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SYNTHESIS AND REACTIVITY OF 10-ALKYLPHENOTELLURAZINES

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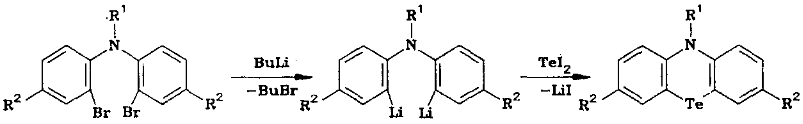
The reaction of N-alkyl-2,2'-dilithium diphenylamines with tellurium diiodide yields derivatives of a new heterocyclic system, phenotellurazine. 10-Alkylphenotellurazines readily form derivatives containing tetra- and tricoordinated tellurium, form complexes with metal salts and rhodium(I) carbonyl chloride, and by bromination and nitration give 3,7-dibromo- or 3-nitro-, 3,7-dinitro, and 1,3,7,9-tetranitro derivatives.

The number of six-membered tricyclic heterocycles containing tellurium that have been described is relatively small: phenoxatellurine [1, 2], phenothiatellurine [3], telluroxanthene [4, 5], telluranthrene [6], and anthracene-10-telluronium perchlorates [7, 8]. Recently we synthesized the first representatives of a new tricyclic system containing tellurium, viz., phenotellurazine [9, 10], the sulfur analogs of which are widely used in medicine as psychotropic agents [11]. Attempts to obtain phenotellurazine by some reactions analogous to those used to synthesize phenothiazines [12] and phenoselenazines [13], by treatment of diarylamines with tellurium metal or tellurium tetrachloride, were unsuccessful. We therefore turned to a very efficient method for constructing a tricyclic system, the reaction of 2,2'-dilithium derivatives of diphenylamines with halides of the respective elements [14].

In the reaction of N-alkyl-2,2'-dilithiumdiphenylamines with tellurium diiodide in an argon atmosphere, the 10-alkylphenotellurazines Ia-d were synthesized in more than 50% yield. The dilithium derivatives were obtained by treating ether solutions of N-alkyl-2,2'-dibromodiphenylamines, IIa-d, with an ether solution of butyllithium at 0°C; in the case of N-alkyl-2,2',4,4'-tetrabromodiphenylamines, at −10°, at which temperature only the bromines in the o-position undergo exchange. It should be noted that recently 10-methyl-5,5-dichlorophenotellurazine was synthesized in 18% yield by the reaction of N-methyl-2,2'-dilithiumdiphenylamine with tellurium tetrachloride [15].



II a-d

I a-d

a, b d $R^1=C_2H_{55}$, c $R^1=CH_3$; a $R^2=H$; b $R^2=CH_3$; c, d $R^2=Br$

The composition and structure of the phenotellurazines I was demonstrated by elemental analysis and PMR spectra. The PMR spectrum of 3,7-dimethyl-10-ethylphenotellurazine (Ib) (Fig. 1) shows successively the triplet and quartet of the ethyl radical, the singlet of the methyls at the 3 and 7 positions, the weakly resolved AB system of the protons at the 1, 2, 8, and 9 positions, and the singlet signal of the aromatic protons at the 4 and 6 positions. The PMR spectrum of 3,7-dibromo-10-ethylphenotellurazine (Id) (Fig. 2) shows the triplet and quartet of the ethyl radical, the doublet of the aromatic protons at the 1 and 9 positions,

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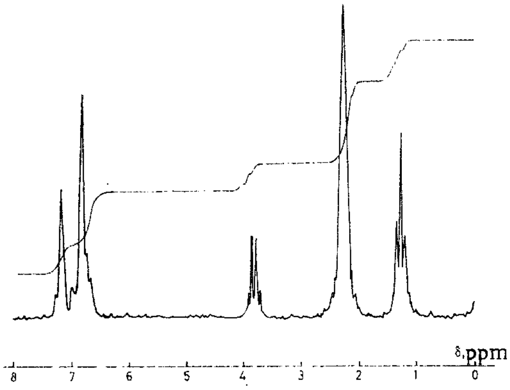


Fig. 1

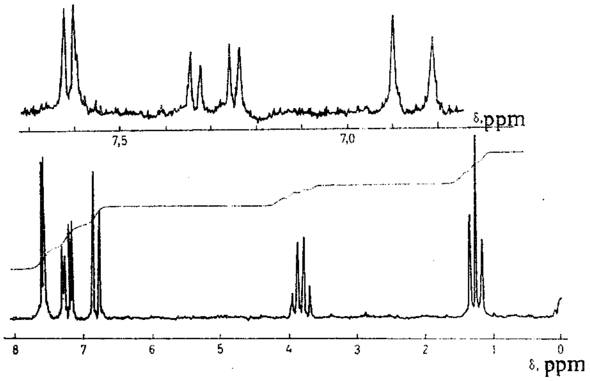


Fig. 2

Fig. 1. PMR spectrum of 3,7-dimethyl-10-ethylphenotellurazine (Ib) in CCl_4 (80 MHz).

Fig. 2. PMR spectrum of 3,7-dibromo-10-ethylphenotellurazine (Id) in CCl_4 (100 MHz).

