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Permanganate–periodate oxidation. Part VIII. The oxidation of some cyclic mono-olefins and monoterpenes[1]

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The reaction of cyclic mono-olefins with the permanganate–periodate reagent was investigated. 4-Terpinenol and its acetate, and to a lesser degree α-terpineol and camphene gave in addition to the expected products, several neutral and acidic products. In contrast, α-pinene, β-pinene, sabinene, pulegone, and several cyclo-olefins which can be considered as simple analogues of these monoterpenes, afforded the predicted products in high yield. Cyclo-hexanone and menthone, though saturated, were oxidized extensively, enolization offering a plausible pathway for this result. Saturated terpene alcohols reacted only very slowly indicating that attack at a tertiary hydrogen is not a significant part of the permanganate–periodate reaction.

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Introduction

Recently we have shown that the common acyclic monoterpenes may be oxidized by the permanganate–periodate reagent in high yield to predicted end products (1). In a preliminary experiment it was found that α-terpineol did not give a high yield of the expected product, homoterpenyl methyl ketone. In view of this, and of the different behavior of some dienes as reported recently by Klein and Rojahn (2), Apsimon *et al.* (3), and von Rudloff (4), the oxidation of some cyclic monoterpenes and related cyclo-olefins was studied with the specific purpose of determining whether or not the cyclic mono-olefins, and in particular monoterpenes, would react as predicted with the permanganate–periodate reagent.

Daly and co-workers (5) have employed the reagent in a preparative oxidation of sabinene to yield sabina ketone. We reported briefly (6) on the excellent yields of sabina ketone and nopinone which may be obtained from sabinene and β-pinene respectively, and that the oxidation proceeds at a satisfactory rate in aqueous suspension. Our previous studies (1, 7–12) have shown that the oxidation of an olefinic double bond proceeds in a predictable manner, involving hydroxylation of the double bond by a permanganate ion (via a π complex and hypomanganate ester (13) (see also Wiberg and Geer (14)), followed by periodate cleavage of the diol or ketols thus formed, and subsequent slower oxidation of the resulting aldehydes. Ketones and esters were found to be stable towards the reagent (at pH 7 to 8), whereas alcohols reacted slowly (12). With water-insoluble olefins good results were obtained when the reaction was carried out in aqueous *tert* butyl alcohol solutions (10–50%) (1, 11, 12).

In a few instances, the reaction with mono-olefins did not proceed to the predicted end products. Thus Lin and Cheng (15) reported that 1-cyclopentene-, 1-cyclohexene-, and 1-cycloheptene-carboxylic acids were oxidized to the next lower dicarboxylic acid rather than the expected keto-dicarboxylic acids. We found that carboxylic acids, including pyruvic acid, are not oxidized, although malonic acid was degraded slowly (12). In the same study we found that tetrahydrofurfurol was oxidized to succinic acid rather than to tetrahydro-2-furoic acid. Thus, in certain instances at least, over-oxidation of the type reported by Lin and Cheng must be considered as a possible side reaction.

Experimental

All compounds investigated were of commercial origin (Aldrich Chemical Co., unless otherwise stated). Sabinene was isolated from the oil of Savin (16). If the purity was satisfactory (see Tables I and II) these compounds were used as such. Impure ones were purified as described.

The purity of the starting materials was determined by gas–liquid chromatography (g.l.c.), employing temperature-programming or isothermal conditions and a flame ionization detector. Stainless steel columns, 0.3 cm outer diameter and 2–3 m long, and helium flow rates of 25–40 ml per min were employed. Of the many liquid phases and solid supports tested, polyethyleneglycol (Carbowax 20 *M*, 2%) on Porasil D, 100–150 mesh (17) was found to give the highest degree of separation of cyclo-olefins. For the oxygenated terpenes a standard 5% polyethylene

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glycol column on Aeropak 30, 70–80 mesh (1, 18) was employed. The quantitative area measurements were obtained with a model 471 Varian Aerograph digital integrater. No correction factors were applied. The standard run was from 55° to 200° at 4° per min (18), but for the lower boiling olefins, a lower starting temperature (40°–50°) and lower rate of heating (2° per min) or isothermal conditions were employed.

