CHAPTER IV

CHROMIC ACID OXIDATION OF OXIRANES

ABSTRACT

Oxidation of several epoxides of flexible and rigid carbon skeleton with chromic acid was investigated with the aim of finding an alternative to the rather complex oxidation of olefins with chromic acid and understanding the mechanism of such oxidations. Oxidation of 3-carene epoxide (3) was studied with a variety of Cr(VI) reagents and Jones' reagent gave the best yields of the keto-acid 4. A number of selected epoxides were oxidised with this reagent and products of rearrangement and C-C bond cleavage were separated and characterised. Based on the results, a mechanism for the oxidation of epoxides with chromic acid is proposed.

CHROMIC ACID OXIDATION OF OXIRANES

INTRODUCTION

Chromic acid is one of the most versatile oxidising agents, reacting with almost all types of oxidisable groups. The oxidation of alkenes may lead to several different products like an epoxide, ketoalcohol, acids or ketones derived by cleavage of double bond, or acids or ketones having the same number of carbon atoms as the alkene *via* a rearrangement, or α,β-unsaturated ketones arising out of allylic oxidation (Eq. 1). As a result of the variety of reactions, chromic acid oxidation of alkenes is not a generally useful synthetic reaction.

Although doubts have sometimes been expressed,[1] the intermediacy of epoxides in the chromic acid oxidation of olefins is fairly certain.[2-4] Kinetic evidence for epoxide formation in the rate-determining step of Cr(VI) oxidation of olefins was presented.[2] The products of oxidation of cyclohexene in glacial HOAc containing $HClO_4$ include cyclopentane carboxaldehyde and *cis*- and *trans*-2-acetoxycyclohexanol in about the same ratio as they are obtained from solvolysis of cyclohexene oxide under similar conditions. Moreover, direct detection (GLC) of cyclohexene oxide in the product of an oxidation quenched after 30 seconds leaves little doubt that epoxide formation is an important path in the oxidation.[3] Cholesterol α-oxide (1) on chromic acid oxidation gave cholestane-3,6-dione-5a-ol (2)[4a] (Eq. 2) and this was the major product of oxidation of cholesterol.[4b]

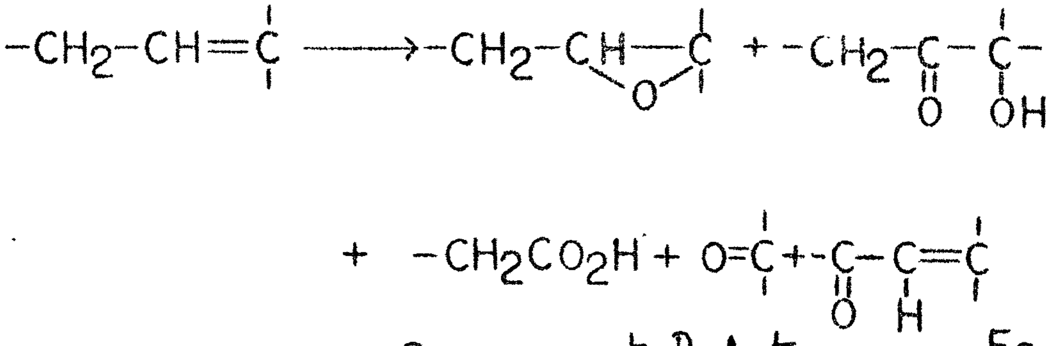
Cr(VI) and Cr(V) are responsible for epoxide formation and further reaction of epoxide, while the allylic oxidation products are not formed via the epoxide and are most probably produced by Cr(IV).

PRESENT WORK

A survey of literature indicates that a systematic investigation of the chromic acid oxidation of epoxides has not been carried out. It was envisaged that oxidation of epoxides instead of olefins would exclude other oxidation pathways like allylic oxidation and provide synthetically useful procedure in some cases. Also, quantitation and characterisation of the products of oxidation of a number of epoxides derived from alkenes of flexible and rigid carbon skeleton may throw some light on the course of the reaction. With these aims in mind it was planned to prepare some selective epoxides and study their oxidation with chromic acid.

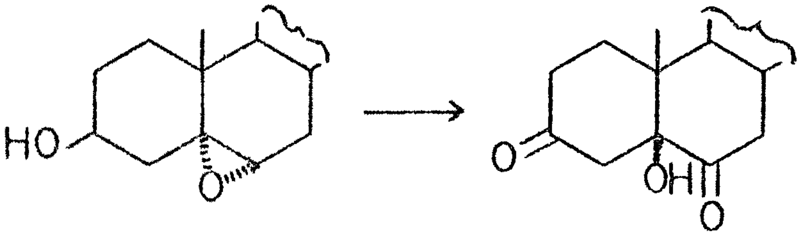
Preparation of epoxides

The epoxides were prepared by reacting the corresponding

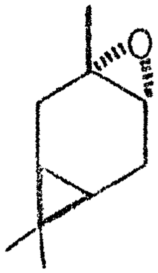


$$-CH_2-CH=\overset{|}{\underset{|}{C}} \longrightarrow -CH_2-CH\overset{O}{-}\overset{|}{\underset{|}{C}} + -CH_2-\underset{O}{\underset{\|}{C}}-\underset{OH}{\underset{|}{\overset{|}{C}}}- + -CH_2CO_2H + O=\overset{|}{\underset{|}{C}} + -\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$

