

Reactions of Carbonyl Compounds with Benzyldibutyltelluronium Bromide Mediated by Different Strong Bases¹

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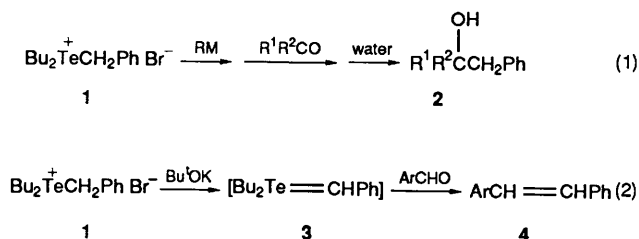
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Reactions of carbonyl compounds with benzyldibutyltelluronium bromide mediated by alkyllithium or Grignard reagent give homobenzylic alcohols, while those mediated by potassium *t*-butoxide give olefins.

Recently, there has been growing interest in the synthetic application of organotellurium reagents.² Osuka *et al.* reported that stabilized and moderately stabilized telluronium ylides are reactive toward carbonyl compounds, giving rise to alkenes and epoxides, respectively.³ We found that diphenyltelluronium methylide – the first non-stabilized telluronium ylide – reacted with carbonyl compounds to afford substituted oxiranes in good yield.⁴ In our previous paper, we reported that the reaction of trimethyl- and methyl-diphenyl-telluronium salts (precursors of non-stabilized telluronium ylides) with aldehydes gave secondary alcohols by the aid of organolithium reagents.⁵ We now report the reactions of carbonyl compounds with benzyldibutyltelluronium bromide **1** – a precursor of semi-stabilized telluronium ylides – mediated by different strong bases.

It was reported that, in the presence of strong bases, carbonyl compounds reacted with benzyltriphenylphosphonium bromide to form olefins,⁶ and with benzyldimethylsulphonium bromide to afford epoxides,⁷ while with benzyltriphenylarsonium bromide either olefins or epoxides are obtained.⁸ We found that carbonyl compounds reacted with benzyldibutyltelluronium bromide to give either homobenzylic alcohols or olefins depending upon the strong base used.

Benzyldibutyltelluronium bromide **1**, after being treated with an alkyllithium, phenyllithium, or a Grignard reagent, reacted with carbonyl compounds to give alcohols [equation (1)], instead of olefins or epoxides which were expected by analogy with the reactions of other heteroatom ylides. However, when the salt **1** was treated with potassium *t*-butoxide and then allowed to react with aldehydes, we did obtain olefins, obviously through an ylide intermediate³ [equation (2)]. As shown in equation (2), we didn't obtain epoxides as described by Osuka *et al.*³



*al.*³ this is because the reactivity of dibutyltelluronium benzylylide is more similar to that of the stabilized telluronium ylide. The results are shown in Table 1 and Table 2, respectively.

The reaction pathway, which is different from that of a Wittig-type reaction, may be proposed as shown in Scheme 1: Alkylation of the telluronium salt **1** with a nucleophilic organolithium or Grignard reagent formed unstable tetraorganyltellurium intermediates,⁹ which through cleavage of one of the substituents undergo nucleophilic addition to carbonyl

Table 1 Synthesis of homobenzylic alcohols **2**^a

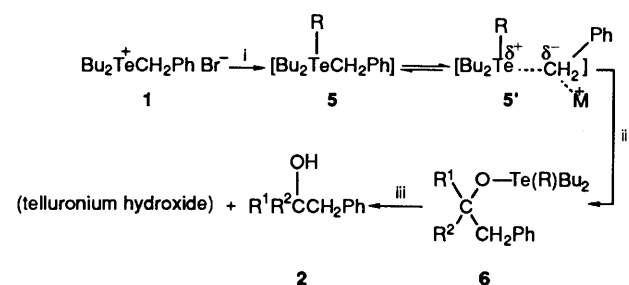
Compound	RM	R ¹	R ²	Yield (%) ^b
2a	BiLi	Ph	H	68
2b	BuLi	<i>p</i> -ClC ₆ H ₄	H	62
2b	PhLi	<i>p</i> -ClC ₆ H ₄	H	91
2b	MeLi	<i>p</i> -ClC ₆ H ₄	H	93
2b	Bu ^t Li	<i>p</i> -ClC ₆ H ₄	H	83
2b	MeMgI	<i>p</i> -ClC ₆ H ₄	H	82
2c	BuLi	<i>p</i> -BrC ₆ H ₄	H	69
2d	BuLi	PhCH=CH	H	96
2e	BuLi	<i>p</i> -NO ₂ C ₆ H ₄	H	63
2f	BuLi	2-pyridyl	H	78
2g	BuLi	-[CH ₂] ₅ -		58

