271. The Reaction of Singlet Oxygen with α- and β-Pinenes

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Summary. The reaction of photogenerated singlet oxygen with α- and β-pinenes has been carefully re-examined. α-Pinene almost exclusively (99.3% yield) furnishes *trans*-3-hydroperoxy-pin-2(10)-ene. However, detectable amounts of the three other possible products are also found, viz., *cis*-3-hydroperoxypin-2(10)-ene (~0.8%), and *cis*- and *trans*-2-hydroperoxypin-3(4)-ene (~0.04%). β-Pinene gives 99.9% of 10-hydroperoxypin-2(3)-ene and a trace (~0.01%) of norpinan-2-one. Rates of reaction and product composition are treated by modal analysis and reflect the operation of steric and stereoelectronic factors in a reactant-like transition state.

Introduction. – The reaction of singlet oxygen with mono-olefins having an allylic hydrogen available produces the allylic hydroperoxide in which the double bond has migrated [1]. The mechanism of this reaction has been widely discussed, and present opinion centers on two alternative processes which appear to be compatible with the experimental evidence, namely, a one-step cyclic concerted mechanism [2] and a two-step mechanism in which a perepoxide is initially formed and subsequently rearranges to hydroperoxide [3]. In spite of this ambiguity, recent studies have revealed that the transition state for photo-oxygenation is reactant-like, and that steric effects largely determine the reaction course [2] [4]. For the case of typical bridged bicyclic olefins, such as 2-methylnorbornene, singlet oxygen attacks the *exo* and *endo* sides in a ratio of 66:1 [4]. On the other hand, the *exo-endo* attack ratio for 2-methylenenorbornane is about 28 [5]. Thus it is seen that photo-oxygenation, compared with typical one-step cyclic additions, *e.g.* the hydroboration [6] and epoxidation [7] of norbornene, which exhibit *exo-endo* ratios of 200, is subject to similar steric constraint. However, there is the difference that ectocyclic double bonds may well show less steric discrimination[2]). Accordingly, in a general way, it should be possible to predict, by extrapolation from the norbornene cases mentioned above, the composition of the products of photo-oxygenation for other bridged bicyclic olefins. In particular the α- and β-pinenes (**1** and **2**) should furnish products deriving from attack on both faces of the molecule. In two previous investigations only a single product was characterized from **1**, viz., *trans*-3-hydroxy-pin-2(10)-ene (**5**), which was obtained in yields of 93 and 94%. We now report on the complete product analysis of the photo-oxygenation of **1** and **2** [8] [9].

Results. – *Products.* Photo-oxygenations of α-pinene (**1**) were carried out in acetonitrile using methylene blue as sensitizer and a 500 W projector lamp as light

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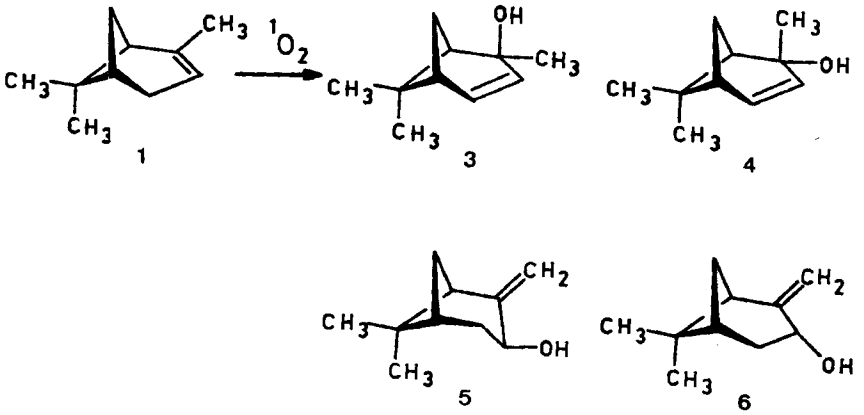
[2]) To avoid ambiguity with the terms *exo* and *endo* commonly employed with bridged bicyclic olefins, the prefixes *ecto* and *en* have been chosen to designate placement of the double bond or the attacking reagent with respect to the outside or inside of the ring (*cf.* ref. [25]).

source. The mixture of hydroperoxides so obtained was reduced either with (a) sodium borohydride in ethanol [10] or with (b) triphenylphosphine in ether [11]. The absolute yield of each alcoholic product was scrupulously determined by gas-liquid chromatographic analysis using an internal standard (Table 1). All the four expected alcohols (**3**, **4**, **5**, and **6**) were formed although some were present in vanishingly small amounts. Nevertheless, the identity of each was verified by direct comparison with independently prepared authentic samples.

