Sodium Arenetellurolate Catalyzed Selective Conversion of Nitroaromatics to Aromatic Azoxy or Azo Compounds and Its Application for Facile Preparation of 3,3'- and 4,4'-Bis[β-(aryltelluro)vinyl]azobenzenes from (3- and 4-Nitrophenyl)acetylenes

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Treatment of aromatic nitro compounds with sodium borohydride in alkaline ethanol in the presence of a catalytic amount of diaryl ditelluride at room temperature affords the corresponding azoxy compounds selectively in fair to excellent yields. Under reflux aromatic azo compounds are obtained as major products. In situ generated sodium arenetellurolate (ArTeNa) is the active species to reduce nitroaromatics into aromatic nitroso compounds, the latter being easily converted into azoxy compounds in alkaline ethanol. Higher temperature enables ArTeNa to reduce the initially produced azoxy compounds into azo compounds. A new vinylic telluride having an azo group in the molecule, 3,3'-bis[β-(aryltelluro)vinyl]azobenzene, was prepared in one pot in 66–91% isolated yield by treating (3-nitrophenyl)acetylene with a stoichiometric amount of ArTeNa in alkaline ethanol at reflux temperature, the structure of which was determined unambiguously by X-ray crystallography. The corresponding 4,4'-isomer was similarly prepared, but in lower yield.

Synthetic applications of tellurium reagents have been rapidly developed.[1] Both inorganic and organic tellurium compounds such as H_2Te,[2] $NaTeH$,[3] M_2Te (M = Li, Na),[4] $PhTeH$,[5] and $ArTeNa$[6] have recently been introduced as mild and efficient reducing agents of various organic compounds and their catalytic use has also been developed in some cases. A great number of methods of the direct synthesis of azoxy and azo compounds from nitroaromatics have so far been reported,[7] but catalytic reactions are limited to the reduction with hydrogen using Pd–C as a catalyst.[8] For the syntheses of azoxy compounds the reductions using a stoichiometric amount of thallium metal,[9] phosphine,[10] and sodium arsenite[11] generally give

good results, but the reagents are toxic and not easily handled. The reduction of a wide variety of nitroaromatics by glucose in alkaline solution has been known to give a high yield of the corresponding azoxy compounds, but a stoichiometric amount of glucose is also required.[12] Sodium arenetellurolate (ArTeNa) is produced by reduction of diaryl ditelluride with $NaBH_4$ in ethanol–benzene in the presence of NaOH,[13] but its use for reduction is still limited to dehalogenation of several organic halides.[6] Here, we describe the selective reduction of nitroaromatics to either the corresponding azoxy or azo compounds by the use of ArTeNa as a catalyst.[14] Furthermore, one-pot prepara-

Table I. Reduction of Nitrobenzene (1a) with (PhTe)₂ and NaBH₄[a]

(PhTe)₂, mmol	NaBH₄, mmol	time, h	convn,[b] %	products and GLC yield, %	
				2a	3a
1.0	20	10	97	89	8
0.05	5	10	71	71	trace
0.05	10	5	73	73	trace
0.05	10	10	93	92	trace
	10	20	1	0	0
c	10	30	1	trace	0

[a] 1a (2 mmol), ethanol (15 mL), and 5 M aqueous NaOH (2.5 mL) were used at 25 °C under N₂. [b] Conversion of 1a (by GLC). [c] (PhSe)₂ (0.05 mmol) was used in place of (PhTe)₂.

(1) For example: (a) Uemura, S. *Kagaku* 1981, *36*, 381. (b) Engman, L. *Acc. Chem. Res.* 1985, *18*, 274. (c) Petragnani, N.; Comasseto, J. V. *Synthesis* 1986, 1. (d) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, Vol. 1, 1986; Vol. 2, 1987.

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(3) (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. I* 1975, 1574. (b) Osuka, A.; Shimizu, H.; Suzuki, H. *Chem. Lett.* 1983, 1373. (c) Uchida, S.; Yanada, K.; Yamaguchi, H.; Meguri, H. *Ibid.* 1986, 1069.

(4) (a) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* 1982, *47*, 1354. (b) Tschugaeff, L.; Chlopin, W. *Ber.* 1914, *47*, 1269. (c) Bergman, J.; Engman, L. *Z. Naturforsch.* 1980, *356*, 217. (d) Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gegne, P. *Organometallics* 1983, *2*, 549. (e) Suzuki, H.; Manabe, H.; Inouye, M. *Chem. Lett.* 1985, 1671. (f) Suzuki, H.; Inouye, M. *Ibid.* 1986, 403. (g) Suzuki, H.; Manabe, H.; Kawaguchi, T.; Inouye, M. *Bull. Chem. Soc. Jpn.* 1987, *60*, 771.

(5) (a) Akiba, M.; Cava, M. P. *Synth. Commun.* 1984, *14*, 1119. (b) Ohira, N.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* 1984, 853. (c) Aso, Y.; Nishioka, T.; Osuka, M.; Nagakawa, K.; Sasaki, K.; Otsubo, T.; Ogura, F. *Nippon Kagaku Kaishi* 1987, 1490.

(6) (a) Engman, L.; Cava, M. P. *J. Org. Chem.* 1982, *47*, 3946. (b) Engman, L. *Tetrahedron Lett.* 1982, *23*, 3601. (c) Engman, L.; Bystrom, S. E. *J. Org. Chem.* 1985, *50*, 3170. (d) Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Bull. Chem. Soc. Jpn.* 1986, *59*, 3013.

(7) For example: (a) Hudlicky, M. *Reduction in Organic Chemistry*; Ellis Horwood Ltd., Chichester, 1984; pp 71–72. (b) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; 1971; Vol. 11, pp 286–382.

(8) Brand, K.; Steiner, J. *Chem. Ber.* 1922, *55*, 875.

(9) McKillop, A.; Raphael, R. A.; Taylor, E. C. *J. Org. Chem.* 1970, *35*, 1670.

(10) Buckler, S. A.; Doll, L.; Lind, F. K.; Epstein, M. *J. Org. Chem.* 1962, *27*, 794.

