0.82 (s, 3, tertiary methyl), 0.80 (d, J = 6.5 Hz, 3, secondary methyl). The vpc retention time[39] (5% UCON, 5% DEGS) and ir and pmr spectra were superimposable on those of naturally occurring (−)-patchouli alcohol.[40] The mass spectrum was also identical with that of the natural product.

Constituent B was the oily acyclic ketone **18g**: ir 1705 cm^{-1} (ketone); pmr δ 1.09 (s, 3, tertiary methyl), 1.07 (s, 3, tertiary methyl), 0.88 (s, 3, tertiary methyl), 0.86 (d, J = 6.5 Hz, 3, C_9 methyl); mass spectrum m/e 222 (M^+).

(39) The synthetic material was mixed with naturally occurring (−)-patchouli alcohol and peak enhancement was observed on the two columns at various temperatures.

(40) Naturally occurring (−)-patchouli alcohol, mp 56°, was isolated from patchouli oil which was generously donated by Plaimar Ltd., Perth. The higher boiling fractions of the oil were chromatographed over neutral alumina to give patchouli alcohol of high purity.

Registry No.—(±)-**2**, 5986-55-0; **4**, 34996-60-6; **6**, 34996-61-7; **7**, 34996-62-8; **8**, 34996-63-9; **9a**, 34996-28-3; **9b**, 34996-64-0; **10a**, 34996-65-1; **10b**, 34996-66-2; (±)-**14a**, 29450-72-4; (±)-**14c**, 29448-20-2; (±)-**15a**, 29448-21-3; (±)-**16**, 34996-70-8; (±)-**18a**, 21682-97-3; (±)-**18c**, 34996-72-0; (±)-**18d**, 21683-01-2; (±)-**18e**, 34996-74-2; (±)-**18g**, 21682-98-4.

Studies with Bicyclo[2.2.2]octenes. VI.[1] The Total Synthesis of (±)-Seychellene[2]

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A stereospecific total synthesis of (±)-seychellene is described from the alcohol **2**, which was previously prepared for the synthesis of patchouli alcohol. The key stage in the sequence was the relatively efficient conversion of the olefinic bridge in **2** to the exocyclic methylene function in **21** *via* a modified hydrochlorination–dehydrochlorination procedure. The sequence was completed *via* the intermediates **22**, **25**, **26a**, and **26c**. Attempts to acylate the olefinic ester **7** gave none of the desired ketone **11**, but afforded instead the rearranged acetate **8** and/or the ketone **9**, depending on the reaction temperature.

The sesquiterpenoid (−)-seychellene was isolated from patchouli oil obtained from the Seychelles Islands, and was assigned the structure and absolute stereochemistry depicted in **1**.[4] The similarity in structure between seychellene and patchouli alcohol suggested a synthetic route to seychellene utilizing alcohol **2**, a key intermediate for the synthesis of patchouli alcohol.[1]

Two approaches to an intramolecular alkylation which could be used to construct the tricyclic seychellene skeleton are outlined in Scheme I. Path A suffers from the disadvantage that either the nitrile, aldehyde, or methyl ketone function of the cyclized product **4** must be converted to a methyl group in seychellene. On the other hand, norseychellanone (**5**), the path B intramolecular alkylation product, ought to be readily converted to seychellene by the reported procedure[5] of reaction with methyllithium, followed by dehydration of the resultant tertiary alcohol with thionyl chloride–pyridine.

Preliminary investigations were carried out on both pathways to assess their relative merits. The unsaturated aldehyde **3b** would have been the most useful of the type A alkylations from the point of view of generation of the C_2 methyl by a Wolff–Kishner reduction.[6] The preparation of this unsaturated aldehyde from the ketone **6**,[1] however, would be far from trivial.[7] The preparation of the unsaturated nitrile **3a** *via* the corresponding cyanohydrin was abandoned when difficulty was experienced in preparing the latter in good yield from the ketone **6** using acetone cyanohydrin.[8]

It is known[9] that acylation of 1-methylcyclohexene with polyphosphoric acid in acetic acid under specified conditions yields 2-acetyl-1-methylcyclohexene, and therefore it was envisaged that a compound of the type **3c** might be prepared by acylation of the corresponding olefin with the same reagent. Initially we studied the acylation of the readily available[10] model ester **7**.

