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Efficient Addition of Aroyl Radicals to Ketene Dithioacetal *S,S*-Dioxides and its Utilization in Organic Synthesis

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On irradiation, an aromatic aldehyde adds efficiently to ketene dithioacetal *S,S* dioxides to give the Kharasch addition-type product.

Keywords: aromaticaldehyde; ketene dithioacetal *S,S*-dioxide; radical addition; the Nazarov cyclization

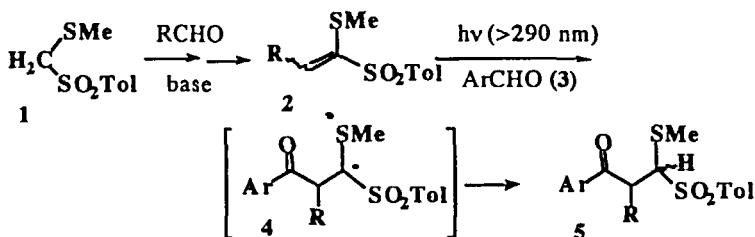
Introduction

Methylthiomethyl *p*-tolyl sulfone (**1**) is a versatile reagent for preparing many kinds of carbonyl compounds.^[1] Ketene dithioacetal *S,S*-dioxides (**2**), easily obtainable from **1**, were shown to have a high ability to accept various radicals such as 1-hydroxyalkyl radicals and 1-alkoxyalkyl radicals. We have also found that aroyl radicals add to **2** with high efficiency, which is realized by the photochemical addition of aromatic aldehydes (**3**) to **2** to give rise to the Kharasch addition-type products, which are useful in organic synthesis.

Photochemical addition of aromatic aldehydes (**3**) to **2**

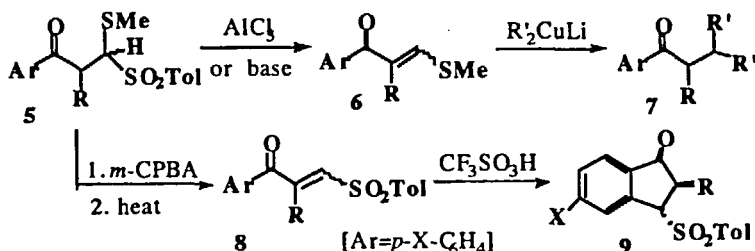
Irradiation (>290 nm) of **2** and **3** (5 equiv) in benzene or chlorobenzene gave an adduct (**5**). This reaction could be rationalized in terms of the addition of an aroyl radical, which was photochemically generated from **3**, to **2** to give rise to an intermediary radical (**4**) stabilized by a

synergistic (captodative) effect of methylthio and *p*-tolylsulfonyl groups.[2] The coexistence of benzophenone accelerated the reaction to improve the yield of **5**.



Utilization of the adducts (**4**) in organic synthesis

We found that **5** is an important precursor of highly substituted aromatic ketones (**7**): Treatment of **5** with AlCl_3 or a base (NaH or DBU) afforded a β -methylthio- α,β -unsaturated ketone (**6**) which was converted to the ketone (**7**) by the reaction with lithium dialkyl cuprate.



On oxidation with *m*-CPBA (1 equiv) followed by pyrolysis in refluxing toluene, the adduct (**5**) afforded an γ -oxo- α,β -unsaturated sulfone (**8**), which was transformed into a 2-alkyl-3-(*p*-tolylsulfonyl)-1-indanone (**9**) by the Nazarov reaction with trifluoromethanesulfonic acid.

References

- [1] "Encyclopedia of Reagents for Organic Synthesis", ed by L. A. Paquette, vol.5, p 3589 (1995).
- [2] (a) K. Ogura, A. Kayano, N. Sumitani, M. Akazome, and M. Fujita, *J. Org. Chem.*, 1995, 60, 1106. (b) A. Kayano, M. Akazome, M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn.*, 1995, 68, 3599. (c) A. Kayano, M. Akazome, M. Fujita, K. Ogura, *Tetrahedron*, 1997, 36, 12101.