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Photo-Induced Ditelluration of Acetylenes with Diphenyl Ditelluride

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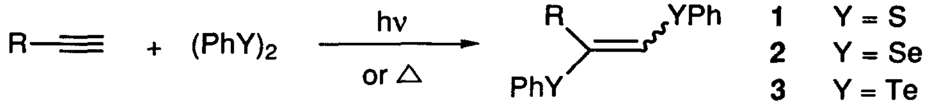
Abstract: *Diphenyl ditelluride (PhTeTePh) adds to a variety of acetylenes upon irradiation with visible light in the absence of solvent to provide vic-bis(phenyltelluro)alkenes in good yields. The reaction may proceed by a radical-chain mechanism that includes the addition to acetylenes of phenyltelluro radical (PhTe•) generated in situ by photolysis of diphenyl ditelluride, followed by the* S_H2 *reaction between thus formed β-(phenyltelluro)alkenyl radicals and diphenyl ditelluride. In the cases of unactivated acetylenes such as 1-octyne, the addition proceeds stereoselectively to provide only (E)-vic-bis(phenyltelluro)alkenes. Contrary to this, activated acetylenes like phenylacetylene give rise to a mixture of E- and Z-isomers of vic-bis(phenyltelluro)alkenes. Since the obtained vic-bis(phenyltelluro)alkenes indicate absorption in the near-UV, irradiation with near-UV light in solvent causes a novel reverse reaction of the adducts to the starting acetylenes and diphenyl ditelluride. Accordingly, irradiation with visible light (>400 nm) under high concentrations of the substrates induces the addition of* $(PhTe)_2$ *to acetylenes, whereas irradiation with near-ultraviolet (>300 nm) under dilution condition causes the reverse reaction.*

Introduction

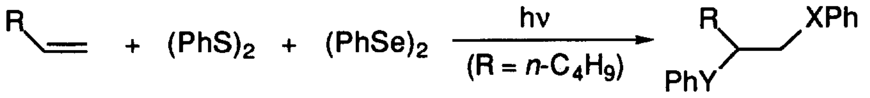
The addition to carbon-carbon unsaturated compounds of heteroatom-centred radicals arising from heteroatom-heteroatom bond homolysis is one of the most basic reactions in organic chemistry.[1] It is well-known that organic dichalcogenides, e. g., organic disulfides and diselenides, undergo photolysis or thermolysis to generate corresponding organic thio and seleno radicals as labile species.[2] However, these chalcogen atom-centred radicals are less reactive toward carbon-carbon unsaturated bonds and are liable to recombine to re-form the starting dichalcogenides; so free-radical additions of organic dichalcogenides to carbon-carbon multiple bonds



(1)

had remained largely undeveloped until very recently ever since the Heiba's pioneering work of the free-radical addition of dialkyl disulfides to terminal acetylenes under irradiation with ultraviolet light (eq 1, Y = S).[3]

Recently, we have found that, upon irradiation through Pyrex with tungsten lamp (>300 nm) for very longer time (330 h), diphenyl disulfide slowly adds to terminal olefins like 1-hexene to give 1,2-bis(phenylthio)-alkanes **4** in *ca.* 20 % yields (eq 2, X = Y = S).[4] Likewise, the photo-initiated addition of diphenyl diselenide to terminal olefins proceeds very slowly to afford 1,2-bis(phenylseleno)alkanes **5** (eq 2, X = Y = Se (270 h)).[5] The inefficiency of the addition of disulfides to olefins is believed to be due to the lower capturing ability of disulfides toward carbon radicals ($k_{PhSeSePh} / k_{PhSSPh}$ = *ca.* 160),[6] whereas the inefficiency of the diselenide-addition is most probably due to the less reactivity of seleno radicals toward carbon-carbon double bonds ($k_{PhS\cdot} / k_{PhSe\cdot}$ = 10~50).[7] Based upon these kinetic features of organic dichalcogenides and chalcogen atom-centered radicals, however, highly selective thioselenation of olefins has been developed by using disulfide-diselenide mixed system (eq 2, X = S; Y = Se (30 h)).[4]



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1 mmol	1 mmol	—	**4**	18 % (X = Y = S)
1 mmol	—	1 mmol	**5**	21 % (X = Y = Se)
1 mmol	1 mmol	1 mmol	**6**	89 % (X = S; Y = Se)

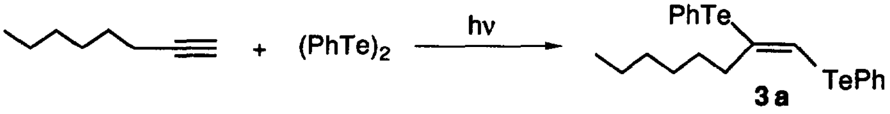
As to the radical addition of organic diselenides to acetylenes, Back and coworker have recently reported that photolysis of diphenyl diselenide with dimethyl acetylenedicarboxylate or methyl propiolate using UV lamp in benzene leads to the formation of corresponding vicinal diselenides (**2**) (eq 1, Y = Se).[8] We have also found that diphenyl diselenide adds to a variety of acetylenes under higher concentrations of the substrates upon heating over 150 °C in the dark[9] or upon irradiation through Pyrex with tungsten lamp (>300 nm) at 40 °C.[10,11] In these radical reactions, *vic*-bis(phenylseleno)alkenes are formed generally as a mixture of *E*- and *Z*-isomers (*E/Z* = 8/2 ~ 9/1), though each stereoisomers can be isolated easily by column chromatography or preparative TLC.[12]

