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REGIOSELECTIVE FORMATION OF 3-tertALKOXY-1,2-GLYCOLS FROM 2,3-O-ALKYLIDENETRIOLS WITH TRIMETHYLALUMINUM

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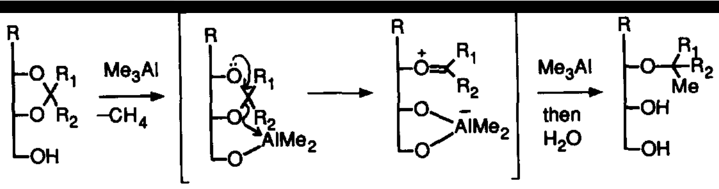
Summary: 2,3-O-Alkylidenetriols undergo nucleophilic cleavage to give 3-tertalkoxy-1,2-glycols regioselectively on treatment with trimethylaluminum.

In relation to our ongoing project,[1] we required α-alkoxyaldehydes whose alkyl group may be removed in later stage. We report here an efficient method for the preparation of 3-tertalkoxy-1,2-glycols serving as stable precursors of the requisite aldehydes from the corresponding 2,3-O-alkylidenetriol employing highly regioselective nucleophilic cleavege of the O-alkylidene bond by [illegible]

Treatment of the substrates 1 with an excess amount of trimethylaluminum in toluene at an ambient temperature furnished the 1,2-diols 4 bearing 3-tertalkoxy group as major to exclusive products in good yield (Table). Interestingly, when a substrate carries alkylidene group remote from hydroxy group or possesses no hydroxy group the reaction proceeded very sluggishly (Entries 5-8). Moreover, when a substrate carries bulky groups around hydroxy groups, no cleavage was observed at all (Entry 4). Diastereoselection was observed (Entries 9-12), however, it was not high (33-17% de by MTPA ester).

The reaction presumed to take place by the formation of metal alkoxide 2 and its transformation to betaine intermediate 3, followed by nucleophilic addition of the second aluminum reagent to the latter (Scheme 1). Since tertbutoxy group may be cleaved to give alcoholic function under relatively mild conditions,[4] the present method is [illegible]



1 2 3 4 Scheme 1

References and Notes

1. Cf. S. Takano, A. Kurotaki, Y. Sekiguchi, S. Satoh, M. Hirama, and K. Ogasawara, Synthesis, 1986, 811.
2. Nucleophilic cleavage of ketal bond with trimethylaluminum, see: J. Fujiwara, Y. Fukutani, M. Hasegawa, K. Maruoka, and H. Yamamoto, J. Am. [illegible]
4. Cf. U. Eder, G. Haffer, G. Neef, G. Sauer, A. Seeger, and R. Wiechert, Chem. Ber., 110, 3161 (1977).