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SYNTHESIS OF MONO- AND SESQUITERPENOIDS—I

RACEMIC NORCARAN-2-ONE, *trans*-CARAN-2-ONE AND *trans*-DIHYDROSESQUICARAN-2-ONE

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Abstract—The title compounds were synthesized by the application of the intramolecular α-ketocarbene-olefin addition reaction.

BICYCLO[4.1.0]HEPTANE ring system is found in some terpenes such as carenes,[1] susquicarene[2] and sirenin.[3] We focused our attention on the synthesis of these compounds because of the interesting biological activity of the last mentioned plant sex hormone, sirenin.

In 1961 Stork and Ficini devised a simple method for the construction of this ring system.[4] They converted the unsaturated α-diazoketone (**A**) into bicyclo[4.1.0] heptan-2-one (**B**) by intramolecular α-ketocarbene-olefin addition. Application of this reaction to some α-diazoketones with a tri-substituted double bond is the theme of this paper.

Racemic norcaran-2-one. 4-Methylpent-3-enyl bromide (Ia)[5] was condensed with diethyl malonate to give a mono-substituted malonic ester (IIa). This gave an acid (IIIa) after hydrolysis and decarboxylation. Its sodium salt was treated with oxalyl chloride to give an acyl chloride (IVa) which was converted into a diazoketone (Va), a solution of which was heated in the presence of powdered copper and cupric sulfate to give crude (±)-norcaran-2-one (VIa)*[6] in 44% yield from IIIa. This was shown to be 90% pure by the GLC analysis. IR and NMR spectra of both the crude ketone (VIa) and its pure crystalline 2,4-dinitrophenylhydrazone supported the assigned structure.

Racemic trans-*caran*-2-one. The bromide (Ia) was condensed with diethyl methylmalonate to give a di-substituted malonic ester (IIb). Subsequent steps (IIb → IIIb → IVb → Vb →) were carried out as described in the preceding section to yield a crude ketone (VIb) in 28% yield from Vb. The ketone was estimated to be 90% pure by GLC on a capillary column. This was purified by chromatography on silicic acid impregnated with silver nitrate.[7] The IR and NMR spectra of the pure ketone are in good accord with the published values of (−)-*trans*-caran-2-one (VIb)[8] which is known to be more stable than *cis*-caran-2-one.[9] A pure crystalline 2,4-dinitrophenylhydrazone was obtained from the crude ketone.

* Although the formulas depicted represent only one enantiomer, they are taken to mean a racemate in the case of synthetic products.

A mixture of racemic trans-*dihydrosesquicaran-2-one and its* C-7 *epimer.* The starting C_{11}-bromide (Ic) was synthesized as follows. Methyl cyclopropyl ketone was added to a Grignard reagent prepared from the bromide (Ia) to give an alcohol (VII).[5] This was hydrogenated over Pd-C to afford a saturated alcohol (VIII) in 61% yield. The rest of the material was a low-boiling mixture of hydrogenolysis products. The alcohol (VIII) was treated with 48% hydrobromic acid to give the desired bromide (Ic) in fair yield. This was condensed with diethyl methylmalonate to give a di-substituted malonic ester (IIc). Subsequent manipulations as described before (IIc → IIIc → IVc → Vc →) yielded a crude ketonic product in 55% yield from the diazoketone (Vc). This was purified by chromatography on silicic acid impregnated with silver nitrate to give an analytically pure product which was shown to be a mixture of racemic *trans*-dihydrosesquicaran-2-one (VIc) and its C-7 epimer (1:1) by the GLC analysis.* The 7β-methyl isomer (VIc) was assumed to exhibit a longer retention time owing to its extending C_6 side chain. The assignment of the α-configuration to the C-3 Me group is in analogy to the formation of *trans*-caran-2-one (VIb) by this carbene-olefin addition.