TABLE 1. The σ-Telluranes, III

Compound	X	mp†, °C	Found, %		Empirical formula	Calculated, %		Yield, %
			C	H		C	H	
IIIa	Cl	250—252	42,9	3,6	$C_{14}H_{13}Cl_2NTe$	42,6	3,3	97
IIIb	Br	239—241	35,0	2,7	$C_{14}H_{13}Br_2NTe$	34,8	2,7	96
IIIc	I	212—214	29,6	2,7	$C_{14}H_{13}I_2NTe$	29,1	2,3	95
IIId	Cl	265—267	45,1	3,8	$C_{16}H_{17}Cl_2NTe$	45,5	4,0	99
IIIe	Br	256—258	37,4	3,6	$C_{16}H_{17}Br_2NTe$	37,7	3,3	98
IIIf	I	218—221	31,4	3,0	$C_{16}H_{17}I_2NTe$	31,7	2,8	97
IIIg	Cl	255	29,5	1,9	$C_{13}H_9Br_2Cl_2NTe$	29,0	1,7	96
IIIh	Br	>250	24,6	1,5	$C_{13}H_9Br_4NTe$	24,9	1,4	97
IIIi	I	233—235	22,1	1,5	$C_{13}H_9Br_2I_2NTe$	21,6	1,3	97
IIIj	Cl	245—247	30,6	2,0	$C_{14}H_{11}Cl_2Br_2NTe$	30,4	2,0	97
IIIk	Br	255	25,8	1,6	$C_{14}H_{11}Br_4NTe$	26,2	1,7	96
IIIl	I	215—217	23,1	1,6	$C_{14}H_{11}Br_2I_2NTe$	22,9	1,5	96
IIIm	F	256	49,0	4,5	$C_{16}H_{17}F_2NTe$	49,3	4,4	85
IIIn	$OCOCH_3$	176—178	51,0	4,6	$C_{20}H_{23}NO_4Te$	51,2	4,9	75
IIIo	ONO_2	227	40,6	3,8	$C_{16}H_{17}N_3O_6Te$	40,4	3,6	65
IIIp	$OCOCF_3$	202—204	41,6	3,3	$C_{20}H_{17}F_6NO_4Te$	41,9	3,4	87
IIIq	$OCOCH_3$	193—195	48,9	4,3	$C_{18}H_{19}NO_4Te$	48,7	4,3	70

*IIIa-f, j-q: $R^1 = C_2H_5$; g-i: $R^1 = CH_3$; a-c,q: $R^2 = H$; d-f,m-p: $R^2 = CH_3$.

†Recrystallization: IIIa, g-i, *l* from toluene; IIIm, n, p, q from ethanol; IIIo from propanol; others from chlorobenzene; IIIa decomposes.

the quartet of aromatic protons at the 2 and 8 positions, and the doublet of aromatic protons at the 4 and 6 positions.

The phenotellurazines Ia-d are yellow or greenish yellow crystalline compounds, without odor, stable when stored, with good solubility in acetone, chloroform, benzene, toluene, limited solubility in octane, and slight solubility in light petroleum ether.

The reactivity of Ia-d is determined by the two main reactive centers, viz., the tellurium atom and the benzene rings that are activated by the electron donor nitrogen and therefore can react relatively easily by electrophilic substitution. Like other compounds that contain dicoordinated tellurium (phenoxatellurines [1, 2] and telluroxanthenes [4, 5]), the 10-alkylphenotellurazines are easily converted to derivatives of tetracoordinated (σ-telluranes) and tricoordinated tellurium, viz., oxides, ylids, and telluronium salts; they also form molecular complexes with various acceptors (metal salts, rhodium(I) carbonyls [16]) in which tellurium is a donor center. When compounds Ia-d react with halogens (chlorine, bromine, iodine) or sulfuryl chloride, the 10-alkyl-5,5-dihalophenotellurazines IIIa-*l* (Table 1) form in quantitative yield; these in turn are quantitatively reduced (by potassium metabisulfite) to the 10-alkylphenotellurazines Ia-d. A number of other σ-telluranes containing

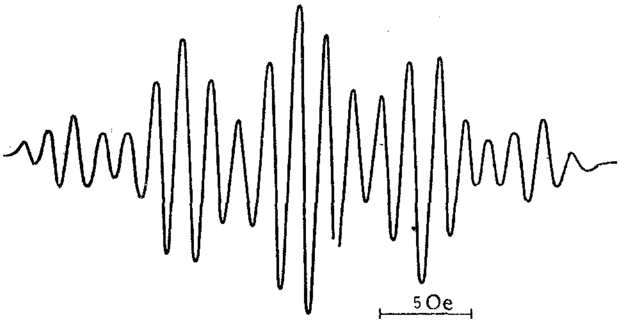


Fig. 3. EPR spectrum of radical cation of 10-ethylphenotellurazine 5,5-di(trifluoroacetate) (VIa).

TABLE 2. Hyperfine Coupling Constants (a, Oe) in Spectra of Radical Cations VIa-d

Radical cation	R^1	R^2	a_1^H	a^N	$a_{CH_2}^H$	$a_{CH_3}^H$
VIa	C_2H_5	H	1,6*	6,2	6,2	—
VIb	C_2H_5	CH_3	1,6	6,3	6,1	—
VIc	CH_3	Br	1,5	6,2	—	9,3
VId	C_2H_5	Br	1,5	6,2	6,0	—

*Relative to $a_{1,3}^H$.

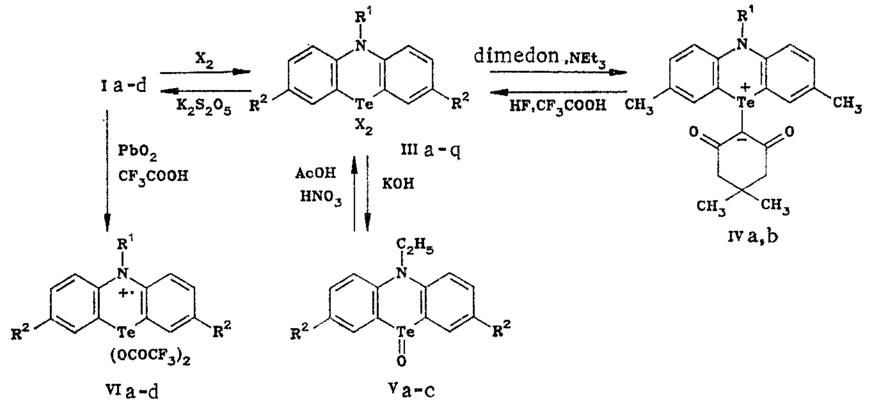
10-alkylphenotellurazine segments were obtained from π-telluranes (ylids or oxides; for their synthesis, see below) analogously to the syntheses from such compounds of the acyclic σ-telluranes. The reaction of telluronium ylids IVa,b with a number of acids (hydrofluoric, trifluoracetic goes, (as in the case of diaryltelluronium ylids [17]) with scission of the ylid bond, and gives III in high yield. Because weak acids do not cleave the ylid bond, the phenotellurazine 5,5-diacetates were synthesized, like the diaryltellurium diacetates [18], by the reaction of telluroxides Va-c with acetic acid. The same reaction was used to obtain 5,5-dinitrates, which in the case of phenoxatellurine were synthesized only by oxidation with nitric acid [2, 19].

