

An Efficient Olefination Method Catalysed by Dibutyl Telluride†

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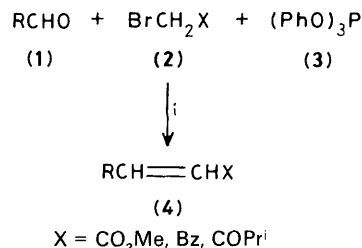
Olefins are formed in excellent yields, stereoselectively, by treating aldehydes and α -bromoesters or α -bromo ketones with potassium carbonate and catalytic amounts of dibutyl telluride regenerated by triphenyl phosphite.

The Wittig reaction is the most general approach toward the synthesis of olefins, and regeneration of the triphenylphosphine from the triphenylphosphine oxide produced has attracted much attention. Several methods have been reported: thus phosgene converts triphenylphosphine oxide into triphenylphosphine dichloride which gives triphenylphosphine and phosphorus trichloride with elemental phosphorus.¹ In a recently disclosed method the methylthiophosphonium salt, prepared with dimethyl sulphate by quaternization of the sulphide, itself obtained from oxide, is electrolysed.² Recently, the conversion of aldehydes to alkenes has also been realized by stoichiometric telluric reagents.^{3,4} Since the bond energy of tellurium–oxygen is weaker than that of phosphorus–oxygen,⁵ dialkyl telluroxide may be more easily reduced to dialkyl telluride. This suggests that the dialkyl telluride might be recycled *via* the dialkyl telluroxide in a catalytic tellurium–Wittig reaction.

Results and Discussion

Diorgano telluroxide is easily reduced to diorgano telluride, the deoxygenation of which by thioketone⁶ or triorgano-phosphine⁷ has been reported. However, since neither reagent is suitable for our purpose, and it has been reported that triphenylarsonium oxide could be reduced to triphenylarsine by triphenyl phosphite,⁸ we reasoned that the triphenyl phosphite should deoxygenate dialkyl telluroxide to dialkyl telluride.

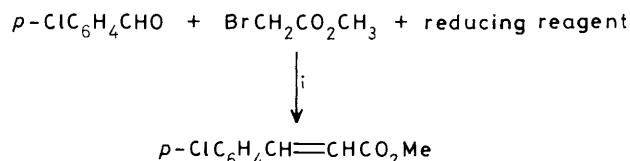
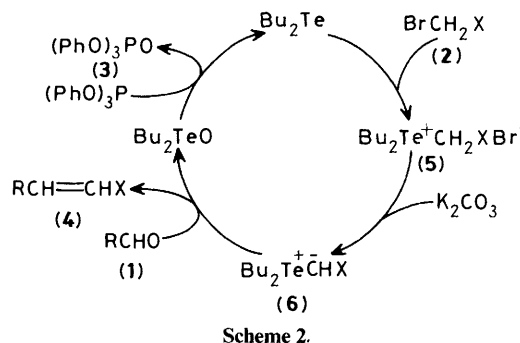
When a mixture of aldehyde, methyl bromoacetate (or α -bromoacetophenone, or 1-bromo-3-methylbutan-2-one), potassium carbonate, triphenyl phosphite, and a catalytic amount of dibutyl telluride (20 mol%) in tetrahydrofuran (THF) was stirred at 50 °C for a specified period, the desired olefination products were obtained in good to excellent yields with high *E* stereoselectivity (see Scheme 1); the results are shown in Table 1



Scheme 1. Reagents and conditions: *i*, Bu₂Te(cat.), K₂CO₃(s), THF, 50 °C, –(PhO)₃PO

and the catalytic reaction path is proposed as shown in Scheme 2.

A catalytic amount of dibutyl telluride reacted easily with the bromo compounds (2) to give the tellurium salt (5) at room



Scheme 3. Reagents and conditions: *i*, Bu₂Te(cat.), K₂CO₃(s), solvent, 50 °C

temperature. Under phase-transfer conditions (solid K₂CO₃–trace H₂O), the ylide (6) was conveniently generated *in situ*, and this reacted immediately with aldehyde to afford the desired product (4). Dibutyl telluroxide, the by-product, was converted into dibutyl telluride in the presence of triphenyl phosphite. Thus we had achieved a catalytic tellurium–Wittig reaction.

