

Highly Regio- and Stereoselective Alkylation of *vic*-Bis(phenyltelluro)alkenes with Organocuprates

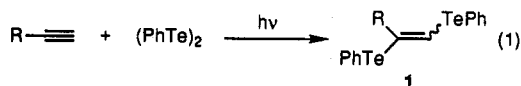
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Summary: Alkylation of *vic*-bis(phenyltelluro)alkenes 1 with lithium dialkylcuprates takes place regioselectively at the terminal carbon of 1 to provide the corresponding 1-alkyl-2-phenyltelluroalkenes (2) stereoselectively in good yields.

Recently, we have developed a preparative method of a series of vicinal bis(phenyltelluro)alkenes (1) by the photoinitiated radical addition of diphenyl ditelluride to acetylenes (eq 1).¹ Vicinal bis(phenyltelluro)alkenes are of interest from a synthetic point of view because of the potential that exists for the selective introduction of vinylic functions into various organic molecules.² Thus, we have made a close study on the reaction of vicinal ditelluroalkenes with carbon nucleophiles in order to accomplish the site-selective C-C bond formation by displacement of the terminal telluro group of 1.

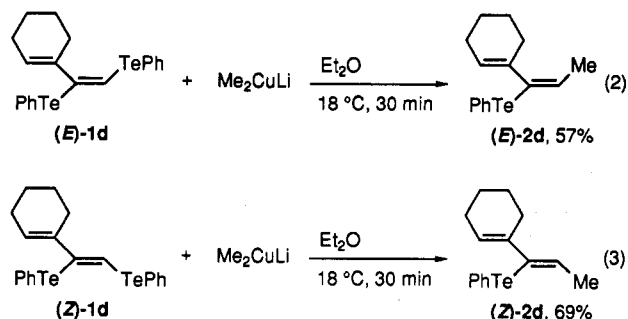


Reaction of 1,2-bis(phenyltelluro)styrene (1a) with equimolar amounts of methylolithium did not cause the desired substitution reaction; instead lithium-tellurium exchange reaction^{2d-f,3} occurred smoothly even at -78°C , affording phenyl methyl telluride and phenylacetylene most probably *via* β -elimination of PhTeLi^4 from the resulting (β -tellurovinyl)lithium (run 1).⁵ A similar result was also obtained in the case using MeMgBr in place of MeLi (run 2). With MeCu , no reaction was detected (run 3). Upon treatment with lithium dimethylcuprate (20°C , 5 min), however, site-selective alkylation at the terminal position of 1a took place successfully to give 2-methyl-1-phenyltellurostyrene (2a) in 92% yield (run 5).⁶ This result is very interesting when compared with the reaction using higher order cuprates as the nucleophiles, because

higher order cuprates are reported to effect transmetalation with vinyl tellurides to provide the corresponding higher order vinyl cuprates.⁷ In fact, attempted reaction of 1a with $\text{Me}_2\text{Cu}(\text{CN})\text{Li}$ provided phenylacetylene and phenyl methyl telluride probably *via* the decomposition of higher order vinyl cuprate.

Site-selective methylation with Me_2CuLi also occurred in a similar manner starting with alkyl- and alkoxy-carbonyl-substituted *vic*-ditelluroalkenes (1b and 1c) (runs 6 and 7). In the arylation with Ph_2CuLi , complete control of regioselectivity was achieved again (run 9). The procedure can be applicable to vinylic monotellurides, providing alkylated products with retention of the olefin geometry (run 10).

To clarify the stereochemistry of this alkylation, the reaction of (*E*)- and (*Z*)-*vic*-ditelluroalkenes with Me_2CuLi was carried out as exemplified in eqs 2 and 3. These



results clearly indicate that the alkylation proceeded stereoselectively in the retention manner. The stereospecificity observed is consistent with the possible reaction path, which includes substitution of the terminal PhTe group with Me_2Cu and subsequent reductive elimination from the resulting $\text{Cu}(\text{III})$ intermediate (I) to give 2 (Scheme 1).^{8,9}

As an extension of our interest in the synthetic utility of *vic*-ditelluroalkenes, we examined the generation of

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(4) PhTeLi was recovered as diphenyl ditelluride by hydrolysis and air oxidation during workup.

(5) Methylolithium was consumed by some side reactions, *i.e.*, the hydrogen abstraction from phenylacetylene to give $\text{PhC}\equiv\text{CLi}$ and the lithium-tellurium exchange reaction with PhTeMe to give PhLi and Me_2Te .

(6) Into a 10-mL two-necked glass flask with a magnetic stirring bar were placed 1a (0.25 mmol) and Et_2O (5 mL) under an argon atmosphere, and the solution was cooled at -78°C . Then, a solution of Me_2CuLi (0.5 mmol, prepared from CuI and 2 equiv of MeLi) in Et_2O (5 mL) was added using a syringe. Immediately, the solution was allowed to warm at 20°C and was stirred for 5 min. The resulting mixture was worked up with saturated NH_4Cl (5 mL) and then extracted with Et_2O (10 mL \times 3). The extract was dried (MgSO_4), concentrated *in vacuo*, and subjected to preparative HPLC (CHCl_3 as an eluent) to give 74.5 mg (92%) of 2a as a yellow oil. Data for 2a: $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 1.69 (d, $J = 6.8$ Hz, 3 H), 6.35 (q, $J = 6.8$ Hz, 1 H), 7.10-7.26 (m, 8 H), 7.65 (d, $J = 6.8$ Hz, 2 H). NOE experiment: Irradiation of the *o*-protons of methylstyrene at δ 7.10-7.26 resulted in a 3% enhancement of the signal at δ 1.69 (methyl doublet); $^{13}\text{C NMR}$ (68 MHz, CDCl_3) δ 17.41, 114.93, 117.81, 126.83, 127.74, 127.94, 128.74, 129.15, 137.83, 138.61, 141.85; IR (NaCl) 3052, 2907, 2850, 1573, 1486, 1473, 1434, 1017, 757, 731, 698 cm^{-1} ; mass spectrum (EI) m/e 324 (M^+ , 6.6), 117 ($\text{M}^+ - \text{PhTe}$, 100); HRMS calcd for $\text{C}_{15}\text{H}_{14}\text{Te}$ 324.0156, found 324.0172.