Diphenyl ditelluride exhibits its absorption maximum in the visible region (λ_{max} = 406 nm, ε_{max} = 777) and also undergoes homolysis upon irradiation with visible light to form *in situ* phenyltelluro radical (PhTe•). The rate for capturing carbon radicals by diphenyl ditelluride is still faster than that by the corresponding diselenide ($k_{PhTeTePh} / k_{PhSeSePh}$ = 4),[6a] whereas the reactivity of phenyltelluro radical toward carbon-carbon unsaturated bonds is presumably poor, compared with phenylseleno radical. These features mean that the addition process of PhTe• to C-C multiple bonds may be difficult to proceed. Accordingly, in order to succeed in the radical-addition of organic ditellurides to carbon-carbon unsaturated bonds, higher concentrations of substrates are conceivably essential. In addition, the stability of vicinal ditelluro products under photo-irradiation conditions is another important factor. We have found that the radical-addition of diphenyl ditelluride to acetylenes takes place efficiently upon irradiation with visible light in the absence of solvent to provide *vic*-bis(phenyltelluro)alkenes **3** in good yields (eq 1, Y = Te).[13] This paper describes full details of this reaction.

Results and Discussion

To overcome the low reactivity of telluro radicals toward carbon-carbon unsaturated bonds, the reaction of diphenyl ditelluride with 1-octyne was examined *under the conditions of high initial concentrations of the starting materials* (Table I). The reaction of $(PhTe)_2$ with 1-octyne in the absence of solvent was conducted by irradiation through Pyrex with a tungsten lamp at 40 °C, but did not proceed at all (entry 1). However, elevated temperature (70 °C) led to the formation of the desired 1,2-bis(phenyltelluro)-1-octene (**3a**), which could be isolated upon treatment with preparative TLC (entries 2-3).

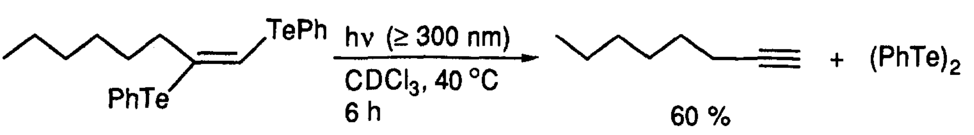
Table I. Photo-Initiated Addition of $(PhTe)_2$ to 1-Octyne[a]



entry	temp, °C	time, h	wave length	yield of **3a**, %[b]
1	40	48	≥ 300 nm[c]	0
2	70	24	≥ 300 nm[c]	20
3	70	115	≥ 300 nm[c]	32
4	70	48	dark	0
5	40	48	≥ 400 nm[d]	43
6	40	96	≥ 400 nm[d]	62

[a] Reaction conditions: 1-octyne (0.25 mmol), $(PhTe)_2$ (0.25 mmol), tungsten lamp (500 W). [b] Determined by ^1H NMR. [c] Irradiation was performed through Pyrex. [d] Irradiation was performed through glass filter.

As shown in Figure 1, the UV-visible spectra of **3a** indicated the absorption in the near-ultraviolet, which possibly caused the reverse reaction of **3a** to the starting materials. Indeed, upon subjection to near-UV irradiation in $CDCl_3$ at 40 °C for 6 h, **3a** decomposed to re-form 1-octyne (60 %) and diphenyl ditelluride (eq 3).



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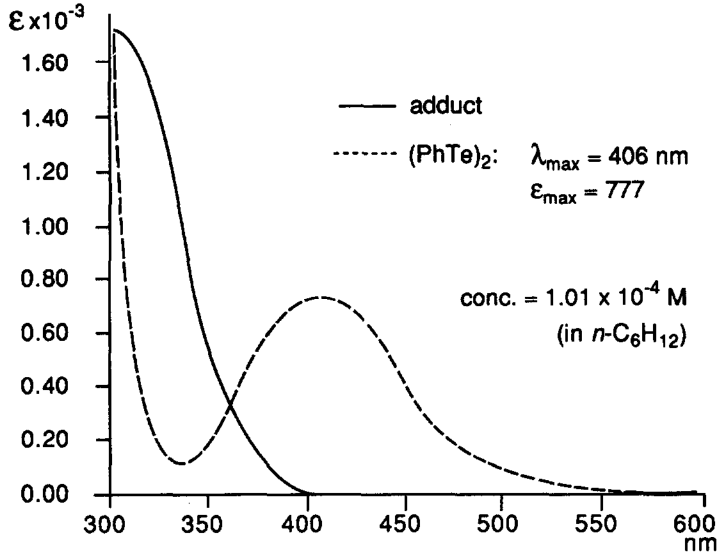


