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Rearrangement of Tetramethyl-*trans*-decalin Derivatives[1)]

Tochiro TATEE, Takahiko TSUYUKI, and Takeyoshi TAKAHASHI
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

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Synopsis. The dihydroxydecalin (**6**) was treated with iodine at 140 °C to give the octalins (**13** and **14**). Treatment of the *β*-epoxide (**8**) with boron trifluoride etherate gave the octalins [**17** and **18** (or **19**)] and the oxide (**20**).

Backbone rearrangements in the steroid and terpenoid fields are well documented.[2a,b)] Intracyclic tension in the rigid polycyclic ring provokes of backbone rearrangements to give the products less constrained. Electronic effects resulting from the presence of functional groups and kinetic effects due to the nature of reagents can modify the development of rearrangement.[3a,b)]

It has been shown that a treatment of the decalols (**1** and **2**) with iodine at 140 °C gave a mixture of olefins (**3**, **4**, and **5**), respectively.[4)] It would be expected that a dihydroxydecalin (**6**) having a hydroxyl group at C-6 might effect a rearrangement to give a ketone (**7**). Similarly, a rearrangement of an epoxide (**8**) to form an enol benzoate (**9**) might be expected.

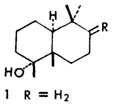
Recent communication on the epoxides of bisnorlabdane derivatives and on related epoxides[5)] prompted us to report our result.[1)] We wish to describe the rearrangements of **6** and **8**.

The hydroxyketone (**10**)[6)] was treated with methylmagnesium iodide to give a mixture of diols (**6** and **11**). Pure **6** was obtained by crystallization from light petroleum. The configuration of the tertiary hydroxyl group in **6** was confirmed by conversion of **6** into **1**[4)] *via* a ketol (**12**). Treatment of **6** with iodine at 140 °C gave the unsaturated alcohols (**13** and **14**).

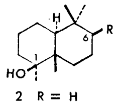
A benzoate (**15**) derived from **13** was epoxidized with *m*-chloroperbenzoic acid to give **8** and **16**. The *β*-epoxide (**8**) was treated with boron trifluoride etherate in benzene to yield three products. The PMR and IR spectra of the most polar product showed the presence of a benzoyloxyl and a hydroxyl group and the absence of olefinic proton. Therefore the structure (**17**) was given for the most polar compound.

The presence of a benzoyloxyl and a hydroxyl group along with an olefinic proton in the second polar product was shown by its PMR and IR spectra, which led to the structure (**18** or **19**) for this substance. The PMR spectrum of the least polar product indicated the presence of one proton (δ 3.90, d, J=4 Hz) on a carbon atom attached to ethereal oxygen on a five membered ring[7)] and of a benzoyloxyl group. No signal due to olefinic proton was observed. The absence of hydroxyl absorption in the IR spectrum and the mass spectrum showing a molecular ion peak at *m/e* 328 along with the observations mentioned above suggested the structure (**20**) for the least polar product.

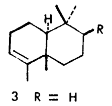
As a result, the dehydration of **6** with iodine and the treatment of **8** with boron trifluoride etherate gave the rearranged products in which the 1,3-diaxial interaction was released. A further rearrangement of a methyl group resulting in new formation of 1,3-diaxial interaction, did not take place. The hydroxyl group (at C-6 of **6**) and the benzoyloxyl group (at C-2 of **8**) did not develop further rearrangement to give **7** and **9**, respectively, under the conditions described above.



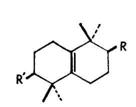
1 R = H₂
6 R = β-OH, α-H
12 R = O



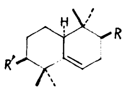
2 R = H
11 R = OH



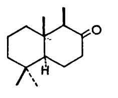
3 R = H
13 R = OH
15 R = OCOPh



4 R = H, R' = H
14 R = OH, R' = H
17 R = OCOPh, R' = OH



5 R = H, R' = H
18 R = OCOPh, R' = OH



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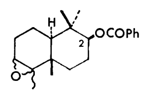
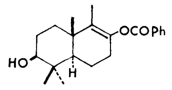


8 β-epoxide
16 α-epoxide



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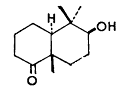

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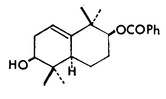

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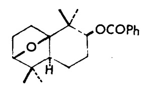

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Experimental

Instruments utilized for measurements of spectral data and the other experimental indications were the same as those described in Ref. 4.