Melting points were recorded on a Leitz hotstage microscope and these are uncorrected. Infrared (i.r.) spectra were obtained as films between sodium chloride plates or as potassium bromide disks, using a Perkin–Elmer model 21 double beam spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were obtained in carbon–tetrachloride solution with tetramethylsilane as internal standard, using a Varian model HA-100 MHz spectrometer.

The quantitative and preparative oxidation procedures were described in detail previously (1, 7, 12). Tables I and II list the purity of the starting materials as determined by g.l.c., the amount of *tert* butyl alcohol used, the results obtained after 1, 6, 24, 144, and 196 h reaction time (the data obtained after 0.5, 2, 3, 48, 72, 96, and 120 h are not included), as well as the products obtained in the preparative oxidations. Neutral products were recovered by extracting the oxidation mixture with ether and removing the solvents as far as possible by fractional distillation. The weakly alkaline aqueous residue was evaporated to a small volume, the distillate being used for formaldehyde determination by the chromotropic acid method (8). The residual aqueous concentrate was acidified and extracted continuously (1–5 days) with ether to recover the acidic oxidation products. A small aliquot was methylated by the addition of freshly distilled diazomethane (best results were obtained by passing the vapors into a concentrated solution of the acidic product) and the resulting methyl esters were analyzed by g.l.c. (5% SE-30). The balance of the acidic product was used for recrystallization or the preparation of suitable crystalline derivatives. The experimental data for those compounds which gave the expected products in high yield have been placed into the Depository of Unpublished Data.[3]

Allyl Cyclohexane

The commercial sample was found to have a purity of 99.9% by g.l.c. (see, however, below). Preparative oxidation (248 mg, 2 mmoles; 20% *tert* butyl alcohol, 24 h) gave formaldehyde and a liquid acidic product (222 mg, 78%, ν_{max} (liquid) 1703, 1293, and 929 cm^{-1}), the methyl ester of which showed only a single peak with the retention time of the methyl ester of cyclohexane acetic acid. The identity was confirmed by conversion to the amide, m.p. 169–170° (lit (19) m.p. 169–171°). In a repeat experiment the neutral fraction (mainly *tert* butyl alcohol) was analyzed by g.l.c. and a peak with the retention time of allyl cyclohexane was recorded. Fractional distillation gave a small amount of a saturated hydro-carbon which had an i.r. spectrum that differed from that of allyl cyclohexane, but *tert* butyl alcohol was an impurity.

(±)-Camphene

The commercial sample (Lights and Co., England) was purified by preparative g.l.c. to give 98.0% pure camphene. Preparative oxidation (544 mg, 4 mmoles, 5–10% *tert* butyl alcohol, 24 h) afforded a neutral (530 mg) and an acidic (12 mg) product. Analysis by g.l.c of the neutral product showed the presence of *tert* butyl alcohol, unchanged camphene, and a major peak with the retention time of camphenilone. The identity of camphenilone was confirmed by conversion to the crystalline semicarbazone, m.p. and mixed m.p. 221.5–223° (lit. (20) m.p. 224°).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.52; H, 8.77; N, 22.0.

When the reaction was carried out in 30% *tert* butyl alcohol solution, virtually all the camphene reacted but in addition to camphenilone, a neutral compound of much higher retention time (not the same as the derived diol or ketol) and a larger amount of acidic products were obtained.

α-Terpineol

The commercial sample (Eastman Organic Chemical) was found to be 98.6% pure; m.p. 33.5–34.5°. In the preparative oxidation (310 mg, 2 mmoles; 10% *tert* butyl alcohol, 48 h) the neutral product (247 mg, 67%) was extracted with chloroform instead of with ether. Although the i.r. spectrum, ν_{max} (liquid) 1760 cm^{-1} (γ-lactone) and 1708 cm^{-1} (carbonyl), was in good agreement with that of homoterpenyl methyl ketone, g.l.c. analysis showed that at least 3 major and 3 minor impurities as well as some unchanged α-terpineol were present. The retention times of the major impurities (5% SE-30 at 120°; 8.7, 10.5, and 11.5 min) were higher than that of α-terpineol (3.5 min) but lower than that of homoterpenyl methyl ketone (18.0 min). Homoterpenyl methyl ketone semicarbazone, m.p. and mixed m.p. 204.5–205.5°, was obtained in fairly good yield from the crude product. A small amount of an acidic product (74.2 mg) was also isolated. The chromatogram of the derived methyl esters showed 4 major and 12 minor peaks.