+ Rearrangement Products Eq.1



1 2 Eq.2



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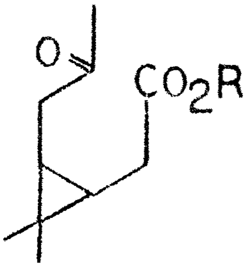
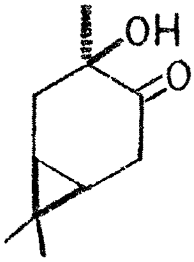


4:R=H
5:R=CH3



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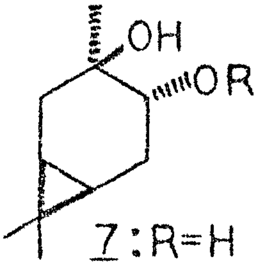


7:R=H
8:R=Ac

CHART I

olefins with perbenzoic acid at -5° in presence of Na_2CO_3 buffer.[5] α,β-Unsaturated ketones were epoxidised using alkaline H_2O_2.[6]

Oxidation of epoxides

Oxidation of $3\alpha,4\alpha$-epoxycarane (3, Chart 1) was studied with a number of Cr(VI) reagents. Oxidation with Fieser's reagent (CrO_3/HOAc)[7] gave 2,2-dimethyl-3-(2'-oxopropyl)-cyclopropane-*cis*-1-acetic acid (4)[8] in 30% yield. Oxidation with Kiliani reagent ($Na_2Cr_2O_7.2H_2O$, H_2SO_4, H_2O)[9] in HOAc gave the keto acid 4 in 37% yield. In the neutral material, 3β-hydroxycaran-4-one (6)[10] (19%), $3\beta,4\alpha$-dihydroxycarane (7)[10] (1%) and 3β-hydroxy-4α-acetoxycarane (8)[11] (9%) were identified by co-injection on GLC (10% carbowax on chromosorb W, 12', 200°, 60 ml/min) with authentic samples. Oxidation of 3 with $Na_2Cr_2O_7.2H_2O$ in benzene/HOAc gave 33% yield of the keto acid 4. Oxidation with chromic acid using the phase transfer catalyst, tetra-n-butylammonium iodide[12] also gave poor yield of the acid 4. Sobti and Sukh Dev[8] reported 44% yield of the keto acid 4 with Jones' reagent (1.08 mole equivalents). The yield of 4 could be improved to 58% by employing 1.4-1.5 moles of Jones' reagent per mole of epoxide. The hydroxyketone 6 was the major product in the neutral material. A small amount (~1%) of the diol 7 was also formed. The acid 4 is a crucial intermediate in the synthesis of *trans*-chrysanthemic acid.[8]

In view of the above results, the rest of the epoxides were oxidised with Jones' reagent. Oxidation was carried out at 15-20° for 30-45 min. The results are presented in Table 1.

Table 1 : Oxidation of epoxides

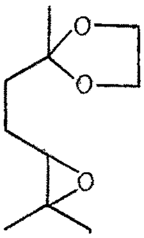
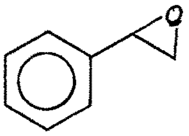
		Product of	
Entry	Epoxide	C-C cleavage	rearrangement
1.	 9	$CH_3COCH_2CH_2CO_2H$ (60%)	-
2.	 10	Benzoic acid (59%)	Phenylacetic acid (6%)

Table 1 contd.

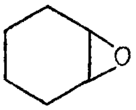
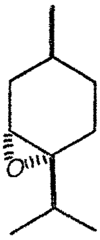
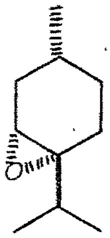
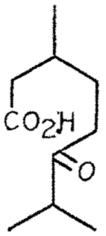
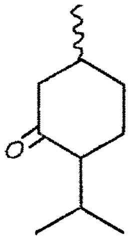
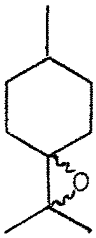
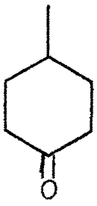
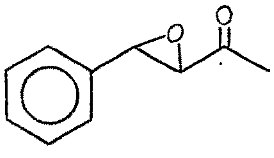
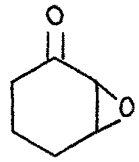
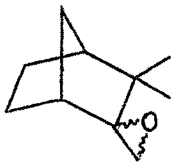
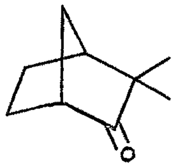
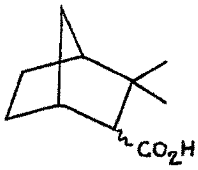
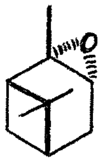
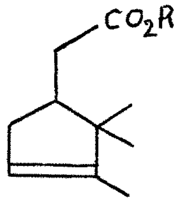
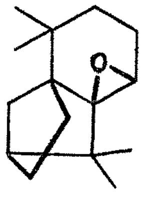
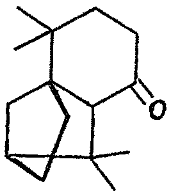
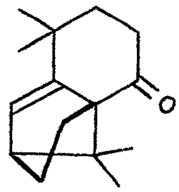
3.	 11	Adipic acid (60%)	Cyclohexanone (20%)
4.	 12 +  13	 14 (58%)	 15(25%)
5.	3	4 (58%)	6(18%) + 7(1%).
6.	 16	 17(80%)	-
7.	 18	Benzoic acid (80%)	-

Table 1 contd.

