). A solution of α-terpineol (154 g) in methanol (1500 ml) was ozonized at 0° until one equivalent of ozone was absorbed (ca. 3 h). To the resulting solution triphenylphosphine (262 g) was added in portions, keeping the temperature between -5° and +5°. The mixture was concentrated under partial vacuum (rotatory evaporator), and the residue used to prepare the isopropylidenecyclopentenyl methyl ketone (4). Of the crude residue, 30 g (corresponding to 14 g of α-terpineol) was chromatographed in hexane-ether (1:1) on silica gel. After the triphenylphosphine oxide, there was eluted first, a mixture of the title acetals followed by 11 g of a more polar fraction. The acetals decomposed on GC, but the proportion of isomers in the crude material was the same as after chromatography (from the integration of the methyl signals in the ^{1}H-NMR spectra - see theoretical part).

4-(Tetrahydro-5-hydroxy-2,2-dimethyl-3-furyl)-2-butanone (2). Ozone was passed through a mixture of α-terpineol (15 g), caprylic acid (13 g) and water (20 g) at 40°5 until ca. 4.7 g (1 equivalent) had been absorbed. After separation of the organic phase, the aqueous phase was extracted with ether, and the combined organic phases were washed with sodium bicarbonate solution. The caprylic acid was not completely removed, so the organic phase was stirred for 2 h with solid potassium carbonate, then filtered and concentrated to yield 11.7 g of material which was mostly 2 (two isomers by ^{1}H-NMR). Chromatography on silica gel in ether was accompanied by some loss and decomposition, but the following fractions were obtained. First, after a small amount of non-polar material, 4.1 g of the title products, identified by the ^{1}H-NMR spectrum (cf.[3]): *cis*-isomer: 1.19, 1.29, 2.15 (each s), 5.55 (dxd, J 4 and 7); *trans*-isomer: 1.09, 1.38, 2.15 (each s), 5.43 (d, J 4). GC of these isomers resulted in extensive decomposition; the major compound observed from the column was shown (by TLC and MS) to be the lactone (3) (see below), but a less important peak with a shorter retention time on the capillary SE 54 column was presumed to be the title product, with MS: 153 (M^+-H_2O-CH_3), 128 (8), 110 (27), 95 (50), 59 (38), 58 (45), 43 (100). The second product eluted from the silica gel column was 1.4 g of a mixture of the hydroxyketones (8, 9, identified by GC-MS coupling and comparison with authentic samples), and finally 2.5 g of the lactone (3), m.p. 59-60°; ^{1}H-NMR: 1.28, 1.47, 2.15 (each 3H, s); 1.54 (1H, mult) and 1.81 (1H, mult) ($COCH_2CH_2CH$); 2.19 (1H, mult, CH_2CHCH_2); 2.28 and 2.59 (each 1H, latter has J 7 and 16, $COCH_2CH$); 2.47 and 2.48 (each 1H, t, J 7; $COCH_2CH_2$). MS: 169 (M-CH_3^+, 3), 166 (18), 151 (10), 111 (23), 98 (28), 43 (100).

1-(4-Isopropylidene-1-cyclopent-1-enyl)-1-ethanone (4).[2] The crude material from the ozonolysis of α-terpineol (154 g) in methanol was mixed with aqueous phosphoric acid (10%, 200 ml) and distilled in steam. Extraction of the distillate with ether yielded after concentration 76 g (51%) of crystals m.p. 47-48° (pentane). λ_{max} 221 nm (ε 11570); ν_{max} 1660, 1625. ^{1}H-NMR: 1.64, 1.66, 2.33 (each 3H, s); 3.19, 3.24 (each 2h, broad s); 6.77 (5 lines, each ca. 2.5 Hz distant). MS 150 (M^+, 55), 135 (38), 107 (45), 91 (56), 43 (100).

