Oxidation of *cis*- and *trans*-pinane with RuO_4 generated *in situ*

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Abstract

The products obtained by oxidation of *cis*- and *trans*-pinane (**1a** and **1b**) by RuO_4 generated *in situ* have been analyzed. Examination of their structure shows that two mechanisms are operating: a concerted mechanism postulated by ourselves and a more energetic mechanism considered by Bakke, which involves the development of a partial positive charge on the carbon to be oxidized.

Key words: Ruthenium complexes; Oxo complexes; Oxidation; Hydroxylation; Alkanes; Carbon–carbon bond cleavage; Bridgehead reactivity

Introduction

In 1953 ruthenium tetraoxide was introduced by Djerassi and Engle as an organic oxidant [1]. Since that time its utility for a variety of oxidative transformations has been recognized [2]. It should be pointed out that the Sharpless multicomponent solvent mixture renders the regeneration of the catalyst particularly efficient [3]. Under such experimental conditions ruthenium tetraoxide can be used in catalytic amounts, generally with sodium periodate or sodium hypochlorite as the stoichiometric reoxidizing reagent.

Ruthenium tetraoxide is a fascinating reagent because it allows the oxyfunctionalization of saturated hydrocarbons [4] which is topic of current interest [5]. The high valent, highly electrophilic RuO_4 is very reactive. This oxo meal species does not require polydentate ligands such as porphyrins [6] which are needed to stabilize the corresponding oxo iron or oxo manganese species to enable to achieve oxyfunctionalization efficiently and selectively. However in order to use ruthenium tetraoxide in a convenient catalytic way, it is more practical to generate it *in situ* from hydrated ruthenium trichloride or ruthenium dioxide. Once reduced after the oxidation of an alkane, it can be regenated by a wide variety of reoxidizing reagents [7] among which sodium periodate is apparently the most active.

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We have recently shown that this kind of reagent is efficient, highly regio- and chemioselective [4d, e]. Hydroxylation occurs exclusively or preferentially on unhindered tertiary carbons with retention of configuration. With bridged bicyclic substrates (involving bicyclo[2.2.1]heptane or bicyclo[3.2.1]octane units) neither Wagner Meerwein rearrangement nor bridgehead hydroxylation were observed. In some cases [4a, c], the oxidation of methylenic groups into the corresponding carbonyl did occur. The latter process can be followed by the cleavage of the nearby carbon–carbon bond, most likely via the corresponding enolic structure [8]. When hydroxylation occurs on a trisubstituted carbon next to a tertiary alcohol, a C–C bond cleavage is also observed [9].

In order to rationalize the hydroxylation process, we have proposed (Fig. 1) a reaction mechanism with the formation of an intermediate alkoxyhydridotrioxo intermediate **I** which yields the corresponding alcohol by reductive elimination. The latter can also be formed via an alkoxyhydroxydioxo ruthenium **II** (resulting from an hydrogen migration on intermediate **I**), followed by hydrolysis. If a hydrogen is available on the β carbon (Fig. 1, R = H), β-elimination followed by reductive elimination can directly yield a carbonyl group. The question of how the oxo ruthenium double bond interacts with the C–H bond (parallel (compare the pathways lateral (a) or (b)), colinear (pathway (c)) or perpendicular (not shown)) is still open, and currently under investigation in our laboratory [10]. However the experimental data presently available (absence of Wagner

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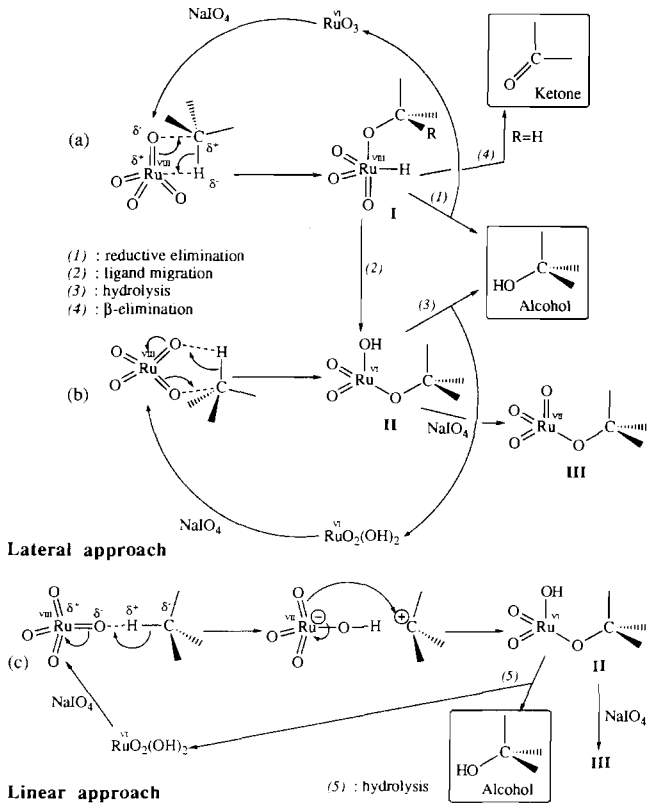

Fig. 1. Lateral and linear approaches of RuO_4 towards a carbon–hydrogen bond.

