NITROGEN-TELLURIUM HETEROCYCLES.

2.* APPROACHES TO THE SYNTHESIS OF 2-SUBSTITUTED BENZOTELLURAZOLES

I. D. Sadekov, G. M. Abakarov, A. A. Shneider, S. G. Kuren', A. G. Starikov, A. D. Garnovskii, and V. I. Minkin

Several 2-substituted benzotellurazoles have been prepared by the reaction of N-allyl derivatives cf o-methyltelluroaniline with $POCl_3$ or $SOCl_2$ followed by reduction of the σ -telluranes which are formed. The use of the zinc and sodium salts of o-aminotellurophenol and 2-chlorotellurenylazobenzene, in a procedure similar to that used to prepare benzothiazoles and benzoselenazoles, did not lead to the formation of benzotellurazoles.

In contrast to benzoselenazoles [2] and benzothiazoles [3], methods for the preparation of benzotellurazoles (I) have received little attention. The first synthesis of azoles with very low yields (2-15%) by the cyclization of N-acyl derivatives of o-ethyltelluroaniline under the action of POCl₃ was reported in [4]. We have shown [1] that the yields of benzotellurazoles, isolated in the form of Te, Te-dichloroderivatives, increases significantly, reaching 35% for 2-methylbenzotellurazole and 65% for 2-phenylbenzotellurazole, if one uses in the reaction N-acyl derivatives of o-methyltelluroaniline II which have been subjected to preliminary purification and if one carries out the cyclization by boiling in POCl₃ for 6 h. The reaction products here are not benzotellurazoles I as in [4], but 1,1-dichlorobenzotellurazoles (III). From this, one can postulate a reaction scheme the first stage of which is probably the formation of either imidoylchlorides or complexes IV analogous to the intermediates of the Vilsmeier reaction [5]. These compounds, splitting off MeCl and HPO_2Cl_2 on heating, are converted to 2-substituted benzotellurazoles I which are oxidized by the conversion product of $POCl_3$ (HPO₂Cl₂) to the σ -telluranes III. In common with other σ -telluranes [6] compounds III are reduced to benzotellurazoles by sodium metabisulfite in practically quantitative yields.



A somewhat different mechanism can be suggested for the conversion of compounds II to benzotellurazoles under the action of thionyl chloride. This reagent, as is well known, on the one hand converts N-acyl groups to imidoylchlorides [7] and, on the other hand, it oxidizes a di-coordinated Te atom to a tetra-coordinated [6]. As a result of this, on treatment of N-acyl-o-methyltelluroanilines (II) with thionyl chloride, compounds were isolated whose elemental composition and PMR spectra corresponded to the σ -telluranes V, i.e., compounds with the Te(CH₃)Cl₂ group in the o-position to the -N=C(Cl)R grouping. Reduction of these compounds by means of an aqueous solution of sodium metabisulfite or hydrazine hydrate gave the benzotellurazoles I. Evidently the Te(II) derivatives which arise from the reduction of the Te(IV) derivatives (V) have the imidoylchloride structure VI and readily split off methyl chloride forming the heterocycles I. Examples of a similar elimination of

*For Communication 1, see [1].

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Com- pound*	R	Formula	Cycliz- ing agent	mp, °C from hexane	Yield, %
la Ib Ic Id Ie If	CH ₃ C ₆ H ₅ <i>p</i> -CH ₃ C ₆ H ₄ <i>p</i> -CH ₃ OC ₆ H ₄ <i>p</i> -BrC ₆ H ₄ <i>p</i> -ClC ₆ H ₄	C₅H7NTe C13H4NTe C14H11NTe C14H11NOTe C13H8BrNTe C13H8CINTe	POCI ₃ POCI ₃ POCI ₃ POCI ₃ SOCI ₂ SOCI ₂	$\begin{array}{r} 96 \dots 98 \\ 101 \dots 103 \\ 110 \dots 112 \\ 106 \dots 108 \\ 136 \dots 138 \\ 123 \dots 125 \end{array}$	$35 \\ 65 \\ 55 \\ 58 \\ 44 \\ 40$

TABLE 1.2-R-Benzotellurazoles (Ia-f)

*PMR spectra of compounds Ic-f corresponded to the proposed structures.

a molecule of methyl chloride from compounds with chlorine atoms activated by electron-acceptor groups are well known and are used for the synthesis of certain tellurium heterocycles: tellurocoumarin [8] and telluroisocoumarin [9].



