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Synthesis of Ketene Phenyltelluroacetals by a Wittig-Horner Route

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Abstract: Ketene phenyltelluroacetals are prepared by the treatment of methylphosphonate or phenyltelluromethylphosphonate with base and PhTeBr and subsequently with aldehydes.

Organotelluro compounds play an important role on organic synthesis.¹ From the several classes of organotelluro compounds, vinyllic tellurides are of particular interest, mainly as precursors of vinyllithium and vinylcopper reagents via transmetallation.^{1e,2}

Vinyllic tellurides have been prepared by several different routes. The major drawback of these methods was with the preparation of vinyllic tellurides with chain elongation, which obviously limits their application in organic synthesis. This problem was partially solved^{3,4} by the preparation of vinyllic tellurides using a Wittig-type reaction. Although 1,1-diaryltelluro ketenes could be a very useful specie as a 1,1-dilithio ethene equivalent,⁵ to our knowledge only one method has been described (with 2 examples in low yield) on their preparation involving the insertion of a vinyllic carbene into a Te-Te bond of a ditelluride.⁶

We wish to describe here a general preparation of ketene phenyltelluroacetals⁷ 6, by the reaction of diethyl methylphosphonate 1 or diethyl phenyltelluromethylphosphonate⁴ 3 with LDA, phenyltellurenyl bromide 2 and then with a carbonyl compound 5, involving probably the intermediary of 4, scheme 1.



A detailed study on the formation of 6 is presented in Table 1, employing different amounts of 1 or 3. Entry 5 shows that 6 was obtained in 45% yield from 1, LDA and PhTeBr. The use of tellurophosphonate 3,

Table 1. Reaction of 1 or 3 with furfural						
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Entry	(EtO) ₂ P(O)CH ₁	(EtO) ₂ P(O)CH ₂ TePh	LDA	PhTeBr	Yield %	
1	•	1.3	2.4	1	30	
2	•	1.5	2.6	1	64	
3	•	1.7	2.8	1	78	
4	•	2.0	3.1	1	94	
5	1	-	3.1	2	45	

easily accessible from methylphosphonate 1, makes the reaction experimentally easier and gives higher yields of 6; the yield is very dependent upon the amount of 3 and LDA (entries 1-4, Table 1), with the best results

achieved using 2 molar eq. of 3 and 3.1 molar eq. of LDA (entry 4, Table 1). This method permits easy access to compounds 6 in good to excellent yields with few exceptions. Even acrolein gives the corresponding diene, albeit in lower yield. The reaction of 3 with ketones was also examined. Unfortunately, we only observed reaction with cyclohexanone and in low yield (16 %, entry 6g, Table 2). All other ketones we have tried (cyclopentanone, acetophenone, 3-pentanone) fail to give the desired products. This result is related to previous observation in that tellurophosphonates 3 reacted with aldehydes at reflux in THF.^{4,8} and we observed that tellurophosphoranes reacted with aldehydes at room temperature to give vinylic tellurides but not with ketones.³ In conclusion, starting from methylphosphonate or phenyltelluromethylphosphonate, a convenient synthesis of almost unknown ketene phenyltelluro acetals has been described.⁹

Table 2. Ketene phenyltelluroacetals 6 prepared from 3 ^a								
Entry	R	R'	Reaction time(h)	Yield (%) ^{b.c}				
6a ^d	C ₆ H ₅ -	Н	1	88				
6b	2-Furyl-	н	1	94				
6c ^e	$4 - NO_2C_6H_4$	н	I	72				
6d	CH ₃ CH ₂ CH ₂ -	Н	2	94				
6e	(CH ₃) ₂ CH-	Н	2	84				
6f	CH ₂ =CH-	Н	2	41				
6g	-CH ₂ (CH ₂) ₂ CH ₂ -		2	16				

a) Reactions were carried out with tellurophosphonate **3** (2 mmol), LDA (3.1 mmol), PhTeBr (1 mmol) and carbonyl compound (1.0mmol); *b)* Refer to isolated yields by column chromatography; *c)* All compounds gave correct elemental analyses C \pm 0.29; H \pm 0.25; *d)* mp : 67.9-69.2 °C (hexane); *c)* mp : 81.9-82.9 °C (hexane).

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- 8. No mention was made by Oh⁴ about the possibility of the reactions at room temperature or on the use of ketones.
- 9. Typical Procedure for 1,1-Bis(phenyltelluro)-1-pentene(6d): To a solution of LDA(3.1 mmol) in THF(4 mL) cooled to -78°C, under nitrogen, was added a solution of 3 (0.71g, 2 mmol) in THF(1 mL) dropwise. The reaction was warmed up to 0°C and stirred 30 min at 0°C, then cooled to -78°C and the PhTeBr(1 mmol) in THF (2 mL) was added. The temperature was again raised to 0°C for 30 min., butyraldehyde (1 mmol) was then added and the reaction mixture stirred at RT for 2h. Usual work-up and column chromatography (SiO₂, hexane) gave : 0.45g (94 %). ¹H NMR (80 MHz, CDCl₃): δ ppm 0.85(t, 3H, J 7.1 Hz); 1.36 (sext, 2H, J 7.1 Hz); 2.20 (q, 2 H, J 7.1 Hz); 6.61 (t, 1H, J 7.0 Hz); 7.0-7.3 (m, 6H); 7.7-7.9 (m, 411); m/z (GC/MS) : 477(65%, M*), 450, 400, 332, 301, 283, 207, 145, 77(100%); Anal. calcd for C₁₇H₁₈Te₂ (477.52) : C, 42.76; H, 3.80. Found: C, 42.75; H, 3.70.

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