At 55–60°, the major product of the reaction of **7** with polyphosphoric acid in acetic acid was the rearranged secondary acetate **8**. There was little or no tertiary acetate **10**, which was perhaps the expected major product, and furthermore, none of the desired ketone **11** was detected. At 75–80°, a mixture of compounds was isolated of which greater than 90% (pmr and vpc) were **8** and **9** in a ratio of 1:1.7. At 85–90°, the sole product was the ketone **9**. The movement of the double bond from the endocyclic to the exocyclic position prior to acylation has also been observed by other workers in the acylation of 1-ethylcyclohexene catalyzed by stannic chloride.[11] It was the remarkable isolation of **9** in good yield which aroused interest in the present case, since ozonolysis of **9** to the corresponding ketone **12** provided the analogy for a useful method of preparing a type B intramolecular alkylation precursor such as **25**. It was found, however, that, when the primary acetate **13** was treated with polyphosphoric acid in acetic acid under identical conditions to those used for the methyl ester **7**, none of the expected conjugated ketone analogous to **9** was obtained. The mixture of

(1) Part V: R. N. Mirrington and K. J. Schmalzl, *J. Org. Chem.*, **37**, 2871 (1972), accompanying paper.

(2) Some of the work described herein has appeared in a preliminary communication: K. J. Schmalzl and R. N. Mirrington, *Tetrahedron Lett.*, 3219 (1970).

(3) (a) Abstracted in part from the Ph.D. thesis of K. J. Schmalzl, University of Western Australia, May 1971. (b) The award of a Commonwealth Postgraduate Scholarship to K. J. S. is gratefully acknowledged.

(4) G. Wolff and G. Ourisson, *Tetrahedron Lett.*, 3849 (1968); *Tetrahedron*, **25**, 4903 (1969).

(5) J. E. McMurry, *J. Amer. Chem. Soc.*, **90**, 6821 (1968).

(6) F. E. King, D. H. Godson, and T. J. King, *J. Chem. Soc.*, 1117 (1955).

(7) M. de Botton, *Bull. Soc. Chim. Fr.*, 2466 (1966).

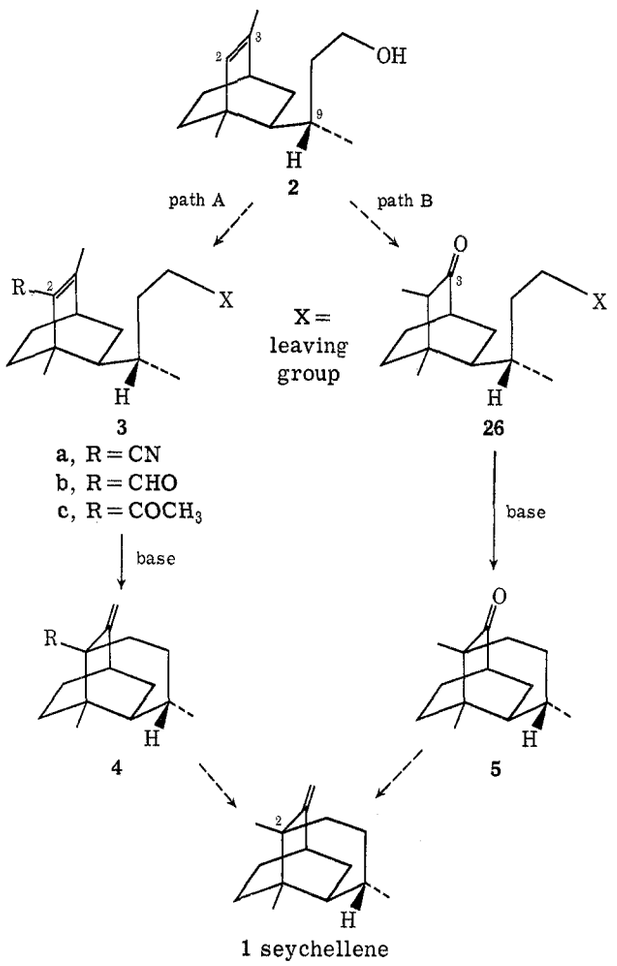
(8) (a) R. Gardi, P. P. Castelli, R. Gandolfi, and A. Ercoli, *Gazz. Chim. Ital.*, **91**, 1250 (1961); (b) A. Ercoli and P. de Ruggieri, *J. Amer. Chem. Soc.*, **75**, 650 (1953).

