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231. An Anomalous Oxidation of β-Pinene

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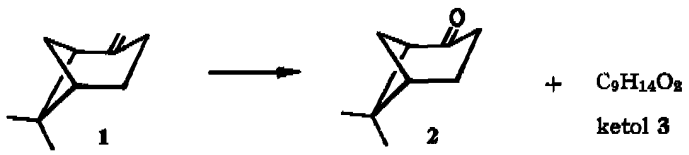
(9. VII. 75)

Summary. The oxidation of β-pinene with aqueous alkaline potassium periodate and catalytic amounts of potassium permanganate gave, in addition to the expected oxidation product nopinone, a β-ketol. The structure of the latter was shown to be 1-(2-hydroxyisopropyl)bicyclo[3.1.0]hexan-2-one. The formation of this anomalous side-product represents a new type of rearrangement of the pinane skeleton.

In connection with a programme of research where sizeable quantities of nopinone were needed, it was decided to oxidatively cleave the double bond of β-pinene with an aqueous solution of sodium periodate in the presence of potassium permanganate as catalyst. This method was originally exploited for the semiquantitative analysis of terminal methylidene and isopropylidene groups [1]. The gross mechanistic features of the oxidation are that permanganate anion converts the double bond to the vicinal diol which is subsequently cleaved by the more powerful oxidant periodate to two carbonyl fragments. As the permanganate is only present in catalytic amounts it is constantly regenerated from the spent manganate ion by excess periodate. As side reactions are claimed to be unimportant this analytical procedure has been adapted to the oxidation on a preparative scale of many cyclic olefins, in particular bicyclic monoterpenes. Both α- and β-pinene and sabinene have been reported to undergo straightforward oxidative cleavage in high yield to the corresponding ketone products. However, camphene, in addition to the expected camphenilone produced in 50% yield, gave numerous acidic by-products [2].

In this paper we report our findings concerning a sideproduct obtained from β-pinene (**1**). We find that the oxidation is extremely sensitive to the precise choice of conditions employed. A typical procedure for *von Rudloff* oxidation of β-pinene is to take 0.25 mol of substrate, 1 mol of sodium periodate, 0.05 mol of potassium permanganate in 5 l of water. It appears to be essential that the pH be maintained between 7 and 10 and to ensure this 0.75 mol of potassium carbonate is added to the mixture. High speed stirring is necessary and for difficultly soluble substrates, small amounts of *t*-butyl alcohol need to be added to the mixture to ensure homogeneity. We confirm that these conditions do in fact give a 95% yield of nopinone, but when *t*-butyl alcohol is omitted, then the oxidation mixture deposits manganese dioxide with the passage of time and only affords a yield of some 20 to 25% of nopinone (**2**) accompanied by 11 to 16% of a ketol of molecular formula $C_9H_{14}O_2$ (**3**) (*Scheme 1*). In this paper we describe the elucidation of the structure of this ketol and in so doing uncover an unprecedented rearrangement of the pinane skeleton.

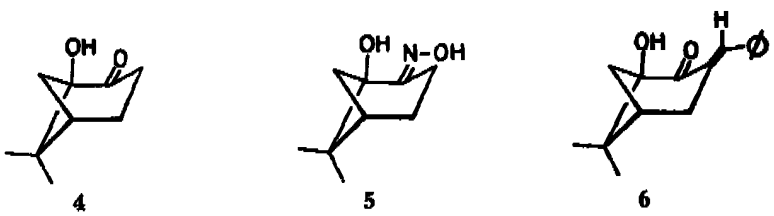
Scheme 1



Discussion. – The first structure put forward for the unknown ketol was the bridgehead hydroxynopinone (**4**). Reaction with hydroxylamine afforded a crystalline oxime (**5**) and equilibration with sodium deuteroxide in deuteriomethanol resulted in the easy replacement of just three hydrogen atoms by deuterium thereby indicating a single methylene group adjacent to carbonyl. Further confirmation of this structural feature was provided by the formation of only a single monobenzylidene derivative on treatment with benzaldehyde (*Scheme 2*). A spectral analysis of this derivative was in reasonable accord with the proposed structure (**5**), however there were disturbing inconsistencies (*v. infra*). Nevertheless, the infrared stretching frequency of 1710 cm^{-1} found for **3** was consistent with a six-membered ring and was similar to that observed for nopinone itself. The hydroxy group was seen to be tertiary from the NMR. spectrum of **3** in dimethyl sulfoxide. The hydroxyl proton showed as a sharp singlet, thereby demonstrating the absence of an H–C(α) [3]. Contiguity of the hydroxyl to the carbonyl group was evidenced by intramolecular hydrogen bonding revealed by the IR. spectra determined at various dilutions.