The use of thionyl chloride leads to benzotellurazoles with yields comparable to those of compounds prepared using $POCl_3$. Thus, the yield of compound Ib when using $POCl_3$ as cyclizing agent is 65%, whereas when using $SOCl_2$ the yield is 59% (Table 1). It should, however, be noted that neither with $POCl_3$ nor with $SOCl_2$ is it possible, notwithstanding [4], to prepare unsubstituted benzotellurazoles; attempts to cyclize the N-acetyl derivative IIa with thionyl chloride led only to tarry products of unknown structure, probably as a result of a side reaction - chlorination at the methyl group [7].

We also undertook experiments in the preparation of benzotellurazoles using compounds the sulfur and selenium analogs of which have been successfully employed to prepare the corresponding benzochalcogenazoles. It is known that the zinc salts of o-aminothiophenol [3, 10-12] and o-aminoselenophenol react with acid chlorides to give the corresponding 2-substituted benzochalcogenazoles in high yield. However, treatment of the zinc salt of o-aminotellurophenol VII, the preparation of which we have reported previously [16], with benzoyl chloride under various conditions was accompanied by partial elimination of tellurium and the N-benzoyl derivative of di(o-aminophenyl)ditelluride (VIII) was isolated as the main product. Compound VIII was identified in the form of the N-benzoyl derivative of o-methyltelluroaniline after reduction with sodium borohydride and subsequent treatment with dimethyl sulfate.

Another way of using the zinc salts of o-aminochalcogenophenols in the preparation of benzochalcogenazoles is to react them with aromatic aldehydes which, depending on the solvent, temperature, and reaction time, leads to either zinc complexes of arylidene-o-aminochalcogenophenols [3, 17], or benzochalcogenazoles [2, 3, 11, 17]. However, treatment of the zinc salt of o-aminotellurophenol with benzaldehyde under various conditions (boiling an equimolar mixture of the compounds in 2-propanol or dioxan, heating the zinc salt of o-aminotellurophenol VII with an excess of benzaldehyde at different temperatures) always led to bis(2-aminobenzylidene)ditelluride (IX), identical with the compound obtained by the reaction of bis(oaminophenyl)ditelluride with 2 moles of benzaldehyde in ethanol.



One of the most generally applicable methods for the synthesis of benzothiazoles is the reaction of o-aminothiophenols with carboxylic acids or their derivatives [3]. In this case, o-acylaminothiophenols are the intermediate products. S-Acyl derivatives of thiophenols are excluded as possible intermediates because of their facile rearrangement to N-acyl derivatives. A similar rearrangement is observed for analogous tellurium derivatives. On treating the sodium salt of o-aminotellurophenol, prepared by reduction of bis(o-aminophenyl)ditelluride with sodium borohydride in ethanol, with benzoyl chloride the product isolated was not the o-aminophenyltellurium ester of benzoic acid (X) but the N-benzoyl derivative of bis(o-aminophenyl)ditelluride (VIII), probably formed by rearrangement of compound X and subsequent oxidation of the TeH group to ditelluride. Compound VIII was identified, as before, in the form of the N-benzoyl derivative of o-methyltelluroaniline IIb. The physical constants of compound IIb obtained in this way were in complete agreement with those of compound IIb prepared [1] by acylation of bis(o-aminophenyl)ditelluride with benzoyl chloride in the presence of triethylamine with subsequent reduction and alkylation.

