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Photoinduced thiotelluration of isocyanides by using a $(PhS)_2$–$(PhTe)_2$ mixed system, and its application to bisthiolation via radical cyclization

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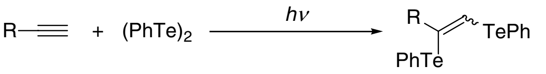
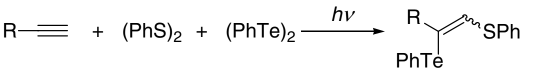
This Letter is dedicated to the memory of the late Professor Yoshihiko Ito of Doshisha University

Abstract—Upon visible light irradiation, highly selective thiotelluration of isocyanides bearing an electron-withdrawing group like nitro or trifluoromethyl group takes place smoothly by the use of a disulfide–ditelluride mixed system. The application of this photoinduced reaction to radical cyclization of *o*-vinyl and *o*-allyl substituted phenylisocyanides successfully leads to the formation of bisthiolated indole and quinoline derivatives, respectively, in moderate yields.

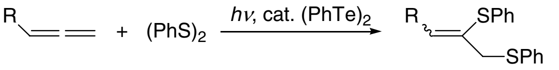
Diphenyl ditelluride (PhTeTePh) has its absorption maximum in visible region ($\lambda_{\max} = 406$ nm), and therefore, the irradiation with visible light causes homolytic cleavage of the tellurium–tellurium single bond, generating the corresponding tellurium-centered radical. When the visible-light irradiation is performed by co-existence of unsaturated compounds in this system, radical addition of the ditelluride to the unsaturated compounds may take place to give the corresponding bistelluration products. However, examples of efficient bistelluration of unsaturated compounds are extremely rare. In 1991, we have found the visible-light-irradiated bistelluration of alkynes with diphenyl ditelluride (Eq. 1).[1]



(1)



(2)



(3)

The combination of the ditelluride and diphenyl disulfide leads to novel regioselective thiotelluration of alkynes, which can be attained based on the higher reactivity of phenylthio radical (compared with phenyltelluro radical),[2] and the higher carbon radical capturing ability of diphenyl ditelluride (compared with diphenyl disulfide)[3] (Eq. 2).[4] On the other hand, the thiotelluration of allenes using the $(PhS)_2$–$(PhTe)_2$ mixed system does not proceed at all, and instead bisthiolation of allenes successfully takes place to give the corresponding terminal adducts regioselectively (Eq. 3).[5] In this reaction, the desired thiotelluration products are unstable under photoirradiation conditions, and the following photoinduced reaction of the thiotelluration products with $(PhS)_2$ takes place to give the corresponding bisthiolation products selectively. In the absence of $(PhTe)_2$, a complex mixture including small amounts of the bisthiolation product is obtained. In this Letter, we wish to report a novel photoinduced introduction of chalcogen functions into isocyanides, as C–N multiple bond compounds, by using the $(PhTe)_2$ single system and the $(PhS)_2$–$(PhTe)_2$ mixed system.[6,7]

When the reaction of aromatic isocyanide[8] (**1**, 0.25 mmol, 0.5 M) with equimolar amounts of diphenyl ditelluride in $CDCl_3$ was conducted for 24 h upon irradiation with a tungsten lamp through a filter (*hν*

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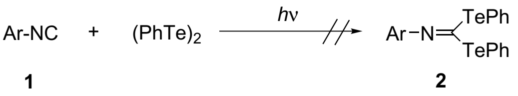
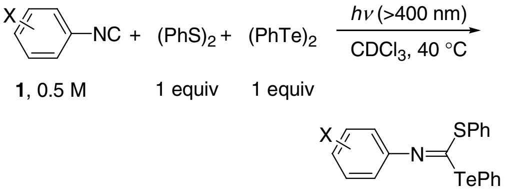
>400 nm), the desired 1,1-bistellurated product (**2**, Ar = 2,6-xylyl or *p*-nitrophenyl) was not obtained at all (Eq. 4).



