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NOVEL REARRANGEMENT OF DIHYDROMAYURONE WITH BORON TRIFLUORIDE IN ACETIC ACID - ACETIC ANHYDRIDE

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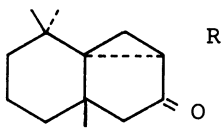
Acid-catalyzed isomerization of dihydromayurone (4) with boron trifluoride etherate in acetic acid - acetic anhydride afforded 4-acetoxy-1β,11,11-trimethylbicyclo[5.4.0]undeca-3,7-diene (5), 4-acetoxy-1β,7β,11-trimethylbicyclo[5.4.0]undeca-3,10-diene (6), 7-acetoxy-2,2,3-trimethyltricyclo[5.2.2.$0^{1,6}$]undec-3-ene (16), and 4-acetyl-7-acetoxy-2,2,3-trimethyltricyclo[5.2.2.$0^{1,6}$]undec-3-ene (17) as the case may be, according to reaction temperature.

In the preceding communication,[1] we have described the formation of the acetates (2) and (3) by acid-catalyzed cleavage of 6,10,10-trimethyl-4-oxotricyclo[4.4.0.$0^{1,3}$]decane (1) with boron trifluoride in AcOH - Ac_2O. Now we wish to report the acid-catalyzed rearrangement of dihydromayurone (4),[2] which provided the different products depending on the reaction temperature.



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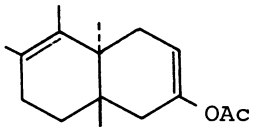


2 R=H
3 R=Ac

Dihydromayurone (4) (2.06 g, 10 mmol) was allowed to react with $BF_3 \cdot Et_2O$ (2 ml, 4.5 mmol) in 20 ml of AcOH - Ac_2O (1:1) under the five different conditions (cf. Table). The reaction mixture obtained in each reaction was separated by column (SiO_2 and SiO_2 impregnated with $AgNO_3$) chromatography. The results are summarized in the Table. The structures of the reaction products were determined in the following ways.

Acetate (5). It exhibits bands at 1750 (OAc) and 1696 cm^{-1} (C=C) in its IR spectrum and signals at δ 0.88 (3H, s), 0.91 (3H, s), 1.01 (3H, s), 2.06 (3H, s, OAc), 5.25 (1H, dd, J=7.5 and 4.0 Hz), 5.45 (1H, t, J=4.0 Hz) in its NMR spectrum. Hydrolysis of 5 with alcoholic KOH at room temperature afforded 7 in quantitative yield, a colorless oil; IR (neat)ν 1704 cm^{-1} (C=O); NMR ($CDCl_3$)δ 0.90 (6H, s), 1.05 (3H, s), 5.45 (1H, t, J=4.0 Hz); 2,4-DNP, mp 122-123 °C. Reaction of 7 with excess methyl lithium gave β-alcohol (8) in 31.2 % yield, a colorless oil; IR (neat)ν 3345 cm^{-1} (-OH); NMR ($CDCl_3$)δ 0.88 (3H, s), 0.93 (3H, s), 0.98 (3H, s), 1.18 (3H, s), 5.38 (1H, m), and α-alcohol (9) in 43.3 % yield, colorless crystals; mp 118-120 °C (hexane) (lit.[3] 118-121 °C); IR (KBr)ν 3335 cm^{-1} (-OH); NMR ($CDCl_3$) δ 0.86 (3H, s), 0.93 (3H, s), 1.00 (3H, s), 1.19 (3H, s), 5.40 (1H, m), whose spectrum data were identical with those reported.[3]