[4-(1-Hydroperoxy-1-methylethyl)-1,3-cyclopentadien-1-yl]-1-ethanone (10). Crystals of the aforementioned compound (4) were left for 3 days in the dark in air. The crystals thus obtained were recrystallized in ether, m.p. 82-84°. λ_{max} 222 nm (ε 6830), 300 nm (ε 2120). ν_{max} 3525 (OH), 1690 (C=O). ^{1}H-NMR: 1.51 (6H, s), 2.37 (3H, s), 3.42 (2H, d, J 1.5 + long-range coupling), AB system at 6.51 and 7.29 (each 1H, J 2 + long-range coupling). ^{13}C-NMR: q at 25.2 (2), 26.0, t at 39.5, d at 128.0,

143.4; s at 81.4, 146.1, 161.7, 194.8. MS: 164 (M^+-H_2O, 7), 149 (100), 121 (40), 93 (32), 77 (27), 43 (30). Found: C, 66.2; H, 7.9. $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.7%.

Reaction of hydroperoxide (10) on silica gel. The crude hydroperoxide (10, 3 g) was chromatographed on silica gel (800 g) in ether-pentane (1:1). At first, 70 mg of 1-(4-isopropylidene-1-cyclopent-1-enyl)-1-ethanone (4) was eluted, then 150 mg of an intermediate fraction. This was followed by 0.4 g of crystals of the dimer 12*, m.p. 139° (from ether). λ_{max} 215 nm (ε 9430), 235 nm (shoulder, ε 7380); ν_{max} 1660, 1705 cm^{-1}. NMR spectra in theoretical part, and ^{13}C q at 21.0, 21.2, 21.5, 21.9, 25.0, 27.4. MS: 285 (M-43$^+$, 3), 271 (4), 227 (11), 185 (15), 164 (28), 149 (43), 148 (48), 133 (65), 121 (34), 43 (100). Found: C, 72.9; H, 7.5. $C_{20}H_{24}O_4$ requires C, 73.1; H, 7.4%.

Continuing elution of the silica gel column then yielded 0.23 g of a mixture, followed by 1.03 g of crystals of dimer 13*, m.p. 152° (from ether). λ_{max} 215 nm (ε 10110), 235 nm (shoulder, ε 6560); ν_{max} 1675, 1705 cm^{-1}. NMR spectra in theoretical part, and ^{13}C q at 20.9, 21.2, 21.5, 22.0, 26.3, 27.0. The only MS obtainable from GC-MS coupling was identical with that of the thermolysis product (20). Found: C, 73.3; H, 7.5. $C_{20}H_{24}O_4$ requires C, 73.1; H, 7.4%.

Hydrogenation of dimer 12. A. A solution of dimer 12 (0.15 g) in ethanol (50 ml) was shaken in hydrogen over Raney nickel. After 1h, ca. 27 ml of hydrogen had been absorbed (theory: 2.6 mol), and after filtering and concentrating, the residue exhibited two spots on TLC. Chromatography on silica gel in ether yielded two fractions: first, 7 mg of a mixture responsible for a yellow spot on TLC (revealed with anisaldehyde). This could not be purified completely, but the NMR data are consistent with structure 15 (see theoretical). MS: 316 (M^+, 4), 301 (5), 298 (4), 273 (4), 255 (3), 107 (18), 91 (22), 43 (100). Continuing elution of the column yielded 0.1 g of compound 14, m.p. 113-115° (from ether). NMR data in theoretical part and ^{13}C q at 14.2, 20.7, 21.3 (2), 23.9, 29.4. MS: 301 (M^+-CH_3, trace), 298 (2), 283 (2),273 (2), 255 (7), 107 (25), 91 (20), 43 (100).

B. The experiment was repeated, but now stopping the reaction after 2.1 mol of hydrogen had been absorbed. Purification of the products by chromatography on silica gel gave the same major compound (14), but this time it was contaminated by ca. 15% (by NMR) of an impurity characterized as 16 (^1H-NMR in theoretical part). GC-MS coupling showed a new peak with retention time slightly longer than 14; this peak had MS: 314 (M^+, 5), 271 (M-43$^+$, 23), 253 (3), 141 (16), 128 (16), 115 (18), 91 (13), 43 (100).

