Rearrangement of *vic*-Diol Monoacetates Promoted by Organoaluminium Compounds

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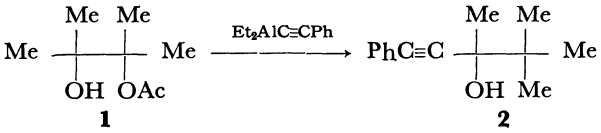
Synopsis. Treatment of pinacol monoacetate with organoaluminium reagent R_3Al caused the rearrangement under uptake of R as a nucleophile on the resulting carbonyl carbon, while R_2AlSPh produced the pinacolone itself upon workup.

Lewis acid catalysis of Diels-Alder reaction[1] or ene reaction[2] has been recently well documented. We have reported that the common Lewis acids such as $TiCl_4$ and $BF_3 \cdot OEt_2$ failed to catalyze the aliphatic Claisen rearrangement, meanwhile amphoteric organoaluminium compounds facilitated the rearrangement.[3] Another application of this new strategy with combined acid-base attack of organoaluminium reagent to the pinacol rearrangement[4] has been studied.

Treatment of pinacol monoacetate **1** with $Et_2AlC{\equiv}CPh$ in hexane provided alcohol **2** which was produced apparently by the rearrangement and successive alkynylation. Hexane, benzene, and dichloromethane were equally effective as the solvents. In ether or THF no rearrangement was observed.

Table 1 summarizes the reaction between *vic*-diol monoacetates and organoaluminium compounds. Epoxide **7** has afforded a rearranged product as *vic*-diol monoacetate (Entry 4). The reagent Et_2AlSPh has been found to be effective for the rearrangement to give ketones without introduction of a nucleophile.

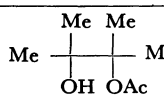
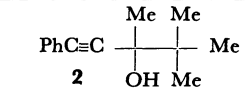
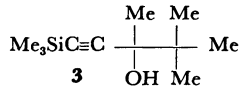
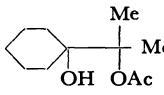
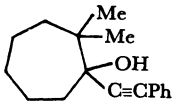
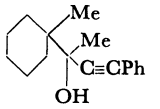
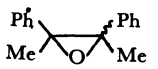
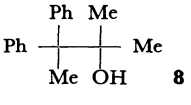
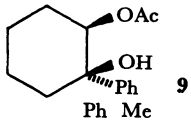
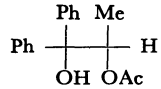
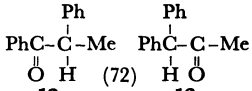
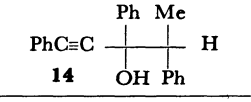


1 **2**

It is worth noting that this new method can be used to change the nature of rearrangement from that expected in a strong acid-catalyzed reaction of the corresponding glycol. In the case of a glycol, $Ph_2C(OH)-CH(Me)-OH$, that contains one secondary and one tertiary hydroxyl, the secondary hydroxyl group could be selectively acetylated and removed preferentially upon treatment with organoaluminium compound (Entry 6 and 7). In contrast, the tertiary hydroxyl was exclusively removed to give $Ph_2CHC(O)Me$ (**13**) under sulfuric acid-catalyzed conditions.

A glycol monoacetate, $PhC(Me)(OH)-CH_2OAc$, that contains a tertiary hydroxyl and a primary acetate did not give any rearranged products on treatment with Et_2AlSPh. Benzenethiolate attacked carbonyl carbon

TABLE 1. REARRANGEMENT OF *vic*-DIOL MONOACETATES PROMOTED BY ORGANOALUMINIUM COMPOUNDS

Entry	Substrate	Organoaluminium reagent	Conditions Temp °C	Conditions Time h	Product (Yield/%)
1	 **1**	$Et_2AlC{\equiv}CPh$	25,1.0; 80,0.5		 **2** (62)
2	**1**	$Et_2AlC{\equiv}CSiMe_3$	80	0.7	 **3** (45)
3		$Et_2AlC{\equiv}CPh$	70	1.5	 **5** (25)  **6** (28)
4	 **7**	Me_3Al	80	1.0	 **8** (69)
5	 **9**	Et_2AlSPh	25	1.5	 **10** (68)
6	 **11**	Et_2AlSPh	25	0.2	 **12** (72) **13** (24)
7	**11**	$Et_2AlC{\equiv}CPh$	80	0.5	 **14** (75)

of the acetate to provide the original diol.

