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SYNTHESIS OF *N*-METHYLPHENOTELLURAZINE

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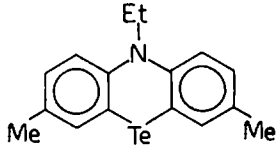
Summary

Various possible synthetic routes to the phenotellurazine system were explored. A two-step synthesis of *N*-methylphenotellurazine from $TeCl_4$ and 2,2′-dibromo-*N*-methyldiphenylamine is described.

A recent Russian communication [1], reporting the first synthesis of a phenotellurazine derivative (3,7-dimethyl-10-ethylphenotellurazine, **1**) by reacting 2,2′-dilithiated 4,4′-dimethyl-*N*-ethyldiphenylamine with TeI_2, has prompted us to disclose our studies in this area.

The lower homologs of phenotellurazine (**2d**): phenoxazine (**2a**), phenothiazine (**2b**) and phenoselenazine (**2c**), have all been known for a long time. However, there are no reports of the synthesis of phenotellurazine itself.



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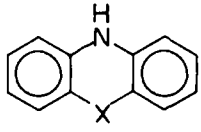

2 a X=O
b X=S
c X=Se
d X=Te

We felt that this new heterocyclic system would be interesting to examine as a donor component in charge-transfer complexes or in ion-radical salts. A number of heterocyclic organotellurium compounds based on tetratellurafulvalene and related systems has recently been designed for this purpose [2–6].

The phenoselenazine system was successfully synthesized directly from selenious chloride and diphenylamine [7,8]. In analogy with this, we tried to react both diphenylamine (**3a**) and *N*-methyldiphenylamine (**3b**) with tellurium tetrachloride in order to obtain the phenotellurazine-5,5-dichlorides (**4**); this direct approach had been used for the synthesis of phenoxatellurine-10,10-dichloride (**5**) from diphenyl

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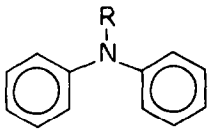
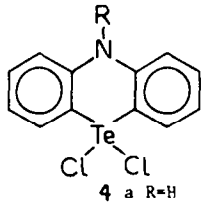
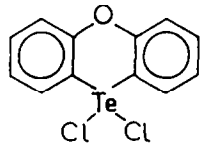
ether and tellurium tetrachloride [4,9]. Fusion of $TeCl_4$ with the diphenylamines, however, failed to give any of the desired products. All the reaction mixtures immediately turned deep blue, probably due to oxidation at nitrogen and subsequent radical-coupling reactions. It should however be noted that this method might be useful with less activated (e.g. *N*-acetylated) diphenylamines, as indicated by results obtained by Zankowska-Jasinska and Burgiel [10], who reported that melting of **6** with $TeCl_4$ produced 4,4-dichlorodibenzo[b,g]-4-tellura-1,8-naphthyridine (**8**) (via **7**) as the hydrochloride.



3 a R=H
b R=CH_3



4 a R=H
b R=CH_3



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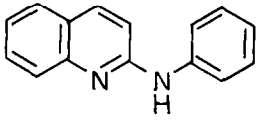

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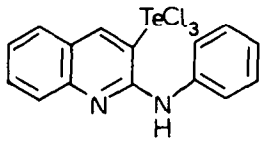

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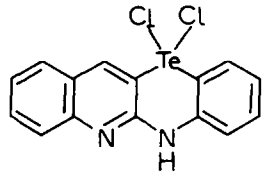

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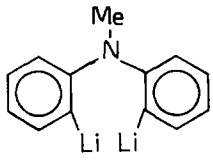
For the synthesis of simple phenotellurazines we therefore turned our attention to another approach, involving the reaction of a dilithiated diphenylamine derivative with tellurium tetrachloride. This approach was used to give the phenophosphazine skeleton [11] and other similar systems. The reaction of 2,2′-dilithio-*N*-methyldiphenylamine (**9**) with tellurium tetrachloride in dry tetrahydrofuran gave the high-melting dichloride **4b** in low yield (18%). Reduction with ethanolic hydrazine hydrate afforded *N*-methylphenotellurazine (**10**) as a yellow highly crystalline material, m.p. 160°C.



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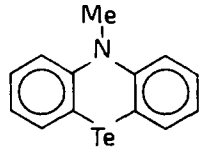

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Experimental

2,2′-Dibromo-*N*-methyldiphenylamine was synthesized by a published method [11,12]. $TeCl_4$ was sublimed immediately before use (200°C/0.1 mmHg).

N-methylphenotellurazine (10)

2,2′-Dibromo-*N*-methyldiphenylamine (1.0 g, 2.9 mmol) was lithiated under N_2 in

dry THF (35 ml) at 0°C with butyllithium (3.7 ml 1.7 *M*, 6.3 mmol). After 1 h at 20°C, $TeCl_4$ (0.79 g, 2.9 mmol) in dry THF (10 ml) was added dropwise during 15 min, producing a greenish-yellow precipitate. After another 2 h the solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (250 ml). The solution was washed with H_2O, dried, and evaporated to leave a yellowish solid, which was recrystallized from CH_3CN to give 0.20 g (18%) of the high-melting dichloride **4b** (m.p. > 270°C). The dichloride **4b** was then heated in EtOH (20 ml) with an excess of hydrazine hydrate for 2 h. Dilution with water and CH_2Cl_2-extraction, drying, evaporation, filtration through a short column (SiO_2/CH_2Cl_2) and recrystallization (light petroleum b.p. 40–60°C) afforded compound **10** as yellow needles, m.p. 160°C. Analysis: Found: C, 50.74; H, 3.67; N, 4.54. $C_{13}H_{11}NTe$ calcd.: C, 50.56; H, 3.59; N, 4.54%. Mass spectrum (*m/e* rel. intensity, selected peaks) M^+ 311(52), 296(6), 181(100). ^1H NMR δ ($CDCl_3$, Me_4Si): 3.50 (s, 3H), 6.93 (t, 2H), 7.05 (d, 2H), 7.25 (t, 2H), 7.54 (d, 2H).

Acknowledgement

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