Hydrogenation of dimer 13. The dimer 13 (0.18 g) was hydrogenated in ethanol over Raney nickel at room temperature. After 12 h, 11 ml of hydrogen had been absorbed (theory for 1 mol, 12 ml). The suspension was filtered and concentrated, and the residue chromatographed on silica gel in ether. At first ca. 20 mg of a substance responsible for a single yellow spot on TLC (anisaldehyde) was eluted. This was identified as the *exo*-acetyl dihydro compound (18) by the ^1H-NMR spectrum (theoretical section) and the MS: 330 (M^+, trace), 315 (1), 255 (3), 213 (10), 157 (9), 149 (18), 115 (15), 107 (11), 43 (100). This was followed by 0.1 g of the *endo*-acetyl dihydro compound (17), with m.p. 159-160° (from ether). NMR spectra in theoretical part and ^{13}C q at 20.7, 20.9, 21.3, 22.3, 25.1, 30.0. MS: 330 (M^+, 3), 315 (5), 302 (2), 201 (10), 159 (12), 91 (13), 59 (28), 43 (100).

Thermolysis of dimers 12 and 13; 4-acetyl-6,6-dimethylcyclohexa-2,4-dienone (20). The dimer (0.2 g) was heated in toluene (15 ml) with a crystal of hydroquinone in a sealed tube for 1 h at 270°. The dark coloured product was filtered through silica gel, when it showed one major spot on TLC, this spot having a shorter retention time than the starting material. Both dimers (12, 13) had identical behaviour. The spot was isolated by preparative TLC, and after workup, the substance had ^1H-NMR: 1.32 (6H, s), 2.45 (3H, s), 6.16 (1H, d, J 10), 7.66 (1H, d, J 2), 7.66 (1H, dxd, J 10, 2). MS: 164 (M^+, 8), 149 (85), 121 (58), 93 (52), 77 (53), 43 (100). In the sample thus prepared, the following evidence supported the presence (ca. 15%) of 4-hydroxy-2,3-dimethylacetophenone (25), ^1H-NMR: 2.20, 2.44, 2.54 (all s), AB system at 6.69 and 7.44 (J 7). MS 164 (M^+, 35), 149 (100), 121 (37), 91 (22), 77 (22), 43 (20). These data were identical with those of an authentic sample of 4-hydroxy-2,3-dimethylacetophenone.[13, 14]

Reaction of hydroperoxide 10 with triphenylphosphine. A small amount of triphenylphosphine was added to the hydroperoxide (5 mg) in $CDCl_3$ in an NMR tube. The following ^1H-signals appeared immediately: 2.36 (s), 3.36 (s), 6.47 (broad), and the signal at 7.29 broadened. Consequently, triphenylphosphine (5.7 g) was added in portions to the hydroperoxide (4 g) in chloroform (20 ml), keeping the temperature <25°. After 1h, the solution was concentrated and the residue chromatographed on silica gel in ether-pentane (1:1). After elution of 6.4 g of triphenylphosphine oxide, 1.5 g of 3,10-diacetyl-11-isopropylidene-7,7-dimethyltricyclo[6.2.1.$0^{2,6}$]undeca-2,5,9-triene (24) was eluted, m.p. 138-139° (from ether). λ_{max} 238 nm (ε 10500) 305 nm (ε 6700); ν_{max} 1632, 1663 cm^{-1}. ^1H-NMR: 1.24, 1.25, 1.70, 1.75, 2.27, 2.69 (each 3H, s), ABX system with A 3.12, B 3.20, X 6.29 (J_{AB} 22, J_{AX} & J_{BX} 2.5), 3.21 (1H, d, J 3), 5.16 (1H, s), 7.08 (1H, d, J 3). ^{13}C: q at 20.1, 20.3, 26.3, 27.6, 29.5, 32.2; t at 40.4; d at 43.3, 53.7, 132.7, 147.7; s at 41.2, 121.9, 135.3, 137.3, 149.4, 152.5, 153.7, 194.6, 194.7. ^1H-^{13}C-correlation[16] showed that the d at 43.3 was due to the C(H) with its proton at 5.16 ppm, that the CH_3 groups on the double bond were at 20.1 and 20.3, and that the two other CH_3 groups were at 27.6 and 32.2, attached to the C atom having a s at 41.2 ppm. For the ^{13}C-^{13}C INADEQUATE spectrum[22] see fig. 1.

