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Synthesis and Photochemical Reaction of 1,5,5,9-Tetramethyl-2-decalone

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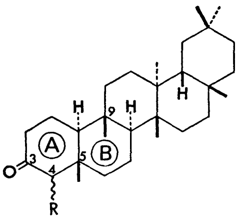
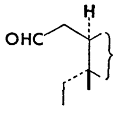
1,5,5,9-Tetramethyl-2-decalone (**6**) was synthesized from 5,5,9-trimethyl-1-decalone (**7**) and irradiated in *n*-hexane under a nitrogen atmosphere using a high pressure mercury lamp. Oxygen was passed through the reaction mixture in the dark to give a seco-nor acid, 1-carboxymethyl-2-ethyl-2,6,6-trimethylcyclohexane (**8a**) and a seco acid, 1-(2-carboxyethyl)-2-ethyl-2,6,6-trimethylcyclohexane (**9a**).

In the photochemical reaction of cycloalkanones, α-cleavage to form a biradical is well known as one of the primary photoreactions.1) The biradical undergoes elimination of carbon monoxide and/or hydrogen shift to afford an unseturated aldehyde and/or a ketene, depending on the structural requirement.2) In protic solvents such as alcohols or aqueous solvents, the ketene immediately reacts with the solvents to afford an ester or a carboxylic acid, respectively. However, the ketene formed in aprotic solvents is inert to the (aprotic) solvents.

In the previous papers3) we reported the photochemical reaction of friedelin (**1a**) in *n*-hexane and isolation of 5α-ethyl-10β-formylmethyl-des-A friedelane (**2**), 10β-carboxymethyl-5α-ethyl-des-A-friedelane (**3**), and 10β-(2-carboxyethyl)-5α-ethyl-des-A-friedelane (**4**). Since a 3,4-seco-friedelin skeleton bears no hydrogen atom on the δ-carbon atoms, the acyl-alkyl biradical produced from **1a** could not afford a δ-unsaturated aldehyde, but could lead to the ketene (**5**).3) During the subsequent separation work-up, the ketene (**5**) gave the seco acid (**4**) by addition of water, while the seco-nor aldehyde (**2**) was formed by autoxidation of the ketene (**5**); **2** was further oxidized by air to give the seco-nor acid (**3**).3)



1a R = 4β-CH$_3$
1b R = 4α-CH$_3$



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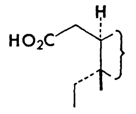

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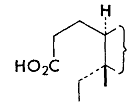

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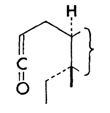

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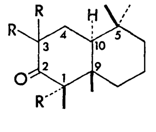
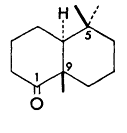


6 R=H
6-d$_3$ R=D



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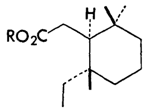
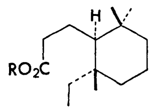
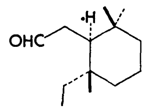


8a R=H
8b R=CH$_3$



9a R=H
9b R=CH$_3$



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In order to examine the general formation of the seco-nor product in a system such as friedelin (**1a**), photochemical behavior of 1,5,5,9-tetramethyl-2-decalone (**6**), as a simple bicyclic model compound corresponding to the A/B ring of **1a**, was investigated.

In this paper, we wish to describe the synthesis of 1,5,5,9-tetramethyl-2-decalone (**6**) from 5,5,9-trimethyl-1-decalone (**7**) and the formation of 1-carboxymethyl-2-ethyl-2,6,6-trimethylcyclohexane (**8a**), 1-(2-carboxyethyl)-2-ethyl-2,6,6-trimethylcyclohexane (**9a**), and 2-ethyl-1-formylmethyl-2,6,6-trimethylcyclohexane (**10**) in the photochemical reaction of **6** in *n*-hexane followed by oxygen introduction in the dark.