(4)

Under similar conditions, photoinduced bisselenation of *p*-nitrophenyl isocyanide with diphenyl diselenide is known to occur efficiently,[9] and therefore, the bistelluration product of isocyanides is most probably unstable under visible light irradiation conditions.

As shown in Eq. 2, the binary system of disulfide and ditelluride is useful for introducing both thio and telluro groups into carbon–carbon triple bonds. Thus, we examined similar photoinduced reactions of isocyanides with $(PhS)_2$ and $(PhTe)_2$ (Eq. 5).[10] Although usual isocyanides such as 2,6-xylyl isocyanide (**1a**, 2,6-$Me_2C_6H_3NC$), *p*-methoxyphenyl isocyanide (**1b**, *p*-MeO–C_6H_4NC), and benzylisocyanide (**1c**, $PhCH_2NC$) did not afford the corresponding thiotellurated product at all, aryl isocyanides (**1d**, **1e**, and **1f**) bearing an electron-withdrawing group such as *p*-nitro, *p*-trifluoromethyl, and *p*-cyano groups, underwent efficient thiotelluration, providing the desired thiotelluration products (**3d**, **3e**, and **3f**) successfully in good yields.[11] Aryl isocyanide (**1g** and **1h**) bearing weak electron-withdrawing groups such as *p*-chloro and *m*-methoxy groups, provided the corresponding products (**3g** and **3h**) in moderate yields.



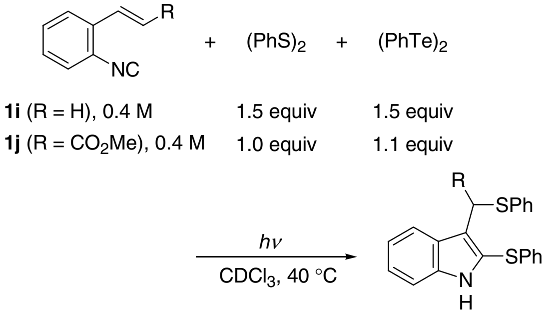
	X =			
1d	*p*-NO_2	3 h	**3d**,	43%
		8 h		54% (70%)
		20 h		(88%)
1e	*p*-CF_3	11 h	**3e**	54%
		20 h		(73%)
1f	*p*-CN	12 h	**3f**	(91%)
1g	*p*-Cl	12 h	**3g**	(46%)
1h	*m*-OMe	8 h	**3h**	(13%)

(5)

*Isolated (NMR) yield.

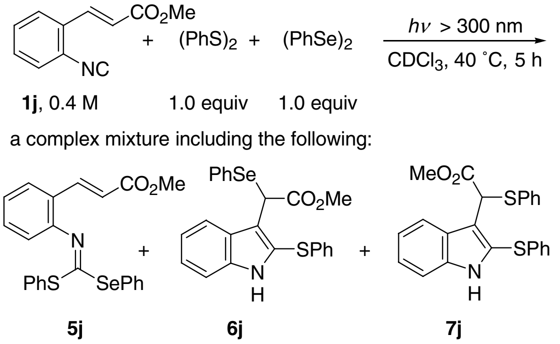
Isocyanides, having an unsaturated bond at a suitable position, are expected to undergo radical cyclization reactions initiated by chalcogen-centered radicals. Thus, we examined intramolecular cyclization reactions of *o*-vinylphenyl isocyanides (**1i**) by using the $(PhS)_2$–$(PhTe)_2$ mixed system. When the reaction of an isocyanide (**1i**) with 1.5 equiv of $(PhS)_2$ and $(PhTe)_2$ was conducted under the photoirradiation conditions (*hν* >400 nm), cyclization reaction occurs successfully, affording bisthiolated indole derivative (**4i**) in 50% yield (Eq. 6).[12] Similar conditions can be employed with methyl *o*-isocyanocinnamate (**1j**), affording the corresponding cyclization product (**4j**) in moderate yield.