Under the same reaction conditions, there was no alkene formation in the absence of dibutyl telluride. Triphenyl phosphite did not react with bromo compounds and aldehydes in our experimental procedure. Furthermore, utilization of the weak base K₂CO₃, in the solid state, avoided side reactions such as aldol condensation and the Cannizzaro reaction. Under the conditions described above, other reducing reagents such as Na₂SO₃, NaHSO₃, and Na₂S₂O₃ were also effective in this catalytic reaction (see Scheme 3). The results are demonstrated in Table 2.

Conclusion.—This one-pot catalytic olefination method provides a practical and economical approach to the synthesis of α,β -unsaturated esters and ketones with the advantages of mild conditions, a simple procedure, excellent yields, and high stereoselectivity.

Experimental

All reactions were carried out under nitrogen. Solvents were dried and redistilled before use. B.p.s. and m.p.s. are uncorrected. Dibutyl telluride was synthesized by the reaction of tellurium powder and butyl bromide in the presence of rong-

† This paper is the 69th Report on the application of elemento-organic compounds of the 15th and 16th groups in organic synthesis.

Table 1. Reactions of various aldehydes with the bromo compounds (2)^a

Entry (4)	R	X	Reaction time (h)	Yield ^{b,c} (%)
(a)	<i>p</i> -ClC ₆ H ₄	CO ₂ Me	13	89
(b)	Ph	CO ₂ Me	13	98
(c)	PhCH=CH	CO ₂ Me	17	80
(d)	Cyclohexyl	CO ₂ Me	12	74
(e)	<i>p</i> -MeC ₆ H ₄	CO ₂ Me	18	95
(f)	Me(CH ₂) ₈	CO ₂ Me	17	83
(g)	2-Furyl	CO ₂ Me	7	76
(h)	<i>p</i> -ClC ₆ H ₄	Bz	17	89
(i)	2-Furyl	Bz	16	91
(j)	Bu	Bz	17	72
(k)	Ph	COPr ⁱ	14.5	98
(l)	2-Pyridyl	COPr ⁱ	14.5	98
(m)	Me(CH ₂) ₈	COPr ⁱ	33	78

^a All the reactions were carried out in THF at 50 °C. ^b All compounds were confirmed by ¹H n.m.r., m.s., i.r.; in no case was any *Z* stereoisomer found by ¹H n.m.r. ^c Isolated yields after t.l.c.

Table 2. Reactions of *p*-ClC₆H₄CHO with BrCH₂CO₂CH₃ in the presence of Bu₂Te(cat.) and inorganic reducing reagents

Solvent	Reaction time (h)	Reducing reagent	Yield ^a (%)
THF	8	NaHSO ₃ ^b	56
THF	12	Na ₂ SO ₃ ^b	59
THF	12	Na ₂ S ₂ O ₃ ^b	64
THF	20	NaHSO ₃ ^c	79
MeCN	15	NaHSO ₃ ^c	71
THF	16	Na ₂ S ₂ O ₃ ^c	60

^a Isolated yields after t.l.c. ^b In order to increase the solubility, Bu₄N⁺Cl⁻(0.05 ml) was added. ^c Trace of water (40 μl) was added.

alite.⁹ 1-Bromo-3-methylbutan-2-one was prepared according to the literature.¹⁰ N.m.r. spectra were recorded on a Varian EM 360-A instrument in tetrachloromethane (CCl₄) solution containing tetramethylsilane (TMS) as internal standard. I.r. and mass spectra were recorded on IR-440 and Finnigan 4021 spectrometers respectively.

Typical Procedure for the Synthesis of α,β -Unsaturated Esters and Ketones.—Methyl (*E*)-3-phenylacrylate (**4b**). Benzaldehyde, (106 mg, 1.0 mmol), methyl bromoacetate (165 mg, 1.1 mmol), triphenyl phosphite (356 mg, 1.2 mmol), dibutyl telluride (48 mg, 0.2 mmol), potassium carbonate (179 mg, 1.3 mmol), and tetrahydrofuran (THF) (4 ml) were mixed and stirred at 50 °C for 13 h (monitored by t.l.c.). The reaction mixture was filtered rapidly through a small amount of silica gel with ethyl acetate as eluant to remove inorganic salts and dibutyl tellurium oxide. Preparative t.l.c. with ethyl acetate–light petroleum (b.p. 60–90 °C) (1:9) as eluant yielded product (**4b**) (160 mg, 98%), b.p. 113 °C/5.0 mmHg (lit.,¹¹ b.p. 263 °C); ν_{\max} (film) 1720s, 1640s, 1315s, 1340s, and 980 cm⁻¹; δ 3.66 (s, 3 H, OCH₃), 6.16, 6.42 (d, *J* 16 Hz, 1 H), and 7.3 (m, 6 H); *m/z* (rel. intensity) 162 (*M*⁺, 41%), 161 (*M*–1, 18), 131 (100), 103 (76), and 77 (39).