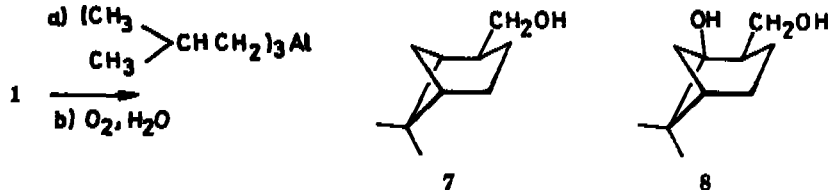
Moreover, it should be observed at this juncture that the hydroxynopinone formula appeared to be a reasonable proposal, especially so in view of the reported aerial

Scheme 2



oxidation of β-pinene in the presence of tris(iso-butyl)aluminium to *trans*-myrtanol (**7**) together with a small percentage of the bridgehead hydroxy derivative (**8**) (*Scheme 3*) [4]. It also seemed reasonable that in alkaline conditions the pinane skeleton, in contrast to its behaviour under acid conditions, would remain unchanged. Therefore it was thought that the normal oxidation product, nopinone, was undergoing further oxidation at the bridgehead by alkaline permanganate or periodate. Good precedent exists for the oxidation of tertiary hydrogen atom to hydroxyl by permanganate in aqueous base [5–7]. However, in a separate experiment it was shown that nopinone after vigorous stirring for a week under the *Lemieux-von Rudloff* conditions was recovered unchanged. Similarly, the 1,2-diol obtained from β-pinene simply underwent oxidation to nopinone.

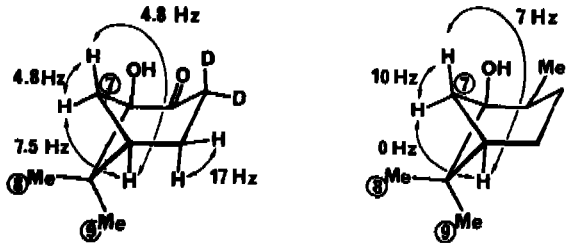
Scheme 3



7 **8**

Although the NMR. data were consistent with hydroxynopinone (**4**) the values of the coupling constants and the chemical shifts of the *gem*-dimethyl grouping were not quite right. The lack of agreement with structure **4** is immediately seen when the data of the corresponding α,α-deuterio-ketol **9** are compared with those of hydroxypinane **10** (*Scheme 4*). The values of the vicinal coupling constants between the bridgehead proton and the methylene bridge protons are at variance with those exhibited for authentic hydroxypinane (**10**). The same is true for the geminal coupling constants; the values of 4.75 and 17 Hz in **9** are too small and too big respectively for a cyclohexane-type ring. Furthermore, the disparity in chemical shifts for the *gem*-dimethyl grouping and the bridge methylene protons is too great to be ascribeable to

Scheme 4. *Comparison of some coupling constants and chemical shifts of the postulated structure* **9** (dideuterio **4**) *with authentic hydroxypinane* **10** (see [4])

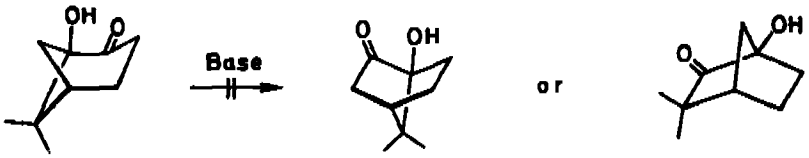


δ Me, 9 Me	= 1.29, 1.39	0.9, 1.35 ppm
C_7H_2	= 0.90, 1.50	1.40, 2.60 ppm

the presence of the ketone function. In fact, the upfield position of the methylene protons suggests the presence of a cyclopropane ring.

