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NITROGEN—TELLURIUM HETEROCYCLES.

1. PREPARATION OF BENZOTELLURAZOLES AND THEIR DERIVATIVES

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Cyclization of previously isolated and purified N-acyl derivatives of σ-methyltelluroaniline under the influence of $POCl_3$ leads to 2-R-benzotellurazoles in yields of 35-65%. 1,1-Dichloro-2-R-benzotellurazoles are intermediates in this reaction.

In recent years there has been marked progress in the study of methods of preparation, structure, and reactivity of five-membered tellurium containing heterocycles [1]. However, in contrast to benzoxazole [2] and its sulfur [3] and selenium [4] analogs, benzotellurazole (I) has been little studied. In an isolated communication [5], devoted to these compounds, a three-stage synthesis of benzotellurazole and its 2-substituted derivatives was described: reaction of o-nitrophenyl diazonium fluoroborate with diethylditelluride in the presence of 18-crown-6 with the formation of o-ethyltelluronitrobenzene [6], reduction of the latter to o-ethyltelluroaniline, acyclation of the aniline with an acyl chloride and cyclization (without previous isolation and purification) of the N-acyl derivative by boiling in $POCl_3$. The yield of compound I by this method amounted to 2-15% overall, calculated on o-ethyltelluronitrobenzene.

As starting materials for the preparation of benzotellurazoles we have used N-acylated derivatives of o-methyltelluroaniline (II), and $POCl_3$ as cyclizing agent as in [5]. Preparation of compound II was carried out in four stages. Reaction of azobenzene with tellurium tetrachloride by the method of [7] yielded o-trichlorotelluroazobenzene. Reduction of this by sodium borohydride in ethanol led to di(o-aminophenyl)ditelluride (III). Acylation of compound III with acyl chloride in the presence of triethylamine gave di(o-acylaminophenyl)ditelluride (IV) reduction of which with sodium borohydride in methanol with subsequent treatment of the telluropheolate with dimethyl sulfate led to compound II. Although the method which we used has four steps whereas the method of [5] has but three, our method

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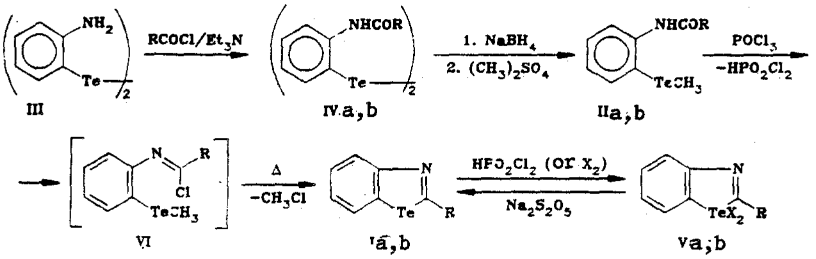
has several advantages since the yield of product at each stage is higher and the process does not require the use of the extremely evil-smelling diethylditelluride.

The use of previously purified N-acyl derivatives (II) in the reaction, and an increase in the reaction time (six hours instead of the three hours used in [5]) effected a considerable increase in the yield of benzotellurazoles (35% for 2-methyl- and 65% for 2-phenylbenzotellurazole). In contrast to the results of [5], the main reaction product here was not the benzotellurazoles, isolated in trace quantities, but their Te,Te-dichloro derivatives (V). The latter are reduced by sodium metabisulfite with practically quantitative yield of benzotelluroazoles which on treatment with halogens are converted again to the tellurohalides V. The isolation of V as the main product of the reaction leads us to propose the following reaction mechanism. The imidochlorides (VI) formed in the first stage of the reaction lose CH_3Cl on heating, passing into the benzotellurazoles (I) chlorination of which by the conversion products of $POCl_3$ (assumed to be HPO_2Cl_2) leads to the tellurodichlorides (V).



Ia, IIa, IVa, Va,c $R=C_6H_5$; Ib, IIb, IVb, Vb,d $R=CH_3$; Va,b X=Cl; c,d X=Br

Experiments in the use of phosphonitrile dichlorides as cyclizing agent by analogy with the preparation of benzothiazoles from N-acyl derivatives of o-methylthioaniline [8] were not successful.

EXPERIMENTAL

Infrared spectra were run on a UR-20 instrument as nujol mulls. Proton NMR spectra were obtained on a Tesla BS-487C (80 MHz) instrument in deuterochloroform using HMDS as internal standard.

Di(o-aminophenyl)ditelluride (III). To a vigorously stirred suspension of 41.5 g (100 mmole) o-trichlorotellurobenzene [7] in 500 ml ethanol at bp was added gradually 9.5 g (255 mmole) $NaBH_4$ in 200 ml 1 N NaOH until the solid had completely dissolved and a colorless solution was obtained. This solution was poured into 800 ml water and air blown through until oxidation of the sodium salt of o-aminotellurophenol was complete. The wine-colored deposit which formed was filtered off, washed with water, dried, and recrystallized from 1:1 benzene-hexane. Yield 19.6 g (89%), mp 99-101°C. Found (%): C 32.6; H 2.7, N 6.5. Calculated for $C_{12}H_{12}N_2Te_2$ (%): C 32.8; H 2.7, N 6.4.

