Dianions of β-Keto-sulphoxides. A New General Synthesis of Vinyl Ketones

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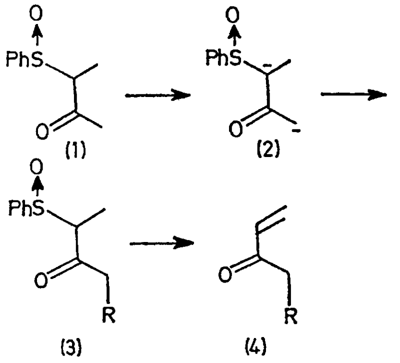
Summary The dianion of the β-keto-sulphoxide (**1**) can be alkylated exclusively on the γ-carbon atom with a variety of alkyl halides; the resultant α-phenylsulphinyl ketones (**3**) undergo ready elimination of benzenesulphenic acid providing a new general route to alkyl vinyl ketones.

The synthetic utility of dianions[1] derived from β-keto-sulphoxides (*e.g.* phenylsulphinylacetone) for the construction of ketones, 1,4-diketones, aldols, and 1,5-dicarbonyl systems has recently been described.[2] We now report a general method for the synthesis of methyl vinyl ketone homologues (see Scheme and Table), providing useful reagents for the annelation of β-diketones and simple cyclic ketones. The method is based on our earlier observations[2] that the dianion of phenylsulphinylacetone undergoes exclusive γ-alkylation and on recent reports that α-phenylsulphinyl carbonyl systems undergo ready thermal elimination of benzenesulphenic acid.[3]

The required β-keto-sulphoxide (**1**) was prepared in very high overall yield by oxidation (periodate–aqueous MeOH)[4] of its corresponding β-keto-sulphide which was synthesized from 3-bromobutan-2-one[5] and C_6H_5SNa in absolute EtOH. The dianion (**2**) can be conveniently prepared by sequential treatment of (**1**) in tetrahydrofuran (THF) containing hexamethylphosphoramide (HMPA) with NaH and $\mathrm{Bu^nLi}$. Addition of a variety of alkylating agents results in a ready reaction to give yields of γ-alkylated β-keto-sulphoxides (**3**) in the range 65—84%.



Scheme

The following is a typical reaction sequence. To a suspension of NaH (1·65 mmol, washed with hexane) in

TABLE. Preparation of vinyl ketones from the β-keto-sulphoxide (**1**).

R–X	Yield (%) of (**3**)	Vinyl ketone R in (**4**)	Time/h	Temp. (t/°C)	Yield (%)
—	—	H	16	75	80
$PhCH_2Br$	72	$PhCH_2$	18	74	75
MeI	65	Me	22	74	78
Bu^{n}I	84	Bu^n	23	70	78
Geranyl chloride	71	$Me_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe:CHCH_2$	42	74	92
$CH_2Cl{\cdot}CH:CClMe$	70	$MeCCl{=}CH{\cdot}CH_2$	16	74	98

anhydrous THF (1·5 ml) at 0° under N_2 was added a solution of (**1**) (1·5 mmol) in THF (2·2 ml) containing HMPA (1 equiv.). After 20 min, Bu^{n}Li (1·65 mmol) was added and the mixture was stirred for an additional 20 min. Addition of $PhCH_2Br$ (1·65 mmol), followed by warming to room temperature (30 min) and work-up afforded a 72% yield of (**3**; R = $PhCH_2$) after purification on silica gel.

Thermolysis of the α-phenylsulphinyl derivative (**3**; R = $PhCH_2$) (0·3 M in CCl_4) was carried out at *ca.* 74° under N_2 for 17 h. The reaction was quenched with $NaHCO_3$ solution and the crude product rapidly chromatographed on silica gel. The Table shows yields of this and other vinyl ketones; thermolysis of sulphoxides neat (120°) or in refluxing toluene gave only moderate yields.

The ready availability of (**1**) coupled with the ability of dianions of β-keto-sulphoxides to undergo exclusive γ-alkylation, condensation with carbonyl systems, ring opening of epoxides, and Michael additions should provide a general route to vinyl ketones. Moreover, the elimination step is quite mild and should be compatible with a variety of functional groups.

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