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Functionalization of *trans*-Decalin. I. Synthesis of 1-Oxo-*trans*-decalin-4a, 6-carbolactone

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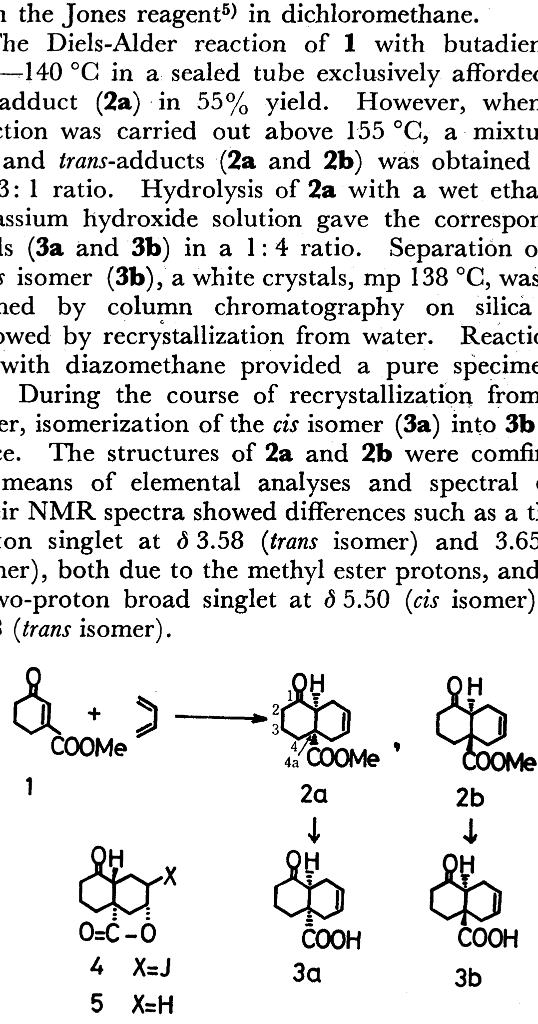
Synopsis. The synthesis of 4a-carbomethoxy-*cis*- and *trans*-Δ^6-octalin-1-ones (**2a** and **2b**), 4a-carboxy-*trans*-Δ^6-octalin-1-one (**3b**), and 1-oxo-*trans*-decalin-4a,6-carbolactone (**5**) from the adduct of 3-carbomethoxy-2-cyclohexen-1-one with butadiene was described.

Although the combinations of some alicyclic β-methyl-α,β-unsaturated ketones with butadienes were unsuccessful,[1] alicyclic β-carbomethoxy-α,β-unsaturated ketone such as 3-carbomethoxy-2-cyclohexen-1-one (**1**) was found to be a reactive dienophile. A similar reaction has been observed in the β-carboxy-α-butenolide system.[2] Thus, the cycloaddition of **1** with butadiene was investigated as a means of preparing functionalized *trans*-decalins (**4** and **5**), which would provide a synthetic intermediate for the preparation of sesquiterpenoids. The starting compound (**1**)[3] was prepared from readily available 1-carbomethoxycyclohexene[4] by oxidation with selenium dioxide[3] followed by treatment with the Jones reagent[5] in dichloromethane.

The Diels-Alder reaction of **1** with butadiene at 130—140 °C in a sealed tube exclusively afforded the *cis* adduct (**2a**) in 55% yield. However, when the reaction was carried out above 155 °C, a mixture of *cis*- and *trans*-adducts (**2a** and **2b**) was obtained in a *ca.* 3: 1 ratio. Hydrolysis of **2a** with a wet ethanolic potassium hydroxide solution gave the corresponding acids (**3a** and **3b**) in a 1: 4 ratio. Separation of the *trans* isomer (**3b**), a white crystals, mp 138 °C, was performed by column chromatography on silica gel, followed by recrystallization from water. Reaction of **3b** with diazomethane provided a pure specimen of **2b**. During the course of recrystallization from hot water, isomerization of the *cis* isomer (**3a**) into **3b** took place. The structures of **2a** and **2b** were comfirmed by means of elemental analyses and spectral data. Their NMR spectra showed differences such as a three-proton singlet at δ 3.58 (*trans* isomer) and 3.65 (*cis* isomer), both due to the methyl ester protons, and also a two-proton broad singlet at δ 5.50 (*cis* isomer) and 5.58 (*trans* isomer).