In contrast, the use of diphenyl diselenide in place of the ditelluride, resulted in the formation of a complex mixture, which included the corresponding cyclic products (**6j** and **7j**) along with an acyclic product (**5j**) (Eq. 7). Accordingly, the $(PhS)_2$–$(PhTe)_2$ mixed system is superior to the $(PhS)_2$–$(PhSe)_2$ mixed system for this radical cyclization reactions of *o*-alkenyl isocyanides.



(6)

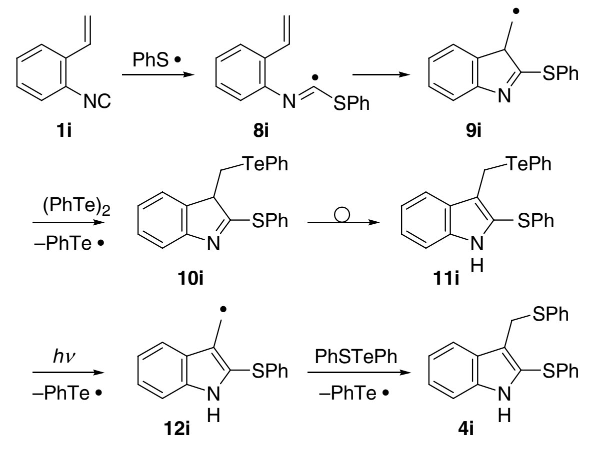
hν > 400 nm	31 h	**4i** (R = H), 50%
hν > 500 nm	15 h	**4j** (R = CO_2Me), 42%



(7)

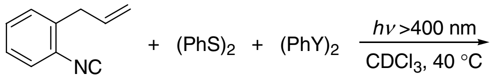
A possible pathway may include the following (see Scheme 1): (i) upon visible light irradiation, comproportionation of $(PhS)_2$ and $(PhTe)_2$ takes place to form PhSTePh,[13–15] which undergoes photoinduced homolytic cleavage, generating PhS$^•$; (ii) PhS$^•$ adds to the isocyano group of **1i** selectively, forming an imidoyl radical intermediate (**8i**); (iii) **8i** cyclizes in the 5-*exo* manner to give the radical intermediate bearing a five-membered ring (**9i**); (iv) **9i** undergoes S_H2 reaction with $(PhTe)_2$, which bears the excellent carbon radical capturing ability. The formed thioltellurated product (**10i**) isomerizes to more stable indole derivative (**11i**); (v) homolytic dissociation of the phenyltelluro group of **11i** under the photoirradiation conditions generates a radical intermediate (**12i**) and PhTe$^•$;[16,17] (vi) S_H2 reaction of **12i** with PhSTePh forms a bisthiolated indole derivative (**4i**).

When 2-allylphenyl isocyanide (**1k**) was used as the substrate, the 6-*exo* radical cyclization reaction takes place successfully by using $(PhS)_2$–$(PhTe)_2$ or $(PhS)_2$–$(PhSe)_2$ mixed systems. The photoinduced reaction of **1k** with



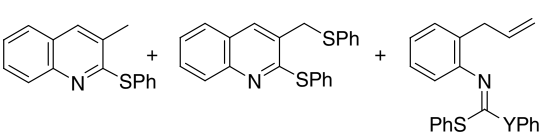
Scheme 1. A possible pathway for the bisthiolative cyclization.