5,5,9-Trimethyl-1-decalone (**7**)4) was treated with methylmagnesium iodide to give two alcohols (**11**) and (**12**) in 63% and 20% yield, respectively, which were separated by silica gel chromatography. Assignment of the hydroxyl group was easily accomplished by PMR measurement using Eu(dpm)$_3$ as a shift reagent (Figs. 1 and 2). The signal due to the methyl group geminal to the hydroxyl group suffered the most significant shift in each alcohol. The shift for the

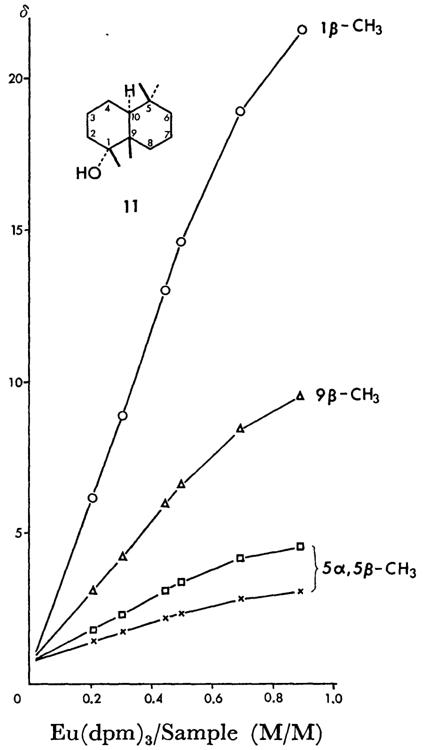


Fig. 1. Induced paramagnetic shifts for the alcohol **11**. [Eu(dpm)$_3$ was added to a 7% (w/v) soln of **11** in CCl$_4$].

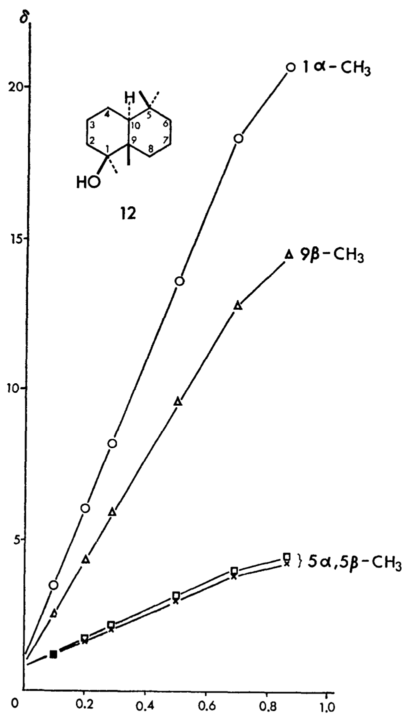
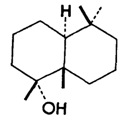


Fig. 2. Induced paramagnetic shifts for the alcohol **12**. [Eu(dpm)$_3$ was added to a 7% (w/v) soln of **12** in CCl$_4$].

angular methyl group of **11** was smaller than that of **12**. Each alcohol (**11** and **12**) was subjected to dehydration with iodine at 140 °C yielding an olefin mixture (**13**, **14**, and **15**) whose ratio was 61 : 8 : 31 and 6 : 18 : 76, respectively. The olefin mixture was separated by silver nitrate-impregnated silica gel chromatography. The main olefin (**13**) obtained by the dehydration of the alcohol (**11**) showed the presence of an olefinic methyl (δ 1.58, d, J=2 Hz), an olefinic proton (δ 5.18, m), and three tertiary methyls (δ 0.87, 0.89, and 1.02; each s) in the PMR spectrum. The structure of **13** was further supported by the formation of the ketone (**6**) (*vide infra*).

Treatment of the olefin mixture with *p*-toluenesulfonic acid in chloroform gave a mixture of **14** and **15** in a ratio of 1 : 4; **13** was absent in the resulting mixture. The mixture of **14** and **15** was separated by a column of silica gel impregnated with silver nitrate. Each olefin (**14** or **15**) gave the same equilibriating mixture of **14** and **15** in a ratio of 1 : 4 by treatment with *p*-toluenesulfonic acid. The structures of these olefins (**14** and **15**) were also confirmed by their PMR and IR spectral data.

