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Preparation and reactivity of phenyltelluroalkylphosphine oxides. Vinylic tellurides

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Abstract—Phenyltelluromethyldiphenylphosphine oxide was prepared by the reaction of methyldiphenylphosphine oxide with base and PhTeBr. The telluromethylphosphine oxide reacts with aldehydes and ketones to give the corresponding vinylic tellurides, with preferential *E* stereochemistry for aryl aldehydes and *Z* for alkyl aldehydes.
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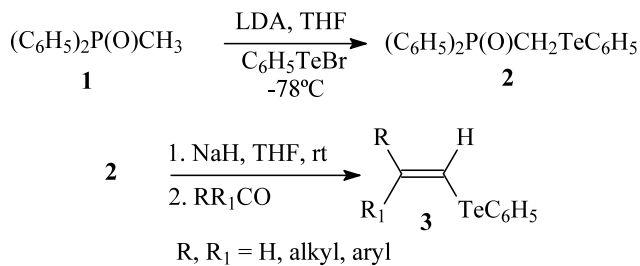
Among the many classes of organotellurium compounds which have recently been recognized as important synthetic reagents or intermediates,^{1,2} vinylic tellurides exhibit a peculiar role.³ Vinylic tellurides are valuable synthetic intermediates and their preparation and usefulness have been recently reviewed.⁴ From the many applications that they can undergo, the most useful are Pd-catalyzed homocoupling⁵ and cross-coupling reactions,⁶ and Ni(II)- or Co(II)-catalyzed cross-coupling reaction with alkynes and Grignard reagents,⁷ carbonylation in the presence of Pd(II) salts leading to carboxylic acids,^{8,9} transmetalation reaction by treatment with lithium,¹⁰ Li/Ce,^{10a} Li/Zn,¹¹ Zn,¹² sodium,¹³ calcium¹³ and Grignard reagents,¹⁴ followed by the capture of the vinyl metals with electrophiles. In the majority of these reactions the geometry of the original double bond is retained. Besides this, higher order vinylcuprates [vinylCu(R)CNLi₂] are provided upon transmetalation of vinyl tellurides with higher order cyanocuprates, and undergo 1,4-addition to enones,¹⁵ to epoxides^{15a,16} as well as bromoalkynes.¹⁷ Substitution of the tellurium moieties by methyl or alkyl groups take place upon treatment with Me₂CuLi,^{10h} with Grignard,¹⁸ magnesium higher order cuprates¹⁹ and alkyl- and alkynylzinc reagents.²⁰

From the several methods for the preparation of vinylic tellurides, the Wittig-type reactions constitute one of the most useful.²¹ In this respect we²² and others²³ have

described methods for their preparation based on Wittig and Horner–Wittig reactions.

Herein we describe our results on the preparation of phenyltelluroalkylphosphine oxides **2** and their conversion into vinylic tellurides. The compound **2** was prepared by the reaction of methyl diphenylphosphine oxides **1** with LDA at –78°C followed by the addition of phenyltellurenyl bromide, in 78% isolated yield.²⁴ Thus, the treatment of the tellurophosphinoyl **2** with base (NaH, *t*-BuOK, see text) in THF, followed by the addition of the carbonyl compound, furnishes the corresponding vinylic tellurides **3a–j**,²⁵ according to Scheme 1.

Initially we have studied the reaction with aromatic aldehydes at room temperature, in THF, using NaH as the base, and the corresponding vinylic tellurides **3** were isolated in good yields (85–64%, entries 1–5, Table 1). In all examples, a high preference for the *E*-isomer could be detected by GC, ¹H and ¹³C NMR. Next we studied it with aliphatic aldehydes. The reaction occurred well at room temperature, with *n*-butyraldehyde and *i*-butyraldehyde, albeit lower yields were



Scheme 1.

Keywords: Wittig reaction; aldehydes; ketones; vinylic tellurides; tellurium and compounds.

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Table 1. Vinylic tellurides prepared according to Scheme 1

Entry	R	R ₁	Compound	E/Z Ratio ^c	Reaction time (h)	Yield%
1	C ₆ H ₅	H	3a	13.7/1	4	66
2	4-CH ₃ C ₆ H ₄	H	3b	15.6/1	3	77
3	4-CH ₃ OC ₆ H ₄	H	3c	14.6/1	3	85
4	4-ClC ₆ H ₄	H	3d	7.3/1	12	64
5 ^a	CH ₃ CH ₂ CH ₂	H	3e	1/4	3	65
6 ^a	(CH ₃) ₂ CH	H	3f	1/4.5	3	66
7 ^b	-CH ₂ (CH ₂) ₄ CH ₂ -		3g	–	24	50
8 ^b	-CH ₂ CH ₂ CH(<i>t</i> -Bu)CH ₂ CH ₂ -		3h	–	24	55
9 ^b	-CH ₂ CH ₂ CH(CH ₃)CH ₂ CH ₂ -		3i	–	24	57
10 ^b	C ₆ H ₅	C ₆ H ₅	3j	–	24	68

^a *t*-BuOK was used as the base.

^b The reactions 7–10 were performed using a mixture of THF/HMPA (3:1) at the temperature of 45°C (oil bath).

