Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Sep 2006.

To cite this article: Zhang-Lin Zhou , Li-Lan Shi & Yao-Zeng Huang (1991) A Novel Olefination of Carbonyl Compounds with Dibromomalonate Promoted by Dibutyl Telluride, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:8-9, 1027-1037, DOI: 10.1080/00397919108019792

To link to this article: http://dx.doi.org/10.1080/00397919108019792

SYNTHETIC COMMUNICATIONS, 21(8&9), 1027-1037 (1991)

A NOVEL OLEFINATION OF CARBONYL COMPOUNDS WITH DIBROMOMALONATE Promoted by Dibutyl Telluride[£]

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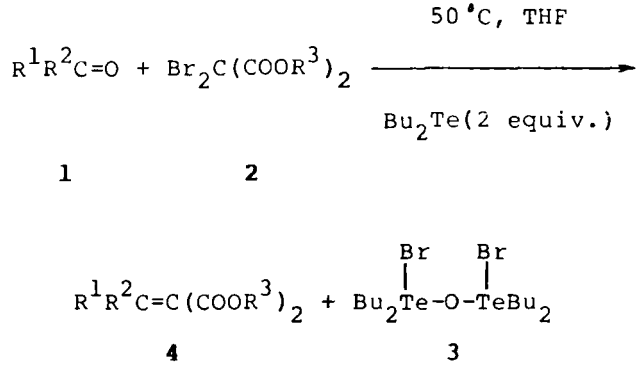
Abstract: α,β-Unsaturated malonic esters are conveniently synthesized from the reaction of dibromomalonate with carbonyl compounds promoted by dibutyl telluride in excellent yields. A possible mechanism involving twice halophilic attacks of dibutyl telluride is proposed. This methodology provides a facile route to α,β-unsaturated malonic esters and represents an alternative to the Knoevenagel reaction.

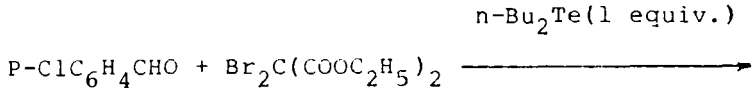
Recently, more and more attention has been paid to the synthetic application of organotellurium reagents[1]. In previous communications, we reported that diphenyltelluronium methylide - a first non-stabilized telluronium ylide reacted with carbonyl compounds to afford substituted oxiranes in good yields[2]; and that the reaction of trimethyl- and methyldiphenyltelluronium salts

(precursors of non-stabilized telluronium ylide) with aldehydes gave sec-alcohols by use of organolithium reagents[3]. Under solid-liquid phase transfer condition, allyldiisobutyltelluronium bromide reacted directly with aromatic aldehydes to afford α,β-unsaturated epoxides in excellent yields[4]. In the presence of cesium carbonate, we achieved the diisobutyl telluride catalyzed epoxidation of aldehydes with allyl bromide — a first example of catalytic ylide epoxidation reaction[5]. However, little attention has been paid to the halophilicity of organotellurium compound[6]. In our previous paper, we described a novel methylenation of carbonyl compounds by a halophilic reaction of dibutyl telluride with iodomethyltriphenylphosphonium iodide[7]. We wish to report herein another example of halophilic reaction of dibutyl telluride ——— a novel olefination of carbonyl compounds with dibromomalonate promoted by dibutyl telluride to afford α,β-unsaturated malonic esters in excellent yields.

It is known that the condensation of aldehydes or ketones with malonic esters is called the Knoevenagel reaction. Under the usual conditions of the reaction, a secondary amine is used as a catalyst and water formed must be removed by azotropic distillation. The procedure is rather troublesome[8]. Moreover, the condensation gives rise to unexpected products which result from



Scheme 1



Scheme 2

secondary reaction[8]. In our continuous studies over the halophilic reaction of dibutyl telluride, we found that the dibutyl telluride-promoted reaction of dibromomalonate with a variety of carbonyl compounds under neutral conditions, conveniently gives α,β-unsaturated malonic esters in excellent yields. The results are listed in **Table 1.**