Continuing elution of the silica gel column yielded 1.5 g of 3,10-diacetyl-11-isopropylidene-7,7-dimethyltricyclo[6.2.1.$0^{2,6}$]undeca-3,5,9-triene (25), with the following spectra:

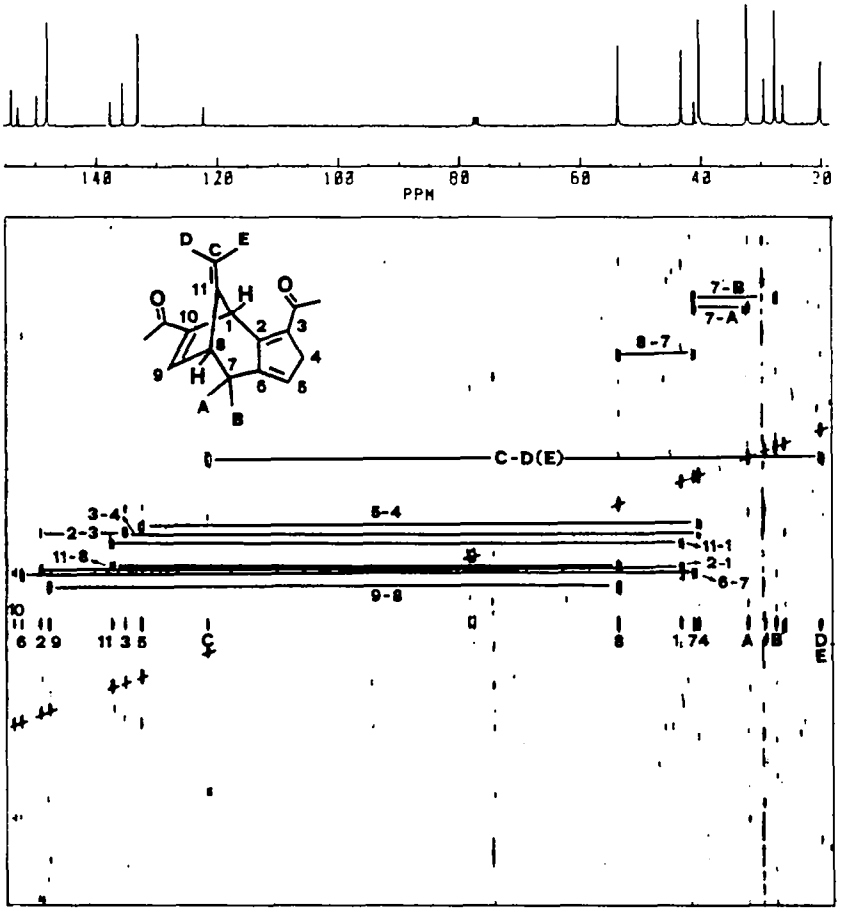
*IUPAC names, 12: 3a',5'-diacetyl-3a',4',7',7a'-tetrahydro-3,3,3",3"-tetramethyldispiro[oxirane-2,1'-[4,7]-methano-[1H]-indene-8',2"]oxirane; 13: 3a',6'diacetyl-3a',4',7',7a'-tetrahydro-3,3,3",3"-tetramethyldispiro[oxirane-2,1'-[4,7]-methano-[1H]-indene-8',2"]oxirane.

λ_{max} 240 nm (ε 8150), 307 nm (ε 5600); ν_{max} 1645, 1660 cm^{-1}. ^{1}H-NMR: 1.26, 1.28, 1.71, 1.87, 2.07, 2.34 (each 3H, s), AB with A at 3.24, B at 6.75, J_{AB} 3, another AB at 3.46 and 4.35 (J_{AB} 3.5), the A proton also coupled (<1 Hz) with both protons of a third AB system having A at 6.1, B at 6.98 (J_{AB} 2). ^{13}C-NMR: q at 19.7, 20.0, 25.6, 26.0, 26.2, 29.0; d at 45.2, 53.4, 56.4. 126.0, 141.0, 146.4; s at 44.2, 119.8, 139.6, 146.8, 148.0, 165.2, 193.9, 194.8.

