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CATECHOLBORANE REDUCTIVE CLEAVAGE OF ALLYL AND PROPARGYL ACETALS AND KETALS: A SIMPLE ROUTE TO ALLYL AND PROP-2-YNYL ETHERS.

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Summary: the chemoselective conversion of allyl and prop-2-ynyl acetals as well as ketals by reductive cleavage with catecholborane into the corresponding allyl and prop-2-ynyl ethers is described.

It is known that catecholborane (CTBH), owing to the minor electrophylicity of its boron atom, is a mild hydroborating agent, as supported by the fact that the hydroboration of carbon-carbon double bonds with this reagent is effective only at temperatures of 80-100°C[1].

At lower temperatures such as room temperature, we observed that CTBH reacts very easily with the benzilic acetals. For example the benzaldehyde dimethyl acetal is

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TABLE

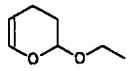
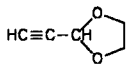
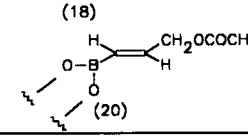
	Substrate	Conditions	Products	(yield %)
1	$CH_2=CH-CH(OCH_3)_2$ (1)	CTBH, r.t.	$CH_2=CH-CH_2OCH_3$ [a] (2)	(88)
2	$CH_2=CH-C(OCH_3)_2-CH_3$ (3)	CTBH, r.t.	$CH_2=CH-CHOCH_3-CH_3$ [a] (4)	(91)
3	 (5)	CTBH, 50°C	 [a] (6)	(75)
4	$HC\equiv C-CH(OCH_3)_2$ (7)	CTBH, r.t.	$HC\equiv C-CH_2OCH_3$ [a] (8)	(71)
5	$HC\equiv C-C(OCH_3)-CH_3$ (9)	CTBH, r.t.	$HC\equiv C-CHOCH_3-CH_3$ [a] (10)	(68)
6	 (11)	CTBH, 50°C	$HC\equiv C-CH_2O(CH_2)_2OH$ [b] (12)	(67)
7	$HC\equiv C-CH_2OTHP$ (13)	CTBH, 50°C	$HC\equiv C-CH_2O(CH_2)_4CH_2OH$ [b] (14)	(22)
			$HC\equiv C-CH_2OH$ [a] (15)	(68)
8	$HC\equiv C-CH_2OTHP$ (13)	CTBH/ $RhCl(PPh_3)_3$, r.t.	$HC\equiv C-CH_2O(CH_2)_4CH_2OH$ [b] (14)	(58)
			$HC\equiv C-CH_2OH$ [a] (15)	(26)
9	$CH_3(CH_2)_{10}CH_2OTHP$ (16)	CTBH, 50°C	$CH_3(CH_2)_{10}CH_2O(CH_2)_4CH_2OH$ [b] (17)	(24)
			$CH_3(CH_2)_{10}CH_2OH$ [a] (18)	(71)
10	$CH_3(CH_2)_{10}CH_2OTHP$ (16)	CTBH/ $RhCl(PPh_3)_3$, r.t.	$CH_3(CH_2)_{10}CH_2O(CH_2)_4CH_2OH$ [b] (17)	(67)
			$CH_3(CH_2)_{10}CH_2OH$ [a] (18)	(24)
11	$HC\equiv C-CH_2OCOCH_3$ (19)	CTBH, 70°C	 [b] (20)	(75)

TABLE 1 (continued)

(a) Identified by comparison with authentic samples.
(b) Identified , after chromatographic purification (see experimental) by spectral data: (12) MS: m/z=100; ^{1}H-NMR ppm: 3.75 (2H, dd -OC$\underline{H}_2$), 3.60 (2H, t, C$\underline{H}_2$OH),3.55 (2H, t, C$\underline{H}_2$O), 2.55 (1H, s, $\underline{H}$C=C); (14) MS: m/z=128; ^{1}H-NMR ppm: 3.70 (2H, dd, C$\underline{H}_2$O-), 3.66 (2H, t, C$\underline{H}_2$OH), 3.53 (2H, t, -OC$\underline{H}_2$), 2.55 (1H, s, $\underline{H}$C=C); (17) MS: m/z= 272; ^{1}H-NMR ppm: 3.65 (2H, t, C$\underline{H}_2$OH), 3.40 (4H, m, C$\underline{H}_2$O-), 1.70-1.20 (26H, m, C$\underline{H}_2$), 1.25 (3H, t C$\underline{H}_3$); (20) MS: m/z= 218; ^{1}H-NMR ppm: 6.90 (1H, m, $\underline{H}$C=C), 6.80 (4H, m, aromatic protons), 6.0 (1H, dt, $\underline{H}$C=C), 4.75 (2H, dd, C$\underline{H}_2$OCOCH$_3$), 2.15 (3H, s, OCOC$\underline{H}_3$).

converted in high yield at r.t. into the corresponding benzyl methyl ether. Therefore we explored the possibility to utilize this reagent for the chemoselective conversion of the allyl acetals and ketals in the corresponding allyl ethers.