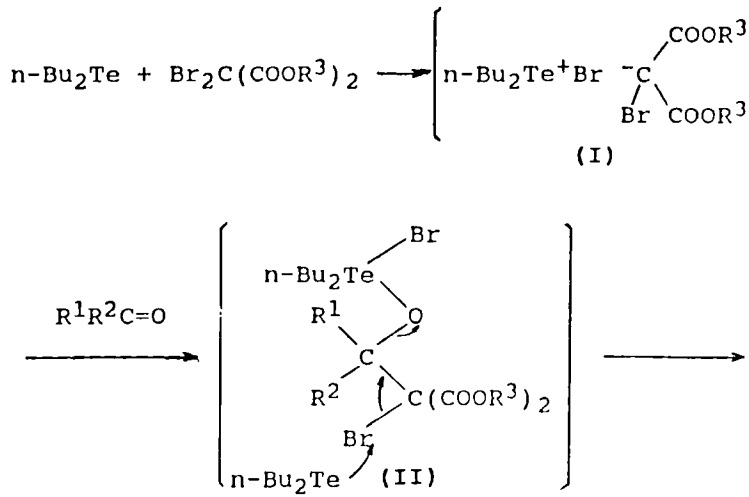
We found that when one equivalent dibutyl telluride was used, only 50% of aldehyde was converted to α,β-unsaturated malonic esters. **(Scheme 2)**

Table 1 Preparation of α,β-unsaturated malonic esters **(4)**[a]

Products	R^1	R^2	R^3	Isolated yield(%)[b]
4a	C_6H_5	H	C_2H_5	93
4b	4-ClC_6H_4	H	C_2H_5	99
4c	2-ClC_6H_4	H	C_2H_5	98
4d	4-$NO_2C_6H_4$	H	C_2H_5	91
4e	4-$CH_3OC_6H_4$	H	C_2H_5	95
4f	2-pyridyl	H	C_2H_5	94
4g		H	C_2H_5	92
4h	n-C_9H_{19}	H	C_2H_5	98
4i	-$(CH_2)_5$-		CH_3	84
4j	i-Bu	H	CH_3	91
4k	2-thiofuryl	H	CH_3	93

a All the products were characterized by ^1H NMR, MS and IR.
b Isolated yields

However, when 2 equivalents of dibutyl telluride were used, carbonyl compounds disappeared completely after 2-8.5 hours. Thus we suggest that the mechanism involves twice halophilic attacks of dibutyl telluride as shown in **Scheme 3.** The reaction is initiated by attack of dibutyl



(Scheme 3)

telluride on dibromomalonate to the intermediate **(I)**, which reacted with carbonyl compounds to form intermediate**(II)**, **(II)** is halophilically attacked by another dibutyl telluride to give the desired products **(4)** and byproduct **(3)**, which has been characterized by ^{1}H-NMR, MS, IR and elemental analysis.

The reaction is of wide scope **(Table 1)**. The carbonyl compounds may be aromatic, aliphatic, heteroaromatic aldehydes and ketones. This one-pot synthesis of α,β-

unsaturated malonic esters is convenient. This methodology may serve as an alternative to the Knoevenagel reaction due to neutral condition, simple procedure and excellent yields.

Experimental section:

The recorded boiling and melting points were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined in $CDCl_3$ with a Varian EM-360L(60MHz) spectrometer using TMS as the internal standard in ppm. Infrared (IR) spectra were recorded on an IR-440 instrument in cm^{-1}. Mass spectral data were obtained with electron ionization(EI) on a Finnigan 4021 spectrometer.

All reactions were carried out under nitrogen. All solvents were dried and redistilled before use. Dibutyl telluride, ethyl dibromomalonate and methyl dibromomalonate were prepared according to references [9], [10], and [11] respectively.

Synthesis of α,β-unsaturated malonic esters (4): General procedure: Dibutyl telluride (2.0mmol) was injected into a solution of the carbonyl compound (1.0 mmol) and dibromomalonate(1.0mmol) in THF under nitrogen. The mixture was stirred and heated for several hours. After the reaction was completed (monitored by TLC), ethyl acetate was added. The resulting mixture was filtered to remove the byproduct. The desired product was obtained by flash chromatography.

Diethyl benzylidene malonate (4a): Yield, 93%; b.p. 165°C/5mmHg (lit.[12] 178°C/12mmHg); ^{1}H NMR δ 1.27(t,J=7.0Hz,3H), 1.33(t,J=7.0Hz,3H), 4.23(q,J=7.0Hz,4H), 7.32 (s,5H), 7.57(s,1H); IR(neat) 1740(vs), 1631(m); MS m/z (rel. intensity) 249(M+1,39), 248(M^+,36), 203(100), 158 (16), 130(15), 102(34).

Diethyl 4-chlorobenzylidene malonate (4b): Yield, 99%; b.p. 165°C/3mmHg (lit.[13] 156-158°C/1.5mmHg); ^{1}H NMR δ 1.26(t,J=7.0Hz,3H), 1.30(t,J=7.0Hz,3H), 4.26(q,J=7.0Hz, 4H), 7.30(s,4H), 7.45(s,1H); IR(neat) 1730(vs), 1638(m); MS m/z(rel. intensity) 283(M+1,83), 282(M^+,35), 237(100), 193(5), 165(8), 136(18).

