Synthesis of Alkenes from 1,2-Diols *via* Cyclic Sulfates

Yung Hyup Joo[†] and Doo Ok Jang*

Department of Chemistry, Yonsei University, Wonju 222-710, Korea
[†]Pacific Corporation, Pharmaceutical Research Institute, Kyounggi-do 449-900, Korea
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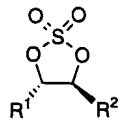
Deoxygenation of 1,2-diols is a valuable transformation which is used for synthesis of alkenes. A number of methods have been developed for the regio- and stereospecific deoxygenation of 1,2-diols.[1] The conversion of 1,2-diols into alkenes can be performed directly by reaction with tungsten reagent,[2] PBr_3-CuBr-Zn,[3] titanium metals,[4] Ph_3P-I_2-imidazole,[5] Me_3SiCl-NaI,[6] or Ph_2PCl-I_2-imidazole.[7] Deoxygenation of 1,2-diols can also be done indirectly *via* precursors which are activated by various functional groups. Among them, Corey-Winter method which involves cyclic thionocarbonates is the most well known. The cyclic thionocarbonates can be transformed into alkenes by trialkyl phosphites,[8] 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine,[9] iron pentacarbonyl,[10] Raney nickel,[11] tributyltin hydride,[12] bis(1,5-cyclooctadecene) nickel,[13] or Zn and an alkyl iodide.[14] Besides the cyclic thionocarbonates, 1,3-dioxolane derivatives,[15] disulfonates,[16] vicinal dixanthates,[17] cyclic phosphates,[18] phosphoroamidates,[18] oxiranes,[19] and episulfides[20] have been applied for the synthesis of alkenes from 1,2-diols.

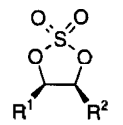
Most recently, it has been reported that cyclic sulfates can be used as activating groups for the transformation of 1, 2-diols to alkenes.[21-24] The cyclic sulfates of 1,2-diols are conveniently synthesized from 1,2-diols by treatment with thionyl chloride and $NaIO_4/RuCl_3 \cdot 3H_2O$ according to Sharpless procedure.[25] The cyclic sulfates show high reactivity towards various nucleophiles.[25] The cyclic sulfates are converted into acyclic sulfate half-esters which could be displaced by another nucleophile intramolecularly. It is thought that if the reaction is controlled to lead to elimination over nucleophilic substitution by the second nucleophile, the desired alkenes could be obtained.

In this communication, we wish to report that alkenes can be obtained from cyclic sulfates of 1,2-diols by treatment with sodium iodide in acetone at room temperature in high isolated yields.

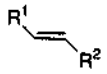
When cyclic sulfate of (±)-hydrobenzoin (**1**) was treated with NaI (3 eq) at room temperature, *trans*-stilbene (**9**) was obtained in 95% yield (Table 1, entry 1). At the end of the reaction, the reaction had deep brown color of iodine. The reaction time was shortened by using excess NaI (up to 5 eq) (entry 2). Potassium iodide is less effective than sodium iodide (entry 3). 1,2-Diols which are activated by phenyl or ester groups are good substrates for the process (entry 1-7). At room temperature, inactivated 1,2-diols **6** and **7** gave precipitates, presumably sulfate salts, which produced alkenes in boiling acetone (entry 8 and 9). Reaction of cyclic sulfate of 1,2-diol **6** with KI in the presence of 18-crown-6 in acetone at room temperature also gave a sulfate salt. Reaction of cyclic sulfate of *meso*-hydrobenzoin (**8**) gave a mixture of *trans*-stilbene (**9**) and *cis*-stilbene (**16**) (42 : 58 ratio) in 96% yield (entry 10). Interestingly, using excess NaI offered *trans*-stilbene (**9**) as a major product (entry 11). It is thought that for *trans*-1,2-diols (entry 1-8), the mechanism of the reaction is very similar to the Tipson-Cohen reaction[16] involving nucleophilic displacement of a cyclic sulfate at a site by an iodide ion followed by elimination by another iodide ion with antiperiplanar geometry. In the case of *cis*-1,2-diols, direct elimination without changing the conformation leads



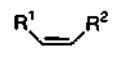
1: (±) $R^1 = R^2 = Ph$
2: $R^1 = R^2 = CO_2CH_3$
3: (±) $R^1 = Ph$, $R^2 = CO_2CH_3$
4: (±) $R^1 = CH_3(CH_2)_4$, $R^2 = CO_2CH_2Ph$
5: (±) $R^1 = Ph$, $R^2 = CH_2OCH_3$
6: (±) $R^1 = CH_3(CH_2)_9$, $R^2 = H$



7: $R^1, R^2 = -(CH_2)_{10}-$
8: $R^1 = R^2 = Ph$



9: $R^1 = R^2 = Ph$
10: $R^1 = R^2 = CO_2CH_3$
11: $R^1 = Ph$, $R^2 = CO_2CH_3$
12: $R^1 = CH_3(CH_2)_4$, $R^2 = CO_2CH_2Ph$
13: $R^1 = Ph$, $R^2 = CH_2OCH_3$
14: $R^1 = CH_3(CH_2)_9$, $R^2 = H$
15: $R^1, R^2 = -(CH_2)_{10}-$



16: $R^1 = R^2 = Ph$
17: $R^1, R^2 = -(CH_2)_{10}-$

Table 1. Transformation of Cyclic Sulfates into Alkenes with NaI in Acetone at Room Temperature

Entry	Substrate	NaI (eq)	Time (hr)	Product	Yield (%)[a]
1	**1**	3	6	**9**	95
2	**1**	3+2[b]	3	**9**	95
3	**1**	3+2[c]	4	**9**	94
4	**2**	3	1	**10**	86
5	**3**	3	0.5	**11**	73
6	**4**	2.5	1	**12**	83
7	**5**	2.2	12	**13**	70
8[d]	**6**	5	4	**14**	86
9[d]	**7**	5	4	**15:17**[e]	80
10	**8**	3	6	**9:16** (42:58)[f]	96
11	**8**	3+2[b]	4	**9:16** (80:20)[f]	80

[a] Isolated yields by column chromatography on silica gel and identified by ^1H NMR and GC-MS. [b] After 1 hr, further 2 eq of NaI was added. [c] Under the same conditions as entry 2 except using KI. [d] In boiling acetone. [e] The ratio was not determined. [f] The ratio was determined by ^1H NMR.

to *cis*-olefin. However, the intermediate, acyclic sulfate half-ester, can be rotated around carbon-carbon bond to have stable conformation which the alkyl groups are *cis* to each other. Then, epimerization takes place to have antiperiplanar geometry for giving *trans*-olefin.

The reaction offers several advantages over existing methods. The reaction generally proceeds smoothly at low temperature. The reagent is readily available. Byproducts deriving from the reagents are conveniently extracted from the organic layer into the aqueous $Na_2S_2O_3$ layer.

Typical experimental procedure: To a solution of the cyclic sulfate of (±)-hydrobenzoin (**1**) (0.10 g, 0.36 mmol) in dry acetone (3 mL) under nitrogen was added NaI (0.17 g, 1.1 mmol) at room temperature. The reaction mixture was stirred for 6 hr (TLC showed the disappearance of the cyclic sulfate). The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $Na_2S_2O_3$ solution until the brown color disappeared. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed and the residue was purified with column chromatography on silica gel (hexanes/EtOAc, 8 : 2) to give *trans*-stilbene (**9**) (62 mg, 95%).

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