Crystallization of the residual oil from ethyl acetate gave 1.08 g (58%) of **20** as colorless prisms. The liquid fraction was concentrated under reduced pressure to give 0.36 g (19%) of **19** as colorless prisms. The butenamides **19** and **20** were identical (by their spectra) with the hydrolysates from the imino ether **5h** and the acetal **7h**, respectively.

Chemical names, physical data, and analytical data for the compounds **1–7** and **15–23** are summarized in Tables VI–VIII (supplementary material).

General Procedure for the Geometrical Photoisomerization of Imino Ethers 5a–c in CD_3OD. Photochemical reaction was carried out with a low-pressure mercury lamp (30 W) through a Corning 9-54 color filter in a quartz NMR tube. CD_3OD was purged with dry nitrogen. The (2*E*)-imino ether (25–30 mg) was irradiated in CD_3OD (0.3–0.4 mL) at 20–25 °C. After irradiation, 20 μL of CD_3ONa–CD_3OD (0.05 M) was added to the reaction mixture. The 2*Z* isomers were quantitatively converted to **9a–c**.

General Procedure for the Irradiation of Imino Ethers (2*E*)-5a–c in CD_3ONa–CD_3OD. Photolysis of the (2*E*)-imino ethers was carried out in CD_3OD (0.3–0.4 mL) containing 0.022–0.029 M of CD_3ONa. The relative yields of the products were monitored by ^1H NMR analysis. After neutralization of the irradiated solution, the solvent was evaporated. The amounts of the products were analyzed by ^1H NMR spectra.

Irradiation of (2*E*)-5a in CD_3ONa–CD_3OD. From 27.8 mg (0.164 mmol) of (2*E*)-**5a** was obtained 24.3 mg (96%) of a mixture of (2*E*)-**5a** (52%) and **9a** (=**1a**) (48%) after a 16.5-h irradiation. The yields of (2*E*)-**5a** and **9a** (=**1a**) were 50% and 46%, respectively.

Irradiation of (2*E*)-5b in CD_3ONa–CD_3OD. From 29.8 mg (0.128 mmol) of (2*E*)-**5b** were obtained 27.5 mg (105%) of a mixture of (2*E*)-**5b** (16%), **9b** (=**1c**, 67%), and **1b** (17%) after a 36-h irradiation. The yields of (2*E*)-**5b**, **9b** (=**1c**), and **1b** were 17%, 70%, and 18%, respectively.

Irradiation of (2*E*)-5c in CD_3ONa–CD_3OD. From 29.8 mg (0.128 mmol) of (2*E*)-**5c** was obtained 27.5 mg (107%) of **9c** (=**1b**) after a 3-h irradiation.

Acknowledgment. This study was supported in part by a Grant-in-Aid (No. 577880) from the Ministry of Education, Science and Culture of Japan. We are indebted to H. Yamazaki for her assistance.

Registry No. **1b**, 86421-66-1; **1c**, 20959-22-2; **1d**, 17758-19-9; **1e**, 86421-67-2; **1f**, 86421-68-3; **1g**, 3240-60-6; **1h**, 17758-38-2; **1i**, 65754-05-4; **1j**, 52090-53-6; **1k**, 32363-53-4; **1k**(D), 86421-75-2; **1l**, 6622-92-0; **2b**, 86421-69-4; **2c**, 86421-70-7; **2d**, 86421-71-8; **2e**, 86421-72-9; **2f**, 86421-73-0; **2g**, 86436-06-8; **3**, 86421-74-1; **3**(D), 86436-07-9; (*E*)-**4b**, 86421-76-3; (*Z*)-**4b**, 86421-77-4; (*E*)-**5a**, 86421-78-5; (*Z*)-**5a**, 86421-79-6; (*E*)-**5b**, 86421-80-9; (*Z*)-**5b**, 86421-81-0; (*E*)-**5c**, 86421-82-1; (*Z*)-**5c**, 86421-83-2; **5d**, 86421-84-3; **5h**, 86421-85-4; **6h**, 86421-86-5; (*E*)-**7d**, 86421-87-6; (*Z*)-**7d**, 86421-88-7; **7h**, 86421-89-8; **7i**, 86421-90-1; **7j**, 86421-91-2; **15**, 86421-92-3; **16**, 86421-93-4; **17**, 73645-41-7; **18**, 73645-38-2; **19**, 73645-40-6; **20**, 73645-39-3; **21**, 86421-94-5; **22**, 86436-08-0; **23**, 86421-95-6; ε-caprolactam, 105-60-2; *N*-methyl-3-amino-2-butenamide, 24392-27-6.