The olefin mixture (**13**, **14** and **15**) derived from the alcohol (**11**), without separation, was subjected to hydroboration and subsequent Jones' oxidation to give 1,5,5,9-tetramethyl-2-decalone (**6**) and several minor oxidation products, which were not further examined. The structure of the main product (**6**) was supported by the PMR and IR spectral data. However, an alternative structure (**16**) might be possible to explain the spectral data for **6**. The ketone (**16**) would be derived from an olefin (**17**) which might be formed by a skeletal rearrangement during dehydration of the alcohol (**11**). In order to confirm that the Jones' oxidation product possesses a decalone skeleton, it was deuterated to give the deuterated ketone (**6**-d_3), which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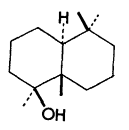
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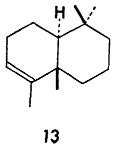
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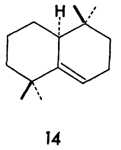
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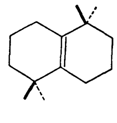
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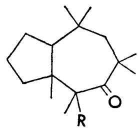
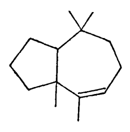

16 R=H
16-d_3 R=D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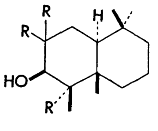
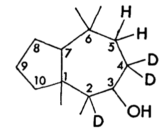

18 R=H
18-d_3 R=D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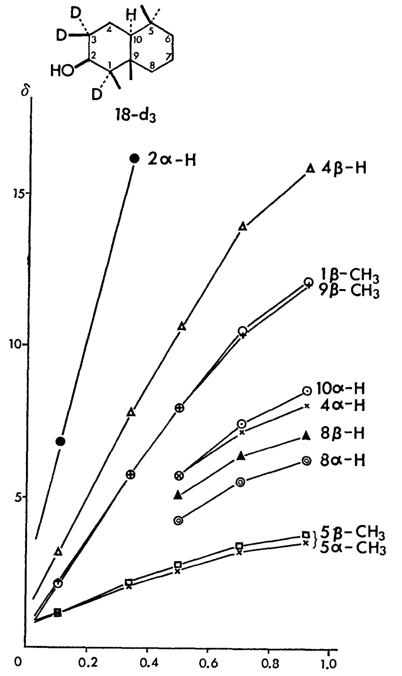


Fig. 3. Induced paramagnetic shifts for the alcohol **18**-d_3. [Eu(dpm)$_3$ was added to a 8% (w/v) soln of **18**-d_3 in CCl$_4$].

was converted with sodium borohydride into an alcohol ($\mathbf{18}$-d_3). The PMR spectral measurement of $\mathbf{18}$-d_3 using $Eu(dpm)_3$ as a shift reagent was then effected. The signals due to 4β, 4α, 10α, 8β, and 8α-hydrogens were separated distinctly (Fig. 3). A triplet (J=13 Hz) due to the 4β-hydrogen coupled with the 4α-hydrogen (geminal) and the 10α-hydrogen (trans) was observed (cf. Experimental). These results are in good accordance with those reported for friedelan-3β-ol.[5] If the alcohol had a structure **19**, which might be derived from the olefin (**17**), the signal due to 5α- and 5β-hydrogens must have been observed as an AB quartet. This was not the case in reality. Thus the structure of the decalone, obtained by Jones' oxidation was shown to be **6** except the configuration at C–1.

The induced paramagnetic shift experiments on **6** using $Eu(fod)_3$-d_{27} as a shift reagent showed a large shift for the signals due to a secondary methyl at C-1 (δ 0.89) and a tertiary methyl at C-9 (δ 0.73), while a smaller shift for the signals due to two tertiary methyls at C-5 (δ 0.88 and 0.98)(Fig. 4). These methyl signals suffer a solvent shift when the solvent was replaced from deuteriochloroform to deuteriobenzene (Table 1). A small downfield shift (Δ −0.02 ppm) observed for the C–1 methyl of **6** was parallel to the shift (Δ −0.10 ppm) observed for the 4β(equatorial)-methyl of friedelin (**1a**), while different from an appreciable upfield shift (Δ +0.25 ppm) for 4α(axial)-methyl of 4-epifriedelin (**1b**).[6] The methyl group at C-1 of **6** was thus inferred to be equatorial (1β).

