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 14. mp. 170-175°C; ¹H NMR (80 MHz, CDCl₃) δ 0.85 (t, 12H, CH₃), 1.31 (m, 40H, CH₂(CH₂)₅CH₃), 2.20 (m, 8H, CH₂ α to methine), 4.42 (s, 8H, CH₂Br), 4.57 (d, 4H, inner OCH₂), 4.79 (t, 4H, methine), 6.04 (d, 4H, outer OCH₂), 7.13 (s, 4H, ArH).
 15. mp. 243-246°C; ¹H NMR (80 MHz, CDCl₃) δ 0.85(t, 12H, CH₃), 1.32 (m, 40H, CH₂(CH₂)₅CH₃), 2.20 (m, 8H, CH₂ α to methine), 3.54 (s, 8H, CH₂CN), 4.47 (d, 4H, inner OCH₂), 4.79 (t, 4H, methine), 6.03 (d, 4H, outer OCH₂), 7.17 (s, 4H, ArH); Mass(EI) m/e (relative intensity) 1084.5 (100, M⁺).

Reaction of Dimethyl L-Tartrate 2,3-Cyclic Sulfate with Dimethyl Sulfide and with Pyridine

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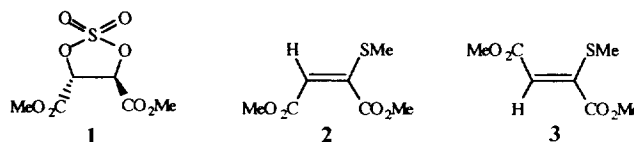
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Synthesis of the cyclic sulfate and its reaction with nucleophiles have been known for a long time,¹ especially in the

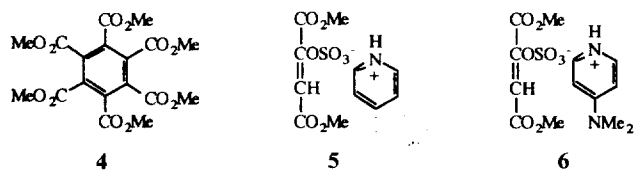
field of carbohydrate chemistry.² Recent works by Sharpless *et al.* have provided an easier access to cyclic sulfates and have shown their usefulness in organic synthesis.³ We have also employed the cyclic sulfates for the efficient synthesis of Ara-U.⁴ We further investigated the reaction of cyclic sulfates with certain nucleophiles and have found that the reactions of dimethyl L-tartrate 2,3-cyclic sulfate(**1**) with dimethyl sulfide and with pyridine give unusual products. Herein we report the preliminary results.

Reaction of cyclic sulfate **1** with dimethyl sulfide in xylene at 80-85°C for 3 days afforded an equal amount of dimethyl 2-(methylthio)maleate(**2**)⁵ and dimethyl 2-(methylthio)fumarate(**3**)⁶ in 40% yield. Prolonged reaction time, higher reaction temperature, or reactions in different solvents did not improve the yield. Reaction of **1** with ethyl phenyl sulfide also afforded **2** and **3** though in low yield, but the reaction using *t*-butyl methyl sulfide did not proceed. The assignment of *E*- and *Z*-isomers, **2** and **3** was made on the basis of NOE experiments. Upon irradiation of the vinyl proton, NOE was observed on methyl protons of methylthio group in *E*-isomer, **2** but not in *Z*-isomer, **3**. Although the reaction mechanism is not clear, the first step might be the sulfate ring opening by dimethyl sulfide.⁷



Since the product mixture was quite acidic, the effect of base on this reaction was examined. The reaction of cyclic sulfate **1** with dimethyl sulfide in the presence of pyridine afforded unexpected hexamethyl mellitate **4**. However, it was found that dimethyl sulfide did not actually participate in the formation of **4**. Heating of cyclic sulfate **1** in refluxing THF in the presence of one or two equivalents of pyridine for 10 hr afforded **4** in 49% yield. Higher reaction temperature and different amount of pyridine did not improve the yield of **4**. Although *N,N*-dimethylaminopyridine was as effective as pyridine for the formation of **4**, the reaction did not occur with other bases such as triethylamine, DBU, potassium carbonate, and potassium *t*-butoxide.

