

Perkin Communications

Formation of Secondary Alcohols from the Reaction of Trimethyl- and Methyl-diphenyl-telluronium Salts with Aldehydes by Use of Organolithium Reagents †

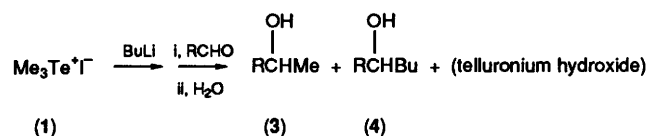
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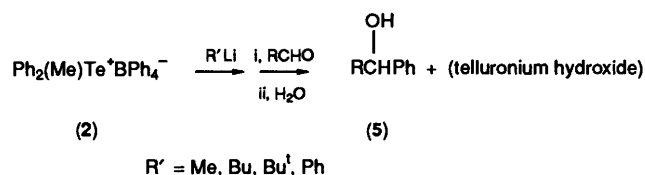
The telluronium salts (1) and (2), precursors of the non-stabilized telluronium ylide, on treatment with organolithium reagents, reacted with aldehydes to afford secondary alcohols *via* tetraorganyl tellurium intermediates.

Synthetic applications of tellurium reagents have recently been reviewed.¹ Osuka² reported that stabilized and moderately stabilized telluronium ylides are reactive toward carbonyl compounds to give alkenes and epoxides respectively. The use of dibutyl telluride in the synthesis of α,β -unsaturated compounds was described by Huang.³ We found that diphenyltelluronium methylide generated from methyl-diphenyltelluronium tetraphenylborate with lithium 2,2,6,6-tetramethylpiperidine (LiTMP), reacted with carbonyl compounds to afford substituted oxiranes in good yields.⁴ We now report that aldehydes react with the trimethyltelluronium iodide (1) and methyl-diphenyltelluronium tetraphenylborate (2), precursors of the non-stabilized telluronium ylide, on treatment with organolithium reagents to give secondary alcohols.

The readily available compound (1),⁵ after being treated with butyl-lithium, reacted with aromatic or heteroaromatic aldehydes to afford the methylated alcohols (3) as major products. Butylated alcohols (4) were also obtained in low yield. While *t*-butyl-lithium was used (entry 9), no *t*-butylated alcohols were observed. The yields of (3) were increased by using methyl-lithium. In the case of phenyl-lithium (entry 11), only the phenylated alcohols were obtained. The results are shown in the Table.



The telluronium salt (2)⁶ was treated under the above conditions, to give the phenylated alcohols (5) as the sole products. No butylated, *t*-butylated, and methylated alcohols were detected (entry 9,10) in our procedure (see Table).



It is proposed that the reaction path, which is different from that for a Wittig-type reaction, is as follows: alkylation of (1) and (2) with nucleophilic organolithium reagents to form unstable tetraorganyltellurium intermediates⁷ which, through

Table. Reaction of telluronium salts (1) and (2) with aldehydes by use of organolithium reagents

Entry	RLi	ArCHO (Ar)	Te salt	Yield (%)		
				Alcohol (3)	Alcohol (4)	Alcohol (5)
1	BuLi	Ph	(1) (2)	57	12	55
2		<i>p</i> -ClC ₆ H ₄	(1) (2)	64	10	85
3		<i>p</i> -BrC ₆ H ₄	(1) (2)	55	13	71
4		<i>p</i> -FC ₆ H ₄	(1) (2)	88	10	72
5		<i>p</i> -MeC ₆ H ₄	(1) (2)	73	23	84
6		<i>p</i> -MeOC ₆ H ₄	(1) (2)	53	10	60
7		2-Naphthyl	(1) (2)	93	6	56
8		2-Pyridyl	(1) (2)	57	12	67
9	Bu ^t Li	<i>p</i> -ClC ₆ H ₄	(1) (2)	67		60
10	MeLi	<i>p</i> -ClC ₆ H ₄	(1) (2)	77		85
11	PhLi	<i>p</i> -ClC ₆ H ₄	(1) (2)			80 70

All the products were confirmed by ¹H NMR, IR, and MS.

cleavage of one of the substituents, undergo nucleophilic addition to aldehydes. The phenyl group is transferred preferentially to the methyl, butyl, and *t*-butyl group.

It is noteworthy that the non-nucleophilic reagents such as Bu^tOK and NaH did not invoke the same reaction, and that under the same reaction conditions, reactions of aromatic ketones with telluronium salt (1) and (2) did not occur.

Typical Procedure.—A solution of butyl-lithium (1.1 mmol) in hexane was added to a solution of telluronium salt (2) (1.2 mmol) in THF (6 ml) at -78°C under N₂. The mixture was then warmed to -60°C and stirred for 10 min. After the mixture had cooled to -78°C , *p*-chlorobenzaldehyde (1.0 mmol) in THF (2 ml) was added to it. The reaction mixture

† This paper is the 83rd report on the synthetic application of elemento-organic compounds of the 15th and 16th groups.

was then allowed to warm to room temperature. After the reaction was complete (monitored by TLC), work-up and flash chromatography gave the products.

Acknowledgements

Financial supports from the National Natural Science Foundation of China and Academia Sinica are gratefully acknowledged.

References

- 1 (a) L. Engman, *Acc. Chem. Res.*, 1985, **18**, 274; (b) N. Petragani and J. V. Comasseto, *Synthesis*, 1986, 1.
- 2 (a) A. Osuka, Y. Mori, H. Shimizo, and H. Suzuki, *Tetrahedron Lett.*, 1983, **24**, 2599; (b) A. Osuka and H. Suzuki, *Tetrahedron Lett.*, 1983, **24**, 5109.
- 3 X. Huang, L. H. Xie, and H. Wu, *J. Org. Chem.*, 1988, **53**, 4862.
- 4 L. L. Shi, Z. L. Zhou, and Y. Z. Huang, *Tetrahedron Lett.*, in the press.
- 5 M. L. Bird and F. Challenger, *J. Chem. Soc.*, 1939, 163.
- 6 Diphenyl telluride reacted with an excess of methyl iodide during 2 days at room temperature to give methyl diphenyltelluronium iodide (7) in almost quantitative yield. To a chloroform solution of the iodide (7), a methanol solution of sodium tetraphenylborate was added to give stable (2) (m.p. 200–202 °C) in 70% yield. Reagent (2) had satisfactory elemental analysis; δ (60 MHz; CD₃COCD₃) 2.40 (s, 3 H) and 6.35–7.14 (m, 30 H); m/z 284, 282, 242, 165, 207, 205, and 77; ν_{\max} 3 010, 1 425, 745, and 682 cm⁻¹.
- 7 D. Hellwinkel and G. Farbach, *Chem. Ber.*, 1968, **101**, 574.

Paper 0/01255F
Received 21st March 1990
Accepted 18th June 1990