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NITROGEN—TELLURIUM-CONTAINING HETEROCYCLES.

3*. REACTION OF 2-PHENYLBENZOTELLURAZOLE AT THE HETEROATOMS

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UDC 547.789.9.04

Reactions of 2-phenylbenzotellurazole at both heteroatoms are studied. σ-Telluranes and molecular complexes with mercury and palladium salts are prepared. Exchange of a tellurium atom by sulfur is achieved. Alkylation of a heteroatom of the pyrrole type, the tellurium atom, is achieved in a series of benzazoles for the first time.

If in benzoxazoles (-thiazoles and -selenazoles) the main reaction centers are the nitrogen atom and the ring annelated to the heterocyclic benzene, then in benzotellurazoles the tellurium atom is added to these reaction centers. It should be noted that tellurium-containing heterocycles are probably unique heterocycles for which a wide variety of reactions is characteristic. These occur at the heteroatom of the pyrrole type, the tellurium atom [2, 3]. The present work reports results of a study of reactions of 2-phenylbenzotellurazole (I) at both heteroatoms, the tellurium and nitrogen.

Reactions at the tellurium atom in this heterocycle, as in others, are caused by the ease of transition of the dicoordinated tellurium atom into tetra- and tricoordinated forms. Similar to other derivatives of dicoordinated tellurium [4], including the heterocyclics of [2, 3], 2-phenylbenzotellurazole is converted with high yields under the action of halogens under mild conditions into the corresponding σ-telluranes, 1,1-dihalo-2-phenylbenzotellurazoles (IIa-c). Another σ-tellurane, 1,1-dinitro-2-phenylbenzotellurazole (IId) is formed upon treatment of compound I with dilute nitric acid. The reaction probably occurs through intermediate formation of the corresponding telluroxide, interaction of which with excess

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*For Communication 2, see [1].

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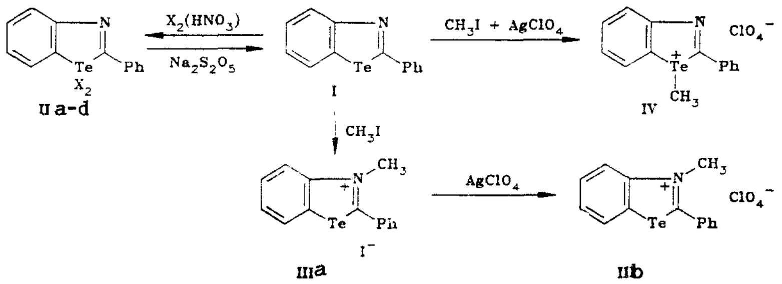
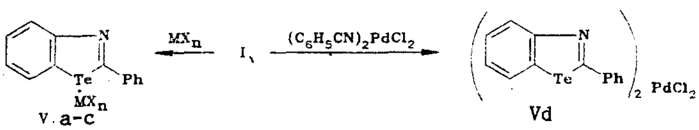
HNO_3 leads to the final product IId. The σ-telluranes obtained are reduced under mild conditions into the starting 2-phenylbenzotellurazole by an aqueous solution of sodium metabisulfite.



II, III a X=Cl, b X=Br, IIc X=I, d X=ONO_2

Two potential alkylation centers, the nitrogen and tellurium atoms, exist in 2-phenylbenzotellurazole. Actually, all other benzazoles are alkylated by methyl iodide at the nitrogen [5-7], forming iodides of N-methylbenzazoles while derivatives of dicoordinate tellurium (dialkyl-, arylalkyl-, and even diaryltellurides) form telluronium salts through reaction with methyl iodide [4]. In this respect, study of alkylation reactions of compound I under various conditions is especially interesting. Alkylation of 2-phenylbenzotellurazole by heating it in excess methyl iodide in a sealed ampul occurs, as in the case of other benzazoles, at the nitrogen atom and leads to N-methyl-2-phenylbenzotellurazolium iodide (IIIa) with high yield [8]. Alkylation at the nitrogen atom is unambiguously confirmed by the δ_{NCH_3} values in the PMR spectra of compound IIIa (3.81 ppm) and 2-phenylbenzoxazolium (3.95 ppm), 2-phenylbenzothiazolium (3.91 ppm), and 2-phenylbenzoselenazolium (3.88 ppm) iodides. The signals of the N-methyl groups for all these structurally related compounds lie in approximately the same region and shift insignificantly to strong field upon going from the benzoxazole to benzotellurazole derivatives. At the same time, 1-methyl-3-azabenzo[b]tellurophenium (IV) [8] perchlorate is formed by reaction of 2-phenylbenzotellurazole with methyl iodide in the presence of an equivalent quantity of silver perchlorate. The signal of the Te-methyl protons in the PMR spectrum of this compound appear at much stronger field than for the N-methyl iodide derivative (IIIa), at 2.28 ppm. For comparison, we cite the chemical shifts of the Te-methyl protons in the perchlorates of 3,7,10-trimethylphenotellurazinium [9] and halides of diarylmethyltelluronium [10], which are at 2.55 and 2.69-3.04 ppm, respectively. The signal of the N-methyl protons for N-methyl-2-benzotellurazolium perchlorate (IIIb), obtained by us by treatment of IIIa with an equimolar quantity of silver perchlorate, is observed at 3.88 ppm, i.e, practically in the same region as for the iodide of IIIa. To our knowledge, formation of the telluronium salt IV is the first example of alkylation at the heteroatom of the pyrrole type in a series of benzazoles.

