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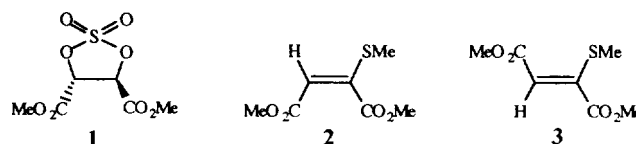
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Synthesis of the cyclic sulfate and its reaction with nucleophiles have been known for a long time,¹ especially in the

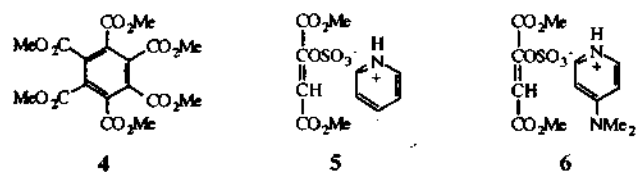
field of carbohydrate chemistry.² Recent works by Sharpless *et al.* have provided an easier access to cyclic sulfates and have shown their usefulness in organic synthesis.³ We have also employed the cyclic sulfates for the efficient synthesis of Ara-U.⁴ We further investigated the reaction of cyclic 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.

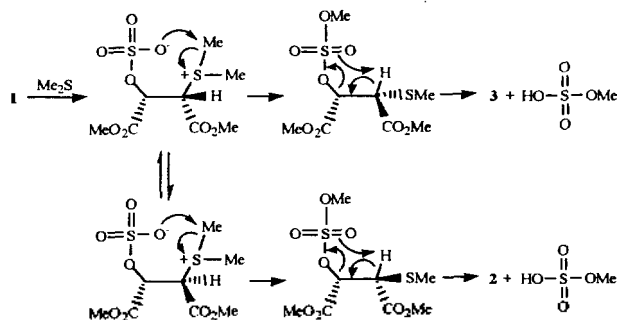


The present reactions of cyclic sulfates **1** with dimethyl sulfide and with pyridine are very special ones. Other cyclic sulfates never showed same reaction patterns as **1**. Further studies are required for the elucidation of the reaction mechanisms.

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- 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.
- 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.
- A plausible mechanism for the formation of **2** and **3** can be suggested as follows:



- 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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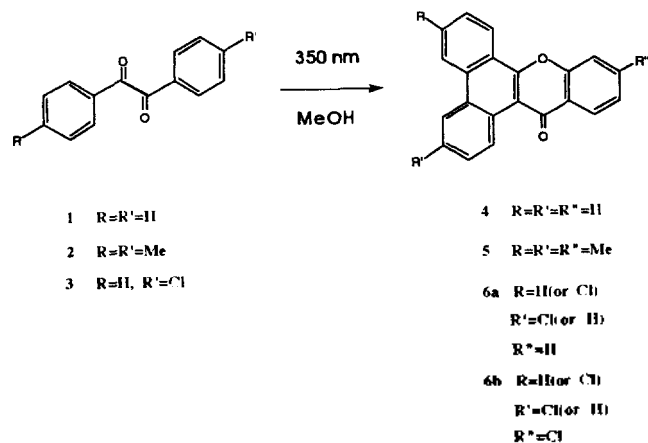
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The photochemistry of α-diketones has been a subject of interest for a century. Since the appearance of comprehensive review articles^{1,2} in 1969 and 1972, activity in this area has continued with investigation of a number of new systems.³⁻¹² The 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 benzoyloxydesyl 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.