8.	 19	Glutaric acid (34%) + Adipic acid (4%)	-
9.	 20	 21 (33%)	 22 (52%)
10.	 23	-	 24: R=H (37%) 25: R=CH_3
11.	 26	-	 27 (60%) +  28 (37%)

Methylheptenone ketal epoxide (9): Ketalisation of methylheptenone (ethylene glycol/PTS) followed by epoxidation gave 9 in 90% yield (IR: epoxide 875 cm^{-1}. PMR: C-$\underline{Me}$'s, 3H, singlets at 1.24, 1.27 and 1.29 ppm; $\overset{O}{C\underline{H} - C}$, 1H, t, 2.53 ppm, J=6 Hz; $\underbrace{C - O - C\underline{H}_2C\underline{H}_2 - O}$, 4H, s, 3.9 ppm). Oxidation of 9 gave a material, which was separated into acidic (60%) and neutral (25%) parts. The former was identified as laevulinic acid by comparison with an authentic sample (IR, PMR). The latter was a complex mixture and not studied further.

Styrene oxide (10): Oxidation of styrene oxide (10) gave a mixture of two acids [GLC of the methyl esters (10% SE-30 on chromosorb W 60-80, 2 m, 170°, 60 ml/min) showed two peaks; RRT 1.0, 1.4], which were identified as benzoic acid (59%) and phenylacetic acid (6%) by co-injection of the methyl esters with authentic samples.

Cyclohexene epoxide (11): Oxidation of 11 gave a material which was separated into acidic (60%) and neutral parts (25%). The former was identified as adipic acid (m.p., IR, GLC of the methyl ester). GLC of the neutral material showed one major (80%) component identified as cyclohexanone by co-injection.

p-3-Menthene oxides (12/13): Epoxidation of p-3-menthene with PBA at -5° gave a mixture (90%) of 12 (PMR: $\overset{O}{C\underline{H} - C}$, bs, 2.8 ppm) and 13 (PMR: $\overset{O}{C\underline{H} - C}$, bd, 2.75 ppm) in the ratio of 7:3.

Bowman and co-workers[13] got 12/13 in the ratio of 3:2 by doing epoxidation with PBA at 20°. Oxidation of 12/13 gave acidic (58%) and neutral (25%) parts, which were identified as 3,7-dimethyl-6-oxo-octanoic acid[14] (14, IR, PMR) and menthones (15, IR, PMR) respectively.

p-4(8)-Menthene oxides (16)[13]: Oxidation of 16 gave a single neutral product (GLC) in 80% yield, identified as 4-methylcyclohexanone (17) by comparison (IR, PMR, GLC) with an authentic sample.

3,4-Epoxy-4-phenyl-2-butanone (18): Reaction of benzalacetone with alkaline H_2O_2[15] gave the epoxyketone 18 in 75% yield (IR: CO 1710 cm^{-1}; epoxide 750 cm^{-1}. PMR: $COC\underline{H}_3$, 3H, s, 2.04 ppm; $\overset{O}{\overbrace{C\underline{H} - C\underline{H}}}$, 1H, doublets at 3.29, 3.92 ppm, J = 3 Hz; Ar$\underline{H}$, 5H, s, 7.24 ppm). Oxidation of 18 gave benzoic acid in 80% yield.

Cyclohexenone epoxide (19)[6]: Oxidation of 19 gave glutaric acid (34%) and adipic acid (4%; estimated by GLC of the methyl esters).

Camphene oxides (20): Oxidation of camphene oxides[16] gave acidic (52%) and neutral (33%) parts, identified as 3,3-dimethylbicyclo(2.2.1)heptane-2-carboxylic acid[17] (22, IR, PMR) and 3,3-dimethylbicyclo(2.2.1)heptan-2-one[18] (21, IR, PMR, co-injection on GLC with an authentic sample) respectively.

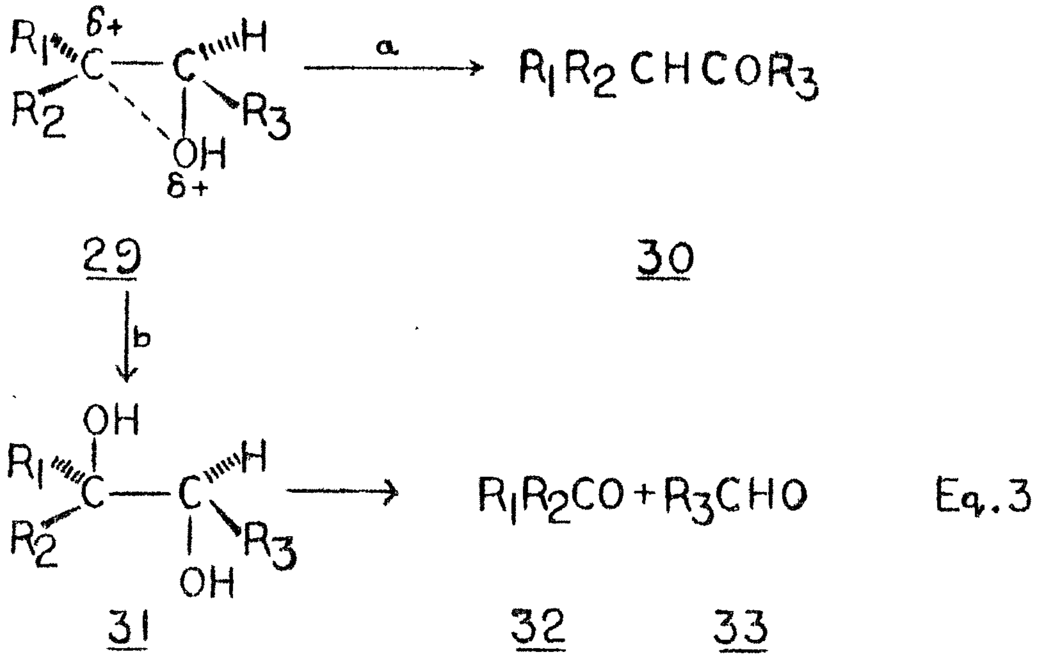
2α,3α-Epoxypinane (23):[19] Oxidation of 23 gave 37% yield of an acid and 40% of neutral material. The acid is a single compound (GLC of the methyl ester). It was identified as 2,2,3-trimethylcyclopent-3-en-1-yl acetic acid[19] (24; IR, PMR of the acid and ester). The neutral material was a complex mixture (8 peaks in GLC) and not investigated further.