* Although it is difficult to entirely exclude the possibility that the mixture consists of two epimers at C-3 instead of C-7 as a referee questioned, the following facts support our assignment. (i) The acid IIIc is a mixture of Δ^5-*cis* and *trans* isomers (1:2·8) as evidenced by the GLC analysis of the corresponding methyl ester (Experimental). Since no reaction is involved in the synthetic sequence which will affect the geometry of the double bond, all the other intermediates, Ic, IIc, IVc and Vc, are also mixtures of each two geometrical isomers. The intramolecular carbene addition of the diazoketone Vc should, therefore, give a mixture of C-7 epimers regardless of the configuration at C-3. Our unpublished observation on the cyclization of a mixture of Δ^6-*cis*- and *trans*-1-diazo-7,11-dimethyldodeca-6,10-dien-2-one, which gives a mixture of 3-demethylsesquicaran-2-one and its C-7 epimer, supports this argument. The discrepancy between the ratio of the Δ^5-*cis* and *trans* isomers of IIIc (1:2·8) and the ratio of the two isomeric ketones (VIc and VIć, 1:1) may be due to the difference in the yields of the two ketones from the corresponding starting diazoketones (Vc). A synthesis of a stereochemically pure diazoketone (Vc) and its cyclization are an interesting problem. (ii) Some information is obtained by the comparison of the NMR data of *cis*- and *trans*-caran-2-ones with that of the mixture of two dihydrosesquicaran-2-ones as shown in the Table. (It is doubtful whether the conformations of *cis*- and *trans*-dihydrosesquicaran-2-ones are similar to those of *cis*- and *trans*-caran-2-ones which have been discussed by Acharya and Brown,[9] and hence the NMR spectral comparison is not on a sound basis.) Firstly, the C-7 Me protons of the dihydrosesquicaranone mixture absorb at $\delta = 1{\cdot}14$ ppm as a broad 3-proton singlet with a half-band width of 4 Hz. This is in accord with our assumption that the mixture consists of two C-7 epimers of *trans*-dihydrosesquicaran-2-ones (VIc). The NMR spectrum of a mixture of any other isomeric ketones should exhibit two separate absorptions due to the C-7 Me protons, for two signals with a difference of 0·05 ppm or more in their chemical shifts are easily distinguishable in the 100 MHz spectrum. Secondly, the C-3 Me protons of the epimeric mixture (VIc and VIc') absorb at $\delta = 0{\cdot}98$ ppm as 3-proton doublet ($J = 6$ Hz). These values including the half-band width (2 Hz) of the each lines are exactly the same as those of *trans*-caran-2-one (VIb) and exclude the possibility that one of the two *cis*-dihydrosesquicaran-2-one is the component of the mixture. The stereoselective formation of *trans*-caran-2-one (VIb) from the diazoketone Vb also supports the view described in the text.