Meerwein rearrangement reaction products, diastereoselectivity of the hydroxylation, absence of chlorinated derivatives in presence of CCl_4) are in agreement with a concerted mechanism. Nevertheless, the development of a partial positive charge on the carbon of the C–H bond which is hydroxylated cannot be excluded. Although initially in favour of a carbonium ion [4b] Bakke no longer excludes [11] a mechanism with two competing pathways (Fig. 1): one via a cyclic transition state with a partially developped positive charge on the carbon atom (lateral approach) and one via a higher energy linear transition state to form an ion pair (linear approach). Evidence for the latter pathways relies upon the production of chloroalkanes during ruthenium tetraoxide oxidations in the presence of chloride ions [11], and the observation of an unexpected large kinetic isotope effect.

We describe here additional results which show that these two mechanisms can indeed compete, provided an appropriate substrate is used for such hydroxylation reactions, with ruthenium tetraoxide generated *in situ*. We have selected the pinane skeleton **1** which could give rise not only to skeletal rearrangements [12] under ionic conditions, but also to fragmentation reactions [12]. Furthermore if a free carbonium ion such as **IV** is involved in the oxidation mechanism, *cis*-pinane (**1a**) and *trans*-pinane (**1b**) should yield the same mixture of hydroxylation, oxidation rearrangement and fragmentation products (Fig. 2). If a concerted or 'intimate ion pair' oxidation mechanism is involved, the distribution of the products formed from either **1a** or **1b** should definitely be different. Due to the original and peculiar flat conformation of the six-membered ring of pinane [13] it was reasonable to expect that the hydroxylation could occur on both stereoisomers **1a** and **1b**. An intermediate ion pair should yield a mixture of two alcohols, except if the ion pair is so intimate that the stereochemistry of the starting hydrocarbon is retained in the tertiary hydroxylation product. If the positive charge develops significantly, it should be prone to yield (pathway (7), Fig. 2) the well known pinane–camphane skeleton rearrangement [12] to yield a primary alcohol which would be further oxidized into corresponding camphor. If a fragmentation should be involved (pathway (8), Fig. 2) the formation of various keto acids should be observed. The latter would result from the oxidative cleavage of the double bond of **10**.

Results

Examination of the results reported in Table 1 shows that neither the products formed from either **1a** or **1b**, nor the product distribution are the same. The oxidation occurs very rapidly in 1 h at 60 °C. Quite curiously no hydroxylation products are formed. Furthermore the chemical behaviour of the *cis/trans* mixture **1** (entry 1) does not reflect what is observed for either pure stereoisomer **1a** or **1b** (entries 2 and 3). In our opinion this is related to the association step(s) between the hydrocarbon and ruthenium tetraoxide (see 'Discussion'). The γ-lactone **2** which is the major compound

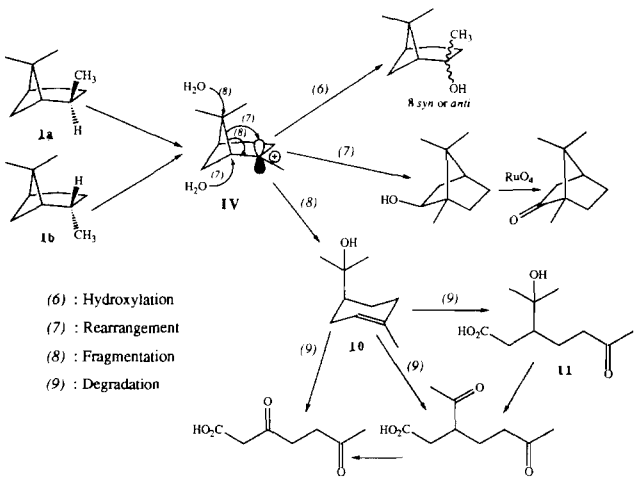

Fig. 2. Hydroxylation, rearrangement and fragmentation products expected from an intermediate free carbonium ion **IV** formed from *cis*- and *trans*-pinane (**1a** and **1b**).

