Reductive Desulfonylation of β-Ketosulfones by $TiCl_4$–Zn†

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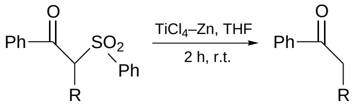
β-Ketosulfones are readily reduced by $TiCl_4$–Zn to give the corresponding ketones in good yields under mild conditions.

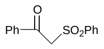
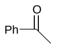
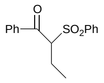
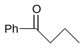
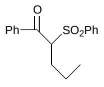
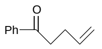
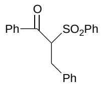
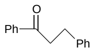
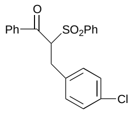
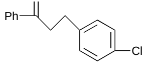
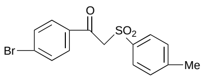
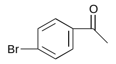
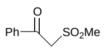
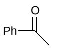
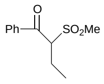
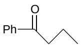
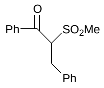
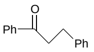
β-Ketosulfones, which are important synthetic intermediates, can be easily prepared by the phase-transfer-catalysed reaction of the corresponding halides with sodium arylsulfinates.[1,2] α-Alkyl-β-ketosulfones can be obtained by the alkylation of β-ketosulfones.[3] A useful transformation is the reductive desulfonylation of β-ketosulfones to the corresponding ketones.

Recently, low-valent titanium reagents[4] have been of great interest in organic synthesis. Herein we report the reductive desulfonylation of β-ketosulfones with $TiCl_4$–Zn to afford corresponding ketones under mild conditions (Scheme 1, Table 1).



Scheme 1

Table 1 Reductive desulfonylation of β-ketosulfones with $TiCl_4$–Zn

Substrate	Product	Yield (%)[a]	mp/°C (Lit.)
		83	oil[11]
		74	oil[12]
		87	oil[13]
		92	67–68 (68.5–69[9])
		82	55–57 (56.5–58[9])
		75	48–50 (51[14])
		75	oil[12]
		76	oil[13]
		82	66–68 (68.5–69[9])

[a]Yields of isolated product.

It was discovered that the corresponding ketones are not obtained from α-disubstituted β-ketosulfones by refluxing in THF for 8 h.

The same reductive desulfonylation can be effected by many existing procedures, for example, ketones can be obtained by the reductive cleavage of β-ketosulfones with aluminum amalgam.[5] The yield of this reaction was lower because the ketones produced can be consumed by further bimolecular reduction to pinacol. Two other widely exploited desulfonylation methods involve zinc metal[6] and chromous ion.[7] These procedures employ acidic media for prolonged periods, often at elevated temperatures. Another two methods use sodium dithionite[8] and sodium hydrogen telluride[9] in basic media to provide the corresponding ketones in moderate yields. Smith[10] has reported that the reductive cleavage of β-ketosulfones with trialkyl- or triphenylstannanes can be achieved under essentially neutral conditions. In order to obtain good to excellent yields, the desulfonylation must be heated at reflux in toluene. It is worth noting that $(C_5H_5)_2TiCl_2$-Zn is not more effective for the reductive desulfonylation. In our experiments, we observed that the yield was lower and the separation of crude product by preparative TLC became more difficult. In contrast, the reductive cleavage of β-ketosulfones with $TiCl_4$–Zn circumvents most of these problems. The present method offers some distinct advantages, such as mild and neutral conditions, high yields, rapid reaction and easy operation.

Experimental

Typical Procedure.—Under an inert atmosphere of nitrogen, $TiCl_4$ (1.14 g, 6 mmol) was added by syringe to a stirred slurry of zinc powder (0.2 g, 3 mmol) in THF (20 ml) in a 50 ml three-neck flask. The mixture was stirred magnetically for 0.5 h at room temperature. A light blue suspension was obtained. A solution of substrate (1 mmol) in THF (2 ml) was then added to this stirred suspension. The mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC. A dilute solution of HCL (5%, 10 ml) and ether (20 ml) were added. The organic layer was separated and the aqueous layer was extracted with either (20 ml × 2). The combined organic solution was washed with a saturated solution of NaCl (20 ml) and dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by preparative TLC on silic gel using cyclohexane–ethyl acetate as eluent. The product had identical spectral data (^1H NMR, IR) to that obtained from an authentic sample.

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