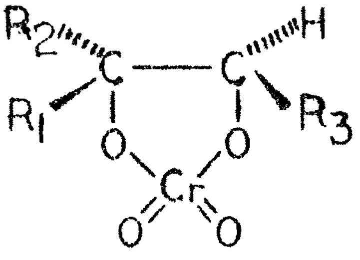
Isolongifolene epoxide (26):[5] Oxidation of 26 gave a neutral product in almost quantitative yield, which showed two peaks in GLC (10% SE-30, chromosorb W 60-80, 2 m, 200°, 60 ml/min; RRT 1.0, 1.44). They were identified as the ketones 27[5] (60%) and 28[20] (37%) by co-injection with authentic samples.

The relevance of this data in understanding the mechanism of oxidation is discussed below.

DISCUSSION

The epoxides are known[21,22] to develop significant carbonium ion character in an acidic medium, as obtained with Jones' reagent. The intermediate 29 can either rearrange *via* hydride transfer[21] (path a) or pinacol-type rearrangement to the corresponding carbonyl compound 30 or may be solvated (path b) to a *trans*-diol 31 (Eq. 3). The latter can undergo





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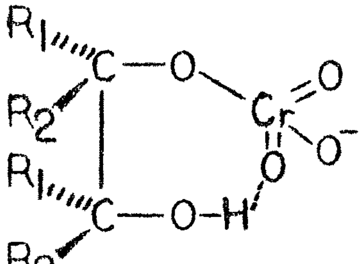

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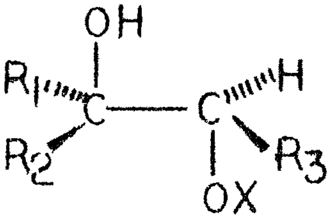

36 : $X = CrO_3^-$

37 : $X = CrO_3SO_3^-$

CHART 2

cleavage *via* a cyclic chromate ester (34)[23] to carbonyl compounds 32 and 33. A seven-membered hydrogen bonded intermediate such as 35 has also been suggested[24] for C-C bond cleavage.

The *trans*-diol 31 is not a mandatory intermediate for the formation of cyclic chromate ester 34. The opening of the oxirane ring with H_2CrO_4 or H_2CrO_4-H_2SO_4 acting as electrophiles[25] can furnish hydroxychromate ester intermediates (36/37) which can reorganise to 34 (Chart 2).

To evaluate factors influencing the extent to which paths a and b are followed, oxidations of a number of epoxides incorporating different stereoelectronic features were studied. In the first place, some acyclic (such as 9, 10) or flexible cyclic epoxides (such as 11) were investigated. In 9 and 10, C-C bond cleavage took place to a larger extent ($\sim$60%) than rearrangement. Even with cyclohexene oxide (11), cleavage product (adipic acid) was major. Since epoxide ring opening in acidic medium is a ‘border line S_N^2’ process and *trans*-diaxial opening is favoured[22] in acyclic epoxides, the formation of adipic acid from cyclohexene oxide (11) can be visualised as proceeding *via* Eq. 4. Such a sequence demands that for efficient C-C cleavage, the cyclic epoxides should possess correct geometry for *trans*-diaxial opening and the resulting diol (or its derivative) should be flexible enough