In the PMR spectrum of 3,7-dimethyl-5,5-dichloro-10-ethylphenotellurazine (IIId) the signals of the aromatic protons in the 1, 2, 8, and 9 positions appear as an AB quartet at 7.63 ppm; those in the 4 and 6 positions appear as a singlet at 8.20 ppm. Thus, going from a dicoordinated tellurium derivative (Ib) to a tetracoordinated (IIId) causes a significant downfield shift of the aromatic proton signals (0.7-0.85 ppm).

Like the phenothiazines [12], the 10-alkylphenotellurazines Ia-d are easily oxidized in acid medium to form the stable radical cations VIa-d. These radical cations, which are generated by the oxidation of phenotellurazines Ia-d in trifluoroacetic acid by lead dioxide, have well resolved EPR spectra that are evidence of the significant delocalization of the unpaired electron. A typical EPR spectrum is shown in Fig. 3. But in contrast to the phenothiazine radical cation [12], the phenotellurazine radical cations contain tetracoordinated tellurium. Apparently in acid medium PbO_2 is converted to lead tetra(trifluoroacetate), which like lead tetraacetate converts tellurides to tellurium di(trifluoroacetate). The hyperfine coupling constants of the radical cations VIa-d are given in Table 2.

Tricoordinated derivatives containing a 10-alkylphenotellurazine residue, viz., ylids IVa,b and oxides Va-c, were synthesized in high yield from σ-telluranes, like the corresponding derivatives of the acyclic diaryl tellurides [21] and telluroxanthene [5]. Ylids IVa,b were obtained by the reaction of 5,5-dibromophenotellurazines III with dimedon in the presence of two equivalents of triethylamine; telluroxides Va-c, by hydrolysis of the dibromotelluride in dilute aqueous potassium hydroxide. When concentrated aqueous KOH containing excess alkali is used, the tellurium atom is pushed out, and the respective diarylamine is formed (see structure on following page).

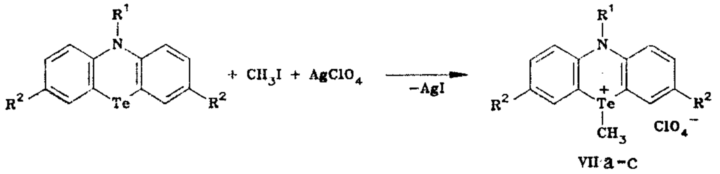
The other type of tricoordinated derivative, which contains a 10-alkylphenotellurazine segment, viz., the telluronium salts VIIa-c, does not form in the alkylation of 10-alkylphenotellurazines with alkyl halides, like dialkyl- and arylalkyl tellurides [1], due to the



IV a $R^1=C_2N_5$, b $R^1=CH_3$; V a $R^2=H$, b $R^2=CH_3$, c $R^2=Br$; X=Cl, Br, I; F, CF_3COO, CH_3COO, NO_3; the values R^1, R^2, and X for IIIa-q are given in Table 1; for VIa-d see Table 2.

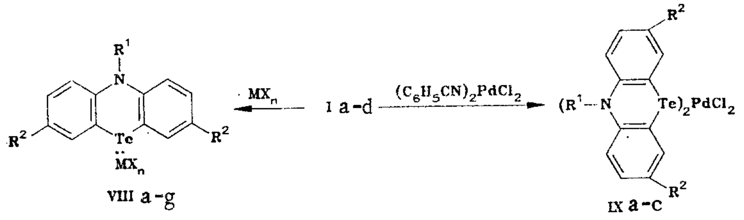
weakening of the nucleophilic properties of tellurium in I under the influence of the condensed benzene rings. But compounds VII were obtained in high yield by treating 10-alkylphenotellurazines with methyl iodide in the presence of an equivalent amount of silver perchlorate.

The PMR spectrum of the telluronium salt VIIb shows a poorly resolved AB quartet at 7.50 ppm of the aromatic protons at the 1, 2, 8, and 9 positions, and a singlet of the protons in the 4 and 6 positions at 7.85 ppm. Consequently the transition from a derivative of dicoordinated tellurium (Ib) to one of tricoordinated tellurium (VIIb) is accompanied by a substantial downfield shift of the aromatic proton signals (0.50-0.55 ppm), which, however, is less than that of the derivative of tetracoordinated tellurium (0.70-0.85 ppm).



VII a,b $R^1=C_2H_5$, c $R^1=CH_3$; a $R^2=H$; b,c $R^2=CH_3$

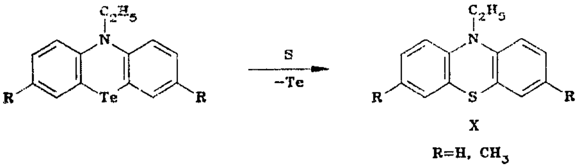
10-Alkylphenotellurazines form various molecular complexes in which tellurium, as in other complexes of dicoordinated tellurium with mild acceptors [16], acts as donor center. Compounds I form 1:1 complexes with mercury and silver salts (VIIIa-g), and a 2:1 complex with the palladium chloride—benzonitrile complex (IXa-c). The complexes with mercury and palladium salts are stable crystalline materials, of yellow or dark cherry color, respectively. However the complexes with silver salts are unstable and rapidly decompose when they are removed from solution (concerning the complexes of 10-alkylphenotellurazines with rhodium(I) carbonyls, see [16]). In contrast, copper dihalides do not form molecular complexes with 10-alkylphenotellurazines, but oxidize them to 5,5-dihalophenotellurazines.