Scheme 1



trans-3-Hydroxypin-2(10)-ene (**5**) was synthesized by two independent routes. The first started with the epoxide of α-pinene (**8**) which on base-induced eliminative opening of the oxirane gave **5** [12] [13]. An alternative procedure was the allylic oxidation of β-pinene (**2**) to the acetate **9** which on hydrolysis gave **5** [14].

Table 1. *The Product Distribution of Pinenols* **3**, **4**, **5** *and* **6** *obtained by Reaction of Singlet Oxygen with α-Pinene* (**1**)

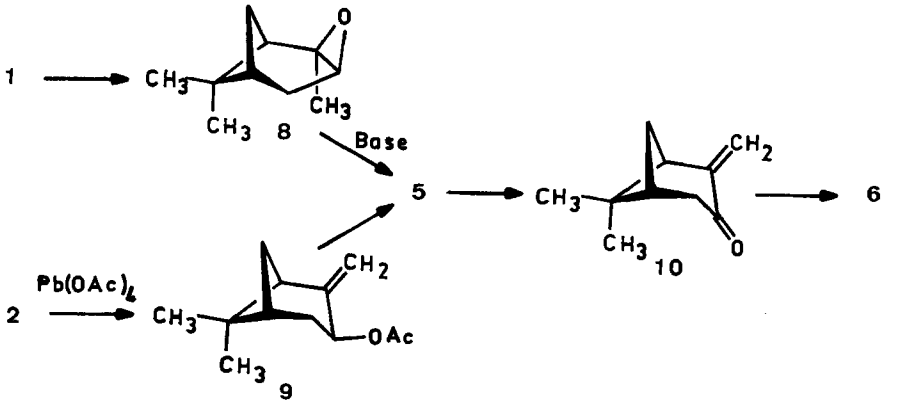
Reductant	Absolute yield [a] (%)	Relative Yields			
		enclinal		ectoclinal	
		3	**4**	**5**	**6**
$NaBH_4$/Ethanol	100 ± 4.7	0.04 [b]	0.01 [b]	99.3	0.8
Triphenylphosphine	96.9 ± 1.8	0.4 [b]	0.08 [b]	98.8	0.7

[a] Recorded as the average of two experiments. The response to the detector was determined for **5** and **4** (see experimental section) and the same response was assumed for the isomeric alcohols **6** and **3** respectively.

[b] These values represent the outer limits of detection by this technique.

cis-3-Hydroxypin-2(10)-ene (**6**) was prepared by oxidation of the *trans* alcohol **5** to pin-2(10)-en-3-one (**10**) with chromium trioxide in pyridine [15] followed by reduction with diisobutylaluminium hydride in light petroleum [16] (scheme 2).

Scheme 2: Preparation of the pinenols **5** and **6**



The procedure of *Whitham* was adopted for the preparation of *trans*-2-hydroxypin-3(4)-ene (**3**) [17]. Treatment of α-pinene (**1**) with dry lead tetraacetate followed by base hydrolysis of the acetate **11** gave **3**.

A search of the literature showed that no feasible laboratory synthesis of *cis*-2-hydroxypin-3(4)-ene (**4**) was available. *Bain* has reported that aerial oxidation of α-pinene (**1**) gave, in very low yield, the alcohol **4** [18]. A previous attempt to synthesize **4** by addition of methyl *Grignard* reagent to norpin-3(4)-en-2-one (**14**) was reported to be unsuccessful [19]. Norpin-3(4)-en-2-one (**14**) was prepared from norpinan-2-one (**12**) [20]; bromination of the latter with N-bromosuccinimide gave 3-bromonorpin-2-one (**13**) which in turn on elimination of hydrogen bromide, gave **14**. The addition of excess methyllithium to **14** in ether at 0° gave **4** stereospecifically and in high yield [21] (scheme 3).