TABLE 1. Products (%) formed from *cis*- and *trans*-pinane. The reactions were performed at 60 °C for 1 h in a 2/2/3 mixture of $CCl_4/CH_3CN/H_2O$ using $RuCl_3 \cdot 3H_2O$ 6% and $NaIO_4$ 4.2 equiv. Alcohol **8** is not formed under these conditions but only by using $Ca(OCl)_2$ 2.1 equiv. as reoxidizing reagent (see 'Experimental')

Entry	1a	1b	Overall yield (%)	2	3	4	5	6	7a	7b	8
1	65	35	65	36	7	12	10				
2	100		58	48	10						
3		100	74		7	26	29	8	6		

formed from **1a** (entry 2) is not observed when **1b** is submitted to strictly the same reaction conditions (entry 3). The formation of 10% of nopinone **3** from **1a** can only result from the cleavage of the carbon–carbon bond linked to the methyl group.

Discussion

Stereoisomer **1a** where the tertiary hydrogen is most likely to undergo hydroxylation because it is unhindered [4c, d], does not yield the expected tertiary alcohol **8** when sodium periodate is used as reoxidizing agent in the catalytic system. However this alcohol could be isolated in 42% yield when $Ca(OCl)_2$ was used (1 h at 60 °C) instead of $NaIO_4$. This observation emphasizes the important role of the reoxidizing reagent [7]. In order to explain the product formation, there are no reasons to consider intermediates different from those which have been considered so far (Fig. 3). The formation of an alkoxyhydroxydioxoruthenium **A** (Fig. 3)* looks reasonable. In the absence of a strong reoxidizing reagent, **A** is transformed into alcohol **8** followed by hydrolysis. The six oxidation state of ruthenium in intermediate **A** can be raised to seven, with sodium

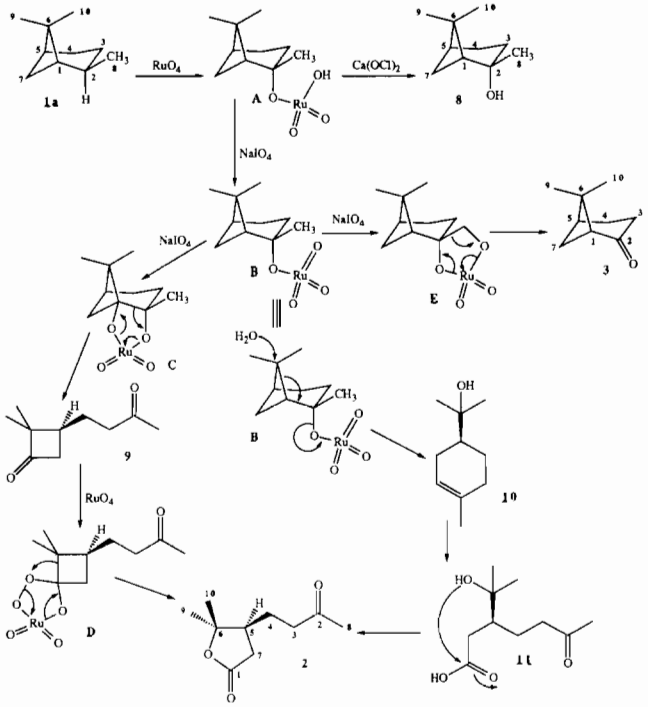

Fig. 3. Proposed mechanistic pathways for the catalytic oxidation of pure *cis*-pinane (**1a**) with RuO_4 generated *in situ*. The reactive intermediates as well as the compounds **9**, **10** and **11** are not isolated.

*Intermediate **A** (Fig. 3) has a structure corresponding to **II** (Fig. 1) which can be formed by a linear or a lateral approach.

periodate, but not with calcium hypochlorite. This explains why tertiary alcohol **8** can be obtained with the later reoxidizing reagent, and not with sodium periodate which oxidizes **A** into **B***. As soon as **B** is formed, it can either give rise to **C** by reaction of an oxoruthenium with the bridgehead hydrogen, or to **E** by reaction with one of the primary hydrogens of the 2-methyl group. Nopinone **3** is formed from the latter by a carbon–carbon single bond cleavage. Intermediate **C**, would be likely to undergo the same kind of reaction to yield cyclobutanone **9**. Baeyer Villiger reactions [14] have been previously observed with RuO_4 generated *in situ* [7]; it was therefore reasonable to assume that the carbonyl double bond of the strained cyclobutanone **9** could undergo an addition of RuO_4 (similar to the one observed for carbon–carbon double bonds with related oxo metals such as OsO_4 or MnO_4^- [15]. However such a reaction seems unlikely because cyclobutanone **9** prepared independently [16] remained unchanged when submitted to oxidation with RuO_4. However the formation of lactone **2** can be easily explained by the occurrence of intermediate **10** (Fig. 2). As shown in Fig. 3, the concerted attack of a water molecule on **B** yields **10** (without the need of having a genuine carbonium ion such as **IV** (Fig. 2)). This process compares to the one which allows the transformation of **G** into **4** or **F** into **7a** (Fig. 4). Further oxidative cleavage of the double bond of **10** yields keto hydroxyacid **11** which lactonizes into **2**. Indeed compound **10** (Fluka) yields lactone **2** with 55% yield when oxidized with RuO_4 generated *in situ*.