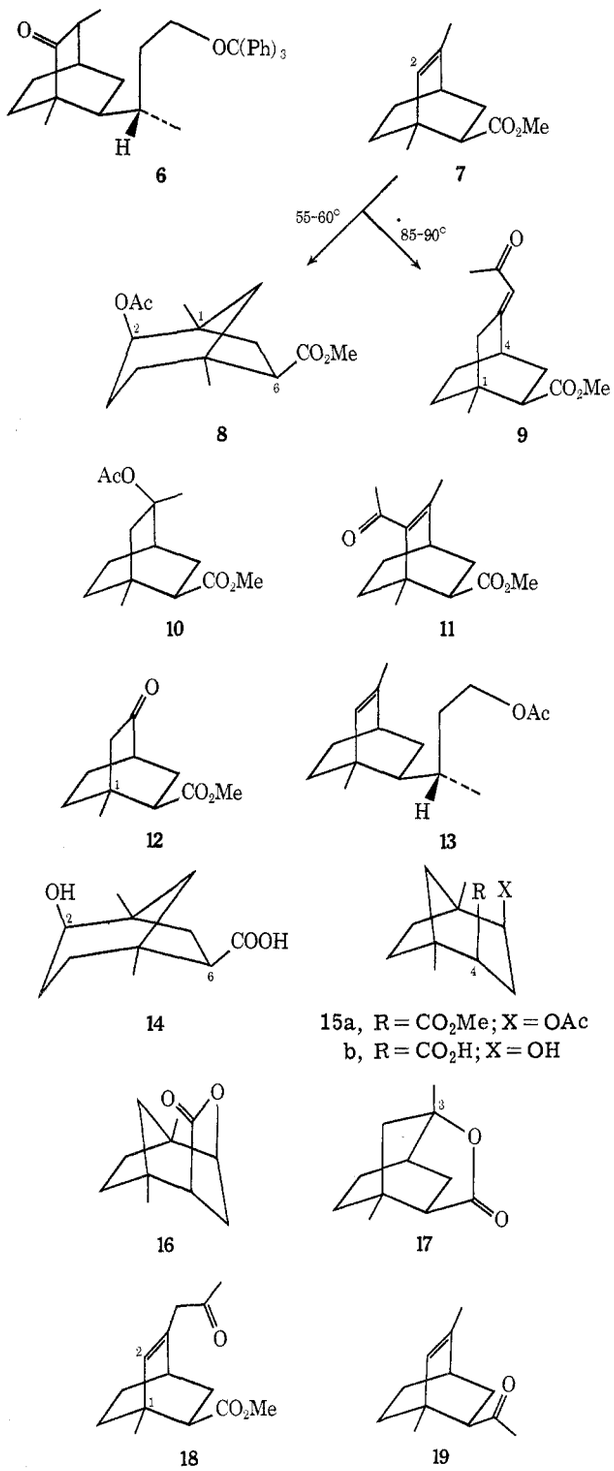
(9) S. B. Kulkarni and Sukh Dev, *Tetrahedron*, **24**, 561 (1968).

(10) R. N. Mirrington and K. J. Schmalzl, *J. Org. Chem.*, **34**, 2358 (1969).

(11) J. K. Groves and N. Jones, *Tetrahedron Lett.*, 1161 (1970).

SCHEME I





acetates that was obtained was not investigated further.

The structures **8** and **9** were assigned to the two products isolated from the attempted acylation of **7** at C_2 on the basis of the following evidence. The pmr spectrum of the acetate **8** showed a broad singlet of width at half height 4.5 Hz, at δ 4.60. The shape of the signal was characteristic of an equatorial proton on the chair form of a six-membered ring.[12] The chemical shift of the signal was consistent with a methine proton on a carbon bearing an acetate function. There were two tertiary methyl singlets and the doublet of doublets for H_6 was also clearly visible. Mild hydrolysis yielded the corresponding hydroxy acid **14**, the pmr spectrum of which showed the expected diamagnetic shift of H_2 to 3.54 ppm, and the doublet of doublets for H_6. The appearance of the doublet of doublets for H_6 ruled out the alternative structure **15a** for the rearranged secondary acetate, since the equatorial proton H_4 in **15a** should give rise to a broad singlet in the pmr spectrum.[12] In addition, if the rearranged secondary acetate had the structure **15a**, the corresponding hydroxy acid **15b** would have been expected to lactonize readily to **16**. The only lactone obtained, however, on treatment of the hydroxy acid with formic acid and sulfuric acid for 20 hr at 20° was the known[10] δ-lactone **17** in low yield. This presumably arose *via* a reversal of the original rearrangement, although the remote possibility of it having been formed from traces of the tertiary hydroxy acid corresponding to **10**, which may have been present in the starting material, could not be overlooked. Acid-catalyzed rearrangements are well known in the bicyclo[2.2.2]octane series[13] and hence the isolation of the rearranged secondary acetate **8** was not exceptional.

The proposed structures for the conjugated ketone **9** and the corresponding ketone **12** obtained by ozonolysis are supported by their spectroscopic data (Experimental Section). Of the two possible configurations, *Z* and *E*, for the conjugated ketone, the more stable *E*

(12) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 1053 (1962).

(13) For example; H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

configuration depicted in **9** was assigned to the product. If the product had the alternative *Z* configuration, the pmr spectrum would have been expected to show strong deshielding of H_4. The absence of any signals downfield from 3.2 ppm, apart from those due to the methyl ester and olefinic protons, thus supported the *E* configuration.

When an attempt was made to purify **9** by preparative vpc, it partly isomerized to the ketone **18**. The characteristic pmr signals of the latter offered supporting evidence for the proposed structures, and, in particular, the paramagnetic shift of the C_1 methyl singlet from δ 0.92 in **9** to δ 1.13 in **18** was found to be entirely consistent with the established trend in related compounds, as shown in Table I.

