Total Synthesis of (±)-Seychellene [1]

By **Narihiko Fukamiya, Michiharu Kato,** and **Akira Yoshikoshi,*** Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai, Japan

The total synthesis of (±)-seychellene (4,7,8-trimethyl-11-methylenetricyclo[5.3.1.$0^{3,8}$]undecane) (I) from 2,3-dimethylcyclohex-2-en-1-one (XIV) is described. The ketone (XIV) was converted into 2-methyl-2-(3-methyl-5-iodopentyl)-3-methylenecyclohexan-1-one (XV), which gave 2-methyl-2-(3-methyl-5-iodopentyl)-3-bromomethylcyclohexa-3,5-dien-1-one (XIX) with *N*-bromosuccinimide. Treatment of bromo-ketone (XIX) with chromium(II) chloride followed by acid gave 2,3-dimethyl-2-(3-methyl-5-iodopentyl)cyclohexa-3,5-dien-1-one (XXI). 2,3-Dimethyl-2-(3-methyl-5-dimethylaminopentyl)cyclohexa-3,5-dien-1-one (XXII) was obtained from the dienone (XXI) and was oxidised; pyrolysis of the resulting *N*-oxide yielded 4,7,8-trimethyltricyclo-[5.3.1.$0^{3,8}$]undec-9-en-11-one (VII). The adduct (VII) was hydrogenated to (±)-norseychellanone (4,7,8-trimethyltricyclo[5.3.1.$0^{3,8}$]undecan-11-one), whose transformation into (±)-seychellene is known.

SEYCHELLENE, a sesquiterpene isolated from patchouli oil as a minor constituent,[2,3] has been assigned a tricyclo[5.3.1.$0^{3,8}$]undecane structure [3] (I) related to patchouli alcohol [4] (II), which occurs in the same essential oil. Recently two total syntheses of seychellene were reported which both involved base-catalysed intramolecular alkylation of suitably functionalised bicyclic or tricyclic precursors to construct the tricyclo-[5.3.1.$0^{3,8}$]undecane skeleton. Thus, base-induced intramolecular cyclisation of the *cis*-decalone (III)

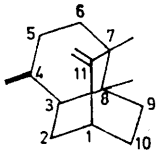
[1] Preliminary report, N. Fukamiya, M. Kato, and A. Yoshikoshi, *Chem. Comm.*, 1971, 1120.

[2] N. Tsubaki, K. Nishimura, and Y. Hirose, *Bull. Chem. Soc. Japan*, 1967, **40**, 597.

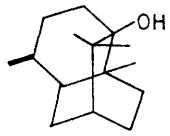
[3] G. Wolff and G. Ourisson, *Tetrahedron Letters*, 1968, **3949**; *Tetrahedron*, 1969, **25**, 4903.

[4] G. Büchi, R. E. Erickson, and N. Wakabayashi, *J. Amer. Chem. Soc.*, 1961, **83**, 927; M. Dobler, J. D. Dunitz, G. Gubler, H. P. Weber, G. Büchi, and J. Padilla O, *Proc. Chem. Soc.*, 1963, 383.

gave norseychellanone (V), which was then converted into seychellene (I) by reaction with methyl-lithium followed by dehydration.[5] Similarly, treatment of bicyclo[2.2.2]octane derivatives (IV; X = TsO or

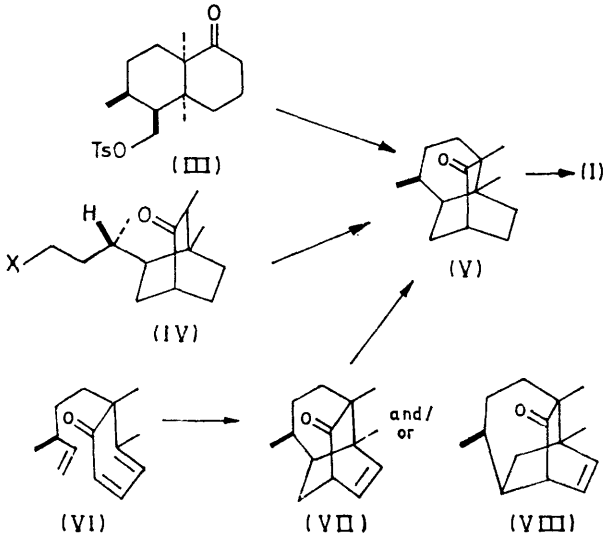


(I)