Supplementary Material Available: Chemical names, melting points, spectral data (IR, UV, ^1H NMR, and MS), and analytical data for the compounds **1–7** and **15–23** (Tables VI–VIII) (6 pages). Ordering information is given on any current masthead page.

New General Synthesis of Diaryl Tellurides from Aromatic Amines

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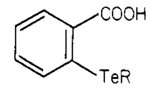
A number of substituted diaryl tellurides were obtained from aryldiazonium tetrafluoroborates and potassium tellurocyanide in dimethyl sulfoxide at ambient temperature. Aryl tellurocyanides were isolated as byproducts in some experiments and postulated as intermediates in the reactions.

Although many methods are available for the preparation of diaryl tellurides,[1] only very few of them are general enough to allow the introduction of a broad variety of substituents. The reaction of diarylmercury and elemental tellurium[2,3] is perhaps the most general method at hand, but it requires the synthesis and high-temperature pyrolysis of hazardous organic mercury compounds, which are serious drawbacks. The complex reaction of aromatic Grignard reagents with tellurium tetrachloride[4] has been used for the synthesis of many diaryl tellurides, but isolation is often difficult due to formation of several byproducts such as diaryl ditellurides, aromatic hydrocarbons, and elemental tellurium. The condensation of $TeCl_4$ with 2 equiv of an aromatic compound, followed by reduction, is a good route to diaryl tellurides containing electron-donating substituents.[5]

We report herein a general synthesis of diaryl tellurides from diazotized aromatic amines and potassium tellurocyanide, KTeCN. Aryldiazonium salts (1) have been frequently used for the synthesis of organotellurium compounds.[6] Renson[7] treated diazotized anthranilic acid with a number of sodium arenetellurolates, $ArTe^-Na^+$, to obtain unsymmetrical tellurides of the general formula **2**. Sadekov[8] similarly prepared a number of unsymmetric diaryl tellurides from aryldiazonium tetrafluoroborates and so-

$ArN_2^+X^-$

1



2, R = phenyl, *p*-tolyl, 3-thienyl

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Table I. Synthesis of Diaryl Tellurides, Ar_2Te, from Aromatic Amines, $ArNH_2$

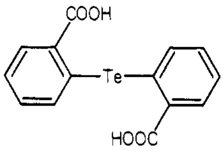
Ar	yield, %	mp, °C	lit.	analysis		Cu(0) treatment
				calcd	found	
4-methylphenyl	47	67	69-70[5]			
4-methoxyphenyl	47	53-54	55-57[5]			+
2-nitrophenyl	39	140	141-142[25]			
4-nitrophenyl	34	170-172	169-171[26]			
2-naphthyl	38	110[a]	126[27]	C, 62.90; H, 3.69	C, 62.88; H, 3.69	+
2-biphenylyl	47	132-133	*b*	C, 66.42; H, 4.18	C, 66.41; H, 4.22	
2-bromophenyl	48	68-69		C, 32.71; H, 1.83	C, 33.06; H, 1.89	+
2,4,6-tribromophenyl	44	190-191		C, 19.09; H, 0.53	C, 19.57; H, 0.63	+
2-cyanophenyl	41	163		C, 50.67; H, 2.43	C, 50.79; H, 2.45	
2,6-dimethylphenyl	42	82-83		C, 56.87; H, 5.37	C, 56.85; H, 5.41	+
2-carboxyphenyl	8	277-279	278[12]			

[a] A melting point of 126 °C was reported for this compound.[27] Our material, which may also be described as "glittering brownish yellow leaflets", melted at 110 °C after several recrystallizations from ethanol. [b] This compound was prepared by a lengthy procedure in 19% yield from 2-biphenylylmercury chloride.[28] No melting point, analysis, or spectroscopic data were given.

dium arenetellurolates. The reaction of diazonium chlorides with elemental tellurium[9,10] has yielded diaryltellurium dichlorides, and their reaction with tellurium tetrachloride and zinc dust has provided diaryl tellurides in low yield.[11] Several attempts have been made to realize the general synthesis of diaryl tellurides from diazonium compounds, as depicted in eq 1. Farrar[12] repeated and

$$2ArN_2X + Na_2Te \rightarrow Ar_2Te + 2NaX + 2N_2 \qquad (1)$$

improved a questionable procedure by Mazza and Melchionna[13] for the synthesis of bis(2-carboxyphenyl) telluride (**3**) by reacting potassium telluride with diazotized anthranilic acid. More recently, Praefcke[14] synthesized telluroxanthone (**4**) in low yield from sodium telluride and diazotized 2,2′-diaminobenzophenone.



