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REACTIONS OF IMMONIUM AND TELLURONIUM SALTS OF 2-PHENYLBENZOTELLURAZOLE

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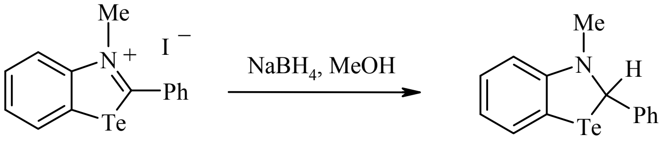
N-methyl-2-phenylbenzotellurazolinium iodide, like other N-methylbenzochalcogenazolium salts, readily undergoes reduction, hydrolysis, and recyclization with hydrazine hydrate and o-phenylene diamine. 1-Methyl-2-phenylbenzotelluronioazole perchlorate is an effective methylating agent in reactions with nucleophiles.

Keywords: N-methyl-2-phenylbenzotellurazolium iodide, 1-methyl-2-phenytelluronioazole perchlorate, reduction, hydrolysis, recyclization.

We have established previously [1, 2] that, depending on the nature of the methylating agent, 2-phenylbenzotellurazole (**1**) is alkylated either at the nitrogen atom or the tellurium atom. N-methyl-2-phenylbenzotellurazolium iodide (**2**) was obtained in 90% yield when compound **1** was heated with an excess of methyl iodide in a sealed ampule. On the other hand treatment of an acetonitrile solution of 2-phenylbenzotellurazole and methyl iodide with silver perchlorate (an equimolar ratio of the reagents) gave an almost quantitative yield (95%) of 1-methyl-2-phenybenzotelluronioazole perchlorate (**3**). In this report we give an account of the results of an investigation of some reactions of the salts **2** and **3**.



2 **4**

On treatment of a suspension of the immonium salt **2** in methanol with dry $NaBH_4$ (A) reduction of the C=N bond occurs to give 3-methyl-2-phenyl-2,3-dihydrobenzotellurazole (**4**) in greater than 70% yield, the structure of which was confirmed by elemental analysis and ^1H NMR spectroscopy. In the latter the signal of the N-methyl group was observed at 2.60 ppm, whereas the analogous signal was observed at 3.81 ppm in the spectrum of salt **2**.

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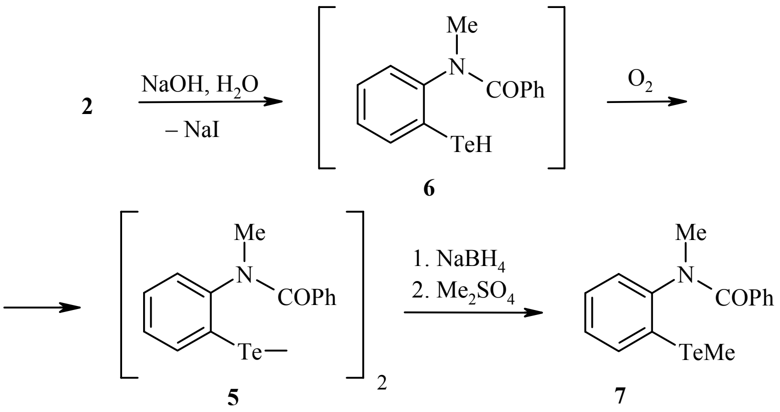
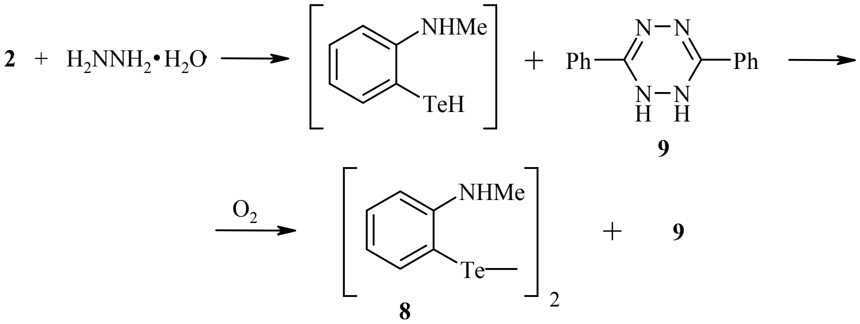
Salt **2** underwent hydrolysis under comparatively mild conditions (maintenance of a suspension in aqueous NaOH (B) at 60-80°C) similarly to other N-methylbenzochalcogenium salts [3, 4]. However, in difference from its thio- and selenoanalogs which gave on hydrolysis the corresponding thio- and selenophenols, which are converted into the disulfides or diselenides by oxidizing agents [I_2, $K_3Fe(CN)_6$], hydrolysis of salt **2** led directly to bis(2-N-methyl-N-benzoylaminophenyl)ditelluride (**5**). This ditelluride is evidently formed by self-oxidation by aerial oxygen of the intermediate tellurophenol (**6**). We identified the ditelluride **5** in the form of N-benzoyl-N-methyl-2-(methyltelluro)aniline **7** obtained by reduction of the ditelluride with sodium borohydride and alkylation of the sodium tellurophenolate formed with dimethyl sulfate.