Attempts to use 2-chlorotellurenylazobenzene [18] for the preparation of benzotellurazoles also proved unsuccessful. In contrast to the corresponding sulfur compound [19], which gives 2-substituted benzothiazoles on reaction with compounds having active methyl or methylene groups (acetone, acetophenone, malonic acid), 2-chlorotellurenylazobenzene did not enter into reaction with such compounds. Thus, one can say that methods for the preparation of benzotellurazoles, as for many other tellurium heterocycles (see reviews [20, 21]) are highly specific and many of the classic reactions for the synthesis of benzothiazoles cannot be used for the preparation of benzotellurazoles.

The hydrogen atoms of the methyl group of 2-methylbenzotellurazole (Ia) prove to be sufficiently mobile for it to be used for the synthesis of a series of new benzotellurazole derivatives. In a similar manner to the other 2-methylbenzochalcogenazoles [2, 3] compound Ia reacts with aromatic aldehydes in the presence of catalytic quantities of zinc chloride with the formation of 2-styrylbenzotellurazoles (XI) in yields of over 60%.



XI a $R=NO_2$, b R=H. c $R=OCH_3$, d $R=OC_2H_5$

On heating 2-methylbenzotellurazole with an excess of methyl iodide in a sealed ampul, the iodide of 2,3-dimethylbenzotellurazole (XII) is formed and this reacts with orthoformic ester and 2-methyl-substituted quaternary heterocycles to form symmetrical and unsymmetrical cyanine dyes XIIIa-d.



It is interesting to note that in the electronic absorption spectrum of compound XIIIa the long-wave band shows a bathochromic shift of 52 nm compared to the sulfur analog (λ_{max} 558 nm [22]).

EXPERIMENTAL

Infrared spectra of the compounds, in the form of mulls in mineral oil, were run on a UR-20 spectrophotometer. PMR spectra were obtained from solutions in $CDCl_3$ on a Tesla BS-487C (80 MHz) instrument with HMDS as internal standard.

N-Acyl derivatives of o-methyltelluroaniline (IIc-f) not described earlier were prepared by the method of [1]. The results of the elemental analyses were in agreement with the calculated data.

<u>o-Methyltelluro-N-(p-methylbenzoyl)aniline (IIc, $C_{15}H_{15}NOTe$)</u>. Colorless needles, mp 118-120°C (from 2-propanol); yield 80%. PMR spectrum (δ , ppm): 1.85 (3H, s, Te-CH₃), 2.25 (3H, s, C-CH₃), 6.70-8.45 (8H, m, aromatic protons), 8.90 (1H, s, NH).

<u>o-Methyltelluro-N-(p-methoxybenzoyl)aniline (IId, $C_{15}H_{15}NO_2Te$).</u> Colorless needles, mp 108-110°C (from 2-propanol); yield 60%. PMR spectrum (δ , ppm): 1.90 (3H, s, TeCH₃), 3.70 (3H, s, OCH₃), 6.65-8.40 (8H, m, aromatic protons), 8.85 (1H, s, NH).

<u>o-Methyltelluro-N-(p-chlorobenzoyl)aniline (IIe, $C_{14}H_{12}CINOTe$)</u>. Colorless needles, mp 100-102°C (from 2-propanol); yield 78%. IR spectrum (cm⁻¹): 3260 (ν_{NH}), 1635 (C=O)

<u>o-Methyltelluro-N-(p-bromobenzoyl)aniline (IIf, $C_{14}H_{12}BrNOTe$).</u> Colorless needles, mp 117-119°C (from 2-propanol); yield 83%. PMR spectrum (δ , ppm): 1.90 (3H, s, TeCH₃), 6.73-8.43 (8H, m, aromatic protons), 8.93 (1H, s, NH). IR spectrum (cm⁻¹): 3267 (ν_{NH}), 1635 (C=0).