Scheme 3: Preparation of the pinenols **3**, **4** and **7**

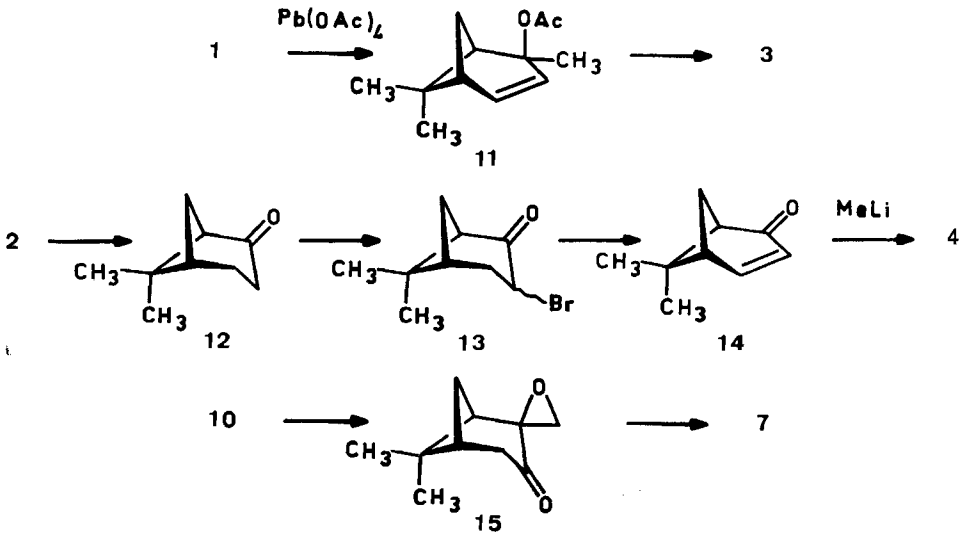
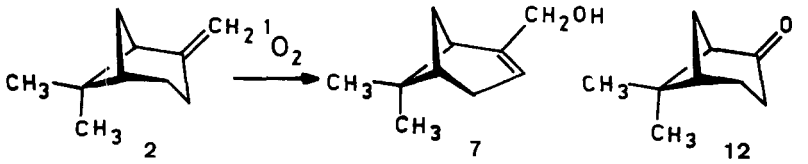


Photo-oxygenation of β-pinene (**2**) gave essentially one product [9], 10-hydroxy-pin-2(3)-ene (**7**) together with a small amount of norpinan-2-one (**12**) (obtained on triphenylphosphine reduction) or *cis*-norpinan-2-ol (**16**) (from the sodium borohydride reduction). The origin of **12** or **16** clearly springs from the cleavage of the ectocyclic double bond of **2**, presumably by way of the dioxetane intermediate [22].

Scheme 4



Although reaction was stopped after absorption of an equivalent of oxygen, the overall yield was less than that obtained with α-pinene (**1**) (Table 2). The identity of **7** was confirmed by synthesis. The enone **10** was epoxidized to **15**. Conversion of **15** to its hydrazone, followed by treatment with base gave **7** [23] (scheme 3).

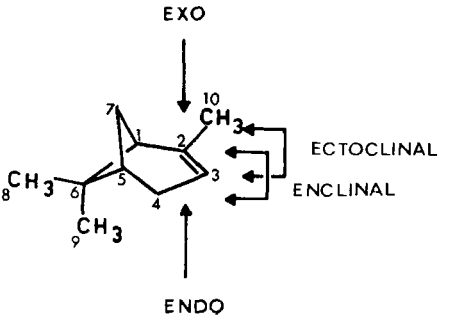
Table 2. *The Product Distribution in the Reaction of Singlet Oxygen with β-Pinene*

Reductant	Absolute Yield[a] (%)	Relative Yields		
		7	**12**	**16**
$NaBH_4$/Ethanol	79.7[b] ± 2.5	99.9	–	0.01
Triphenylphosphine	72.5[b] ± 1.6	99.9	0.01	–

[a] Recorded as the average of two experiments.
[b] Compare ref. [9].