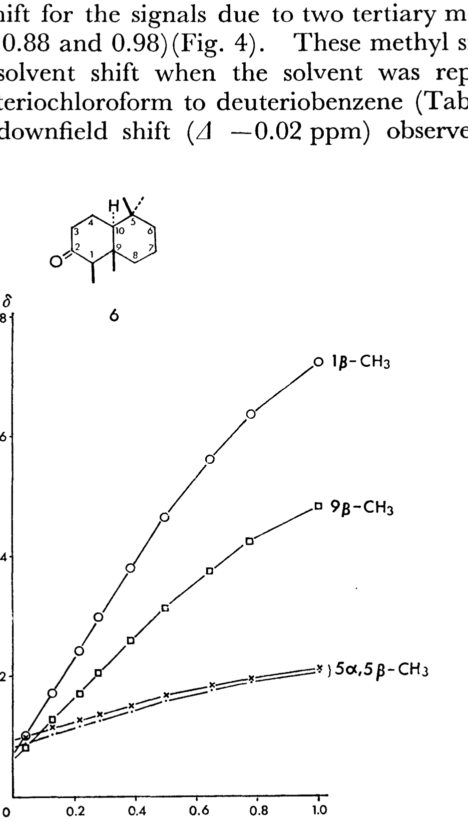
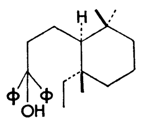


Fig. 4. Induced paramagnetic shifts for the ketone **6**. [$Eu(fod)_3$-d_{27} was added to a 5% (w/v) soln of **6** in CCl_4].

1,5,5,9-Tetramethyl-2-decalone (**6**) was irradiated in *n*-hexane with a high pressure mercury lamp under a nitrogen atmosphere at room temperature and then slow stream of oxygen was introduced into the solution in the dark. The reaction product was subjected to GC-MS examination and the formation of the seco-nor aldehyde, 2-ethyl-1-formylmethyl-2,6,6-trimethylcyclohexane [**10**; *m/e* 196 (M^+ $C_{13}H_{24}O$)] was suggested. However, a further confirmation was not furnished, because of lack of the material.

The reaction product was separated by silica gel chromatography to give an acid fraction. On treatment with diazomethane, the acid fraction was converted into the methyl esters in about 10% yield from **6**, which were found to consist of two components (**8b** and **9b**). The mixture of the esters was separated by preparative glc to give two esters. One methyl ester with lower R_f value on tlc showed a molecular ion peak at *m/e* 240 and was shown to be identical with 2-ethyl-1-(2-methoxycarbonylethyl)-2,6,6-trimethylcyclohexane (**9b**) in respect to IR, mass, glc, and tlc, which was prepared by the photochemical reaction of **6** in methanol.

The other methyl ester gave a molecular ion peak at *m/e* 226. This suggested that the ester would be a methyl ester derived from a seco-nor acid, 1-carboxymethyl-2-ethyl-2,6,6-trimethylcyclohexane (**8a**). This was confirmed by the synthesis of the seco-nor ester, 2-ethyl-1-methoxycarbonylmethyl-2,6,6-trimethylcyclohexane (**8b**) from the seco ester (**9b**) by the Barbier-Wieland degradation *via* a diphenylcarbinol (**20**) and a diphenylethylene derivative (**21**). Therefore, the structure of the original seco-nor acid was shown to be 1-carboxymethyl-2-ethyl-2,6,6-trimethylcyclohexane (**8a**). The formation mechanism of **8a** from 1,5,5,9-tetramethyl-2-decalone (**6**) could be inferred to be the same as that of the seco-nor acid (**3**) from friedelin (**1a**).[3]



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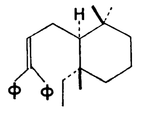

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TABLE 1. SOLVENT SHIFTS IN THE PMR SPECTRA[a)]

		δ_{CDCl_3}	$\delta_{C_6D_6}$	Δ		δ_{CDCl_3}	$\delta_{C_6D_6}$	Δ		δ_{CDCl_3}	$\delta_{C_6D_6}$	Δ
1a	4β-CH_3	0.87	0.97	−0.10	5β-CH_3	0.72	0.63	+0.09	9β-CH_3	0.87	0.74	+0.13
1b	4α-CH_3	1.11	0.86	+0.25	5β-CH_3	0.87	0.69	+0.18	9β-CH_3	0.92	0.85	+0.07
6	1β-CH_3	0.89	0.91	−0.02	9β-CH_3	0.73	0.57	+0.16	5β-CH_3 and 5α-CH_3	0.88 0.98	0.67 0.78	+0.21 +0.20