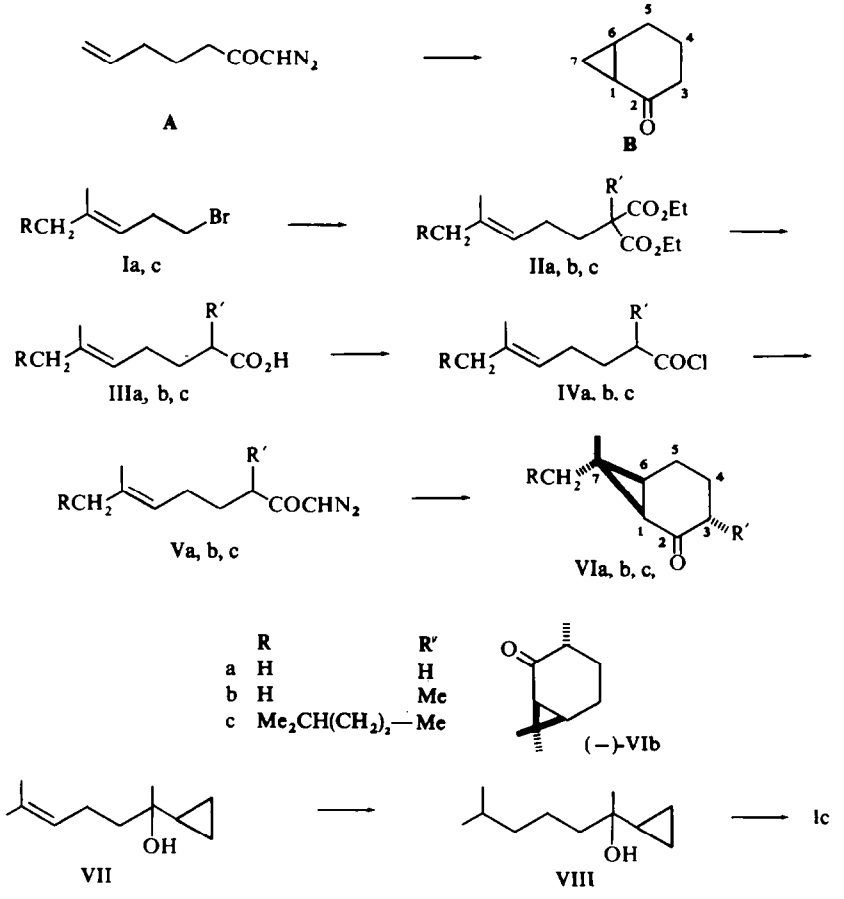
TABLE 1. CHEMICAL SHIFT (δ FROM TMS, PPM) OF THE METHYL PROTONS IN CARANONES

Name	Methyl at C-3	β-Methyl at C-7	α-Methyl at C-7
cis-Caran-2-one[8, 9]	0·96 (d, $J = 6$ Hz)	1·07	1·12
trans-Caran-2-one[8, 9]	0·98 (d, $J = 6$ Hz)	1·17	1·19
The mixture of dihydrosesquicaran-2-ones	0·98 (d, $J = 6$ Hz)	1·14	

GCMS measurements revealed that the mass spectra of both the racemic ketone (VIc) and its C-7 epimer were identical with that of the optically active ketone (VIc). This established the identity of the plane structure of the three compounds. The position of the major absorptions in the IR and NMR spectra of the synthetic mixture are almost identical with those of the optically active dihydrosesquicaran-2-one, although small differences are observed in the relative intensities of the major absorptions and in the position and intensity of small peaks. This may be due to the presence of the C-7 epimer in the synthetic product.

The direct GLC comparison of the synthetic product with the optically active ketone was impossible, since an authentic sample was not available.

In conclusion this study added further examples to the application of the α-ketocarbene-olefin addition[10, 11] in terpene synthesis[12] and opened the way to the synthesis of sesquicarene[13] and sirenin.



EXPERIMENTAL

All m.ps and b.ps were uncorrected. IR spectra refer to Nujol mulls for solid samples and films for liquids. NMR spectra were recorded at 100 MHz in CCl_4 with TMS as an internal standard unless otherwise stated.

Diethyl 4-methylpent-3-enylmalonate (IIa). A soln of diethyl malonate (80 g) in EtOH (50 ml) was added to a soln of NaOEt (from 11·5 g of Na) in EtOH (200 ml). To this mixture Ia (80 g) in EtOH (50 ml) was

added with stirring at 0–5°. After stirring for 1 hr at 0–5°, the mixture was heated under reflux for 2 hr with stirring, concentrated *in vacuo*, poured into water and extracted with ether. The ethereal soln was washed with sat NaCl aq, dried ($MgSO_4$) and concentrated. The residue was distilled to give 90 g (75%) of IIa, b.p. 103–123°/5 mm. An analytical sample boiled at 104–105°/2 mm, n_D^{19} 1·4432; ν_{max} 1730 (broad), 1290, 1240, 1220, 1130, 1080, 1040, 1020, 855 cm^{-1}; δ 1·23 (6H, t, J = 6 Hz), 1·55 (3H, s), 1·65 (3H, s), 4·05 (4H, q, J = 6 Hz) 5·00 (1H, broad t) ppm. (Found: C, 64·64; H, 9·02. $C_{13}H_{22}O_4$ requires: C, 64·44; H, 9·15%).