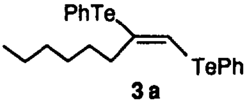
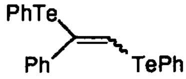
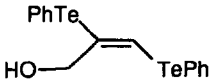
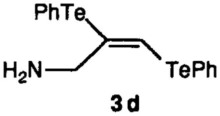
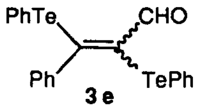
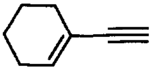
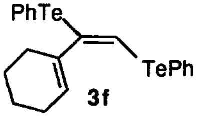
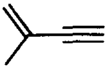
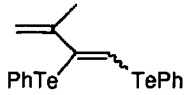
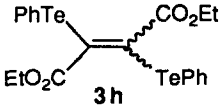
Figure 1. Ultraviolet-visible spectra of $(PhTe)_2$ and 1,2-bis(phenylseleno)-1-octene

To avoid the reverse reaction induced by near-UV light, the reaction of $(PhTe)_2$ with 1-octyne was examined by shading from the near-ultraviolet with a filter. Thus, irradiation with a tungsten lamp through a filter (>400 nm) at 40 °C for 98 h successfully afforded satisfactory yield of **3a** as a single stereoisomer (*E*) (entry 6).

Table II indicates the results of the addition of $(PhTe)_2$ to some other acetylenes. In analogy with 1-octyne, ditelluration of propargyl alcohol and propargylamine with diphenyl ditelluride efficiently proceeded with visible light irradiation (> 400 nm), to give corresponding vicinal ditelluroalkenes **3c** and **3d** in high yields (entries 3-4). Again, *E*-isomers were obtained predominantly in these cases. The same reaction by irradiation through Pyrex (>300 nm) resulted in the formation of **3c** and **3d** in lower yields, most probably due to the reverse reaction caused by near-ultraviolet.

In contrast to unactivated acetylenes like 1-octyne, the addition to activated acetylenes such as aryl group-substituted acetylenes and conjugated acetylenes proceeded even upon irradiation with the light of wavelength over 300 nm. For example, the reaction of phenylacetylene with diphenyl ditelluride provided the desired 1,2-bis(phenyltelluro)styrene (**3b**) in excellent yield (97 % by ^{1}H NMR) upon irradiation through Pyrex (>300 nm) at 40 °C for 24 h. Irradiation with visible light (>400 nm) shortened the reaction time (entry 2). In the cases of conjugated acetylenes, the yields of ditelluration products were generally high, but the stereoselectivity was lost (entries 5-8). The photo-induced *E* to *Z* isomerization of vicinal ditelluroalkenes may contribute the lower stereoselectivity. In the case of 2-methyl-1-buten-3-yne, for example, the *E*-selectivity decreased with the irradiation time (entry 7).

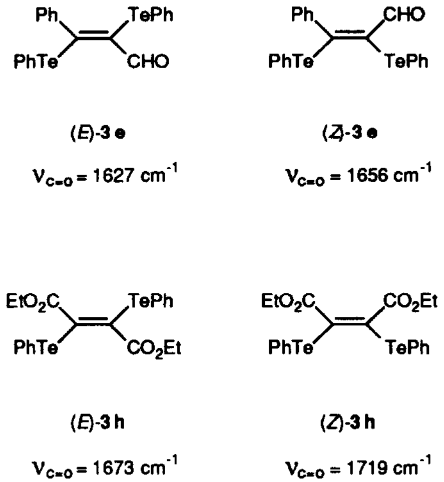
Table II. Photo-Initiated Addition of Diphenyl Ditelluride to Acetylenes[a]

entry	substrate	conditions	product	yield, %[b]	E/Z[c]
1		40°C, 48 h, >400 nm 40°C, 96 h, >400 nm	 **3a**	(43) 29(62)	[100/0] [100/0]
2	Ph—≡	40°C, 24 h, >300 nm 40°C, 3 h, >400 nm	 **3b**	(97) 73(98)	[90/10] [94/6]
3		70°C, 24 h, >400 nm 70°C, 24 h, >300 nm	 **3c**	78(86) (16)	[100/0] [100/0]
4		40°C, 24 h, >400 nm 40°C, 24 h, >300 nm	 **3d**	68(81) (25)	[100/0] [100/0]
5	Ph—≡—CHO	40°C, 34 h, >300 nm	 **3e**	80[d](95)	[64/36]
6		40°C, 36 h, >300 nm	 **3f**	78(96)	[65/35]
7		40°C, 2 h, >300 nm 40°C, 6 h, >300 nm 40°C, 20 h, >300 nm	 **3g**	(72) (90) 41(97)	[95/5] [78/22] [52/48]
8	EtO_2C—≡—CO_2Et	40°C, 12 h, >300 nm	 **3h**	90[e](99)	[82/18]

[a] Acetylene (1 mmol), PhTeTePh (1 mmol), hν (tungsten lamp, 500 W, filter), without solvent. [b] Isolated yield (NMR yield). [c] *E/Z* ratio was determined by ^1H NMR. [d] 49 % (*E*); 31 % (*Z*). [e] 85 % (*E*); 5 % (*Z*).