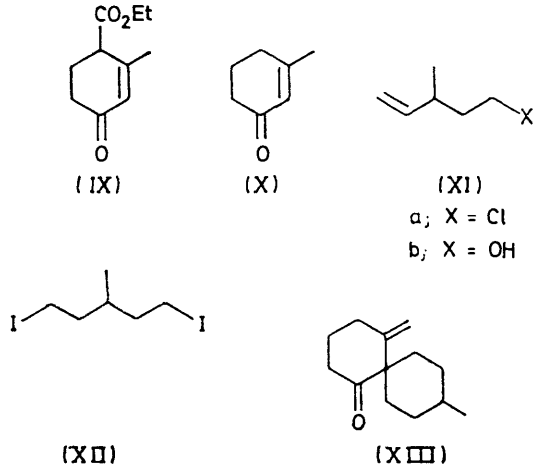
(II)

Cl) with base gave norseychellanone (V).[6] As an alternative, we presumed that on intramolecular Diels–Alder addition, the cyclohexadienone derivative (VI) might yield the tricyclic ketone (VII) or the isomeric adduct (VIII), the former being easily convertible into norseychellanone (V).



We report here the one-step construction of the tricyclo[5.3.1.$0^{3,8}$]undecane skeleton from the monocyclic precursor (XXIII) by this route.*

Initially we attempted to introduce an appropriate side-chain into Haagemann's ester (IX) or 3-methylcyclohex-2-en-1-one (X) using 3-methyl-5-chloropent-1-ene (XIa) [prepared from the known alcohol[7] (XIb)] or 3-methyl-1,5-di-iodopentane[8] (XII) as alkylating agents. Despite reports[9] of the introduction of an alkenyl group into Haagemann's ester at C-2 in moderate yield, treatment of Haagemann's ester with these halides [(XIa) and (XII)] under similar conditions gave no reaction. On the other hand, alkylation of 3-methylcyclohex-2-en-1-one[10] (X) with 1,5-di-iodo-3-methylpentane (XII) gave a spiroketone (XIII) using sodium amide in liquid ammonia as base.† Under similar conditions, 2,3-dimethylcyclohex-2-en-1-one[10] (XIV)



afforded the 2-alkylated product (XV),‡ which could be converted into the final product (V) in 35% yield. Treatment of the iodo-ketone (XV) with potassium t-butoxide in dimethyl sulphoxide § did not give the desired compound (XVIII) but an intramolecular alkylation product (XVI) as shown by the spectra. Silver fluoride in dry pyridine[11] also failed to give dehydro-iodination. The iodo-ketone (XV) was converted into the amino-ketone (XVII) by treatment with dimethylamine in ethanol. The product (XVII) was treated with hydrogen peroxide, and the resulting *N*-oxide was heated to produce the vinyl ketone (XVIII) in moderate overall yield. Attempts to produce the required cyclohexadienone system from the amino-ketone (XVII) were unsuccessful: bromination of the amino-ketone (XVII) with 2 equiv. of bromine in acetic acid, and treatment of the crude product with lithium carbonate and lithium bromide in dimethylformamide gave an oily product. This showed absorptions characteristic[12] of the αβγδ-conjugated cyclohexadi-

* Intramolecular Diels–Alder addition has been successfully employed for the synthesis of γ-apopicropodophillin (L. H. Klemm and K. W. Gopijoth, *Tetrahedron Letters*, 1963, 1243).

† The spiro-alkylation of the ketone (X) with some polymethylene dibromides under these conditions has been reported (M. S. Newman, V. Devries, and R. Darlok, *J. Org. Chem.*, 1966, **31**, 2171).

‡ The anticipated formation of diastereoisomers was not indicated by g.l.c., t.l.c., or n.m.r. data. Of the synthetic intermediates [(XV)—(XXII)] only the ketone (XVI) gave an n.m.r. spectrum indicative of a mixture of diastereoisomers.

§ These reaction conditions effected dehydro-iodination of a primary iodide in the synthesis of β-elemene (N. F. Wood and F. C. Chang, *J. Org. Chem.*, 1965, **30**, 2054).