2-Phenylbenzotellurazole forms molecular complexes with some soft Lewis acids, mercury, silver, and palladium salts (Va-d). As in the case of other derivatives of dicoordinated tellurium, complexes of 2-phenylbenzotellurazole with mercury salts have a 1:1 composition and the palladium salt, 2:1. Although direct, and in particular, x-ray structural data, which indicate that the tellurium atom acts in these complexes as the donor center, are absent, the formation itself of complexes of similar composition with diaryltellurides [4], phenotellurazines [9], and telluroxanthenes [11] support this proposal. It should be mentioned that the complex with silver perchlorate is exceedingly unstable and is easily decomposed at room temperature by light.

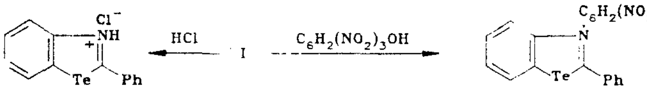


V a MX_n=$HgCl_2$; b MX_n=$HgBr_2$; c MX_n=$AgClO_4$

The tellurium atom in some of its cyclic derivatives, phenoxatellurines [12-16] and phenotellurazines [9], is known under rather forcing conditions to be capable of replacement by a sulfur atom. The behavior of 2-phenylbenzotellurazole has definite interest in this respect since these heterocycles do not have aromatic character. Heating of compound I with excess sulfur at 180°C leads to replacement of the tellurium by sulfur and formation of 2-phenylbenzothiazole with 42% yield. Undoubtedly, this reaction can be used further for establishing the structure of newly prepared benzotellurazoles since benzothiazoles into which they convert upon heating with sulfur are comparatively well-studied compounds.

Thus, reactions which lead to an increase of tellurium coordination number to four (formation of σ-telluranes) or three (telluronium salts, molecular complexes with metal salts) and replacement of it by a sulfur atom are characteristic for the tellurium atom in 2-phenylbenzotellurazole.

The nitrogen atom in 2-phenylbenzotellurazole acts as a reaction center in salt formation reactions besides being N-alkylated upon reaction with methyl iodide. 2-Phenylbenzotellurazole (VI) is formed practically with quantitative yield upon passage of gaseous HCl through a benzene solution of compound I. The same compound is obtained upon reaction of 2-phenylbenzotellurazole with hydrochloric acid, while extended boiling of the latter in concentrated HCl does not lead to destruction of the ring. Probably, a complex of 2-phenylbenzotellurazole with picric acid (VII) is formed due to the nitrogen atom, as in the case of the analogous complex of dibenzotellurophene, the more the π-electron system of the heterocycle [17] acts as the donor center, judging from Mössbauer spectra.



VI VII

EXPERIMENTAL

PMR spectra of the compounds were recorded on a Tesla BS-487C (80 MHz) instrument in DMSO-D_6 or CF_3COOH (HMDS internal standard). Elemental analyses of compounds II-VII for C and H corresponded with those calculated.

1,1-Dichloro-2-phenylbenzotellurazole (IIa, $C_{13}H_9Cl_2NTe$). A stream of dry chlorine was slowly passed through a solution of 1.53 g (55 mmole) of 2-phenylbenzotellurazole [1] in 20 ml CCl_4 cooled in an ice bath until cessation of formation of precipitate. The precipitate was filtered off, washed with CCl_4, dried, and recrystallized from acetone. The light yellow crystals had mp > 250°C (dec.). The yield was practically quantitative.