Iodolactonization[6] of **3b** gave a lactone iodide (**4**) in 95% yield, mp 119 °C. Reduction of **4** with tri-*n*-butyltin hydride[7] afforded a keto lactone (**5**) in 80% yield, mp 104 °C. The structures of **4** and **5** were confirmed by their elemental analyses and spectral data. Characteristic carbonyl bands of **4** were seen at 1770 (iodolactone carbonyl) and 1708 (ketone carbonyl) cm^{-1}, whereas those of **5** appeared at 1762 (lactone carbonyl) and 1715 (ketone carbonyl) cm^{-1}, indicating that both decalin-1-ones have a γ-lactone function.

Experimental

All the melting points are uncorrected. The IR spectra were recorded on a Hitachi EPI-S2 spectrophotometer. The NMR spectra were observed with Hitachi R-24 and/or R-22 spectrometers. Mass spectral analyses were carried out on a Hitachi RMS-4 mass spectrometer, ionizing at the order of 70 eV.

3-Carbomethoxy-2-cyclohexen-1-one (1). A mixture of 3.33 g (30 mmol) of selenium dioxide and 3.50 g (25 mmol) of 1-carbomethoxy-1-cyclohexene[4] in 35 ml of dioxane was stirred at 70—80 °C for 18—20 hr and at 90 °C for 3 hr. The precipitate was filtered and washed with 20 ml of dichloromethane. The combined filtrates were concentrated in a rotary evaporator. The residue, a reddish-brown viscous oil, was taken up in ether–*n*-hexane (4: 1). The mixture was stirred for some minutes, after which the organic layer was separated. Removal of the solvent gave crude 3-carbomethoxy-2-cyclohexen-1-ol. Without further purification, a solution of the crude alcohol in 50 ml of dichloromethane was treated with 12 ml of a chromic acid solution[5b] with vigorous stirring for 25 min under nitrogen atmosphere at 0 °C. After being left to stand for a few minutes, the organic layer was separated. The aqueous layer was washed with 30 ml of dichloromethane. The combined extracts were washed with water and dried (Na_2SO_4). The solvent was concentrated and the residue was taken up in ether and the insoluble material was filtered off. The filtrate was concentrated in a rotary evaporator to afford a brown oil. The crude oil was purified by column chromatography on silica gel with *n*-hexane–dichloromethane (2: 1), which eluted 0.89 g (23%) of **1**; bp 126—128 °C/8 mmHg; IR (Neat) 1725 (ester C=O), 1685 (conj. ketone), 1628 (C=C) cm^{-1}; NMR (CCl_4) δ 1.97—2.71 (m, 6H, CH_2), 3.78 (s, 3H, CH_3O), 6.59 (m, 1H, HC=C). Found: C, 62.24; H, 6.53%. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54%.

*4a-Carbomethoxy-*cis*-Δ^6-octalin-1-one (2a).* A mixture of 462 mg (3.0 mmol) of 3-carbomethoxy-2-cyclohexenone (**1**), 1 mg of 2,5-di-*tert*-butylhydroquinone, and 1.35 ml of butadiene in 1 ml of benzene was charged in a sealed tube. The tube was allowed to stand in an oil bath at 130—140 °C for 3 day. The mixture was then poured into 15 ml of methanol. The precipitate was filtered and washed with methanol. The combined filtrates were concentrated in a rotary evaporator. The residue was purified by chromatography on a silica gel column with dichloromethane–*n*-hexane (1 : 3), which eluted 343 mg (54.9%) of **2a**, mp 78.0—78.5 °C, bp 111—114 °C/1 mmHg; IR (Neat) 1725 (ester C=O), 1715 (ketone C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.83—2.46 (m, 10H, CH_2), 3.00 (broad, d, 1H, CHC=O), 3.65 (s, 3H, CH_3O), 5.50 (broad s, 2H, HC=C); MS (*m/e*) 208 (M^+). Found: C, 69.20; H, 7.72%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

A mixture of *cis-* and *trans*-adducts (**2a** and **2b**) (3 : 1) was obtained when the sealed tube was heated above 155 °C for 3 day.