^a All the products were characterized by ¹H NMR, IR and MS as reported in the Experimental section. ^b Isolated yield.

Table 2 Synthesis of olefins **4**^a

Compound	Ar	Yield (%) ^b
4a	Ph	72
4b	<i>p</i> -ClC ₆ H ₄	63
4c	<i>p</i> -MeC ₆ H ₄	72
4d	PhCH=CH	81
4e	2-naphthyl	84

^a All the products had the *E* configuration. ^b Isolated yield.



Scheme 1 Reagents: i, RM; ii, R¹R²CO; iii, water

compounds. The benzyl group is transferred preferentially over the alkyl group, so we obtained only the homobenzylic alcohols without other alkylated alcohols.

Experimental

M.p.s were measured on a Thiele apparatus and are uncorrected. ¹H NMR spectra were recorded in CDCl₃ with SiMe₄ as internal standard on a Varian-360L instrument; *J*-values are given in Hz. IR spectra were obtained with an IR-440

spectrophotometer. Mass spectra were measured with a Finnigan GC-MC 4021 spectrometer. Dibutyl telluride was prepared according to the literature procedure.¹⁰

Synthesis of Benzyldibutyltelluronium Bromide 1.—An equimolar mixture of dibutyl telluride and benzyl bromide was stirred under nitrogen at room temperature to afford white crystals (76%), m.p. 120–122 °C; δ_{H} 7.29 (5 H, m), 4.40 (2 H, s), 2.75 (4 H, m), 1.78 (8 H, m) and 0.97 (6 H, m) (Found: C, 43.4; H, 6.0; Br, 19.5. Calc. for $\text{C}_{15}\text{H}_{25}\text{BrTe}$: C, 43.58; H, 6.05; Br, 19.37%).

Synthesis of Homobenzylic Alcohols 2. General Procedure.—A solution of an organometallic RM (1.2 mmol) in hexane (0.6 cm^3) was syringed into a solution of benzyldibutyltelluronium bromide (1.2 mmol) in dry tetrahydrofuran (THF) (4 cm^3) at -70 °C under nitrogen. After 30 min, a solution of a carbonyl compound (1.0 mmol) in THF (2 cm^3) was added. The mixture was then allowed to warm to room temperature. After the reaction was complete (monitored by TLC), usual work-up and flash chromatography gave the corresponding product **2**.

1,2-Diphenylethanol 2a. M.p. 67–68 °C (lit.,¹¹ 67 °C); δ_{H} 7.18 (10 H, m), 4.67 (1 H, t, *J* 6), 2.85 (2 H, d, *J* 7) and 2.05 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3400.

1-(4-Chlorophenyl)-2-phenylethanol 2b. M.p. 50–52 °C (lit.,¹² 52.5–53.6 °C); δ_{H} 6.67 (9 H, m), 4.17 (1 H, t, *J* 6), 2.35 (2 H, d, *J* 6) and 1.79 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3360; EIMS *m/z* 232 (M^+ , 6%), 215 (45), 141 (70), 92 (100) and 77 (66).

1-(4-Bromophenyl)-2-phenylethanol 2c. M.p. 50–52 °C (lit.,¹³ 51–52 °C); δ_{H} 7.10 (9 H, m), 4.63 (1 H, t, *J* 6), 2.80 (2 H, d, *J* 6) and 2.60 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3450; EIMS *m/z* 277 (M^+ , 5%), 185 (100), 92 (64) and 77 (78).