Acetate (6). It has two tert-methyl [δ 0.93 (3H, s) and 0.98 (3H, s)],

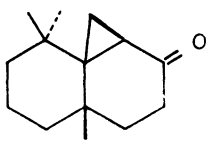
a vinyl methyl [δ 1.65 (3H, d, J=2.0 Hz)], an acetyl group [ν 1740 cm^{-1}, δ 2.10 (3H, s)] and two olefins [ν 1660 cm^{-1}, δ 5.45 (2H, m)]. Hydrolysis of 6 with alcoholic KOH at room temperature afforded ketone (10), a colorless oil; IR (neat) ν 1702 cm^{-1} (>C=O); NMR ($CDCl_3$) δ 0.97 (3H, s), 1.02 (3H, s), 1.67 (3H, d, J=2.0 Hz, vinyl methyl), 5.50 (1H, m); 2,4-DNP, mp 142-144 °C. Methylation of 10 with excess methyl lithium afforded alcohol (11) in 61.7 % yield. Dehydration of 11 with p-TsOH catalyst in benzene at room temperature for 4 h gave dienes (13) in 38 % yield, a colorless oil; NMR ($CDCl_3$) δ 0.88 (6H, s), 1.70 (6H, m, vinyl methyl), 5.30 (2H, m), and (15) in 36 % yield, a colorless oil; NMR ($CDCl_3$) δ 0.85 (3H, s), 0.95 (3H, s), 1.67 (6H, m, vinyl methyl), 5.41 (2H, m). The spectral data of 13 were identical with those of the authentic sample synthesized from the compound (12)[4] as follows. Wolff-Kishner reduction of the ketone (12) gave ketone (14) in 23 % yield, mp 54-55 °C (hexane); IR (KBr) ν 3255 (-OH), 1685 cm^{-1} (>C=O); NMR ($CDCl_3$) δ 0.90 (3H, s), 1.02 (3H, s), 1.60 (3H, d, J=1.5 Hz, vinyl methyl), 2.13 (3H, broad s, vinyl methyl), 5.63 (1H, m), 5.98 (1H, m), and diene (13) in 14 % yield.

Table. Isomerization products of dihydromayurone (4) at various reaction temperatures

Reaction temp., °C	Time, h	Product, No	Yield, %
20	2	(5)	70
35	2	(5)	35
		(6)	48
50	2	(16)	45
			70*
100	2	(16)	20
		(17)	15
	4	(17)	25

*Yield: from (5)

Acetate (16). It exhibits bands at 1740 cm^{-1} (OAc) in its IR spectrum and signals at δ 0.82 (3H, s), 1.03 (3H, s), 1.65 (3H, d, J=1.5 Hz, vinyl methyl), 2.01 (3H, s, OAc), 5.35 (1H, m). Hydrolysis of 16 with alcoholic KOH at room temperature gave a compound (18) in 80.4 % yield, colorless crystals, mp 122-123 °C (hexane); IR (KBr) ν 3255 cm^{-1} (-OH); NMR ($CDCl_3$) δ 0.82 (3H, s), 1.04 (3H, s), 1.68 (3H, d, J=1.5 Hz, vinyl methyl), 5.31 (1H, m); CMR ($CDCl_3$) δ 19.0 (q), 20.8 (q), 22.6 (t), 25.9 (q), 28.3 (t), 30.5 (t), 34.4 (t), 36.6 (t), 37.6 (s), 45.0 (d, C_6), 48.9 (s), 82.2 (s, C_7), 119.7 (d, C_4), 139.4 (s, C_3); MS m/e 206 (M^+). Bromination of 18 with PBr_3 in benzene at room temperature afforded bromide (19) in 76.6 % yield, colorless crystals, mp 150-153 °C (hexane); NMR ($CDCl_3$) δ 0.83 (3H, s), 1.01 (3H, s), 1.68 (3H, broad s, vinyl methyl), 5.32 (1H, m), and methylation of bromide (19) with excess methyl lithium in ether at boiling for 5 days gave an olefin (20) in 5.3 % yield, a colorless oil; NMR ($CDCl_3$) δ 0.85 (3H, s), 0.92 (3H, s), 1.03 (3H, s), 1.65 (3H, broad s, vinyl methyl), 5.17 (1H, m), whose NMR spectral data were identical with those reported.[5a-b] Furthermore, ozonolysis of 18 in AcOH gave keto-aldehyde (21) in 23 % yield, a colorless oil; IR (neat) ν 3400 (-OH), 2720 and 1722 (-CHO), 1700 cm^{-1} (>C=O); NMR