α-Terpinyl Acetate

Commercial α-terpineol was acetylated by heating under reflux with a 6-fold amount of acetic anhydride, an equal amount of sodium acetate, and a 15-fold amount of xylene for 12 h. Crude α-terpinyl acetate was purified by fractional distillation, b.p. 78–78.5° (1 mm), n_D^{25} 1.4621, 95% (g.l.c.).

Preparative oxidation (400 mg, 2.04 mmole; 10% *tert* butyl alcohol, 72 h) gave a small amount of neutral product (24 mg) and a liquid acidic product (489 mg, 98.5% based on the assumption of it being the expected acidic product). The neutral product showed at least 8 peaks in g.l.c. analysis, one of which corresponded to α-terpinyl acetate. Analysis by g.l.c. of the derived methyl esters of the acidic product showed one major peak (95%) and a broad tail (3–5%), indicating an impurity or decomposition. The acidic product was hydrolyzed with sodium ethoxide in excess ethanol. On acidification a neutral product was obtained which had an i.r. spectrum that was superimposable with that of homoterpenyl

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[3] Photocopies may be obtained upon request to: The Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Canada.

TABLE I

Permanganate–periodate oxidation of some cyclo-olefins

Compound	Purity* %	Oxidant consumed (atoms oxygen/mole)						% *tert* Butyl alcohol	Oxidation product (% yield) and remarks
		1 h	6 h	24 h	144 h	196 h	Calcd.		
Cyclopentene	98.5	3.54	3.92	3.97	4.10	—	4	20	Glutaric acid (99)
Cyclohexene	99.2	3.64	3.75	3.79	3.98	—	4	20	Adipic acid (98)
1-Methyl cyclopentene	99.7	2.59	2.71	2.72	3.19	—	3	20	5-Ketohexanoic acid (92)
1-Methyl cyclohexene	100.0	2.35	2.73	2.82	3.09	—	3	20	6-Ketoheptanoic acid (94)
3-Methyl cyclohexene	99.4	3.64	3.91	3.92	4.09	—	4	20	2-Methyl adipic acid (96)
4-Methyl cyclohexene	94.8	3.58	3.74	3.79	4.04	—	4	20	3-Methyl adipic acid (94)
Methylene cyclohexane	99.8	2.99	3.21	3.37	—	4.11	4	20	Cyclohexanone (95) + CH_2O
Vinyl cyclohexane	100.0	3.80	4.05	4.15	—	4.56	5	10	Cyclohexane carboxylic acid (91) + CH_2O
Allyl cyclohexane	99.9†	3.69	3.90	3.99	4.29	—	5	20	Cyclohexane acetic acid (78) + CH_2O
1-Methyl cycloheptene	99.5	2.61	2.96	3.01	3.10	—	3	20	7-Keto octanoic acid (95)
4-Vinyl cyclohexene	97.4	5.04	5.34	5.58	—	6.05	9	20	Butane-1,2,4-tricarboxylic acid (58)
Cyclohexanol	100.0	0.08	0.10	0.17	—	1.39	1	0	—
Cyclohexane-methanol	100.0	0.06	0.13	0.16	—	0.58	2	0	—
2-Cyclohexen-1-ol	98.1	4.65	5.38	5.85	—	—	6	10	Glutaric acid (98)
Cyclohexene oxide	99.5	0.00	0.08	0.20	1.00	—	0	10	—
3-Cyclohexene-1-carboxylic acid	98.2	3.40	3.85	3.97	4.12	—	4	0	Butane-1,2,4-tricarboxylic acid (58)
Cyclohexanone	100.0								Adipic acid
a)		0.02	0.18	0.78	2.21	—	(3)	0	0.5 times K_2CO_3
b)		0.05	0.20	1.09	2.60	—		0	1.0 times K_2CO_3
c)		0.05	0.46	1.13	2.59	—		0	2.0 times K_2CO_3

*As determined by g.l.c.