TABLE I

DESHIELDING EFFECT OF THE C_2=C_3 DOUBLE BOND ON THE C_1 METHYL GROUP[a]

Compounds with olefinic bridge	C_1 methyl singlet[b]	Compounds without olefinic bridge	C_1 methyl singlet[b]
7	1.09	**12**	0.96
13	1.07	**23**	0.87
2	1.08	**21**	0.91
20	1.15	**22**	0.94
18	1.13	**9**	0.92

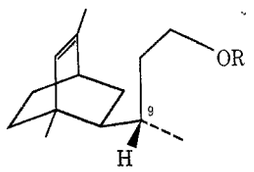
[a] There were obviously many other factors which influenced chemical shift of the C_1 methyl group. Nevertheless, these data gave a rough estimate for the magnitude of the deshielding effect of the olefinic bridge. [b] Pmr spectra were measured for CCl_4 solutions on a Varian A60 spectrometer. Chemical shifts are in parts per million downfield from TMS as internal standard.

The obvious sequel to this work on the acylation reactions was the search for a more reliable method of introducing a carbonyl group at C_3 (path B, Scheme I). Some preliminary experiments using Brown's hydrochlorination–elimination procedure[14] on the model compound **19**[10] showed some promise, although the ratio of exocyclic to endocyclic olefin, obtained from the reaction of potassium triethylmethoxide[14] with the hydrochloride of **19**, was disappointingly low (1:2). However, elimination with the weaker base sodium ethoxide not only gave a much more favorable ratio (up to 2:1), but also avoided the problem, when using triethyl methoxide, of separating the products from the relatively nonvolatile triethylmethanol.

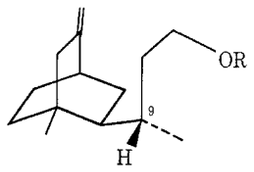
The alcohol **2**[1] was protected as its acetate **13**, which was then hydrochlorinated to give **23**. Dehydrochlorination of **23** with sodium ethoxide proceeded with concomitant transesterification of the protecting acetate group as desired to yield a mixture of olefins **2** and **21** in the ratio 2:3. After chromatography on silver nitrate–alumina the alcohol **21** was isolated in a yield of 50%, based on unrecovered **2**. A by-product was assigned the structure **24** on the basis of its pmr spectrum, which contained no signals for olefinic protons but an ethyl quartet at δ 3.30.

The preparation of the exocyclic olefin **21** by this simple and relatively high-yielding procedure from the endocyclic isomer **2** was an important contribution to the success of the total synthesis of (±)-seychellene.

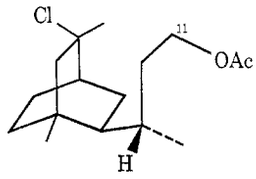
The alcohol function in **21** was protected as the trityl



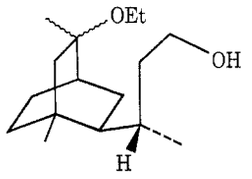
2, R = H
13, R = Ac
20, R = C(Ph)$_3$



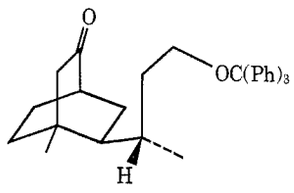
21, R = H
22, R = C(Ph)$_3$



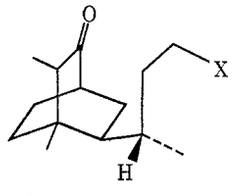
23



24



25



26a, X = OH
b, X = OC(Ph)$_3$
c, X = OTs
d, X = Cl

ether **22**, whose exocyclic double bond was cleaved, using osmium tetroxide and sodium metaperiodate in aqueous dioxane,[15] to yield the ketone **25**. Originally this cleavage was attempted on a mixture of exocyclic and endocyclic olefins **22** and **20** using catalytic amounts of osmium tetroxide, but the unreacted olefins were recovered. The color of the reaction mixture in these cases was a deep green. When pure exocyclic olefin **22** was used, the reaction proceeded smoothly and the color of the reaction mixture was deep brown. It was thus apparent that the endocyclic olefin **20** reacted with osmium tetroxide, but that the intermediate osmate ester was not breaking down readily to regenerate the osmium tetroxide, and hence the reaction did not proceed. Similarly, 1-methylcyclohexene has been reported[15] to undergo oxidative cleavage very slowly.

The ketone **25** was monomethylated using potassium triphenylmethide and methyl iodide. The relative stereochemistry of the C_2 methyl group in the product **26b** was assigned on the basis of the assumption that the enolate would be attacked by the alkylating agent from the less hindered side.[16] This issue was not crucial, since the system could be cyclized to norseychellanone regardless of the relative stereochemistry at C_2.