(11) Bigelow, H. E.; Palmer, A. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. 2, p 57.

(12) Galbraith, H. W.; Degering, E. F.; Hitch, E. F. *J. Am. Chem. Soc.* 1951, *73*, 1323.

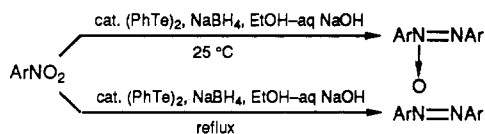(13) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* 1970, *79*, 353, 367, 383.

(14) Preliminary communication: Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Chem. Soc., Chem. Commun.* 1988, 591.

Table II. PhTeNa-Catalyzed Reduction of Aromatic Nitro Compounds 1 to Aromatic Azoxy Compounds 2[a]

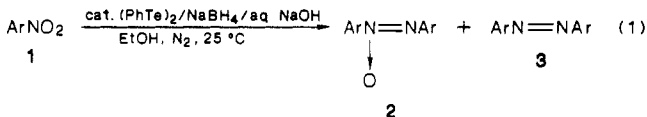| 1	(PhTe)$_2$, mmol	time, h	convn of 1, %	products and isolated yield, %
1a	0.05	10	93	2a 91 (92)[b]
1b	0.05	40	93	2b 78 (91)[b,c]
1c	0.05	10	91	2c 83[b]
1d	0.05	20	90	2d 85[b]
1e	0.10	12	100	2e 99
1f	0.10	12	100	2f 96
1g	0.10	40	83	2g 60
1h	0.05	7	100	2[d] 82

[a] Carried out with 1 (2 mmol), (PhTe)$_2$, and NaBH$_4$ (10 mmol) in ethanol (15 mL) and 5 M aqueous NaOH (2.5 mL) at 25 °C under N$_2$. [b] GLC yield. [c] A side product: 3b 2%. [d] 2 (Ar = 4-MeCH-(OH)C$_6$H$_4$).

tions of new vinylic tellurides, 3,3'- and 4,4'-bis[β-(aryltelluro)vinyl]azobenzenes, from (3- and 4-nitrophenyl)-acetylenes are also reported as the results of the application of this reduction.

$$ArNO_2 \xrightarrow[\substack{\text{cat. (PhTe)}_2, \text{ NaBH}_4, \text{ EtOH–aq NaOH} \\ 25\ °C}]{} ArN{=}NAr$$
$$\downarrow O$$
$$\xrightarrow[\substack{\text{cat. (PhTe)}_2, \text{ NaBH}_4, \text{ EtOH–aq NaOH} \\ \text{reflux}}]{} ArN{=}NAr$$

Results and Discussion

On treatment of nitrobenzene (1a; 2 mmol) with an equimolar amount of sodium benzenetellurolate (PhTeNa) generated in situ from diphenyl ditelluride [(PhTe)$_2$, 1 mmol] and NaBH$_4$ (20 mmol) in ethanol (15 mL) containing aqueous 5 M NaOH (2.5 mL) at 25 °C for 10 h under nitrogen atmosphere, azoxybenzene (2a) and azobenzene (3a) were obtained in 89% and 8% yields, respectively.[15] Interestingly, further work revealed that the reduction proceeds catalytically in (PhTe)$_2$ to give 2a from 1a selectively when excess NaBH$_4$ to 1a is used (eq 1).
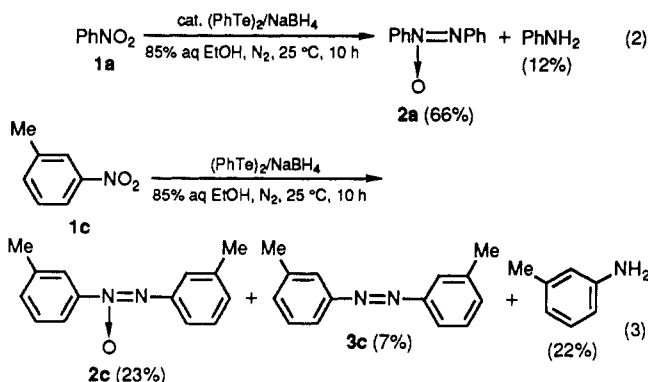
$$ArNO_2 \xrightarrow[\text{EtOH, N}_2, 25\ °C]{\text{cat. (PhTe)}_2/\text{NaBH}_4/\text{aq NaOH}} ArN{=}NAr + ArN{=}NAr \quad (1)$$
$$\underset{1}{} \qquad \underset{\underset{2}{\overset{\downarrow}{O}}}{} \qquad \underset{3}{}$$

a, Ar = C$_6$H$_5$; **b**, Ar = 2-MeC$_6$H$_4$; **c**, Ar = 3-MeC$_6$H$_4$; **d**, Ar = 4-MeC$_6$H$_4$; **e**, Ar = 4-ClC$_6$H$_4$; **f**, Ar = 4-BrC$_6$H$_4$; **g**, Ar = 4-MeOC$_6$H$_4$; **h**, Ar = 4-MeCOC$_6$H$_4$; **i**, Ar = 2,4-Me$_2$C$_6$H$_3$

Without (PhTe)$_2$ the reduction did not occur at all, 1a being recovered intact. It has been shown[16] that benzeneselenol and its diazabicyclo[2.2.2]octane (DABCO) complex reduce nitroaromatics 1 to anilines and aromatic hydrazo compounds respectively. We determined, however, that sodium benzeneselenolate (PhSeNa) prepared in situ from diphenyl diselenide and NaBH$_4$ did not show any catalytic activity for the reduction of nitroaromatics into azoxy compounds in our reaction system. Typical results are shown in Table I.