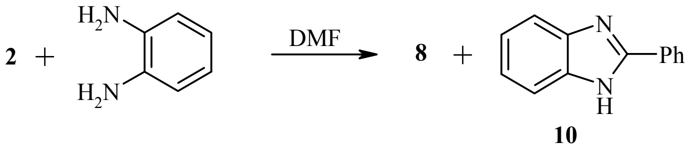


In the ^1H NMR spectrum there are, apart from the signals of the aromatic protons, singlets of the protons of the NCH_3 and $TeCH_3$ groups at 3.30 and 2.08 ppm respectively.

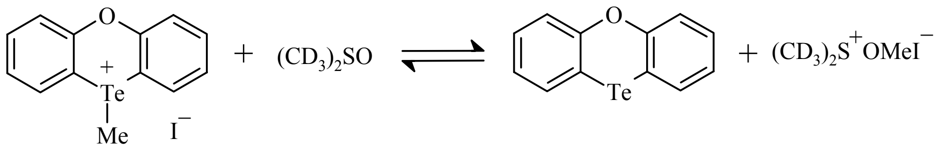
One of the characteristic properties of N-methylbenzochalcogenazolium salts is their ability to undergo recyclization with bifunctional compounds: hydrazine [5] and *o*-phenylenediamine [6]. Reaction of salt **2** with hydrazine hydrate (C) gave di(2-N-methylaminophenyl)ditelluride (**8**) in greater than 50% yield and also 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine (**9**) (with a yield of about 40%).



Reaction of salt **2** with *o*-phenylenediamine (D) gave the ditelluride **8** (yield 43%) and 2-phenylbenzimidazole (**10**) (yield 39%).



It is known that diphenylalkylsulfonium salts [7] and trimethylselenonium hydroxide [8] are effective alkylating agents. In a series of telluro-organic compounds similar properties were observed for Te-methylphenoxatelluronium iodide (**11**) [9]. The following equilibrium was established in a solution of this compound in DMSO-d_6.



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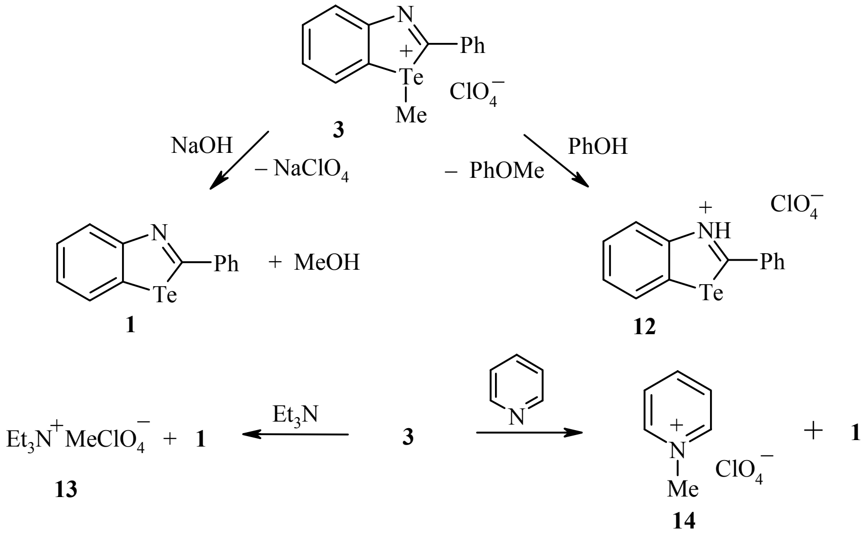
Starting from this observation it might be expected that the telluronium salt **3** would have methylation properties on reaction with nucleophilic reagents. On reaction with sodium hydroxide and phenol compound **1** 2-phenylbenzotellurazolium perchlorate (**12**) were isolated in 70 and 85% yields respectively. Reaction of compound **3** with triethylamine and pyridine gave methyltriethylammonium perchlorate (**13**) and N-methylpyridinium perchlorate (**14**) in yields of 75 and 60% The yields of compound **1** were 73 and 65 % respectively.