With the pure *trans* isomer **1b** (Fig. 4), the formation of an intermediate of type **II** (Fig. 1) is no longer possible, because of the steric hindrance of the 2-tertiary hydrogen which is *cis* with one of the methyl groups on carbon 6. The major products are diketones **4** and **5** which have a characteristic *trans* stereochemistry. These diketones are likely to result from a concerted fragmentation process where the cyclobutane ring has been cleaved. The attack of primary hydrogens of a methyl group appears to be a difficult process, and has not been observed until now; however the occurrence of an intermediate such as **E** (Fig. 3) is an indication in favour of such a process. The pseudo equatorial 9-methyl group is more prone to give an intermediate **G** (Fig. 4) that the more hindered pseudo axial 8-methyl group. Once, intermediate **G** is formed, the cyclobutane ring fragmentation can easily occur with simultaneous attack of a water molecule on bridgehead carbon 1 to yield **12** which is further oxidized into **13** to finally yield diketone **4**. Similarly, formation of diketone **5** can be explained by the attack of water on bridgehead carbon 5 of intermediate **G**. These considerations provide support for the ionic mechanism proposed by Bakke *et al.* [11] as a positive partial charge must develop on carbon 9 in order to explain the fragmentation reaction occurring on **G**.

It is also possible to consider the transformation of **G** into **H** because of the peculiar reactivity of the bridgehead hydrogens in bridged bicyclo[3.1.1]heptane derivatives [17]. Intermediate **H** can then be easily transformed into **13** and **4**. The bridgehead reactivity can be explained by the peculiar hybridation by which it is possible to describe the bridgehead C–H bond [17]. Until now, no bridgehead hydroxylation due to ruthenium tetraoxide had been observed except in the case of adamantane [4b]. However it was necessary to consider such a bridgehead hydrogen reactivity (Fig. 5) in the case of **14** which yields alcohol **15** (probably via the intermediate perruthenate **I**) and after further

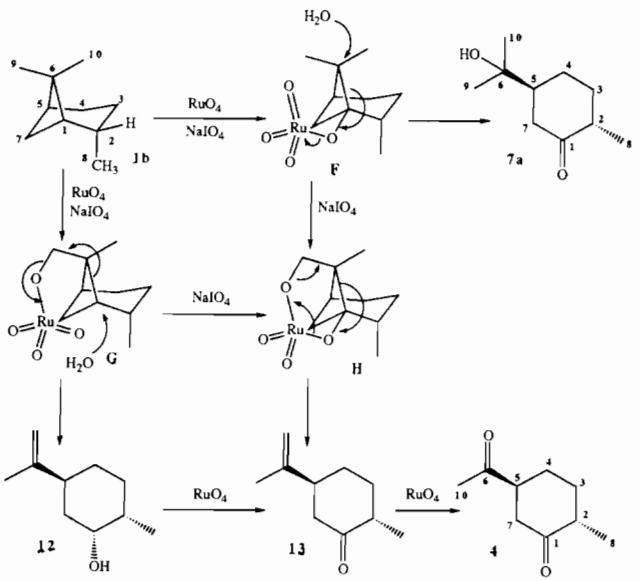

Fig. 4. Proposed mechanistic pathways for the catalytic oxidation of pure *trans*-pinane (**1b**) with RuO_4 generated *in situ*. The reactive intermediates as well as **12** and **13** are not isolated.

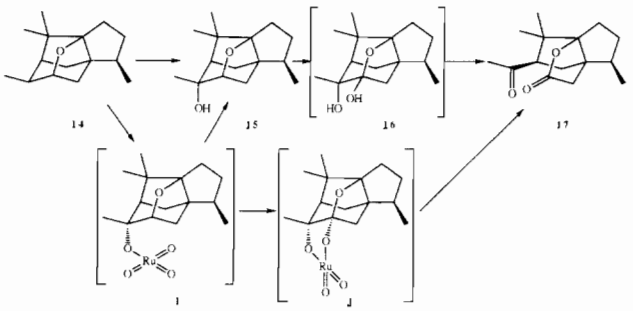

Fig. 5. Peruthenate and ruthenate intermediates involved in the hydroxylation (formation of **15**) and carbon–carbon bond oxidative cleavage (formation of **17**) of neoisocedranol oxide **14**.