The lack of agreement between the data for the proposed ketol structure **4** and the authentic pinane skeleton was confirmed by further chemical testing. Treatment of the ketol with strong base did not result in the expected rearrangement of the pinane to the bornane or fenchane skeleton (**11** or **12**) (*Scheme 5*). This rearrangement

Scheme 5

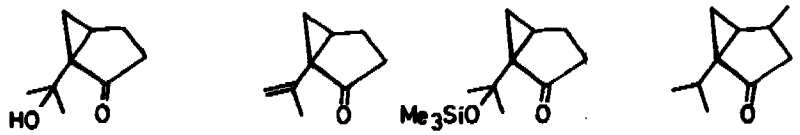


4 **11** **12**

would be expected by analogy with the base-catalyzed isomerization of hydroxynorcamphor to hydroxyfenchone [8]. In the present case the strained pinane skeleton ought to isomerize readily to its bornylic derivative. However, no rearrangement occured in this sense. The cationic counterpart of this reaction, namely the treatment of the ketol oxime (**5**) with acid, in the expectation of bringing about an abnormal *Beckmann* reaction, also failed. Either the α-ketol grouping is absent or if present, the attached skeleton is not permitting rearrangement or cleavage. Conclusive evidence against the α-ketol was provided by reduction to the diol which was subsequently found to be inert to periodic acid. Accordingly, the hydroxynopinone formulation (**4**) can be discarded, which leaves only one alternative, the isomeric hydroxysabinone (**13**). The correctness of the isopropyl alcohol grouping was confirmed by its ready dehydration with thionyl chloride and pyridine to give 1-isopropenyl-bicyclo[3.1.0]-hexan-2-one (**14**). Suppression of the hydroxy group, either by elimination or by silylation (**13** → **15**) produces a dramatic change in the carbonyl stretching frequency, which increases from 1710 to 1725 cm^{-1}. This latter value is entirely compatible with the five-membered ring and is confirmed by that exhibited for dihydro-umbellulone (**16**) [9] [10] (*Scheme 6*). Further comparison of the NMR. data of the ketol was that found for thujanol (**17**) reveals that the vicinal coupling constants are very nearly the same (*Scheme 7*).

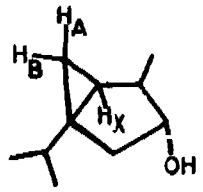
Final proof for the β-ketol (**13**) was obtained from hydrogenation experiments. Hydrogenation of the isopropenyl derivative (**14**) over palladium-on-charcoal gave only *trans*-2-isopropyl-3-methylcyclopentanone (**18**). Here it is seen that the weakest cyclopropane bond, that which has the best σ–π overlap with the carbonyl group, is

Scheme 6. *IR. stretching frequencies of the carbonyl group of some bicyclo[3.1.0]hexan-2-ones*



13	**14**	**15**	**16**
IR. ν_{CO} 1710	1725	1725	1726 cm^{-1}

Scheme 7. *Proton coupling constants belonging to the cyclopropane part of thujanol* **17** (see [11] [12])

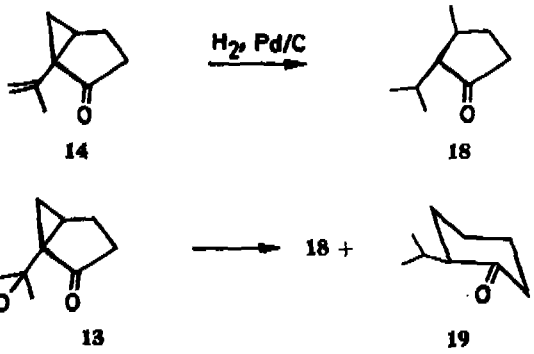


J_{AB} = 4.5 Hz
J_{AX} = 4.5
J_{BX} = 7.0

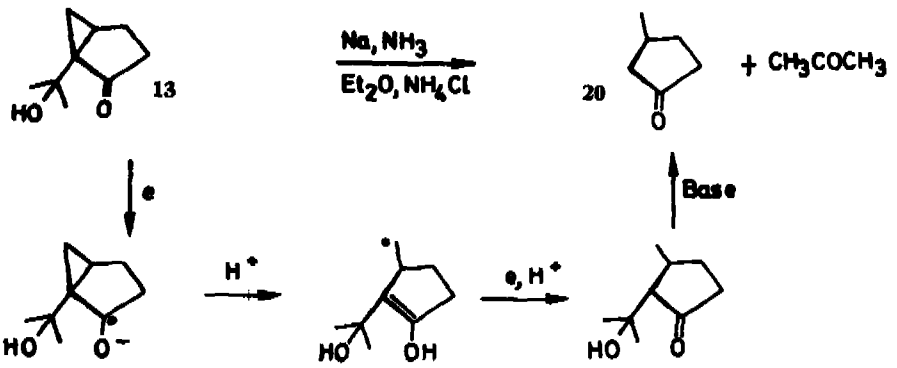
17

cleaved [13] [14]. When the same reduction is carried out in acetic acid at 90°, but on the ketol itself (**13**), 2-isopropylcyclohexane (**19**) is obtained together with **18** in a ratio of 1:2.5 (*Scheme 8*). These experiments provide a complete confirmation of structure, however a nice variant, relative to the β-ketol grouping, is provided by *Birch* reduction of **13**. Under these conditions, only 3-methylcyclopentanone (**20**) is obtained. Here, the consecutive addition of an electron and a proton twice over is responsible for the reductive rupture of the homo-conjugated cyclopropane sigma bond. Once the quaternary bridgehead is demolished, the base present permits the operation of the retro-aldol reaction. Acetone is lost to give **20** (*Scheme 9*).