6-*Methylhept-5-en*-1-*oic acid* (IIIa). A soln of IIa (87 g) in 95% EtOH (150 ml) was mixed with KOH aq (87 g in 200 ml). The mixture was heated under reflux for 2 hr with stirring and concentrated *in vacuo* to remove EtOH. After acidification with AcOH (200 ml) the mixture was heated under reflux for 2 days, cooled, diluted with water and extracted with ether. The ethereal soln was washed with water and sat NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was distilled to give 46 g (92%) of IIIa, b.p. 125–126°/13 mm. An analytical sample boiled at 110–111°/4 mm, n_D^{20} 1·4492; ν_{max} ~3400–~2600, 1705, 960 cm^{-1}; δ 1·58 (3H, s), 1·67 (3H, s), 5·00 (1H, t), 12·08 (1H, s) ppm. (Found: C, 67·46; H, 9·98. $C_8H_{14}O_2$ requires: C, 67·57; H, 9·93%).

6-*Methylhept-5-en*-1-*oyl chloride* (IVa). A soln of IIIa (23 g) in 95% EtOH (100 ml) was neutralized with NaOH aq employing phenolphthalein as an indicator. The soln was concentrated *in vacuo*. The wet Na salt of IIIa was suspended in benzene and the benzene was removed *in vacuo*. This was repeated several times to remove water and the dry Na salt was suspended in dry benzene (150 ml). Oxalyl chloride (35 g) was added to the suspension with shaking at 0–5°. The mixture was stirred for 1 hr at 0–5°, filtered through celite and concentrated *in vacuo* to give an oily IVa. This was employed for the next step without further purification.

1-*Diazo*-7-*methyloct*-6-*en*-2-*one* (Va). A soln of the above IVa in dry benzene (50 ml) was added to a soln of CH_2N_2 (from 50 g of N-nitroso-N-methylurea) in ether (ca. 600 ml) under ice-cooling. The mixture was left to stand at 0–5° for 2 hr and then at room temp for 16 hr, filtered and concentrated *in vacuo* to give crude Va, ν_{max} 2130, 1730 (w, due to impurities), 1645, 1380, 1150, 1040 cm^{-1}. This was employed for the next step without further purification.

(±)-3-*Norcaran*-2-*one* (VIa). A soln of the above Va in cyclohexane (300 ml) was added dropwise to a stirred and refluxing suspension of powdered Cu (1·5 g) and $CuSO_4$ (0·4 g) in cyclohexane (700 ml) during 1·5 hr. After the addition the mixture was stirred and heated under reflux for 8 hr, then cooled, filtered and concentrated *in vacuo*. The residue was distilled to give 10·0 g (44% from IIIa) of crude VIa, b.p. 88–102°/12 mm. An analytical sample boiled at 91–92°/15 mm, n_D^{22} 1·4783; ν_{max} 173((w, due to impurities), 1675 (s), 1450, 1420, 1370, 1340, 1325, 1240, 1210, 1180, 1115, 1070, 1040, 890, 755 cm^{-1}; δ 1·18 (3H, s), 1·20 (3H, s) ppm. (Found: C, 76·97; H, 10·22. $C_9H_{14}O$ requires: C, 78·21; H, 10·21%). This figure indicates the presence of impurities. GLC analysis: Column, SE30 2·0 m × 3 mm; Column temp, 105°; Carrier gas, He 1·0 kg/cm^2; Retention time: 5·0 min, 7·8 min (area ratio = 1:9). 2,4-*Dinitrophenylhydrazone*: orange-colored elongated prisms from EtOH, m.p. 150–151°, ν_{max} 3380, 1625, 1590, 1540, 1510, 1425, 1380, 1350, 1315, 1280, 1260, 1220, 1145, 1080, 915, 830, 770, 745, 725 cm^{-1}: δ ($CDCl_3$) 1·06 (3H, s), 1·45 (3H, s), 7·90–8·75 (3H) ppm. (Found: C, 56·55; H, 5·73; N, 17·75. $C_{15}H_{18}O_4N_4$ requires: C, 56·59; H, 5·70; N, 17·60%).