[5] E. Piers, R. W. Britton, and W. de Waal, *Chem. Comm.*, 1969, 1069; *J. Amer. Chem. Soc.*, 1971, **93**, 5113.

[6] K. J. Schmalzl and R. N. Mirrington, *Tetrahedron Letters*, 1970, 3219; *J. Org. Chem.*, 1972, **37**, 2877.

[7] O. P. Vig, K. L. Matta, and I. Raj, *J. Indian Chem. Soc.*, 1964, **41**, 752; L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, 1967, **89**, 923.

[8] P. Karrer and J. Lee, *Helv. Chim. Acta*, 1934, **17**, 543; C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, 1963, **85**, 3743.

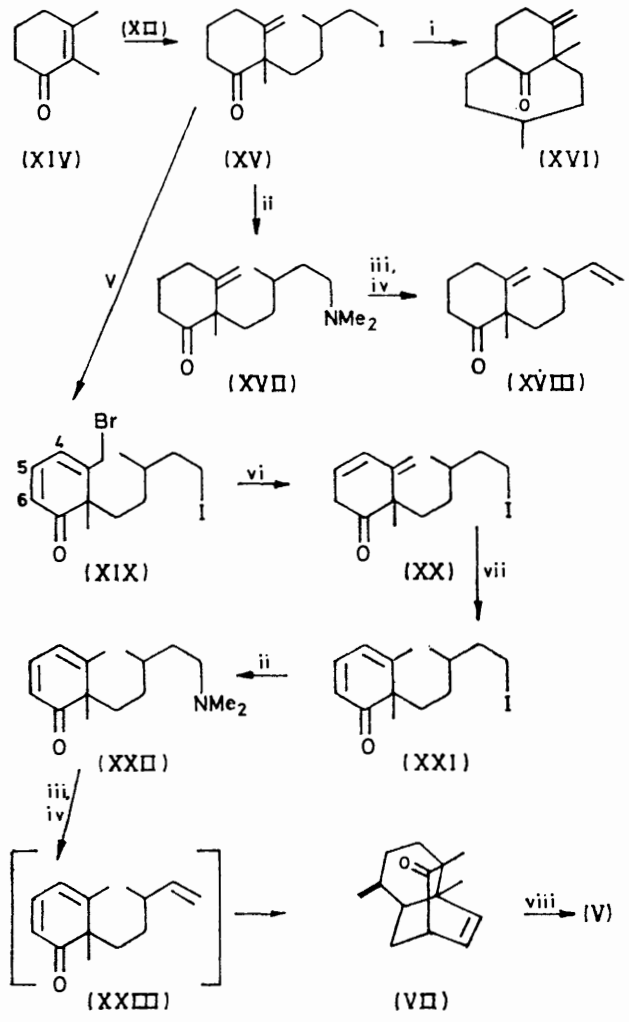
[9] W. S. Johnson, N. P. Jensen, J. Hooz, and E. J. Leopold, *J. Amer. Chem. Soc.*, 1968, **90**, 5872.

[10] L. I. Smith and G. F. Rouault, *J. Amer. Chem. Soc.*, 1943, **65**, 631.

[11] M. Fieser and L. Fieser, 'Reagents for Organic Synthesis,' Wiley-Interscience, New York, vol. 2, 1969, p. 364, and references cited therein.

[12] C. Ganter, K. D. Greuter, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1964, **47**, 427.

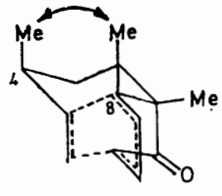
enone system at 1665, 1632, and 1566 cm^{-1}, but purification was difficult owing to the product's instability. Thus we decided to elaborate the iodo-ketone (XV).