Scheme 8



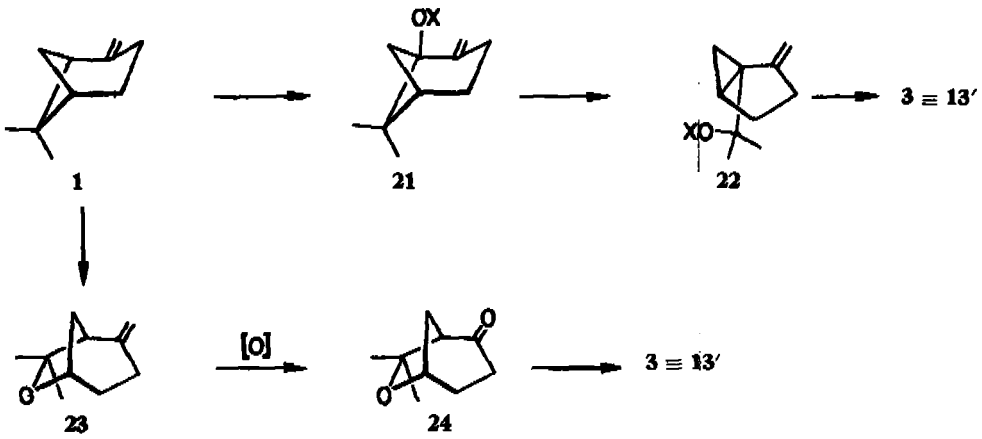
Scheme 9



Epilogue. – The rearrangements and eliminations which pinene and its derivatives can undergo in acid or under solvolytic conditions are legion [15]. However, in every case eliminations lead to derivatives of cyclohexene. On the other hand, skeletal rearrangements give derivatives of bicyclo[2.2.1]heptane. The present findings unambiguously confirm that oxidation under alkaline conditions generates the bicyclo[3.1.0]hexane skeleton. Mechanistically this rearrangement is neither expected nor plausible. Nevertheless, the combined weight of the chemical and spectral evidence confirms the sabinane or thujane β-ketol structure[1]).

How does the ketol **13** arise? Although a precise answer is difficult to give, a general mechanistic pathway can be outlined. The inertness of nopinone and the usual cleavage of the 1,2-diol derived from β-pinene indicate that the presence of the exocyclic methylidene grouping is a mechanistically important feature. Consequently it is suggested that β-pinene undergoes formal electrophilic substitution by an oxygen substituent (OX) at the allylic bridgehead position. Next, diplotropic rearrangement converts the resulting cyclobutyl derivative (**21**) into its cyclopropylmethyl isomer (**22**) [20]. Oxidative cleavage of the double bond in **22** proceeds normally to yield the β-ketol **3** (≡ **13**) or rather its enantiomer **13'**. Alternatively, **1** is oxidized to the β-pinol structure **23**, which subsequently undergoes oxidative cleavage of the double bond to the ether-ketone **24**. Base then brings about rearrangement of **24** to the ketol **13'**, in a *Favorskii* type reaction[2]) (*Scheme 10*).

Scheme 10



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Experimental Part

IR. spectra were recorded, as films on NaCl plates (unless otherwise stated) on a *Perkin-Elmer* model 257 spectrometer. Gas liquid chromatography (GLC.) was carried out on model F 11 (analytical) and 990 (semipreparative) *Perkin-Elmer* instruments, using Apiezon L, Carbowax and FFAP columns. Microanalyses were performed by Dr. *K. Eder*, Ecole de Chimie, Genève. A *Perkin-*

[1]) 7-Hydroxysabina ketone, an isomer of **13**, has been recently synthesized [16]. Several syntheses of sabina ketone itself, have also been reported [17–19].

[2]) Pinol has been found as a product in the oxidation of α-pinene with chromyl chloride [21].