Ethyl 2-*carbethoxy*-2,6-*dimethylhept*-5-*en*-1-*oate* (IIb). The bromide Ia (25 g) and diethyl methylmalonate (25 g) were condensed as described for IIa to give 23·3 g (57%) of IIb, b.p. 115–120°/4 mm. An analytical sample boiled at 110–111°/4 mm; n_D^{14} 1·4470; ν_{max} 1730, 1280, 1250, 1190, 1130, 1050, 860 cm^{-1}; δ 1·26 (6H, t, J = 6 Hz), 1·36 (3H, s), 1·58 (3H, s), 1·66 (3H, s), 4·10 (4H, q, J = 6 Hz), 5·05 (1H, broad t) ppm. (Found: C, 67·38; H, 9·06. $C_{14}H_{24}O_4$ requires: C, 67·13; H, 9·02%).

2,6-*Dimethylhept*-5-*en*-1-*oic acid* (IIIb). The ester IIb (22 g) was processed as described for IIIa to give 11·0 g (86%) of IIIb, b.p. 110–120°/4 mm. An analytical sample boiled at 104–105°/4 mm, n_D^{20} 1·4482; ν_{max} ~3400–~2600, 1700, 1290, 1240, 940 cm^{-1}; δ 1·18 (3H, d, J = 7 Hz), 1·59 (3H, s), 1·67 (3H, s), 5·04 (1H, broad t) ppm. (Found: C, 68·43; H, 10·11. $C_9H_{16}O_2$ requires: C, 69·19; H, 10·32%).

2,6-*Dimethylhept*-5-*en*-1-*oyl chloride* (IVb). The acid IIIb (11 g) was converted into its Na salt by neutralizing with NaOMe (3·8 g) in EtOH. The Na salt was treated with oxalyl chloride (25 g) as described in the preparation of IVa to give an oily IVb.

1-*Diazo*-3,7-*dimethyloct*-6-*en*-2-*one* (Vb). The above IVb was treated with ethereal CH_2N_2 (from 25 g of N-nitroso-N-methylurea) to give crude oily Vb, ν_{max} 2150, 1730 (w, due to impurities), 1640, 1370, 1325, 1150, 1110, 1040 cm^{-1}.

(±)-*trans*-Caran-2-one (VIb). A soln of the above Vb in cyclohexane (150 ml) was added dropwise to a stirred and refluxing suspension of powdered Cu (0·75 g) and $CuSO_4$ (0·2 g) in cyclohexane (350 ml) during 1·5 hr. After the addition the mixture was stirred and heated under reflux for 8 hr, then cooled, filtered and

concentrated *in vacuo*. The residue was distilled to give 3·0 g (28% from IIIb) of crude VIb, b.p. 95–102°/20 mm. Redistillation afforded a purer sample, b.p. 97–98°/15 mm, n_D^{21} 1·4760, ν_{max} 1735 (w, due to impurities), 1700 (sh, due to impurities), 1680 (s), 1635 (w, due to impurities), 885 cm^{-1}; δ 0·98 (3H, d, J = 6 Hz), 1·18 (3H, s), 1·20 (3H, s) ppm. GLC analysis: Column, Castor wax 45 m × 0·5 mm; Column temp 170°; Carrier gas, N_2, 0·5 kg/cm^2; Retention time: 2·3 min, 4·9 min (area ratio = 1:9).

This was purified by chromatography on SiO_2-$AgNO_3$. A column (27 cm × 2·5 cm) in pet. ether was prepared from SiO_2 (50 g) and $AgNO_3$ aq (4 g in 20 ml). The crude VIb (1·3 g) in a small amount of pet. ether was placed on the top of the column. The eluant was saturated with Ag^+ by shaking with $AgNO_3$ aq in a separatory funnel prior to use. All fractions were 200 ml. Fractions No. 1–6 (pet. ether) gave 56 mg of oily impurities. Fractions 7–15 (pet. ether: benzene = 9:1) gave 536 mg of almost pure VIb. An analytical sample boiled at 98–100°/20 mm, n_D^{17} 1·4775; ν_{max} 1680, 1380, 1240, 1225, 1180, 1120, 1050, 1030, 990, 890, 765 cm^{-1}; δ 0·98 (3H, d, J = 6 Hz), 1·17 (3H, s), 1·19 (3H, s) ppm. The spectra were identical with those of the optically active ketone. (Found: C, 79·55; H, 10·21. $C_{10}H_{16}O$ requires: C, 78·89; H, 10·59%). *2,4-Dinitrophenylhydrazone* Orange leaflets from EtOH, m.p. 118–119°, ν_{max} 3360, 3120, 1614, 1585, 1340, 1315, 1280, 1135 cm^{-1}; δ ($CDCl_3$) 1·02 (3H, s), 1·28 (3H, d, J = 6 Hz), 1·43 (3H, s), 7·90–8·40 (3H) ppm. (Found: C, 57·29; H, 6·34; N, 16·83. $C_{16}H_{20}O_4N_4$ requires: C, 57·82; H, 6·07; N, 16·86%).