Experimental

Infrared spectra were determined on a Shimadzu IR-27-G spectrometer, mass spectra on a Hitachi M-80. NMR spectra were recorded on a Varian EM-390H spectrometer using TMS as an internal standard. Microanalysis was performed at the Elemental Analyses Center of Kyoto University. All the experiments were carried out under an argon atmosphere. Purification of the product was performed by preparative thin layer chromatography (TLC) or column chromatography on silica gel (Merck Kiesel Gel 60).

Preparation of Diol Monoacetates **1**[5] *and* **4**: The title compounds were prepared by acetylation of the corresponding diols with acetic anhydride in the presence of 4-dimethylaminopyridine.[6]

Reaction between Pinacol Monoacetate **1** *and* $Et_2AlC{\equiv}CPh$: Butyllithium (1.6 M, 1.75 ml, 2.8 mmol) was added to a solution of phenylacetylene (0.21 g, 3.0 mmol) in benzene (2.0 ml) at 0 °C under an argon atmosphere. A solution of Et_2AlCl in hexane (1.0 M, 2.8 ml, 2.8 mmol) was added to the resulting suspension and the whole was stirred for 30 min at 25 °C. A solution of pinacol monoacetate **1** (0.16 g, 1.0 mmol) in benzene (2.0 ml) was added dropwise and the resulting mixture was stirred at 25 °C for 1 h, then at 80 °C for an additional 0.5 h. The mixture was diluted with dichloromethane (30 ml) and successively treated with NaF[7] (1.8 g) and water (0.6 ml). Vigorous stirring of the resulting suspension was continued at 25 °C for 0.5 h. The semi-solid was filtered and the remaining solid was washed with ether (3×10 ml). The combined filtrate and washings were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was submitted to preparative TLC (hexane : ethyl acetate=5 : 1) to give the rearranged product **2** (0.13 g, 62% yield) as a yellow oil: bp 103—107 °C (bath temp, 133 Pa); IR (neat) 3450, 2980, 1495, 1375, 1135, 900, 750, 685 cm^{-1}; NMR (CCl_4) δ 1.08 (s, 9H), 1.45 (s, 3H), 7.06—7.49 (m, 5H). Found: C, 83.32; H, 9.18%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

3,4,4-Trimethyl-1-trimethylsilyl-1-pentyn-3-ol (**3**): Bp 100 °C (bath temp, 1995 Pa); IR (neat) 3475, 2980, 2180, 1368, 1259, 1160, 842, 759 cm^{-1}; NMR (CCl_4, benzene as an internal standard) δ 0.08 (s, 9H), 0.93 (s, 9H), 1.27 (s, 3H), 1.70 (bs, 1H). The compound **3** was treated with potassium fluoride in *N,N*-dimethylformamide[8] to give 3,4,4-trimethyl-1-pentyn-3-ol whose IR and NMR spectra were identical with those reported.[9]

2,2-Dimethyl-1-(phenylethynyl)cycloheptanol (**5**): Bp 135—137 °C (bath temp, 133 Pa); IR (neat) 3470, 2940, 1600, 1497, 1448, 993, 750, 688 cm^{-1}; NMR (CCl_4) δ 1.06 (s, 3H), 1.13 (s, 3H), 1.3—2.3 (m, 10H), 7.1—7.5 (m, 5H). Found: *m/e* 242.1750. Calcd for $C_{17}H_{22}O$: M, 242.1668.