Elmer 141 polarimeter was used for the measurement of optical rotations using $CHCl_3$ as the solvent. Mass spectra were taken with an *Atlas* model CH-4 operating at 12 eV. NMR. were determined on model XL-100 *Varian* (at 100 MHz) and R-12 *Perkin-Elmer* (at 60 MHz) spectrometers, using deuteriochloroform and carbon tetrachloride, respectively as solvents; chemical shifts are expressed in ppm and measured downfield from tetramethylsilane (TMS) as internal standard (0.0 ppm). Signal intensities are reported in proton units (1 H, 2 H, etc.); multiplicities are expressed as singlet (*s*), doublet (*d*), triplet (*t*) and multiplet (*m*), and coupling constants in Hz.

β-Pinene was obtained from *Aldrich* and *Fluka* and was distilled before use.

Abnormal oxidation of (−)-β-pinene (**1**). To a suspension of 7.5 g (0.048 M) of potassium permanganate, 210 g (0.98 M) of sodium periodate and 75 g (0.76 M) of potassium carbonate in 4.5 l of water was added 36.7 g (0.37 M) of (−)-*β*-pinene ($[\alpha]_D^{25} = -18.2°$ ($c = 7.6$)). The mixture was stirred vigorously for 26 h. Manganese dioxide was removed by filtration and the filtrate extracted twice with large volumes of ether. The combined ethereal layers were washed with sodium chloride solution, water, and dried over anhydrous sodium sulfate. Removal of solvent gave 21.6 g of yellow liquid. Distillation gave 7.8 g nopinone (**2**), b.p. 45°/0.2 Torr (21% yield) and 4.7 g of the ketol **3**, b.p. 76°/0.2 Torr (11% yield). Yields up to 16% for **3** have been obtained, on prolonging reaction time (3 days).

1-[2-Hydroxyisopropyl]-bicyclo[3.1.0]hexan-2-one (**3** ≡ **13'**).

It was a viscous liquid, $[\alpha]_D^{25} = +18.5°$ ($c = 2.0$) with the following spectral characteristics: IR. spectrum: max. at 3430 *s* (OH), 3077 *w* (C—H of cyclopropane), 3040 *w* (C—H of cyclopropane), 2930 *s*, 1710 *s* (C=O), 1458 *w*, 1412 *w*, 1368 *m*, 1300 *m*, 1260 *w*, 1205 *w*, 1178 *m*, 1150 *w*, 1088 *w*, 1061 *m*, 1035 *w*, 1015 *m*, 1000 *m*, 975 *w*, 950 *w*, 880 *m*, 865 *m*, 840 *w*, 798 *m*, and 769 cm^{-1}.

IR. spectra in carbon tetrachloride at different concentrations reveals two important changes: (i) increasing dilution results in the shift of the $\nu(CO) = 1710\ cm^{-1}$ to bigger values by diminishing intermolecular hydrogen bonding, (ii) at high dilution (less than 0.001 M) a band due to intramolecular hydrogen bonding ($\Delta\nu = 107\ cm^{-1}$) is still observed.

NMR. spectrum: 0.84 ($d \times d$, 1 H, H_A—C(6)); 1.15 and 1.27 (*s*, each 3 H, methyl groups); 1.30 ($d \times d$, partially hidden by the Me peak at 1.15, 1 H, H_B—C(6)); 2.05 (*m*, 5 H, C(3) + C(4) methylene and C(5) bridgehead proton); 2.88 (*s*, 1 H, OH). – MS.: M^+ at 154.

$C_9H_{14}O_2$ (154) Calc. C 70.13 H 9.09% Found C 70.01 H 9.19%

Deuteriation of ketol **3**. 100 mg of **3** in methanol (CH_3OD) was treated with a few drops of sodium deuteroxide. It was left for three days at room temperature with occasional shaking. Integration of the NMR. spectrum (using one of the methyl groups as an internal standard), indicated the exchange of three hydrogens (including the OH group) by deuterium (**26**) (NMR. data, Table 3).