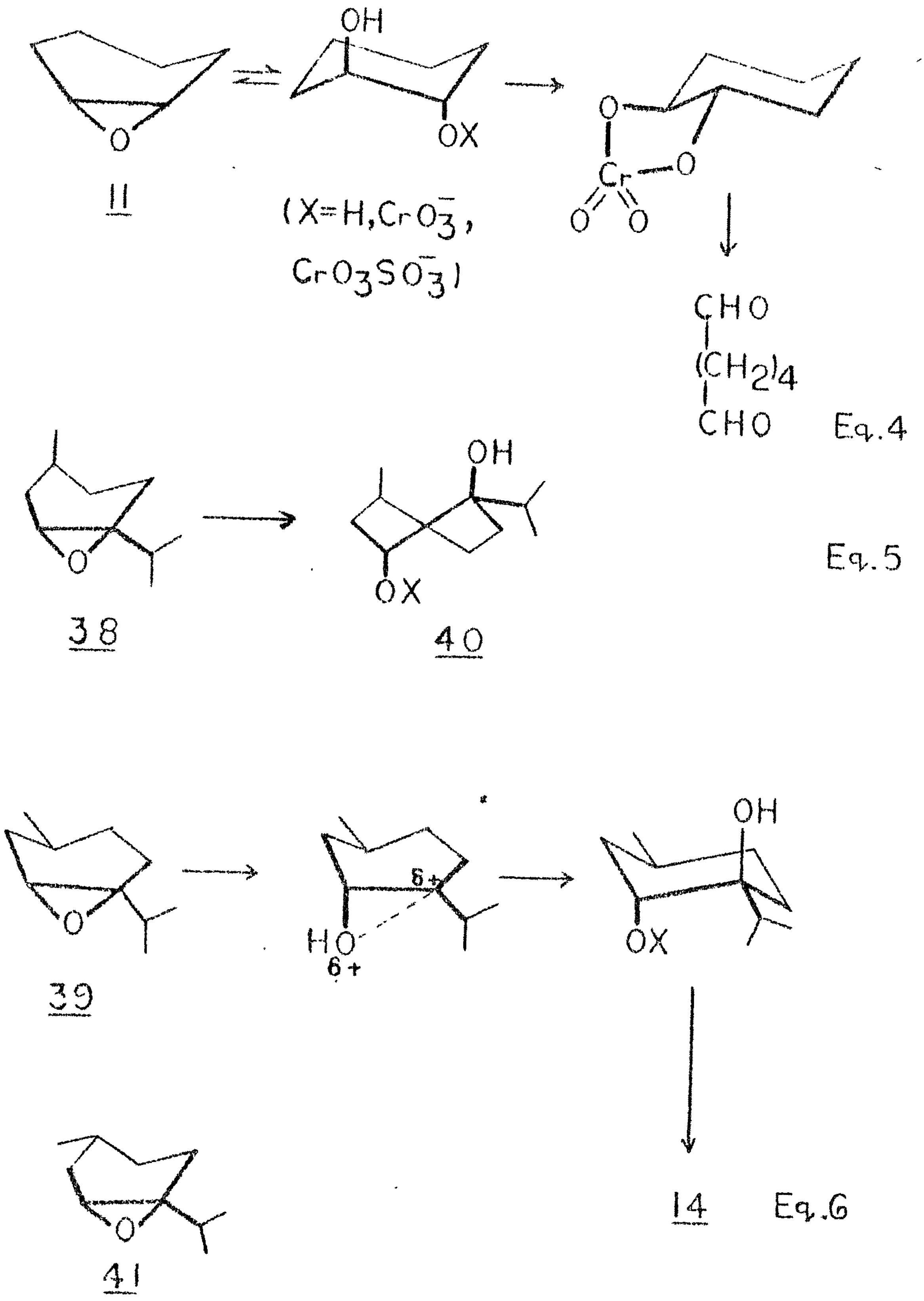
OH
OX
11
(X=H,CrO$_3^-$,
CrO$_3$SO$_3^-$)
O
Cr
O
O
O
CHO
(CH$_2$)$_4$
CHO
Eq.4
O
OH
OX
38
40
Eq.5
O
δ+
HO
δ+
OH
OX
39
14
Eq.6
O
41

CHART 3

to form a cyclic chromate ester intermediate. Cleavage products become prominent in cases where these conditions are fulfilled or path a is inhibited by other steric or electronic factors.

p-3-Menthene epoxides (12/13): Of the two possible conformations 38 and 39 (Chart 3), the major isomer 12 should preferentially exist in conformation 39 with equatorial methyl group. That a methyl group can exert a strong conformational preference in such systems is on record.[26] The conformation 39 is well suited to give cleavage products in good yield for the following reasons. In such a system, the carbonium ion at C_4 will be stabilised and the external nucleophile should be captured at this position. Only in conformation 39, *trans*-diaxial opening can give the product in chair conformation. Similar opening in 38 will give product in a 'twist-chair' conformation 40. Since the transition state in such systems is believed[27] to be more product-like, conformation 38 required to cleave *via* 40 would have rendered rearrangement process more competitive. The minor isomer 13, which should preferentially exist in conformation 41, for reasons indicated above should be more prone to rearrangement.

3-Carene epoxide (3): This epoxide believed[28] to exist in conformation 42 on opening must acquire the half-chair conformation before it can form the cyclic chromate ester intermediate 43 necessary for cleavage (Eq. 7).