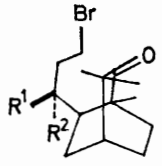


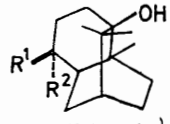
Reagents. i, Bu^tOK–DMSO; ii, Me_2NH; iii, H_2O_2; iv, heat; v, NBS; vi, $CrCl_2$; vii, H_3O^+; viii, H_2–Pd(C)

SCHEME

The iodo-ketone (XV) was treated with 1 equiv. of *N*-bromosuccinimide in carbon tetrachloride under standard conditions to give a bromo-ketone (*ca.* 30% yield). This showed absorptions due to the cyclohexa-1,3-dienone chromophore in the u.v. and i.r. spectra at 317 nm and 1658, 1632, and 1563 cm^{-1} and the n.m.r. spectrum was also consistent with the structure (XIX). The yield of the dienone (XIX) was increased to 64% by using 2 equiv. of the brominating agent. Reductive elimination of the allylic bromine atom of the dienone (XIX) by treatment with chromium(II) chloride in aqueous acetone gave the deconjugated ketone (XX) contaminated with a conjugated dienone (indicated in the i.r. spectrum). The ketone (XX) was unstable and was gradually transformed into the conjugated dienone; this transformation into the desired conjugated dienone (XXI) was also accomplished by heating ketone (XX) with toluene-*p*-sulphonic acid in ethanol. The terminal iodine atom of the dienone (XXI) was substituted by dimethylamine to give the amino-ketone (XXII), which was then treated with hydrogen peroxide. The resulting *N*-oxide was pyrolysed without purification. To avoid intermolecular Diels–Alder addition of the intermediate (XXIII), reaction in dilute solution was considered, but a suitable solvent could not be discovered. When the crude *N*-oxide was pyrolysed in the vaporiser of a g.l.c. apparatus, a main peak accompanied by three minor peaks was observed. The product corresponding to the main peak was collected by preparative g.l.c. in low yield (because of considerable polymerisation), and analytical g.l.c. indicated that the condensate was still contaminated by minor products. Preparative t.l.c. effectively separated the main component, and the oily product obtained was homogeneous by n.m.r., t.l.c., and g.l.c. and showed a saturated carbonyl absorption at 1718 cm^{-1} and an olefinic two-proton signal in the n.m.r. spectrum. Pyrolysis of the *N*-oxide under reduced pressure and concurrent distillation of volatile products afforded the adduct in improved yield (*ca.* 13%). Upon hydrogenation the above adduct gave a saturated ketone, which was identified as (±)-norseychellanone (V) by comparison with the spectra of authentic ketone. The formation of (±)-norseychellanone (V) indicated that the desired adduct (VII) was produced as the main product in the intramolecular Diels–Alder addition. The formation of the C-4 epimer of the adduct (VII) and the regioisomeric adducts [ketone (VIII) and its C-4 epimer] could not be confirmed, because insufficient material was available.







The formation of the C-4 epimer of (VII) may be hindered by a severe non-bonded interaction betwen the axial methyl groups at C-4 and C-8 in the transition state (XXIV). A similar argument has been used to explain the large difference in yields observed in the reductive

cyclisation of a pair of epimeric bromo-ketones [(XXVa) and (XXVb)] leading to patchouli alcohol (XXVIa) and epipatchouli alcohol (XXVIb),[13] respectively.

EXPERIMENTAL

U.v. spectra were run on a Cary model 14 spectrophotometer, and i.r. spectra on a Hitachi EPI-S2 or G-2 spectrophotometer. N.m.r. spectra with carbon tetrachloride as solvent (unless otherwise stated) and tetramethylsilane as internal standard were recorded on a JNMC-60HL spectrometer. Coupling constants (J) are given in Hz.

5-Chloro-3-methylpent-1-ene (XIa).—Thionyl chloride (1·1 ml) was added dropwise to a stirred solution of 3-methylpent-4-en-1-ol (1 g) in pyridine (5 ml) in an ice-bath. The mixture was stirred for 12 h and poured into ice–water. The product was extracted with ether, and the combined extracts were washed with water, dilute hydrochloric acid, and water. The solvent was evaporated off, and the residue was chromatographed on a silica gel column. *5-Chloro-3-methylpent-1-ene* (XIa) (679 mg) was eluted with light petroleum; $\nu_{max.}$ (CCl_4) 3050, 1644, 997, and 915 cm^{-1}, δ 1·05 (3H, J 7), 3·95 (2H, m), and 4·86—6·02 (3H, ABX m) (Found: C, 60·9; H, 9·4. $C_6H_{11}Cl$ requires C, 60·8; H, 9·5%).