The MS of both isomers (24, 25) was: 148 (57), 133 (100), 105 (50), 103 (20), 79 (28), 77 (30), 63 (12), 51 (14), 43 (13), 39 (10).

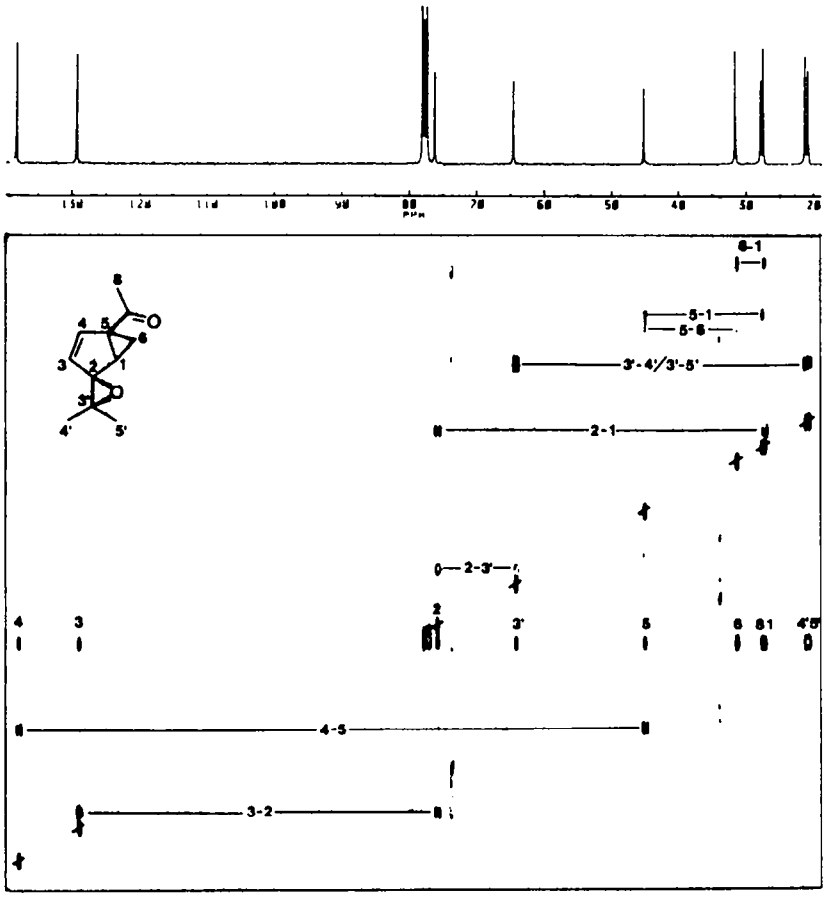
A solution of 25 (0.5 g) in 10 ml ether was stirred overnight with aluminium oxide (Fluka, basic, activity 1, 0.5 g). Filtration and concentration gave a residue with identical ^{1}H-NMR spectrum as described for 24.

Fig. 1. ^{13}C-^{13}C INADEQUATE spectrum[22] of compound 24. The signals of the C=O carbon atoms are not shown because no connectivities were discernable from them. Atoms extraneous to the tricyclo[6.2.1.$0^{2,6}$]undecatriene skeleton are lettered A-E.