It is interesting to note that the frequencies of the CO stretching vibrations ($\nu_{C=O}$) in the carbonyl groups of the *E*-adducts **3e** and **3h** were lower than anticipated. Similar observation was reported on the corresponding diselenide-adduct to methyl propiolate ($\nu_{C=O}$ = 1683 cm^{-1} for *E*-isomer of $MeO_2C(PhSe)C{=}CHSePh$; 1714 cm^{-1} for *Z*-isomer).[8] However, the diselenide-adduct to dimethyl acetylenedicarboxylate did not exhibit significant difference between the frequency of *E*-isomer and that of *Z*-isomers ($\nu_{C=O}$ = 1724 cm^{-1} for *E*-isomer; 1725 cm^{-1} for *Z*-isomer). The lower frequencies ($\nu_{C=O}$) observed for (*E*)-**3e** and (*E*)-**3h** are most probably due to an interaction between the carbonyl oxygen and the *cis* tellurium atom of vicinal ditelluroalkenes. Indeed, the X-ray analysis[14] of (*E*)-**3h** indicates that the distance between the carbonyl oxygen and the *cis* tellurium atom is 3.51 Å and is shorter than the van der Waals' internuclear distance calculated (3.60 Å for Te•••O).

Chart I


(*E*)-**3e** $\nu_{C=O}$ = 1627 cm^{-1}

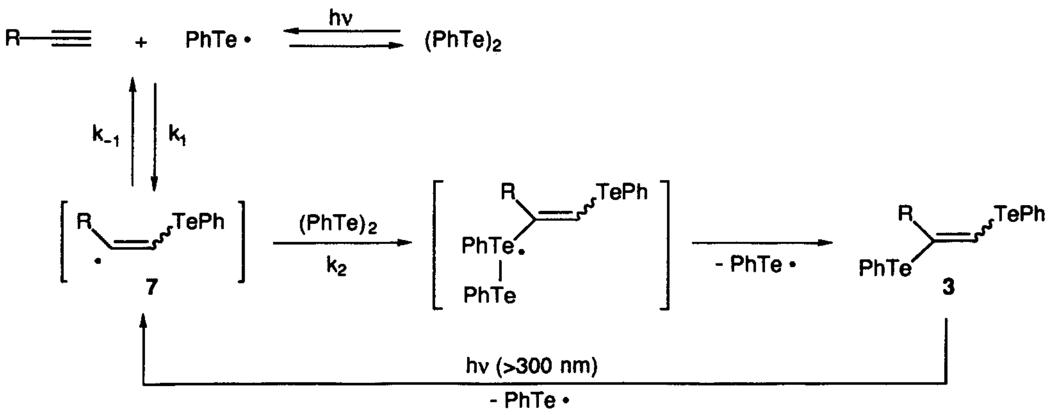
(*Z*)-**3e** $\nu_{C=O}$ = 1656 cm^{-1}

(*E*)-**3h** $\nu_{C=O}$ = 1673 cm^{-1}

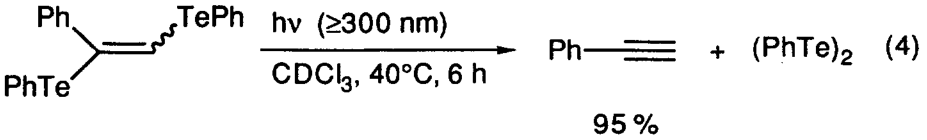
(*Z*)-**3h** $\nu_{C=O}$ = 1719 cm^{-1}

A mechanistic proposal includes the addition of phenyltelluro radical (PhTe•) to acetylenes to form the alkenyl radical intermediates (**7**) and the subsequent S_H2 reaction of **7** with $(PhTe)_2$ leading to 1,2-bis(phenyltelluro)alkenes (**3**) with regeneration of PhTe• (Scheme I).

Scheme I



The stability of vinyl radical **7** is greatly affected by the α-substituent (R). α-Alkyl substituted vinyl radicals are accepted as σ-radical[15] and are less stable than α-aryl substituted vinyl radicals, which are believed to be π-radical.[16] Accordingly, in the cases of unactivated acetylenes like 1-octyne, the decomposition of **7** (which gave the acetylenes and PhTe•) is suggested to take place easily. Contrary to this, activated acetylenes like phenylacetylene form vinylic radicals (**7**) stabilized by the carbonyl, vinyl, or aryl group; so, under high concentrations of substrates, the reverse reaction of these vicinal ditelluroalkenes to the starting acetylenes and the ditelluride was suppressed even under irradiation with near-UV. However, decreasing the initial concentrations of the substrates retarded both the addition of PhTe• to acetylenes and the S_H2 reaction of **7** with $(PhTe)_2$, and resulted in the decomposition of the double telluration products. For example, **3b** (0.025 mol/l in $CDCl_3$) decomposed almost quantitatively upon irradiation with near-UV to re-form phenylacetylene in 95 % yield (eq 4), whereas 1 mol/l of **3b** gave only 48 % of phenylacetylene with the same treatment.