2-Cyclopropyl-6-methylheptan-2-ol (VIII). An alcohol VII (59 g) in 95% EtOH (200 ml) was hydrogenated over 10% Pd-C (3 g) at room temp under atm press for 4 hr. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was fractionally distilled to give 36 g (61%) of VIII, b.p. 82–100°/12 mm. A forerun (b.p. 75–82°/12 mm) weighed 13 g. An analytical sample of VIII boiled at 88–95°/12 mm, n_D^{20} 1·4452; ν_{max} 3400, 1150, 1070, 1040, 1015, 980, 920, 910, 870, 820 cm^{-1}; δ 0·25–0·33 (4H), 0·91 (6H, d, J = 7 Hz), 1·08 (3H, s) ppm. (Found: C, 77·37; H, 12·61. $C_{11}H_{22}O$ requires: C, 77·58; H, 13·02%).

4,8-Dimethylnon-3-enyl bromide (Ic). Crude VIII (32 g) was added portionwise to 48% HBr (100 ml) at 5–10° with stirring. After stirring for 30 min at 10–15°, the mixture was extracted with pet. ether. The extract was dried ($MgSO_4$) and concentrated. The residue was distilled *in vacuo* to give 34·8 g (78·5%) of crude Ic, b.p. 76–80°/0·5 mm, n_D^{18} 1·4668; ν_{max} 1270, 1205, 1170, 1130, 1080, 1020 cm^{-1}; δ 0·89 (6H, d, J = 7 Hz), 1·56 and 1·62 (3H), 5·15 (1H, broad t) ppm. (Found: C, 61·93; H, 9·26. $C_{11}H_{21}Br$ requires: C, 56·65; H, 9·08%). This figure indicates that crude Ic is contaminated with impurities.

Ethyl 2-carbethoxy-2,6,10-trimethylundec-5-en-1-oate (IIc). The bromide Ic (34·5 g) and diethyl methylmalonate (35 g) were condensed as described in the prep of IIa to give 23·2 g (48%) of IIc, b.p. 140–160°/5 mm. An analytical sample boiled at 148–149°/4 mm, n_D^{20} 1·4490; ν_{max} 1730, 1250, 1220, 1160, 1100, 1020, 850 cm^{-1}; δ 0·88 (6H, d, J = 6 Hz), 1·25 (6H, t, J = 6 Hz), 1·35 (3H, s), 1·56 and 1·65 (3H), 4·10 (4H, q, J = 6 Hz), 5·05 (1H, broad) ppm. (Found: C, 69·95; H, 10·51. $C_{19}H_{34}O_4$ requires: C, 69·90; H, 10·50%).

2,6,10-Trimethylundec-5-en-1-oic acid (IIIc). The ester IIIb (23 g) was processed as described in the prep of IIIa to give 14·1 g (90%) of IIIc, b.p. 140–150°/0·5 mm. An analytical sample boiled at 146–147°/0·5 mm, n_D^{21} 1·4548: ν_{max} ~3400–~2600, 1700, 1290, 1240, 1170, 1110, 940 cm^{-1}; δ 0·88 (6H, d, J = 6 Hz), 1·18 (3H, d, J = 7 Hz), 1·57 and 1·65 (3H, area ratio = ca. 3:1), 5·10 (1H, broad t) ppm. (Found: C, 74·32; H, 11·56. $C_{14}H_{26}O_2$ requires: C, 74·28; H, 11·58%). GLC analysis of the corresponding methyl ester: Column, Castor wax 45 m × 0·5 mm; Column temp 170°; Carrier gas, N_2, 0·5 kg/cm^2; Retention time, 8·4 min (Δ^5 *cis*), 9·4 min (Δ^5 *trans*) (area ratio = 1:2·8).