Methyl (*E*)-3-(4-chlorophenyl)acrylate (**4a**) (170 mg, 89%), m.p. 70–72 °C (lit.,¹² 70–72 °C); ν_{\max} (KCl) 1720s, 1640s, 1500, 1320s, 1180, and 1200 cm⁻¹; δ 3.65 (s, 3 H, OCH₃), 6.09, 6.34 (d, *J* 16 Hz, 1 H), and 7.3 (m, 5 H); *m/z* (rel. intensity) 197 (*M*⁺ + 1, 30%), 196 (*M*⁺, 47), 165 (100), 137 (25), and 102 (35).

Methyl (*E,E*)-5-phenylpent-2,4-dienoate (**4c**) (150 mg, 80%), m.p. 69–70 °C (lit.,¹³ 70–71 °C); ν_{\max} (KCl) 1720s, 1630s, 1440, 1240, 1140, and 1000 cm⁻¹; δ 3.61 (s, 3 H, OCH₃), 6.04, 6.11 (d, *J* 15 Hz, 1 H), 6.59 (m, 2 H), 7.20 (m, 5 H), and 7.55 (m, 1

H); *m/z* (rel. intensity) 189 (*M*⁺ + 1, 32%), 188 (*M*⁺, 42), 157 (32), 129 (100), 115 (9), and 102 (7).

Methyl (*E*)-3-cyclohexyl acrylate (**4d**) (130 mg, 74%), b.p. 90 °C/15 mmHg (lit.,¹⁴ 92–93 °C/10 mmHg); ν_{\max} (film) 1710s, 1640, 1320, 1170, 1000, and 820 cm⁻¹; δ 1.48 (m, 11 H), 3.68 (s, 3 H, OCH₃), 5.19, 5.36 (d, *J* 16 Hz, 1 H), and 7.10 (m, 1 H).

Methyl (*E*)-3-(*p*-tolyl)acrylate (**4e**) (168 mg, 95%), m.p. 54.5–55.5 °C (lit.,¹² m.p. 55–56 °C); ν_{\max} (KCl) 1710s, 1590, 1160, and 960 cm⁻¹; δ 2.37 (s, 3 H, CH₃), 3.72 (s, 3 H, OCH₃), 6.16, 6.43 (d, *J* 16 Hz, 1 H), and 7.05–7.73 (m, 5 H); *m/z* (rel. intensity) 192 (*M*⁺, 77%), 161 (100), 133 (41), 118 (13), and 89 (21).

Methyl (*E*)-dodec-2-enoate (**4f**) (176 mg, 83%), ν_{\max} (film) 3350 m, 2900s, 1710s, 1610s, 750, and 690 cm⁻¹; δ 0.85 (t, 3 H, CH₃), 1.30 (m, 14 H), 2.14 (m, 2 H), 3.70 (s, 3 H, OCH₃), 5.66, 5.81 (d, *J* 16 Hz, 1 H), and 6.21 (m, 1 H).

Methyl (*E*)-3-(2-furyl)acrylate (**4g**) (115 mg, 76%), b.p. 105 °C/15 mmHg (lit.,¹⁵ 145 °C/20 mmHg); ν_{\max} (film) 1730s, 1640, 1440, and 970 cm⁻¹; δ 3.70 (s, 3 H, OCH₃), 6.10, 6.35 (d, *J* 16 Hz, 1 H), 6.55 (m, 1 H), and 7.38 (m, 3 H); *m/z* (rel. intensity) 152 (*M*⁺, 39%), 121 (100), 109 (46), 94 (51), and 65 (88).