(4)

Conclusion

This paper described the full details of the radical addition of organic ditellurides to acetylenes. The reaction of diphenyl ditelluride with activated acetylenes like phenylacetylene under irradiation through Pyrex with tungsten lamp at 45°C in the absence of solvent provided vicinal ditelluroalkenes in good yields. Contrary to this, the addition to unactivated acetylenes such as 1-octyne hardly proceeded under the same conditions, because near UV-induced decomposition of the ditelluration products to the starting materials took place easily. Thus, irradiation with the light of wavelength over 400 nm successfully produced corresponding vicinal ditelluroalkenes.

The products, 1,2-bis(phenyltelluro)olefins, are of interest from the synthetic point of view, because the vinyl tellurides are widely accepted as the useful intermediates for introducing vinyl functions into various organic molecules.[17] We believe that the present paper offers a novel approach for utilizing unreactive tellurium-centred radicals for synthetic reactions.

Acknowledgment. This work was supported in part by Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. We thank Professor Y. Kai and Dr. N. Kanehisa for their helpful assistance in X-ray analysis. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University for assistance in obtaining NMR and Mass spectra on a JEOL JNM-GSX-400 and a JEOL JMS-DX303.

Experimental Section

General Comments. Unless otherwise noted, materials were obtained commercially and were purified by distillation. Diphenyl ditelluride was prepared by the air-oxidation of the product of the reaction of phenylmagnesium bromide with an equimolar amount of metallic tellurium, and was recrystallized from *n*-hexane.

^{1}H NMR spectra were recorded on JOEL JNM-GSX-270 (270 MHz) and JNM-GSX-400 (400 MHz) spectrometers using $CDCl_3$ as the solvent with Me_4Si as the internal standard. ^{13}C NMR spectra were taken on a JOEL JNM-GSX-270 using $CDCl_3$ as the solvent. Chemical shifts in ^{13}C NMR were measured relative to $CDCl_3$ and converted to δ (Me_4Si) value by using δ ($CDCl_3$) = 76.9 ppm. IR spectra were determined on a Perkin Elmer Model 1600 spectrometer. UV spectra were recorded on a Hitachi U-3500 spectrometer. Mass spectra were obtained on a JEOL JMS-DX303 in the analytical section of our department. Elemental analyses were also performed there.

(*E*)-1,2-Bis(phenyltelluro)-1-octene (3a). In a glass tube (Pyrex), were placed 1-octyne (0.25 mmol) and diphenyl ditelluride (0.25 mmol), and the tube was sealed under reduced pressure. The mixture was irradiated through a filter (>400 nm) with tungsten lamp (500 W) at 40 °C for 96 h. After the measurement of ^{1}H NMR spectrum of the resulting mixture (NMR yield of **3a**: 62 %, *E*/*Z* = 100/0), the mixture was treated with column chromatography (silica gel) using *n*-hexane as an eluent to provide 38 mg (29 %) of (*E*)-1,2-bis(phenyltelluro)-1-octene (**3a**): yellow oil; ^{1}H NMR (270 MHz) [$CDCl_3$]: δ 0.88 (t, 3H, *J* = 6.8 Hz), 1.26 (brs, 6H), 1.52 (m, 2H), 2.37 (t, 2H, *J* = 7.6 Hz), 7.18~7.32 (m, 7H), 7.61 (d, 2H, *J* = 6.8 Hz), 7.77 (d, 2H, *J* = 6.4 Hz). [benzene-d_6]: δ 0.85 (t, 3H, J = 6.8 Hz), 1.18~1.23 (m, 6H), 1.59 (m, 2H), 2.44 (t, 2H, *J* = 7.2 Hz), 6.84~6.98 (m, 6H), 7.414 (s, 1H), 7.54 (d, 2H, *J* = 7.1 Hz), 7.72 (d, 2H, *J* = 6.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.09, 22.56, 28.59, 29.16, 31.64, 44.19, 112.36 (C=$\underline{C}$H), 114.78 (ipso), 114.45 (ipso), 126.35 ($\underline{C}$=CH), 127.70 (p), 128.10 (p), 129.41 (m), 129.50 (m), 137.30 (o), 139.02 (o); IR (NaCl) 3064, 2925, 2853, 1574, 1474, 1433, 1017, 998, 729, 690 cm^{-1}; MS, m/e = 524 (M^+, 41); Anal. Calcd for $C_{20}H_{24}Te_2$: C, 46.23; H, 4.66. Found : C, 46.13; H, 4.69.