1,1-Dibromo-2-phenylbenzotellurazole (IIb, $C_{13}H_9Br_2NTe$). A solution of 0.8 g (5 mmole) bromine in 5 ml CCl_4 was slowly added dropwise with vigorous mixing to a solution of 1.53 g (5 mmole) of I in 20 ml CCl_4 cooled in an ice bath. The yellow precipitate which formed was filtered off, washed with CCl_4, and recrystallized from acetone. The yellow crystals had mp > 250°C (dec.). The yield was practically quantitative.

1,1-Diiodo-2-phenylbenzotellurazole (IIc, $C_{13}H_9I_2NTe$) was obtained analogously with 98% yield as dark red crystals with mp > 250°C (dec.).

1,1-Dinitrato-2-phenylbenzotellurazole (IId, $C_{13}H_9N_3O_4Te$). Compound I (0.612 g, 2 mmole) was added in small portions to 10 ml 20% HNO_3 with vigorous mixing and heating on a water bath at 40-50°C. After 30 min heating, the yellow precipitate was filtered off, washed with water, and dried. Yield 0.73 g (92%). The yellow crystals had mp 190-192°C (dec.).

N-Methyl-2-phenylbenzotellurazolium iodide (IIIa, $C_{14}H_{12}INTe$). A mixture of 0.92 g (3 mmole) compound I and 8 ml methyl iodide was heated for 16 h in a sealed ampul on a boiling water bath. After cooling, the contents of the ampul were filtered, washed with hexane, and dried. Yield 1.22 g (91%) of yellow crystals with mp > 250°C. PMR spectrum (CF_3COOH): 3.81 (3H, s, CH_3); 7.13-8.15 ppm (9H, m, 4-7.2'-6'-H_9).

N-Methyl-2-phenylbenzotellurazolium Perchlorate (IIIb, $C_{14}H_{12}ClNO_4Te$). A mixture of 0.90 g (2 mmole) of N-methyl-2-phenylbenzotellurazolium iodide and 0.66 g (2 mmole) of the silver perchlorate acetonitrile complex in 10 ml acetonitrile was stirred vigorously at room temperature for 3 h. The precipitate of AgI (0.46 g, 97%) was filtered off and the filtrate was evaporated. Yield 0.78 g (93%) of small yellow crystals with mp 228-230°C (expl.). PMR spectrum (CF_3COOH): 3.88 (3H, s, CH_3), 7.20-8.00 ppm (9H, m, 4-7.2'-6'-H_9).

1-Methyl-3-azabenzo[b]tellurophenium Perchlorate (IV, $C_{14}H_{12}ClNO_4Te$). A solution of 1 g (3 mmole) of the silver perchlorate acetonitrile complex in 10 ml acetonitrile was added with vigorous mixing to a solution of 0.92 g (3 mmole) of 2-phenylbenzotellurazole and 0.57 g (4 mmole) methyl iodide in 20 ml dry acetonitrile. The mixture was stirred with boiling for 1 h 30 min. After cooling, the AgI precipitate (0.68 g, 96%) was filtered off and the filtrate evaporated. Yield 1.2 g (95%) of yellow needle-like crystals of IV, mp 210-212°C (expl.). PMR spectrum (DMSO-D_6): 2.28 (3H, s, CH_3), 7.20-8.50 ppm (9H, m, 4-7.2'-6'-H_9).

(2-Phenylbenzotellurazole)mercury(II) Chloride (Va, $C_{13}H_9Cl_2HgNTe$). A solution of 0.543 g (2 mmole) of mercury chloride in 4 ml ethanol was added dropwise to a solution of 0.612 g (2 mmole) of 2-phenylbenzotellurazole in 6 ml ethanol. The yellow precipitate which formed was filtered off, washed with ether, and dried. Yield 1.0 g (87%) of complex Va as yellow needles with mp 153-155°C (ethanol-benzene).

2-(Phenylbenzotellurazole)mercury(II) Bromide (Vb, $C_{13}H_9Br_2HgNTe$). This was obtained analogously to Va. Yellow crystals with mp 155-157°C (ethanol-benzene). Yield 89%.

Bis(2-phenylbenzotellurazole)palladium (II) Chloride (Vd, $C_{26}H_{18}Cl_2N_2PdTe_2$). A solution of 0.383 g (1 mmole) of dichlorobis(benzonitrile)palladium in 10 ml acetonitrile was added with stirring to a solution of 0.612 g (2 mmole) of compound I in 10 ml acetonitrile. The reddish-orange precipitate which formed was filtered off, washed with ether, and dried. Yield 0.79 g (99%), mp 216-218°C.