†See text.

methyl ketone. The melting point of the derived semicarbazone, m.p. 202.5–204.5° was undepressed in admixture with the authentic specimen. This confirmed that the oxidation product from α-terpinyl acetate was the acetate of homoterpenyl methyl ketone.

4-Terpinenol

The commercial sample (Lights and Co., England) was found to be 98.5% pure. Preparative oxidation (616 mg, 4 mmoles; 10% *tert* butyl alcohol, 6 h) gave a neutral (62.8 mg) and an acidic (426.7 mg) product. The neutral product showed 5 peaks with higher retention times than 4-terpinenol, and the derived methyl esters of the acidic product 1 major and 10 minor peaks. The spectrum of the crude acidic product ν_{max} (liquid) 1718, 1285, 1205, and 918 cm^{-1} (COOH), confirmed that the major product was a keto acid but no crystalline semicarbazone or 2,4-dinitrophenyl hydrazone could be obtained.

4-Terpinenyl Acetate

This acetate was prepared from 4-terpinenol in the same manner as α-terpinyl acetate (see above); b.p. 71–73° (1.3 mm), n_D^{25} 1.4623; 95% (g.l.c.). Preparative oxidation (785 mg, 4 mmoles; 10% *tert* butyl alcohol, 6 h) afforded a small amount of a neutral product (27.3 mg) and a liquid acidic product (416 mg); g.l.c. analysis of the derived methyl esters showed it to be composed of 3 major and 4 minor components. The i.r. spectrum of the sodium salts, ν_{max} (KBr) 1735 (OCOCH$_3$), 1707 (CO), 1566 and 1398 cm^{-1} (COO$^{\ominus}$) confirmed that the acetate of a keto acid was present, but no crystalline derivatives were obtained.

Results and Discussion

The amounts of oxidant consumed by the cyclic olefins at different reaction times are shown in Table I. Cyclopentene, cyclohexene, the methyl substituted derivatives, and 1-methyl cycloheptene, as well as the cyclohexanes with exocyclic double bonds all reacted in the expected manner and the predicted end products were isolated in high yield. The 1-methyl cyclo-olefins reacted more slowly than the other cyclo-alkenes. Allyl cyclohexane consumed less than the calculated 5 atoms of oxygen per mole and cyclohexane acetic acid was obtained in only about 78% yield. A saturated impurity having the same retention time on the PEG-Porasil column as allyl cyclohexane was found to be present and this can account for the low results obtained. Similarly, 4-vinyl cyclohexene afforded only a 58% yield of the expected butane-1,2,4-tricarboxylic acid.

Several oxygenated cyclohexane derivatives were also oxidized (see Table I). As expected (7, 12) cyclohexanol, cyclohexane-methanol and cyclohexene oxide consumed oxidant only at a very slow rate. Cyclohexanone consumed very little oxidant during the first 6 h, but thereafter a steady increase was measured, which reached the equivalent of 2.60 atoms of oxygen per mole of cyclohexanone after 7 days. Hence, it appeared that cyclohexanone enolized under conditions which did not produce any oxidation with aliphatic ketones (12). Once a double bond is formed, one would expect hydroxylation, cleavage, and further oxidation to proceed in the normal manner. It was confirmed that enolization is involved by employing one-half and twice the normal concentration of potassium carbonate, when a corresponding decrease and increase in the rates of oxidation was obtained (see Table I). 2-Cyclohexen-1-ol consumed the calculated amount of oxidant in about 3 days and the predicted end product, glutaric acid, was obtained in 98% yield. Similarly, the oxidation of 3-cyclohexene-1-carboxylic acid proceeded as expected. This is in contrast to the results reported by Lin and Cheng for the oxidation of 1-carboxyl cyclo-olefins (15), but the latter must be considered a special case because of the conjugated nature for the double bond.