5-Acetyl-3',3'-dimethylbicyclo[3.1.0]hex-3-ene-2-spiro-2'-oxirane (29). A solution of the hydroperoxide (10, 18 g) in ether (600 ml) at 0° was treated with diazomethane in ether (1%, 415 ml) by adding small amounts at a time with swirling. After 30 min. at 0°, the solvent was concentrated at reduced pressure at <35°. TLC showed one main spot, and after purification of a small amount by chromatography on silica gel, this was identified as 6a-acetyl-3,3a,4,6a-tetrahydro-2',2'-dimethylspiro[cyclopentapyrazol-4,2'-oxirane] (28) by the following spectra: ^{1}H-NMR: 1.36, 1.38, 2.58 (each 3H, s), ABX system with A 4.64, B 4.76, X 2.94 (J_{AB} 19, J_{AX} 10, J_{BX} 4.5, O-C*H*H_2-N=); AB at 5.62 and 4.76 (J 5.5). ^{13}C-NMR: q difficult to identify because of impurities; t at 80.4; d at 34.6, 133.2, 133.7; s at 64.0, 74.0, 76.6, 200.9. Elemental analysis was not possible because the sample lost weight on the balance. Heating this material in toluene for 1 h in toluene at 100° yielded a product which after purification by chromatography on silica gel gave 9 g of crystals, m.p. 46° (from pentane), identified as 29 by the following spectra. λ_{max} 260 nm (ε 2900); ν_{max} 1685 cm^{-1}. ^{1}H-NMR: 1.37, 1.44, 2.21 (each 3H, s); AMX system with A 1.36, M 1.90, X 2.21 (J_{AM} 4, J_{AX} 5, J_{MX} 9, protons on cyclopropane, respectively *endo* and *exo* of CH_2 and bridgehead proton); 5.30 and 6.57 (each 1H, d, J 5). ^{13}C-NMR: q at 21.0, 21.3, 27.8; t at 31.7; d at 27.6, 129.5, 138.2; s at 45.4, 64.7, 76.3, 205.1. For the ^{13}C-^{13}C INADEQUATE spectrum containing all C-C connectivities, see fig. 2. MS: 177 (M^+-H, 6), 163 (11), 135 (40), 120 (48), 105 (63), 77 (45), 43 (100). Found: C, 73.9; H, 8.2. $C_{11}H_{14}O_2$ requires C, 74.2; H, 7.9%.

Fig. 2. ^{13}C-^{13}C INADEQUATE spectrum[22] of compound 29. All connectivities are visible except 5-7-8.



Thermolysis of 29. A solution of the epoxide (29, 0.1 g) in cyclohexane (2 ml) was heated in a sealed tube at 250° for 1 h. After concentration, two spots were visible on TLC, and were separated by preparative TLC. The major substance was the more polar, 4'-(1-hydroxy-1-methylethyl)-acetophenone (30).[23] Only the ^{13}C-NMR spectrum is quoted in ref. [23], so we give: ^1H-NMR: 1.60 (6H, s), 2.60 (3H, s), 7.59 and 7.94 (each 1H, d, J 7). MS: 178 (M^+, 3), 163 (63), 121 (18), 77 (10), 43 (100). The other spot gave a very small amount of substance whose MS was as expected for 4-isopropenyl-acetophenone (31)[24]: 160 (M^+, 28), 145 (100), 115 (48), 91 (23), 43 (13).