<u>Benzotellurazoles (Ia-d)</u> were prepared using $POCl_3$ as cyclizing agent by the method of [1].

<u>N-(2-Methyltellurodichlorophenyl)-4-bromobenzimidochloride (Vf, $C_{1.4}H_{1.1}BrCl_{3}NTe$).</u> A solution of 4.18 g (10 mmoles) compound IIf in 20 ml SOCl₂ was heated at bp for 5 h. The remaining thionyl chloride was removed under reduced pressure and the yellow residue recrystallized from 1:1 benzene-hexane. Yellow crystals, mp 166-168°C; yield 4.71 g (93%). PMR spectrum (δ , ppm): 3.13 (3H, s, TeCH₃), 7.33-8.13 (8H, m, aromatic protons). IR spectrum (cm⁻¹): 1640 (C=N).

Compounds Vb and Ve were prepared in a similar manner.

<u>N-(2-Methyltellurodichlorophenyl)benzimidochloride (Vb, $C_{14}H_{12}Cl_3NTe$).</u> Yellow crystals, mp 153-155°C (from 1:1 benzene-hexane); yield 90%. PMR spectrum (δ , ppm): 3.10 (3H, s, TeCH₃), 7.13-8.25 (9H, m, aromatic protons). IR spectrum (cm⁻¹): 1647 (C=N).

<u>N-(2-Methyltellurodichlorophenyl)-4-chlorobenzimidochloride (Ve, C₁₄H₁₁Cl₄NTe).</u> Yellow crystals, mp 153-155°C (from 1:1 benzene-hexane); yield 92%. IR spectrum (cm⁻¹): 1643 (C-N).

<u>2-(p-Bromophenyl)benzotellurazole (If).</u> A suspension of 4.71 g (9.3 mmoles) σ -tellurane Vf in 100 ml water was vigorously stirred at 60-80°C with a solution of 10 g (52.6 mmoles) sodium metabisulfite in 100 ml water for 30 min. The precipitate which formed was filtered off, washed with water, and dried. Yield 1.58 g (44%). Yellowish crystals, mp 136-138°C (from hexane).

<u>2-Phenylbenzotellurazole (Ib) and 2-(p-chlorophenyl)benzotellurazole (Ie)</u> were prepared similarly (Table 1).

<u>Bis(2-aminophenyltellurato)zinc (VII, $C_{12}H_{12}N_2TeZn$).</u> To a solution of 1.46 g (3.3 mmoles) bis(o-aminophenyl)ditelluride in 40 ml dry methanol, NaBH₄ was added in small portions with vigorous stirring under argon until the initial deep red color was discharged. To the solution so obtained a deaerated solution of 0.61 g (3.3 mmoles) zinc acetate in 20 ml methanol was added with stirring. A precipitate of the zinc salt VII was immediately formed and was filtered off, washed with ether, and dried in a vacuum desiccator. Yield 1.36 g (81%). Fine, light cream-colored crystals, mp 183-185°C (decomp.). IR spectrum (cm⁻¹): 3200 (NH).

<u>o-Methyltelluro-N-benzoylaniline (IIb).</u> To a suspension of 2.62 g (5.2 mmoles) compound VII in 4 ml dry pyridine was added, with stirring at room temperature, a solution of 1.45 g (10.4 mmoles) benzoyl chloride in 4 ml CHCl₃. An exothermic reaction occurred accompanied by the separation of a small amount of metallic tellurium. The reaction mixture was heated at bp for 3 min and poured into 50 ml cold water. The precipitate of the ditelluride VIII was filtered off, washed with water, dried, and converted into o-methyltelluro-N-benzoylaniline (IIb) by the method of [1]. Yield 2.66 g [77% on bis(o-aminophenyl)ditelluride], mp 123-125°C (from 2-propanol); from the results of [1], 123-125°C.

