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A NEW SYNTHESIS OF β-KETO-PHENYLSULFOXIDES

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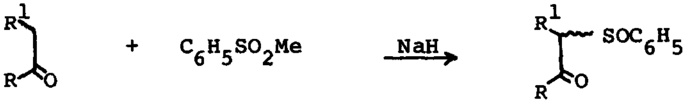
β-Keto-sulfoxides have been widely used in organic chemistry as synthetic intermediates[1]. The most common method of preparation of such compounds involves the reaction of esters with sodium methylsulfinylmethide[2]. More recently β-Keto-sulfoxides have also been prepared via rearrangement of 1-chloro-2-hydroxy - alkyl phenylsulfoxides with alkyl lithium[3] or oxidation of the appropriate β-ketothioethers[3,4].

In the course of our researches it became necessary to develop a convenient synthetic method for the introduction of the sulfoxide moiety alpha to a carbonyl group. We now wish to report a new method of preparation of β-keto-phenylsulfoxides.

When carbonyl compounds bearing an active methylene group were stirred overnight, at room temperature, with equimolar amounts of methyl benzenesulfinate[5] and sodium hydride in anhydrous ether, a smooth reaction took place. After the conventional work up the corresponding β-keto-phenylsulfoxides could be isolated in good yields (see table).

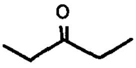
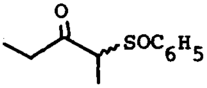
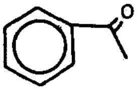
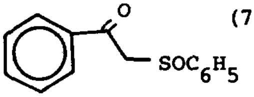
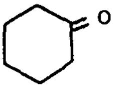
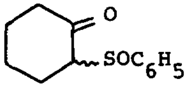
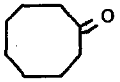
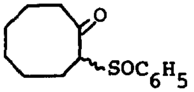
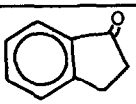
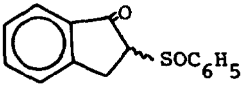
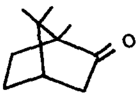
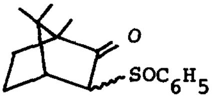


In a typical reaction, a suspension of sodium hydride (0.370 g, 15.4 mmoles) in 70 ml of anhydrous ethyl ether was treated with a mixture of cyclohexanone (1.38 g, 14.1 mmoles) and methyl benzenesulfinate (2.40 g, 15.4 mmoles) with vigorous stirring, at room temperature under nitrogen. After stirring overnight the resulting slurry was cooled in an ice bath, acidified with 10% sulfuric acid and the ethereal layer separated. The water layer was extracted with ether (20 ml x 2) and the combined extracts washed with 10% sodium bicarbonate, brine, and dried over sodium sulfate. Evaporation of the solvent under vacuum gave a crystalline residue which was recrystallized from ether to give α-phenylsulfinyl-cyclohexanone (2,3 g, 74%).

As shown by the examples in the table the new procedure allows the direct preparation of β-keto-sulfoxides derived from cyclanones, which are not readily available by other means. The generality of the method is presently under investigation in our laboratory.

TABLE

The Reaction of Methyl Benzenesulfinate with Carbonyl Compounds

Carbonyl Compounds	Product (isolated yield, m.p./Et_2O)[a]
	 (65%, 82-83°)
	 (70%, 70-71°, lit.[6]70.5-71.5°)
	 (74%, 104-105°)
	 (83%, oil)[b]
	 (60%, 95-97°)
	 (50%, 112-113°)[b,c]

a - All new compounds exhibited spectral and analytical data in agreement with the proposed structures.

b - In a preliminarly experiment methyl p-toluenesulfinate was used with similar results.

c - n-Hexane used as crystallization solvent.

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