A Novel Methylenation Method of Aldehydes Mediated by Dibutyl Telluride[1)]

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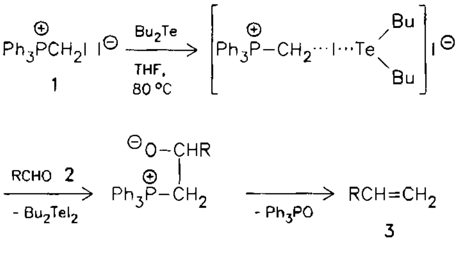
In the presence of dibutyl telluride, (iodomethyl)triphenylphosphonium iodide (**1**) reacted with aldehydes **2** in THF at 80°C yielding the methylenation products **3** under neutral conditions in good yields.

Methylenation of carbonyl compounds is usually accomplished by the Wittig reaction[2)], the Horner-Wadsworth-Emmons reaction[3)], or the Peterson reaction[4)]. Hauffmann et al. reported a method for a highly aldehyde-selective olefination with $G-CH_2-TiCl_3$ ($G = Me_3Si$, Me_3Ge) and $Me_3Si-CH_2-CrCl_3$[5)], and Takai et al. reported a method for chemoselective methylenation with a methylene dianion synthon[6)]. Recently, Vedejs et al. found that the desilylation of α-trimethylsilylphosphonium salts with fluoride followed by addition of an aldehyde gave alkenes[7)]. However, most of the reactions reported previously are carried out in basic or acidic media (including Lewis acid) or are treated with bases during workup.



2, 3	R
a	C_6H_5
b	$4-F-C_6H_4$
c	$4-Cl-C_6H_4$
d	$4-Br-C_6H_4$
e	$C_6H_5CH=CH$
f	2-naphthyl
g	$CH_3[CH_2]_8$

Table 1. Methylenation of Aldehydes Mediated by Bu_2Te[a)]

2	Reaction time [h]	3[b)]	Yield[c)] (%)	Ref.
a	28	a	58	12)
b	20	b	80	13)
c	22	c	85	14)
d	30	d	87	15)
e	25	e	51	16)
f	22	f	82	17)
g	28	g	75	18)

[a)] All reactions were carried out at 80°C in THF. – [b)] All products were characterized by ^{1}H NMR, IR, and MS. – [c)] Isolated yields.

In our previous communications, we described a facile olefination method catalyzed by dibutyl telluride[8)], and the reaction of benzyldibutyltelluronium bromide with aldehydes mediated by different strong bases[9)]. Owing to the great halophilicity of diorganyl telluride[10)], we developed a novel methylenation method. The advantage of this method is that the reaction is carried out under neutral conditions. Thus, (iodomethyl)triphenylphosphonium iodide (**1**), which is readily obtained from triphenylphosphine and an excess amount of diiodomethane at 40°C in benzene[11)], was mixed with dibutyl telluride and an aldehyde **2** in THF and heated for about one day at reflux to afford the methylenation products **3** in good yields. The results are summarized in Table 1.

In the presence of the halophilic dibutyl telluride, the α-carbon of the phosphonium salt **1** became nucleophilic and then reacted with an aldehyde **2**, a betain intermediate was formed, and alkene **3** was eventually produced, as in the Wittig reaction.

Owing to the halophilicity of dibutyl telluride, a methylenation method of aldehydes was realized under neutral conditions. Our method is an alternative approach for preparing ylides and seems to be interesting and especially suitable for base-sensitive substrates.

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Experimental

All reactions were conducted under nitrogen. – Melting points and boiling points were not corrected. – ^{1}H NMR: EM-360A, Varian XL-200, tetramethylsilane as internal standard. – MS: Finnigan 4021. – IR: IR-440. – All solvents were dried and redistilled before use. – Dibutyl telluride was prepared according to a literature procedure[19)].