Diethyl 2-chlorobenzylidene malonate (4c): Yield, 98%; b.p. 163°C/1mmHg (lit.[14] 141-142°C/0.3mmHg); ^{1}H NMR δ 1.33(t,J=7.0Hz,3H), 1.43(t,J=7.0Hz,3H), 4.15(q,J=7.0Hz, 2H), 4.26(q,J=7.0Hz,2H), 7.40(m,4H), 7.96(s,1H); IR(neat) 1735(vs), 1637(m); MS m/z(rel. intensity) 283(M+1,72), 247(80), 237(81), 219(15), 173(100), 136(8).

Diethyl 4-nitrobenzylidene malonate (4d): Yield, 91%; m.p. 94-95°C (lit.[15] 93-94°C); ^{1}H NMR δ 1.26(t,J=8.0Hz, 3H), 1.35(t,J=8.0Hz,3H), 4.27(q,J=8.0Hz,4H), 7.59(d,J= 8.0Hz,2H), 7.63(s,1H), 8.14(d,J=8.0Hz,2H); IR(KCl) 1730 (vs), 1628(m); MS m/z(rel. intensity) 294(M+1,19), 293(M^+,27), 264(10), 248(100), 220(30), 203(77), 175(39), 157(36), 147(50).

Diethyl 4-methoxybenzylidene malonate (4e): Yield, 95%; b.p. 160°C/1.0mmHg (lit.[13] 166-168°C/1.5mmHg); ^{1}H NMR 1.26(t,J=7.0Hz,3H), 1.29(t,J=7.0Hz,3H), 3.76(s, 3H), 4.20(q,J=7.0Hz,4H), 6.80(d,J=8.5Hz,2H), 7.33(d,J= 8.5Hz,2H), 7.48(s,1H); IR(neat) 1730(vs), 1631(w); MS m/z (rel.intensity) 279(M+1,29), 278(M^+,100), 233(85), 205(14), 188(6), 132(46).

Diethyl 2-pyridylmethylidene malonate (4f): Yield, 94%; m.p. 81-82°C(lit.[16] 83.4-84.5°C); ^{1}H NMR δ 1.40 (t,J=8.0Hz,6H), 4.37(q,J=8.0Hz,4H), 7.10-7.80(m,4H), 8.63(d,J=2.0Hz,1H); IR(KCl) 1735(vs), 1630(w); MS m/z (rel. intensity) 250(M+1,20), 249(M^+,4), 220(97), 204 (100), 176(58), 159(14), 132(58).

Diethyl 2-(3-bromothiofuryl)methylidene malonate (4g): Yield, 92%; oil; ^{1}H NMR δ 1.30(t,J=7.0Hz,3H), 1.35(t,J= 7.0Hz,3H), 4.20(q,J=7.0Hz,2H), 4.27(q,J=7.0Hz,2H), 6.99 (d,J=4.0Hz,1H), 7.04(d,J=4.0Hz,1H), 7.54(s,1H); IR(neat) 1720(s), 1614(s); MS m/z(rel. intensity) 335,333(M+1,14), 334,332(M^+,54), 289,287(36), 253(46), 129(100), 108(27). Anal. Found: C,42.84; H,3.85; Br,24.32. Calc. for $C_{12}H_{13}BrO_4S$: C,43.26; H,3.93; Br,23.98.

Diethyl n-decylidene malonate (4h): Yield, 98%; b.p. 155°C/1mmHg; ^{1}H NMR δ 0.93(t,J=5.0Hz,3H), 1.30(m,20H), 2.30(m,2H), 4.23(q,J=7.0Hz,4H), 6.86(t,J=8.0Hz,1H); IR (neat) 1730(vs), 1650(m); MS m/z(rel. intensity) 299 (M+1,100), 298(M^+,4), 253(27), 225(5), 140(14), 127(29).

Anal. Found: C,68.21; H,10.22. Calc. for $C_{17}H_{30}O_4$: C, 68.42, H,10.13.

Dimethyl cyclohexylidene malonate (4i): Yield, 84%; b.p. 130°C/5mmHg; ^{1}H NMR δ 1.70(m,6H), 2.50(m,4H), 3.70 (s,6H); IR(neat) 1730(vs), 1640(m); MS m/z(rel. intensity) 213(M+1,4), 181(22), 153(14), 125(100), 97 (49). Anal. Found: C,62.18; H,7.88. Calc. for $C_{11}H_{16}O_4$: C,62.25; H,7.60.

