5-AZA-10-TELLURA-5,10-DIHYDROANTHRACENES (PHENOTELLURAZINES)

Thomas Junk and Kurt J. Irgolic

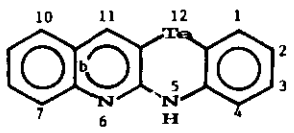
Department of Chemistry, Texas A&M University

College Station, Texas 77840 USA

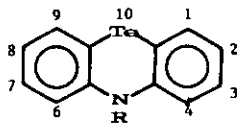
Abstract 5-Aza-10-tellura-5,10-dihydroanthracene (phenotellurazine) was prepared in seven percent yield by mercurating diphenylamine with mercury(II) acetate, converting the 4-acetatomercurodiphenylamine to the chloro derivative, and reacting it with tellurium tetrachloride. The 4-(phenylamino)phenyltellurium trichloride was not isolated but refluxed in glacial acetic acid for twelve hours to cause isomerization to 2-(phenylamino)phenyltellurium trichloride and cyclization to phenotellurazine 10,10-dichloride, which was reduced with aqueous sodium sulfide to phenotellurazine. Benzo[a]phenotellurazine was similarly obtained in 53 percent yield starting with 2-(phenylamino)naphthalene. The phenotellurazines were characterized by elemental analyses, ^{1}H-, ^{13}C- and ^{125}Te- nmr spectroscopy, and mass spectrometry.

The first phenotellurazine, 5,6-diaza-12-tellura-5,12-dihydrobenzo[b]anthracene **1** was reported[1] in 1977. The compound was obtained by heating 2-phenylaminoquinoline and tellurium tetrachloride at 200°C and reducing the resulting Te,Te-dichloride with sodium disulfite. Attempts to prepare phenotellurazine **2** (R = H), the parent compound of this class of heterocycles, by condensation of diphenylamine with tellurium tetrachloride failed.

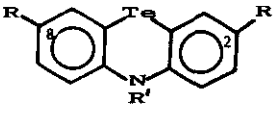
Sadekov[2-4], Bergman[5], and coworkers succeeded in preparing N-alkylphenotellurazines **2** ($R = CH_3$[5], C_2H_5[4]) and 2,8-disubstituted N-alkylphenotellurazines **3** ($R = CH_3$, $R' = C_2H_5$[2,3]; R = Br, $R' = CH_3$[4]; R = Br, $R' = C_2H_5$[4]) from tellurium diiodide and bis(2-lithiophenyl)alkylamines. The N-alkylphenotellurazines are stable, yellow to greenish-yellow, odorless, crystalline compounds with good solubility in acetone, chloroform, benzene, and toluene and slight solubility in light petroleum ether.



1



2



3

EXPERIMENTAL

Diphenylamine (Fisher Scientific), dichloromethane, methanol (A. T. Baker Chemical Co.), mercury(II) acetate, anhydrous lithium chloride (Aldrich), 2-(phenylamino)naphthalene (ICN Biochemicals), and sodium sulfide

nonahydrate (Fluka Chemie AG) were purchased from the vendors indicated and used as received. Tellurium powder was donated by ASARCO and converted to tellurium tetrachloride in a reaction with chlorine[6].

Mass spectra were recorded on a VG Analytical 70 S high resolution, double-focusing mass spectrometer with an attached VG Analytical 11/250 J data system. All samples were introduced via the direct probe inlet (probe temperature 115°C for phenotellurazine, 82°C for benzo[a]phenotellurazine) and ionized with a 70-eV electron beam. The nominal masses were determined by reference to a perfluorokerosene standard. The identities of the molecular ion peaks were confirmed comparing experimental with calculated peak clusters generated by the Te isotopes. ^{1}H-nmr spectra were recorded on Varian XL-200 and XL-400 Fourier Transform spectrometers using 0.5 M solutions in $CDCl_3$. ^{13}C-Proton-noise-decoupled nmr spectra (600 transients) and ^{125}Te-nmr spectra (8000 transients) were obtained on a Varian FT-80 spectrometer. Elemental analyses were performed by Gailbraith Laboratories, Knoxville, TN.