Typical Procedure: A mixture of 530 mg (1.0 mmol) of (iodomethyl)triphenylphosphonium iodide (**1**), 242 mg (1.0 mmol) of dibutyl telluride and 96.0 mg (0.5 mmol) of 4-bromobenzaldehyde (**2d**) in 5 ml of THF, was heated for 30 h at reflux, cooled, and filtered. The residue was purified by TLC yielding 80.0 mg (87%) of 4-bromostyrene (**3d**).

All the methylenation products **3** are known and were identified by direct comparison with authentic samples.

CAS Registry Numbers

C_6H_5CHO: 100-52-7 / p-FC_6H_4CHO: 459-57-4 / p-ClC_6H_4CHO: 104-88-1 / p-BrC_6H_4CHO: 1122-91-4 / $C_6H_5CH=CHCHO$: 104-55-2 / $CH_3[CH_2]_8CHO$: 112-31-2 / $C_6H_5CH=CH_2$: 100-42-5 / p-$FC_6H_4CH=CH_2$: 405-99-2 / p-$ClC_6H_4CH=CH_2$: 1073-67-2 / p-$BrC_6H_4CH=CH_2$: 2039-82-9 / $C_6H_5CH=CHCH=CH_2$: 1515-78-2 / $CH_3[CH_2]_8CH=CH_2$: 821-95-4 / (iodomethyl)triphenylphosphonium bromide: 3020-28-8 / dibutyl telluride: 38788-38-4 / 2-formylnaphthalene: 66-99-9 / 2-cthenylnaphthalene: 827-54-3

[1] This paper is the 84th report on the studies of the application of elemento-organic compounds of the 15th and 16th group in organic synthesis.

[2] G. Wittig, G. Geissler, *Liebigs Ann. Chem.* **580** (1953) 44.

[3] W. S. Wadsworth, Jr., *Org. Reac.* **24** (1977) 73.

[4] D. J. Peterson, *J. Org. Chem.* **33** (1968) 780.

[5] T. Hauffmann, R. Konig, C. Pahde, A. Tannert, *Tetrahedron Lett.* **22** (1981) 5031.

[6] T. Okazoe, J. Hibino, K. Takai, H. Nozaki, *Tetrahedron Lett.* **26** (1985) 5581.

[7] E. Vedejs, F. G. West, *Chem. Rev.* **86** (1986) 941.

[8] Y. Z. Huang, L. L. Shi, S. W. Li, X. Q. Wen, *J. Chem. Soc., Perkin Trans. 1,* **1989**, 2397.

[9] S. W. Li, Y. Z. Huang, L. L. Shi, manuscript submitted.

[10] N. Petragnani, J. V. Comasseto, *Synthesis* **1986**, 1; X. Huang, L. H. Xie, H. Wu, *J. Org. Chem.* **53** (1988) 4862.

[11] D. Seyferth, J. K. Heeren, G. Singh, *J. Organomet. Chem.* **5** (1966) 267.

[12] *Org. Synth.*, Coll. Vol. **1** (1947) 440.

[13] G. B. Bachman, L. L. Lewis, *J. Am. Chem. Soc.* **69** (1947) 2022.

[14] H. Staudinger, E. Suter, *Ber. Dtsch. Chem. Ges.* **53** (1920) 1099.

[15] R. Broos, M. Anteunis, *Synth. Commun.* **6** (1976) 53.

[16] O. Grummitt, F. J. Christoph, *J. Am. Chem. Soc.* **71** (1949) 4157.

[17] Yu. S. Zal'kind, S. A. Zonis, *J. Gen. Chem. U.S.S.R. (Engl. Transl.)* **6** (1936) 988; *Chem. Abstr.* **31** (1937) 676.

[18] B. A. Kazanski, A. L. Liberman, A. F. Plate, M. I. Rosengart, G. A. Tarasova, *J. Gen. Chem. U.S.S.R. (Engl. Transl.)* **17** (1947) 1503; *Chem. Abstr.* **42** (1948) 2226.

[19] M. P. Balfe, C. A. Chaplin, H. Philips, *J. Chem. Soc.* **1938**, 341.

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