Next, the effect of alkaline concentration on both the yield and selectivity of products was investigated in the reduction of 1a by the use of a catalytic amount of (PhTe)$_2$ at 25 °C for 10 h. Even without aqueous NaOH the reduction occurred, but the yield of 2a was low (66%) and aniline was obtained as a byproduct (12%). Several ex-

periments revealed that the use of ca. 0.7 M NaOH solution [the addition of 5 M aq NaOH (2.5 mL) to ethanol (15 mL)] was the best for obtaining 2a in high yield (92%) and high selectivity. Suitable alkaline concentration seems to be necessary not only for generating PhTeNa favorably but also for making the reaction system homogeneous. Under these best conditions the reduction of several nitroaromatics was carried out to give azoxy compounds 2 almost selectively, azo compounds 3 being scarcely formed (Table II). The reduction of each nitrotoluene (1b–d) occurred to give the corresponding azoxytoluene (2b–d). The rate of reduction of 1 bearing an electron-donating group was generally slower than that of 1 bearing an electron-withdrawing one. The carbonyl group in 4-nitroacetophenone (1h) was reduced to the hydroxy group and 4,4'-bis(1-hydroxyethyl)azoxybenzene was the product. On the other hand, the reduction of 4-cyanonitrobenzene and 4-(ethoxycarbonyl)nitrobenzene afforded a complex mixture of products, respectively, from which no desirable azoxy compounds were obtained.

Here we would like to consider briefly the active species for reduction. Ogura et al. have reported[5c] that the reduction of nitroaromatics with 7 equiv of benzenetellurol (PhTeH) in benzene at room temperature gave anilines in very high yields. On the other hand, the main reduction products in our catalytic system were azoxy compounds as described above. In the absence of NaOH the reduction of 1a and 1c with either catalytic or stoichiometric amounts of (PhTe)$_2$ and excess NaBH$_4$ afforded a mixture of 2a and aniline and a mixture of 2c, 3,3'-dimethylazobenzene (3c), and 3-methylaniline, respectively (eq 2 and 3). The formation of anilines is worth noting and in this

$$PhNO_2 \xrightarrow[\text{85\% aq EtOH, N}_2, 25\ °C, 10\ h]{\text{cat. (PhTe)}_2/\text{NaBH}_4} PhN{=}NPh + PhNH_2 \quad (2)$$
$$\underset{1a}{} \qquad \underset{\underset{2a\ (66\%)}{\overset{\downarrow}{O}}}{} \qquad \underset{(12\%)}{}$$

case the active species may be mainly sodium (phenyltelluro)triethoxyborate (4) by considering the formation of the corresponding selenium analogue from (PhSe)$_2$ and NaBH$_4$ in ethanol.[17] Some benzenetellurol and/or PhTeNa could also be present in the reaction mixture to give 2 and/or 3. In order to obtain more information on the active species in our reduction system, we carried out the reduction of 1a and 1c with PhTeNa, prepared in situ from (PhTe)$_2$ and sodium wire in tetrahydrofuran (THF). The products were the corresponding azoxy and azo compounds in both cases (eq 4 and 5) and anilines were not formed at all. Here, further reduction of the initially formed 2 to 3 may be induced by unreacted sodium.[18] We also clarified separately that the reduction of 1a did not occur at all with a stoichiometric amount of triethyl borate [B(OEt)$_3$] in alkaline ethanol, although the in situ for-

(15) Under identical conditions 3,3'-dimethylazoxybenzene (2c) was obtained in 88% yield from 3-nitrotoluene (1c) together with a trace amount of 3,3'-dimethylazobenzene (3c).

(16) Fujimori, K.; Yoshimoto, H.; Oae, S. *Tetrahedron Lett.* **1979**, 4397.

(17) Miyashita, M.; Hoshino, M.; Yoshikoshi, A. *Tetrahedron Lett.* **1988**, *29*, 347.

(18) In fact, we disclosed in a separate experiment that 2a was converted to 3a (28% GLC yield) by treatment with 3 equiv of sodium in THF at 25 °C for 10 h, with no aniline and starting compound 2a being detected in the products.

(4)

(5)

Scheme I
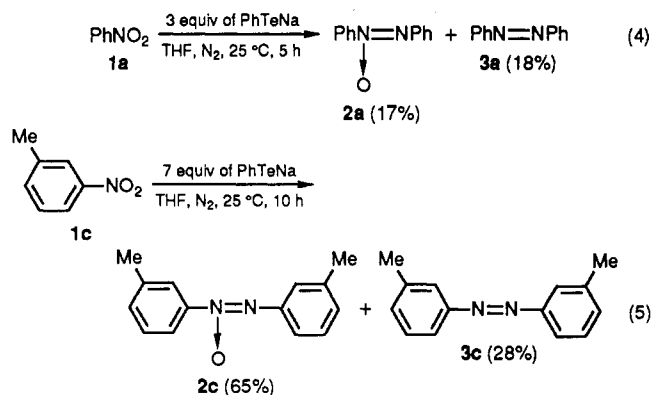
mation of the borate as an active species might be expected in our reaction system. By considering these observations the active species in our catalytic reduction in alkaline ethanol can be supposed to be PhTeNa which is a milder reducing agent than PhTeH and produces azoxy compounds selectively. The species 4 may be converted to PhTeNa in the presence of NaOH.

Although PhTeNa is shown to be a mild reducing agent, it was disclosed that the species can reduce **2a** to **3a** at reflux temperature in ethanol (eq 6). Then, it is con-


(6)
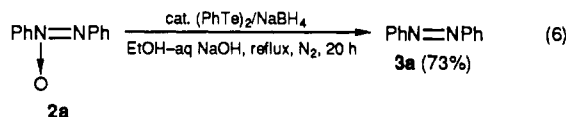
ceivable that the direct conversion of 1 to 3 may generally occur by use of a catalytic amount of (PhTe)$_2$ when the reduction is carried out at higher temperature. In fact, this is the case as summarized in Table III (eq 7). A longer