(*E*)-1,2-Bis(phenyltelluro)styrene (3b). The reaction of phenylacetylene (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through a filter (>400 nm) with tungsten lamp (500 W) at 40 °C for 3 h. After the determination of the NMR yield (98 %, *E*/*Z* = 94/6) of the desired adduct (**3b**), purification by recrystallization from ethanol provided 93 mg (73 %) of (*E*)-1,2-bis(phenyltelluro)styrene (**3b**): yellow solid (mp 100~101°C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.18~7.32 (m, 11H), 7.57 (d, 2H, *J* = 6.8 Hz), 7.73 (d, 2H, *J* = 6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 114.92 (ipso), 115.65 (C=$\underline{C}$HTePh), 115.99 (ipso), 120.77 (ipso), 127.47 (m), 127.83 (p), 128.20 (p), 128.20 (p), 128.58 (o), 129.34 (m), 129.50 (m), 137.49 (o), 139.05 (o), 144.74 ($\underline{C}$=CHTePh); IR (KBr) 3045, 1472, 1432, 1015, 779, 730, 694 cm^{-1}; MS, m/e = 516 (M^+, 40); Anal. Calcd for $C_{20}H_{16}Te_2$: C, 46.76; H, 3.15. Found: C, 46.69; H, 3.14. Attempted isolation of (Z)-**3b** by column chromatography on silica gel resulted in the formation of a 1:1-mixture of (*E*)- and (Z)-isomers. By using this sample was obtained the following ^{1}H NMR spectra of (Z)-isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.16~7.37 (m, 11H), 7.76 (d, 2H, *J* = 6.9 Hz), 7.84 (d, 2H, *J* = 7.0 Hz).

(*E*)-1,2-Bis(phenyltelluro)-3-hydroxy-1-propene (3c). The reaction of propargyl alcohol (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through a filter (>400 nm) with tungsten lamp (500 W) at 70 °C for 24 h. After the determination of the NMR yield (86 %, *E/Z* = 100/0), the same workups as described in the synthesis of **3a** provided 92 mg (78 %) of (*E*)-1,2-bis(phenyltelluro)-3-hydroxy-1-propene (**3c**): yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.00 (brs, 1H), 4.34 (s, 2H), 7.15~7.45 (m, 6H), 7.37 (s, 1H), 7.65 (d, 2H, *J* = 6.4 Hz), 7.76 (d, 2H, *J* = 6.6 Hz); ^{13}C NMR (68 MHz, CDCl$_3$) δ 71.01, 112.50 (C=$\underline{\mathrm{C}}$H), 114.13 (ipso), 121.76 (ipso), 126.01 ($\underline{\mathrm{C}}$=CH), 127.85 (p), 128.27 (p), 129.42 (m), 129.65 (m), 137.44 (o), 138.86 (o); IR (NaCl) 3377, 3054, 2915, 2846, 1569, 1471, 1425, 1212, 1033, 1010, 992, 727, 687 cm^{-1}; MS, m/e = 470 (M$^+$, 34); Anal. Calcd for $C_{15}H_{14}OTe_2$: C, 38.71; H, 3.03. Found : C, 38.83; H, 3.18.

(*E*)-1,2-Bis(phenyltelluro)-3-amino-1-propene (3d). The reaction of propargyl-amine (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through a filter (>400 nm) with tungsten lamp (500 W) at 70 °C for 24 h. After the determination of the NMR yield (82 %, *E/Z* = 100/0), the same workups as described in the synthesis of **3a** provided 79 mg (68 %) of (*E*)-1,2-bis(phenyltelluro)-3-amino-1-propene (**3d**): yellow oil; ^{1}H NMR (270 MHz) [CDCl$_3$]: δ 1.45 (brs, 2H), 3.59 (s, 2H), 7.15~7.33 (m, 7H), 7.59 (d, 2H, *J* = 7.0 Hz), 7.76 (d, 2H, *J* = 7.3 Hz). [benzene-d$_6$]: δ 0.58 (brs, 2H), 3.21 (s, 2H), 6.88~7.01 (m, 6H), 7.38 (s, 1H), 7.63 (d, 2H, *J* = 7.2 Hz), 7.74 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (68 MHz, CDCl$_3$) δ 52.66, 109.32 (C=$\underline{\mathrm{C}}$H), 115.13 (ipso), 118.88 (ipso), 125.92 ($\underline{\mathrm{C}}$=CH), 127.38 (p), 128.01 (p), 129.21 (m), 129.49 (m), 136.79 (o), 139.11 (o); IR (NaCl) 3389, 3056, 2867, 1572, 1478, 1422, 1189, 1056, 1017, 989, 783, 722, 694 cm^{-1}; MS, m/e = 469 (M$^+$, 47). Anal. Calcd for $C_{15}H_{15}NTe_2$: C, 38.78; H, 3.25; N, 3.02. Found : C, 38.85; H, 3.36; N, 2.96.