1,4-Diphenylbut-3-ene-2-ol 2d. M.p. 64–66 °C (lit.,¹⁴ 65–66 °C); δ_{H} 7.12 (10 H, m), 6.24 (2 H, m), 4.27 (1 H, m), 2.61 (2 H, d, *J* 6) and 2.18 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3400; EIMS *m/z* 223 ($\text{M} - 1$, 5%) and 207 (100).

1-(4-Nitrophenyl)-2-phenylethanol 2e. M.p. 110–111 °C (lit.,¹³ 109–110 °C); δ_{H} 7.83 (9 H, m), 5.13 (1 H, t, *J* 6), 3.12 (2 H, d, *J* 6) and 2.20 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3360; EIMS *m/z* 244 ($\text{M} + 1$, 14%), 152 (45) and 92 (100).

2-phenyl-1-(2-pyridyl)ethanol 2f. M.p. 117–119 °C (lit.,¹⁵ 119–121 °C); δ_{H} 8.72 (1 H, d, *J* 6), 7.33 (8 H, m), 5.32 (1 H, t, *J* 6), 3.26 (2 H, d, *J* 6) and 2.71 (1 H, br); $\nu_{\text{max}}/\text{cm}^{-1}$ 3350; EIMS *m/z* 200 ($\text{M} + 1$, 5%), 180 (18), 108 (100), 91 (18) and 78 (22).

1-Benzylcyclohexanol 2g. M.p. 53–54 °C (lit.,¹¹ 53–55 °C); δ_{H} 7.52 (5 H, m), 3.05 (2 H, m), 2.38 (1 H, br) and 1.87 (10 H, m); $\nu_{\text{max}}/\text{cm}^{-1}$ 3420.

Synthesis of Olefins 4. General Procedure.—A solution of benzyldibutyltelluronium bromide (1.1 mmol) in dry THF (4 cm^3) was syringed into a solution of potassium *t*-butoxide (1.1 mmol) in THF (8 cm^3) at -70 °C under nitrogen. After 30 min, a solution of an aldehyde (1.0 mmol) in THF (2 cm^3) was added. The mixture was then allowed to warm to room temperature. After the reaction was complete (TLC), the mixture was filtered, and the filtrate was evaporated. The residue was purified by flash chromatography to afford the corresponding pure product **4**.

(*E*)-1,2-Diphenylethene **4a.** M.p. 123–124 °C (lit.,¹⁶ 124 °C); δ_{H} 7.30 (10 H, m) and 7.23 (2 H, d, *J* 17).

(*E*)-1-(4-Chlorophenyl)-2-phenylethene **4b.** M.p. 129–130 °C (lit.,⁶ 129 °C); δ_{H} 7.20 (10 H, m) and 7.03 (1 H, d, *J* 17).

(*E*)-1-(4-Methylphenyl)-2-phenylethene **4c.** M.p. 119–120 °C (lit.,¹⁷ 120 °C); δ_{H} 7.28 (1 H, d, *J* 18), 7.15 (9 H, m), 7.13 (1 H, d, *J* 18) and 2.30 (3 H, s); $\nu_{\text{max}}/\text{cm}^{-1}$ 1590, 1450, 810 and 750; EIMS *m/z* 195 ($\text{M} + 1$, 30%), 194 (M^+ , 100) and 179 (37).

(*E*)-1,4-Diphenylbuta-1,3-diene **4d.** M.p. 148–149 °C (lit.,¹⁸ 147–148 °C); δ_{H} 7.18 (10 H, m) and 6.67 (4 H, m); EIMS *m/z* 206 (M^+ , 100%), 191 (31), 128 (31) and 91 (55).

(*E*)-1-(2-Naphthyl)-2-phenylethene **4e.** M.p. 143–145 °C (lit.,¹⁹ 145–146 °C); δ_{H} 7.50 (12 H, m), 7.20 (1 H, d, *J* 16) and 7.14 (1 H, d, *J* 16); EIMS *m/z* 230 (M^+ , 14%), 217 (100), 139 (73) and 89 (94).

Acknowledgements

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