Rates. It has been stated that α-pinene (**1**) reacts sluggishly and that it is much less reactive than 1-methylcyclohexene [8]. On the other hand, it appears from earlier reports that β-pinene is far more reactive than methylenecyclohexane [9] [24]. In

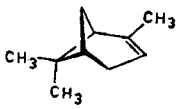
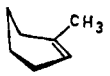
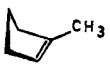
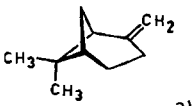
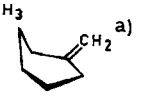
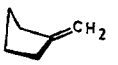
Scheme 5: Modes of attack by singlet oxygen on α-pinene; I) *exo*-ectoclinal, II) *exo*-enclinal, III) *endo*-ectoclinal and IV) *endo*-enclinal



order to get a quantitative measure of reactivity, both α- and β-pinene have been compared to standard bridged bicyclic and mono-cyclic olefins (see Table 3). Molecular rates have been normalized by partition into their modal contributions on the assumption that products are entirely kinetic in origin [25]. For α-pinene, photo-oxygenation proceeds *via* four modes of attack (scheme 5). The reference mode chosen is the main one, namely the *exo*-ectoclinal mode.

Discussion. – We have proposed elsewhere that the reaction of singlet oxygen with mono-olefins can be conveniently evaluated by recourse to modal analysis [25]. Regardless of the nature of the mechanism, photo-induced hydroperoxidation of α-

Table 3. *Relative Rates of Photo-oxygenation*

Entry	Acceptor	Total Rate	Ectoclinal Rate[b] *Endo*	*Exo*
1		3.9	0.03	3.87
2		15.4	3.28	3.28
3		2.20	0.03	2.17
4		118.00	3.30	3.30
5		3.00	–	~3.0
6		–	–	–
7		1.00	0.04	0.96
8		3.6	0.9	0.9

[a] Inert under the present conditions. [b] See footnote 2 and [25].

pinene formally involves C–O bond making either at C(2) or C(3) with associated hydrogen abstraction either at C(4) or C(10); these processes pass through, what are called, the enclinal and ectoclinal modes respectively. Moreover, as each mode has *exo* and *endo* sides, singlet oxygen attacks the allylic moiety in four modes (scheme 5).

Partitioning of oxygen attack between these modes will depend on the relative importance of electronic, stereoelectronic and steric factors in the transition states corresponding to each mode. It has already been amply demonstrated that C–O bond making is sensitive to steric hindrance [4] [26–27], whereas ease of rupture of the allylic C–H bond depends on its orientation with respect to the double bond. When the σ–π overlap is good, abstraction by singlet oxygen of allylic hydrogen is easy [26] [28]. In conformationally free cyclohexene derivatives, which exist preferentially in unencumbered half-chair configurations, the quasi-axial allylic hydrogen is abstracted some three times more easily than quasi-equatorial hydrogen by singlet oxygen [2].

In α-pinene, the cyclohexene moiety is held flat by the *gem*-dimethylmethylene bridge [29]. Consequently, stereoelectronic preferences springing from axiality of the ring allylic C–H bonds should be effectively suppressed. However, the C(10) methyl group will be unaffected and its C–H bonds will be able to adopt the best overlap possible with the double bond. The proportion of ectoclinal to enclinal product, which is overwhelmingly in favour of the former, clearly reflects the paramouncy of the stereoelectronic factor. Indeed, any benefit which might have accrued from preferential formation of a tertiary over a secondary hydroperoxide [30] (attack by oxygen at C(2) rather than C(3)) is simply not in evidence. It might also be argued that favouring of the ectoclinal mode could be due to the switching of the double bond out of what is tantamount to a cyclopentene ring to the thermodynamically more favourable ectocyclic position. However, rate studies (*v. infra*) enable this possibility to be discounted.