Phenotellurazine. Diphenylamine (26.5 g, 0.16 mol), mercury(II) acetate (50 g, 0.16 mol), and methanol (500 mL) were placed into a 1-l round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The mixture containing some precipitate was stirred and gently refluxed for 12 h, and then cooled to room temperature. A solution of lithium chloride (14 g, 0.33 mol) in methanol (50 ml) was added. The mixture was stirred for 12 h at room temperature. The white product (4-chloromercurodiphenylamine) precipitated, was collected by filtration, and dried in a desiccator over silica gel. Yield: 56 g (80%); mp >250°.

Crude chloromercurodiphenylamine[7] (20 g, 50 mmol), tellurium tetrachloride (13.3 g, 50 mmol), and glacial acetic acid (100 ml) were placed into a 250-ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The greenish mixture was refluxed and stirred for 12 h. The solvent was subsequently removed on a rotary evaporator at 70°C under an aspirator vacuum. A saturated aqueous solution of sodium sulfide (50 ml) was then added to the green residue. The mixture that had turned black was stirred at room temperature for 30 min. Then dichloromethane (100 ml) was added and the mixture stirred for 1 h. The mixture was filtered through a Buchner funnel and the filter cake washed with two portions of dichloromethane (50 ml each). The washings were combined with the filtrate. The organic layer was separated and dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator at 40°C under an aspirator vacuum. The concentrate was subsequently placed on a column (1.5 x 10 cm) of silica gel (activity I) and eluted with dichloromethane. The yellow fractions that eluted close to the solvent front were collected. The solvent was evaporated. The solid residue was placed into a sublimator equipped with a Dry Ice-cooled coldfinger. The sublimator was evacuated (0.5 Torr) and heated to 180°C in an oil bath. Yellow needles slowly condensed on the coldfinger. After 1 h the sublimation was complete. The sublimator was removed from the oil bath, the vacuum broken, and the sublimate dissolved in dichloromethane (30 ml). Evaporation of the solvent produced 1.0 g (7%) phenotellurazine **2** (R = H) mp 176° (dec). Found (calcd) for $C_{12}H_9NTe$ (294.81): C 49.15 (48.89); H 3.18 (3.08).

Benzo[a]phenotellurazine. 2-(Phenylamino)naphthalene (34.3 g, 0.16 mol), mercury(II) acetate (50 g, 0.16 mol) and methanol (600 ml) were placed in a 1-l round-bottomed flask equipped with a magnetic stirrer and reflux condenser. The mixture was refluxed for 8 h (heating mantle). Lithium chloride (6.7 g, 0.16 mol) in methanol (50 ml) was added. The heating mantle was removed, and the mixture allowed to cool to room temperature. The product [1-chloromercuro-2-(phenylamino)naphthalene] precipitated and was collected on a Buchner funnel. Yield: 64 g (90%); decomp. 180°.

Chloromercuro-2-(phenylamino)naphthalene (8.44 g, 18.6 mmol), tellurium tetrachloride (5.0 g, 18.6 mmol), and glacial acetic acid (40 ml) were placed in a 100-ml round-bottomed flask equipped with magnetic stirrer and a reflux condenser. The mixture was refluxed for 12 h (heating mantle) and then allowed to cool. The precipitated solid was collected by filtration and washed with dichloromethane (50 ml). The solid was placed in a 250-ml round-bottomed flask. Dichloromethane (100 ml), sodium sulfide nonahydrate (20 g), and water (100 ml) were added. The mixture was stirred at ambient temperature for 5 h. Large lumps were broken up with a glass rod to ensure complete reduction. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed at 50°C under an aspirator vacuum, the yellow crystalline residue dissolved in boiling methanol (250 ml), and insoluble material removed by filtration. The solution was concentrated to 40 ml. The concentrate was cooled in an ice bath. Benzo[a]phenotellurazine **4** crystallized as yellow needles, which were collected by filtration. Yield: 3.4 g (53%); mp 164 - 166°. Found (calcd) for $C_{16}H_{11}NTe$ (344.87): C 55.26 (55.72); H 2.87 (3.22).