2-Phenylbenzothiazole. A thoroughly powdered and mixed mixture of 1.23 g (4 mmole) of 2-phenylbenzotellurazole and 0.16 g (5 mmole) of sulfur was heated for 8 h at 180°C. The cooled mixture was dissolved in 20 ml benzene. The precipitate of tellurium (0.22 g, 43%) was filtered off, washed with 5 ml benzene, and dried. The benzene solution was chromatographed on aluminum oxide (benzene eluent). After evaporation of solvent, 0.35 g (42%) of 2-phenylbenzothiazole with mp 112-113°C were obtained. According to [18], mp is 114°C.

2-Phenylbenzotellurazolium chloride (VI, $C_{13}H_{10}ClNTe$). A stream of dry HCl was passed through a solution of 0.92 g (3 mmole) of 2-phenylbenzotellurazole in 10 ml benzene. After cessation of precipitate formation, it was filtered, washed with ether, and dried. Yield 1.01 g (98%) of VI as bright yellow crystals with mp 160-162°C.

2-Phenylbenzotellurazole Picrate (VII, $C_{19}H_{12}N_4O_7Te$). A solution of 0.46 g (2 mmole) of picric acid in 5 ml ethanol was added with mixing at room temperature to a solution of 0.612 g (2 mmole) of 2-phenylbenzotellurazole in 6 ml ethanol. The precipitate which formed was filtered off, washed with ether, and dried. The orange plates had mp 153-154°C. Yield 1 g (93%).

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STEREOCHEMICAL FEATURES OF TRANSESTERIFICATION (N—B)-PERHYDRO-2-ISOPROPYL-1,3-DIOXA-6-AZA-2-BORACINE BY 2-ALKYL-1,3-BUTANEDIOLS

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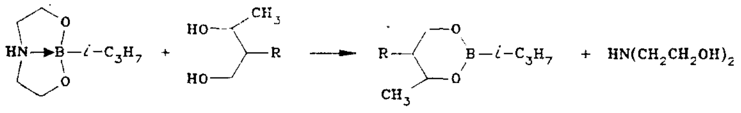
The stereoisomeric composition of 2,4,5-substituted 1,3,2-dioxaborinanes, products of transesterification of the diethanolamine ester of isopropylboric acid by 2-alkyl-1,3-butanediols, are shown by GLC not to correspond to the ratio of erythro-threo-forms of the starting diols. The fraction of trans-isomer of 2,4,5-substituted 1,3,2-dioxaborinane which is elevated by comparison with that expected is explained by stereoselective reaction of the erythro-form of the 1,3-diol with diethalnolaminoborate.

Reaction of the erythro-isomer of 2-alkyl-1,3-butanediol with esters of monosubstituted boric acids was shown earlier [1-3] to occur stereoselectively and to lead not only to cis- but also to trans-isomers of the corresponding 2,4,5-substituted 1,3,2-dioxaborinanes. Reaction of alkylborondichlorides with 4,5-substituted 1,3-dioxanes [4], interaction of 2,4,5-substituted 1,3,2-dioxaborinanes with aldehydes [5], and hydrolysis of 2,4,5-substituted 1,3,2-dioxaborinanes [6] also obey similar principles. In order to expand studies of stereochemical features of formation of the 1,3,2-dioxaborinane ring, we investigated transestericication of (N—B)-perhydro-2-isopropyl-1,3-dioxa-6-aza-2-boracine (I) by 2-alkyl-1,3-butanediols (IIa-d).



I IIa-d IIIa-d

As a result of the reaction, 2-isopropyl-4-methyl-5-alkyl-1,3,2-dioxaborinanes IIIa-d are formed. The stereoisomeric composition of the starting diols II was established from the corresponding 4,5-dialkyl-1,3-dioxanes [7, 8]. The composition of the reaction products III was monitored by GLC taking into account the configurational references which were found earlier [9, 10]. The data obtained (Table 1) indicate a sharp discrepancy between the stereoisomeric composition of the starting (IIa-d) and final (IIIa-d) compounds with an increase of 1,3,2-dioxaborinane trans-isomer which was evident in all cases. The stereoisomeric composition of the III compounds does not depend on the reaction yield (see Experimental). The ratio of cis- and trans-isomers of the III compounds, which are prepared by reaction of diols II and boracine I, are in excellent agreement with the stereochemical result of the reaction of diols II with acyclic boric esters [1-3]. Thus, both of these processes obey the same stereochemical principles. Hence it follows that reaction of threo- and erythro-isomers II

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