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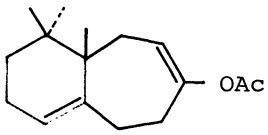

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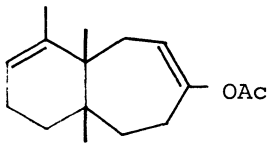

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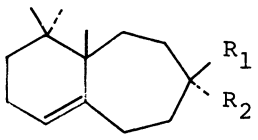
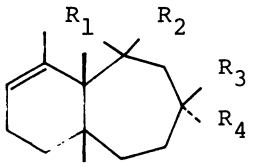
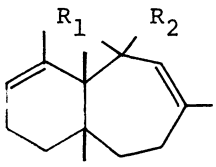


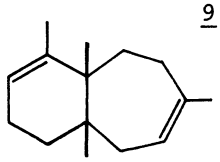
7 $R_1=R_2=O$
8 $R_1=OH$, $R_2=CH_3$
9 $R_1=CH_3$, $R_2=OH$



10 $R_1=R_2=H$, $R_3=R_4=O$
11 $R_1=R_2=H$,
$R_3=R_4=H$ or OH
12 $R_1=R_2=O$, $R_3=OH$, $R_4=CH_3$



13 $R_1=R_2=H$
14 $R_1=R_2=O$



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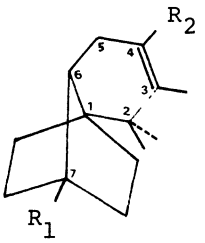
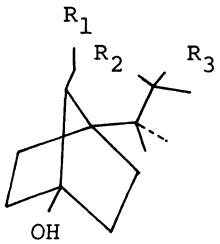
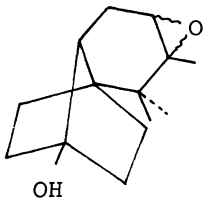


16 R_1=OAc, R_2=H
17 R_1=OAc, R_2=Ac
18 R_1=OH, R_2=H
19 R_1=Br, R_2=H
20 $R_1=CH_3$, R_2=H
24 R_1=OH, R_2=Ac
25 R_1=OH, R_2=COOH