Hydrogenolysis of the trityl ether **26b** afforded the alcohol **26a**. This was converted to the tosylate **26c**, which readily cyclized to norseychellanone (**5**) when treated with potassium triphenylmethide in 1,2-dimethoxyethane. An indication of the speed of this reaction was gained from the fact that, upon dropwise addition of the triphenylmethide solution to the tosylate **26c** in 1,2-dimethoxyethane at 20°, an instantaneous

(14) (a) S. P. Acharya and H. C. Brown, *Chem. Commun.*, 305 (1968); (b) H. C. Brown and Min-Hon Rei, *J. Org. Chem.*, **31**, 1090 (1966).

(15) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

(16) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Amer. Chem. Soc.*, **84**, 2611 (1962).

precipitate of potassium tosylate was observed. The chloride **26d** did not cyclize at 20° under similar conditions, but heating at 90° for 1.5 hr was required before complete precipitation of potassium chloride was observed. This chloride **26d** was prepared by accident from the alcohol **26a**, when the temperature during tosylation and subsequent hydrolysis of excess reagent was not kept below 20°. The chloride ion present in solution presumably displaced the initially formed tosylate group. Analogous observations have been made by other workers.[17]

This synthesis of (±)-norseychellanone (**5**) constitutes a total synthesis of (±)-seychellene, because the conversion of **5** to (±)-seychellene has been carried out by Piers, Britton, and de Waal, who synthesized the racemic ketone by quite a different route.[18]

Experimental Section

For general details, refer to the previous paper.[1] An aluminum column 10 ft × 0.375 in. of 15% Apiezon on nonacid-washed Chromosorb W (60–80 mesh) was also used for preparative vpc.

Reaction of Methyl Ester 7 with Polyphosphoric Acid in Acetic Acid. A. At 55–60°.—The polyphosphoric acid in acetic acid reaction medium was prepared according to the method of Kulkarni and Dev[9] using 7 g of phosphorus pentoxide, 3 ml of 85% orthophosphoric acid, and 12 g of acetic acid. To one third of this solution at 55–60°, 0.50 g of the methyl ester[10] was added dropwise over 2 min and the temperature was maintained at 55–60° for 1 hr. The product was then poured into ice water and extracted with hexane. The hexane extract was washed with dilute aqueous sodium carbonate and water, then dried over anhydrous sodium sulfate. Evaporation of solvent yielded 0.55 g of a yellow oil, identified as predominantly the rearranged secondary acetate **8** (see below).

B. At 75–80°.—The reaction medium was prepared as above using 35 g of phosphorus pentoxide, 15 ml of 85% orthophosphoric acid, and 60 g of acetic acid. The olefin **7** (5 g) was added dropwise with stirring over 2 min to the reaction medium at 75–80°, and this temperature was maintained for 1 hr. Work-up as above yielded 5.6 g of product; vpc analysis showed the presence of two major components, A and B (1.7:1), which accounted for approximately 90% of the mixture. The retention times of A and B on 3% SE-30 at 160° were 4.7 and 2.8 min, respectively. A and B were separated by preparative vpc on 15% Apiezon at 180°.

B, a colorless oil, was the rearranged secondary acetate **8**: ir 1730 cm^{-1} (ester and acetate); pmr δ 4.60 (br s, 1, H_2), 3.60 (s, 3, methyl ester), 2.48 (dd, $J_{6,7n} + J_{6,7x} = 14.5$ Hz, 1, H_6), 2.00 (s, 3, acetate methyl), 1.02 (s, 3, tertiary methyl), 0.93 (s, 3, tertiary methyl); mass spectrum *m/e* 194 ($M^+ - 60$) (the molecular ion was of negligible abundance). The analytical sample was obtained by microdistillation, bp 86° (0.1 mm). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.38; H, 8.85.

The higher retention time component A was found to be a mixture of the two double bond isomers **9** and **18** (2.5:1). Since **18** was not present in the crude product (pmr), it must have been formed by isomerization of **9** on the preparative column. The ir and pmr spectra of **9** are given below. The characteristic pmr signals of the nonconjugated ketone **18** were δ 5.67 (br s, H_2), 3.14 (br s, $-CH_2CO-$), 1.13 (s, C_1 methyl).

C. At 85–90°.—The reaction medium was prepared as before using 7 g of phosphorus pentoxide, 3 ml of 85% orthophosphoric acid, and 12 g of acetic acid. The olefin **7** (1.0 g) was added with stirring over 2 min to the reaction medium at 85–90° and this temperature was maintained for 1 hr. Work-up as before yielded 1.0 g of the oily conjugated ketone **9**: ir 1730 (ester), 1680 (conjugated ketone), 1610 cm^{-1} (conjugated double bond); pmr δ 5.99 (br t, $J_t = 2.3$ Hz, 1, olefinic proton), 3.62 (s, 3, methyl ester), 2.10 (s, 3, methyl ketone), 0.92 (s, 3, C_1 methyl).