^c Ratio determined by GC or ¹H NMR, compared with authentic samples.²²

obtained (55–58%). Concerning stereochemistry, ¹H NMR analysis indicated that using NaH as the base, an isomeric *Z*+*E* mixture (3:1) was formed. However, better results were obtained when the base was changed from NaH to *t*-BuOK. Moderate yields of these vinylic tellurides were then observed (65 and 66%, entries 5 and 6, Table 1), with the same *Z* preference (\approx 4:1 *Z*/*E* ratio). The use of LDA as the base, in the reaction with *i*-butanal, gave the corresponding vinylic telluride in 63% yield, with a 3:1 *E*/*Z* ratio.

Besides aldehydes, we decided to perform reaction with ketones, since trisubstituted vinylic tellurides could be easily prepared, species not affordable by most of the other methods described.⁴ In this way, interesting vinylic nucleophiles could be easily accessible, by the well known transmetallation of vinylic tellurides (see above). The first example studied was the reaction with cyclohexanone, which gave the desired product in 50% isolated yield after 24 h of reaction under a small heating (45°C). A small amount of HMPA as a co-solvent was necessary and NaH was found to be the best base. The reaction showed to be quite general and was also successful with other substituted cyclohexanones (entries 8 and 9, Table 1) and even benzophenone could be employed (entry 10, 68% yield). In all cases, THF was observed to be the best solvent. These results nicely complement other methods based on Wittig-type reactions, since no reaction with aliphatic aldehydes and ketones was previously observed.^{22,23,26} Unfortunately, we could not observe a reaction with acyclic aliphatic ketones, such as 3-pentanone and acetophenone.

In summary, we described a very convenient method for the preparation of vinylic tellurides by a Wittig-type route, by the reaction of phenyltelluroalkyl diphenyl phosphinoides with aromatic and aliphatic aldehydes and with ketones.

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24. *Preparation of the telluromethyldiphenylphosphine oxide 2*: To a solution of LDA (10 mmol) in dry THF (10 mL), at -78°C , under argon, was added a solution of methyl diphenylphosphine oxide (2.16 g, 10 mmol) in dry THF (10 mL). After stirring at -78°C for 30 min a solution of PhTeBr (prepared in situ from bromine and diphenyl ditelluride; 10 mmol) in dry THF (10 mL) was added. The dark brownish color turned to pale-yellow immediately. The reaction mixture was stirred at -78°C for 1 h, warmed up to -10°C for 1 h, then an aq sol. NH_4Cl was added and the mixture was extracted with ethyl acetate. The organic layer was dried (MgSO_4) and the solvent removed. The residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:9); yellow powder mp: $123\text{--}124^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.54 (d, 2H, $J=7.44$ Hz), 7.10–7.75 (m, 15H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 4.86 (d, $J_{\text{CP}}=67.6$ Hz, CH_2), 111.6, 127.8, 128.1, 128.2, 128.8, 130.5, 130.6, 131.4, 131.8, 132.8, 138.7. GC/MS m/z 422 (M^++2), 291, 215, 201, 91 (100%).
25. *General procedure for the preparation of vinylic tellurides 3*: To a solution of phenyltelluroalkylphosphine oxide **2** (0.42 g; 1 mmol) in THF (5 mL) under argon at room temperature was added the base (NaH for aromatic aldehydes and ketones or *t*-BuOK for aliphatic aldehydes; 2 mmol). After 30 min of stirring, the appropriate carbonyl compound (2 mmol) was added and stirring continued by the time indicated in Table 1. The reaction was stopped by adding water (10 mL) and extracted with ethyl acetate. The organics were washed with water and aq. NH_4Cl , dried over MgSO_4 and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel, eluting with hexane or hexane/ethyl acetate. Selected spectroscopic data. Compound **3g**: $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 1.55 (br s, 6H), 2.23–2.34 (m, 4H), 6.32 (s, 1H), 7.15–7.25 (m, 3H), 7.60–7.70 (m, 2H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): δ 26.16, 26.97, 36.76, 38.46, 27.57, 93.65, 153.75, 114.62, 127.08, 129.18, 136.54; IR (film, cm^{-1}) 2918, 1572, 1433, 1269; GC/MS m/z 302 (M^+), 207, 172, 129, 77 (100%). Anal. calcd for $\text{C}_{13}\text{H}_{16}\text{Te}$: C, 52.07; H, 5.38. Found: C, 52.18; H, 5.34. Compound **3h**: $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 0.83 (s, 9H); 1.80–2.65 (m, 9H), 6.32 (s, 1H); 7.10–7.25 (m, 3H), 7.55–7.75 (m, 2H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): δ 27.60, 28.27, 29.09, 32.34, 36.61, 38.23, 47.79, 93.33, 114.55, 127.10, 129.18, 136.56, 153.69; IR (film, cm^{-1}) 2946, 1573, 1475, 1435, 1365, 1276; GC/MS m/z 356 (M^+), 207, 129, 91, 57 (100%). Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{Te}$: C, 57.36, H, 6.80. Found: C, 56.68, H, 6.57. Compound **3j**: $^1\text{H NMR}$ (200 MHz, CDCl_3): δ 7.16–7.39 (m, 14H), 7.74–7.79 (m, 2H); $^{13}\text{C NMR}$ (50 MHz, CDCl_3): δ 108.75, 115.21, 127.11, 127.17, 127.9, 128.02, 128.14, 128.61, 128.67, 129.37, 137.97, 141.75, 142.80, 149.11; IR (film, cm^{-1}) 3055, 1573, 1492, 1437, 1264; GC/MS m/z 386 (M^+), 256, 178 (100%). Anal. calcd for $\text{C}_{20}\text{H}_{16}\text{Te}$: C, 62.57; H, 4.20. Found: C, 62.32; H, 4.10.
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