*1α,6β-Dihydroxy-1β,5,5,9β-tetramethyl-*trans*-decalin (6).* To the Grignard reagent prepared from methyl iodide (5 g) and magnesium (637 mg) in dry ether (25 ml) at 0 °C was added a solution of the ketol (**10**;[6)] 1.31 g) in dry ether (20 ml). The reaction mixture was stirred at 0 °C for 2 hr. After usual treatment, the residue (1.43 g) was chromatographed on a column of silica gel (150 g). Elution with a mixture of light petroleum and ether (2: 1) gave a mixture of epimeric diols (**6** and **11**; 1.07 g; yield: 76% from **10**), which was crystallized from light petroleum to afford the pure **6**, mp 151.5—152.5 °C, IR (Nujol) 3570, 3400, 3350 cm^{-1}; PMR (CDCl$_3$) δ 0.83, 0.97, 1.02, and 1.11 (each 3H, s; *t*-CH$_3$), 3.26 (1H, m; -C$\underline{H}$-OH); mass *m/e* 226 (M$^+$; 1%) and *m/e* 43 (100%); Found: C, 74.04; H, 11.51%. Calcd for $C_{14}H_{26}O_2$: C, 74.28; 11.58%. The mother liquid of crystallization containing the epimeric diol (**11**) was not examined further.

The Decalol (1). The diol (**6**; 40 mg) in acetone (5 ml) was oxidized with Jones' reagent (0.1 ml) at 0 °C. After usual work-up, a ketol (**12**; 41 mg) was obtained as an oil, IR (liquid) 3480 and 1700 cm^{-1}; mass *m/e* 224 [M$^+$ ($C_{14}H_{24}O_2$); 26%] and *m/e* 43 (100%). To the ketol (**12**) were added diethyleneglycol (2 ml), 80% hydrazine hydrate (0.3 ml) and potassium hydroxide (20 mg), and the resulting mixture was refluxed for 3 hr and the temperature of the reaction mixture was raised to 200 °C. Water was added and the mixture was extracted with ether. After usual work-up, the residue was chromatographed on a column of silica gel (5 g). Elution with a mixture of light petroleum and ether (10: 1) gave the known decalol (**1**;[4] 8 mg).

Dehydration of the Diol (6) with Iodine. The diol (**6**; 167 mg) was heated at 165 °C. To the resulting melted material cooled to 140 °C was added iodine (6.7 mg) and the mixture was kept for 20 sec. The cooled reaction mixture was extracted with ether. After usual work-up, the residue was chromatographed on a column of silica gel (12 g) impregnated with 20% silver nitrate. Elution with a mixture of light petroleum and ether (10: 1) gave 2-hydroxy-1,1,5,5-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (**14**; 31 mg; y: 21%), as an oil, IR (liquid) 3380 cm^{-1}; PMR ($CDCl_3$) δ 0.97 (9H, s; 3×*t*-CH_3), 1.02 (3H, s; *t*-CH_3), and 3.47 (1H, q, J= 4 and 8 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OH); mass *m/e* 208 [M$^+$($C_{14}H_{24}O$); 16%] and *m/e* 175 (100%). Elution with a mixture of light petroleum and ether (5: 1) gave 3β-hydroxy-4,4,8,8aβ-tetramethyl-*trans*-1,2,3,4,4a,5,6,8a-octahydronaphthalene (**13**; 70 mg; y: 45%), mp 99—99.5 °C (from light petroleum), IR (Nujol) 3280 and 1655 cm^{-1}; PMR ($CDCl_3$) δ 0.82 (3H, s; *t*-CH_3), 1.00 (6H, s; 2×*t*-CH_3), 1.58 (3H, d, J=2 Hz; C=C–CH_3), 3.25 (1H, q, J=5 and 11 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OH), and 5.16 (1H, m; CH=C); mass *m/e* 208 [M$^+$; 14%] and *m/e* 175 (100%); Found: C, 80.97; H, 11.65%. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61%.

Benzoylation of the Unsaturated Alcohol (13). The unsaturated alcohol (**13**; 50 mg) in pyridine (0.5 ml) was heated at 95 °C with benzoic anhydride (143 mg) for 24 hr. After usual treatment, the unsaturated benzoate (**15**; 55 mg; y: 74%) was obtained; mp 146—147.5 °C, IR (Nujol) 1710 cm^{-1}; PMR ($CDCl_3$) δ 0.98 (3H, s; *t*-CH_3), 1.08 (6H, s; 2× *t*-CH_3), 1.60 (3H, d, J=2 Hz; C=C–CH_3), 4.6—4.9 (1H, m; –$\overset{|}{\text{C}}\underline{\text{H}}$–OBz), and 5.1—5.3 (1H, m; CH=C); mass *m/e* 312 [M$^+$; 4%] and *m/e* 105 (100%); Found: C, 80.67; H, 9.18%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