The results obtained in the oxidation of some cyclic monoterpenes are shown in Table II. (−)-α-Pinene was oxidized smoothly to (−)-pinonic acid. The almost quantitative oxidation of β-pinene and sabinene to nopinone and sabina ketone respectively employing the aqueous reagent (6) was confirmed. It is noteworthy that the retentions of nopinone and sabina ketone differ considerably on most g.l.c. columns, whereas β-pinene and sabinene are not easily separated. The facile oxidation of the latter to the corresponding ketones offers a convenient method for detecting one terpene in the other.

Camphene did not react appreciably with the aqueous reagent, presumably because this terpene is a solid at room temperature. The reaction proceeded only at a satisfactory rate when 30% *tert* butyl alcohol was added. The expected product, camphenilone, was obtained in only about 50% yield. In addition to this, a mixture of acidic products and at least one higher boiling neutral compound was formed. Upon reducing the *tert* butyl alcohol content of the reaction mixture, the relative yield of camphenilone increased but the amount of camphene which reacted was reduced. Hence it appears that the presence of *tert* butyl alcohol tends to increase side-reaction and undesirable by-products.

α-Terpineol was oxidized to the predicted homoterpenyl methyl ketone, but g.l.c. analysis of the neutral fraction showed the presence of 3

TABLE II

Permanganate-periodate oxidation of some cyclic monoterpenes

Compound	Purity* %	Oxidant consumed (atoms oxygen/mole)					% *tert* Butyl alcohol	Oxidation products (% yield) and remarks
		1 h	6 h	24 h	144 h	Calcd.		
(−)-α-Pinene	98.9	2.79	3.06	3.18	3.48	3	20	(−)-Pinonic acid (84)
(−)-β-Pinene	96.5	2.30	2.98	3.50	4.02	4	20†	(−)-Nopinone (95)
(+)-Sabinene	97.3	2.46	2.79	3.23	3.84	4	20†	(−)-Sabina ketone (96)
(±)-Camphene	98.0	0.72	2.60	2.93	3.88	4	30†	(±)-Camphenilone (~50)
α-Terpineol	98.6	2.15	2.31	2.39	3.22	3	10	Homoterpenyl methyl ketone (~50)
α-Terpinyl acetate	95.0	2.60	2.68	2.83	3.34	3	10	Homoterpenyl methyl ketone acetate (94)
4-Terpinenol	98.5	2.35	2.85	3.30	4.09	3	10	Complex mixture of products
4-Terpinenyl acetate	95.0	2.85	3.07	3.33	4.53	3	10	
(+)-Pulegone	94.0	2.93	3.15	3.28	—	3	10	3-Methyl adipic acid (75)
Dihydro-α-terpineol	98.3	—	0.30	0.30	0.72	0	10	—
(−)-Menthol	99.8	0.00	0.05	0.05	0.10	0	10	—
(±)-Borneol	99.5	0.00	0.05	0.05	0.15	0	10	—
(±)-Isoborneol	100.0	0.00	0.10	0.10	0.15	0	10	—
(−)-Menthone	99.5							
a)		0.00	0.25	0.74	1.65	(3–4)	10	0.5 times K_2CO_3
b)		0.00	0.25	0.80	1.75		10	1.0 times K_2CO_3
c)		0.05	0.40	0.82	1.83		10	2.0 times K_2CO_3

*As determined by g.l.c.

†Preparative oxidation also carried out in aqueous suspensions.

major and 3 minor compounds. The formation of additional neutral products cannot be explained by over-oxidation, as the amount of oxidant consumed did not exceed the theoretical to any appreciable extent (see Table II). Hence, the possibility of the introduction of hydroxyl groups at tertiary hydrogen atoms by reaction with permanganate as reported by Eastman and Quinn (21) was investigated. Dihydro-α-terpineol, menthol, borneol, and isoborneol were oxidized under the same conditions. These saturated alcohols consumed oxidant at a very low rate (see Table II). Hence, any oxidation of a tertiary hydrogen with the permanganate–periodate reagent proceeds at such a slow rate, if at all, that it cannot account for the formation of the additional neutral products in the reaction with α-terpineol. When α-terpinyl acetate was oxidized, both the rate of oxidation (Table II) and the high yield of a single acidic product, which gave homoterpenyl methyl ketone on hydrolysis and acidification, indicated that the typical route of permanganate–periodate oxidation was followed. It appears likely that the side reactions encountered with α-terpineol are not of a general nature, but rather arise from some specific property of this terpene alcohol. This concept was strengthened by the results obtained in the oxidation of 4-terpinenol and its acetate. Not only did both mono-olefins consume more than the calculated amount of oxidant (Table II, 4.1 and 4.5 respectively instead of 3.0 atoms of oxygen per mole), but both gave a rather large number of neutral and acidic products. With these two terpenes it is possible that a reactive methylene group is produced which is oxidized further and may thus lead to a variety of products. Also, one cannot rule out the formation of oxides, as found by Klein and Rojahn (2) in the permanganate oxidation of 1,5-dienes, by Apsimon *et al.* (3) in the oxidation of methyl pimarate, and by us (4) in the oxidation of occidentalol.