(7)
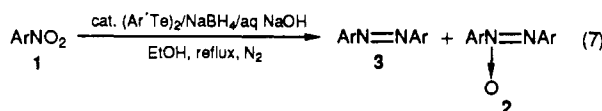
reaction time was necessary to obtain a satisfactory yield of **3**, and hydrazine derivatives such as *N,N'*-bis(4-chlorophenyl)hydrazine and *N,N'*-bis(4-bromophenyl)-hydrazine were also obtained from 4-chloro- and 4-bromonitrobenzene (**1e** and **1f**) in 13% and 19% yields, respectively, as side products. Other organyltellurolates such as sodium 4-methoxybenzenetellurolate (**5**), sodium 2-naphthalenetellurolate (**6**), and sodium 2-thienetellurolate (**7**) generated in situ from the corresponding ditelluride were also used in place of PhTeNa to reduce 1 to 3 (Table III).
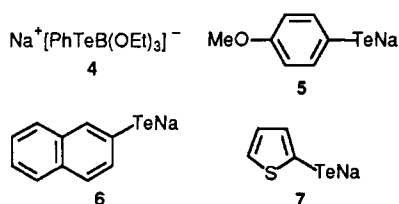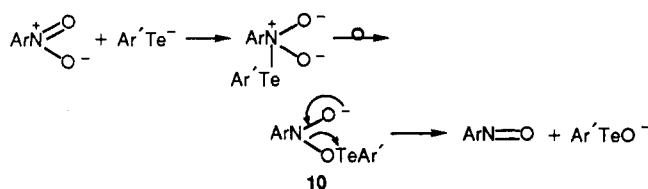

When the reduction using a catalytic amount of PhTeNa at 25 °C was applied to 2,2'-dinitrobiphenyl (**8**), the almost quantitative formation of benzo[*c*]cinnoline dioxide (**9**) was observed (eq 8). This fact strongly suggests the inter-


(8)
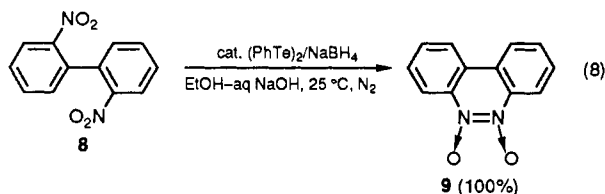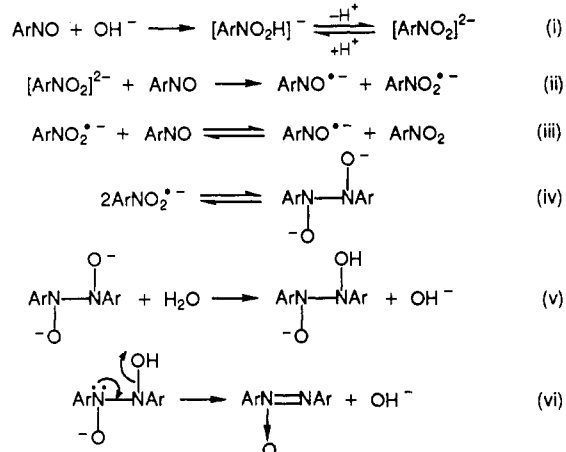
Scheme II

vention of a nitroso compound as an intermediate. Although no such nitrosoaromatics were detected in the reaction products from any nitroaromatics shown in Table II, this seems to be due to a facile conversion of nitroso compounds to azoxy compounds under alkaline conditions as has already been reported by Russell et al. (Scheme I).[19] We also confirmed in our hands that nitrosobenzene was converted to **2a** almost quantitatively by stirring it in alkaline ethanol (ca. 0.7 M NaOH solution) at 25 °C for 6–10 h either in the presence or absence of NaBH$_4$ and/or (PhTe)$_2$.[20] Therefore, the key step of this reduction is probably the formation of a nitroso compound and one of the possible schemes is shown in Scheme II. Namely, a nucleophilic attack of arenetellurolate ion (Ar''Te$^-$) upon nitrogen of nitroaromatics followed by rearrangement of the Ar''Te moiety from nitrogen to oxygen gives an intermediate (**10**) that liberates arenetellurenate ion (Ar''TeO$^-$) and a nitroso compound.[21]

The catalytic cycle of this reduction is shown in Scheme III. Sodium arenetellurenate (Ar''TeONa), which is formed by the reaction of Ar''TeNa with 1 or 2, regenerates Ar''TeNa by reduction with NaBH$_4$. Another possibility is the disproportionation of Ar''TeONa to Ar''TeNa and Ar''TeO$_2$Na,[22] the latter reagent having been also revealed separately to work as a catalyst for the reduction of 1 to

(19) (a) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807. (b) Russell, G. A.; Geels, E. J.; Smentowski, F. J.; Chang, K.-Y.; Reynolds, J.; Kaupp, G. *J. Am. Chem. Soc.* **1967**, *89*, 3821. (c) Russell, G. A.; Geels, E. J. *J. Am. Chem. Soc.* **1965**, *87*, 122.

(20) We also disclosed separately that β-phenylhydroxylamine (PhNHOH) is converted to **2a** (93% yield) by stirring it in alkaline ethanol (ca. 0.7 M NaOH solution) at 25 °C for 12 h. Although we described in a preliminary communication[14] that **2a** was not produced from β-phenylhydroxylamine, that was incorrect.

(21) The mechanism involving one-electron transfer from Ar''Te$^-$ to 1 shown below is another possibility.
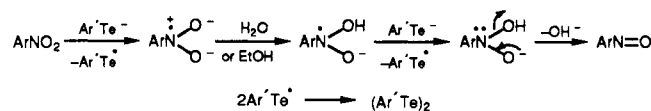

(22) Uemura, S.; Fukuzawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 2748.