(17) B. W. Metcalf, Ph.D. Thesis, University of Western Australia, 1970.

(18) E. Piers, R. W. Britton, and W. de Waal, *Chem. Commun.*, 1069 (1969); E. Piers, W. de Waal, and R. W. Britton, *J. Amer. Chem. Soc.*, **93**, 5113 (1971).

The analytical sample was prepared by chromatography over neutral alumina and subsequent microdistillation, bp 90° (0.08 mm). *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.89; H, 8.29.

Ozonolysis of Conjugated Ketone 9.—Ozone was bubbled through a solution of 0.50 g of the ketone in 35 ml of purified acetone at −70° until a faint blue color was apparent. The solution was allowed to warm to 20° and 1.5 ml of Jones reagent was added dropwise. After standing for 30 min, excess reagent was destroyed by the addition of ethanol and the reaction mixture was poured into water. Extraction with ether and evaporation of the washed and dried extracts yielded 0.35 g of the ketone **12** as a colorless liquid: ir 1720–1730 cm^{-1} (ketone and ester); pmr δ 3.67 (s, 3, methyl ester), 0.96 (s, 3, C_1 methyl); mass spectrum *m/e* 196 (M^+). *Anal.* Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.44; H, 8.24.

Hydrolysis of Acetate 8.—The acetate (45 mg) was refluxed with 400 mg of sodium hydroxide in 5 ml of 50% aqueous ethanol for 12 hr. The mixture was poured into water, acidified with dilute hydrochloric acid, and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated to yield 26 mg (74%) of glassy hydroxy acid **14** which crystallized from benzene–ethanol as colorless prisms: mp 160–161°; ir 3620 (OH), 1695 cm^{-1} (acid); pmr ($CDCl_3$) δ 6.16 (very br s, 2, OH protons), 3.54 (br s, 1, H_2), 2.52 (dd, $J_{6,7n} + J_{6,7x} = 14$ Hz, 1, H_6), 1.11 (s, 3, tertiary methyl), 1.07 (s, 3, tertiary methyl); mass spectrum *m/e* 198 (M^+).

Attempted Lactonization of Hydroxy Acid 14.—A solution of 70 mg of the hydroxy acid in 5 ml of formic acid containing 5 drops of concentrated sulfuric acid was left at 20° for 22 hr. The solution was then poured cautiously into excess aqueous sodium bicarbonate and extracted with ether. The extract was washed with aqueous sodium carbonate and water, then dried over anhydrous sodium sulfate. Evaporation of solvent yielded 5 mg of the crude δ-lactone **17**.[10]

Acetylation of Alcohol 2.—A solution of 9.9 g of the alcohol[1] in 70 ml of pyridine and 70 ml of acetic anhydride was left overnight at 20°. The reaction mixture was then poured into ice water and extracted with hexane. The extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of solvent yielded 11.6 g (97%) of the acetate **13**: ir 1735 cm^{-1} (acetate); pmr δ 5.46 (br s, 1, H_2), 3.98 (m, 2, C_{11} methylene), 2.29 (br s, 1, H_4), 1.98 (s, 3, acetate methyl), 1.75 (d, $J = 1.5$ Hz, 3, C_3 vinyl methyl), 1.07 (s, 3, C_1 methyl), 0.81 (d, $J = 6.5$ Hz, 3, C_9 methyl). The analytical sample was obtained by microdistillation, bp 100° (0.7 mm). *Anal.* Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 77.11; H, 10.40.

A 4:1 mixture of the alcohol **2** and its C_9 epimer[1] was also acetylated according to the above procedure to yield a mixture of acetates whose pmr analysis showed the characteristic C_9 methyl doublet of the minor epimer at δ 0.57 ($J = 6.5$ Hz).

Preparation of Olefin 21.—Gaseous hydrogen chloride was passed through a stirred solution of 41 g of the acetate **13** in 200 ml of ether at −70°, using apparatus similar to Brown's automatic hydrochlorinator.[14b] Evaporation of the ether at low temperature yielded the unstable chloride **23**, which was used in the next reaction without delay: pmr δ 4.02 (br t, $J = 6.5$ Hz, 2, C_{11} methylene), 1.97 (s, 3, acetate methyl), 1.68 (s, 3, C_3 methyl), 0.87 (s, 3, C_1 methyl).