a) $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$

Experimental

IR spectra were measured on a Hitachi EPI-G2 spectrometer. Mass spectra were taken on a Hitachi RMU-6-Tokugata mass spectrometer operating at 70 eV with an indirect inlet system unless otherwise stated. High resolution mass spectra were taken using a Hitachi RMH-2 mass spectrometer operating at 70 eV. PMR spectra were measured using a JEOL JNM PS-100 (100 MHz), a Hitachi R-20 (60 MHz) or a Hitachi R-24 (60 MHz) spectrometer. Chemical shifts were expressed in δ downfield from TMS as an internal standard and coupling constants in Hz. Gas chromatography-mass spectrometry (GC-MS) was performed on a Hitachi gas chromatograph model K-53 connected with the mass spectrometer mentioned above. Analytical gas chromatography (glc) was carried on a Shimadzu gas chromatograph model GC-4APF, and preparative gas chromatography was carried on a Hitachi gas chromatograph model K-53. Thin layer chromatography (tlc) was carried out on Kieselgel G (E. Merck) in 0.25 mm thickness. For column chromatography, Wakogel C-200 (Wako Pure Chemical Ind.) was used. All melting points were determined on a hot block and reported uncorrected. Liquid samples for elemental analyses were purified by rechromatography on silica gel.

*1-Hydroxy-1,5,5,9-tetramethyl-*trans*-decalins (**11** and **12**).* To the Grignard reagent prepared from methyl iodide (15 g) and magnesium (1 g) in dry ether (15 ml) at 0 °C was added a solution of 5,5,9-trimethyl-1-decalone (**7**[4]; 1.84 g) in dry ether (30 ml). The reaction mixture was stirred for 1.5 hr at 0 °C, then decomposed with aqueous ammonium chloride solution, and extracted with ether three times. The ethereal layer was washed with brine twice, and dried over magnesium sulfate. Evaporation of the solvent gave a residue (2.16 g), which was chromatographed on a column of silica gel (100 g) using the following solvents as eluents: light petroleum–ether (20 : 1) frs 1—4, each 150 ml; fr 5, 100 ml; frs 6—12, each 50 ml; light petroleum–ether (10 : 1) frs 13—22, each 50 ml; light petroleum–ether (5 : 1) frs 23—30, each 75 ml. Fractions 4—13 gave 1α-hydroxy-1β,5α,5β,9β-tetramethyl-*trans*-decalin (**11**; 1.26 g, 63%) as an oil, IR (liquid) 3480 cm^{-1}; PMR ($CDCl_3$) δ 0.84, 0.88, 0.97, and 1.08 (each 3H, s, t-CH_3); mass *m/e* 210 [M^+ ($C_{14}H_{26}O$); 13%] and *m/e* 81 (100 %): Found: C, 79.81; H, 12.40%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%. Fractions 16—23 afforded 1β-hydroxy-1α,5α,5β,9β-tetramethyl-*trans*-decalin (**12**; 0.41 g, 20%), mp 52—53 °C (sublimation at 50 °C/1 mmHg), IR (Nujol) 3430 cm^{-1}; PMR ($CDCl_3$) δ 0.86 (6H, s, 2×*t*-CH_3), 1.03, and 1.28 (each 3H, s, t-CH_3); mass *m/e* 210 [M^+ ($C_{14}H_{26}O$); 7%] and *m/e* 81 (100%); Found: C, 79.66; H, 12.23%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%.

*1,5,5,9-Tetramethyl-2-decalone (**6**).* The alcohol (**11**; 2.00 g) was heated at 140 °C and iodine (34 mg) was added at 5 min intervals over a period of 20 min. To the reaction mixture, after cooling, ether was added, and the ethereal solution was washed with aqueous sodium thiosulfate and sodium hydrogen carbonate solutions and with brine, and then dried over magnesium sulfate. On evaporation of the solvent, a residue (1.58 g) was obtained, which was shown to be a mixture of three olefins in a ratio of 61 : 8 : 31 for **13**, **14**, and **15**, respectively, by glc analysis (column: C-20M, 150 °C; N_2 65 ml/min; retention time: 10.3, 6.3, and 5.5 min for **13**, **14**, and **15**, respectively). The olefin mixture obtained from the alcohol (**12**; 295 mg) and iodine (6 mg) at 140 °C was shown to consist of **13**, **14**, and **15** in a ratio of 6 : 18 : 76 by glc analysis.

