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NEW REACTIONS OF ORGANIC SULFUR COMPOUNDS WITH THALLIUM TRINITRATE : A SYNTHESIS OF α-OXODIMETHYLKETALS[1]

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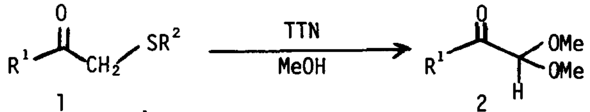
We have exploited new reactions utilizing "Soft-Soft specific affinity" between trivalent thallium atom and divalent sulfur atom.[2,3]

As a part of this investigation, we reported the conversions of β-oxosulfides (1) into the corresponding α-oxodimethylacetals (2) by treatment with thallium trinitrate [$Tl(ONO_2)_3 \cdot 3H_2O$] (TTN) in methanol.[3]



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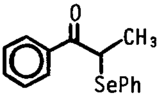
R^1= alkyl, aryl, or alkoxyl

We have extended this reaction to a general synthesis of the α-oxodimethylketal, which is reported here.

As shown in Table, β-oxosulfides, 4, 7, 10, 14, and 17, were prepared under the conditions indicated, and they were treated with TTN in methanol to give α-diketone 5 and α-oxodimethylketals (8, 12, 15, and 18) in good yields.

On the other hand, β-oxoselenide 19 on treatment with TTN (3 mol equiv) in methanol afforded αβ-unsaturated ketone 20 in 50% yield.[4]

Compound 12 was treated with hydrobromic acid in dichloromethane at 50° to give flavonol (21)[7] (mp 169-172°) in 76% yield.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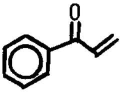
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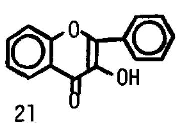
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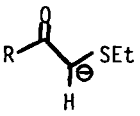
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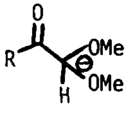
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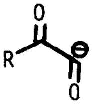
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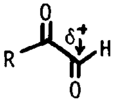
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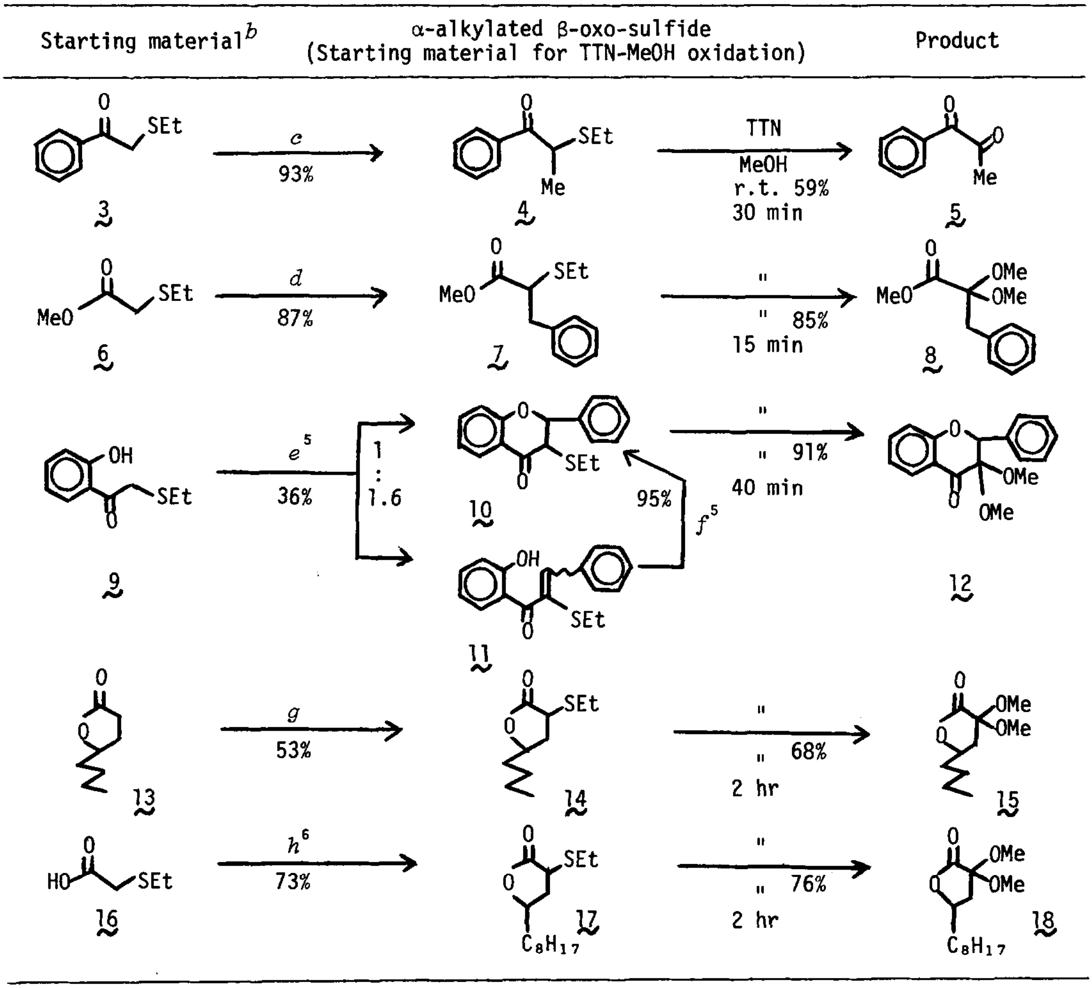
The foregoing experiments indicate that anion 22 can be utilized as the latent synthon of anion 23 and a hypothetical anion 24. Thus, an "Umpolung" of the formyl group in an α-oxoaldehyde 25 is achieved.

Application of this new reaction to the syntheses of the biologically active α-ketoacids, flavonol derivatives, and avenaciolides is in progress.

Table. Synthesis of α-Oxodimethylketals[a]



a All of the new compounds indicate the reasonable IR, NMR, and mass spectra. In all of the oxidation reactions, 2.2 mol equivs. of TTN were used. The yields(%) are isolated yields. *b* β-Oxosulfides, 3, 6, and 9 were prepared from the corresponding bromide by treatment with thallous ethanethiolate (TlSEt).[3] *c* 1) NaH/THF-HMPT, 0°; 2) MeI, 0°. *d* 1) $(i\text{-}Pr)_2NLi$/THF-HMPT, -78°; 2) $PhCH_2Br$, -78°. *e* 1) 50% KOH-MeOH, 0°; 2) PhCHO, 0°→r.t. *f* Pyridine-H_2O(1:4), r.t. *g* 1) $(i\text{-}Pr)_2NLi$/THF, -78°; 2) EtSSEt, -78°→0°. *h* 1) $(i\text{-}Pr)_2NLi$/THF, -78°; 2) , -78°→r.t.

References and Notes

1 The IUPAC's nomenclature rule has rejected the word "ketal" and unified it as "acetal". In this communication, however, we dare to use "ketal", because of convenience of distinction between them.
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