<u>Bis(2-benzylideneaminophenyl)ditelluride (IX, $C_{26}H_{20}N_2Te_2$).</u> <u>A.</u> To a boiling solution of 0.504 g (1 mmole) tellurophenolate VII in 30 ml dry 2-propanol was added 0.32 g (3 mmoles) freshly distilled benzaldehyde and boiling continued for 2 h. Three-fourths of the solvent was distilled off and the solution cooled. The crystalline precipitate was filtered off and dried. Yellow-orange crystals, mp 202-204°C (from 1:1 ethanol-benzene). Yield quantitative.

<u>B.</u> To a solution of 2.2 g (5 mmoles) bis(o-aminophenyl)ditelluride in 50 ml 2-propanol was added, dropwise, 1.06 g (10 mmoles) freshly distilled benzaldehyde and the solution held at bp until yellow-orange crystals deposited. The crystals were filtered off, washed with hexane, and dried. Yellow-orange crystals, mp 202-204°C (from 1:1 ethanol-benzene). Yield 3.54 g (89%).

<u>1-(2-Benzotellurazoly1)-2-(4-nitropheny1)ethene (XIa, $C_{15}H_{10}N_2O_2Te$).</u> A mixture of 0.98 g (4 mmoles) 2-methylbenzotellurazole, 0.6 g (4 mmoles) 4-nitrobenzaldehyde, and 0.05 g (0.37 mmole) zinc chloride was melted and heated at 140-160°C for 3 h. The cooled reaction mixture was treated with 40 ml methanol, the insoluble precipitate filtered off, washed with hexane, and recrystallized from toluene. Orange crystals, mp 194-196°C, yield 0.94 g (62%).

 $\frac{1-(2-\text{Benzotellurazolyl})-2-\text{phenylethane (XIb, C_{15}H_1)NTe}}{(\text{yellow crystals, mp 183-184°C (from toluene), yield 61%], 1-(2-benzotellurazolyl)-2-(4-methoxyphenyl)ethene (XIc, C_{16}H_{13}NOTe)}{(\text{yellow crystals, mp 152-154°C (from toluene), yield 65%}), and 1-(2-benzotellurazolyl)-2-(4-ethoxyphenyl)ethene (XId, C_{17}H_{15}NOTe)}{(\text{lemon-yellow crystals, mp 172-174°C (from toluene), yield 64%})} were prepared in a similar manner.}$

<u>2,3-Dimethylbenzotellurazole iodide (XII, $C_{g}H_{10}INTe$)</u>. A mixture of 0.8 g (3.3 mmoles) 2-methylbenzotellurazole and 5 ml (80 mmoles) freshly distilled methyl iodide was heated in a sealed ampul in a boiling water bath for 8 h. The mixture was cooled and the fine crystalline precipitate filtered off, washed with ether, and dried. Yield 1.23 g (98%). Deep yellow powder, mp 248-250°C. PMR spectrum (in DMSO-D₆) (δ , ppm): 2.78 (3H, s, 2-CH₃), 3.78 (3H, s, 3-CH₃), 6.87-8.11 (4H, m, aromatic protons).

Cyanines XIIIa-d were prepared by methods similar to those described previously [23].

 $\frac{2-[3-(2,3-\text{Dihydro-3-methyl-2-benzotellurazolidene)-1-propenyl]-3-methylbenzotellurazole}{\text{Iodide (XIIIa, C₁₉H₁₇IN₂Te). A mixture of 0.387 g (1 mmole) compound XII and 0.4 ml (2.7 mmoles) orthoformic ester in 15 ml acetic anhydride was heated at bp for 20 min. After cooling, the precipitate was filtered off, washed with ether, and dried. Deep green crystals, mp 300-303°C (from DMF); yield 0.53 g (81%). UV spectrum (in DMF) [<math>\lambda_{max}$, nm (log ε)]: 316 (2.93), 373 (2.90), 610 (3.78).

