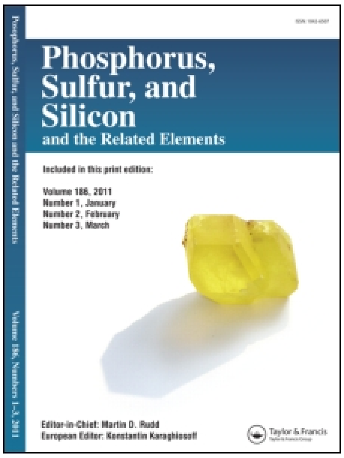

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Carbotelluration of Phenylacetylene

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CARBOTELLURATION OF PHENYLACETYLENE

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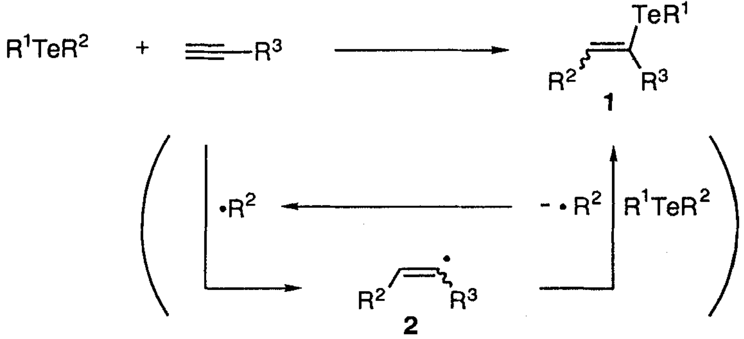
Abstract The addition of diorganyl tellurides (PhTePr^i and ^{n}BuTeBu^t) to phenylacetylene took place efficiently via a radical mechanism with a perfect regioselectivity to give corresponding vinyl tellurides. The *E* isomer was formed exclusively in the case of ^{n}BuTeBu^t, whereas PhTePr^i gave a *E/Z* mixture.

INTRODUCTION

We have recently developed a novel carbotelluration reaction of alkynes with tellurides[1] which has proven to be a synthetically useful methodology for the preparation of vinyl tellurides (**1**).[2, 3] This reaction takes place in the presence of AIBN (2, 2'-azobisisobutyronitrile) via a free radical chain mechanism involving a S_H2 reaction on tellurium as a key chain-propagating step as shown in Scheme **1**.

Scheme **1**

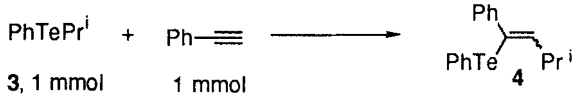


In this paper we describe the results of carbotelluration of phenylacetylene performed under various conditions using two different tellurides. The reactions were conducted by use of PhTePr^i and ^{n}BuTeBu^t as the representative examples of tellurides having *sec*- and *tert*-alkyl substituents.

RESULTS AND DISCUSSION

Reactions of $PhTePr^i$ with phenylacetylene were performed under different conditions as shown in Table 1. When the reaction was conducted at 80°C in the presence of AIBN, 80% yield of **4** was obtained as a mixture of *E* and *Z* isomers with ca. 1:1 ratio (run 1). Under more concentrated conditions, the reaction proceeded almost quantitatively (run 2). Similar reactions at lower temperatures using In as an initiator gave moderate yields of adducts with the *Z*/*E* ratio of ca. 4/6 (runs 3, 4). Less satisfactory results were obtained when $(Bu_3Sn)_2$[4] and Et_3B[5] were employed as radical initiators.

Table 1. Carbotelluration of phenylacetylene with $PhTePr^i$.