The former olefin mixture (65 mg) obtained from **11** was dissolved in light petroleum and passed through a column of silica gel (7 g) impregnated with 20% silver nitrate. Elution with light petroleum (each 20 ml) gave the olefin (**13**; 30 mg, frs 4 and 5) as an oil; IR (liquid) 1660 and 795 cm^{-1}; PMR ($CDCl_3$) δ 0.87, 0.89, 1.02 (each 3H, s, t-CH_3), 1.58 (3H, d, J=2 Hz, C=C–CH_3), and 5.18 (1H, m, C=CH); MW 192.1858, Calcd for $C_{14}H_{24}$: 192.1876; mass *m/e* 192 (M^+, 9%) and *m/e* 41 (100%).

The latter olefin mixture (280 mg), obtained from the alcohol (**12**), was dissolved in chloroform (5.5 ml). After *p*-toluenesulfonic acid (51 mg) was added, the resulting solution was allowed to stand at 60 °C for 4 hr. Extraction with ether and usual treatment gave an oil, which was shown to be a mixture of **14** and **15** in a ratio of 1 : 4 by glc analysis. The mixture was chromatographed on a column of silica gel (22 g) impregnated with 20% silver nitrate. Elution with light petroleum (each 10 ml) afforded the olefin (**15**; 137 mg, from frs 1 and 2) as an oil; IR (liquid) neither absorption band due to C=C–H nor C=C was observed. PMR ($CDCl_3$) δ 0.97 (12H, s, 4×*t*-CH_3); mass *m/e* 192 [M^+($C_{14}H_{24}$); 15%] and *m/e* 177 (100%). From the fractions 4—6, the olefin (**14**, 7 mg) was obtained as an oil; IR (liquid 3050 and 1635 cm^{-1}; PMR ($CDCl_3$) δ 0.81, 0.88, 1.01, and 1.05 (each 3H, s, *t*-CH_3) and 5.45 (1H, m, C=C–H); mass *m/e* 192 [M^+ ($C_{14}H_{24}$), 13%], *m/e* 136 (39%, a peak due to retro-Diels Alder fragmentation), and *m/e* 55 (100%).

Treatment of each olefin (**14** and **15**) in chloroform with *p*-toluenesulfonic acid as described above gave an oil, which was shown to consist of **14** and **15** in a ratio of 1 : 4 by glc analysis.

To the crude olefin mixture (**13**, **14**, and **15**; 1.49 g; obtained by the dehydration reaction of **11**) in tetrahydrofuran (20 ml) was added a tetrahydrofuran solution (20 ml) of diborane prepared from boron trifluoride etherate (15 g) and sodium borohydride (2 g). The mixture was kept at room temperature for 70 min and the excess diborane was decomposed by addition of water (1.8 ml). The organoborane solution, kept at 40 °C, was oxidized with 3M sodium hydroxide (3 ml) and 30% hydrogen peroxide (3 ml). After the reaction mixture was kept at room temperature for 1 hr, potassium carbonate (9 g) and water were added. Extraction with ether and usual work-up afforded a residue (1.77 g).

The crude alcohol, obtained above, was dissolved in acetone (20 ml) and oxidized with Jones' reagent (2 ml) at 0 °C. The reaction mixture was stirred for 40 min and then diluted with brine (40 ml). Extraction with ether and usual work-up gave a residue (1.57 g), which was subjected to column chromatographic separation on silica gel (200 g) and eluted with light petroleum–ether (20 : 1, each 60 ml). On removal of the solvents (frs 6—12), 1,5,5,9-tetramethyl-2-decalone (**6**; 838 mg, one spot on tlc) was obtained in 45% yield from **11**. Mp 55—56 °C (from light petroleum), IR (Nujol) 1715 cm^{-1}; PMR ($CDCl_3$) δ 0.73, 0.88, 0.98 (each 3H, s, *t*-CH_3), and 0.89 (3H, d, J=7 Hz, *s*-CH_3); mass *m/e* 208 [M^+($C_{14}H_{24}O$), 5%] and *m/e* 41 (100%); Found: C, 80.41; H, 11.51%. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61%. 2,4-Dinitrophenylhydrazone (crystallized from ethanol): mp 159—160 °C, Found: C, 61.60; H, 7.26; N, 14.27%. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42%.