Table III. ArTeNa-Catalyzed Reduction of Aromatic Nitro Compounds 1 to Aromatic Azo Compounds 3[a]

| 1	cat., ditelluride[b]	time, h	convn of 1, %	products and isolated yield, %	
				3	2
1a	A	3	99	3a 43[c]	2a 53[c]
1a	A	10	99	3a 71[c]	2a 24[c]
1a	A	20	100	3a 88[c]	2a 10[c]
1a	B	20	100	3a 84[c]	2a 1[c]
1a	C	20	100	3a 91[c]	2a 7[c]
1a	D	20	100	3a 58[c,d]	2a 0
1b	A	20	e	3b 61	2b 4
1c	A	20	100	3c 90	2c 10
1d	A	24	100	3d 71	2d 26
1e	A	15	100	3e 75[f]	2e 0
1f	A	15	100	3f 66[g]	2f 0
1g	A[h]	48	100	3g 71	2g 8
1i	A	48	e	3i 52	2i e

[a] Carried out with 1 (2 mmol), catalyst (0.05 mmol), and NaBH$_4$ (10 mmol) in ethanol (15 mL) and 5 M NaOH (2.5 mL) at reflux temperature under N$_2$. [b] A, (PhTe)$_2$; B, (4-MeOC$_6$H$_4$Te)$_2$; C, di(2-naphthyl) ditelluride; D, di(2-thienyl) ditelluride. [c] GLC yield based on 1. [d] A side product: C$_6$H$_5$NH$_2$ 3%. [e] Not determined. [f] A side product: (4-ClC$_6$H$_4$NH)$_2$ 13%. [g] A side product: (4-BrC$_6$H$_4$NH)$_2$ 19%. [h] (PhTe)$_2$ (0.1 mmol) was used.

Scheme III
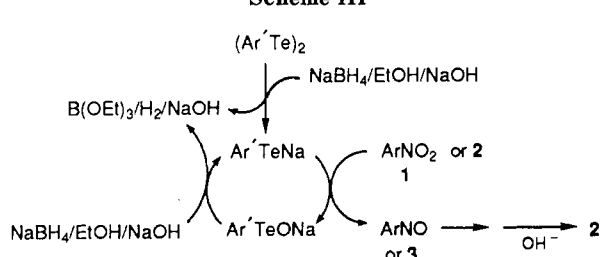
2: i.e., by the reduction using a catalytic amount of PhTeO$_2$H, NaBH$_4$, and aqueous NaOH in EtOH at 25 °C for 10 h, 88% of 2a was obtained from 1a, while without NaBH$_4$ no reduction occurred. At higher temperature Ar'TeNa reduces 2 to 3 in this catalytic cycle.

We have previously reported that the treatment of arylacetylenes with (PhTe)$_2$ and NaBH$_4$ in ethanol at reflux temperature gives the corresponding (Z)-vinyl phenyl tellurides via addition of PhTe⁻ to triple bonds.[23] In the case of (3-nitrophenyl)acetylene (11) the addition was accompanied by the reduction of a nitro group to an amino group to give (Z)-2-(3'-aminophenyl)vinyl phenyl telluride (12), although a controlled addition of NaBH$_4$ was necessary to obtain it in a good yield (Scheme IV).[23] When the so-far described preparative method for azo compounds was applied to 11 using a stoichiometric amount of (PhTe)$_2$ and under alkaline conditions, a new vinylic telluride having an azo group in the molecule, 3,3'-bis[β-(phenyltelluro)vinyl]azobenzene (13a), was obtained in 91% isolated yield as a golden solid (Scheme IV). Its 4-methoxy derivative (13b) was also prepared in 67% isolated yield. Under identical conditions (4-nitrophenyl)acetylene gave a similar telluride, 4,4'-bis[β-(phenyltelluro)vinyl]azobenzene (14) in 23% yield together with 27% of the unexpected 4,4'-azostyrene (15), while the reduction of (2-nitrophenyl)acetylene was slow and a mixture of several unidentified compounds was obtained in a low yield.

The configuration of the carbon–carbon double bond of 13a and 13b is suggested to be cis by ¹H NMR spectroscopy (vinylic protons, J_{H-H} = 10.4 Hz). This was established unambiguously by X-ray crystal structure analysis of 13a, which had the cis configuration at C=C bonds, C(7)–C(8) and C(7)'–C(8)', and further the trans configuration at the N=N bond was also revealed (Figure 1). The
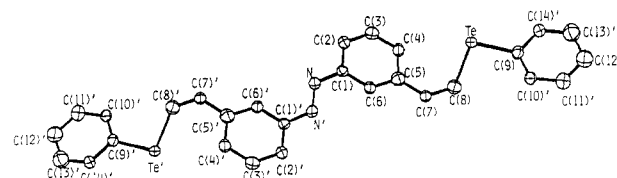
Figure 1. Structure of 13a.

bond lengths of vinylic carbon–Te [C(8)–Te] and carbon–carbon double bonds [C(7)–C(8)] are 2.095 Å and 1.330 Å, respectively, which are almost identical with those reported for hexamethylenetetratellurafulvalene (2.098 Å and 1.356 Å, respectively.[24]

The cyclic voltammogram of 13a in dichloromethane containing n-Bu$_4$NClO$_4$ as supporting electrolyte displays a reduction couple at $E_{1/2}$ = −1.23 V vs the saturated calomel electrode (SCE) and an oxidation peak at $E_{p,a}$ = 1.16 V vs SCE (Figure 2). This shows that 13a is chemically reversible with its anion, while oxidation is not chemically reversible. Similarly the cyclic voltammogram of 13b (Figure 3) showed a reduction couple at $E_{1/2}$ = −1.28 V vs SCE and an oxidation peak at $E_{p,a}$ = 1.16 V vs SCE.

Experimental Section

General Procedures. ¹H NMR spectra were recorded on Varian VXR-200 (200-MHz) and JEOLCO GX-400 (400-MHz) spectrometers as solutions in CDCl$_3$. ¹³C NMR spectra were determined on Varian VXR-200 and JNM FX-100 spectrometers in CDCl$_3$. Chemical shifts are reported in δ units downfield from the internal reference Me$_4$Si. The coupling constants (J) are in hertz (Hz). IR spectra were recorded on a Jasco IR-810 infrared spectrophotometer as KBr pellets. Mass spectra were measured on a JEOL JMS-DX 300 mass spectrometer, equipped with a JMA-3500 data processing system. UV spectra were measured on a Jasco UVIDEC-610B double beam spectrophotometer. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses (1 m × 0.5 cm column packed with 5% Silicone DC QF-1 on Chromosorb W, 60–80 mesh) were performed on a Yanaco G 2800 instrument with flame-ionization detectors and N$_2$ as carrier gas. All column chromatographies on SiO$_2$ were performed with Wakogel C-200 (100–200 mesh).