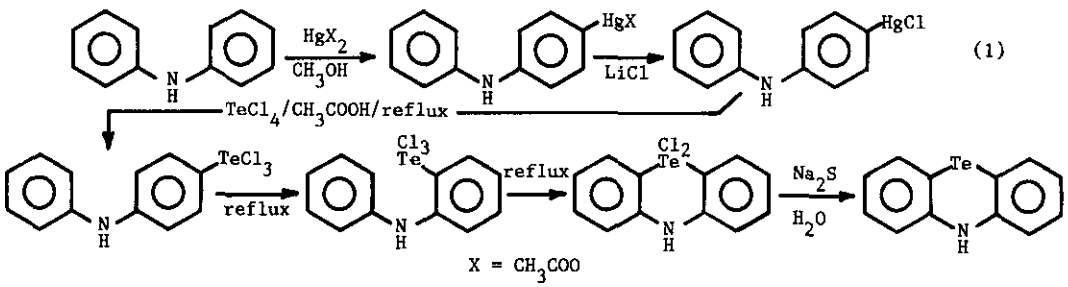
Phenotellurazine 10,10-dibromide. Phenotellurazine **2** (0.50 g, 1.69 mmol) was dissolved in chloroform (20 ml) and bromine added until the brown color persisted. A reddish-brown precipitate formed and was collected by filtration. Yield: 0.63 g (82%); mp >250°. Found (calcd) for $C_{12}H_9Br_2NTe$ (454.62): C 31.34 (31.70); H 2.03 (2.00).

Benzo[a]phenotellurazine 10,10-dibromide. Benzo[a]phenotellurazine **4** (0.50 g, 1.45 mmol) was dissolved in chloroform (20 ml) and bromine added until the brown color persisted. A yellow precipitate formed and was collected by filtration. Yield: 0.46 g (63%); mp >250°. Found (calcd) for $C_{16}H_{11}Br_2NTe$ (504.60): C 37.90 (38.08); H 1.76 (2.20).

RESULTS AND DISCUSSION

Because the condensation of tellurium tetrachloride and diphenylamine had failed to produce phenotellurazine, an alternate route was developed that does not require the replacement of the amine-hydrogen by a protective group. Diphenylamine was mercurated with mercury(II) acetate to 4-(acetatomercuro)diphenylamine[7]. The acetate group was exchanged for chloride by addition of lithium chloride. The precipitated 4-chloromercurodiphenylamine was isolated and then reacted with tellurium tetrachloride in glacial acetic acid to produce 4-(phenylamino)phenyl-

tellurium trichloride. This compound isomerized in refluxing glacial acetic acid to 2-(phenylamino)phenyltellurium trichloride, which in turn was cyclized to phenotellurazine 10,10-dichloride. A saturated aqueous solution of sodium sulfide was used to reduce the dichloride to the phenotellurazine (eqn. 1), which was purified by column



(1)

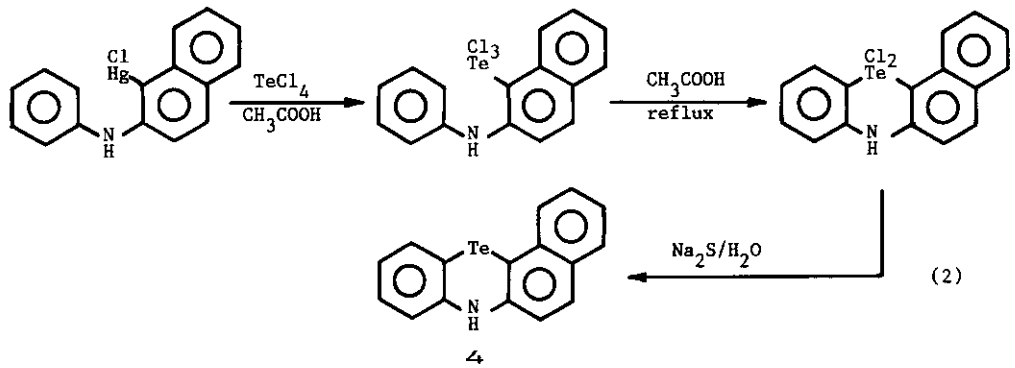
chromatography (SiO_2) and vacuum-sublimation. Phenotellurazine could not be obtained in more than seven percent yield based on tellurium tetrachloride in spite of valiant attempts to improve the yield. Neither dioxane that precipitates the mercury(II) chloride formed in the transmetallation reaction as an insoluble adduct nor trifluoroacetic acid was suitable as the solvent. Heating the reactants in glacial acetic acid for three hours gave no phenotellurazine. Reflux periods longer than twelve hours did not increase the yield above seven percent. The refluxing reaction mixtures became homogeneous but deposited later a whitish precipitate and acquired a greenish color. Black tellurium did not form during this phase of the reaction.