VIIIa,b $R^1=C_2H_5$, $R^2=H$, c-f $R^1=C_2H_5$, $R^2=CH_3$, VIIIa-g $R^1=C_2H_5$; a,b $R^2=H$; c-f $R^2=CH_3$, g $R^2=Br$; a,c,g $MX_n=HgCl_2$; b,c $MX_n=HgBr_2$; e $MX_n=AgNO_3$; f $MX_n=AgClO_4$; IX a,b $R^1=C_2H_5$, c $R^1=CH_3$, a $R^2=H$, b $R^2=CH_3$, $R^2=Br$

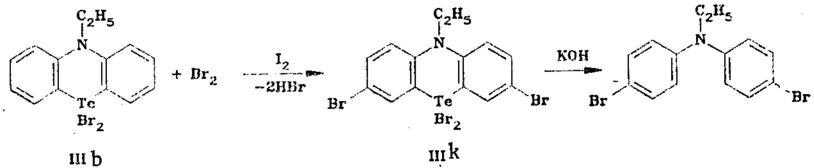
Like the phenoxatellurines [22-26], 10-alkylphenotellurazines can replace tellurium with sulfur when they are heated with sulfur at high temperature. In this way 10-ethylphenotellurazines gave 10-ethylphenothiazines X in more than 50% yield. (See structure on following page.)

Electrophilic substitution of benzene-ring hydrogen is a typical reaction of 10-alkylphenotellurazines, e.g., bromination and nitration. Bromination of 10-ethylphenotellurazine



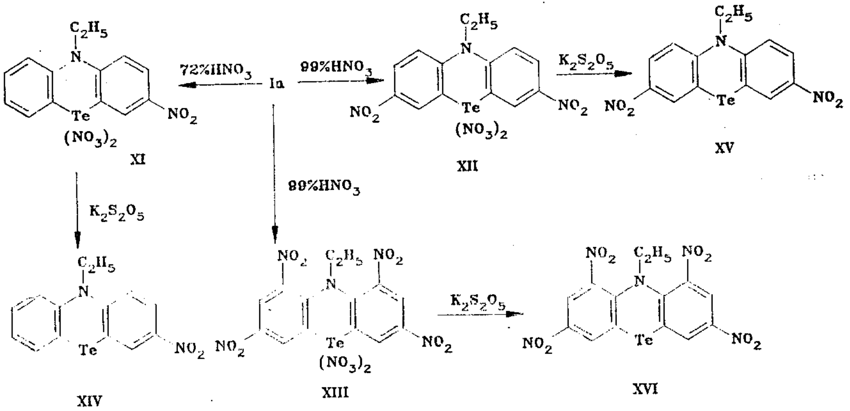
(Ia) occurs upon heating with bromine in CCl_4 solution in the presence of iodine catalyst. But it is not 10-ethylphenotellurazine that undergoes electrophilic substitution, but its 5,5-dibromo derivative IIIb that forms in the first state of the reaction of bromine with the phenotellurazine. In 5,5-dibromo-10-ethylphenotellurazine the nitrogen is the strong electron donor; the $TeBr_2$ group, which like other groups containing tetracoordinated tellurium [27] is a strong electron acceptor, accordingly orients the incoming bromine atoms to the 3 and 7 positions to give 3,5,5,7-tetrabromo-10-ethylphenotellurazine (IIIk). This result is analogous to that obtained with phenoxatellurine [28].

The same results were obtained in the bromination of 5,5-dibromo-10-ethylphenotellurazine (in the presence of iodine) or 5,5-diiodo-10-ethylphenotellurazine. In the latter case, as with the corresponding phenoxatellurine [29], there is first displacement by bromine of iodine, which then catalyzes the electrophilic substitution.



The structure of the product was demonstrated by its identity with a sample synthesized by oxidation of 3,7-dibromo-10-ethylphenotellurazine with bromine (see above), and by converting it to 4,4'-dibromo-N-ethyldiphenylamine by boiling with concentrated aqueous KOH.

10-Ethylphenotellurazine was nitrated by reaction with concentrated nitric acid in the absence of a solvent. Mono-, di-, or tetranitro derivatives form, depending on nitric acid concentration and reaction conditions (time, temperature). The final products are 10-ethylphenotellurazine 5,5-dinitrates, since before nitration occurs, tellurium is undoubtedly oxidized by the nitric acid. Just as in bromination, due to the concordant orienting influences of the $Te(NO_3)_2$ and NC_2H_5 groups the nitro groups are directed to the 3, 7, 1, and 9 positions. Treatment of 10-ethylphenotellurazine (Ia) with 70% nitric acid in a boiling water bath for 10 min gives 3-nitro-5,5-dinitrate phenotellurazine (XI). It should be noted that in the nitration of 10-ethylphenotellurazine, in contrast to that of phenoxatellurine [19], no isomer containing a nitro group at the 1 position could be separated [9]. The reaction of 10-ethylphenotellurazine with fuming nitric acid (heating in boiling water bath for 30 min) gives 10-ethyl-3,7-dinitrophenotellurazine 5,5-dinitrate (XII); longer heating (2 h) gives 1,3,7,9-tetranitro-10-ethylphenotellurazine 5,5-dinitrate (XIII). Thus in nitration 10-ethylphenotellurazine behaves like the phenothiazines [12], but it differs from phenoxatellurine, for which only mono- and dinitro derivatives were obtained [19]. The dinitrates XI-XIII are reduced to the nitrophenotellurazines XIV-XVI with potassium metabisulfite in high yield.



EXPERIMENTAL

PMR spectra of Ia-d were recorded on a Varian XL-100 instrument (100 MHz); those of IIId and VIIb, on a Tesla BS-487C (80 MHz) in carbon tetrachloride or deuteroacetone solution, with HMDS (internal standard) EPR spectra were obtained on a Carl Zeiss ER-9 instrument.