*4a-Carboxy-*trans*-Δ^6-octalin-1-one (3b).* To a stirred solution of 112 mg (2.0 mmol) of potassium hydroxide in 1 ml of water was added a solution of 250 mg (1.2 mmol) of **2a** in 2 ml of ethanol. After stirring at room temperature for 15—20 hr, the solution was heated at 60 °C for 2 hr and then concentrated. The residual solution was acidified with 10% aqueous hydrogen chloride and extracted with chloroform. The extracts were washed with brine and dried (Na_2SO_4). Removal of the solvent gave 210 mg of crude acids (**3a** and **3b**) (*ca.* 1 : 4). The crude product was chromatographed over silica gel (Wako Gel C-200). Elution of the column with dichloromethane gave 80 mg of a mixture of **3a** and **3b** (*ca.* 1 : 1) as an oil. The following elution with dichloromethane–ethyl acetate (4 : 1) gave 110 mg (48% yield) of **3b** as a white crystals, mp 138.0 °C (from water); IR (Nujol) 3400—2500 (COOH), 1723 (C=O), 1682 (COOH) cm^{-1}; NMR ($CDCl_3$) δ 1.55—2.53 (m, 10H, CH_2), 2.66 (m, 1H, CHC=O), 5.69 (broad s, 2H, CH=C), 10.93 (s, 1H, COOH). Found: C, 68.20; H, 7.40%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

*4a-Carbomethoxy-*trans*-Δ^6-octalin-1-one (2b).* Mp 71.5—73.0 °C, bp 83—86 °C/0.02 mmHg, obtained by treatment of **3b** with diazomethane: IR (Nujol) 1724 (ester C=O), 1712 (ketone C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.67—2.67 (m, 10H, CH_2), 2.83 (m, 1H, CHC=O), 3.58 (s, 3H, CH_3O), 5.58 (broad s, 2H, HC=C). Found: C, 69.38; H, 7.89%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

*1-Oxo-*trans*-decalin-4a,6-carbolactone (5).* To a stirred solution of 160 mg (0.82 mmol) of **3b** in 5 ml of 0.5 M aqueous sodium bicarbonate was added a mixture of 317 mg (1.25 mmol) of iodine and 1.33 g (8.0 mmol) of potassium iodide in 3 ml of water for 5 min under cooling in an ice-water bath. The flask was covered with a black napkin and stirring was continued for 24 hr at room temperature. The reaction mixture was extracted with ether. The extracts were washed with aqueous sodium thiosulfate and saturated aqueous sodium carbonate and dried (Na_2SO_4). Removal of the solvent gave 250 mg (95%) of the iodolactone (**4**), mp 119 °C, as a white crystal (from *n*-hexane–benzene, 2 : 3): IR (Nujol) 1770 (lactone C=O), 1708 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.74—3.04 (m, 11H), 4.47—4.88 (m, 2H, HCI, HC–O). Found: C, 41.42; H, 4.15%. Calcd for $C_{11}H_{13}O_3I$: C, 41.27; H, 4.09%.

To a solution of 250 mg of **4** in 5 ml of dry benzene was added 450 mg (1.55 mmol) of tri-*n*-butyltin hydride dropwise with stirring for 5 min at 5 °C under nitrogen atmosphere. Stirring was continued for 48 hr at room temperature and the solvent was removed in a rotary evaporator to afford 128 mg (80% yield) of **5**, a columnar crystals, mp 104 °C (from benzene–*n*-hexane, 3 : 2): IR (Nujol) 1762 (γ-lactone C=O), 1710 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.68—2.43 (m, 13H, CH_2, CH), 4.73 (t, 1H, HC–O); MS (*m/e*) 194 (M^+). Found: C, 68.25; H, 7.25%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

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