The high *exo-endo* ratio of 130 for the ectoclinal mode shows that pure steric effects are also extremely important. An equally high, if not higher, ratio would have been expected for the enclinal mode. The actual value of 4 probably constitutes an unreliable index in view of the poor accuracy of analysis for the minor photo-oxygenation products. Comparable high *exo-endo* ratios are found for typical one-step cycloadditions such as hydroboration [31], epoxidation [32] and cyclopropanation [33] of α-pinene. Thus the ratio found for photo-oxygenation reveals the operation of a one-step cycloaddition in the rate determining step. The question immediately arises concerning the number of atoms in this transition state, is it three or six ? In other words could the value of the *exo-endo* ratio itself provide a distinction between the supposed initial formation of perepoxide and the ene-reaction, assuming that the steric exigencies of each process differ sufficiently [34]. Unfortunately this appears not to be possible, as the diimide reduction of both α- and β-pinene displays an equally high *exo-endo* ratio [35].

In summary, the overwhelming disposition of α-pinene for the *exo*-ectoclinal mode demonstrates that steric and stereoelectronic effects work together and simultaneously in the transition state. If a perepoxide were responsible for the formation of hydroperoxide, then steric and stereoelectronic effects would manifest themselves separately in the addition and abstraction steps respectively. As this is not the case, such a two-step process can be ruled out. It is also worth noting at this juncture that the reaction of iodine azide in acetonitrile with α- and β-pinenes leads to products of the menthane skeleton. The mechanism involves initial formation of an iodonium

ion which causes cleavage of the adjoining four-membered ring. Although not a proof against the intermediacy of the related perepoxide the absence of ring cleavage products from the photo-oxygenation of the pinenes is noteworthy [39].

β-Pinene, as previously reported, gives the expected hydroperoxide plus some cleavage product [9]. Clearly, subtle factors are responsible for its reactivity, as the closely related methylenecyclopentane, methylenecyclohexane and $\Delta^{1(17)}$-*p*-menthene were previously reported to be inert [24]. Re-examination of the relative rates by modal analysis is revealing. The *exo*-ectoclinal rates for the ectocyclic olefins (entries 5–8, Table 3) are all of the same order of magnitude, except for methylenecyclohexane. Steric effects, as such, are evidently unimportant, and this is expected as C–O bond formation is far removed from possible hindrance by the body of the molecule. Thus it can be concluded that the stereoelectronic factor is the sole one controlling rate in the ectoclinal mode. In methylenecyclohexane the chair conformation apparently does not permit a favourable overlap of the allylic C–H bond with the double bond[3]). In the five-membered rings (entries 7 and 8) favourable overlap obtains. At first sight, β-pinene appears to be an exception (entry 5), but its six-membered ring experiences the inverse reflex effect due to the constraint of the *gem*-dimethylmethylene bridge, and accordingly the ring behaves like cyclopentane [29].

The encyclic olefins (entries 1–4) also exhibit reasonably similar rates in their *exo*-ectoclinal mode. Here the stereoelectronic factor must be constant as the freely rotating methyl group provides the allylic hydrogen. As a result, it can be inferred that steric factors to C–O bond formation are very similar and largely independent of ring size or bridging.

The rates for the *endo*-ectoclinal modes vary widely; this will be discussed elsewhere [25].

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Experimental Part

General. IR. were recorded as films on NaCl on a *Perkin-Elmer* 257 spectrometer. The characteristics of the absorption maxima (cm^{-1}) are expressed as follows: s, strong; m, medium; w, weak; b, broad. NMR. spectra were determined either on a model R-12 *Perkin-Elmer* instrument (60 MHz) or on a *Varian* XL-100 spectrometer (100 MHz) using carbon tetrachloride or deuteriochloroform as solvent. Chemical shifts are expressed as ppm with reference to tetramethylsilane. All important NMR. data is assembled in Table 5.