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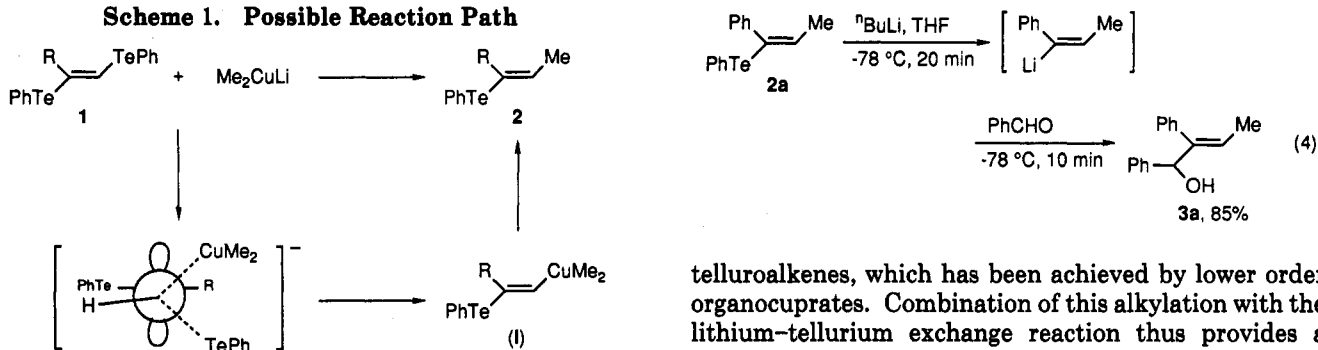
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Table 1. Regioselective Alkylation of *vic*-Ditelluroalkenes

run	substrate	R'-M (equiv)	condns	product(s) (yield, %) ^a
1 ^b	Ph (1a)	MeLi (1.0)	Et ₂ O/-78 °C/1 h	Ph—≡ (48) PhTeMe (34) (PhTe) ₂ (25)
2 ^c		MeMgBr (1.0)	Et ₂ O/19 °C/1 h	Ph—≡ (48) PhTeMe (39) (PhTe) ₂ (24)
3		MeCu (1.0)	Et ₂ O/20 °C/20 min	no reaction
4		Me ₂ CuLi (1.2)	Et ₂ O/20 °C/5 min	2a [R = Ph; R' = Me] (68)
5		Me ₂ CuLi (2.0)	Et ₂ O/20 °C/5 min	2a [R = Ph; R' = Me] (92)
6	ⁿ C ₆ H ₁₃ (1b)	Me ₂ CuLi (2.0)	Et ₂ O/18 °C/10 min	2b [R = ⁿ C ₆ H ₁₃ ; R' = Me] (84)
7	EtO ₂ C (1c)	Me ₂ CuLi (2.0)	Et ₂ O/-78 °C/5 min	2c [R = EtO ₂ C; R' = Me] (62) ^d
8	Ph (1a)	ⁿ Bu ₂ CuLi (2.0)	THF/0 °C/5 min	2a' [R = Ph; R' = ⁿ Bu] (61)
9		Ph ₂ CuLi (2.0)	Et ₂ O/0 °C/30 min	2a'' [R = R' = Ph] (72)
10	Ph—≡—TePh	Me ₂ CuLi (2.0)	Et ₂ O/20 °C/5 min	Ph—≡—Me (69) ^d

^a Isolated yield. ^b 52% of 1a was recovered. ^c 49% of 1a was recovered. ^d NMR yield.

Scheme 1. Possible Reaction Path



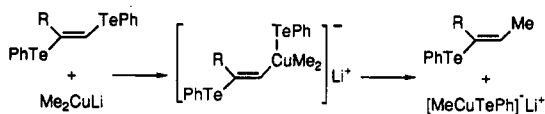
vinylolithiums by the lithium-tellurium exchange reaction utilizing the remaining telluro group of 2. The reaction of 2a with ⁿBuLi in THF at -78 °C followed by quenching with benzaldehyde successfully led to allylic alcohol 3a in 85% yield (eq 4).

In conclusion, this work describes the first example of site-selective and stereoselective alkylation of *vic*-di-

telluroalkenes, which has been achieved by lower order organocuprates. Combination of this alkylation with the lithium-tellurium exchange reaction thus provides a convenient access to trisubstituted alkenes. Further studies on the scope and the precise mechanism of this alkylation reaction are underway.

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(9) An alternative mechanism may include the oxidative addition of Me₂Cu to vinylic telluride, followed by reductive elimination. We cannot specify at present which, if either, of these processes is operative.



Supplementary Material Available: Characterization data and ¹H and ¹³C NMR spectra of 2a, 2a', 2a'', 2b, 2c (*E*)-2d, and (*Z*)-2d (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.