Photo-initiated Addition of Diphenyl Ditelluride to Acetylenes

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Diphenyl ditelluride **2** has been found to add efficiently to various acetylenes **1** upon irradiation with visible light (>400 nm), providing *vic*-bis(phenyltelluro)alkenes **3** in good yields.

The addition to unsaturated compounds of heteroatom-centred radicals arising from heteroatom–heteroatom bond homolysis is a basic reaction in organic chemistry.[1] Although organic ditellurides are well known to generate the corresponding telluro radicals by photolysis,[2] there exist no reports of free-radical addition of organic ditellurides to carbon–carbon multiple bonds. This is partly due to the lower reactivity of the telluro radicals, compared to thio and seleno radicals, towards carbon–carbon unsaturated bonds. We have made a close study of the photo-initiated addition of organic ditellurides to acetylenes and have found that 1,2-addition of diphenyl ditelluride to a variety of acetylenes indeed takes place *via* a radical pathway [eqn. (1)].

To overcome the low reactivity of the telluro radicals towards carbon–carbon unsaturated bonds, the reaction of diphenyl ditelluride **2** with oct-1-yne **1a** was examined under

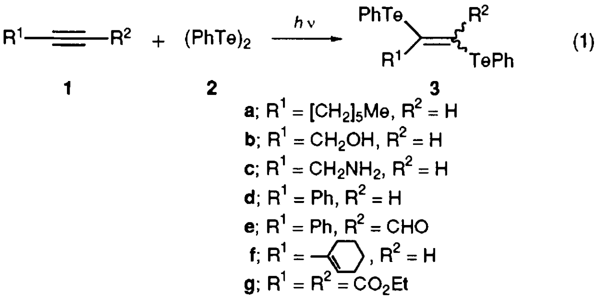


Table 1 Photo-initiated addition of $(PhTe)_2$ **2** to oct-1-yne **1a** to give **3a**[a]

Run	λ/nm	Temp./°C	Time/h	Yield[b] (%) of **3a**[e]
1	⩾300[c]	40	48	0
2	⩾300[c]	70	24	20
3	⩾300[c]	70	115	32
4	Dark	70	48	0
5	⩾400[d]	40	48	43
6	⩾400[d]	40	96	62

[a] *Reagents and conditions*: oct-1-yne (0.25 mmol), $(PhTe)_2$ (0.25 mmol), tungsten lamp (500 W). [b] Determined by ^1H NMR. [c] Irradiation through Pyrex. [d] Irradiation through a glass filter. [e] Only (*E*)-isomer.

conditions of high initial concentrations of the starting materials **1a** and **2** (Table 1).[3] The attempted reaction of **2** with **1a** by irradiation through Pyrex with a tungsten lamp at 40 °C in the absence of solvent did not proceed (run 1), but elevated temperatures led to the formation of the desired 1,2-bis(phenyltelluro)oct-1-ene **3a** in low yields (runs 2, 3). The UV-VIS spectra of the isolated adduct **3a** indicated absorption in the near-UV, which possibly caused the reverse reaction of **3a** to the starting materials **1a** and **2** (Fig. 1).

Thus, when a $CDCl_3$ solution of the adduct **3a** was irradiated with near-UV light at 40 °C for 6 h, the reverse reaction took place to give the acetylene **1a** (60%) and the ditelluride **2**. These results prompted us to examine the reaction of **1a** with **2** using a near-UV filter. Upon irradiation with a tungsten lamp through the filter (>400 nm) at 40 °C for 98 h, the desired 1,2-adduct **3a** was successfully produced as a single stereoisomer (*E*) (run 6).

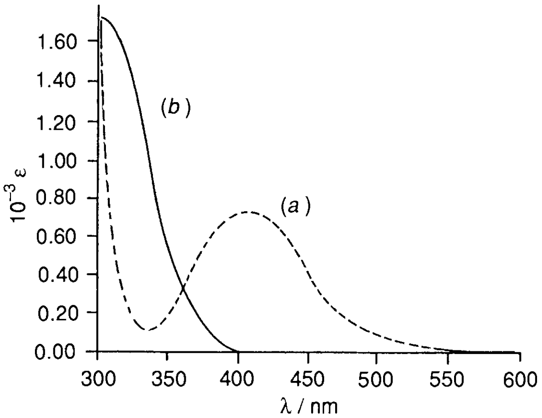


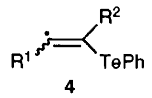
Fig. 1 UV-VIS spectra of (*a*) $(PhTe)_2$ and (*b*) 1,2-bis(phenyltelluro) oct-1-ene. Concentration 1.01×10^{-4} mol dm^{-3}; for $(PhTe)_2$, λ_{max} = 406 nm (ε 777).