Spiro-alkylation of 3-Methylcyclohex-2-en-1-one (X) *with 1,5-Di-iodo-3-methylpentane* (XII).—An ethereal solution of 3-methylcyclohex-2-en-1-one [10] (X) (553 mg) was added to a stirred solution of sodium amide [from sodium (149 mg) and liquid ammonia (*ca.* 40 ml)], and the mixture was stirred for an additional 30 min. An ethereal solution of 1,5-di-iodo-3-methylpentane [8] (1·61 g) was added and the mixture was refluxed for 1 h. The reaction was quenched by adding ammonium chloride, the liquid ammonia was evaporated off, and the residue was extracted with ether. The ethereal solution was washed with water, dilute hydrochloric acid, water, and then brine. Removal of the solvent left an oil (1·09 g), which was chromatographed on a silica gel column. Ether–light petroleum (1 : 10) eluted *9-methyl-5-methylenespiro[5.5]undecan-1-one* (XIII) (384 mg, 40%), $\nu_{max.}$ (film) 3110, 1709, 1625, and 896 cm^{-1}, δ 0·90 (3H, d, J 6) and 4·77br (2H, m) (Found: C, 81·4; H, 10·5. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%).

Alkylation of 2,3-Dimethylcyclohex-2-en-1-one (XIV) *with 1,5-Di-iodo-3-methylpentane* (XII).—An ethereal solution of 2,3-dimethylcyclohex-2-en-1-one [10] (XIV) (15·6 g) was added to sodium amide solution [from sodium (3·50 g) and liquid ammonia (*ca.* 400 ml)], and the mixture was stirred for 1 h. 1,5-Di-iodo-3-methylpentane [8] (XII) (51·5 g) was added to the mixture over 30 min, and stirring was continued for 1·5 h. Ammonium chloride (9·72 g) was added to quench the reaction, and liquid ammonia was evaporated off to leave an oil, which was dissolved in ether. The solution was washed with water, dilute hydrochloric acid, and then water, and dried. The residue obtained by evaporation was chromatographed on a silica gel column, and ether–light petroleum (1 : 20) eluted *2-(5-iodo-3-methylpentyl)-2-methyl-3-methylenecyclohexan-1-one* (XV) (14·4 g, 35%) as an oil, $\nu_{max.}$ (film) 3080, 1707, 1638, and 895 cm^{-1}, δ 0·88 (3H, d, J 6), 1·14 (3H, s), 3·20br (2H, t, J 7), and 4·78br and 4·89br (both 1H, s) (Found: C, 49·9; H, 6·7. $C_{14}H_{23}IO$ requires C, 50·3; H, 6·95%).

1,4-Dimethyl-10-methylenebicyclo[5.3.1]undecan-11-one (XVI).—Dimethyl sulphoxide (3 ml) was added to potassium t-butoxide solution [from potassium (104 mg) and t-butyl alcohol (2 ml)]. A solution of the iodo-ketone (XV) (336 mg) in dimethyl sulphoxide (1 ml) was added, and the mixture was stirred for 1 h at room temperature and extracted with light petroleum. The combined extracts were washed with water and evaporated to give an oil (266 mg). P.l.c. [ether–light petroleum (1 : 10)] gave the *product* (XVI), $\nu_{max.}$ (film) 3120, 1695 (CO), 1630, and 890 cm^{-1}, δ 0·85 and 0·88 (total 3H, both d, J 6), 1·10 (3H, s), and 4·77 and 4·80 (both 1H, d), *m/e* 206 (M^+) (Found: C, 81·0; H, 10·8. $C_{14}H_{22}O$ requires C, 81·5; H, 10·8%).

2-(5-Dimethylamino-3-methylpentyl)-2-methyl-3-methylenecyclohexan-1-one (XVII).—Dimethylamine, generated by adding potassium hydroxide solution to aqueous 40% dimethylamine hydrochloride solution and purged by nitrogen, was passed through an ethanolic solution of the iodo-ketone (XV) (123 mg) at room temperature with stirring for several h. After the starting material was consumed, the solvent was evaporated off, and N-sodium hydroxide was added to the residue. The mixture was extracted with ether, and the combined extracts were washed with water and brine. Evaporation gave the *amino-ketone* (XVII) (89 mg, 95%) as an oil, $\nu_{max.}$ (film) 3070, 2780, 2730, 1710, 1645, and 895 cm^{-1}, δ 0·88 (3H, d, J 6), 1·15 (3H, s), 2·13 (6H, s), and 4·80br and 4·88br (both 1H, s) (Found: C, 76·2; H, 11·6. $C_{16}H_{39}NO$ requires C, 76·2; H, 11·6%).