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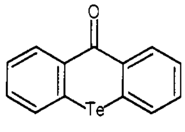


4

Results and Discussion

We have found that aryldiazonium tetrafluoroborates can be converted to symmetrical diaryl tellurides in moderate yields by treatment with potassium tellurocyanide in dimethyl sulfoxide at ambient temperature.

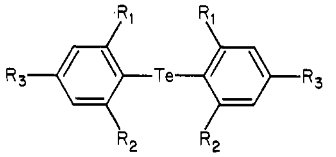
The expected aryl tellurocyanides are seldom stable enough to be isolable (vide infra). This is in contrast to the behavior of aryl selenocyanides,[15] which are stable under similar reaction conditions. A probable mechanism for the reaction (eq 2) involves the formation of aryl tellurocyanides as primary products that disproportionate

$$ArN_2^+BF_4^- + KTeCN \rightarrow ArTeCN + KBF_4 + N_2 \qquad (2)$$

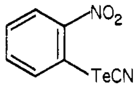
$$2ArTeCN \rightarrow Ar_2Te + Te(CN)_2 \rightarrow Te + (CN)_2$$

to diaryl tellurides and tellurium dicyanide, $Te(CN)_2$. $Te(CN)_2$ is a known[16] but very unstable compound that could be expected to decompose into elemental tellurium (an observed byproduct) and dicyanogen (not isolated).

Potassium tellurocyanide was prepared according to a procedure by Cava[17] from elemental tellurium and potassium cyanide in dimethyl sulfoxide. The solid aryldiazonium salts[18] were added to an ice-cooled and partly crystallized solution of the tellurocyanide, causing a violent gas evolution. Workup after stirring several hours at ambient temperature usually afforded the diaryl tellurides in 30–50% yield. A number of representative examples are given in Table I, including the four new compounds **5a–d**. The products were sometimes contaminated by small amounts of the corresponding ditelluride, $(ArTe)_2$, causing a red coloration. However, treatment with copper powder in refluxing dioxane for several hours cleanly converted the ditellurides to tellurides according to a literature procedure.[19]



5a, $R_1 = CN; R_2 = R_3 = H$
b, $R_1 = Br; R_2 = R_3 = H$
c, $R_1 = R_2 = R_3 = Br$
d, $R_1 = R_2 = CH_3; R_3 = H$



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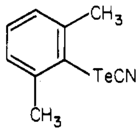

7

In only two cases were aryl tellurocyanides formed in isolable yields in addition to the diaryl tellurides. 2-Nitrophenyl tellurocyanide (**6**) and 2,6-dimethylphenyl tellurocyanide (**7**) were isolated after chromatography in 11% and 40% yields, respectively.

Of the few aromatic tellurocyanides known, most seem to have a stabilizing group in the 2-position that coordinates to the electron-deficient tellurium. Renson has synthesized the aromatic tellurocyanides **8** with 2-formyl,[20] 2-acetyl,[21] and 2-benzoyl[7] substituents. The only unsubstituted aromatic tellurocyanide seems to be the azulene derivative **9** obtained by Nefedov.[22]

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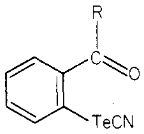
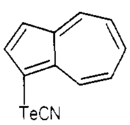


8, R = H, CH_3, C_6H_5



9

The relative stability of the 2-nitrophenyl tellurocyanide (**6**) can be understood in view of the theory for ortho stabilization.[23,24] On the other hand, the high yield of 2,6-dimethylphenyl tellurocyanide (**7**) is remarkable but might be attributed to steric factors. The two ortho methyl groups should serve to protect the labile tellurocyanide functionality. Surprisingly, no aryl tellurocyanide could be isolated when diazotized 2,4,6-tribromoaniline was treated with KTeCN.

In summary, the present synthesis of diaryl tellurides from aryldiazonium tetrafluoroborates and potassium tellurocyanide shows a generallity that has not been obtained by other methods. Our procedure is mild (essentially carried out at room temperature), compatible with a large variety of functional groups, and utilizes readily available starting materials (substituted aromatic amines are commercially available in a great variety). Although the yields are modest, we still feel that the present method should be the one of choice for the synthesis of many aromatic tellurides.

Experimental Section

Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 257 instrument. NMR spectra were obtained with a Bruker WP 200 instrument. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. All preparations of aryldiazonium tetrafluoroborates were performed in analogy with a literature procedure.[18] Copper powder was prepared according to Vogel.[29] Elemental analyses were performed by Centrala Analyslaboratoriet, Uppsala, Sweden.