Benzylidene derivative of **3** (**25**). 178 mg (1.28 mmol) of ketol **3**, 274 mg (2.56 mmol) of freshly distilled benzaldehyde, in 2 ml of methanol, was treated dropwise with a sodium hydroxide solution (60 mg in 60 ml water). The mixture turned yellow, stirring was continued for 15 h at 23°; work-up gave 334 mg of the benzylidene derivative and unreacted ketol **3** (as checked by TLC.). Chromatography on a silica gel column gave 160 mg of pure monobenzylidene derivative. – IR.: max. at 3425 *s* (OH), 3090 *m*, 3020 *w*, 2968 *s*, 2918 *s*, 1687 *s* (C=O), 1620 *m* (double bond and aromatic), 1490 *m*, 1447 *m*, 1365 *s*, 1300 *s*, 1270 *m*, 1241 *w*, 1175 *m*, 1110 *m*, 1040 *m*, 1028 *m*, 964 *m*, 850 *m* (CH out-of-plane deformation of olefin), 770 *m*, 685 *m* (aromatic). – MS.: M^+ at 242 (Calc. for $C_{16}H_{18}O_2$: 242).

Trimethylsilyl ether (**15**). To 320 mg of ketol **3** in 3 ml of dry pyridine was added dropwise 2.0 g of hexamethyldisilazane in 0.2 g of trimethylchlorosilane at room temperature. The mixture was stirred under nitrogen for 48 h. Excess reagent and pyridine were removed under vacuum, moisture was excluded by a $CaCl_2$-tube placed between the water-pump and the apparatus. The reaction mixture was extracted with carbon tetrachloride and the solid removed by centrifugation. – IR.: max. at 3078 *w* (C—H of cyclopropane), 3048 *w* (C—H of cyclopropane), 2950 *s*, 2870 *s*, 1720 *s* (C=O), 1460 *w*, 1415 *w*, 1378 *s*, 1360 *m*, 1310 *m*, 1300 *m*, 1260 *s*, 1250 *s*, (Si—CH_3), 1198 *w*, 1175 *s*, 1090 *m*, 1065 *m*, 1040 *s*, 1015 *w*, 998 *m*, 900 *s*, 865 *w*, 840 *s* (Si—CH_3), 753 *m* and 705 *w* cm^{-1}. – NMR.: 0.02 (*s*, 9 H, $Si(CH_3)_3$); 0.65 ($d \times d$, 1 H, H_A—C(6)); 1.25 and 1.40 (2 *s*, 6 H, methyl groups); 1.95 (*m*, 5 H). – MS.: M^+ at 226 (Calc. for $C_{12}H_{22}O_2Si$: 226).

Oxime derivative of **3**. To 1.0 g of **3** in 4 ml of ethanol was added dropwise a mixture of 1.0 g hydroxylamine hydrochloride and 1.3 g of sodium acetate in 5 ml of water. Stirring was maintained for 48 h at room temperature. The mixture was diluted with 20 ml of water and neutralized with dil. hydrochloric acid. The solution was extracted with ether and the latter was washed with water. Removal of solvent gave 1.38 g of thick liquid which crystallized on standing. Recrystallization from *n*-hexane/ethyl acetate gave a colorless solid, m.p. 165–166°. $[\alpha]^{25} = -10.0°$ ($c = 0.41$). – IR.: max. at 3379 *s* (–OH), 3250 *s* (OH), 2920 *s*, 2840 *s*, 1650 *m* (C=N), 1455 *m*, 1370 *m*, 1310 *m*, 1265 *m*, 1150 *m*, 1030 *m*, 960 *s*, 945 *m*, 905 *s*, 995 *s*, 868 *m*, 835 *w*, 815 *w*, and 798 *w* cm^{-1}. – NMR.: 0.59 ($d \times d$, 1 H, $^2J = {}^3J = 5.0$, H_A–C(6)); 1.10 and 1.31 (2 *s*, each 3 H, methyl groups); 1.25 ppm (*m*, 1 H, H_B–C(6)); 2.30–1.50 (*m*, 4 H); 2.87 (*m*, 1 H); 4.70 (*s*, OH); 8.80 (br. *s*, N–OH). – MS.: M^+ at 169 (Calc. for $C_9H_{15}NO_2$: 169).

Attempted Beckmann Reaction. 338 mg (2 mmol) of the above oxime in 10 ml of carbon tetrachloride was treated with 126 mg (2 mmol) of freshly distilled acetyl chloride, at 0° under nitrogen with stirring. The mixture was allowed to warm to room temperature and stirred overnight. Analysis of the mixture revealed at least five compounds. However, no nitrilic cleavage products were characterized.

