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REDUCTIVE ELIMINATION OF β-BENZOYLOXY SULFIDES BY THE USE OF TiCl$_4$-Zn. A CONVENIENT METHOD FOR KETONE METHYLENATION

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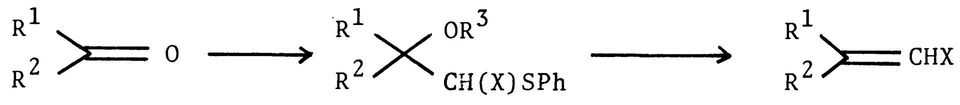
Exo methylene compounds were prepared in good yields by the reductive eliminations of β-benzoyloxy sulfides, produced by the reactions between ketones and phenylthiomethyllithium and subsequent benzoylations, with TiCl$_4$-Zn.

In the preceding paper, it was reported that lower valent titanium chloride, produced from titanium tetrachloride and zinc, is a useful reagent for the reductive β-elimination of β-hydroxy sulfides (II, X=H) and β-hydroxy thioacetals (II, X=SPh) to yield olefins and vinyl sulfides (IV), respectively.[1] Recently, it was also reported that a variety of styrene derivatives is prepared in high yields from II according to this procedure.[2] These observations directed us to examine a general synthetic utility of this method for the exo methylenation of ketones via the corresponding β-hydroxy sulfides (II, X=H), which are readily available by the reaction of ketones with phenylthiomethyllithium.[3] Concerning the reductive elimination reaction preparing olefins, Sowerby and Coates[4] have reported that the exo methylene compounds were produced in fairly good yields by the treatment of acyloxy sulfides (III, X=H) with Li-liq.NH$_3$.

In the present study, sulfide (V), derived from phenyl propyl ketone and phenylthiomethyllithium, having hydroxy group situated on the benzylic carbon atom was chosen as a model compound. When V was treated with lower valent titanium chloride, prepared in situ by the reaction between titanium tetrachloride and zinc in refluxing pyridine, the expected olefin was isolated in 85% yield. In a similar manner, 4-phenyl-2-methylbut-1-ene was obtained in good yield when β-hydroxy sulfide (VI), produced from benzylacetone and phenylthiomethyllithium, was treated with titanium tetrachloride and zinc in refluxing β-picoline, whereas the reaction was very sluggish in pyridine. It was further found that the same reductive elimination took place even at room temperature when the benzoyl ester[5] was used in place of VI in above experiment. Thereafter, the methylenation of several ketones via benzoyloxy sulfides (III) was studied under appropriate conditions shown in the Table.



I

II, R^3=H
III, R^3=COR

IV

Table. Exo Methylenation of Ketones

Ketone		Yield (%)			Condition (III→IV)	
R^1	R^2	II	III	IV	Temp.	Time (hr)
$PhCH_2CH_2$	CH_3	93	75	93	refl.	3
$PhCH_2$	$PhCH_2$	59	75	94	refl.	3
PhCH=CH	CH_3	90	--[a]	90	r.t.	8
$-(CH_2)_2CH(CH_3)(CH_2)_2-$		--	79	90[b]	r.t.	24
$-(CH_2)_3CH(CH_2Ph)-$		--	36[c]	83	refl.	4
Cholestan-3-one		--	62	87	refl.	4

a) The crude ester was characterized by ir and nmr spectroscopy, and used without further purification. b) Yield analyzed by glc. c) Fifty-eight percent yield of the hydroxy sulfide was obtained along with the ester.

The following is a typical procedure for the reductive elimination reaction. A suspended pyridine solution containing titanium tetrachloride (2 molar amounts) and zinc (4 molar amounts) was either refluxed or stirred at room temperature for 1-2 hours. After the solution changed from yellow to dark green, benzoyloxy sulfide (1 molar amount) in pyridine was added dropwise and the reaction mixture was stirred under the conditions indicated in the Table. The reaction mixture was then poured into an aqueous potassium hydroxide solution and extracted with ether. The combined ethereal solution was washed successively with KOH, dil.HCl, $KHSO_4$ aqueous solutions and then with water, and dried over anhydrous sodium sulfate. The product was isolated by preparative tlc. In a similar fashion, exo methylene compounds were obtained in high yields starting from benzylacetone, dibenzyl ketone, benzalacetone, 4-methylcyclohexanone, 2-benzylcyclopentanone, and cholestan-3-one.[6] The results are summarized in the Table. In all cases, no products formed by the isomerization of double bonds or polymerization could be detected.

It is noted that the present method for the reductive elimination reaction of β-benzoyloxy sulfides is very useful in respect that yields are high and that the procedure is simple, moreover that titanium tetrachloride is readily available as a common reagent. Therefore, the present method would be newly added as a general method for the exo methylenation of ketones.

Further works on the scope and utility of the reaction are now in progress.

References and Notes

1) T. Mukaiyama, M. Shiono, and T. Sato, Chem. Lett., 37 (1974).
2) S. Z. Song, M. Shiono, and T. Mukaiyama, ibid., 1161 (1974).
3) E. J. Corey and D. Seebach, J. Org. Chem., 31, 4097 (1966).
4) R. L. Sowerby and R. M. Coates, J. Amer. Chem. Soc., 94, 4758 (1972).
5) Hydroxy sulfides (II) and these benzoyl esters (III) were prepared according to Sowerby and Choates' method.[4]
6) Unfortunately, this method is not generally applicable to aldehyde methylenations. For example, treatment of 1-(phenylthiomethyl)dodecyl benzoate under similar conditions resulted in the formation of the parent β-hydroxy sulfide as a main product. The desired olefin was formed only in low yield.

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