Table 2 Photo-initiated addition of $(PhTe)_2$ **2** to acetylenes[a]

Run		λ/nm	Time/h	Product	Yield[b] (%)	*E*:*Z*
1	**1b**	⩾400	24[d]	**3b**	78(86)	100:0
2	**1c**	⩾400	24	**3c**	68(82)	100:0
3	**1d**	⩾400	3	**3d**	73(98)	94:6
4	**1e**	⩾300	34	**3e**	80(95)[e]	64:36
5	**1f**	⩾300	24	**3f**	78(96)	65:35
6	**1g**	⩾300	12	**3g**	90(99)[f]	82:18

[a] *Reagents and conditions*: acetylene (0.25 mmol), $(PhTe)_2$ (0.25 mmol), *hv* (tungsten lamp, 500 W), 40 °C. [b] Isolated yield (NMR yield). [c] *E*:*Z* ratio was determined by ^1H NMR. [d] 70 °C. [e] Isolated yield 49% for (*E*)-**3e**; 31% for (*Z*)-**3e**. [f] Isolated yield 85% for (*E*)-**3g**; 5% for (*Z*)-**3g**.

Table 2 indicates the results of the addition of **2** to other acetylenes. Prop-2-ynyl alcohol **1b** and prop-2-ynyl amine **1c** underwent addition of **2** efficiently with visible light irradiation, giving the corresponding 1,2-adducts **3b** and **c** with excellent stereoselectivities [again, only (*E*)-isomers were formed] (runs 1, 2).† In contrast to unactivated acetylenes like **1a–c**, the addition to activated acetylenes **1d–g** proceeded even upon irradiation with light of wavelength >300 nm (runs 3–6). For example, phenylacetylene **1d** and $(PhTe)_2$ provided the corresponding adduct **3d** in excellent yield (97% by ^1H NMR) upon irradiation through Pyrex at 40 °C for 24 h. Irradiation with visible light (>400 nm) shortened the reaction time (run 3). In the cases of the conjugated acetylenes **1e**, **f** and **g**, the addition proceeded smoothly, but was less stereoselective (runs 4–6).‡ It is interesting that the frequencies of the CO stretching vibrations in the carbonyl groups of the (*E*)-adducts **3e** and **g** were lower than expected [$\nu_{C=O}/cm^{-1}$ 1627 for (*E*)-**3e**; 1656 for (*Z*)-**3e**; 1673 for (*E*)-**3e**; 1719 for (*Z*)-**3e**].[4]



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A possible mechanism includes the formation of the alkenyl radical intermediates **4** by the addition of the phenyltelluro radical to acetylenes and the subsequent S_H2 reaction of **4** with $(PhTe)_2$ leading to 1,2-bis(phenyltelluro)alkenes **3** with regeneration of PhTe•. In the cases of the activated acetylenes **1d–g**, the alkenyl radicals **4** are stabilized by the conjugated carbonyl, vinyl or aryl group; this may suppress the photo-induced reverse reaction of the 1,2-adducts **3d–g** to the acetylenes **1d–g** and the ditelluride.

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† Typical procedure: in a Pyrex glass tube were placed prop-2-ynyl alcohol **1b** (0.25 mmol) and diphenyl ditelluride **2** (0.25 mmol). The tube was filled with Ar and sealed under reduced pressure. The mixture was irradiated at 70 °C for 24 h through a filter (>400 nm) with a tungsten lamp (500 W) positioned approximately 20 cm from the tube. The mixture was purified by preparative TLC on silica gel (n-hexane) to provide (*E*)-1,2-bis(phenyltelluro)-3-hydroxyprop-1-ene **3b** (78%): ^1H NMR (270 MHz, $CDCl_3$): δ 2.00 (br s, 1H, OH), 4.34 (s, 2H, CH_2), 7.15–7.45 (m, 6H, *m*- and *p*-Ph), 7.37 (s, 1H, =CH), 7.65 (d, 2H, $^3J_{HH}$ 6.4 Hz, *o*-Ph) and 7.76 (d, 2H, $^3J_{HH}$ 6.6 Hz, *o*-Ph); ^{13}C NMR (68 MHz, $CDCl_3$): δ 71.01, 112.50 (=CH), 114.13 (*ipso*), 121.76 (*ipso*), 126.01 (C=), 127.85 (*p*), 128.27 (*p*), 129.42 (*m*), 129.65 (*m*), 137.44 (*o*) and 138.86 (*o*); IR (NaCl): ν/cm^{-1} 3377, 3054, 2846, 1569, 1471, 1425, 1212, 1033, 1010, 992, 727 and 687; MS: *m/z* 466 (M^+, 17%); satisfactory C, H analysis.

The same reaction with irradiation through Pyrex (>300 nm) resulted in the formation of **3b** and **c** in lower yields, probably owing to the reverse reaction caused by the near-UV component (16% for **3b**; 25% for **3c**).

‡ (*E*)- to (*Z*)-isomerisation was observed during the irradiation. In the case of enyne **1f**, for example, the (*E*)-selectivity decreased with the irradiation time [24% (*E*:*Z* = 92:8) after 1 h; 31% (90:10) after 2 h; 33% (83:17) after 4 h].

In summary, this paper indicates the first example of the radical addition of organic ditellurides to acetylenes. The products, *vic*-bis(phenyltelluro)alkenes, are of interest from the synthetic point of view, because vinyl tellurides are widely accepted as useful intermediates for introducing vinyl functions into various organic molecules.[5]§

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§ The selective alkylation of *vic*-ditelluroalkenes with organometallic reagents is now under investigation. For example, the methylation of **3d** with Me_2CuLi (1.2 equiv.) proceeded regioselectively at the terminal carbon to provide (*E*)-1-phenyl-1-(phenyltelluro)prop-1-ene in good yield.