 $\frac{2-[3-(2,3-\text{Dihydro-3-methyl-2-benzoxazolidene)-1-propenyl]-3-methylbenzotellurazole}{\text{Iodide (XIIIb, C₁₉H₁₇IN₂OTe). A mixture of 0.48 g (1.5 mmoles) 2,3-dimethylbenzotazole p-toluene sulfonate, 0.5 ml (3 mmoles) orthoformic ester, and 15 ml acetic anhydride was heated until the color deepened and added to a mixture of 0.58 g (1.5 mmoles) compound XII, 1 ml (17 mmoles) triethylamine, and 10 ml acetic anhydride. This mixture was then heated for 15 min on a water bath, cooled, and diluted with 120 ml ether. The crystals which separated were filtered off, washed with ether, and recrystallized from methanol. Deep claret-colored crystals, mp 243-246°C, yield 0.31 g (82%). UV spectrum (in DMF) [<math>\lambda_{max}$, nm (log ε)]: 309 (2.92), 368 (2.91), 546 (3.89).

 $\frac{2-[3-(2,3-\text{Dihydro-3-methyl-2-benzeneselenazolidene)-1-propenyl]-3-\text{methylbenzotellur-}}{\text{azole iodide (XIIIc, C_{19}H_{17}IN_2SeTe)} [deep violet crystals, mp 274-277°C (from DMF), yield 70%. UV spectrum (in DMF) (<math>\lambda_{max}$, nm (log ε)]: 305 (3.05), 574 (3.99).

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9-IMINO(AMINO)-10-SILA-2-AZAANTHRACENES

N. S. Prostakov, A. V. Varlamov, A. A. Fomichev, A. É. Aliev, V. M. Polosin, V. A. Rezakov, and Hussein Annan
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9-Imino derivatives of dihydrosilaazaanthracenes were obtained from 10,10-diorganosila-2-azaanthrones. It was shown by PMR spectroscopy that they exist in the form of Z and E isomers. The azomethines were reduced to secondary amines, from which the N-acyl derivatives were obtained.

The previously undescribed azomethines 10,10-dimethyl- and 3-methyl-10,10-diphenyl-9phenylimino-10-sila-2-azaanthracenes (III, IV) and also 10,10-dimethyl-9-(2,4-dinitrophenylhydrazono)-10-sila-2-azaanthracene (V) were obtained by the condensation of the corresponding 10-sila-2-azaanthrones (I) and (II) [1, 2] with aniline or 2,4-dinitrophenylhydrazine in the presence of boron trifluoride etherate or anhydrous zinc chloride, where the latter proved more effective.



I, III, V R=CH₃, R¹=H; II, IV R=C₆H₅, R¹=CH₃; III, IV R²=C₆H₅; V R²= =NH--C₆H₃(NO₂)₂-2,4

In view of the analogy between the carbonyl and imino groups [3] we investigated the reaction of (III) with organometallic compounds. The azomethine (III) does not react with phenylmagnesium bromide on account, evidently, of steric hindrances. The action of phenyllithium leads to phenylation of the pyridine fragment of the azomethine molecule at position 1. 10,10-Dimethyl-1-phenyl-9-phenylimino-10-sila-2-azaanthracene (VI) and 10,10-dimethyl-9-phenylamino-10-sila-2-azaanthracene (VII) were isolated from the reaction mixture with identical yields (30%). The secondary amine is evidently formed as a result of reduction of the azomethine bond by the lithium hydride produced during nucleophilic substitution of another azomethine molecule at position 1. The data from the PMR spectrum of (VI) confirm its structure (Table 1) (see scheme below).

At room temperature, according to the data from PMR spectroscopy, the azomethines (III, IV) and the dinitrophenylhydrazone (V) represent mixtures of the Z and E isomers (Table 1). The latter were identified on the basis of the effect of the magnetic anisotropy of the ben-

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