Synthesis of Diaryl Tellurides. General Procedure. Potassium tellurocyanide was prepared accordig to a literature procedure[17] from freshly crushed and finely ground tellurium (1.60 g, 12.5 mmol) and potassium cyanide (0.82 g, 12.5 mmol) in dry dimethyl sulfoxide (20 mL) under N_2. This solution was then cooled in an ice bath until most of the solvent had crystallized. The diazonium tetrafluoroborate (12.5 mmol) was added rapidly while a brisk stream of nitrogen was passed through the open system to prevent any introduction of air. When the initial violent gas evolution had ceased, the ice bath was removed and stirring was continued at ambient temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (250 mL), filtered from the dark insoluble material (Te), and washed several times with water. Drying ($CaCl_2$) and evaporation yielded an oil or a semisolid that was filtered (CH_2Cl_2) through a short silica column. (In the few cases where mixtures of diaryl telluride and aryl tellurocyanide were formed, more careful chromatography was required, with CH_2Cl_2/hexane (1:1) as eluent.) The diaryl tellurides were frequently contaminated by small amounts of diaryl ditellurides. These impurities were conventiently removed (converted to diaryl tellurides) by treatment with copper powder in refluxing dioxane.[19] In the preparation of bis(2-carboxyphenyl) telluride, the crude product was extracted with aqueous sodium carbonate and precipitated with acid. No chromatographic purification was required in this case. All yields and melting points of the synthesized diaryl tellurides are listed in Table I. ^{1}H NMR and IR data for the new compounds **5**–**7** are given below.

5a: ^{1}H NMR δ 7.43–7.47 (several peaks, 2 H), 7.71 (m, 1 H), 7.87 (m, 1 H); IR 2220, 2230 cm^{-1} (C$\equiv$N).

5b: ^{1}H NMR δ 7.13–7.20 (several peaks, 2 H), 7.47 (m, 1 H), 7.63 (m, 1 H).

5c: ^{1}H NMR δ 7.71 (s).

5d: ^{1}H NMR δ 2.37 (s, 6 H), 7.04–7.09 (several peaks, 3 H).

6: yield after chromatography 0.38 g (11%); mp 160 °C (ligroin); ^{1}H NMR δ 7.62 (t, 1 H), 7.74 (t, 1 H), 8.46–8.52 (several peaks, 2 H); IR 2150 cm^{-1} (C$\equiv$N). Anal. Calcd for $C_7H_4N_2O_2Te$: C, 30.49; H, 1.46; N, 10.16. Found: C, 31.15; H, 1.59; N, 10.01.

7: yield after chromatography 1.31 g (40%); mp 114–115 °C (ligroin); ^{1}H NMR δ 2.69 (s, 6 H), 7.23–7.26 (several peaks, 3 H); IR 2140 cm^{-1} (C$\equiv$N). Anal. Calcd for C_9H_9NTe: C, 41.77; H, 3.51. Found: C, 42.16; H, 3.64.

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. **1** (Ar = 4-methylphenyl; X = BF_4), 459-44-9; **1** (Ar = 4-methoxyphenyl; X = BF_4), 459-64-3; **1** (Ar = 2-nitrophenyl; X = BF_4, 365-33-3; **1** (Ar = 4-nitrophenyl; X = BF_4), 456-27-9; **1** (Ar = 2-naphthyl, X = BF_4), 450-58-8; **1** (Ar = 2-biphenylyl; X = BF_4), 318-13-8; **1** (Ar = 2-bromophenyl; X = BF_4), 10448-07-4; **1** (Ar = 2,4,6-tribromophenyl; X = BF_4), 4639-13-8; **1** (Ar = 2-cyanophenyl; X = BF_4), 55165-45-2; **1** (Ar = 2,6-dimethylphenyl; X = BF_4), 2192-33-8; **1** (Ar = 2-carboxyphenyl; X = BF_4), 14783-89-2; **3**, 86436-77-3; **5a**, 86436-75-1; **5b**, 86436-73-9; **5c**, 86436-74-0; **5d**, 86436-76-2; **6**, 72726-15-9; **7**, 86436-78-4; Ar_2Te (Ar = 4-methylphenyl), 834-15-1; Ar_2Te (Ar = 4-methoxyphenyl), 4456-34-2; Ar_2Te (Ar = 2-nitrophenyl), 71129-54-9; Ar_2Te (Ar = 4-nitrophenyl), 63212-74-8; Ar_2Te (Ar = 2-naphthyl), 63212-75-9; Ar_2Te (Ar = 2-biphenylyl), 67684-62-2; KTeCN, 75437-09-1; Te, 13494-80-9; potassium cyanide, 151-50-8.

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