2-(1-Methylcyclohexyl)-4-phenyl-3-butyn-2-ol (**6**): Bp 140 °C (bath temp, 133 Pa); IR ($CHCl_3$) 3300, 2925, 1595, 1490, 1105, 895 cm^{-1}; NMR (CCl_4) δ 1.03 (s, 3H), 1.46 (s, 3H), 1.2—2.5 (m, 10H), 7.12—7.67 (m, 5H). Found: *m/e* 242.1668. Calcd for $C_{17}H_{22}O$: M, 242.1668.

Reaction between 2,3-Diphenyl-2,3-epoxybutane (**7**) *and* Me_3Al: A mixture of **7** (0.13 g, 0.58 mmol) and Me_3Al (1.0 M hexane solution, 2.9 ml, 2.9 mmol) in hexane was heated at reflux for 1 h. The resulting mixture was worked-up as described above and the purification by preparative TLC gave alcohol **8** (97 mg, 69% yield) as an oil: bp 150 °C (bath temp, 133 Pa); IR (neat) 3560, 2990, 1600, 1497, 1023, 742, 698 cm^{-1}; NMR (CCl_4) δ 1.3 (s, 6H), 1.05 (s, 3H), 7.0—7.45 (m, 10H). Found: *m/e* 240.1434. Calcd for $C_{17}H_{20}O$: M, 240.1512.

Preparation of 2-Acetoxy-1-phenylcyclohexanol (**9**): Treatment of 1-phenylcyclohexene (4.0 g, 25 mmol) with *N*-methylmorpholine *N*-oxide (4.0 g, 26 mmol) in the presence of OsO_4 (76 mg, 0.3 mmol) according to the reported procedure[10] gave 1-phenyl-1,2-cyclohexanediol (2.9 g, 60% yield) which was transformed into monoacetate with acetic anhydride in pyridine quantitatively.

2-Phenylcyclohexanone: Benzenethiol (0.28 g, 2.5 mmol) was added dropwise to a solution of triethylaluminium (1.0 M hexane solution, 2.5 ml, 2.5 mmol) in hexane (3.0 ml) at 0 °C. After stirring for 30 min, a solution of monoacetate **9** (0.12 g, 0.5 mmol) in dichloromethane (2.0 ml) was added to the resulting solution at 0 °C and the mixture was stirred for another 30 min at 0 °C. Workup followed by purification by preparative TLC afforded a title compound as white crystals which was spectrometrically identical with an authentic sample.[11]

2-Phenylpropiophenone (**12**) *and 1,1-Diphenyl-2-propanone* (**13**): Reaction between diol monoacetate **11** (0.14 g, 0.5 mmol) and Et_2AlSPh (2.5 mmol) gave two isomeric ketones **12** and **13** (**12**/**13**=3/1) which were spectrometrically identical with authentic samples.[5,12]

Sulfuric Acid-catalyzed Rearrangement of Ph_2COH–$CH(Me)OH$: Two drops of concentrated sulfuric acid (≈40 mg) was added to a solution of diol (76 mg, 0.33 mmol) in dichloromethane (2.0 ml) at 25 °C and the whole was stirred for 15 min. Workup (ether, $NaHCO_3$) and purification gave methyl ketone **13** (56 mg, 80% yield) as a single product.

1,3,4-Triphenyl-1-pentyn-3-ol (**14**): Bp 167—168 °C (bath temp, 133 Pa); IR (neat) 3430, 3070, 2990, 2945, 2245, 1600, 1500, 1450, 1270, 1122, 757, 700 cm^{-1}; NMR (CCl_4) δ 1.24 (d, J=6.0 Hz, 3H), 4.38—4.78 (m, 1H), 6.87—8.22 (m, 15H). Found: C, 88.65; H, 6.32%. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%.

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