*In the presence of $NaIO_4$, **A** can be further oxidized into **B** (Fig. 3) which has a structure which corresponds to **III** (Fig. 1); intermediates **F** or **G** (Fig. 4) have an analogous structure.

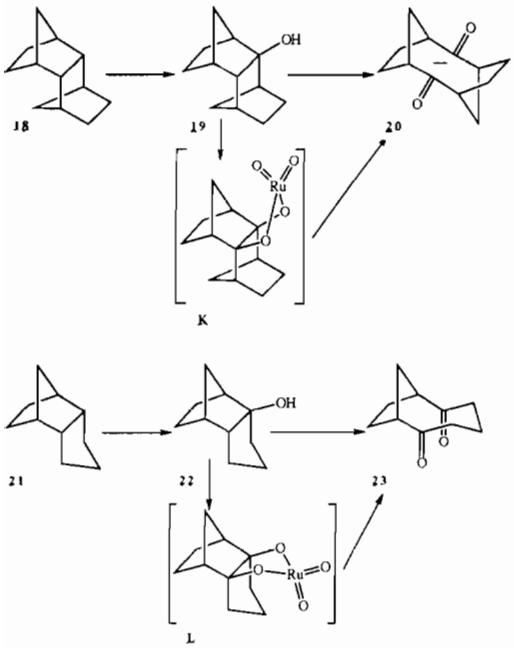

Fig. 6. Hydroxylation and carbon–carbon bond cleavage observed with RuO_4 generated *in situ* on *exo* vicinal hydrogens.

oxidation ketolactone **17**. The latter is likely to result from an oxidative degradation of the non-isolated glycol **16** or via ruthenate **J**. Structures such as **K** and **L** (Fig. 6) analogous to **J** have been considered by Bakke *et al.* [11] and ourselves [9] to explain the formation of **20** and **23**, respectively, from **18** and **21** although in both these cases the hydroxylation occurs on tertiary hydrogens located at ring junctions to yield **19** and **22**, respectively.

In view of all these considerations, it is reasonable to consider that a perruthenate **F** can be formed at the 1-bridgehead hydrogen of **1b** (Fig. 4). A fragmentation process followed by attack of water, similar to the one described for the formation of **4**, is then likely to occur to yield **7a**. Ketoalcohol **7b** can be formed by a similar process from a perruthenate similar to **F** formed on the bridgehead carbon 5 of **1b**. Because of the fragmentation of the cyclobutane ring in both cases, the partial positive charge does not develop on carbon 1 (or 5) which is going to be oxidized into a carbonyl, but on the nearby tetrasubstituted cyclobutane carbon.

Conclusions

Examination of the products formed by oxidation with RuO_4 generated *in situ* of *cis*- and *trans*-pinane (**1a** and **1b**) has shed more light on the intimate mechanism involved. Although carbon–carbon bond cleavage had already been observed, it is apparently the first time that the cleavage of a carbon–methyl bond is reported. It is now clear from our work that although disfavoured, primary hydrogens can nevertheless be attacked by RuO_4. Such oxidations can also lead to fragmentation products, provided a partial positive charge – as postulated by Bakke [11] – develops on the corresponding carbon. Finally the peculiar structure of the bicyclo[3.1.1] skeleton [13, 17] is at the origin of the reactivity of bridgehead hydrogens of the pinane skeleton. Until now, such a reactivity had only been observed in adamantane and does not exist in bridged bicyclo[2.2.1]heptane or bicyclo[3.2.1]octane derivatives.

Experimental

Analytical vapor phase chromatography (VPC) was performed with a Delsi Serial 330 apparatus using hydrogen as carrier gas (capillary column DB-1, 25 m) associated with a Spectra-Physics SP-4290 integrator.

'Merck Kieselgel 60' silica for flash chromatography (0.040–0.063 mm, 230–400 mesh ASTM) was used for separations by column liquid chromatography.

'Merck $60F_{254}$' silica on aluminium sheet was used for thin layer chromatography (TLC). Products were detected with a UV lamp operating at 254 or 365 nm. In some cases, spots were developed chemically with a solution of 5 ml of *p*-anisaldehyde in 90 ml of absolute EtOH with 5 ml of 98% H_2SO_4 and 1 ml AcOH (solution A).