Aliquots of the reaction mixture taken two hours after the reagents had been mixed produced upon reduction with aqueous sodium sulfide black materials, from which a very unstable red ditelluride was extracted that decomposed quickly to elemental tellurium. The instability of the ditelluride prevented its identification. Reduction of aliquots at later times resulted also in black materials, but a ditelluride could not be extracted from them. Tellurium tetrachloride is known to form complexes with amines[8]. Complex formation with the diphenylamine moiety very likely competes with the transmetallation reaction. The 4-(phenylamino)phenyltellurium trichloride formed isomerizes to the 2-(phenylamino)phenyltellurium trichloride, which then condenses to the heterocycle. A similar isomerization reaction leads from 4-phenoxyphenyltellurium trichloride to phenoxtellurine 10,10-dichloride[9]. Early in the reaction, when isomerization and cyclization are not complete, the tellurium trichlorides can be reduced to unstable ditellurides. When isomerization and cyclization are complete, the aqueous sodium sulfide decomposes the $TeCl_4$ • amine adduct to elemental tellurium. The adduct once formed does not appear to dissociate into its components. Such a dissociation would allow additional transmetallation and formation of the heterocycle. Prolonged heating did not produce more phenotellurazine.

Alternatively, the mercuration of diphenylamine could have produced 4-chloromercurodiphenylamine and some 2-chloromercurodiphenylamine. Both compounds are expected to react with tellurium tetrachloride to yield the corresponding aryl tellurium trichlorides. Perhaps only the ortho-isomer condensed to phenotellurazine

10,10-dichloride and the para-isomer did not convert to the ortho-isomer. Mercury-199 nmr spectra of the crude chloromercurodiphenylamine dissolved in trifluoroacetic acid contained several signals that could not be assigned unambiguously. No definite statement about the presence of isomers can be made on the basis of the complex proton spectrum. Attempts to isolate the (phenylamino)phenyltellurium trichlorides gave only intractable mixtures. Although definitive reasons for the low yields of phenotellurazines cannot be given, we favor the sequence of steps shown in eqn. 1 and believe, that the formation of an adduct between tellurium tetrachloride and diphenylamine is responsible for the low yield of phenotellurazine.

Reaction of tellurium tetrachloride with 1-chloromercuro-2-phenylaminonaphthaline produced similarly benzo[a]phenotellurazine 10,10-dichloride, which was reduced with sodium sulfide to benzo[a]phenotellurazine **4** (eqn. 2). The yield based on tellurium tetrachloride was 53 percent. The reason for the high yield of the benzo[c]phenotellurazine might lie with the transmetallation reaction that is favored over the adduct formation or the fact that an isomerization of the aryltellurium trichloride is not required.



(2)

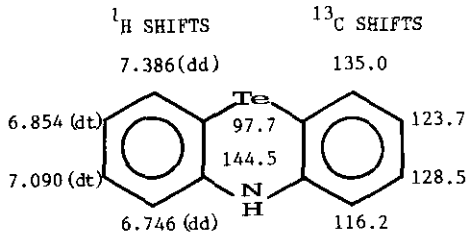
4

Phenotellurazine and benzo[a]phenotellurazine were obtained as yellow, crystalline compounds. Phenotellurazine is isomorphous with phenoxtellurine (5-oxa-10-tellura-5,10-dihydroanthracene) and is folded along the N-Te axis. The central ring is in the boat conformation. Each of the two phenyl rings is planar with a dihedral angle of 38.0° between the two planes of the phenyl rings. The molecule is bent back along the C-C axes of the central ring achieving a butterfly-like conformation[10]. The presence of an N-H group in these phenotellurazines results in thermal and chemical stabilities lower than those observed for N-alkylphenotellurazines. Prolonged exposure of solid phenotellurazine to air caused a green discoloration. Phenotellurazine decomposed at its melting point of 176°C. Addition of concentrated hydrochloric or perchloric acid to solid phenotellurazine produced dark blue solids. Like other divalent tellurium compounds, the phenotellurazines are easily converted to compounds of tetravalent tellurium. The phenotellurazines formed the Te,Te-dibromides on treatment with bromine.