2,6,10-Trimethylundec-5-en-1-oyl chloride (IVc). The acid IIIc (14·0 g) was converted into its Na salt by neutralizing with $NaOCH_3$ (3·3 g) in EtOH. The Na salt was treated with oxalyl chloride (25 g) as described in the prep of IVa to give an oily IVc.

1-Diazo-3,7,11-trimethyldodec-6-en-2-one (Vc). The above IVc was treated with ethereal CH_2N_2 to give crude oily Vc, ν_{max} 2120 (s), 1720 (w, due to impurities), 1640 (s) cm^{-1}.

A mixture of (±)-trans-*dihydrosesquicaran-2-one* (VIc) *and its* C-7 *epimer* (VIc'). A soln of the above described Vc in cyclohexane (200 ml) was added dropwise to a stirred and refluxing suspension of powdered Cu (1·0 g) and $CuSO_4$ (0·2 g) in cyclohexane (350 ml) during 40 min. After the addition the mixture was stirred and heated under reflux for 6 hr, then cooled, filtered and concentrated *in vacuo*. The residue was distilled to give 7·8 g (55% from IIIc) of crude product, b.p. 122–130°/5 mm. The following spectral and analytical data indicate that this is contaminated with some impurities; ν_{max} 1724 (w, due to impurities), 1675 (s), 1240, 1220, 1175, 1115, 1020, 885 cm^{-1}; δ 0·92 (6H, d, J = 6 Hz), 1·02 (3H, d, J = 7 Hz), 1·17 (3H, s) ppm. (Found: C, 79·79; H, 11·25. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%).

This was purified by chromatography on SiO_2-$AgNO_3$. A column (55 cm × 4 cm) in pet. ether was prepared from SiO_2 (200 g) and $AgNO_3$ aq (14 g in 70 ml). The crude ketone (VIc + VIc', 4·0 g) in a small amount of pet. ether was placed on the top of the column. The eluant was saturated with Ag^+ by shaking

with $AgNO_3$ aq in a separatory funnel prior to use. All fractions were 250 ml. Eluants were as follows: fractions No. 1–3, pet. ether; No. 4–17, pet. ether: benzene = 5:1; No. 18–20, pet. ether: benzene = 1:1. Fractions No. 1–5 gave 326 mg of oily impurity. Fractions No. 6–12 gave 2·982 g of almost pure VIc + VIc', b.p. 130–133°/7 mm, n_D^{22} 1·4692; ν_{max} 1680 (s), 1724 (w, due to impurities). Fractions No. 13–19 gave 528 mg of pure VIc + VIc', b.p. 123–124°/5 mm, n_D^{21} 1·4720; ν_{max} 1680, 1460, 1380, 1370, 1360, 1350, 1325, 1230, 1215, 1190, 1170, 1120, 1095, 1045, 1010, 885 cm^{-1}; δ 0·88 (6H, d, J = 6 Hz), 0·98 (3H, d, J = 6 Hz), 1·14 (3H, s) ppm. The positions of major absorptions in these two spectra are in good accord with those of the optically active dihydrosesquicaran-2-one derived from the natural product. The details, however, were somewhat different. (Found: C, 81·09; H, 11·82. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%). GLC analysis: Column, Castor wax 45 m × 0·5 mm; Column temp 190°; Carrier gas, N_2, 0·5 kg/cm^2; Retention time: 14·9 min (VIc'), 19·2 min (VIc) (area ratio 1:1). MS of VIc: *m/e* 222, 151, 138, 125, 109, 96, 81, 69, 55, 41 (base peak). VIc' exhibited an entirely identical mass spectrum with that of VIc. The mass spectra of both VIc and VIc' were identical with that of the optically active dihydrosesquicaran-2-one.

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