Hydrogenation of 29. A solution of the epoxide (29, 0.3 g) in ethanol (20 ml) was shaken in hydrogen over Raney nickel. After 6 h, 39 ml of hydrogen had been absorbed (calc. for 1 mol, 40 ml), and the product was purified by preparative TLC (ether-pentane 2:1). The major spot (more polar) consisted of 150 mg of a mixture of 1-acetyl-4-(1-hydroxy-1-methylethyl)-bicyclo[3.1.0]hex-2-ene (36) and 1-acetyl-4-(1-hydroxy-1-methylethyl)-bicyclo[3.1.0]-hex-3-ene (35). These were only separable by capillary GC (Chrompak, silicone 8 CB). The ^1H-NMR spectrum of 36 is discussed in the theoretical part except for the CH_3 signals at 1.30, 1.41 and 2.06 ppm. ^{13}C-NMR of 36: q at 28.6, 30.1 (2); t at 24.8; d at 30.3, 57.6, 130.5, 133.1; s at 46.0, 72.3, 207.1. MS: 147 (M^+-CH_3-H_2O, 2), 137 (5), 122 (15), 121 (12), 107 (18), 79 (17), 59 (100), 43 (70). Spectra of 35: ^1H-NMR: 1.33, 1.41, 2.16 (each s); cyclopropane AMX system with A 0.68, M 1.88, X 2.55 (J_{AM} 4, J_{AX} 5, J_{MX} 8); AB system at 2.44 and 3.16 (J 18), the latter coupled (J 2) with a proton at 5.28 (narrow d). ^{13}C-NMR: q at 25.8, 28.9 (2); t at 27.1, 34.8; d at 39.6, 119.7; s at 39.4, 70.1, 153.7, 207.3. MS: 165 (M^+-CH_3, 2), 162 (2), 147 (4), 122 (22), 121 (18), 119 (23), 105 (30), 91 (18), 79 (13), 59 (50), 43 (100). Repetition of this experiment using the identical starting material (1.24 g in 100 ml ethanol) and Raney nickel resulted in much more rapid hydrogenation; one mol was absorbed in 20 min., at which point the reaction was interrupted. After filtration and concentration, the residue was purified by chromatography in ether on silica gel. At first 100 mg of a mixture of compounds not containing a hydroxyl group was eluted. These were purified by GC on Carbowax. The first (major) compound eluted was 32, with ^1H-NMR: 1.07 (6H, d, J 7), 2.07 (3H, s); cyclopropane AMX system with A 0.62, M 1.83, X ca. 2.4 (superimposed on two other protons) (J_{AM} 4, J_{AX} 5, J_{MX} 7); AB system at ca. 2.39 and 3.11 (J 17); the q of the isopropyl group is hidden under the signals around 2.4; 5.04 (1H, broad s). MS: 149 (M^+-CH_3, 2), 121 (88), 105 (17), 93 (21), 91 (23), 79 (40), 77 (22), 43 (100). The second compound eluted from Carbowax was a trace of the saturated ketone (34) described below, and the third was the ketone 33, with ^1H-NMR: 1.62, 1.77, 2.10 (each s); cyclopropane AMX system with A 1.03, M 1.66, X 2.50 (J_{AM} 4, J_{AX} 5, J_{MX} 8), CH_2CH_2 signals centred on 1.89, 1.95, 2.32 and ca. 2.5

ppm. MS: 164 (M^+, 30), 149 (5), 121 (100), 105 (17), 93 (40), 91 (25), 79 (33), 77 (30), 43 (53). The saturated ketone (34) was recognized as an impurity in the ^{1}H-NMR spectrum of crude 32 by the presence of signals for the $(CH_3)_2CH$ group at 0.88 and 1.00 (d, J 7), the *syn* proton of the cyclopropane methylene group at 0.98 (t), and by its elution from the capillary SE-54 column immediately after 32, when it gave the following MS: 166 (M^+, 6), 151 (5), 138 (4), 123 (48), 109 (15), 95 (16), 81 (20), 79 (21), 67 (20), 43 (100).

A sample of practically pure 1-acetyl-4-(1-hydroxy-1-methylethyl)-bicyclo[3.1.0]hex-3-ene (35 0.1 g) was shaken for 12 h in ethanol (20 ml) over Raney nickel with ca. 5 ml hydrogen. Filtration and concentration yielded a mixture in which the major compound was 1-acetyl-4-(1-hydroxy-1-methylethylbycyclo[3.1.0]hexane (37) recognizable by ^{1}H-NMR: 1.22, 1.29, 2.08 (each 3H, s), multiplets centred on 1.2 (1H), 1.25 (1H), 1.3 (1H), 1.93 (2H), and 2.2 (2H) with more clearly defined signals at 1.38 (1H, dxd, J 9, 5), 1.65 (1H, txd, J 13, 7.5); and by the MS: 182 (M^+, 1), 164 (4), 149 (3), 124 (12), 121 (18), 113 (25), 109 (17), 81 (34), 59 (100), 43 (75). The remainder was mostly 35, but no 36 was detected.

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