Gas liquid chromatography (GLC.) was carried out on a model F11 (analytical) and F21 or 990 (preparative) *Perkin-Elmer* instruments. The F21 and F11 models were equipped with flame ionization detectors and used nitrogen as carrier gas. The 990 instrument was operated with a thermal conductivity detector and helium as carrier gas.

The following GLC. columns were used: A. FFAP, 9%, 2 m × 2 mm; B. FFAP, 7%, 3 m × 2 mm; C. Apiezon, 5%, 2 m × 2 mm; D. FFAP, 20%, 5 m × 5 mm; E. Apiezon, 20%, 3 m × 5 mm; F. FFAP, 20%, 3 m × 5 mm.

All boiling (b.p.) and melting points (m.p.) are uncorrected.

[3]) The cause of this discrepancy remains to be elucidated and is under investigation (work of *W. T. Wipke, P. Gund* and *C. G. Rimbault*).

Materials. α-Pinene (**1**): *Fluka* (practical grade) α-pinene was carefully fractionated through a vacuum-jacketed column (70 cm) packed with glass helices and fitted with a variable drop ratio distillation head. The fraction b.p. 154.5° was collected, but further purification by preparative GLC. (D) was necessary to remove the last traces of β-pinene. – *β-Pinene* (**2**): *Fluka* (practical grade) β-pinene was distilled b.p. 164°, as described above and purified by preparative GLC. (D). – *Acetonitrile: Fluka* (puriss grade) acetonitrile was used without purification. – *Methylene blue*: Puriss grade reagent (*Fluka*) was utilized as the dye sensitizer. – *Apparatus*: This will be described in detail in a later publication.

Irradiation of the solution of olefin was carried out, in a water-cooled (10–12°) reaction vessel, with two 500 W tungsten projector lamps (*Silvania* FFX) as light source.

Photo-oxygenation. In a typical experiment, a vigorously stirred solution of an accurately weighed sample of olefin (*ca.* 0.05 g, *ca.* 0.0004 mol) and methylene blue (*ca.* 0.02 g) in acetonitrile (*ca.* 2 ml) was irradiated under an atmosphere of oxygen. Absorption decreased sharply as the uptake of the theoretical amount of oxygen was approached. At this point, irradiation was stopped and the resulting solution of hydroperoxides treated in one of two ways: a) *Reduction with triphenylphosphine* [15]. A solution of triphenylphosphine (*ca.* 0.15 g) and an accurately weighed sample of the standard hexamethylbenzene (*ca.* 0.05 g) in ether (3 ml) were added, at room temperature, to the mixture of hydroperoxides. After stirring for 10 min, the solution was analysed directly by GLC. b) *Reduction with sodium borohydride* [10]. The mixture of hydroperoxides in acetonitrile was diluted with dry ethanol (5 ml) and the solution (0°) was stirred with excess sodium borohydride. After 2 h the mixture was diluted with water (300 ml) and an accurately weighed sample of the standard, hexamethylbenzene, was added. Extraction with ether (3 × 50 ml) gave an organic phase which was dried over magnesium sulfate and carefully concentrated by distillation of the solvent on a water bath (50°). The residue was analysed directly by GLC. (A).

Each reaction was performed in duplicate and the absolute and relative yields were found to be well within the limits of experimental accuracy.

Attempted oxygenation with chemogenerated singlet oxygen. The procedure of *Pitts et al.* was investigated [36]. In a typical experiment, a solution of potassium chromate (9.94 g, 0.051 mol) and potassium hydroxide (2.06 g, 0.037 mol) in water (117 ml) was slowly added to a stirred mixture of 33% aqueous methanol (176 ml), 30% hydrogen peroxide (17.6 g) and the olefin (2.0 g, 0.015 mol). After stirring gently for 18 h, during which time gas evolved, the mixture was concentrated under reduced pressure to a volume of *ca.* 50 ml then diluted with water (500 ml). This residue was extracted with ether (3 × 100 ml), dried and concentrated to yield a liquid which was treated with excess sodium borohydride in ethanol. After the usual working-up procedure, the product was analysed by GLC. Both α- and β-pinene were recovered unchanged from the reaction; no products of oxidation being formed.