10-Ethylphenotellurazine (Ia). To a solution of 10 g (28 mmole) of N-ethyl-2,2'-dibromodiphenylamine [30] in 100 ml of absolute ether in an argon atmosphere was added 43 ml of 1.45 N (62.35 mmole) butyllithium in ether with vigorous stirring and cooling to 0 to –2°. The mixture was stirred for 1 h at 0°, and 12.5 g (35 mmole) of tellurium diiodide was added in small portions. The mixture was boiled for 1 h, during which time most of the tellurium diiodide dissolved. The mixture was cooled and poured into 250 ml of ice water. Excess TeI_2 was filtered off and the precipitate on the filter was washed with two 50-ml portions of ether. The ether solution was dried with anhydrous Na_2SO_4 and the ether was evaporated. Recrystallization from nitromethane gave 4.52 g (50%) of 10-ethylphenotellurazine, a yellowish green crystalline material with mp 138-140°. PMR spectrum (CCl_4): 1.28 (3H, t, J = 7 Hz, CH_2CH_3), 3.93 (2H, q, J = 7 Hz, CH_2CH_3), 6.90-7.60 (8H, m, 1,2,3,4,6,7,8,9-H_8). Found: C 52.4; H 3.9%. $C_{14}H_{13}NTe$. Calculated: C 52.0; H 4.0%.

3,7-Dimethyl-10-ethylphenotellurazine (Ib) was obtained by the preceding procedure. Yield 55%. Yellow crystals, mp 88-90° (from octane). PMR spectrum (CCl_4): 1.31 (3H, t, J = 7 Hz, CH_2CH_3), 2.27 [6H, s, 3,7-$(CH_3)_2$], 3.90 (2H, q, J = 7 Hz, CH_2CH_3), 6.95 (4H, unresolves system of protons in 1, 2, 8, 9 positions), 7.35 (2H, s, 4,6H_2). Found: C 55.2; H 5.1%. $C_{16}H_{17}NTe$. Calculated: C 54.8; H 5.4%.

3,5,5,7-Tetrabromo-10-methylphenotellurazine (IIIh). To a suspension of 17 g (34 mmole) of N-methyl-2,2',4,4'-tetrabromodiphenylamine [31] in 200 ml absolute ether in an argon atmosphere was added 50 ml of 1.45 N (73 mmole) butyllithium in ether with vigorous stirring and cooling to –10°. The amine dissolved and the solution turned light brown. The mixture was stirred for 1 h at –10° and 15 g (42 mmole) of tellurium diiodide was added in small portions. The mixture was boiled for 1 h, cooled, and poured into 250 ml of ice water. Excess TeI_2 was filtered off, and the residue was washed twice on the filter with 50-ml portions of ether. The ether solution was dried with anhydrous $CaCl_2$, filtered, and mixed with 5.44 g (34 mmole) of bromine in 10 ml ether with cooling in ice water. A precipitate of IIIh formed at once. Recrystallization from toluene gave 9.60 g (45%) of dark red crystals, mp >250°.

3,7-Dibromo-10-methylphenotellurazine (Ic). To a suspension of 7 g (11 mmole) of IIIh in 50 ml of water was added 15 g (68 mmole) of potassium metabisulfite in small portions with stirring over 20 min. The mixture was heated to 70-80° and held at that temperature for 1 h. It was cooled and the precipitate was filtered off, washed on the filter with a small amount of cold water, and dried. Recrystallization from propanol gave 4.78 g (93%) of golden yellow crystals of Ic, mp 150-152°. PMR spectrum (CCl_4): 3.45 (3H, s, 10-CH_3), 6.80 (2H, d, J_{12} = 9 Hz, 1,9H_2), 7.29 (2H, q, J_{24} = 2.5 Hz, 2,8-H_2), 7.57 (2H, d, J_{24} = 2.5 Hz, 4,6-H_2). Found: C 32.8; H 1.9%. $C_{13}H_9BrNTe$. Calculated: C 33.4; H 1.9%.

3,7-Dibromo-10-ethylphenotellurazine (Id). To a suspension of 15.4 g (30 mmole) of N-ethyl-2,2',4,4'-tetrabromodiphenylamine [32] in 150 ml of absolute ether in an argon atmosphere was added 45 ml of 1.45 N (62 mmole) butyllithium in ether with vigorous stirring and cooling to –10°. The solution turned light brown, It was stirred for 1 h at –10°; 14.3 g (40 mmole) of tellurium diiodide was added in small portions and the mixture was boiled for 1 h. After cooling it was poured into 250 ml of ice water, excess tellurium diiodide was filtered off, and the precipitate was washed with two 50-ml portions of ether. The ether solution was dried with anhydrous Na_2SO_4 and the ether was evaporated. Recrystallization from propanol gave 7.95 g (55%) of Id, light yellow crystals, mp 112-114°. PMR spectrum (CCl_4): 1.29 (3H, t, J = 7 Hz, CH_2CH_3), 3.89 (2H, q, J = 7 Hz, CH_2CH_3), 6.85 (2H, d, J_{12} = 9 Hz, 1,9-H_2), 7.27 (2H, q, J_{24} = 2.5 Hz, 2,8-H_2), 7.57 (2H, d, J_{24} = 2.5 Hz, 4,6-H_2). Found: C 35.0; H 2.4%. $C_{14}H_{11}Br_2NTe$. Calculated: C 34.9; H 2.3%.

5,5-Dichloro-3,7-dimethyl-10-ethylphenotellurazine (IIId). A. To a solution of 1.76 g (5 mmole) of Ib in 50 ml absolute ether was added a solution of 0.68 g (5 mmole) of sulfuryl chloride in 15 ml of ether, slowly with stirring and cooling in ice water; or a current of dry chlorine was passed through for 15 min. The precipitate was filtered off, washed with water, and dried. Recrystallization from chlorobenzene gave 2.09 g (99%) of IIId, yellow crystals, mp 265-267°. PMR spectrum (acetone-D_6): 1.53 (3H, t, J = 7 Hz, CH_2CH_3), 2.60 [6H, s, 3,7-$(CH_3)_2$], 4.47 (2H, q, J = 7 Hz, CH_2CH_3), 7.63 (4H, weakly resolved AB system of protons in 1, 2, 8, 9 positions), 8.20 (2H, s, 4,6-H_2).