*1,3,3-Trideuterio-1,5,5,9-tetramethyl-2-decalone (**6**-d_3).* 1,5,5,9-Tetramethyl-2-decalone (**6**; 46 mg) in tetradeuteriomethanol (1 ml) was allowed to stand with 2 drops of 30% sodium deuterioxide (isotopic purity: 99 atom % D) in deuterioxide. Diluted hydrochloric acid was added and the mixture was extracted with ether three times, washed with aqueous sodium hydrogen carbonate solution and with brine, and dried over magnesium sulfate. After evaporation of the solvent, a residue (38 mg), without further purification, was subjected to mass spectrometric analysis with a direct inlet system operating at 70 eV. The deuterated decalone (**6**-d_3) was shown to consist of -d_3 (71%), -d_2 (25%), and -d_1 (4%). IR (liquid) 1715 cm^{-1}; PMR (CCl_4) δ 0.71, 0.82, 0.89, and 0.98 (each 3H, s, *t*-CH_3).

*1,3,3-Trideuterio-2β-hydroxy-1,5,5,9-tetramethyldecalin (**18**-d_3).* The above-obtained decalone-d_3 (**6**-d_3; 26 mg) was dissolved in methanol (0.5 ml), cooled with ice-salt, and reduced with sodium borohydride (10 mg). After the solution was maintained at 0 °C for 30 min, acetic acid (2 drops) was added. The reaction mixture was extracted with ether, washed with aqueous sodium hydrogen carbonate solution and with brine, and dried over magnesium sulfate. Evaporation of the solvent gave a residue (32 mg), which was chromatographed on a column of silica gel (3 g) and eluted with light petroleum–ether (20 : 1) to afford 1,3,3-trideuterio-2β-hydroxy-1,5,5,9-tetramethyldecalin (**18**-d_3; 21 mg), IR (Nujol) 3360 cm^{-1}; PMR spectral data using Eu(dpm)$_3$ was shown in Fig. 3. Signals due to a proton at C-4β appeared at δ 16.00 as a triplet ($J_{4\alpha,4\beta}=13$ and $J_{4\beta,10\alpha}=13$ Hz) [Eu(dpm)$_3$/**18**-d_3 (M/M): 0.92].

*Photochemical Reaction of 1,5,5,9-Tetramethyl-2-decalone (**6**) in n-Hexane Followed by Introduction of Oxygen in the Dark.* A solution of 1,5,5,9-tetramethyl-2-decalone (**6**; 185 mg) in *n*-hexane (650 ml) was irradiated with a high pressure mercury lamp (100 W, Rikosha) under a nitrogen atmosphere for 11 hr at room temperature. After the irradiation, dry oxygen was passed through the solution for 6 hr in the dark. On evaporation of the solvent, a residue (199 mg) was obtained, which was examined by GC-MS and the formation of 2-ethyl-1-formylmethyl-2,6,6-trimethylcyclohexane (**10**) was inferred [column: OV-17, 150 °C, He 0.8 kg/cm^2; retention time 4.2 min; mass *m/e* 196 ($M^+(C_{13}H_{24}O)$, 6%) and *m/e* 69 (100%)].

The reaction mixture was chromatographed on silica gel (20 g). After the starting ketone (**6**) was eluted with light petroleum–ether (20 : 1), elution with ether afforded an acid fraction (62 mg), which was treated with diazomethane to give a mixture (20 mg) of methyl esters (**8b** and **9b**; 20% silver nitrate-impregnated silica gel tlc showed two spots, R_f 0.42 and 0.38 for **8b** and **9b**, respectively). The mixture was separated by preparative glc (column: OV-17, 140 °C, N_2 1 kg/cm^2, retention time 3.8 min and 7.7 min for **8b** and **9b**, respectively).

The methyl ester (**8b**), an oil, showed IR (liquid) 1745 cm^{-1}; mass *m/e* 226 [$M^+(C_{14}H_{26}O_2)$, 2%] and *m/e* 69 (100%). IR, tlc, glc, and mass of this substance were identical with those of the authentic specimen prepared from **9b** by the Barbier-Wieland degradation (*vide infra*).

The other methyl ester (**9b**), an oil, showed IR (liquid) 1745 cm^{-1}; mass *m/e* 240 [$M^+(C_{15}H_{28}O_2)$, 1%] and *m/e* 69 (100%). This substance was identified to be 2-ethyl-1-(2-methoxycarbonylethyl)-2,6,6-trimethylcyclohexane by comparison (IR, tlc, glc, and mass) with the authentic sample prepared by photoreaction of **6** in methanol (*vide infra*).