2-Methyl-3-methylene-2-(3-methylpent-4-enyl)cyclohexan-1-one (XVIII).—Aqueous hydrogen peroxide solution (30%; 630 mg) was added to a solution of the amino-ketone (XVIII) (1·387 g) in methanol (4 ml), and the mixture was set aside at 30° for 24 h. Two additional portions of hydrogen peroxide solution (*ca.* 630 mg each) were added at intervals of 2 h, and the end-point of the reaction was checked by phenolphthalein. The solvent was removed *in vacuo* at room temperature, and the oily residue was heated at 150° for 1 h. The *vinyl ketone* (XVIII) (696 mg, 62%), $\nu_{max.}$ (film) 3070, 1708, 1640, 990, 910sh, and 895 cm^{-1}, δ 0·96 (3H, d, J 7), 1·11 (3H, s), 4·70—5·10 (4H), and 5·35—5·95 (1H), was obtained on evaporative distillation at 180—190° (bath) and 6 mmHg (Found: C, 81·3; H, 10·5. $C_{14}H_{22}O$ requires C, 81·5; H, 10·75%).

3-Bromomethyl-2-(5-iodo-3-methylpentyl)-2-methylcyclohexa-3,5-dien-1-one (XIX).—A solution of the iodo-ketone (XV) (341 mg), *N*-bromosuccinimide (362 mg), and benzoyl peroxide (16 mg) in carbon tetrachloride (8 ml) was heated under reflux for 20 min. Succinimide was filtered off, and the filtrate was evaporated to leave an oil (869 mg). The oil was subjected to column chromatography on silica gel using ether–light petroleum (1 : 10) as eluant, and the *dienone* (XIX) (333 mg, 65%) was obtained as an oil, $\lambda_{max.}$ (ethanol) 317 nm (ε 7250), $\nu_{max.}$ (film) 1658, 1632, 1563, 820, and 710 cm^{-1}, δ 0·88 (3H, d, J 6), 1·30 (3H, s), 3·17br (2H, t, J 7, CH_2I), 4·15 (2H, s, CH_2Br), 6·04 [1H, d, J 9, C(6)H], 6·65 [1H, d, J 6, C(4)H], and 7·07 [1H, dd, J 9 and 6, C(5)H] (Found: C, 40·8; H, 4·8. $C_{14}H_{20}BrIO$ requires C, 40·9; H, 4·9%).

2-(5-Iodo-3-methylpentyl)-2,3-dimethylcyclohexa-3,5-dien-1-one (XXI).—A large excess of aqueous chromium(II) chloride solution [14] was added to a solution of the dienone (XIX) (1·352 g) in acetone (4 ml), and the mixture was

[13] S. Danishefsky and D. Dumas, *Chem. Comm.*, 1968, 1268.
[14] G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Amer. Chem. Soc.*, 1950, **72**, 4077.

stirred under nitrogen for 5 min. The solvent was evaporated off *in vacuo*, and the residue was extracted with ether. The combined extracts were washed with water and brine, and dried. Removal of the ether left an oil (985 mg). The i.r. spectrum (film) showed strong absorptions due to a saturated carbonyl group and an exocyclic double bond at 1715 and 888 cm^{-1}, respectively; weak absorptions due to a conjugated dienone were observed at 1665, 1645, and 1607 cm^{-1}. At room temperature, the spectrum indicated the gradual increase of the proportion of conjugated dienone. Since isolation of the primary reduction product (XX) was not feasible, the crude product was converted into conjugated ketone by treatment with acid.

A solution of the reduction product (806 mg) and toluene-*p*-sulphonic acid (89 mg) in ethanol (8 ml) was heated under reflux for 1 h. The solvent was removed, water was added to the residue, and the solution was extracted with ether. Work-up gave the *conjugated dienone* (XXI) (830 mg) as an oil, $\nu_{max.}$ (film) 1662, 1630, 1565, 820, and 710 cm^{-1}, δ 0·85 (3H, d, *J* 6), 1·20 (3H, s), 1·91 (3H, s), 3·20br (2H, t, *J* 7), 5·87 [d, *J* 9·5, C(6)H], 6·02 [d, *J* 6, C(4)H], and 6·85 [1H, dd, *J* 9·5 and 6, C(5)H] (Found: C, 50·3; H, 6·2. $C_{14}H_{21}IO$ requires C, 50·6; H, 6·4%).