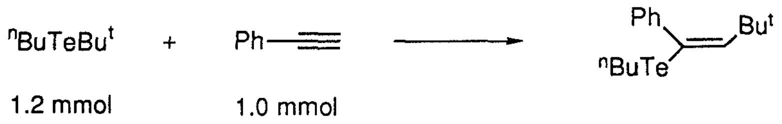


run	conditions	results a)	
		3 (%)	4 (%), *Z*/*E*
1	AIBN (0.1 mmol), benzene (3 mL), 80°C, 6 h	9	80, 48/52
2	AIBN (0.1 mmol), benzene (1 mL), 80°C, 6 h	<1	97, 44/56
3	In (0.1 mmol),b) benzene (3 mL), 30°C, 12 h	46	20, 38/62
4	In (0.1 mmol),b) benzene (1 mL), 50°C, 19 h	21	71, 39/61
5	$(Bu_3Sn)_2$ (0.1 mmol)/hν,c) benzene (3 mL), 45°C, 16 h	6	50, 47/53
6	$(Bu_3Sn)_2$ (0.1 mmol)/hν,c) benzene (3 mL), 30°C, 12 h	35	22, 47/53
7	Et_3B (0.1 mmol)/O_2, benzene (1 mL), 30°C, 25 h	91	8, 22/78

a) The yield of **4** and its *Z*/*E* ratio were determined by GC using octadecane as an internal standard. The percentage of recovered **3** was determined by GC using dodecane as an internal standard. b) In = 2,2-Azobis(4-methoxy-2,4-dimethylvaleronitrile), $t_{1/2}$ = 10h at 30°C in toluene. c) Tungsten lamp.

Table 2 summarized the results of the reactions of $^nBuTeBu^t$ with phenylacetylene. It should be noted that only *E* isomer was obtained, and *Z* isomer was not detected in any cases examined. When a mixture of $^nBuTeBu^t$ and phenylacetylene was heated at 80°C in benzene in the presence of AIBN, all of the telluride was consumed within 1h affording 67% yield of the adduct (run 1). In contrast with the case of PhTePr^i, the yield was improved when the reaction was performed at a lower temperature using In as an initiator (run 2). Although the reaction did not take place at 10°C in the absence of a radical initiator (run 3), it did proceed when a mixture of ^{n}BuTeBu^t and phenylacetylene was irradiated using a tungsten lamp at the same temperature (run 4) or when the mixture was heated at 50°C (run 5). These results may suggest that the C-Te bond between Te and ^{t}Bu is cleft photochemically by irradiation with a tungsten lamp[6] or thermally on heating at 50°C.[7] When the reaction was conducted under light at 50°C the yield was increased (run 6).

Table 2. Carbotelluration of phenylacetylene with ^{n}BuTeBu^t.

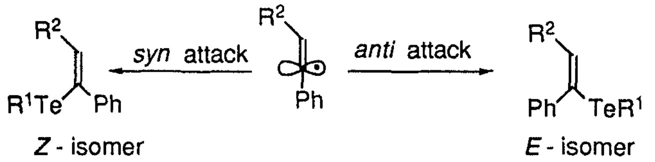


run	conditions	yield (%), *E/Z*$^{a)}$
1	AIBN(0.1 mmol), benzene(1 mL), 80°C, 1h	67, 100/0
2	In(0.1 mmol),$^{b)}$ benzene(1 mL), 25°C, 22 h	93, 100/0
3	neat, 10°C, 10 h	0
4	hv,$^{c)}$ neat, 10°C, 10 h	34, 100/0
5	neat, 50°C, 3 h	33, 100/0
6	hv,$^{c)}$ neat, 50°C, 3 h	84, 100/0

a) The yield of adduct and its *E/Z* ratio were determined by ^{1}H NMR using trioxane as an internal standard. b) In = 2,2-Azobis(4-methoxy-2,4-dimethylvaleronitrile), $t_{1/2}$ = 10h at 30°C in toluene. c) Tungsten lamp.

The stereoselectivity of vinyl telluride **1** is determined by the mode of attack of the telluride on a vinyl radical intermediate (Scheme **2**). The vinyl radical having Ph group is a π radical[8] and the substituent R^2 shields the two sides of this π radical to different extents. When R^2 is ^{t}Bu, the telluride can react with the vinyl radical only at the *anti* side to ^{t}Bu resulting in the formation of only *E* isomer. The ^{i}Pr radical is not bulky enough to prevent the attack from the *syn* direction of the vinyl radical, and hence a mixture of *E*/*Z* isomers was formed.

Scheme 2



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