Dehydration of **3** *to* **14**. 357 mg of **3** in 10 ml dry pyridine was treated dropwise with 2 ml of phosphorous oxychloride at 0–5°, and stirred for 16 h. Excess phosphorous oxychloride was decomposed with ice, and then the mixture was extracted with ether. The extract was washed with aqueous 3% hydrochloric acid, water, and then dried. Removal of ether gave 110 mg of pale yellow liquid. GLC. (Carbowax column, 120°) revealed one major product (**14**) which was isolated. – IR.: max. at 3080 *m* (C–H adjacent to double bond), 3040 *w* (C–H of cyclopropyl), 2948 *s*, 2880 *s*, 1722 *s* (5-membered ring ketone conjugated with cyclopropane), 1647 *m* (disubstituted double bond), 1447 *m*, 1419 *m*, 1383 *m*, 1317 *w*, 1303 *m*, 1268 *m*, 1252 *m*, 1205 *w*, 1158 *w*, 1098 *m*, 1012 *s*, 898 *s* (C–H out-of-plane stretching of $>C=CH_2$), 802 *w*, and 733 *w* cm^{-1}. – NMR.: 1.12 ($d \times d$, 1 H, $^2J = 4.75$, $^3J = 4.75$); 1.35 (multiplet, 1 H); 1.85 (*s*, 3 H); 2.0–2.31 (*m*, 5 H); 4.88 (*d*, 1 H, $^2J = 1.75$); 4.97 (*d*, 1 H, $^2J = 1.75$). – MS.: M^+ at 136.

Hydrogenation of **3**. 500 mg of **3** in 10 ml of acetic acid was hydrogenated over 300 mg 10% Pd/C at 90° and 2 atm. pressure for 16 h. The reaction mixture was cooled, filtered, and washed with a saturated solution of sodium hydrogen carbonate until free of acid. It was extracted with 30 ml of ether, the latter was washed several times with water, and dried. Evaporation gave 350 mg of yellow liquid in 60% yield which was a mixture of the cyclopentanone **18** and the cyclohexanone **19** in a ratio of 2.5:1.0 (GCL., Carbowax column 150°).

Compound **19** was identical with authentic 2-isopropylcyclohexanone (NMR. and IR.) prepared from 2-isopropylphenol by hydrogenation over *Raney* nickel at 100 atm pressure, 180° and followed by oxidation [22].

Compound **19** was identified as *trans*-2-isopropyl-3-methylcyclopentanone. – IR.: max. at 2963 *s*, 2880 *s*, 1740 *s* (C=O of a cyclopentanone), 1645 *m*, 1412 *m*, 1385 *m*, 1370 *m*, 1290 *m*, 1270 *m*, 1240 *m*, 1155 *s*, 1060 *m*, 995 *m*, 945 *w* and 926 *w* cm^{-1}. – NMR.: 0.98 (*d*, 6 H, $^3J = 6.75$); 1.15 (*d*, 3 H, $^3J = 6.05$); 1.20–1.70 (*m*, 2 H); 1.75–2.45 (*m*, 5 H). – MS.: M^+ at 140.

Hydrogenation of **14**. 13 mg of **14** on catalytic hydrogenation over 5 mg 10% Pd/C at 25° in 15 ml of ether absorbed approximately 5 ml of hydrogen (2 molar proportions) to give *trans*-2-isopropyl-3-methylcyclopentanone (**18**). No cyclohexanone **19** was detected by GLC.

Treatment of ketol **3** *with sodium in liquid ammonia*. To 1.0 g of sodium in 300 ml of liquid ammonia was added dropwise 1.7 g of **3** in 20 ml dry ether over 30 min. Stirring was continued for 1½ h and the mixture was treated with a saturated solution of ammonium chloride. Evaporation and work-up gave 0.8 of pale yellow liquid containing 3-methylcyclopentanone (**20**) as major product in 60% yield as indicated by GLC. **20** was identified (NMR., IR. and GLC.) with an authentic sample of 3-methylcyclopentanone.

Treatment of ketol **3** *with lithium aluminium hydride*. 0.85 g **3** was reduced with 0.5 g lithium aluminium hydride in 20 ml of dry ether. Excess reagent was decomposed by dropwise addition of water. The organic layer was dried and evaporated to give 0.80 g of viscous liquid which consisted of one main product (GLC., Apiezon L column, 160°); presumed to be the appropriate diol. Testing with a solution of periodic acid showed it to be oxidatively inert [23]. Attempted isolation of the diol by preparative GLC. resulted in its dehydration to isopropenyl-bicyclo[3.1.0]hexan-

2-ol. – IR. (in CCl_4): max. at 3607 *s* (free OH), 3450 *m* (bridged OH), 3090 *m* (C—H adjacent to double bond), 3040 and 3020 *m* (C—H of cyclopropane), 2980 *s*, 2950 *s*, 2880 *s*, 1633 *s* (C=C), 1458 *s*, 1395 *m*, 1320 *m*, 1305 *m*, 1261 *w*, 1160 *m*, 1086 *w*, 1050 *s*, 1012 *w*, 986 *m* (C—H, out-of-plane stretching of $>C=CH_2$). – NMR.: 0.30–1.10 (*m*, 3 H, cyclopropyl); 1.10–2.00 (*m*, 5 H); 1.70 (br. *s*, 3 H, Me adjacent to double bond); 4.55 (*m*, 1 H, H—C(α)); 4.85 (br. *s*, 2 H, $>C=CH_2$).