2,3-Bis(phenyltelluro)cinnamaldehyde (3e). The reaction of phenylpropargylaldehyde (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through Pyrex (>300 nm) with tungsten lamp (500 W) at 40 °C for 34 h. After the determination of the NMR yield (95 %, *E/Z* = 64/36), the mixture was treated with column chromatography on silica gel (0-25 % ether in *n*-hexane) to provide 70 mg (49 %) of (*E*)-2,3-bis(phenyltelluro)cinnamaldehyde ((*E*)-**3e**) and 44 mg (31 %) of (*Z*)-2,3-bis(phenyltelluro)-cinnamaldehyde ((*Z*)-**3e**): [*E*-isomer]: red crystal (mp 114.5~115 °C); ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.76 (d, 2H, *J* = 7.3 Hz), 6.88~7.10 (m, 6H), 7.17~7.30 (m, 3H), 7.37 (d, 2H, *J* = 7.6 Hz), 7.61 (d, 2H, *J* = 6.7 Hz), 9.89 (s, 1H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 113.63 (ipso), 114.98 (ipso), 121.70 (ipso), 127.03 (p), 127.41 (p), 127.68, 127.89, 128.25 (m), 129.65 (m), 138.29 (o), 140.12 (o), 143.75 (C=), 161.32 (C=), 193.81 (CHO); IR (KBr) 3056, 2856, 1628, 1467, 1428, 1078, 1044, 722, 689 cm^{-1}; MS, m/e = 544 (M$^+$, 33); Anal. Calcd for $C_{21}H_{16}OTe_2$: C, 46.74; H, 2.99. Found: C, 46.70; H, 3.04. [*Z*-isomer]: yellow crystal (mp 103~103.5 °C); ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.87~7.03 (m, 6H), 7.14 (t, 1H, *J* = 7.3 Hz), 7.27 (d, 2H, *J* = 7.6 Hz), 7.29 (dd, 2H, *J* = 7.3, 7.2 Hz), 7.39 (d, 2H, *J* = 7.0 Hz), 7.85 (d, 2H, *J* = 7.2 Hz), 8.60 (s, 1H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 114.45 (ipso), 123.78 (ipso), 127.44 (p), 127.66 (p), 127.95, 128.16, 128.42, 128.93 (m), 129.60 (m), 130.31 (ipso), 137.69 (o), 139.40 (C=), 140.13 (o), 160.80 (C=), 185.50 (CHO); IR (KBr) 3047, 1656, 1515, 1471, 1434, 1117, 1016, 732, 714, 689 cm^{-1} ; exact mass (M$^+$) calcd for $C_{21}H_{16}OTe_2$: 543.9325. Found: 543.9337.

1,2-Bis(phenyltelluro)-1-(1'-cyclohexenyl)ethene (3f). The reaction of 1-ethynyl-cyclohexene (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through Pyrex (>300 nm) with tungsten lamp (500 W) at 40 °C for 24 h. After the determination of the NMR yield (96 %, *E/Z* = 65/35), the mixture was treated with column chromatography on silica gel (2.5 % ether in *n*-hexane) to provide 101 mg (78 %, *E/Z* = 48/52) of 1,2-bis(phenyltelluro)-1-(1'-cyclohexenyl)ethene (**3f**) as a mixture of *E*- and *Z*-isomers. Owing to the similar polarities of (*E*)-**3f** and (*Z*)-**3f**, the isolation of each isomers did not meet success, and so the following spectral and analytical data were obtained using the *E*:*Z*-mixture: yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 1.43~1.64 (m, 4H), 1.95~2.01 (m, 2H), 2.24 (brs, 2H), 5.59 (s, 1H, C=C$\underline{H}$), 7.12 (s, 1H, C=C$\underline{H}$-TePh), 7.16~7.34 (m, 6H), 7.63 (d, 2H, *J* = 6.7 Hz), 7.72 (d, 2H, *J* = 7.2 Hz). [Z-isomer]: δ 1.43~1.64 (m, 4H), 1.95~2.01 (m, 2H), 2.24 (brs, 2H), 6.07 (s, 1H, C=C$\underline{H}$), 7.16~7.34 (m, 6H), 7.63 (d, 2H, *J* = 6.7 Hz), 7.82 (d, 2H, *J* = 7.2 Hz), 8.13 (s, 1H, C=C$\underline{H}$-TePh). NOE study: Irradiation of allylic methylene singlet at δ 2.24 resulted in 8 % increase at δ 8.13; ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer]: δ 21.97, 22.50, 25.11, 27.60, 114.19, 115.34 (ipso), 115.98 (ipso), 127.02, 127.66 (p), 127.82 (p), 129.20 (m), 129.26 (m), 131.25, 137.52 (o), 138.62 (o), 143.88. [Z-isomer]: δ 22.10, 22.78, 26.10, 26.87, 115.69, 115.69 (ipso), 118.48 (ipso), 124.53, 127.36 (p), 127.87 (p), 129.34 (m), 129.48 (m), 135.19, 136.20 (o), 138.21 (o), 139.60; IR (NaCl) 3063, 2926, 2854, 2828, 1573, 1473, 1445, 1017, 998, 729, 690 cm^{-1}; MS, m/e = 520 (M^+, 21). Anal. Calcd for $C_{20}H_{20}Te_2$: C, 46.59; H, 3.91. Found : C, 46.04; H, 3.91.