*2-Ethyl-1-(2-methoxycarbonylethyl)-2,6,6-trimethylcyclohexane (**9b**).* 1,5,5,9-Tetramethyl-2-decalone (**6**; 201 mg) in methanol (750 ml) was irradiated with a high pressure mercury lamp 100 W, Rikosha) under nitrogen for 20 hr. After evaporation of the solvent, the residue (254 mg) was chromatographed on silica gel (20 g). Elution with light petroleum–benzene (100 : 1) and removal of the solvents afforded the methyl ester (**9b**; 179 mg, 77%) as an oil, IR (liquid) 1745 cm^{-1}; PMR ($CDCl_3$) δ 0.82, 0.88, 0.90 (each 3H, s, t-CH_3), 2.20—2.53 (2H, m, $C\underline{H}_2CO_2CH_3$), and 3.65 (3H, s, CO_2CH_3); mass *m/e* 240 [$M^+(C_{15}H_{28}O_2)$, 1%] and *m/e* 69 (100%); Found: C, 74.83; H, 11.96%. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%.

*2-Ethyl-1-methoxycarbonylmethyl-2,6,6-trimethylcyclohexane (**8b**).* To the methyl ester (**9b**; 150 mg) dissolved in tetrahydrofuran (20 ml) was added bromobenzene (950 mg) and magnesium (150 mg), and the reaction mixture was heated under reflux for 2.5 hr. After usual treatment, the residue (660 mg) was chromatographed on silica gel (20 g) and elution with light petroleum–ether (50 : 1) gave a diphenylcarbinol (**20**; 222 mg, 98%), as an oil. IR (liquid) 3600, 3550, and 3460 cm^{-1}; PMR ($CDCl_3$) δ 0.70, 0.78, and 0.80 (each 3H, s, t-CH_3); mass *m/e* 346 [$(M-H_2O)^+$; 8%] *m/e* 71 (100%); Found: C, 86.15; H, 9.71%. Calcd for $C_{26}H_{36}O$: C, 85.66; H, 9.95%.

The diphenylcarbinol (**20**; 200 mg) in benzene (3 ml) was refluxed with iodine (9 mg) for 4 hr. To the reaction mixture aqueous sodium thiosulfate solution was added. Extraction with ether and usual work-up afforded a residue (210 mg), which was passed through a column of silica gel (10 g) and eluted with light petroleum. A diphenylethylene derivative (**21**; 170 mg, 90% from **20**), as an oil, was obtained, IR (liquid) 1660 cm^{-1}; PMR ($CDCl_3$) δ 0.68, 0.76, 0.88 (each 3H, s, t-CH_3), 2.00—2.37 (2H, m, $-C\underline{H}_2-CH=C$), and 6.07 (1H, t, $J=7$ Hz, $CH=C$); mass *m/e* 346 [M^+ ($C_{26}H_{34}$), 5%] and *m/e* 71 (100%); Found: C, 90.33; H, 9.99%. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89%.

The diphenylethylene derivative (**21**; 138 mg) in acetic acid (10 ml) was oxidized with chromium trioxide (0.4 g) in acetic acid (6 ml) and water (0.3 ml) at room temperature for 69 hr. The excess oxidizing reagent was destroyed by addition of methanol, and usual treatment gave a residue (183 mg), which was dissolved in ether and allowed to stand with diazomethane in ether. After evaporation of the solvent, the residue (196 mg) was subjected to separation by silica gel (20 g) column chromatography. Elution with light petroleum–ether (100 : 1) gave the methyl ester (**8b**; 68 mg, 75% from **21**), an oil, IR (liquid) 1745 cm^{-1}; PMR ($CDZl_3$) δ 0.81, 0.84, 0.90 (each 3H, s, t-CH_3), 2.25 (2H, d, $J=5$ Hz, $C\underline{H}_2CO_2CH_3$), and 3.64 (3H, s, CO_2CH_3); MW 226.1920, Calcd for $C_{14}H_{26}O_2$: 226.1930; mass *m/e* 226 [$M^+(C_{14}H_{26}O_2)$, 1%] and *m/e* 69 (100%).

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