The total amount of hydrochloride above was refluxed for 30 min with sodium ethoxide solution (16 g of sodium in 650 ml of ethanol). The reaction mixture was poured into water and extracted with hexane. The extract was washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated to yield 33 g of crude alcohols. A portion (3.2 g) of this mixture was chromatographed on a column of 165 g of 10% silver nitrate–alumina. Elution with hexane–ether (9:1) yielded 0.8 g of the endocyclic olefin **2**. The substitution product **24** (0.3 g) was eluted with hexane–ether (4:1) and 1.3 g of the desired exocyclic olefin **21** was eluted with ether. The isolated yield of **21** was 38% (50% based on unrecovered endocyclic olefin **2**): pmr δ 4.65 (m, 1, exocyclic olefinic proton), 4.47 (m, 1, exocyclic olefinic proton), 3.56 (m, 2, C_{11} methylene), 3.25 (br s, 1, OH), 0.91 (s, 3, C_1 methyl), 0.88 (d, $J = 6.5$ Hz, 3, C_9 methyl). The analytical sample was obtained by microdistillation, bp 80° (0.03 mm). *Anal.* Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.37; H, 11.45.

Tritylation of Alcohol 21.—A mixture of 1.15 g of the alcohol in 50 ml of benzene and 1 ml of pyridine was refluxed gently with

1.9 g of trityl chloride for 12 hr. The trityl ether **22** (2.1 g, 84%), which was isolated in the manner previously described[1] for **20**, crystallized from ethanol as colorless prisms: mp 104–105°; pmr δ 4.66 (m, 1, exocyclic olefinic proton), 4.49 (m, 1, exocyclic olefinic proton), 3.10 (m, 2, C_{11} methylene), 0.94 (s, 3, C_1 methyl), 0.73 (d, J = 6.5 Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{33}H_{38}O$: C, 87.95; H, 8.50. Found: C, 88.09; H, 8.50.

Preparation of Ketone 25.—To a solution of 4.9 g of the trityl ether **22** in 450 ml of purified dioxane and 150 ml of water was added 0.19 g of osmium tetroxide; the solution rapidly became dark brown. Finely powdered sodium metaperiodate (26 g) was added to the stirred solution over a period of 30 min and a flocculent precipitate of sodium iodate soon appeared. The mixture was stirred at 20° for an additional 22.5 hr, after which time the dark brown color of the solution had faded to a light yellow. The reaction mixture was poured into water and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product was purified by chromatography on 240 g of neutral activity I alumina. Elution with benzene yielded 3.45 g (75%) of the ketone **25**, which crystallized from ethyl acetate as colorless prisms: mp 176°; ir 1720 cm^{-1} (ketone); pmr δ 3.11 (m, 2, C_{11} methylene), 1.06 (s, 3, C_1 methyl), 0.73 (d, J = 6.5 Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{32}H_{36}O_2$: C, 84.91; H, 8.02. Found: C, 84.72; H, 7.80.

Preparation of Alcohol 26a.—A solution of 0.89 g of the ketone **25** in 30 ml of 1,2-dimethoxyethane was alkylated using potassium triphenylmethide[19] and methyl iodide (4 ml) in the manner described[1] for the ketone **6**. The trityl ether **26b** was not isolated, but the crude product was dissolved in 250 ml of ethanol and hydrogenated (2.5 atm) with 0.5 g of 5% palladium on charcoal at 20° for 14 hr. After removal of the catalyst by filtration and evaporation of ethanol, the product was purified by chromatography on 150 g of neutral activity I alumina. Elution with hexane and hexane–ether (9:1) yielded triphenylmethane, while 0.35 g (80%) of the alcohol **26a** was eluted with hexane–ether (1:1). Vpc analysis showed a single peak on 3% SE-30 at 160°: ir 3630 and 3450 (OH), 1715 cm^{-1} (ketone); pmr δ 3.56 (m, 2, C_{11} methylene), 3.37 (br s, 1, OH), 2.46 (br q, J = 7 Hz, 1, H_2), 0.99 (d, J = 7 Hz, 3, C_2 methyl), 0.98 (s, 3, C_1 methyl), 0.93 (d, J = 6.5 Hz, 3, C_9 methyl). The analytical sample was obtained by microdistillation, bp 114° (0.04 mm). *Anal.* Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.30; H, 10.99.

Preparation of Chloride 26d.—A mixture of 0.14 g of the alcohol **26a** and 0.17 g of *p*-toluenesulfonyl chloride in 5 ml of pyridine was left at 20° for 42 hr. Water (0.15 ml) was then added and the mixture was left for a further 6 hr at 20°, after which it was poured into excess dilute hydrochloric acid at 0° and extracted with hexane. The hexane extract was washed with dilute aqueous sodium carbonate and water, and then dried over anhydrous sodium sulfate. Evaporation of solvent yielded 0.11 g of a colorless oil, identified as the chloride **26d**: pmr δ 3.55 (m, 2, C_{11} methylene), 1.00 (d, J = 7 Hz, 3, C_2 methyl), 0.99 (s, 3, C_1 methyl), 0.97 (d, J = 6.5 Hz, 3, C_9 methyl). The ir spectrum showed no hydroxyl absorption.