EXPERIMENTAL

^{1}H NMR spectra were recorded on a Varian Unity-300 (300 MHz) instrument with residual H of the solvent as internal standard.

The salts **2** and **3** were synthesized by known methods [2].

Reactions of N-Methyl-2-phenylbenzotellurazolium Iodide (2). A. **With NaBH$_4$. 3-Methyl-2-phenyl-2,3-dihydrobenzotellurazole (4).** Dry sodium borohydride (1 g, 26 mmol) was added in small portions with stirring to a suspension of compound **2** (2.25 g, 5 mmol) in methanol (100 ml) in an atmosphere of argon. Stirring was continued for 1 h, then the product **4** was filtered off, dried, and recrystallized from 2-propanol to give orange plates, mp 141-143°C, yield 1.22 g (76%). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.15-7.28 (10H, m, H-2 and 9H$_{\text{arom}}$); 2.60 (3H, s, NCH$_3$). Found, %: C 51.90; H 3.89. $C_{14}H_{13}NTe$. Calculated, %: C 52.08; H 4.07.

B. **With NaOH. (N-Benzoyl-N-methyl)-2-methyltelluroaniline (7).** A suspension of compound **2** (0.90 g, 2 mmol) in 1N aqueous NaOH (100 ml) was stirred for 1 h at 80-90°C. After cooling the reaction mass the orange precipitate of ditelluride **5** was filtered off, dried, and suspended in methanol (20 ml) without further purification. Dry sodium borohydride was added in small portions to the stirred suspension under argon until the precipitate had completely dissolved to give a colorless solution. Dimethyl sulfate (0.5 g, 4 mmol) was added rapidly to the colorless solution, the reaction mixture was stirred for 40 min with mild heating, cooled, poured into water (100 ml), and extracted with chloroform (3×15 ml). The extract was dried over Na_2SO_4 and the solvent evaporated to give a colorless crystalline product **7** (0.46 g, 65%), mp 145-147° (2-propanol). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.75-7.57 (9H, m, H_{arom}); 3.30 (3H, s, NCH_3); 2.08 (3H, s, $TeCH_3$). Found, %: C 50.91; H 4.07. $C_{15}H_{15}NOTe$. Calculated, %: C 51.04; H 4.29.

C. **With $NH_2NH_2 \cdot H_2O$. Di(2-N-methylaminophenyl)ditelluride (8).** A suspension of compound **2** (2.25 g, 5 mmol) in hydrazine hydrate (10 ml) was stirred while boiling for 10 min. The red pasty mass was separated by decanting the boiling liquid phase of the reaction mixture, dried and crystallized from 2-propanol to give claret-red crystals of ditelluride **8** (0.6 g, 51%), mp 100-102°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.30-7.80 (4H, m, H_{arom}); 4.25 (1H, s, NH); 2.65 (3H, s, NCH_3). Found, %: C 36.52; H 3.61. $C_{14}H_{16}N_2Te_2$. Calculated, %: C 35.96; H 3.46.

The orange-yellow precipitate which formed on cooling the decanted liquid phase was filtered off, dried, and recrystallized from ethanol to give orange-yellow crystals of compound **9** (0.28 g, 48%), mp 190-191°C (mp 191-192°C [5]).