IR spectra (IR) were recorded on a Philips PU-9706 spectrometer either in solution or as films. Frequencies are reported in cm^{-1}.

Proton NMR spectra (^1H NMR) were recorded either on a Bruker AC-200 or a Varian Gemini for the 200 MHz spectra, or on a Bruker AMX-400 for the 400 MHz spectra. Chemical shifts (δ 10^{-6}) are given in ppm relative to TMS taken as an internal reference. Singlets, doublets, triplets, quadruplets and unresolved broad signals are identified by the letters s, d, t, q and m, respectively, placed after the value of the corresponding chemical shift. Coupling constants *J* are given in Hertz.

Carbon-13 NMR spectra (^{13}C NMR) were recorded on a Bruker AC-200 or a Varian Gemini at 50.3 MHz, or on a Bruker AMX-400 at 100.6 MHz. Assignments were made with APT (attached proton test) or/and by DEPT (distorsionless enhancement by polarisation transfert). Chemical shifts (δ 10^{-6}) are given in ppm relatively to TMS. Letters p, s, t and q, which follow these values, are relative to primary, secondary, tertiary and quaternary carbons, respectively.

Mass spectrometry coupled with vapor phase chromatography (MS/VPC) was carried out with an R-10-10 Nermag machine (capillary column DB1, 30 m).

Elemental analysis were done at the 'Service de Microanalyse de la Faculté des Sciences et Techniques de Marseille'.

Melting points were recorded with a Reichert Microscope.

Preparation of pinane (1)

3 g of β-pinene (22.1 mmol) (or α-pinene) in 20 ml of diethyl ether are introduced into a 50 ml one-necked round bottomed flask. Palladium (10%) on charcoal (254 mg) is added with a spatula (altogether 1% Pd relatively to pinene), and the mixture is stirred with a magnetic stirrer. Air is removed from the flask by vacuum, and the flask is fitted with a stopcock connected with a rubber balloon filled up with hydrogen. The reaction mixture is energetically stirred for 24 h. Afterwards it is filtered on celite. Ether is removed at atmospheric pressure, and the residue is distilled at atmospheric pressure to yield 2.98 g of colourless pinane (**1**) (98%) which is a mixture of *cis*- and *trans*-pinane (65:35) according to VPC.

B.p. (P_{atm} = 170 °C).

IR ($CHCl_3$): 2920, 2880, 1460, 1380, 1370, 1120.

^{1}H NMR ($CDCl_3$): *cis*: 2.40–2.20 (m, 1H), 2.20–1.20 (m, 8H), 1.17 (s, 3H), 1.01 (s, 3H), 0.84 (d, 3H J = 6.7 Hz); *trans*: observation of 8-methyl group at 0.87 (d, 3H, J = 6.8 Hz).

^{13}C NMR ($CDCl_3$): *cis*: 48.16 (t, C_1), 41.44 (t, C_5), 38.86 (q, C_6), 36.03 (t, C_2), 34.01 (s, C_7), 28.35 (p, C_8), 26.60 (s, C_4), 23.90 (s, C_3), 23.24 (p, C_9), 22.92 (p, C_{10}); *trans*: 47.72 (t, C_1), 40.97 (t, C_5), 39.53 (q, C_6), 29.41 (t, C_2), 26.87 (p, C_8), 24.66 (s, C_7), 24.00 (s, C_3), 23.08 (s, C_4), 21.63 (p, C_{10}), 20.10 (p, C_9).

Oxidation of pinane (1)

Typical procedure

1.38 g (10 mmol) of pinane (**1**) dissolved in the ternary mixture (CCl_4/CH_3CN/H_2O:12/12/18 by volume) are introduced into a 100 ml one-necked round bottomed flask fitted with a condenser. The $RuCl_3 \cdot 3H_2O$ (160 mg, 6%) catalyst and the reoxidizing reagent $NaIO_4$ (9 g, 4.2 equiv.) are introduced with a spatula. The mixture is stirred magnetically for 1 h at 60 °C. The reaction medium becomes yellow (presence of RuO_4) and then progressively black as the reaction proceeds (formation of RuO_2). After the reaction mixture has returned to room temperature, it is filtered on celite and washed with 20 ml brine, whereas the aqueous phase is extracted successively with 20 ml and twice 10 ml of CH_2Cl_2. The organic phases are brought together, dried on $MgSO_4$ and filtered on celite. The product obtained after concentration with a rotavapor is chromatographed on silica. The following products are eluted with pentane/ether mixture.

When 1.38 g (10 mmol) of *cis/trans* mixture of pinane (**1**) are treated for 1 h at 60 °C, under the above described conditions, one obtains successively: 660 mg (36%) of keto-lactone **2**, 100 mg (7%) of nopinone **3**, 180 mg (12%) of diketone **4** and 160 mg (10%) of diketone **5**.