Gas liquid chromatographic analysis. – *Qualitative analysis*: Qualitative analyses (GLC. (A) and (C)) were performed by a comparison of retention times with authentic compounds and by the technique of peak enhancement. *Quantitative analysis*: In order to estimate absolute yields of products, the responses (to the GLC. flame ionization detector) of the authentic compounds were compared with that of an internal standard. Solutions of accurately weighed samples of the compound (*ca.* 0.01–0.03 g) and the internal standard (*ca.* 0.01 g) in which the ratio of compound to internal standard varied, were analysed by GLC. under the same conditions as those used for the product analysis. The areas of the peaks were determined by the technique of cutting and weighing.

The "response ratio" (Rr) of a particular compound was obtained by substitution in the following formula:

$$\frac{\text{weight of the compound}}{\text{weight of the standard}} \Big/ \frac{\text{area of compound peak}}{\text{area of standard peak}} = \text{Rr}$$

From the various values of Rr obtained, the absolute yields in the photo-oxygenations were calculated.

For a pair of epimeric alcohols the response ratio was assumed to be the same for each isomer (Table 4).

Identification of products: Compounds **5** and **3** were isolated by preparative GLC. (F) from the photo-oxygenation of α-pinene (**1**). The structures were confirmed by a comparison of their spectral and GLC. properties with the authentic compounds and also by analysis of their respective NMR. spectra (100 MHz) which were determined in the presence and absence of Europium shift reagent (see Table 5 at end of experimental section). Identification of the remaining two alcohols **6** and **4** was by a comparison of GLC. properties with the authentic compounds. This was also the case for norpinan-2-one (**12**) and *cis*-norpinan-2-ol (**16**). However, the major product from β-pinene (**2**), that is 10-hydroxypin-2(3)-ene (**7**), was isolated by preparative GLC. (D, 175°) and identified by comparison with the authentic alcohol.

Table 4. *GLC. Characteristics of the Products of Photo-oxygenation*

Product	Response Ratio	Retention Time[a])
trans-3-hydroxypin-2(10)-ene (**5**)	1.23	10 min 47 s
cis-3-hydroxypin-2(10)-ene (**6**)	1.23	18 min 18 s
cis-2-hydroxypin-3(4)-ene (**4**)	1.08	6 min 5 s
trans-2-hydroxypin-3(4)-ene (**3**)	1.08	7 min 47 s
10-hydroxypin-2(3)-ene (**7**)	1.19	19 min 6 s
norpinan-2-one (**12**)	–	9 min 15 s
cis-norpinan-2-ol (**16**)	–	10 min 27 s
hexamethylbenzene (standard)	–	28 min 51 s

[a]) GLC. (A), col 130°, N_2 flow 30 ml/min.

Syntheses. – trans-*3-Hydroxypin-2(10)-ene* (**5**) was prepared by standard procedures [12–14]. Typically, **5** had b.p. 95–97°/17 Torr; GLC. analysis (A) indicated a purity of 96%.

cis-*3-Hydroxypin-2(10)-ene* (**6**) was obtained from pin-2(10)-en-3-one (**10**) [15] by reduction with diisobutylaluminium hydride [16].

trans-*2-Hydroxypin-3(4)-ene* (**3**) was prepared by hydrolysis of *trans*-2-acetoxypin-3(4)-ene [17]. GLC. analysis (B) indicated that the product contained ~60% of alcohol **3** which was obtained pure, b.p. ~83°/14 Torr by preparative GLC. (F).