Preparation of Tosylate 26c.—A mixture of 0.10 g of the alcohol **26a** and 0.23 g of *p*-toluenesulfonyl chloride in 3 ml of cold pyridine was left at −15° for 12 hr, and water (0.15 ml) was then added. The reaction mixture was left for a further 45 min at −15°, after which it was poured into excess dilute hydrochloric acid at 0° and extracted with hexane. The extract was washed with dilute aqueous sodium carbonate and water and dried over anhydrous sodium sulfate, and the solvent was evaporated to yield 0.16 g (93%) of the crude tosylate **26c** which crystallized from benzene–hexane as colorless prisms: mp 91–93°; ir 1715 cm^{-1} (ketone); pmr δ 4.02 (m, 2, C_{11} methylene), 2.46 (s, 3, aromatic methyl), 0.93 (d, J = 7 Hz, 3, C_2 methyl), 0.89 (s, 3, C_1 methyl), 0.85 (d, J = 6.5 Hz, 3, C_9 methyl). *Anal.* Calcd for $C_{21}H_{30}O_4S$: C, 66.64 H, 7.99 S, 8.46. Found: C, 66.98; H, 8.12; S, 8.20.

Cyclization of Tosylate 26c.—Potassium triphenylmethide solution[19] was added dropwise with a syringe to 80 mg of the tosylate in 3 ml of 1,2-dimethoxyethane. An immediate white precipitate of potassium tosylate was observed at 20°. The base was added until the red color of the triphenylmethide ion just persisted. The reaction mixture was left at 20° for 1.5 hr and then poured into water. Extraction with hexane followed by evaporation of the dried extracts yielded a crude product which was purified by chromatography on a small column of 10 g of neutral activity I alumina. Elution with hexane and hexane–benzene (9:1) gave triphenylmethane, while 35 mg (80%) of norseychellanone **5** was eluted with hexane–benzene (1:1). Vpc analysis (5% Ucon) showed the product to be homogeneous. The pmr, ir, and mass spectra of this compound were identical with the spectra[20] of authentic norseychellanone: ir (liquid film) 1715 cm^{-1} (ketone); pmr ($CDCl_3$) δ 0.97 (s, 3, tertiary methyl), 0.94 (s, 3, tertiary methyl), 0.79 (d, J = 6.5 Hz,[21] 3, secondary methyl).

Cyclization of Chloride 26d.—Potassium triphenylmethide solution was added with a syringe to 50 mg of the chloride in 2 ml of 1,2-dimethoxyethane until the red color of the triphenylmethide ion just persisted. The sealed flask was heated at 80–90° for 1.5 hr and by this time precipitation of potassium chloride was complete. The reaction mixture was then poured into water and the cyclic ketone norseychellanone (30 mg, 70%) was isolated as above.

Registry No.—(±)-**1**, 24568-69-2; (±)-**2**, 29450-72-4; (±)-**5**, 24461-21-0; **8**, 34993-78-7; **9**, 34993-79-8; **12**, 34996-50-4; (±)-**13**, 29448-19-9; **14**, 34996-52-6; **18**, 34996-53-7; (±)-**21**, 34996-54-8; (±)-**22**, 29448-16-6; (±)-**25**, 29448-15-5; (±)-**26a**, 29448-22-4; (±)-**26c**, 29448-23-5; (±)-**26d**, 34996-59-3.

(19) H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962).

(20) Copies of spectra were very kindly forwarded by Professor Ourisson.

(21) This coupling constant was incorrectly reported[4] as 5.5 Hz.

The Oxidation of Tetramethylethylene in the Presence of Rhodium(I) and Iridium(I) Complexes

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The oxidation of tetramethylethylene (TME) was studied in the presence of the oxygen-carrying complexes *trans*-$MCl(CO)(Ph_3P)_2$ (M = Rh, Ir). The oxidation was found to be rapid and quite selective under mild conditions, yielding 2,3-dimethyl-2,3-epoxybutane and 2,3-dimethyl-3-hydroxybutene-1 as the major oxidation products. The reactions are inhibited by hydroquinone, which is consistent with a free radical initiated autoxidation. The reaction of TME with oxygen was far more rapid than was oxidation of less substituted olefins in the presence of the Rh(I) and Ir(I) complexes, suggesting that initial coordinative interaction between the olefin and the metal center is not an important factor. A mechanistic pathway involving an allylic hydroperoxide intermediate is proposed.

Current interest in the oxidation of olefins in the presence of hydrocarbon-soluble, oxygen-carrying transition metal complexes has been stimulated by the possibility of novel oxidation pathways in these systems. The results of recent studies concerning the role of transition metal complexes in the oxidation of olefinic