Epoxidation of the Unsaturated Benzoate (15). The unsaturated benzoate (**15**; 51 mg) in benzene (5 ml) was treated with *m*-chloroperbenzoic acid (33 mg) at room temperature for 24 hr. After usual work-up, the residue (107 mg) was chromatographed on a column of silica gel (10 g). Elution with benzene–ether (20: 1) afforded a mixture of the α- and β-epoxides (**16** and **8**). The mixture was subjected to further separation on a column of silica gel (8 g). Elution with a mixture of light petroleum–benzene–ether (25: 25: 2) gave 2β-benzoyloxy-5β,6β-epoxy-1,1,5α,10β-tetramethyl-*trans*-decalin (**8**; 13 mg; y: 24%), mp 190—190.5 °C (from light petroleum), IR (Nujol) 1710 cm^{-1}; PMR ($CDCl_3$) δ 0.95, 1.01, 1.15, and 1.23 (each 3H, s; CH_3), 2.96 (1H, triplet-like singlet; $\underset{\diagdown O \diagup}{\text{CH–C}}$), and 4.6—4.9 (1H, m; –$\overset{|}{\text{C}}\underline{\text{H}}$–OBz); mass *m/e* 328 [M$^+$; 0.5%] and *m/e* 105 (100%); Found: C, 76.93; H, 8.34%. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. Further elution with the same solvent mixture gave 2β-benzoyloxy-5α,6α-epoxy-1,1,5β,10β-tetramethyl-*trans*-decalin (**16**; 19 mg; y: 36%), mp 151—152 °C (from light petroleum), IR (Nujol) 1710 cm^{-1}; PMR ($CDCl_3$) δ 0.94, 1.04, 1.15, and 1.24 (each 3H, s; CH_3), 2.90 (1H, t, J=2.5 Hz, $\underset{\diagdown O \diagup}{\text{CH–C}}$), and 4.6—4.9 (1H, m; –CH–OBz), mass *m/e* 328 [M$^+$ ($C_{21}H_{28}O_3$); 0.1%] and *m/e* 105 (100%).

Treatment of the β-Epoxide (8) with Boron Trifluoride Etherate. The β-epoxide (**8**; 14 mg) in dry benzene (0.2 ml) was treated with freshly distilled boron trifluoride etherate at room temperature for 17 min. Aqueous sodium hydrogen carbonate solution (0.3 ml) was added and the ethereal extract was passed through a column of silica gel (2 g). Light petroleum–ether (1: 1) eluents, after evaporation of the solvents, were subjected to separation by preparative thin-layer chromatography [solv. benzene–ether (3: 1)]. The material corresponding to the most polar spot (R_f 0.45—0.55) gave 6β-benzoyloxy-2β-hydroxy-1,1,5,5-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (**17**; 4 mg), as an oil, IR (liquid) 3500 and 1715 cm^{-1}; PMR ($CDCl_3$) δ 0.99, 1.03, 1.06, and 1.14 (each 3H, s; *t*-CH_3), 3.44 (1H, q, J=4 and 10 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OH; axial-H), and 4.88 (1H, q, J=4 and 9 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OBz; axial-H); mass *m/e* 328 [M$^+$ ($C_{21}H_{28}O_3$); 0.4%] and *m/e* 105 (100%). The product corresponding to the second polar spot (R_f 0.55—0.62) gave 6β-benzoyloxy-2β-hydroxy-1,1,5,5-tetramethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**18**) or 2β-benzoyloxy-6β-hydroxy-1,1,5,5-tetramethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**19**), as an oil, (3.5 mg), IR (liquid) 3520 and 1695 cm^{-1}; PMR ($CDCl_3$) δ 1.00 (6H, s; 2×*t*-CH_3), 1.09 (3H, s; *t*-CH_3), 1.16 (3H, s; *t*-CH_3), 3.48 (1H, br. s, $W_{1/2}$ *ca.* 5.5 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OH; equatorial-H), 4.88 (1H, q, J=5.5 and 8 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OBz; axial-H), and 5.42 (1H, triplet like singlet; CH=C); mass *m/e* 328 [M$^+$ ($C_{21}H_{28}O_3$); 0.2%] and *m/e* 105 (100%). The product corresponding to the least polar spot (R_f 0.71—0.86) gave 2β-benzoyloxy-6β,9β-epoxy-1,1,5,5-tetramethyl-*trans*-decalin (**20**; 4.5 mg), as an oil, IR (liquid) 1710 cm^{-1}; PMR ($CDCl_3$) δ 1.00 (3H, s; *t*-CH_3), 1.05 (6H, s; 2×*t*-CH_3); 1.08 (3H, s; *t*-CH_3), 3.90 (1H, d, J=4 Hz; –$\overset{|}{\text{C}}$H–O–$\underset{|}{\overset{|}{\text{C}}}$–), and 4.86 (1H, t, J=2.5 Hz; –$\overset{|}{\text{C}}\underline{\text{H}}$–OBz; equatorial-H); mass *m/e* 328 [M$^+$ ($C_{21}H_{28}O_3$); 9%] and *m/e* 105 (100%).

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1) A part of this paper was presented at the 31st Annual Meeting of the Chemical Society of Japan, Sendai, October 4, 1974 (Proceedings, Vol. I, p. 37).

2) a) *e.g.*: D. N. Kirk and M. P. Hartshorn, "Steroid Reaction Mechanism," Elsevier Publishing Company, Amsterdam (1968), p. 291 and p. 354. b) *e.g.*: P. de Mayo, "Molecular Rearrangements," Vol. 2, John Wiley & Sons, Inc., New York (1964), p. 821.

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