21 R_1=CHO, $R_2=R_3=O$
23 $R_1=CH_2OH$, R_2=OH, R_3=H



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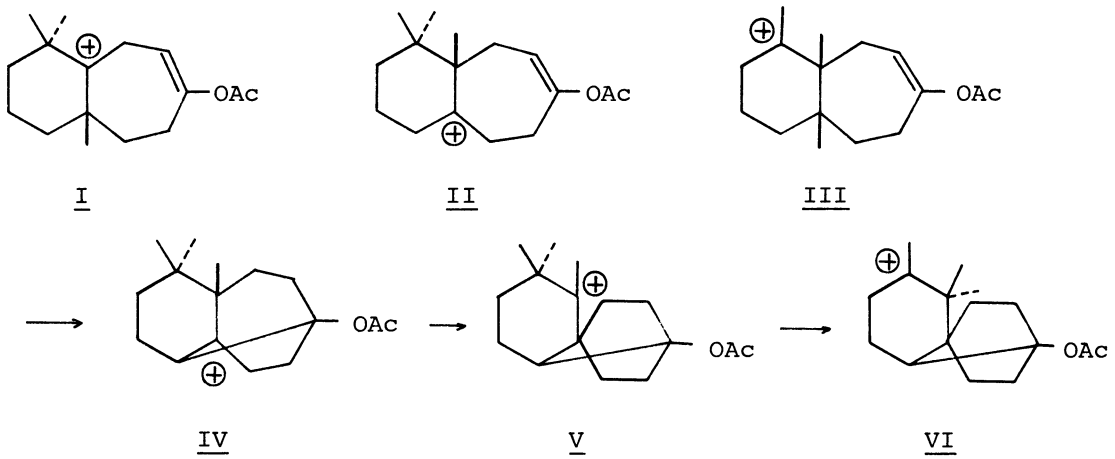
($CDCl_3$)δ 1.16 (6H, s), 2.15 (3H, s, Ac), 9.83 (1H, broad t, -CHO), and 50 % yield of compound (22), colorless crystals, mp 107-108 °C (hexane); IR (KBr)ν 3395 (-OH); NMR ($CDCl_3$)δ 0.97 (3H, s), 1.01 (3H, s), 1.25 (3H, s), 3.21 (1H, t, J=2.0 Hz), whose spectral data were identical with those of the product obtained on the oxidation of 18 with m-chloroperbenzoic acid. Reduction of 21 with $NaBH_4$ in methanol afforded triol (23) in 97 % yield, colorless crystals, mp 148-150 °C (benzene); NMR ($CDCl_3$)δ 0.87 (3H, s), 0.93 (3H, s), 1.10 (3H, d, J=7.5 Hz), 3.83 (2H, t, J=7.0 Hz), 4.00 (1H, q, J=7.5 Hz). These results give a proof of the chemical structure of the product (18).

Acetate (17). It shows bands at 1725 (OAc) and 1702 cm^{-1} (α,β-unsaturated ketone) in its IR spectrum and signals at δ0.90 (3H, s), 1.05 (3H, s), 1.72 (3H, s, vinyl methyl), 2.00 (3H, s, OAc), 2.25 (3H, s, Ac). Hydrolysis of 17 with alcoholic KOH at room temperature gave alcohol (24) in 78.3 % yield, a colorless oil; MS m/e 248 (M^+); IR (neat)ν 3450 (-OH), 1700 cm^{-1} (>C=O); NMR ($CDCl_3$)δ 0.90

(3H, s), 1.05 (3H, s), 1.71 (3H, s), 2.25 (3H, s, Ac). Haloform reaction of keto-alcohol (24) (8 % NaOCl, 80 % dioxane, KOH, at 100 °C, 40 min) afforded hydroxy acid (25) in 51.8 % yield, colorless crystals, mp 175-176 °C (benzene); IR (KBr)ν 1676 cm^{-1} (-COOH); NMR ($CDCl_3$)δ 0.92 (3H, s), 1.07 (3H, s), 2.00 (3H, s), 6.97 (2H, broad s, -COOH and -OH). Decarboxylation of 25 at 260-275 °C (1.5 mmHg) afforded 18.



I II III

IV V VI

Concerning the pathway of acetylations mentioned above which involves by skeletal rearrangement and/or methyl migration, one must first consider the formation of cation I as a precursor of cations II and III. Although cation II is more stable than cation III, it might be assumed that at moderately high temperature cation II would formed easily. Naturally, Cation II, III, and VI correspond to product 5, product 6, and products 16 and 17, respectively.

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References

1) H. Sekizaki, M. Ito, and S. Inoue, Chem. Lett., 1978, 811.
2) M. Ito, K. Abe, H. Abe, K. Yamada, and T. Masamune, Bull. Chem. Soc. Jpn., 42, 3173 (1974).
3) W. G. Dauben, L. E. Friedrich, P. Oberhansli, and E. I. Aoyagi, J. Org. Chem., 37, 9 (1972).
4) C. Enzell, Acta Chem. Scand., 16, 1553 (1962).
5) a) H. V. Daeniker, A. R. Hochstetler, K. Kaiser, and G. C. Kitchens, J. Org. Chem., 37, 1 (1972); b) W. G. Dauben and L. E. Friedrich, ibid., 37, 241 (1972).

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