Other 5,5-dichlorophenotellurazines were obtained similarly; their properties are given in Table 1.

B. To a solution of 1.76 g (5 mmole) of Ib in 50 ml of acetone was added to a solution of 1.40 g (11 mmole) of $CuCl_2$ in a mixture of 25 ml water and 25 ml of acetone, slowly with stirring. The mixture was boiled for 0.5 h, cuprous chloride was filtered off, the filtrate was poured into water, the precipitate was filtered off, washed with water, and dried. Recrystallization from chlorobenzene gave 1.58 g (75%) of IIId, mp 265-267°.

5,5-Dibromo-3,7-dimethyl-10-ethylphenotellurazine (IIIe). A. To a solution of 1.76 g (5 mmole) of Ib in 50 ml of absolute ether was added a solution of 1 g (6.3 mmole) of bromine in 10 ml of absolute ether, slowly with stirring and cooling in ice water. The red precipitate was filtered off, washed with ether and dried. Recrystallization from chlorobenzene gave 2.50 g (98%) of IIIe, brick-red crystals, mp 256-258°.

Other 5,5-dibromophenotellurazines were obtained similarly (Table 1).

B. To a solution of 1.76 g (5 mmole) of Ib in 50 ml of acetone was added a solution of 2.24 g (10 mmole) of $CuBr_2$ in a mixture of 25 ml water and 25 ml acetone, dropwise with stirring. The solution was boiled for 0.5 h, cuprous bromide was filtered off, and the filtrate was poured into water. The precipitate was filtered off, washed with water, and dried. Recrystallization from chlorobenzene gave 2.04 g (80%) of IIIe, mp 256-258°.

5,5-Diiodo-3,7-dimethyl-10-ethylphenotellurazine (IIIf). To a solution of 1.76 g (5 mmole) of Ib in 50 ml of absolute ether was added a solution of 2.54 g (10 mmole) of iodine in 40 ml of ether at room temperature with stirring. The dark brick-colored precipitate was filtered off, washed with ether, and dried. There was obtained 2.96 g (97%) of dark cherry-colored crystals, mp 218-221°.

Other 5,5-diiodophenotellurazines were obtained similarly (Table 1).

5,5-Difluoro-3,7-dimethyl-10-ethylphenotellurazine (IIIm). To a solution of 1 g (2.1 mmole) of 3,7-dimethyl-10-ethylphenotelluronium azine dimedonylide (IVa) in 30 ml of ethanol was added 0.25 g (5 mmole) of 40% HF with stirring. The solution was heated to boiling. When it was cooled a fine crystalline precipitate formed, IIIm, yield 0.69 g (85%), faintly yellowish crystals, mp 256°.

3,7-Dimethyl-10-ethylphenotellurazine 5,5-Dinitrate (IIIo). To a solution of 1 g (2.7 mmole) of 3,7-dimethyl-10-ethylphenotellurazine 5-oxide (Vc) in 25 ml of propanol was added 1.5 ml (6.7 mmole) of 25% HNO_3 at room temperature, slowly with stirring. The mixture was cooled in an ice bath. The bright red precipitate was filtered off, washed with alcohol, and dried. There was obtained 0.83 g (65%) of IIIo, mp 228° (with decomposition).

3,7-Dimethyl-10-ethylphenotellurazine 5,5-Diacetate (IIIn). To a solution of 1.84 g (5 mmole) of Vc in 20 ml or propanol heated to 70-80° was added 0.75 g (12.5 mmole) of glacial acetic acid with stirring. The precipitate that formed when the solution was cooled was filtered off, washed with propanol, and dried. Recrystallization from ethanol gave 1.76 g (75%) of IIIn, colorless crystals, mp 176-178°.

Compounds IIIp, q were obtained similarly (Table 1).

3,7,10-Trimethylphenotelluronium Azinedimedonylid (IVb). To a boiling solution of 4.32 g (8.7 mmole) of 5,5-dibromo-3,7,10-trimethylphenotellurazine and 1.22 g (8.7 mmole) of dimedon in 70 ml of absolute benzene was added 2.5 ml (17 mmole) of freshly distilled triethylamine dropwise with stirring. As the amine was added, colorless crystalline triethylamine hydrobromide precipitated. After cooling, the precipitate was filtered off and washed with benzene, and the filtrate was evaporated in air. The resulting oil crystallized when rubbed with petroleum ether. There was obtained 4.06 g (98%) of light cream-colored crystals, mp 214-216° (from 1:1 benzene—octane). Found: C 58.6; H 5.8%. $C_{23}H_{25}NO_2Te$. Calculated: C 58.1; H 5.3%.

3,7-Dimethyl-10-ethylphenotelluronium azinedimedonylid (IVa) was obtained analogously to IVb. Yield, 80%. Light brown crystals, mp 212-214° (from 1:1 benzene—petroleum ether). Found: C59.0; H 5.5%. $C_{24}H_{27}NO_2Te$. Calculated: C 58.9; H 5.5%.

3,7-Dimethyl-10-ethylphenotellurazine 5-Oxide (Vb). To a suspension of 2.11 g (5 mmole) of IIId in 20 ml of water was added a solution of 0.4 g (10 mmole) of NaOH in 5 ml of water.

The mixture was held at this temperature for 30 min.* The yellow dichloride color disappeared and colorless oxide crystals precipitated; they were filtered off, washed carefully with water, and dried. Yield, 1.56 g (85%), mp 148-150° (from benzene). Found: C 52.3; H 4.6%. $C_{16}H_{17}NOTe$. Calculated: C 52.4; H 4.6%.

3,7-Dibromo-10-ethylphenotellurazine 5-oxide (Vc) was obtained analogously to Vb. Yield, 83%. Colorless crystals, mp 255-257° (from benzene—propanol mixture). Found: C 33.4; H 2.7%. $C_{14}H_{11}Br_2NOTe$. Calculated: C 33.8; H 2.2%.