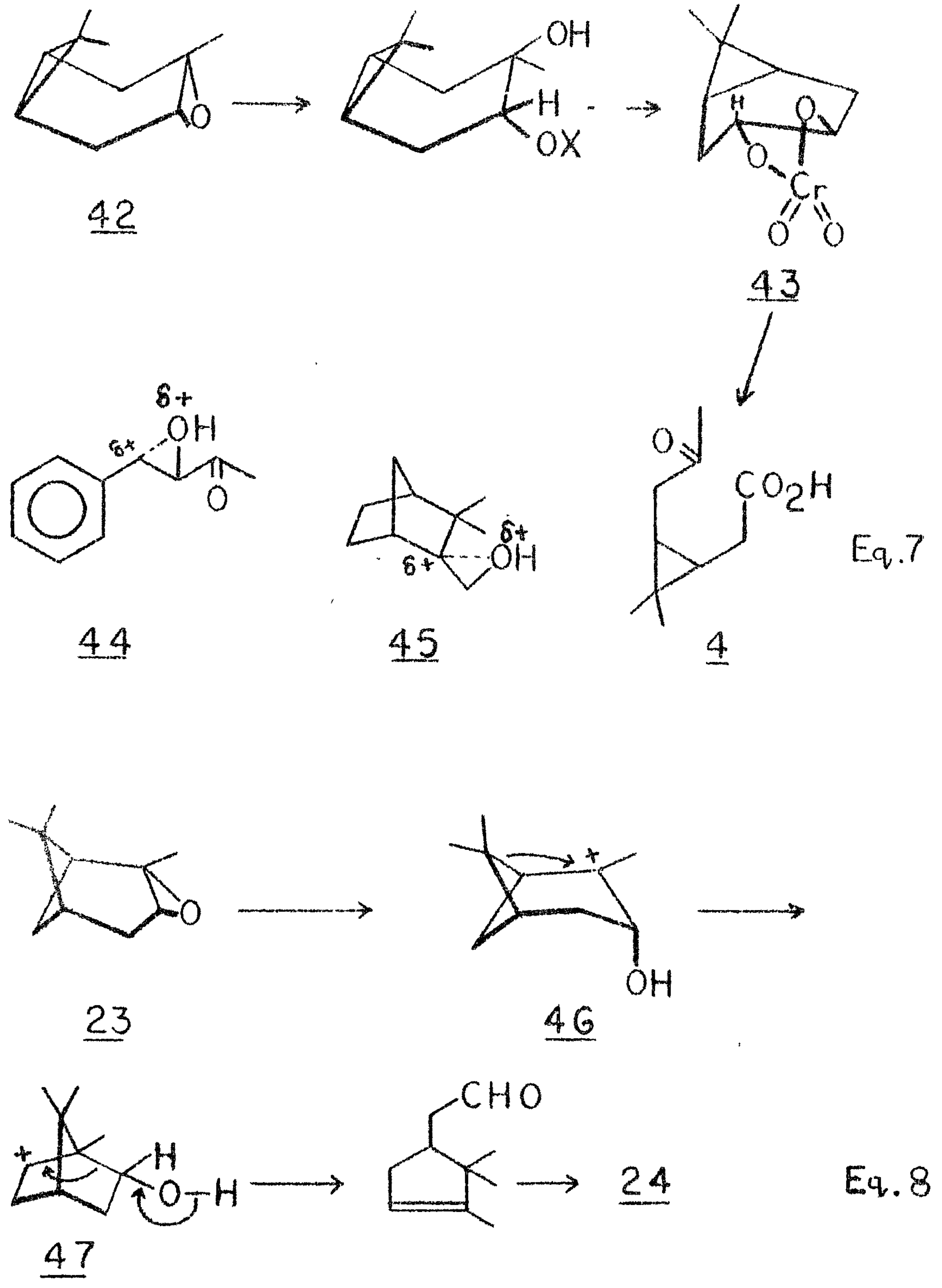
OH
H
OX
O
H
O
O
Cr
O
O
42
43
δ+
OH
δ+
O
44
δ+
δ+
OH
45
O
CO2H
4
Eq.7
O
23
+
OH
46
+
H
O
H
47
CHO
24
Eq.8

CHART 4

p-4(8)-Menthene oxides (16): On treatment with Jones' reagent, 16 gives 4-methyl cyclohexanone (17) in 80% yield. Lack of possibility of hydride transfer and low migratory aptitude of methyl or alkyl group make path b predominant.

Benzalacetone epoxide (18) and cyclohexenone epoxide (19): In the case of 18, both COMe and benzene ring dictate the regiochemistry of oxirane ring opening[21] as shown in 44 (Chart 4). In 44, hydride transfer is inhibited by the inductive effect of the vicinal carbonyl group, thus leading to high yield of cleavage product. For similar reasons, in the oxidation of 19, the only isolable products were due to cleavage.

Camphene oxides (20): Since the capture of external nucleophile in carbonium ion 45 is less favoured compared to other alternatives available, cleavage becomes a minor process.

α-Pinene epoxide (23): The initially formed carbonium in 46, being very prone to rearrangement gives 47, which *via* Grob fragmentation gives 24 as the major product (Eq. 8).

Isolongifolene epoxide (26): Isolongifolene is known[29] not to undergo normal electrophilic addition reactions. For similar reasons, the epoxide 26 does not yield the diol or its derivative and only products 27 and 28 are formed by rearrangement.

The above considerations can help estimate the possible product composition to be expected from the Jones' oxidation of any epoxide.

EXPERIMENTAL

For General Remarks, see Chapter I, Section I.

General procedure for the preparation of epoxides.

Perbenzoic acid (0.12 mole) in benzene was added dropwise to a stirred mixture of the olefin (0.1 mole) in CH_2Cl_2 (25 ml) and Na_2CO_3 (0.2 mole). The reaction mixture was kept at 0 to -5^o for 24-36 h. It was then filtered; the filtrate was washed with 5% Na_2SO_3 aq (10 ml), water (10 ml) and brine (10 ml) and dried (Na_2SO_4). Removal of solvent followed by distillation furnished the epoxide in 85-90% yield. α,β-Unsaturated ketones were epoxidised following the usual procedure.[6]

3α,4α-Epoxycarane ($\underline{3}$): Colorless liquid, b.p. $82-5^o$/10 mm (lit.[19] b.p. $102-3^o$/48 mm).

IR (liq. film): Epoxide 840 cm^{-1}.

PMR (CCl_4): Cyclopropane $C\underline{H}$'s, 2H, bt, 0.44 ppm; $C-\underline{Me}$'s, 3H, singlets at 0.72, 1.02, 1.18 ppm; $C\underline{H}\overset{O}{-}C$, 1H, bs, 2.6 ppm.

Methylheptenone ketal epoxide ($\underline{9}$): Colorless liquid, b.p. $72-4^o$/3 mm.