$(PhS)_2$ and $(PhTe)_2$ under several conditions gave the corresponding 6-*exo* radical cyclization products (**13k** and **14k**), but no 1,1-thiotellulated adduct (**3k**) was obtained (Eq. 8). To get the desired bisthiolated cyclic product (**14k**) selectively, higher concentration of disulfide is favorable. On the other hand, in the case using the $(PhS)_2$–$(PhSe)_2$ mixed system, 1,1-thioselenated adduct (**5k**) was obtained mainly along with cyclic product (**13k**) (Eq. 8).[18]



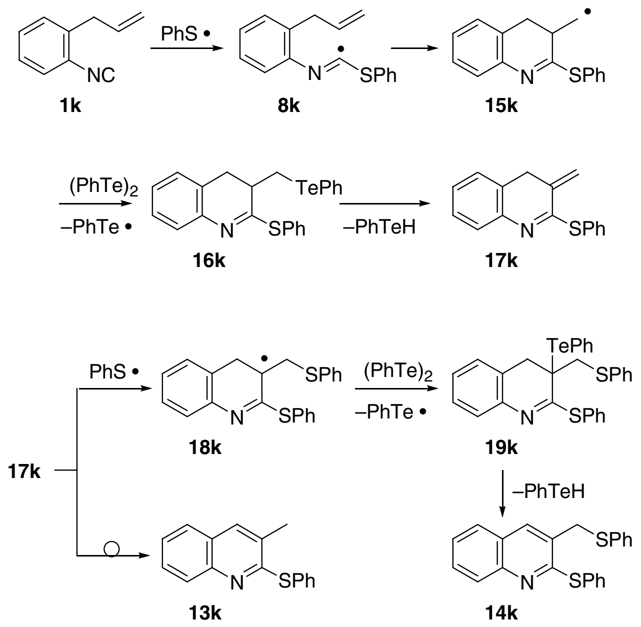
1k, 0.4 M	1.0 equiv	Y = Te, 0.5 equiv	30 h
0.2 M	1.2 equiv	Te, 1.0 equiv	30 h
0.4 M	2.0 equiv	Te, 0.5 equiv	15 h
0.4 M	1.0 equiv	Se, 0.6 equiv	8 h
0.1 M	1.0 equiv	Se, 0.5 equiv	7 h

(8)



13k, 17%	**14k**, 17%	**3k**, 0%
13%	22%	0%
14%	31%	0%
26%	0%	**5k**, 58%
39%	0%	33%

In the reaction of this $(PhS)_2$–$(PhTe)_2$ mixed system, a quinoline (**17k**) was obtained as an initial product upon photoirradiation for 5 h (Scheme 2). Therefore, a possible mechanistic pathway may include the following: (i) the imidoyl radical intermediate (**8k**), which is formed by the addition of $PhS^\cdot$ to **1 k**, cyclizes in the 6-*exo* manner to give the six-membered cyclic radical intermediate (**15k**); (ii) **15k** undergoes S_H2 reaction with $(PhTe)_2$ to provide a thiotellurated quinoline (**16k**); (iii) an elimination of PhTeH from **16k** gives **17k**;[19] (iv) $PhS^\cdot$ attacks **17k** to provide a radical intermediate (**18k**), and then **18k** is trapped by $(PhTe)_2$, yielding the cyclic product (**19k**); (v) an elimination of PhTeH from **19k** affords **14k**. On the other hand, the isomerization of **17k** produces the cyclic product (**13k**).



Scheme 2. A possible pathway for the thiolative cyclization.

In summary, we have disclosed the characteristic features of diphenyl ditelluride in the photoinduced reaction with isocyanides. Although the ditelluride itself does not add to isocyanides, the combination with diphenyl disulfide successfully leads to the desired thiotelluration products of aromatic isocyanides bearing electron-withdrawing groups. Moreover, the present $(PhS)_2$–$(PhTe)_2$ mixed system is useful for radical cyclization of *o*-alkenylphenyl isocyanides.