1,2-Bis(phenyltelluro)-3-methyl-1,3-butadiene (3g). The reaction of 1-methyl-1-buten-3-yne (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through Pyrex (>300 nm) with tungsten lamp (500 W) at 40 °C for 20 h. After the determination of the NMR yield (97 %, *E/Z* = 52/48), the mixture was treated with preparative TLC (silica gel, *n*-hexane) to provide 49 mg (41 %) of 1,2-bis(phenyltelluro)-3-methyl-1,3-butadiene (**3g**) as a 1:1-mixture of *E*- and *Z*-isomers. Owing to the similar polarities of (*E*)-**3g** and (*Z*)-**3g**, the isolation of each isomers did not meet success, and so the following spectral and analytical data were obtained using the *E*:*Z*-mixture: brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) [*E*-isomer]: δ 1.96 (s, 3H), 4.85 (s, 1H), 4.94 (s, 1H), 7.11~7.33 (m, 6H), 7.31 (s, 1H), 7.63 (d, 2H, *J* = 6.7 Hz), 7.70 (d, 2H, *J* = 7.2 Hz). [Z-isomer]: δ 1.96 (s, 3H), 5.00 (s, 1H), 5.32 (s, 1H), 7.21~7.37 (m, 6H), 7.65 (d, 2H, *J* = 7.3 Hz), 7.85 (d, 2H, *J* = 7.0 Hz), 8.33 (s, 1H, $J_{Te\text{-}H}$ = 20.1, 34.8 Hz). NOE study: Irradiation of allylic methyl singlet at δ 1.96 resulted in 16 % increase at δ 8.33; ^{13}C NMR (68 MHz, $CDCl_3$) [*E*-isomer]: δ 21.81, 114.39 (C=$\underline{C}$H-TePh), 115.16 (ipso), 118.87 (ipso), 116.91 ($\underline{C}$=CH-TePh), 123.24 (C=$\underline{C}H_2$), 127.80 (p), 127.88 (p), 129.30 (m), 129.40 (m), 137.65 (o), 138.18 (o), 150.20 ($\underline{C}$=CH_2). [Z-isomer]: δ 20.11, 115.28 (ipso), 118.61 (ipso), 119.11 (C=$\underline{C}$H-TePh), 127.53 (p), 128.08 (p), 129.50 (m), 129.58 (m), 132.34 ($\underline{C}$=CH-TePh), 134.27 (C=$\underline{C}H_2$), 136.08 (o), 138.38 (o), 145.51 ($\underline{C}$=CH_2); IR (NaCl) 3064, 2927, 1573, 1473, 1433, 1017, 998, 890, 728, 690 cm^{-1}; MS, m/e = 480 (M^+, 25). Anal. Calcd for $C_{17}H_{16}Te_2$: C, 42.94; H, 3.39. Found : C, 42.82; H, 3.40.

Ditelluration of Diethyl Acetylenedicarboxylate (1h). The reaction of diethyl acetylenedicarboxylate (0.25 mmol) with diphenyl ditelluride (0.25 mmol) was performed by irradiation through Pyrex (>300 nm) with tungsten lamp (500 W) at 40 °C for 12 h. After the determination of the NMR yield (99 %, *E/Z* = 82/18), the mixture was treated with preparative TLC on silica gel (*n*-hexane) to provide 118 mg (85 %) of diethyl 1,2-

bis(phenyltelluro)fumarate ((*E*)-**3h**) and 7 mg (5 %) of diethyl 1,2-bis(phenyltelluro)maleate ((*Z*)-**3h**): [*E*-isomer]: orange crystal (mp 85~85.5 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (t, 6H, *J* = 7.0 Hz), 3.80 (q, 4H, *J* = 7.0 Hz), 7.21~7.36 (m, 6H), 7.82 (d, 4H, *J* = 7.48 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.75, 62.23, 117.29 (ipso), 128.67 (p), 128.98 (m), 139.96 (o), 167.69 (CO_2Et), 127.20 (C=); IR (KBr) 3065, 2998, 1673, 1574, 1474, 1433, 1294, 1240, 1024, 728, 691 cm^{-1}; MS, m/e = 584 (M^+, 40). Anal. Calcd for $C_{20}H_{20}O_4Te_2$: C, 41.44; H, 3.49. Found : C, 41.69; H, 3.54. [Z-isomer]: brown oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.03 (t, 6H, *J* = 7.0 Hz), 3.77 (q, 4H, *J* = 7.0 Hz), 7.26~7.40 (m, 6H), 7.87 (d, 4H, *J* = 7.3 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.71, 61.68, 116.92 (ipso), 129.02 (p), 129.45 (m), 139.77 (o), 165.07 (CO_2Et), 137.50 (C=); IR (NaCl) 3051, 2981, 1719, 1572, 1534, 1224, 1017, 735, 691 cm^{-1}; exact mass (M^+) calcd for $C_{20}H_{20}O_4Te_2$: 583.9486. Found: 583.9503.

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