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PHASE TRANSFER CATALYZED REACTION OF SOME TELLURONIUM SALTS WITH AROMATIC ALDEHYDES

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Abstract: Under the liquid-liquid phase transfer condition, the reaction of aromatic aldehydes with benzyl dibutyl telluronium bromide were found to give epoxy compounds, while the reactions with p-chlorobenzyl dibutyl telluronium bromide were found to give epoxy compounds or olefins.

Formation of C-C bond is one of the research topics of general interest to synthetic organic chemists. Some applications of telluronium ylides to the formation of C-C bond have been reported in the literature.[1-6] We once described a facile method for the synthesis of 2,4-unsaturated ketones, esters, nitriles and amides via the condensation of some telluronium salts with carbonyl compounds using potassium carbonate as a base in acetonitrile containing trace formamide at room temperature.[7]

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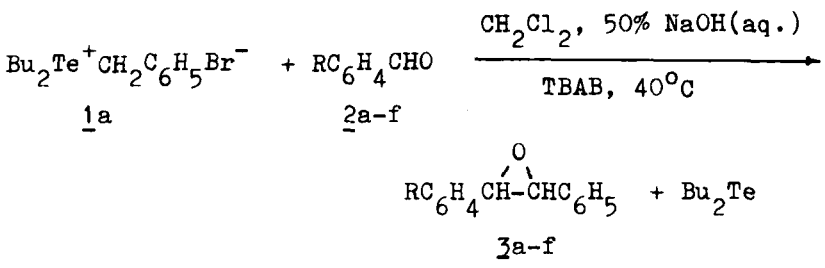
In our investigation, we found that, because of their poor reactivity, benzyl dibutyl telluronium bromide(1a) and p-chlorobenzyl dibutyl telluronium bromide(1b) could not condense with aromatic aldehydes(2) under the above conditions. They(1) could not react with 2 even in the presence of such strong bases as sodium amide, potassium t-butoxide at -30°C in anhydrous tetrahydrofuran. However, under the phase transfer condition, 1a,b could react readily with 2 to give epoxy compounds or olefins in high yields. In the meantime, we also investigated the effect of different phase transfer catalysts, bases and phase systems on the reaction. The results show that, polyglycol can not catalyze the reaction at all, while tetrabutylammonium bromide(TBAB) is superior to triethyl benzylammonium bromide(TEBA). For example, in the liquid -liquid phase system made up of 50% sodium hydroxide aqueous solution and dichloromethane, 1a reacted with p-nitrobenzaldehyde at 40°C for 4 hours in the presence of TEBA and TBAB respectively. The yields of the resulting product 3a are 62% and 87%, respectively. Different phase system(e.g. solid-liquid or liquid-liquid) and different base (e.g. sodium hydroxide or potassium hydroxide) made little difference to the results.

Under the phase transfer condition, 1a reacted with 2 (Scheme 1) to yield epoxy compounds. The reaction conditions and results are listed in Table 1. 1b reacted

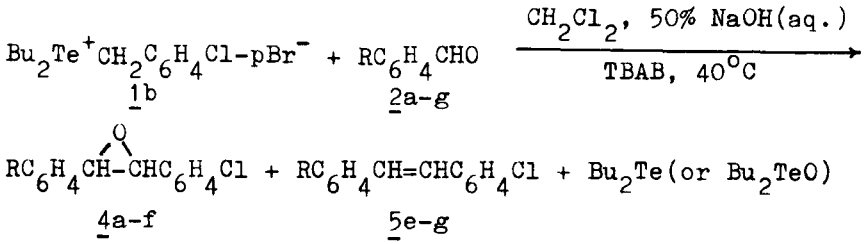


Scheme 1

Table 1

Entry	R	Reaction time(h)	Yield[a] (%)
3a	p-NO_2	4	87
3b	p-Cl	4	86
3c	p-F	4	97
3d	p-H	4	89
3e	p-CH_3	8	72
3f	p-OCH_3	8	72

a. Isolated yields.



Scheme 2

Table 2

Entry	R	Reaction time(h)	Yield[a] (%)	4 : 5[c]
a	p-NO_2	2	84	100 : 0
b	p-Cl	2	87	100 : 0
c	p-F	2	89	100 : 0
d	p-H	4	75	100 : 0
e	p-CH_3	8	80[b]	65 : 35
f	p-OCH_3	8	77[b]	50 : 50
g	p-$N(CH_3)_2$	24	76	0 : 100

a. Isolated yields.
b. Yields of the mixture of 4 and 5.
c. The ratio of 4 to 5 is determined with ^1H NMR.

with 2 (Scheme 2) to yield epoxy compounds or olefins due to the reactivity of aromatic aldehydes. The reaction conditions and results are listed in Table 2.

Experimental

Melting points are uncorrected and were taken on a Büch 535 apparatus. Elemental analysis were carried out on Carlo Erba 1106 apparatus. IR spectra measured with a Nicolet 740 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a JNM-FX 90Q spectrometer in $CDCl_3$ using TMS as internal standard.

General procedure for the preparation of 1a,b.

The mixture of equimolar benzyl bromide or p-chlorobenzyl bromide and dibutyl telluride in ethyl ether was refluxed and stirred for 7 hours. The reaction mixture was filtered after cooling to give the telluronium salt which was washed with ethyl ether and dried.