2-(5-*Dimethylamino*-3-*methylpentyl*)-2,3-*dimethylcyclohexa*-3,5-*dien*-1-*one* (XXII).—Dimethylamine was passed through a solution of the dienone (XXI) (830 mg) in ethanol (30 ml) until no starting material was detected by t.l.c. The solvent was evaporated off, the residue was dissolved in ether, and the amino-ketone (XXII) was extracted with N-hydrochloric acid. Work-up afforded the *amino-ketone* (XXII) (509 mg), $\nu_{max.}$ (film) 2830, 2790, 1664, 1632, 1565, 813, and 710 cm^{-1}, δ 0·85 (3H, d, *J* 6), 1·17 (3H, s), 1·97 (3H, s), 2·23 (6H, s), 6·02 [d, *J* 9·5, C(4)H], 6·19 [d, *J* 6, C(6)H], and 7·05 [1H, dd, *J* 9·5 and 6, C(5)H] (Found: C, 76·8; H, 10·7. $C_{14}H_{27}ON$ requires C, 77·1; H, 10·9%).

4,7,8-*Trimethyltricyclo*[5.3.1.$0^{3,8}$]*undec*-9-*en*-11-*one* (VII).—(*a*) Hydrogen peroxide solution (30%; 415 mg) was added in portions to a solution of the amino-ketone (XXII) (508 mg) in methanol (3 ml), and the mixture was left at room temperature. After treatment as for the vinyl ketone (XVIII), the crude oily *N*-oxide was obtained. The crude product was pyrolysed in the vaporiser (230°) of a g.l.c. apparatus equipped with a 20% SE-30 column (3 mm × 2 m; column temperature, 200°; helium flow, 9 ml min^{-1}). Four peaks were observed on the chromatogram with t_R 10, 15·5, 16·5 (shoulder), and 33 min, in the ratio 1 : 5 (including the shoulder) : 1. The main peak including the shoulder was separated to give an oil (14 mg), which was further purified by p.l.c. on silica gel using ether–light petroleum (1 : 10) as eluant. The *adduct* (VII) (8·4 mg), $\nu_{max.}$ (CCl_4) 3050, 1718, and 705 cm^{-1}, δ 0·85 (d, *J* 6), 0·85 and 1·25 (both 3H, s), and 6·20 (2H, m), was obtained as an oil (Found: M^+, 204·1490. $C_{14}H_{20}O$ requires *M*, 204·1415).*

(*b*) By similar treatment the crude *N*-oxide was obtained from the amino-ketone (XXII) (40 mg), which was heated in an oil-bath at 150° under reduced pressure (10 mmHg) with stirring. The volatile part of the pyrolysate was evaporatively distilled giving an oil (16 mg), which was purified as before to give the adduct (VII) (4 mg).

(±)-*Norseychellanone* (4,7,8-*Trimethyltricyclo*[5.3.1.$0^{3,8}$]-*undecan*-11-*one*).—A solution of the adduct (VII) (13·2 mg) in methanol (3 ml) was hydrogenated over 10% palladium–carbon (7 mg) to give an oil. Purification by p.l.c. on silica gel using light petroleum as eluant gave (±)-norseychellanone (V) (10·2 mg). The i.r. [$\nu_{max.}$ (film) 1718 cm^{-1}] and n.m.r. spectra [δ($CDCl_3$) 0·82 (3H, d, *J* 6), 0·95 (3H, s), and 0·97 (3H, s)] of the product were identical with those of the authentic ketone † (Found: M^+, 206·1697. Calc. for $C_{14}H_{22}O$: *M*, 206·1670).*

[3/004 *Received*, 1*st January*, 1973]

* High resolution mass spectra were taken with a JEOL JMS-015 G mass spectrometer by courtesy of Japan Electron Optics Laboratory, whom we thank.

† We thank Professors G. Ourisson and E. Piers for providing the spectra.