Materials. Diphenyl ditelluride,[25] bis(4-methoxyphenyl) ditelluride,[26] di(2-naphthyl) ditelluride,[27] and di-(2-thienyl) di-

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<div align="center">Scheme IV</div>

13a: Ar = C₆H₅
b: Ar = 4-MeOC₆H₄
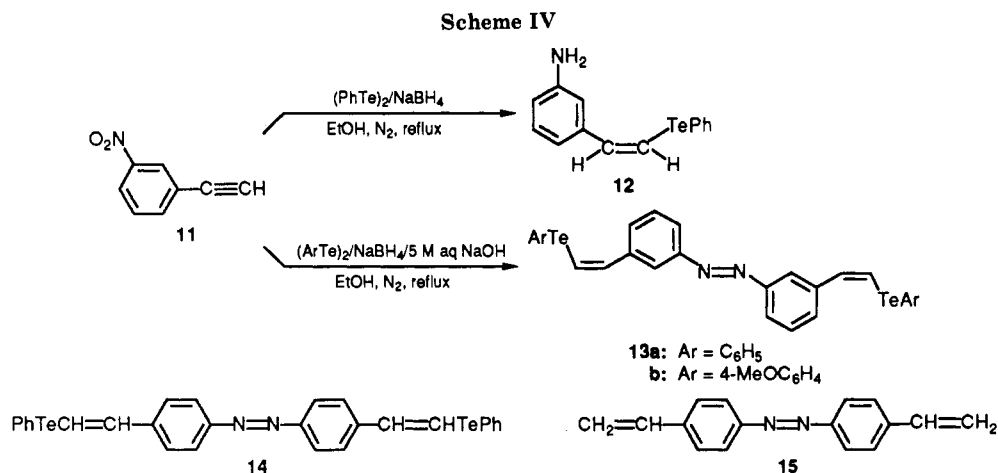
telluride[6a] were prepared by the reported methods. All nitro-aromatics, nitrosobenzene, and diphenyl diselenide as well as inorganic compounds were commercial products and used without further purification. β-Phenylhydroxylamine[28] and (2-, 3-, and 4-nitrophenyl)acetylenes[29] were prepared by literature procedures. Commercially available azoxybenzene (2a), 4,4′-dimethoxyazoxybenzene (2g), and azobenzene (3a) were used as authentic samples. All other 2 and 3 except 2 (Ar = 4-MeCH(OH)C₆H₄) were known compounds and were isolated and identified by ¹H NMR: 2b,[30] 2c,[31] 2d,[30] 2e,[30] 2f,[30] 2g,[32] 3b,[33] 3c,[33] 3d,[34] 3e,[33,35] 3f,[35] 3g,[35] 3i.[36]

General Procedure for the Syntheses of Azoxy Compounds by the Use of a Catalytic Amount of Diphenyl Ditelluride. To a mixture of diphenyl ditelluride (0.021 g, 0.05 mmol) and NaBH₄ (0.378 g, 10 mmol) in a two-necked 50-mL flask were added EtOH (10 mL) and 5 M aqueous NaOH solution (2.5 mL) successively at room temperature under a N₂ atmosphere. An ethanol (5 mL) solution of nitrobenzene (1a) (0.246 g, 2.0 mmol) was then added to the colorless, homogeneous solution and the mixture was stirred at room temperature for 10 h, during which the yellow color turned to orange. The mixture was poured into brine and then extracted with CHCl₃ (3 × 50 mL), and the extract was dried over MgSO₄. Evaporation of the solvent left a yellow oil, which was subjected to column chromatography on SiO₂ using hexane/ethyl acetate (10:1) as eluent to give 0.181 g (0.913 mmol, 91.3% yield) of pure 2a as a yellow solid.

4,4′-(1-Hydroxyethyl)azoxybenzene (2; Ar = 4-MeCH-(OH)C₆H₄). The compound was formed by reduction of 1h and isolated by column chromatography on SiO₂ [hexane/EtOAc (1:1) as eluent]: 0.235 g (0.821 mmol, 82% yield); ¹H NMR (200 MHz) 1.52 (d, *J* = 6.6, 6 H), 1.93 (br, 2 H), 4.91–5.05 (m, 2 H), 7.46–7.53 (m, 4 H), 8.16 (d, *J* = 8.6, 2 H), 8.27 (d, *J* = 8.6, 2 H). Anal. Calcd for C₁₆H₁₈N₂O₃: C, 67.12; H, 6.34; N, 9.78. Found: C, 66.72; H, 6.29; N, 9.74.

General Procedure for the Syntheses of Azo Compounds by the Use of a Catalytic Amount of Diphenyl Ditelluride. To a mixture containing diphenyl ditelluride (0.021 g, 0.05 mmol) and NaBH₄ (0.378 g, 10 mmol) in a two-necked 50-mL flask was added EtOH (10 mL) followed by 5 M aqueous NaOH solution (2.5 mL) at reflux temperature. A solution of 4-bromonitrobenzene (1f) (0.404 g, 2.0 mmol) in ethanol (5 mL) was then added to the colorless homogeneous solution and the mixture was stirred at reflux temperature for 15 h, during which the yellow color turned to red. After it had been cooled, the mixture was poured into

water and then was extracted with CHCl₃ (3 × 50 mL), and the extract was dried over MgSO₄. The products, 3f and 4,4′-dibromo-N,N′-diphenylhydrazine, were isolated by column chromatography on SiO₂. 3f [hexane/CHCl₃ (3:1) as eluent]: 0.224 g (0.66 mmol, 66% yield); mp 206–207 °C (lit.[35] mp 204 °C); ¹H NMR (200 MHz) 7.64 (d, *J* = 8.8, 4 H), 7.79 (d, *J* = 8.8, 4 H). 4,4′-Dibromo-N,N′-diphenylhydrazine ((4-BrC₆H₄NH)₂) [hexane/CHCl₃ (1:1) as eluent]: 0.065 g (0.189 mmol, 19%); ¹H NMR (200 MHz) 5.62 (s, 2 H), 6.70 (d, *J* = 8.8, 4 H), 7.29 (d, *J* = 8.8, 4 H).