Product 2

White crystals, m.p. = 45 °C; b.p. (1 mmHg) = 160 °C; R_f = 0.24 (pure ether); solution A (yellow spot).

IR ($CHCl_3$): 2960, 2920, 1750, 1700, 1400, 1370, 1270, 1200, 1160, 1120, 1090, 950.

^{1}H NMR ($CDCl_3$): 2.60–2.00 (m, 5H), 2.11 (s, 3H), 1.85–1.65 (m, 1H), 1.60–1.40 (m, 1H), 1.39 (s, 3H), 1.21 (s, 3H).

^{13}C NMR ($CDCl_3$): 207.15 (q, C_7), 175.08 (q, C_1), 86.53 (q, C_4), 44.97 (p, C_8), 41.68 (s, C_6), 34.61 (s, C_2), 29.92 (t, C_3), 27.24 (p, C_9), 23.07 (s, C_5), 21.72 (p, C_{10}).

MS/VPC (*m/z* (%)): 184 (0), 166 (7), 151 (3), 127 (4), 111 (11), 98 (12), 82 (4), 68 (6), 55 (10), 43 (100), 27 (4).

Anal. Calc. for $C_{10}H_{16}O_3$ (M = 184.237): C, 65.19; H, 8.75. Found: C, 65.40; H, 9.12%.

Product 3

Light yellow liquid; R_f = 0.62 (pure ether); solution A (violet spot).

IR ($CHCl_3$): 2950, 1700, 1470, 1370, 1320, 1290, 1220.

^{1}H NMR ($CDCl_3$): 2.68–1.84 (m, 7H), 1.62–1.56 (m, 1H), 1.34 (s, 3H), 0.86 (s, 3H).

^{13}C NMR ($CDCl_3$): 214.87 (q, C_2), 57.96 (t, C_1), 41.21 (q, C_6), 40.39 (t, C_5), 32.79 (s, C_3), 25.90 (p, C_8), 25.25 (s, C_7), 22.12 (p, C_9), 21.40 (s, C_4).

Product 4

Colourless liquid; R_f = 0.48 (pure ether); solution A (green spot).

IR ($CHCl_3$): 2960, 2920, 2860, 1700, 1450, 1420, 1340, 1210, 1160.

^{1}H NMR ($CDCl_3$): 2.85–2.60 (m, 1H), 2.50–2.20 (m, 3H), 2.20–1.95 (m, 1H), 2.12 (s, 3H), 1.80–1.10 (m, 3H), 0.97 (d, 3H, J = 6.5 Hz).

^{13}C NMR ($CDCl_3$): 211.45 (q, C_7), 208.19 (q, C_1), 52.10 (t, C_5), 44.55 (t, C_2), 42.69 (s, C_6), 34.51 (s, C_3), 28.25 (p, C_8), 27.78 (s, C_4), 14.23 (p, C_9).

MS/VPC (*m/z* (%)): 154 (9), 111 (100), 97 (9), 83 (13), 71 (8), 55 (100), 43 (100), 27 (12).

Anal. Calc. for $C_9H_{14}O_2$ (M = 154.211): C, 70.10; H, 9.15. Found: C, 69.95; H, 9.60%.

Product 5

Colourless liquid; R_f = 0.46 (pure ether); solution A (brown spot).

IR ($CHCl_3$): 2960, 2920, 2860, 1700, 1450, 1420, 1340, 1210, 1160.

^{1}H NMR ($CDCl_3$): 2.65–2.25 (m, 4H), 2.13 (s, 3H), 2.10–1.85 (m, 2H), 1.55–1.10 (m, 2H), 0.93 (d, 3H, J=6.5 Hz).

^{13}C NMR ($CDCl_3$): 209.51 (q, C_7), 209.46 (q, C_1), 57.03 (t, C_3), 42.27 (s, C_2), 40.42 (s, C_6), 33.49 (s, C_5), 32.94 (p, C_8), 30.14 (t, C_4), 19.06 (p, C_9).

MS/VPC (*m/z* (%)): 154 (9), 125 (3), 111 (46), 97 (18), 83 (8), 70 (21), 55 (100), 43 (86), 27 (12).

Anal. Calc. for $C_9H_{14}O_2$ (M=154.211): C, 70.10; H, 9.15. Found: C, 70.00; H, 9.50%.