IR (liq. film): Epoxide 875 cm^{-1}.

PMR (CCl_4): $C-\underline{Me}$'s, 3H, singlets at 1.24, 1.27, 1.29 ppm; $C\underline{H}\overset{O}{-}C$, 1H, t, 2.53 ppm, J = 6 Hz; $\underbrace{C - O -(C\underline{H}_2)_2- O}$, 4H, s, 3.9 ppm.

Styrene oxide (10): Colorless liquid, b.p. 188-90° (lit.[30] b.p. 188-92°).

IR (liq. film): Epoxide 870 cm^{-1}.

PMR (CCl_4): $C\underline{H}\overset{O}{-}C\underline{H}_2$, 1H, quartets 2.61, 3.0, 3.74ppm;
ArH, 5H, s, 7.2 ppm.

Cyclohexene oxide (11): Colorless liquid, b.p. 129-31° (lit.[31] b.p. 129-34°).

IR (liq. film): Epoxide 835 cm^{-1}.

PMR (CCl_4): $C\underline{H}\overset{O}{-}C\underline{H}$, 2H, bs, 2.95 ppm.

p-3-Menthene oxides (12/13): Colorless liquid, b.p. 94-8° (bath)/15 mm (lit.[13] 96-100°/40mm).

IR (liq. film): Epoxide 855 cm^{-1}.

PMR (CCl_4): $C\underline{H}\overset{O}{-}C$, bd, 2.75 ppm and bs, 2.8 ppm.

p-4(8)-Menthene oxides (16): Colorless liquid, b.p. 74-5°/14 mm (lit.[13] b.p. 120-2°/70 mm).

IR (liq. film): Epoxide 865 cm^{-1}.

PMR (CCl_4): $C\underline{Me}_2$, 3H, singlets at 1.28, 1.30 ppm.

3,4-Epoxy-4-phenyl-2-butanone (18): Pale yellow liquid, b.p. 125-30°/10 mm (lit.[15] b.p. 146-9°/15 mm).

IR (liq. film): CO 1710 cm^{-1}; epoxide 750 cm^{-1}.

PMR (CCl_4): $COC\underline{H}_3$, 3H, s, 2.04 ppm; $C\underline{H}\overset{O}{-}C\underline{H}$, 1H, doublets at
3.29, 3.92 ppm, J = 3Hz; ArH, 5H, s, 7.24 ppm.

Cyclohexenone epoxide (19): Colorless liquid, b.p. 77-80°/10 mm (lit.[6] b.p. 75-7°/11 mm).

IR (liq. film): CO 1710 cm^{-1}; epoxide 825 cm^{-1}.

PMR (CCl_4): $(C\underline{H}_2)_3$, 6H, m, 1.5-2.8 ppm; $C\underline{H}\overset{O}{-}C\underline{H}$, 1H, d, 3.1 ppm, J = 4 Hz and 1H, bs, 3.5 ppm.

Camphene oxides (20): White solid, m.p. 80-2° (lit.[16] m.p. 86-8°).

IR (nujol): Epoxide 845 cm^{-1}.

PMR (CCl_4): C-$\underline{Me}$'s, singlets at 0.76, 0.84, 0.90 and 0.94 ppm (two isomers); $C\overset{O}{-}C\underline{H}_2$, singlets at 2.51, 2.60 ppm.

2α,3α-Epoxypinane (23): Colorless liquid, b.p. 105-10°(bath)/25 mm (lit.[19] b.p. 91-3°/27 mm).

IR (liq. film): Epoxide 860 cm^{-1}.

PMR (CCl_4): C-$\underline{Me}$'s, 3H, singlets at 0.94, 1.29, 1.29 ppm; $C\underset{O}{-}C\underline{H}$, 1H, bs, 2.9 ppm.

Isolongifolene epoxide (26): White crystalline solid, m.p. 40° (lit.[5] m.p. 40.5-41.5°).

IR (nujol): Epoxide 810 cm^{-1}.

PMR (CCl_4): C-$\underline{Me}$'s, 3H, singlets at 0.75, 0.92, 0.92, 1.08 ppm; $C\underline{H}\overset{O}{-}C$, 1H, t, 3.0 ppm, J = 3 Hz.

General procedure for the oxidation of epoxides:

Jones' reagent (stock soln:[8] CrO_3 13.35 g, conc. H_2SO_4 11.5 ml and H_2O 20 ml made up to 50 ml) (1.5 mole equivalents of H_2CrO_4) was added dropwise with stirring to the epoxide (1 g) in acetone (5-10ml) at 20°. After stirring at 15-20° for 30 min, excess of reagent was destroyed by adding a few drops of isopropanol. The mixture was diluted with water (10 ml) and extracted with EtOAc (15 ml x 3). The extract was separated into acidic and neutral portions with 10% Na_2CO_3 aq in the usual manner.

Run 1. Oxidation of methylheptenone ketal epoxide (<u>9</u>, 1 g, 5.4 mmol) gave laevulinic acid (375 mg, 60%; m.p. 33°) and neutral material (0.5 g, complex mixture).

Run 2. Oxidation of styrene oxide (<u>10</u>, 1g, 8.3 mmol) gave a mixture of acids (0.666 g), which was esterified with CH_2N_2. GLC of the ester mixture showed two peaks, which were identified as methyl benzoate and methyl phenylacetate by co-injection with authentic samples. The yields of benzoic acid and phenylacetic acid were 59 and 6% respectively (according to GLC).