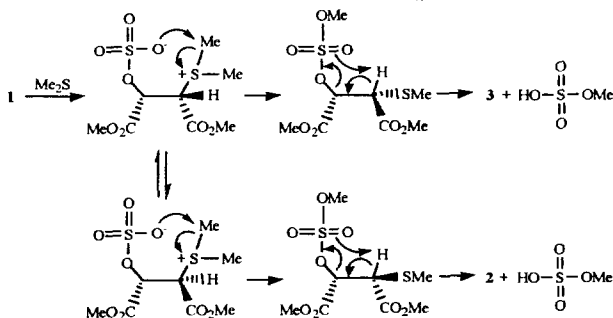
At room temperature, on the other hand, the reaction of **1** with pyridine in THF gave pyridinium salt **5** in 82% yield. Salt **5** was very hygroscopic and could not be completely purified, while *N,N*-dimethylaminopyridinium salt **6** was stable solid and fully characterized by NMR.⁸ Heating of salt **5** or **6** in various solvents gave only very small amount of mellitate **4** even in the prolonged reaction time. We examined the possibility of involvement of dimethyl acetylenedicarboxylate(DMAD) as an intermediate although trimerization of DMAD to mellitate **4** is known to require special conditions.⁹ Attempts to detect or trap DMAD during reaction employing various methods were not fruitful.



The present reactions of cyclic sulfates **1** with dimethyl sulfide and with pyridine are very special ones. Other cyclic sulfates never showed same reaction patterns as **1**. Further studies are required for the elucidation of the reaction mechanisms.

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 5. Compound **2**: TLC (SiO₂, 1 : 1 ethyl acetate/hexanes) *R_f* = 0.68; ¹H NMR (CDCl₃, 300 MHz) δ 2.34 (s, 3H), 3.60 (s, 3H), 3.86 (s, 3H), 5.62 (s, 1H); GC MS *m/e* 190 (M⁺), 159, 131, 130, 105, 85, 72, 59.
 6. Compound **3**: TLC (SiO₂, 1 : 1 ethyl acetate/hexanes) *R_f* = 0.59; ¹H NMR (CDCl₃, 300 MHz) δ 2.32 (s, 3H), 3.74 (s, 3H), 3.84 (s, 3H), 6.28 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 15.6, 51.6, 52.6, 110.0, 150.7, 165.0, 166.0.
 7. A plausible mechanism for the formation of **2** and **3** can be suggested as follows:
- 
8. Compound **6**: ¹H NMR (DMSO-d₆, 80 MHz) δ 3.27 (s, 6H), 3.67 (s, 3H), 3.83 (s, 3H), 7.11 (d, 2H, *J* = 8.0 Hz), 7.25 (s, 1H), 8.24 (d, 2H, *J* = 8.0 Hz).
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One-Pot Preparation of Xanthone Derivatives from Aromatic α-Diketones

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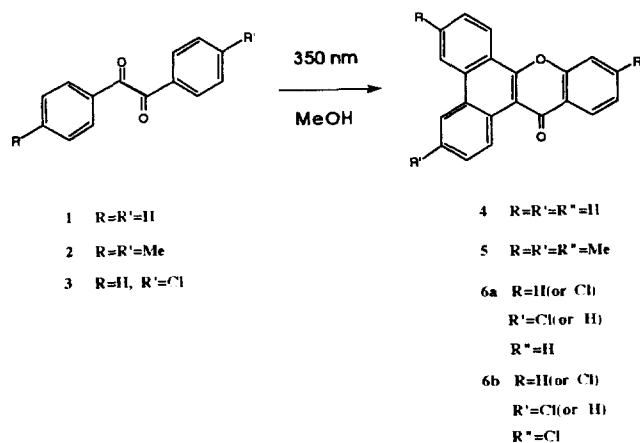
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The photochemistry of α-diketones has been a subject of interest for a century. Since the appearance of comprehensive review articles^{1,2} in 1969 and 1972, activity in this area has continued with investigation of a number of new systems.³⁻¹² The classical photochemistry of saturated and aryl diketones is well known. It has been known that irradiation of benzil in solution gives rise to a variety of reaction products, such as benzaldehyde, benzoic acid, benzoin, benzil pinacol and benzoin benzoate.¹²⁻¹⁵ Irradiation of benzil in ethylene glycol gave α,α'-dihydrostilbene.^{11,15} Irradiation of benzil in cyclohexane yielded benzoic acid, benzoin, desyl benzoyloxidesyl ether and unknown compound.¹⁶ When 2-propanol is used as the solvent, a new product appears which is most probably the dimer of ketyl radical which is formed when an excited benzil abstracts a hydrogen atom.¹² Irradiation of benzil in tetrahydrofuran gave a mixture of product containing benzaldehyde, a small amount of benzoin and unidentified photoproduct.¹⁴

We have reported that irradiation of benzil in methanol gave the unexpected photoproduct, *i.e.*, xanthone derivatives in 18% yield.¹⁷ Here we now describe the photochemical formation of xanthone derivatives from α-diketones, such as benzil **1**, 4,4'-dimethylbenzil **2** and 4-chlorobenzil **3** in methanol (Scheme 1).

Normal scale preparations of the new photoproducts were conducted in a photoreactor composed of water-cooled pyrex reaction vessel, which is equipped with a nitrogen gas inlet.



Scheme 1.