Oxidation of cis-pinane (1a)

(a) When 1.38 g (10 mmol) of *cis*-pinane (**1a**) are treated for 1 h at 60 °C, under the above described conditions (reoxidizing reagent: 4.2 equiv. $NaIO_4$), one obtains successively: 880 mg (48%) of keto-lactone **2** and 130 mg (10%) of nopinone **3**.

(b) When 1.38 g (10 mmol) of *cis*-pinane (**1a**) are treated for 1 h at 60 °C, under the above described conditions (reoxidizing reagent: 2.1 equiv. $Ca(OCl)_2$, one obtains 650 mg (42%) of alcohol **8**.

Product 8

White solid; m.p. = 58–60 °C; R_f=0.60 (pentane:ether =1:1); solution A (blue spot).

IR ($CHCl_3$): 3420, 2880, 1450, 1370, 1160, 1120, 1090, 1070, 910, 890, 850.

^{1}H NMR ($CDCl_3$): 2.15–2.02 (m, 1H), 1.86–1.66 (m, 7H), 1.39–1.25 (m, 1H), 1.22 (s, 3H), 1.16 (s, 3H), 0.86 (s, 3H).

^{13}C NMR ($CDCl_3$): 75.03 (q, C_2), 54.47 (t, C_1), 40.77 (t, C_5), 38.30 (q, C_6), 31.80 (s, C_7), 31.35 (p, C_8), 27.69 (p, C_9), 27.38 (s, C_4), 24.95 (s, C_3), 23.51 (p, C_{10}).

Anal. Calc. for $C_{10}H_{18}O$ (M=154.254): C, 77.87; H, 11.76. Found: C, 77.80; H, 11.60%.

Oxidation of trans-pinane (1b)

When 1.38 g (10 mmol) of *trans*-pinane (**1b**) are treated for 1 h at 60 °C, under the above described conditions (reoxidizing reagent: 4.2 equiv. $NaIO_4$), one obtains successively: 100 mg (7%) of nopinone **3**, 390 mg (26%) of diketone **4** and 440 mg (29%) of diketone **5**, 120 mg (8%) of ketone **6** and 100 mg (6%) of the mixture of alcohols **7a** and **7b**.

Product 6

Liquid.

IR ($CHCl_3$): 2960, 2880, 1690, 1450, 1380, 1270, 1220, 910.

^{1}H NMR ($CDCl_3$): 2.60–1.40 (m, 7H), 1.27 (s, 3H), 1.00 (d, 3H, J=6.7 Hz), 0.78 (s, 3H).

^{13}C NMR ($CDCl_3$): 214.64 (q, C_2), 57.89 (t, C_1), 47.15 (t, C_5), 41.99 (s, C_3), 41.64 (q, C_6), 26.52 (t, C_4), 26.04 (p, C_8), 22.08 (s, C_7), 21.76 (p, C_{10}), 20.34 (p, C_9).

MS/VPC (*m/z* (%)): 152 (5), 137 (13), 123 (2), 109 (25), 95 (31), 83 (94), 67 (23), 55 (100), 41 (50), 27 (27).

Products 7a and 7b

Liquid (the mixture could not be separated); R_f=0.34 (pure ether); solution A (yellow spot).

IR ($CHCl_3$): 3420, 2940, 2880, 1690, 1450, 1380, 1320, 1220, 1130, 940, 920.

^{1}H NMR ($CDCl_3$): 2.52–1.78 (m, 6H), 1.76–1.18 (m, 3H), 1.18–0.80 (m, 9H).

^{13}C NMR ($CDCl_3$): **a**: 213.81 (q, C_1), 71.81 (q, C_8), 50.69 (t, C_5), 44.68 (t, C_2), 43.16 (s, C_6), 34.64 (s, C_3), 27.05 (p, C_9), 26.97 (p, C_{10}), 26.29 (s, C_4), 14.23 (p, C_7); **b**: 214.60 (q, C_1), 73.19 (q, C_7), 51.44 (t, C_3), 40.15 (s, C_2), 37.43 (s, C_6), 30.15 (s, C_5), 29.20 (t, C_4), 27.99 (p, C_8), 27.58 (p, C_9), 22.19 (p, C_{10}).

Oxidation of cyclobutanone 9 (prepared according to ref. 16)

When 340 mg (2 mmol) of cyclobutanone **1a** are treated for 1 h at 60 °C under the above described conditions (reoxidizing reagent: 4.2 equiv. $NaIO_4$), no reaction is observed.

Oxidation of α-terpineol 10 (Fluka)

When 1.54 g (10 mmol) of α-terpineol **10** (Fluka) are treated for 1 h at 60 °C, under the above described conditions (reoxidizing reagent: 4.2 equiv. $NaIO_4$), 1.00 g (55%) of keto-lactone **2** is obtained.

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