Similarly, 3e and 4,4′-dichloro-N,N′-diphenylhydrazine were isolated from reduction of 1e. 3e [hexane/CHCl₃ (3:1) as eluent]: 0.189 g (0.751 mmol, 75% yield); mp 186–188 °C (lit.[35] mp 185 °C); ¹H NMR (200 MHz) 7.48 (d, *J* = 8.8, 4 H), 7.86 (d, *J* = 8.8, 4 H). 4,4′-Dichloro-N,N′-diphenylhydrazine ((4-ClC₆H₄NH)₂) [hexane/CHCl₃ (1:1) as eluent]: 0.032 g (0.128 mmol, 13%); ¹H NMR (200 MHz) 5.62 (s, 2 H), 6.75 (d, *J* = 8.8, 4 H), 7.16 (d, *J* = 8.8, 4 H); IR (KBr) 3350 (NH) cm⁻¹.

Reduction of 3-Nitrotoluene (1c) by the Use of Sodium Benzenetellurolate Generated in Situ from Sodium and Diphenyl Ditelluride in Dry THF. To a mixture of diphenyl ditelluride (1.43 g, 3.5 mmol) and Na wire (0.163 g, 7.1 mmol) in a two-necked 50-mL flask was added tetrahydrofuran (THF) (20 mL) at room temperature under N₂, and the resulting red suspension was stirred at reflux temperature for 2 h. After it had been cooled, a THF (5 mL) solution of 3-nitrotoluene (1c) (0.137 g, 1.0 mmol) was added at 25 °C. The color of the solution changed immediately from red to dark red. After the solution was stirred for 10 h at 25 °C, methanol (5 mL) was added to it to decompose the unreacted sodium followed by the addition of brine. It was extracted with CHCl₃ and the extract was dried over MgSO₄. GLC analysis of the extract using a Silicone DC QF-1 5% (1 m) column and 2a as an internal standard revealed the presence of 3-methylazoxybenzene (2c) (0.33 mmol, 65%) and 3-methylazobenzene (3c) (0.14 mmol, 28%).

Reduction of 2,2′-Dinitrobiphenyl (8) by the Use of a Catalytic Amount of Diphenyl Ditelluride. To a mixture of diphenyl ditelluride (0.021 g, 0.05 mmol) and NaBH₄ (0.378 g, 10 mmol) in a two-necked 50-mL flask with a stirring bar was added ethanol (12 mL) and a 5 M aqueous NaOH solution (2.5 mL) at 25 °C. A solution of 2,2′-dinitrobiphenyl (8) (0.245 g, 1 mmol) in benzene (3 mL) was then added to the colorless homogeneous solution and the mixture was stirred at 25 °C for 10 h, during which the yellow homogeneous solution turned to a yellow heterogeneous solution. The resulting mixture was poured into brine and then was extracted with CHCl₃ (3 × 50 mL), and the extract was dried over MgSO₄. Evaporation of the solvent left a yellow solid and it was washed with hexane to leave a pale yellow solid (0.213 g, 100% yield). Recrystallization from benzene–ethanol afforded white plates of pure 9: 0.165 g, 0.78 mmol, 78% yield; mp 251–252 °C (lit.[37] mp 233–236 °C); ¹H NMR (200 MHz) 7.75–7.85 (m, 4 H), 8.40–8.45 (m, 2 H), 8.50–8.55 (m, 2 H); IR (KBr) 1570, 1510, 1475, 1470, 1420, 1390, 1370, 1360,

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1340, 1305, 1240, 1220, 1120, 1090, 1040, 950, 860, 760, 740, 705, 690, 670, 625, 540 cm^{-1}; mass spectrum, m/e 212 (M$^+$). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.78; H, 3.77; N, 13.15.

Preparation of 3,3'-Bis[β-(phenyltelluro)vinyl]azobenzene (13a). In a 50-mL, round-bottom flask containing a magnetic stirring bar were placed diphenyl ditelluride (0.450 g, 1.1 mmol) and NaBH$_4$ (0.757 g, 20 mmol) under N$_2$. Ethanol (10 mL) was added to the flask at 0 °C, and the mixture became homogeneous after being stirred for 0.5 h at room temperature and then 5 M aqueous NaOH (3 mL) was added. The resulting solution was warmed up to reflux temperature and then an ethanol (5 mL) solution of (3-nitrophenyl) acetylene (0.295 g, 2.0 mmol) was added. The mixture was stirred at reflux for 20 h, during which the color of the solution turned from orange to yellow. After it had been cooled, the mixture was treated with brine and then extracted with CHCl$_3$ (3 × 50 mL), and the extract was dried over MgSO$_4$. Evaporation of CHCl$_3$ left a crude product, which was subjected to column chromatography on SiO$_2$ using hexane/CHCl$_3$ (3:1) as eluent to afford a golden solid of **13a**: 0.582 g, 91% yield; mp 129–130 °C (hexane–CHCl$_3$); ^{1}H NMR (400 MHz) 7.26 (d, J = 10.4, 2 H, vinylic H), 7.28 (d, J = 7.2, 4 H), 7.33 (d, J = 7.2, 2 H), 7.39 (d, J = 8.0, 2 H), 7.56 (dd, J = 8.0, 2 H), 7.59 (d, J = 10.4, 2 H, vinylic H), 7.80 (d, J = 7.2, 4 H), 7.83 (s, 2 H), 7.88 (d, J = 8.0, 2 H); IR (KBr) 1600, 1575, 1475, 1430, 1320, 1020, 905, 810, 720, 685 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} 230, 320 nm; mass spectrum, m/e 642 (M$^+$). Anal. Calcd for $C_{28}H_{22}N_2Te_2$: C, 52.41; H, 3.46; N, 4.37. Found: C, 52.52; H, 3.47; N, 4.37.