Dimethyl iso-pentylidene malonate (4j): Yield, 91%; b.p. 110°C/2mmHg; ^{1}H NMR δ 0.96(d,J=6.0Hz,6H), 1.36-1.94(m,1H), 2.12(dd,J=6.0Hz,7.0Hz,2H), 3.72(s,6H), 6.85 (t,J=7.0Hz,1H); IR(neat) 1730(vs), 1642(m); MS m/z(rel. intensity) 201(M+1,100), 169(17), 157(10), 99(20). Anal. Found: C,59.95; H,8.19. Calc. for $C_{10}H_{16}O_4$: C,59.98; H, 8.05.

Dimethyl 2-thiofurylmethylidene malonate (4K): Yield, 93%; m.p. 44-45°C; ^{1}H NMR δ 3.78(s,3H), 3.84(s,3H), 7.00 (dd,J=4.0,4.0Hz,1H), 7.31(d,J=4.0Hz,1H), 7.45(d,J=4.0Hz, 1H), 7.55(d,J=4.0Hz,1H); IR(KCl) 1710(vs), 1610(s); MS m/z (rel. intensity): 227(M+1,22), 226(M^+,43), 195(44), 169(5), 108(22), 83(11), 43(100). Anal. Found: C,52.96; H,4.45. Calc. for $C_{10}H_{10}O_4S$: C,53.09; H,4.46.

Characterization of organotellurium compound (3): Dibutyl telluride (2.0mmol) was injected into a solution of p-nitrobenzaldehyde (1.0mmol), diethyl dibromomalonate (1.0mmol) in 8ml THF under nitrogen. After heated at 50°C

for 1.5h, the mixture was filtered to obtain a white crystal. Yield, 80%; m.p. 140-142°C (from chloroform-petroleum ether); ^{1}H NMR δ 1.00(t,J=6.0Hz,12H), 1.20-1.60 (m,8H), 1.60-2.06(m,8H), 2.90-3.50(m,8H); IR(KCl) 2990(s), 1380(vs), 1210(vs), 790(m); MS m/z(rel. intensity) 325,323 (10), 266(3), 244(6), 187(20), 57(100). Anal. Found: C, 29.05; H,5.39; Br,24.30. Calc. for $C_{16}H_{36}Br_2Te_2O$: C,29.14; H,5.50; Br,24.23.

Acknowledgement: Financial support from the National Natural Science Foundation and Academia Sinica is gratefully acknowledged.

References and Notes:

£ This paper is 89th report on the synthetic application of elemento-organic compounds of 15th and 16th groups.

[1] a) Back, T.G., in " The Chemistry of Organic Selenium and Tellurium Compounds " Ed. Patai, S. and John Wiley & Sons 1987, 2; b) Engman, L. Acc. Chem. Res., 1985, **18**, 274; c) Petragnani, N. and Comasset, J.V., Synthesis, 1986, 1.

[2] Shi, L.L., Zhou, Z.L. and Huang, Y.Z., Tetrahedron Lett., 1990, **31**, 4173.

[3] Shi, L.L., Zhou, Z.L. and Huang, Y.Z., J. Chem. Soc., Perkin Trans. 1, 1990, 2847.

[4] Zhou, Z.L., Sun, Y.S., Shi, L.L. and Huang, Y.Z., J. Chem. Soc., Chem. Commun., 1990, 1439.

[5] Zhou, Z.L., Shi, L.L. and Huang, Y.Z., Tetrahedron Lett., in the press.

[6] Campos M.M. and Petragnani, N., Tetrahedron Lett., 1960, 5.

[7] Li, S.W., Huang, Y.Z. and Shi, L.L., Chem. Ber., 1990, **123**, 1441.

[8] Jones, G., Org. React., 1967, **15**, 229.

[9] Balfe, M.P., Chaplin, C.A. and Phillips, H., J. Chem. Soc., 1938, 341.

[10] Conrad M. and Bruckner, C., Ber., 1891, **24**, 2993.

[11] Willstatler, R., Ber., 1902, **35**, 1374.

[12] Wittig, G., Todt, U. and Nagel, K., Chem. Ber., 1950, **83**, 110.

[13] Pratt, E.F. and Werble, E., J. Am. Chem. Soc., 1950, **72**, 4638.

[14] Meyer, H., Bossert, F. and Horstman, H., Sustus Liebig Ann. Chem., 1978, 1483.

[15] Knoevenagel, E., Ber. Dtsch. Chem. Ges., 1898, **31**, 2585.

[16] Mohrbacker, R.J., Chem. Abs., 1966, **64**, 17557c.

(Received in The Netherlands 4 March, 1991)