Acknowledgments

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11. General procedure for the synthesis of the thiotellurated product, for example, **3d**, is as follows: the reaction of *p*-nitrophenyl isocyanide (**1d**, 37.5 mg, 0.23 mmol) with diphenyl disulfide (54.6 mg, 0.25 mmol) and diphenyl ditelluride (102 mg, 0.25 mmol) in CDCl$_3$ (0.5 mL) was performed at 40 °C for 8 h upon irradiation with a tungsten lamp (500 W) through a glass filter ($h\nu$ >400 nm). During the reaction, a red precipitate was formed, and the precipitate was separated by filteration. Purification of the precipitate was performed on a recycling preparative HPLC, yielding 62.4 mg (54%) of *N*-(*p*-nitrophenyl)(phenyltelluro)(phenylthio)ethanimine (**3d**) as yellow solid: mp 120.0 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.84 (d, $J = 9.3$ Hz, 2H), 7.25–7.50 (m, 6H), 7.50–7.54 (m, 2H), 7.92 (d, $J = 6.8$ Hz, 2H), 8.12 (d, $J = 9.3$ Hz, 2H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 112.6, 120.0, 124.9, 129.2, 129.5, 129.6, 129.8, 130.9, 134.8, 141.9, 144.4, 150.0, 158.0; IR (KBr) 3065, 2359, 1583, 1563, 1512, 1343, 1217, 876, 747, 687 cm^{-1}; MS (CI) *m*/*z* 465 (M$^+$+1, 6); Anal. Calcd for C$_{19}$H$_{14}$N$_2$O$_2$STe: C, 49.40; H, 3.05; N, 6.06. Found: C, 48.99; H, 3.00; N, 5.98.

    The spectral and analytical data for *N*-(*p*-trifluoromethylphenyl)(phenyltelluro)(phenylthio)methanimine (**3e**) is as follows: yellow solid; mp 107.0 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.86 (d, $J = 8.3$ Hz, 2H), 7.24–7.45 (m, 6H), 7.51 (d, $J = 7.8$ Hz, 4H), 7.94 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 119.7, 120.3, 126.3, 126.6, 129.1, 129.4, 129.5, 131.3, 134.7, 142.1, 148.8, 155.6; IR (KBr) 1598, 1320, 1154, 1124, 1102, 1064, 862 cm^{-1}; MS (CI) *m*/*z* 488 (M$^+$+1, 5); Anal. Calcd for C$_{20}$H$_{14}$F$_3$NSTe: C, 49.53; H, 2.91; N, 2.89. Found: C, 49.78; H, 2.88; N, 2.88.
12. General procedure for the synthesis of the cyclized product, for example, **4j**, is as follows: the reaction of an isocyanide (**1j**, 37.4 mg, 0.20 mmol) with diphenyl disulfide (43.6 mg, 0.20 mmol) and diphenyl ditelluride (90.1 mg, 0.22 mmol) in CDCl$_3$ (0.5 mL) was conducted upon irradiation with a tungsten lamp (500 W) through a filter ($h\nu$ >500 nm) at 40 °C for 15 h. Isolation of the product was performed on a recycling preparative HPLC, yielding 34.0 mg (42%) of (phenylthio)(2-phenylthio-1*H*-indol-3-yl)acetic acid methyl ester (**4j**) as yellow oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.62 (s, 3H), 5.59 (s, 1H), 7.03 (dd, $J = 8.3$, 7.8 Hz, 2H), 7.12–7.27 (m, 9H), 7.33 (dd, $J = 7.3$, 7.8 Hz, 2H), 8.10 (d, $J = 8.3$ Hz, 1H), 8.13 (br s, 1H); ^{13}C NMR (68 MHz, CDCl$_3$) δ 49.9, 52.6, 111.0, 117.3, 120.5, 121.6, 124.0, 124.9, 126.0, 126.4, 127.8, 127.9, 128.8, 129.1, 133.3, 133.9, 135.7, 137.1, 170.6; IR (NaCl) 3360, 3057, 2950, 1732, 1479, 1439, 1151, 743, 690 cm^{-1}; MS (EI) *m*/*z* 405 (M$^+$, 2); HRMS Calcd for C$_{23}$H$_{19}$NO$_2$S$_2$: 405.0857, found: 405.0856.

