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CYCLIC SULFATE FORMATION FROM EPOXIDES

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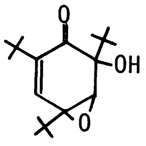
The reactions of 2,4,6-tri-tert-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenone and 2,4,6-tri-tert-butyl-2,3,4,5-diepoxy-6-hydroxycyclohexanone with sulfuric acid in acetic anhydride led to opening of the epoxy ring at 4-position to give the corresponding 4,5-sulfonyldioxy derivatives (cyclic sulfates).

Organic cyclic sulfates are normally formaed by permanganate oxidation of cyclic sulfites,[1] treatment of ethylene dibromide or trimethylene dibromide with silver sulfate,[1] reaction of diols with sulfuryl chloride,[1] and photochemical reaction of quinones with sulfur dioxide.[2] Recently, it has been demonstrated that cyclic sulfate (5) was formed in the photolysis of 3,5-dimethyl-4-pyrone in sulfuric acid.[3] Little information has, however, been available about cyclic sulfate formation from epoxides.



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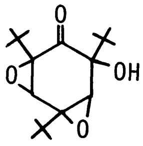

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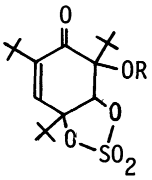
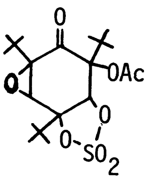


3

a; R=H b; R=Ac



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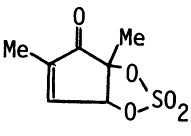

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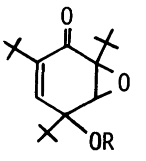

6

a; R=H b; R=Ac

Herein, we wish to report unusual cyclic sulfate formation from 2,4,6-tri-tert-butyl-4,5-epoxy-6-hydroxy-2-cyclohexenone (1) and from 2,4,6-tri-tert-butyl-2,3,4,5-diepoxy-6-hydroxycyclohexanone (2). When epoxide 1, specifically formed in the t-BuOK-catalyzed oxidation of 2,4,6-tri-tert-butylphenol with O_2 in t-BuOH at 40 °C,[4] was treated with an equimolar amount of sulfuric acid in acetic anhydride at 0 °C, the reaction was complete within 10 min. The reaction mixture was poured into ice-water to give 2,4,6-tri-tert-butyl-6-hydroxy-4,5-sulfonyldioxy-2-cyclohexenone (3a) in quantitative yield as colorless prisms; $C_{18}H_{30}O_6S$, mp 112-113 °C; IR(Nujol) 3600, 1730, 1220 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ 1.02 (s, 9H), 1.16 (s, 9H), 1.23 (s, 9H), 3.12 (s, 1H, OH), 5.17 (s, 1H), 6.18 (s, 1H). Further treatment of **3a** with sulfuric acid in acetic anhydride at 0 °C gave the corresponding acetate **3b** in quantitative yield as colorless prisms; $C_{20}H_{32}O_7S$, mp 124-126 °C; IR(Nujol) 1750, 1720, 1220 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 1.02 (s, 9H), 1.23 (s, 18H), 2.07 (s, 3H), 5.12 (s, 1H), 6.37 (s, 1H). Acetate **3b** was also obtained quantitatively when **1** was mixed with an excess of sulfuric acid in acetic anhydride at 0 °C. Similar cyclic sulfate formation was observed in the reaction of **2**[5] with an excess of sulfuric acid in acetic anhydride to give **4**; colorless prisms, mp 153-155 °C; ^{1}H-NMR(CDCl$_3$) δ 1.13 (s, 9H), 1.15 (s, 18H), 2.20 (s, 3H), 3.76 (s, 1H), 5.04 (s, 1H). Chemical shifts of protons attached to the cyclic sulfate rings of **3a** (5.17), **3b** (5.12), **4** (5.04), and **5** (5.43)[3] are satisfactorily compatible. Cyclic sulfates usually undergo base- or acid-catalyzed hydrolysis giving rise to the corresponding diols.[1, 2] Interestingly, however, unusual behavior of the cyclic sulfates **3** toward base and acid has been observed. The cyclic sulfate **3a** was quantitatively reverted to **1** upon treating with trifluoroacetic acid in methanol. When **3b** was treated with KOH or MeOK in methanol at room temperature, **1** was obtained in quantitative yield. These chemical reactions of **3** provide additional evidence for their structures. Attempts for hydrolysis of **3b** to **3a** was unsuccessful.

On the other hand, the reaction of an isomer of **1**, 2,4,6-tri-*tert*-butyl-5,6-epoxy-4-hydroxy-2-cyclohexenone (**6a**), with sulfuric acid in acetic anhydride at 0 °C gave the corresponding acetate (**6b**) instead of a cyclic sulfate. This fact as well as the formation of **4** from **2** indicates that reactivity of 4,5-epoxy group is much higher than that of 5,6-epoxy group, and that the present cyclic sulfate formation is reasonably assumed to be initiated by the opening of the epoxy ring at 4-position of **1** and **2**.

Styrene oxide, tetraphenylethylene oxide, or epoxychalcone does not give cyclic sulfate with sulfuric acid in acetic anhydride.[6] Investigation on structural requirement for the formation of cyclic sulfates from epoxides is now in progress.

References and Notes

1) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, J. Am. Chem. Soc., 85, 602 (1963); 87, 3781 (1965). E. T. Kaiser, Accounts Chem. Res., 3, 145 (1970).

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5) The compound **2** is readily obtained by epoxidation of **1** with *m*-chloroperbenzoic acid.

6) In the reaction with sulfuric acid in acetic anhydride, styrene oxide gave 1-phenyl-1,2-diacetoxyethane, tetraphenylethylene oxide gave pheny trityl ketone, and epoxychalcone gave a complex reaction mixture.

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