When the oxidation of menthone was carried out with different amounts of potassium carbonate, similar results (Table II) as those with cyclohexanone were obtained (see Table I). Hence, enolization may play a considerable role with saturated cyclic ketones unless the pH is kept below 7.5. The reaction with pulegone proceeded in the typical manner and a high yield of the predicted product, 3-methyl adipic acid, was obtained. Therefore, the hydroxylation of the double bond and subsequent cleavage of the diols and ketols produced proceeds rapidly and without any significant side reaction with a conjugated ketone.

It may be concluded that most cyclic mono-olefins react with the permanganate–periodate reagent as predicted to give high yields of the expected products. However, the side-reactions encountered with 4-terpinenol and its acetate, and to a lesser extent with α-terpineol and camphene, indicate that with certain monoterpenes random degradation may take place to such a large degree that the reagent cannot be used for analytical purposes. The facile enolization of the saturated cyclic ketones is a factor which must also be considered when the reagent is applied in terpene analysis.

1. E. von Rudloff. Can. J. Chem. **43**, 2660 (1965).
2. E. Klein and W. Rojahn. Tetrahedron, **21**, 2353 (1965).
3. J. W. Apsimon, A. S. Y. Chau, W. G. Craig, and H. Krehm. Can. J. Chem. **45**, 1439 (1967).
4. E. von Rudloff. Tetrahedron Letters, No. 10, 993 (1966).
5. J. W. Daly, F. C. Green, and R. H. Eastman. J. Amer. Chem. Soc. **80**, 6330 (1958).
6. E. von Rudloff. 47th Annu. Meet. Chem. Inst. Canada, Kingston, Ontario. June 1–4. 1961.
7. R. U. Lemieux and E. von Rudloff. Can. J. Chem. **33**, 1701 (1955).
8. R. U. Lemieux and E. von Rudloff. Can. J. Chem. **33**, 1710 (1955).
9. E. von Rudloff. Can. J. Chem. **33**, 1714 (1955).
10. E. von Rudloff. J. Amer. Oil Chemists' Soc. **33**, 126 (1956).
11. E. von Rudloff. Can. J. Chem. **34**, 1413 (1956).
12. E. von Rudloff. Can. J. Chem. **43**, 1784 (1965).
13. S. Wolfe. Ph.D. Dissertation, University of Ottawa, Ottawa, 1957.
14. K. B. Wiberg and R. D. Geer. J. Amer. Chem. Soc. **88**, 5827 (1966).
15. Y. T. Lin and Y. S. Cheng. J. Chin. Chem. Soc. (Taiwan), **7**, 58 (1960).
16. E. von Rudloff. Can. J. Chem. **41**, 2876 (1963).
17. Pechiney. Saint-Gobain, France. Distributed by Water Associates, Inc., Framingham, Mass. U.S.A.
18. A. R. Vinutha and E. von Rudloff. Can. J. Chem. **46**, 3743 (1968).
19. K. Hofmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey. J. Amer. Chem. Soc. **81**, 992 (1959).
20. J. L. Simonsen and L. N. Owen. *In* The terpenes. Vol. II. University Press, Cambridge. 1949. p. 369.
21. R. H. Eastman and R. A. Quinn. J. Amer. Chem. Soc. **82**, 4249 (1960).