D. **With $1,2\text{-}(H_2N)_2C_6H_4$. Compound 8**. Compound **2** (2.25 g, 5 mmol) and *o*-phenylenediamine (0.55g, 5 mmol) were stirred in DMF (50 ml) with mild boiling for 3 h. The claret-red reaction mixture was cooled and the unreacted salt **2** was filtered off. From the filtrate some of the solvent (40 ml) was evaporated under reduced pressure, the residue was poured into water and extracted with benzene (2×20 ml). The extract was dried over Na_2SO_4, the solvent was evaporated, and the residue was chromatographed on an Al_2O_3 column (eluent chloroform). Fine shining claret-red crystals of compound **8** were obtained (0.51 g, 43%), mp 100-102°C (2-propanol). The yellow residue which was not extracted by benzene was filtered off, dried, and recrystallized from benzene to give fine colorless crystals of 2-phenylbenzimidazole **10** (0.38 g, 39%), mp 292-293°C (mp 294°C [6]).

Reactions of 1-Methyl-2-phenylbenzotelluronioazole Perchlorate (3). With NaOH. 2-Phenylbenzotellurazole (1). A suspension of salt **3** (0.42 g, 1 mmol) in 1 N alcoholic NaOH (50 ml) was stirred with reflux for 1 h. The solution obtained was cooled, poured into water (100 ml), and extracted with chloroform (3×15 ml). The extract was evaporated and the residue washed with hexane to give compound **1** (0.214 g, 70%) as large yellow crystals, mp 102-103°C (mp 102-103°C [10]).

With Phenol. 2-Phenylbenzotellurazolium Perchlorate (12). Phenol (0.21 g, 2 mmol) in acetonitrile (10 ml) was added to a solution of salt **3** (0.84 g, 2 mmol) in acetonitrile (10 ml) and the reaction mixture was boiled with stirring for 2 h. The solvent was partially evaporated and ether (20 ml) was added to the reaction mixture. The precipitate formed was filtered off and dried to give product **12** as fine yellow crystals (0.69 g, 85%), mp 180-182°C (dec.). Found, %: C 38.70; H 2.30. $C_{13}H_{10}ClNO_4Te$. Calculated, %: C 38.30; H 2.48.

The product **12** was identical to a sample of **12** prepared by the reaction of 2-phenylbenzotellurazole (**1**) with perchloric acid in ethanol (no depression of the melting point in a mixed determination).

With Et_3N. Methyltriethylammonium Perchlorate (13). Triethylamine (0.3 g, 3 mmol) was added stepwise to a solution of salt **3** (0.84 g, 2 mmol) in acetonitrile (20 ml), the reaction mixture was stirred while boiling for 1 h and then some solvent (10 ml) was evaporated. Ether (20 ml) was added to the remaining cooled solution, the colorless precipitate was filtered off and recrystallized from ethanol to give fine colorless crystals of the perchlorate **13** (0.321 g, 75%), mp 200-202°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.55 (6H, q, $CH_3\underline{CH_2}$); 3.20 (3H, s, NCH_3); 1.50 (9H, t, $\underline{CH_3}CH_2$). Found, %: C 38.40; H 8.42. $C_7H_{18}ClNO_4$. Calculated, %: C 39.0; H 8.42. The solvent was evaporated from the filtrate and the residue recrystallized from hexane to give large yellow crystals of compound **1** (0.445 g, 73%), mp 101-102°C.

With Pyridine. N-Methylpyridinium Perchlorate (14). Pyridine (0.47 g, 6 mmol) was added to a solution of salt **3** (1.26 g, 3 mmol) in acetone (15 ml) and the mixture was stirred with boiling for 1 h. The colorless precipitate was filtered off and recrystallized from ethanol to give perchlorate **14** (0.35 g, 60%) as colorless crystals, mp 260°C (dec.). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 9.10-8.15 (5H, H_{Het}); 4.75 (3H, s, NCH_3). Found, %: C 37.0; H 3.90. $C_6H_8ClNO_4$. Calculated, %: C 37.2; H 4.17.

The filtrate was evaporated to dryness and the residue recrystallized from hexane to give compound **1** as large yellow crystals (0.6 g, 65%), mp 101-102°C.

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