3,5,7-Trimethyl-10-ethylphenotelluronium Azine Perchlorate (VIIb). To a solution of 1.76 g (25 mmole) of Ib and 0.72 g (5 mmole) of methyl iodide in 20 ml of absolute acetonitrile was added a solution of 1.04 g (5 mmole) of silver perchlorate in 10 ml of acetonitrile at room temperature with stirring. The solution was heated to boiling, the silver iodide precipitate (1.15 g, 98%) was filtered off, and the filtrate was evaporated. There was obtained 2.09 g (90%) of VIIb perchlorate; colorless crystals, mp 204-206° (with explosion, from acetonitrile—octane mixture). PMR spectrum (acetone-D_6): 1.30 (3H, t, J = 7 Hz, CH_2CH_3), 2.35 [6H, s, 3,7-$(CH_3]_2$), 2.55 (3H, s, 5-CH_3), 4.20 (2H, q, J = 7 Hz, CH_2CH_3), 7.50 (4H, AB quartet, J = 8 Hz, 1,2,8,9-H_4), 7.85 (2H, s, 4,6-H_2). Found: C 43.3; H 4.5%. $C_{17}H_{20}ClNOTe$. Calculated: C 43.7; H 4.3%.

3,5,7,10-Tetramethylphenotelluronium azine perchlorate (VIIc) was obtained by the preceding procedure. Yield, 88%. Colorless crystals, mp 232-234° (with explosion, from acetonitrile—octane mixture). Found: C 42.3; H 4.5%. $C_{16}H_{18}ClNO_4Te$. Calculated: C 42.5; H 4.0%.

10-Ethyl-5-methylphenotelluronium azine perchlorate (VIIa) was obtained by an analogous procedure. Yield, 89%. Colorless crystals, mp 238° (with decomposition, from acetonitrile—octane mixture. Found: C 41.6; H 3.8%. $C_{15}H_{16}ClNO_4Te$. Calculated: C 41.1; H 3.7%.

(3,7-Dimethyl-10-ethylphenotellurazine)mercury(II) Chloride (VIIIc). To a solution of 1.76 g (5 mmole) of tellurazine Ib in 50 ml of absolute ether was added 1.36 g (5 mmole) of mercuric chloride in 10 ml of absolute ethanol, dropwise with stirring at room temperature. The yellow precipitate was filtered off, washed with ether, and dried. There was obtained 2.64 g (85%) of VIIIc, mp 158-160° (with decomposition). Found: C 30.6; H 3.1%. $C_{16}H_{17}Cl_2HgNTe$. Calculated: C 30.9; H 2.7%.

(10-Ethylphenotellurazine)mercury(II) chloride (VIIIa) was obtained by the preceding procedure. Yield, 78%. Light yellow crystals, mp 187-189°. Found: C 28.7; H 2.5%. $C_{14}H_{13}Cl_2HgNTe$. Calculated: C 28.3; H 2.2%.

(3,7-Dibromo-10-ethylphenotellurazine)mercury(II) chloride (VIIIg) was obtained analogously to VIIIc. Yield, 65%. Light yellow crystals, mp 156-158°. Found: C 22.5; H 1.6%. $C_{14}H_{13}Br_2Cl_2HgNTe$. Calculated: C 22.3; H 1.5%.

(10-Ethylphenotellurazine)mercury(II) bromide (VIIIb) was obtained analogously to VIIIc. Yield, 75%. Orange crystals, mp 160-162°. Found: C 24.2; H 1.9%. $C_{14}H_{13}Br_2HgNTe$. Calculated: C 24.6; H 1.9%.

(3,7-Dimethyl-10-ethylphenotellurazine)mercury(II) bromide (VIIId) was obtained analogously to VIIc. Yield, 81%. Orange crystals, mp 210-212°. Found: C 26.4; H 2.4%. $C_{16}H_{17}Br_1HgNTe$. Calculated: C 26.9; H 2.5%.

(3,7-Dimethyl-10-ethylphenotellurazine)silver(I) nitrate (VIIIe) and (3,7-dimethyl-10-ethylphenotellurazine)silver(I) perchlorate (VIIIf) were obtained by mixing toluene solutions of 3,7-dimethyl-10-ethylphenotellurazine with equimolar amounts of silver perchlorate or nitrate in acetonitrile solution. The fine crystalline precipitate that forms when the reaction mixture is boiled decomposed rapidly during filtration, with separation of silver metal; therefore acceptable elemental analysis data could not be obtained.

Bis-(3,7-dimethyl-10-ethylphenotellurazine)palladium(II) Chloride (IXb). To a solution of 1.76 g (5 mmole) of tellurazine Ib in 20 ml of acetone were added 0.70 g (2.5 mmole) of the benzonitrile complex of palladium dichloride in 10 ml acetone at room temperature with stirring. The dark cherry red precipitate was filtered off, washed with acetone, and dried. There was obtained 2.09 g (95%) of IXb, mp 255° (with decomposition). Found: C 43.4; H 3.9%. $C_{32}H_{34}Cl_2N_2PdTe$. Calculated: C 43.6; H 3.9%.

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*Temperature omitted from Russian original — Editor.

Bis-(10-ethylphenotellurazine)palladium(II) chloride (IXa) was obtained by an analogous procedure. Yield, 93%. Dark cherry red crystals, mp 247°. Found: C 40.6; H 3.5%. $C_{28}H_{26}Cl_2N_2PdTe$. Calculated: C 40.9; H 3.2%.

Bis(3,7-dibromo-10-ethylphenotellurazine)palladium(II) chloride (IXc) was obtained by an analogous procedure. Yield, 96%. Dark cherry red crystals, mp >255° (with decomposition). Found: C 24.8; H 1.7%. $C_{26}H_{18}Br_2Cl_2N_2PdTe$. Calculated: C 28.1; H 1.6%.