The mass spectrum of phenotellurazine shows a molecular-ion peak cluster (m/z 297 for $^{12}C_{12}{}^{1}H_{9}{}^{14}N^{130}Te^{+}$) easily

recognizable by the tellurium isotope pattern. The base peak at m/z 167 ($C_{12}H_8NH^+$) is formed by extrusion of tellurium from the molecular ion. The ion at m/z 167 loses HNC to give benzotropylium-like fragments at m/z 140 and 139 ($C_{11}H_8^{+\cdot}$, $C_{11}H_7^+$). Benzo[a]phenotellurazine fragments similarly producing from the molecular ion at m/z 347 the ions at m/z 217 and 190/189.

The proton and carbon chemical shifts of phenotellurazine are listed below. The proton spectrum consists of two doublets (H-1, H-4) and two triplets (H-2, H-3) with J_{12}, J_{23}, and J_{34} coupling constants all equal at 7.57 Hz. Four-bond couplings (J_{13}, J_{24} = 1.32 Hz) split each signal into a doublet. The assignments are based on nmr data reported for related compounds (phenothiazine, phenoxachalcogenines)[11]. The carbon atoms bonded to the tellurium atom resonate at 97.7 ppm in the range found for similar carbon atoms in diphenyl ditelluride[12] (108 ppm) and phenoxtellurine[13] (102 ppm). Whereas the C-Te carbon atoms are shielded, the C-N carbon atoms resonating at 144.5 ppm are deshielded with respect to the carbon atoms in benzene (128.8 ppm). The ^{125}Te-resonance for phenotellurazine was located at 409.0 ppm and for benzo[a]phenotellurazine at 293.6 ppm relative to dimethyl telluride. These ^{125}Te shifts are in the range found for similar tricyclic compounds (phenoxtellurine 424 ppm, 5-tellura-5,10-dihydroanthracene 512 ppm).[14] The upfield shift change of 115 ppm upon annelation of a benzene ring to phenotellurazine is noteworthy.



ACKNOWLEDGEMENTS

The financial support of these investigations by the Robert A. Welch Foundation of Houston, Texas and a gift of elemental tellurium by ASARCO Incorporated, Amarillo, Texas are greatfully acknowledged.

REFERENCES

1. W. Zankovska-Jasinska and M. M. Burgiel, Zeszyty Naukowe Univ. Jagiellonskiego, Prace Chem., 1977, **22**, 49.

2. I. D. Sadekov, G. M. Abakarov, A. D. Garnovskii, Yu. S. Varshavskii, T. G. Cherkasova, and V. I. Minkin, Dokl. Akad. Nauk SSSR, Ser. Khim., 1982, **271**, 1164.

3. I. D. Sadekov, G. M. Abakarov, A. D. Garnovskii, and V. I. Minkin, Khim. Geterotsikl. Soedin., 1982, 707.

4. I. D. Sadekov, G. M. Abakarov, V. B. Panov, L. Yu. Ukhin, A. D. Garnovskii, and V. I. Minkin, Khim. Geterotsikl. Soedin., 1985, 757.

5. J. Bergman and L. Engman, J. Organomet. Chem., 1983, **251**, 223.

6. L. Vanino," Handbuch der Präparativen Chemie", Vol. 1, Ferdinand Enke, Stuttgart, Germany, 1913, p. 105.

7. L. Prussia, Gaz. Chim. Ital., 1898, **28**, 31 and 129.

8. Gmelin Handbuch der Anorganischen Chemie, Tellur, Ergänzungsband B3, 1978, p. 166 and references therein.

9. H. D. K. Drew, J. Chem. Soc., 1926, 223.

10. E. A. Meyers, T. Junk, and K. J. Irgolic, unpublished.

11. I. C. Calder, R. B. Johns, and J. M. Desmarchelier, Aust. J. Chem., 1971, **24**, 325.

12. A. Forchioni, V. Galasso, K. J. Irgolic, and G. C. Pappalardo, J. Organomet. Chem., 1977, **135**, 327.

13. V. Galasso, K. J. Irgolic, and G. C. Pappalardo, J. Organomet. Chem., 1979, **181**, 329.

14. D. H. O'Brien, K. J. Irgolic, and C. -K. Huang, Proc. 4th Intern. Symp. Organic Se, Te Chemistry, 1983, Univ. Aston, Birmingham, U.K., University Aston Press, 1983, p. 468; and references therein.

Received, 19th September, 1988