Run 3. Oxidation of cyclohexene oxide (<u>11</u>, 1 g, 10.2 mmol) gave adipic acid (0.89 g, 60%; m.p. 147-9°) and neutral material (0.25 g). The latter showed one major component (80%) in GLC, which was identified as cyclohexanone by co-injection with an authentic sample.

Run 4. Oxidation of p-3-menthene oxides (12/13, 1 g, 6.5 mmol) furnished acidic and neutral products. The acidic part was 3,7-dimethyl-6-oxo-octanoic acid (14, 0.7 g, 58%), b.p. 125-30°(bth)/0.3 mm (lit.[14] b.p. 171-5°/1.5 mm).

IR (liq. film): CO_2H 3300, 1720 cm^{-1}.

PMR (CCl_4): $CHCH_3$, 3H, d, 0.97 ppm, J = 7 Hz; $CHMe_2$, 6H, d, 1.06 ppm, J = 7 Hz; CO_2H, 1H, bs, 9.85 ppm.

The neutral part was menthones (15, 0.25 g, 25%), b.p. 85-90°(bath)/3 mm.

IR (liq. film): CO 1705 cm^{-1}.

PMR (CCl_4): $CHCH_3$, 3H, d, 0.67 ppm; $CH(CH_3)_2$, 6H, d, 0.97 ppm; J = 7 Hz.

Run 5. Oxidation of 3α, 4α-epoxycarane (3, 1 g, 6.5 mmol) gave neutral and acidic parts. The neutral part (0.2 g) is a complex mixture as shown by GLC (7 peaks). The acidic part (0.7 g, 58%) was esterified (MeOH/HCl) to give methyl ester 5; b.p. 115-20°(bath)/1 mm (lit.[8] b.p. 102-5°/1 mm).

IR (liq. film): CO 1720, 1740 cm^{-1}.

PMR (CCl_4): $C\text{-}Me_2$, 3H, singlets at 0.88, 1.0 ppm; $COCH_3$, 3H, s, 2.08 ppm; CO_2CH_3, 3H, s, 3.62 ppm.

Run 6. Oxidation of p-4(8)-menthene oxides (16, 1g, 6.5 mmol) gave 4-methylcyclohexanone (17, 0.582 g, 80%), b.p. 95-100°

(bath)/30 mm (lit.[32] 170°/761 mm).

IR (liq. film): CO 1710 cm^{-1}.

PMR (CCl_4): $CH\underline{H_3}$, 3H, d, 1.04 ppm, J = 6 Hz.

Run 7. Oxidation of 3,4-epoxy-4-phenyl-2-butanone (<u>18</u>, 1 g, 6.2 mmol) gave benzoic acid (0.6 g, 80%), m.p. 120°.

Run 8. Oxidation of cyclohexenone oxide (<u>19</u>, 1 g, 8.9 mmol) gave a mixture of acids (0.5 g), which was esterified (CH_2N_2). GLC (10% SE-30 on chromosorb W 60÷80, 2m, 140°, 60 ml/min) of the ester mixture showed 3 peaks (RRT 1.0, 1.6, 2.7), of which the middle peak is major (∾80%). Two esters (RRT 1.6, 2.7) were identified as methyl glutarate and methyl adipate by co-injection and the estimated yields are 34 and 4% respectively.

Run 9. Oxidation of camphene oxides (<u>20</u>, 1 g, 6.5 mmol) gave acidic and neutral parts. The acid was 3,3-dimethylbicyclo-(2.2.1)heptane-2-carboxylic acids[17] (<u>22</u>, 0.567 g, 52%), b.p. 125-30°(bath)/0.5 mm.

IR (liq. film): CO_2H 3200, 1700 cm^{-1}.

PMR ($CDCl_3$): $C\underline{Me_2}$, 3H, singlets at 1.08, 1.15 ppm; $CO_2\underline{H}$,
1H, bs, 10.84 ppm.

The neutral portion was 3,3-dimethylbicyclo(2.2.1)-heptan-2-one (<u>21</u>, 0.33 g, 33%), b.p. 100-5°(bath)/3 mm (lit.[18] b.p. 70-80°/11 mm).

IR (liq. film): CO 1740 cm^{-1}.

PMR (CCl_4): $C\underline{Me_2}$, 3H, singlets at 1.0, 1.04 ppm.

Run 10. Oxidation of 2α,3α-epoxypinane (23, 1 g, 6.5 mmol) gave a complex mixture of neutral compounds (0.4 g, 8 peaks in GLC) and single acidic compound (GLC of the methyl ester). The latter (0.404 g, 37%) was esterified (CH_2N_2) to give the methyl ester 25, b.p. 110-5°(bath)/2 mm (lit.[19] b.p. 110°(bath)/ 2 mm).

IR (liq. film): CO 1750 cm^{-1}; C=C 800 cm^{-1}.

PMR (CCl_4): C$\underline{Me}_2$, 3H, singlets at 0.78, 0.99, ppm;
C=C-C$\underline{H}_3$, 3H, s, 1.57 ppm; $CO_2C\underline{H}_3$, 3H, s, 3.62 ppm;
C=C$\underline{H}$, 1H, bs, 5.18 ppm, W_h = 6 Hz.

Run 11. Oxidation of isolongifolene oxide (26, 1 g, 4.5 mmol) gave only neutral product (0.99 g), GLC of which showed two peaks (RRT 1.0, 1.44). They were identified as the ketones 27 (60%) and 28 (37%) by co-injection with authentic samples.

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