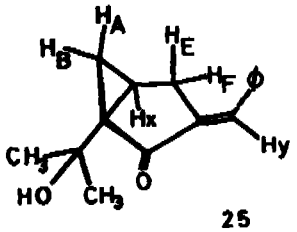
NMR. Data. The monobenzylidene derivative of **3** was analyzed by double resonance experiments and by using the paramagnetic shift reagent Eu (fod)$_3$ whence the relative positions of the protons were established for **25** (*Table 1*). The geminal protons A and B on C(6) were readily distinguishable by the difference in magnitude of their coupling with the C(5) proton X (Table 2). The appearance of A and B at low field can be attributed to deshielding by the carbonyl and hydroxyl groups. Moreover, the fact that proton A is more deshielded than B is concordant with previous data found for derivatives having the bicyclo[3.1.0]hexane skeleton [12].

Table 1. *Chemical shifts*[a]) *of benzylidene derivative* **25**

Protons[b])	X	Δ[c])	A	Δ	B	Δ	E	Δ	F	Δ
In absence of shift reagent	2.16	0	0.68	0	1.48	0	3.0	0	3.0	0
With increasing	2.20	0.04	0.70	0.02	1.43	0	3.0	0	3.0	0
amounts of	2.35	0.19	0.80	0.12	1.68	0.20	3.07	0.07	3.07	0.07
Eu(fod)$_3$ reagent	3.02	0.86	1.22	0.54	2.32	0.84	3.25	0.25	3.54	0.54
	2.85	0.69	1.15	0.47	2.15	0.67	3.20	0.20	3.46	0.46

Protons[b])	OH	Δ	CH_3	Δ	CH_3	Δ	Y	Δ	Φ	Δ
In absence of shift reagent	3.5	0	1.42	0	1.24	0	7.42	0	7.42	0
With increasing	3.92	0.42	1.54	0.02	1.30	0.06	7.42	0	7.42	0
amounts of	4.82	0.32	1.75	0.33	1.45	0.21	7.45	0.03	7.45	0.03
Eu(fod)$_3$ reagent	9.30	5.80	2.84	1.42	2.14	0.90	7.64	0.22	7.48	0
	8.19	4.69	2.60	1.18	1.98	0.74	7.60	0.18	7.46	0.04

a) In $CDCl_3$ as solvent.
b) Chemical shifts are expressed as ppm downfield from TMS. For labelling see below.
c) $\Delta = \nu_{Eu} - \nu_0$; ν_{Eu} = chemical shift in presence of Eu(fod)$_3$ reagent; ν_0 = shift without reagent.



25

Table 2. *Coupling constants of some protons of* **25**

	Multiplicity of signal	Coupling constants
	A, doublet of doublets	$^2J_{AB} = -4.25$ Hz $^3J_{AX} = 4.25$ Hz
	B, doublet of doublets	$^2J_{AB} = -4.25$ Hz $^3J_{BX} = 7.25$ Hz
	E and F, each a doublet of doublets	$^2J_{EF} = 17$ Hz $^4J_{EY}$ or $^4J_{FY} = 2$ Hz

Table 3. *Some chemical shifts*[a]) *and coupling constants*[b]) *of deuteriated ketol* (**26**)

X	A	B	E, F	CH_3	CH_3
2.26 ppm sextet	0.97 ppm doublet of doublets	1.50 ppm octet	2.02 ppm multiplet	1.39 ppm singlet	1.29 ppm singlet
$^3J_{XA} = 4.75$ Hz	$^2J_{AB} = 4.75$ Hz	$^2J_{BA} = 4.75$ Hz			
$^3J_{XB} = 7.5$ Hz	$^3J_{AX} = 4.75$ Hz	$^3J_{BX} = 7.5$ Hz			
		$^4J = 1.25$ Hz			

[a]) In CH_3OD in solvent downfield from TMS.
[b]) Coupling constants determined in $CDCl_3$.

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