As reported in the table, the hydroboration with CTBH of representative allyl acetals gives the desired ethers in good yields, while we observed that BH_3.THF or BH_3.Me_2S in the same reaction conditions give a mixture of the corresponding saturated acetals as well as unsaturated ethers.

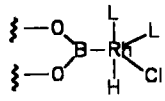
The above procedure was usefully extended to the conversion of prop-2-ynyl acetals or ketals into the corresponding alkynyl ethers. As shown in table, a good chemoselective reduction occurs with the formation of the desired prop-2-ynyl ethers.

These unsaturated ethers are important since they may be used as starting materials for the preparation of the

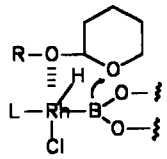
relatively inaccessible allenyl ethers, cyclopropane derivatives, pyrazoles; the prop-2-ynyl ethers are present in several natural materials and posses high antibiotic activity[2]. Moreover they retard metal corrosion, and aid the floctation of rare metals. For example compound (12) of the table finds application in electroplating as brightening agent[3].

It is noteworthy that CTBH prefers to react with the acetalic function of prop-2-ynyl pyranylethers, also at higher temp. (50°C), giving the propargyl alcohols. This reactivity of CTBH with the acetalic or ketalic function is specific as we consider that the propargyl acetate (19) is hydroborated with an opposite chemoselectivity with respect to the propargyl acetal, the acetyl vinyl borane (20) being formed (table).

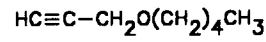
With the aim to obtain the reductive cleavage of the pyranylether group at the ring carbon-oxygen bond, we also operated the reduction with CTBH in presence of the Rhodium chloride tris triphenylphosphine, since this catalyst, as recently reported[4], forms with CTBH an intermediate complex A (scheme) able to hydroborate olefinic double bonds with a change of the usual regioselectivity. In these conditions CTBH converted the alkynyl pyranyl ether (13) mainly into the 1,5-pentandiol-1-propargyl ether (14) (table), thus confirming the inversion in the regioselectivity already observed. The catalyst role is further



(A)



(B)



(23)

Scheme

confirmed as the reduction of (13) is effective(entry 8, table) also at room temp.

A reasonable explanation of this result is reported in scheme (figure B) where the preliminary complexation of Rhodium with the exo oxygen may orient the boron attack to the endo oxygen with the formation of (14). THP ether (16) was converted likewise into the monoetherate diol (17) (table).

The mono pro-2-ynyl ether of 1,2-pentandiol (14) is an intermediate to prepare (23) (scheme), a pharmaceutical compound with beneficial effects on the blood formation[3].

No reaction occurred nevertheless between CTBH and the glucosidic acetals also by forcing the condition reactions. The acetonide of D-glucose (21) (scheme) was therefore cleaved only at the eso ketalic function giving the monoetherate diol (22) in good yields, the preferential opening of ketal at C_5 oxygen being ascribed to the anchimeric assistance of the benzylic group to the boron atom (scheme).

In conclusion this new simple access to the prop-2-ynyl ethers appears to be complementary to the other based on the dehydroalogenation of halogenoalkynyl ethers as well on the reaction between alkoxides and pro-2-ynyl halides[2].

Experimental

Acetals and ketals reduction with catecholborane. General procedure.

Starting compound (1 mmol) was added to a solution of catecholborane (1 mmol) in anhydrous benzene (0.2 ml) under Argon atmosphere, then stirred overnight.

The reaction mixture was diluted with diethyl ether then cathecol extracted with sodium hydroxide solution (10% in water). The ethereal solution was then washed with water to neutrality, dried over anhydrous sodium sulphate and the solvent evaporated at reduced pressure.

The crude product was purified via cromatography on silica gel eluting with petroleum ether 40-60° - diethyl ether 90:10 and the pure product identified by 200MHz 1H-NMR and mass spectra (table) or in comparison with autentic samples.

Reduction of (13) and (16) with catecholborane in presence of Rhodium chloride tris tryphenylphosphine.

To a solution of catecholborane (2 mmol) in anhydrous benzene (0.2 ml) degassed with Argon, the catalyst (20 mg) was added with stirring at r.t. in Argon atmosphere. After 15 min. (13) (2 mmol) was added. The reaction, monitored via gas-cromatography, was stopped after 5 hours.

After the usual work-up the reaction product (14) was isolated via cromatography on silica gel eluting with petroleum ether 40-60° - diethyl ether 90:10 then identified via 1H-NMR and mass spectroscopy (table).

With the same procedure (16) was reduced to (17).

Reduction of (19) with catecholborane, formation of (20).

Catecholborane (2 mmol) was added by stirring to a solution of (19) (2 mmol) in benzene under Argon. The reaction temperature was raised to 70°C then the solution stirred overnight.

After the usual work-up (20) was isolated as a liquid compound and characterized as usual (table).

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