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A CONVENIENT METHOD FOR METHYLENATION OF CARBONYL COMPOUNDS. THE REDUCTIVE β-ELIMINATION OF 2-(PHENYLTHIO)ETHANOLS INTO TERMINAL OLEFINS USING $TiCl_4$-$LiAlH_4$

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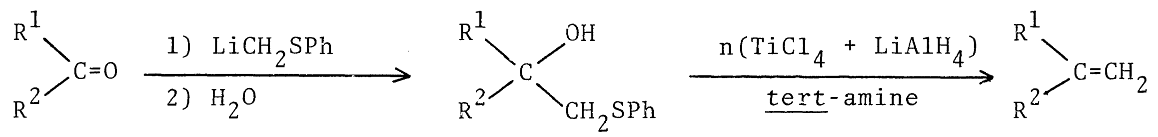
2-(Phenylthio)ethanols readily accessible from carbonyl compounds and phenylthiomethyllithium were converted into terminal olefins in high yields by way of the reductive β-elimination on treatment with $TiCl_4$ and $LiAlH_4$ in the presence of tertiary amine such as 1,8-bis(dimethylamino)naphthalene or tri-n-butylamine.

In the preceding paper,1) it was reported that terminal olefins (III) were produced in good yields by the reductive β-elimination of benzoates of 2-(phenylthio)ethanols (II), prepared from ketones and phenylthiomethyllithium (IV), on treatment with $TiCl_4$-Zn. It provides a convenient method for ketone methylenation, but the benzoylation of II is not always satisfactory, especially in the case of highly hindered alcohols.

In the present communication, we wish to report a method for the preparation of terminal olefins by the direct β-elimination of 2-(phenylthio)ethanols. The application of the $TiCl_4$-$LiAlH_4$ reagent,2) in the presence of 1,8-bis(dimethylamino)naphthalene, to 1,1-dibenzyl-2-(phenylthio)ethanol derived from dibenzyl ketone and IV resulted in the formation of 2-benzyl-3-phenylpropene in excellent yield. A remarkable shortening of the reaction time was accomplished when the reduction was carried out in a mixed solvent of benzene and dioxane, whereas it took 16 hr to complete the reaction in dioxane.



I II III

The following experimental procedure is illustrative;3) after addition of $LiAlH_4$ (10.5 mmol) to a suspension of the $TiCl_4$ (10.5 mmol)-dioxane complex in benzene (24 ml) and dioxane (19 ml), the mixture was refluxed for about 1 hr under an argon atmosphere to give a black colored solution. To metal complexes thus obtained was added 2-octyl-1-phenylthiomethylcyclopentan-1-ol and 1,8-bis(dimethylamino)naphthalene (1.5 mmol each) in benzene and dioxane (1 ml each) under refluxing and the reaction mixture was refluxed for additional 4 hr. The mixture was poured into 2N KOH aq. solution, extracted with petroleum ether after filtration, washed with water and then dried (Na_2SO_4). 2-Octyl-1-methylenecyclopentane$^{4)}$ was obtained in 88% yield by distillation under reduced pressure; bp ca. 120°C/6 mmHg (bath temperature).

Table. Methylenation of Carbonyl Compounds via 2-(phenylthio)ethanols

R^1	R^2	Yields(%) $II^{4)}$	 $III^{4)}$	Conditions (II→III) $n^{a)}$	 $Base^{b)}$	 Time(hr)
$PhCH_2$	$PhCH_2$	59	96	6.5	A	5
$PhCH_2$	$PhCH_2$	59	97	6.0	B	4
$CH_3(CH_2)_7\overset{\mid}{C}H(CH_2)_3$-		87	88	7.0	A	4
Cholestan-3-one		61(α-OH)	95	6.5	A	5
		30(β-OH)	88	7.0	A	6
$CH_3(CH_2)_{10}$	H	93	$74^{c)}$	5.0	B	5
$Ph(CH_2)_2$	CH_3	d)	$86^{e)}$	$6.0^{f)}$	-	5

a) Molar ratio of $TiCl_4$-$LiAlH_4$/2-(phenylthio)ethanol.
b) A=1,8-bis(dimethylamino)naphthalene, B=tri-n-butylamine.
c) A mixed solvent of toluene and dioxane was used. d) Not isolated.
e) Overall yield from ketone. f) Molar ratio based on ketone.

Various 2-(phenylthio)ethanols were successfully converted into the corresponding terminal olefins in high yields as shown in the Table. 1,8-Bis(dimethylamino)naphthalene or tri-n-butylamine was effectively used in the reductive β-elimination reaction to avoid side reactions such as dehydration of the alcohol forming inner olefins or vinyl sulfide, whereas triethylamine did not give a good result. A simplicity and usefulness of the present method was proved by the following experiment; when a THF solution of the 2-(phenylthio)ethanol obtained from 4-phenyl-2-butanone and IV was successively treated with the $TiCl_4$-$LiAlH_4$ reagent without isolation according to a procedure described above, 2-methyl-4-phenyl-1-butene$^{4)}$ was isolated in 86% yield by distillation under reduced pressure; bp ca. 120°C/30 mmHg (bath temperature).

It is noted that the transformation reaction of carbonyl compounds to terminal olefins via 2-(phenylthio)ethanols reported here would provide a convenient alternative method for the methylenation of ketones and aldehydes.

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References and Notes

1) T. Mukaiyama, Y. Watanabe, and M. Shiono, Chem. Lett., 1523 (1974).
2) The $TiCl_4$-$LiAlH_4$ reagent was already reported from our laboratory as a characteristic reducing agent [T. Mukaiyama, N. Hayashi, and K. Narasaka, Chem. Lett., 291 (1973)]. More recently, it was reported by Mc Murry and Fleming that reductive coupling of carbonyl compounds including aliphatic ketones to olefins was satisfactorily performed by using the $LiAlH_4$-$TiCl_3$ system [J. E. Mc Murry and M. O. Fleming, J. Amer. Chem. Soc., 96, 4708 (1974)].
3) 2-(Phenylthio)ethanols (II) were prepared according to the method of Corey and Seebach except that N,N,N',N'-tetramethylethylenediamine was used in place of triethylenediamine [E. J. Corey and D. Seebach, J. Org. Chem., 31, 4097 (1966)].
4) These compounds were identified by ir and nmr spectra.

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