1a: Yield 91%; m.p. 109-110°C; Anal. calcd. for $C_{15}H_{25}BrTe$: C 43.64, H 6.10; Found. C 43.78, H 6.05; IR(KBr): 1601, 760, 702cm^{-1}; ^{1}H NMR(δppm): 0.89(6H, t), 1.2-1.9(8H, m), 2.0-3.05(4H, m), 4.50(2H, s), 7.35(5H, s).

1b: Yield 87%; m.p. 112-113°C; Anal. calcd. for $C_{15}H_{24}BrClTe$: C 40.10, H 5.71; Found. C 40.28, H 5.41; IR(KBr): 1594, 820cm^{-1}; ^{1}H NMR(δppm): 0.91(6H, t), 1.2-1.9(8H, m), 2.0-3.05(4H, m), 4.48(2H, s), 7.35(4H, m).

General procedure for the condensation of 1 with 2.

1 (1.1 mmol) and 0.1 g TBAB were added to the mixture of 5 mL dichloromethane and 1 mL 50% NaOH aqueous solution and stirred. Added drop by drop to the mixture was the solution of aromatic aldehyde(1 mmol) in 1 mL dichloromethane. The reaction was monitored with HPLC. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2. The organic phase was dried and evaporated. The residue was recrystallized with 95% ethanol to give the pure product 3, 4 or 5.

3a: m.p. 126-127°C; Anal. calcd. for $C_{14}H_{11}NO_3$: C 69.70, H 4.59, N 5.81; Found. C 69.50 H 4.31, N 6.12; IR(KBr): 1243, 880(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.84(1H, d, J=1.7), 3.96(1H, d, J=1.7), 7.37(5H, s), 7.45(2H, d, J=9.0), 8.18(2H, d, J=9.0).

3b: m.p. 99-100°C; Anal. calcd. for $C_{14}H_{11}ClO$: C 72.89, H 4.80; Found. C 72.81, H 4.55; IR(KBr): 1244, 890(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.79(1H, d, J=1.8), 3.83(1H, d, J=1.8), 7.29-7.31(9H, m).

3c: m.p. 76-77°C; Anal. calcd. for $C_{14}H_{11}FO$: C 78.49, H 5.17; Found. C 78.31, H 4.99; IR(KBr): 1234, 889(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.80(1H, d, J=1.8), 3.83(1H, d, J=1.8), 6.94(2H, d, J=9.0), 7.14(2H, d, J=9.0), 7.34(5H, s).

3d: m.p. 68-69°C; Anal. calcd. for $C_{14}H_{12}O$: C 85.68 , H 6.16; Found. C 85.45, H 5.89; IR(KBr): 1265, 890 (-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.85(2H, s), 7.34(10H, s).

3e: m.p. 61-62°C; Anal. calcd. for $C_{15}H_{14}O$: c 85.68 , H 6.71; Found. C 85.70, H 6.88; IR(KBr): 125o, 880 (-CH-CH-)cm^{-1}; ^1H NMR(δppm): 2.35(3H, s), 3.85(2H, s), 6.95-7.25(4H, m), 7.37(5H, s).

3f: m.p. 71-72°C; Anal. calcd. for $C_{15}H_{14}O_2$: C 79.62, H 6.24; Found. C 79.36, H 5.98; IR(KBr): 1252, 880(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.71(1H,d,J=1.8), 3.84 (1H, d, J=1.8), 3.81(3H,s), 6.85-7.24(4H, m), 7.34(5H, s).

4a: m.p. 124-126°C; Anal. calcd for $C_{14}H_{10}ClNO_3$: C 60.99, H 3.66, N 5.08; Found. C 61.22, H 3.49, N 5.33 ; IR(KBr): 1243, 884(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.82 (1H, d, J=1.8), 3.93(1H, d, J=1.8), 7.14-7.34(4H, m), 7.44(2H, d, J=9.0), 8.19(2H, d, J=9.0).

4b: m.p. 112-113°C; Anal. calcd. for $C_{14}H_{10}Cl_2O$: C 63.42, H 3.80; Found. C 63.11, H 3.95; IR(KBr): 1243, 883(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.18(2H, s), 7.19(4H, d, J=8.1), 7.31(4H, d, J=8.1).

4c: m.p. 181-182°C; Anal. calcd. for $C_{14}H_{10}ClFO$: C 67.62, H 4.05; Found. C 67.43, H 3.76; IR(KBr). 1243, 884(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.08(2H, s), 7.23(4H, d, J=8.1), 7.31(4H, d, J=8.1).

4d: m.p. 99-100°C; Anal. calcd. for $C_{14}H_{11}ClO$: C 72.89, H 4.80; Found. C 72.81, H 4.55; IR(KBr): 1244 , 890(-CH-CH-)cm^{-1}; ^1H NMR(δppm): 3.79(1H, d, J=1.8), 3.83(1H, d, J=1.8), 7.29-7.31(9H, m).

5e: m.p. 71-72°C; Anal. calcd. for $C_{16}H_{16}ClN$: C 74.55, H 6.26, N 5.44; Found. C 74.37, H 6.03, N 5.57; IR(KBr): 1637, 870(-CH=CH-)cm^{-1}; ^1H NMR(δppm): 3.79(6H, s), 6.98(1H, d, J=15.3), 7.15(1H, d, J=15.3), 6.95-7.42(8H, m).

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