(*E*)-3-(4-Chlorophenyl)-1-phenylprop-2-enone (**4h**) (215 mg, 89%), m.p. 110–111 °C (lit.,¹⁶ m.p. 112–113 °C); ν_{\max} (KCl) 1650 m, 1590s, 1180s, and 960s cm⁻¹; δ 7.50 (m, 9 H) and 7.90 (m, 2 H); *m/z* (rel. intensity) 243 (*M*⁺ + 1, 9%), 242 (*M*⁺, 26), 207 (25), 179 (25), 165 (45), 137 (26), 105 (97), and 77 (100).

(*E*)-3-(2-Furyl)-1-phenylprop-2-enone (**4i**) (180 mg, 91%), b.p. 160 °C/5 mmHg (lit.,¹⁷ 179 °C/7 mmHg); ν_{\max} (film) 3100w, 1670s, 1600s, and 1010s cm⁻¹; δ 6.33, 6.48 (m, 2 H), 7.34 (m, 6 H), and 7.82 (m, 2 H).

(*E*)-1-Phenylhept-2-en-1-one (**4j**) (135 mg, 72%), b.p. 150 °C/1 mmHg (lit.,¹⁸ 107 °C/0.1 mmHg); ν_{\max} (film) 2800s, 1670s, 1620s, 1450, 1470, 980s, and 700 cm⁻¹; δ 0.84 (t, 3 H), 1.34 (m, 4 H), 2.30 (m, 2 H), 5.85, 6.11 (d, *J* 16 Hz, 1 H), 6.79 (m, 1 H), 7.40 (m, 3 H), and 7.83 (m, 2 H).

(*E*)-4-Methyl-1-phenylpent-1-en-3-one (**4k**) (170 mg, 98%), b.p. 109 °C/2 mmHg (lit.,¹⁹ 138 °C/9 mmHg); ν_{\max} (film) 3226, 1688s, 1663s, 1612s, 1349, and 981 cm⁻¹; δ 1.09, 1.20 (d, 6 H, 2 CH₃), 2.85 (m, 1 H), 6.58, 6.85 (d, *J* 16 Hz, 1 H), and 7.42 (m, 6 H); *m/z* (rel. intensity) 175 (*M*⁺ + 1, 25%), 174 (*M*⁺, 4), 132 (100), and 103 (24).

(*E*)-4-Methyl-1-(2-pyridyl)pent-1-en-3-one (**4l**) (175 mg, 98%), b.p. 120 °C/2 mmHg (lit.,¹⁹ 120 °C/2 mmHg); ν_{\max} (film) 2950, 1691s, 1665s, 1622, 1470, 1430, 1200, and 990 cm⁻¹; δ 1.11, 1.15 (d, 6 H, 2 × CH₃), 2.82 (m, 1 H), 7.22, 7.30 (d, 1 H, *J* 16 Hz), 7.49, 7.58 (d, 1 H, *J* 16 Hz), 7.44 (m, 3 H), and 8.58, 8.60 (d, 1 H); *m/z* 176 (*M*⁺ + 1, 30%), 175 (*M*⁺, 1), 158 (6), 133 (100), 104 (24), and 78 (15).

(*E*)-2-Methyltetradec-4-en-3-one (**4m**) (175 mg, 78%), b.p. 104 °C/2 mmHg (lit.,¹⁹ 104 °C/2 mmHg); ν_{\max} (film) 2900s, 1695s, 1673s, 1628, 1460, and 980 cm⁻¹; δ 0.69, 1.66 (m, 23 H), 2.23 (m, 2 H), 2.63 (m, 1 H), 6.00, 6.27 (d, 1 H, *J* 16 Hz), and 6.84 (m, 1 H); *m/z* (rel. intensity) 225 (*M*⁺ + 1, 59%), 224 (*M*⁺, 4), 181 (59), and 55 (100).

Typical Procedure Using Inorganic Reducing Reagent.—4-Chlorobenzaldehyde (141 mg, 1.0 mmol), methyl bromoacetate (165 mg, 1.1 mmol), potassium carbonate (179 mg, 1.3 mmol), sodium hydrosulphite (208 mg, 2.0 mmol), dibutyl telluride (48 mg, 0.2 mmol), and THF (4 ml) were mixed and stirred at 50 °C for 20 h. The reaction mixture was filtered rapidly through a short column of silica gel and eluted with ethyl acetate to remove inorganic salts and to give the product (**4b**). The physical properties of the latter were consistent with those for the product previously obtained using triphenyl phosphite as reducing reagent.

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