3,3'-Bis[β-[(4-methoxyphenyl)telluro]vinyl]azobenzene (13b). A similar reaction using bis(4-methoxyphenyl) ditelluride afforded a golden solid of **13b** after column chromatography on SiO$_2$ [hexane/CHCl$_3$ (1:1) as eluent]: 0.468 g (0.667 mmol, 67% yield); mp 164–165 °C (hexane–CHCl$_3$); ^{1}H NMR (400 MHz) 3.82 (s, 6 H), 6.82 (d, J = 8.8, 4 H), 7.19 (d, J = 10.4, 2 H, vinylic H), 7.36 (d, J = 7.6, 2 H), 7.53 (d, J = 10.4, 2 H, vinylic H), 7.55 (dd, J = 7.6, 2 H), 7.74 (d, J = 8.8, 4 H), 7.82 (s, 2 H), 7.87 (d, J = 7.6, 2 H); IR (KBr) 3020, 2940, 2845, 1590, 1570, 1490, 1280, 1245, 1180, 1020, 900, 815, 685, 590 cm^{-1}; UV (CH$_2$Cl$_2$) λ_{max} 240, 313 nm; mass spectrum, m/e 702 (M$^+$). Anal. Calcd for $C_{30}H_{26}N_2O_2Te_2$: C, 51.35; H, 3.73; N, 3.99. Found: C, 51.30; H, 3.95; N, 4.07.

4,4'-Bis[β-(phenyltelluro)vinyl]azobenzene (14) and 4,4'-Divinylazobenzene (15). From (4-nitrophenyl)acetylene, **14** and **15** were obtained under identical conditions of preparation of **13a**, 53% of diphenyl ditelluride being recovered. They were isolated by column chromatography on SiO$_2$. **14** [hexane/CHCl$_3$ (3:1) as eluent]: 0.150 g (0.234 mmol, 23% yield); mp 171 °C (hexane–CHCl$_3$); ^{1}H NMR (400 MHz) 7.28 (d, J = 7.3, 4 H), 7.29 (d, J = 10.7, 2 H, vinylic H), 7.35 (d, J = 7.3, 2 H), 7.40 (d, J = 8.3, 4 H), 7.55 (d, J = 10.7, 2 H, vinylic H), 7.69 (d, J = 8.3, 4 H), 7.97 (d, J = 8.3, 4 H). **15** [hexane/CHCl$_3$ (5:1) as eluent]: 0.063 g (0.269 mmol, 27% yield); mp 135–136 °C (lit.[38] mp 138–138.5 °C); ^{1}H NMR (200 MHz) 5.36 (d, J = 11.0, 2 H), 5.86 (d, J = 17.6, 2 H), 6.79 (dd, J = 11.0, 17.6, 2 H), 7.55 (d, J = 8.6, 4 H), 7.90 (d, J = 8.6, 4 H).

Electrochemistry of 13a. Cyclic voltammetry was conducted by using a Hokuto-Denko HB-70 A function generator and a HB-104 A potentiostat/galvanostat and was recorded on a Hitachi 057-1001 X-Y recorder. The cell for electrochemical measurements was composed of two compartments connected by a sintered-glass disk. The main compartment was equipped with a Pt working electrode (area 0.06 cm^2) for cyclic voltammetry. The reference electrode was SCE, which was isolated from the bulk solution by a sintered-glass disk. To the electrolysis cell was added 10 mL of electrolyte solution, dichloromethane containing 0.1 mol L^{-1} of n-Bu$_4$NClO$_4$, deaerrated by Ar bubbling, and then 4.0 mg (6.2 × 10^{-3} mmol) of **13a** was added into the main compartment. Cyclic voltammograms of the reduced and oxidized solution were obtained by using the Pt working electrode.

X-ray Structure Determination. Crystal data: $C_{28}H_{22}N_2Te_2$, M_r = 641.68, monoclinic, space group $C2/c$; a = 51.239 (10), b = 5.926 (2), and c = 7.719 (2) Å; β = 93.50 (2)°, V = 2339.4 Å^3, Z = 4, D_{calcd} = 1.829 g cm^{-3}, $\bar{\lambda}$ = 0.71073 Å, and (Mo K$_\alpha$) = 25.17 cm^{-1}.

Yellow single crystals of **13a** suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$. The diffraction intensities were measured on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo K$_\alpha$ radiation. Intensity data in the range 2θ < 60° were collected in the ω–2θ scan mode with a 1.5° scan range and a scan rate of 4° min^{-1} on a crystal with dimensions of 0.38 × 0.25 × 0.037 mm^3. During the course of data collection, three reflections were monitored every 100 reflections. The intensity data were converted to F_0 data in the usual manner. Absorption correction was applied. The standard deviations, $\sigma(F_0)$, were estimated by counting statistics. A total of 2158 independent reflections with $F_0 > 3\sigma(F_0)$ were retained as observed and were used in solving and refining the structure.

The structure was solved by the heavy-atom method. The complete structure was elucidated by iterative synthesis of Fourier maps and was refined by the full-matrix least-squares method. Several cycles of the refinement including anisotropic thermal parameters were carried out with the weighting scheme w^{-1} = $\sigma^2(F_0)$ + $(0.015F_0)^2$. Atomic scattering factors[39a] and anomalous dispersion terms[39b] were taken from the International Tables for X-Ray Crystallography, Vol. IV. The hydrogen atoms were included as being isotropical in the last cycle; their positions were introduced in calculated positions (C–H = 1.09 Å). The final R and R_w values were 0.076 and 0.092, respectively. The final difference Fourier map showed no peaks greater than 0.4 e/Å^3; most of the largest peaks were around the tellurium atoms. All computations were performed on a Hitac M-680H computer at the Computer Center of the Institute for Molecular Science, Okazaki National Research Institute by using the program system UNICS III.[40]

The final positional and isotropic temperature factors of the non-hydrogen atoms are listed in Table IV (supplementary material). The bond lengths and angles are listed in Table V (supplementary material).

Supplementary Material Available: Table IV (fractional coordinates and isotropic thermal parameters), Table V (bond lengths and angles), and Figures 2 and 3 (cyclic voltammograms of **13a** and **13b**, respectively) (4 pages). Ordering information is given on any current masthead page.

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