Di(o-acylaminophenyl)ditellurides (IVa, b). To a solution of 4.4 g (10 mmole) di(o-aminophenyl)ditelluride (III) and 2.12 (21 mmole) triethylamine in 50 ml ether, stirred at 20°C, a solution of 20 mmole of the appropriate acyl chloride in 20 ml ether was slowly added. After stirring for 1 h at room temperature the precipitate which formed was filtered off, washed with water to remove triethylamine hydrochloride and dried. Di(o-acylaminophenyl) ditellurides (Iva, b) were obtained in 88-90% yield and were used without further purification.

o-Methyltelluro-N-benzoylaniline (IIa). To a suspension of 12.94 g (20 mmole) compound IVa in 200 ml methanol, vigorously stirred at room temperature in an atmosphere of argon, dry sodium borohydride was added in small portions until all the suspended solid had dissolved and a colorless solution was obtained. To the solution thus obtained, a solution of 5.3 g (42 mmole) dimethyl sulfate in 10 ml methanol was added in one portion and the solution stirred at bp for 1 h. The solution was then cooled and poured into 500 ml water and the precipitate filtered off, washed with water, and dried. Yield 11.78 g (87%). Lustrous needles, mp 123-125°C (from 2-propanol). IR spectrum (cm^{-1}): 1650 (C=O), 3200 (NH). Proton NMR spectrum (δ, ppm): 8.90 s (1H, N–H), 8.48-6.76 m (9H, Ar–H), 1.93 s (3H, $TeCH_3$). Found (%): C 50.0, H 3.7. Calculated for $C_{14}H_{13}NOTe$ (%). C 49.6; H 3.8.

o-Methyltelluro-N-acetylaniline (IIb) was prepared in a similar manner. Lustrous crystals, mp 97-99°C (from 2-propanol), yield 75%. IR spectrum (cm^{-}): 1640 (C=O), 3220 (NH). Proton NMR spectrum (δ, ppm): 8.13-6.75 m (5H, Ar–H, N–H), 2.10 s (3H, $COCH_3$), 1.93 s (3H, $TeCH_3$). Found (%): C 39.2, H 3.8. Calculated for $C_9H_{11}NOTe$ (%): C 39.0, H 4.0.

2-Phenylbenzotellurazole (Ia). A solution of 5.1 g (15 mmole) o-methyltelluro-N-benzoylaniline (IIa) in 20 ml $POCl_3$ was heated at bp for 6 h. After cooling, the clear yellow solution was poured with stirring into 150 ml water and neutralized with Na_2CO_3 to pH 7. The precipitate of 1,1-dichloro-2-phenylbenzotellurazole (Va) which formed was filtered off, washed with water, suspended in 60 ml water and treated with 7.6 g (40 mole) $Na_2S_2O_5$ while stirring and heating in a waterbath. The product was filtered off, washed with water, dried and recrystallized from hexane. Yield 3.0 g (65%) coarse yellow crystals, mp 101-103°C. Found (%) C 51.1, H 3.1. Calculated for $C_{13}H_9NTe$ (%): C 50.9, H 2.9.

2-Methylbenzotellurazole (Ib) was prepared in a similar manner. Light orange crystals, mp 93-95°C (from hexane), yield 35%. Proton NMR spectrum (δ, ppm): 8.10-6.95 m (4H, Ar-H), 2.78 s (3H, CH_3). Found (%): C 39.7, H 3.2. Calculated for C_8H_7NTe (%): C 39.3, H 2.9.

1,1-Dichloro-2-phenylbenzotellurazole (Va). A virogous current of dry chlorine was passed through a solution of 1.53 g (5 mmole) 2-phenylbenzotellurazole in 20 ml CCl_4, cooled in an ice bath, for 15 min. The precipitate which formed was filtered off, washed with hexane and dried. Soft colorless crystals, mp 200-202°C (decomp.) yield quantitative. Found (%): C 41.1, H 2.7. Calculated for $C_{13}H_9Cl_2NTe$ (%): C 41.3, H 2.4.

1,4-Dichloro-2-methylbenzotellurazole (Vb) was prepared in a similar manner. Soft, colorless crystals, mp 198-200°C (decom.), yield quantitative. Found (%): C 30.8, H 2.4. Calculated for $C_8H_7Cl_2NTe$ (%): C 30.4, H 2.2.

1,1-Dibromo-2-phenylbenzotellurazole (Vc). A solution of 0.80 g (5 mmole) bromine in 5 ml CCl_4 was added with stirring to a solution of 1.53 g (5 mmole) 2-phenylbenzotellurazole in 20 ml CCl_4, cooled in an ice bath. The precipitate which formed was filtered off, washed with hexane and dried. Soft yellow crystals, mp 193-195°C, yield quantitative. Found (%): C 33.2, H 2.1. Calculated for $C_{13}H_9Br_2NTe$ (%): C 33.4, H 1.9.

1,1-Dibromo-2-methylbenzotellurazole (Vd) was prepared in a similar manner. Soft yellow crystals, mp 188-190°C, yield quantitative. Found (%) C 24.0, H 2.0. Calculated for $C_8H_7Br_2NTe$ (%): C 23.7, H 1.7.

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