cis-*2-Hydroxypin-3(4)-ene* (**4**). a) Norpinan-2-one (**12**), b.p. 77°/12 Torr was prepared in 52% yield by the ozonolysis of β-pinene (**2**). Bromination gave an epimeric mixture of 3-bromonorpinan-2-ones (**13**) in 34% yield [20]. Base treatment of **13** gave norpin-3(4)-en-2-one (**14**), b.p. 76°/11 Torr in 27% yield [20]. b) A solution of **14** (0.21 g, 0.0014 mol) in anhydrous ether (7 ml) was added slowly to methyllithium in ether (7 ml of a 4.4% solution, *ca.* 0.014 mol) at 0° under nitrogen. After the addition was complete, the mixture was stirred at 20° for 3 h then it was hydrolyzed with saturated ammonium chloride solution at 0°. Distillation of the crude product gave the alcohol **4** (0.17 g, 81%), m.p. 41–43°. – IR. spectrum: max. at 3330 s b, 3025 w, 1620 w, 730 m cm^{-1}.

cis-*Norpinan-2-ol* (**16**). A solution of norpinan-2-one (**12**) (0.21 g) in ethanol was treated with excess sodium borohydride. After working-up, distillation gave **16** (0.20 g, 95%), b.p. 105°/9 Torr [38].

10-Hydroxypin-2(3)-ene (**7**). Pin-2(10)-en-3-one (**10**) was first converted into a mixture of *cis*- and *trans*-2(10)-epoxypinan-3-ones (**15**), b.p. 104–108°/8 Torr in 59% yield. Alcohol **7** was obtained from **15** by the *Wharton* reaction in 54% yield [23]. Purification was accomplished by preparative GLC. (E).

Table 5. *NMR. Data of the Bicyclo*[3.1.1]*heptane Derivatives*[a])

Compound[b])	C(3)	C(4)	C(7)	C(8)	C(9)	C(10)
4	5.59 *m* $^4J = 8.5$ $^1J = 2.0$ $^5J = 1.0$	6.27 *m* $^3J = 8.5$ $^5J = 6.0$ $^7J = 1.0$	1.48 *d* $^7J = 7.0$	1.10 *s*	1.21 *s*	1.35 *s*
7	5.53 *m*	–	1.23 *d* $^7J = 9.0$	0.88 *s*	1.33 *s*	4.01 *m*
5	4.43 *d* of *m* $^4J = 7.5$	–	1.72 *d* $^7J = 9.0$	1.28 *s*	0.64 *s*	4.94[c]) *m* $^{10}J = 20.5$[d])
5 with shift reagent[e])	4.62	–	1.85	1.29	0.66	4.98
6	4.66 *m*	–	1.47 *d* $^7J = 10$	1.26	0.75	4.86[c]) *m* $^{10}J = 35$[d])
3	5.56 *m* $^4J = 8.5$ $^1J = 2.0$ $^5J = 0.9$	6.28 *m* $^3J = 8.5$ $^5J = 6.0$ $^7J = 1.0$	1.48 *d* $^7J = 9.5$	1.37 *s*	0.97 *s*	1.32 *s*
3 with shift reagent[f])	5.92 6.06	6.46 6.52	1.91 2.02	1.14 1.19	1.48 1.52	1.78 1.92
12	–	–	1.62 *d* $^7J = 9.0$	1.38 *s*	0.88 *s*	–
10	–	–	–	1.40 *s*	0.83 *s*	5.50[c]) $^{10}J = 55.0$[d])
16	–	–	0.91 *d* $^7J = 9.0$	1.27 *s*	1.14 *s*	
13	4.90 *m* $^4J + {}^4J = 17.8$		1.81 *d* $^7J = 10$	1.42 *s*	0.87 *s*	
14	5.88 *d* of *m* $^4J = 9$	7.51 *d* of *m* $^3J = 9$ $^5J = 5$	2.09 *d* $^7J = 9$	1.53 *s*	1.03 *s*	

a) Coupling constants are expressed in Hz, chemical shifts are recorded in ppm.
b) See Scheme 5 for numbering.
c) Geometric centre of *AB*/*AM* spin system.
d) Distance between resonance lines 2 and 3 of *AB*/*AM* spin system.
e) Europium tris[1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione] was used as shift reagent. Concentration is not specified.
f) Two concentrations of shift reagent used.

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