Reaction of Phenotellurazines with Sulfur. A carefully pulverized mixture of 1.62 g (5 mmole) of 10-ethylphenotellurazine and 0.2 g (6 mmole) of sulfur was placed in a one-necked flask with a dephlegmator, and heated at 140-150° for 1.5 h. The mixture became dark red, and metallic tellurium separated as a finely crystalline gray powder. The mixture was cooled, dissolved in 20 ml of benzene, and filtered from Te; the precipitate was washed with benzene and dried; it weighed 0.3 g (47%). The filtrate was treated with activated charcoal, filtered, and chromatographed on aluminum oxide (benzene eluent). The solvent was evaporated and the residue was recrystallized from ethanol. There was obtained 0.51 g (45%) of 10-ethylphenothiazine, mp 103-103.5° (103-103.5° according to [33]). Found: C 74.5; H 5.6%. $C_{14}H_{13}NS$. Calculated: C 74.0; H 5.7%.

10-Ethyl-3-7-dimethylphenothiazine was obtained analogously from 10-ethyl-3,7-dimethylphenotellurazine; mp 56-58°.

Bromination of 5,5-Diiodo-10-ethylphenotellurazine (IIIc). To a solution of 2.89 g (5 mmole) of IIIc in 50 ml of CCl_4 was added a solution of 2.4 g (15 mmole) of bromine in 10 ml CCl_4 at room temperature slowly with stirring. The mixture was boiled for 3 h, cooled to room temperature, and treated with activated charcoal, and the solvent was evaporated. There was obtained 2.31 g (72%) of 3,5,5,7-tetrabromo-10-ethylphenotellurazine (IIIk). Orange crystals, mp 255° (from chlorobenzene). To a suspension of 1.6 g (2.5 mmole) of IIIk in 50 ml of water was added 25 g (11 mmole) of potassium metabisulfite. The mixture was heated 0.5 h at 70-80° and cooled, and the precipitate was extracted with toluene. The solvent was evaporated and the residue was recrystallized from butanol. There was obtained 1.2 g (97%) of 3,7-dibromo-10-ethylphenotellurazine (Id), mp 112-114° (from propanol).

Reaction of 3,5,5,7-Tetrabromo-10-ethylphenotellurazine with KOH. To a suspension of 1.6 g (2.5 mmole) of tetrabromo derivative IIIk in 20 ml of water was added 20 ml of 50% KOH solution. The mixture was boiled for 1.5 h, cooled, and poured into 100 ml of water. The precipitate was extracted with benzene, the solvent was evaporated, and the residue was recrystallized from ethanol. There was obtained 0.46 g (52%) of 4,4'-dibromo-N-ethyldiphenylamine as colorless crystals, mp 105-107° (107-108° according to [34]). Found: C 47.5; H 4.0%. $C_{14}H_{13}Br_2N$. Calculated: C 47.3; H 3.7%.

3-Nitro-10-ethylphenotellurazine (XIV). Powdered 10-ethylphenotellurazine (Ia), 1.5 g (4.6 mmole) was added in small portions with stirring at room temperature to 10 ml of 72% HNO_3 (d 1.42). The phenotellurazine dissolved to give an orange-red solution. The mixture was heated in a boiling water bath for 10 min, cooled, and poured into 30 ml of water. The yellow precipitate was filtered off, washed carefully with cold water, and dried. There was obtained 2.15 g (95%) of 3-nitro-10-ethylphenotellurazine 5,5-dinitrate (XI). To a suspension of 2.15 g (4.4 mmole) of XI in 50 ml of water was added 4.5 g (20 mmole) of potassium metabisulfite in small portions with stirring. The mixture was heated to 70-80°, held for 0.5 h, and cooled. The dark-red precipitate was extracted with benzene, the solvent was evaporated, and the residue was recrystallized from ethanol. There was obtained 1.04 g (75%) of XIV, mp 153-155°. Found: C 45.3; H 3.2%. $C_{14}H_{12}N_2O_2Te$. Calculated: C 45.7; H 3.5%.

3,7-Dinitro-10-ethylphenotellurazine (XV). Powdered Ia, 1.3 g (4 mmole), was added slowly to 3 ml of conc. HNO_3 (d 1.51) with stirring at 0 to −2°. The dark-red solution was allowed to warm up to room temperature and was then heated in a boiling water bath for 0.5 h. The mixture was cooled and poured with stirring into 50 ml of water. The yellow precipitate was filtered off, washed with cold water, and dried. There was obtained 2.08 g (97%) of 3,7-dinitro-10-phenotellurazine 5,5-dinitrate (XII) yellow crystals mp >250°. Found: C 31.7; H 2.2%. $C_{14}H_{11}N_5O_{10}Te$. Calculated: C 31.3; H 2.1%.

To a suspension of 1.34 g (2.5 mmole) of XII in 50 ml of water was added 2.5 g (11 mmole) of potassium metabisulfite in small portions with stirring. The mixture was heated for 20 min at 40-50° and cooled. The dark red precipitate was extracted with benzene. The benzene was distilled off and the residue was recrystallized from toluene. There was obtained 0.88 g

(85%) of brick-red crystals of XV, mp 200-202°. Found: C 41.1; H 3.0%. $C_{14}H_{11}N_3O_4Te$. Calculated: C 40.7; H 2.7%.

1,3,7,9-Tetranitro-10-ethylphenotellurazine (XVI). Ia, 1.5 g (4.6 mmole) was added to 12 ml of conc. HNO_3 (d 1.51) in small portions with stirring at 0° to −2°. The dark-red solution was allowed to warm up to room temperature, heated in a boiling water bath for 2 h, cooled, and poured into 50 ml of cold water. The yellow precipitate was filtered off, washed with water, and dried. There was obtained 2.77 g (96%) of 1,3,7,9-tetranitro-10-ethylphenotellurazine 5,5-dinitrate (XIII).

To a suspension of 1.57 g (2.5 mmole) of XIII in 50 ml of water was added 2.5 g (11 mmole) of potassium metabisulfite in small portions at room temperature. The mixture was heated for 20 min at 70-80°. After cooling the precipitate was filtered off and extracted with benzene. The solvent was distilled off. Recrystallization from ethanol gave 1.1 g (87%) of XVI. Found: C 33.3; H 1.8%. $C_{14}H_9N_5O_8Te$. Calculated: C 33.4; H 1.8%.

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