    For the spectral and analytical data for 2-phenylthio-3-phenylthiomethyl-1*H*-indole (**4i**) is as follows: yellow oil; ^{1}H NMR (270 MHz, CDCl$_3$): δ 4.46 (s, 2H), 7.04–7.37 (m, 14H), 7.76 (d, $J = 8.4$ Hz, 1H), 8.02 (s, 1H); ^{13}C NMR (68 MHz, CDCl$_3$): δ 29.8, 111.0, 118.7, 120.0, 120.1, 123.8, 123.9, 126.2, 126.4, 127.2, 127.4, 128.7, 129.2, 130.6, 136.2, 136.6, 137.0. IR (NaCl) 3371, 3229, 3057, 2924, 2853, 1719, 1582, 1477, 1439, 1340, 1290, 1242, 1192, 1069, 1024, 997, 739, 689 cm^{-1}; MS (EI) *m*/*z* 347 (M$^+$, 6); HRMS Calcd for C$_{21}$H$_{17}$NS$_2$: 347.4964, found: 347.3173.

13. Under photoirradiation conditions (>1 h), $(PhS)_2$ and $(PhTe)_2$ are in equilibrium with PhSTePh, and the ratio of $(PhS)_2$–$(PhTe)_2$–PhSTePh is about 2:2:1.
14. Measurement of UV–visible spectrum of PhSTePh in $CHCl_3$ indicates that its λ_{max} value is 400 nm. Therefore, visible-light irradiation induces homolytic cleavage of PhSTePh, generating $PhS^{\cdot}$ in situ.
15. The reaction of isocyanides with PhSTePh did not take place in the dark. This fact rules out the ionic process for this thiotelluration.
16. Thermal isomerization of allylic tellurides is also possible: Yamago, S.; Hashidume, M.; Yoshida, J.-i. *Tetrahedron* **2002**, *58*, 6805.
17. The thiotellurated indole derivative (**11i**) was observed by ^{1}H NMR (4.15 ppm, C–CH_2–Te) and MS spectra: MS (EI) *m*/*z* 443 (M^+, 0.8).
18. The spectral and analytical data for cyclized products, is as follows: 3-Methyl-2-(phenylthio)quinoline (**13k**): yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.36–7.46 (m, 4H), 7.51 (ddd, $J = 1.5, 6.8, 8.3$ Hz, 1H), 7.59–7.63 (m, 2H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 1H), 7.78 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.0, 125.6, 126.6, 126.8, 128.3 (2 C), 128.5, 128.8, 129.7, 130.8, 134.5, 135.1, 146.8, 159.1; IR (NaCl) 3059, 1600, 1389, 1132, 1039, 687 cm^{-1}; MS (EI) *m*/*z* 251 (M^+, 58); HRMS Calcd for $C_{16}H_{13}NS$: 251.0769, found: 251.0763.
    2-Phenylthio-3-(phenylthiomethyl)quinoline (**14k**): yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.34 (s, 2H), 7.17–7.28 (m, 4H), 7.32–7.43 (m, 6H), 7.54 (ddd, $J = 1.5, 6.8, 8.3$ Hz, 1H), 7.60 (d, $J = 7.3$ Hz, 2H), 7.73 (d, $J = 8.3$ Hz, 1H), 7.81 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 36.3, 125.9, 126.4, 126.9, 127.2, 128.3 (2 C), 128.9, 129.0, 129.3, 130.7, 131.0, 134.4, 135.4, 135.5, 147.3, 158.2; IR (NaCl) 3057, 1593, 1582, 1478, 1438, 1134, 1040, 1024, 746, 689 cm^{-1}; MS (EI) *m*/*z* 359 (M^+, 76); HRMS Calcd for $C_{22}H_{17}NS_2$: 359.0802, found: 359.0813.
19. Several attempts of detection of benzenetellurol failed, owing to its instability. However, the formation of diphenyl monotelluride and benzenethiol suggests the possibility of the generation of PhTeH.