having lowered the temperature to −50°C, 0.02 mole of the respective N-acetylaminothiophene (IIIa or IIIb) was added in the minimum quantity of chloroform. The reaction mixture was agitated for 1 h at −30°C, poured into 200 ml of water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform extracts were washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized or chromatographed on an Al_2O_3 column in the system ether—hexane (1:3) and compounds IV-VI were obtained.

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REACTIONS OF 2H-TELLUROCHROMENE

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2-H-Tellurochromene is characterized by reactions (halogenation, alkylation, and complex-formation) which result in an increase in the coordination number of the tellurium atom to 4 or 3, to give σ-telluranes, telluronium salts, and complexes with metal salts. Oxidation of 2-H-tellurochromene with trityl perchlorate affords tellurochromyllium perchlorate, and with dichromate 2-formylbenzo[b]tellurophene.

Although 2H-tellurochromene (I) was first obtained more than ten years ago [1], information on its reactivity, apart from oxidation with seleneium dioxide to give the 2-formyl derivative of benzo[b]tellurophene [2], is absent from the literature. Such information is nevertheless valuable in comparing the properties of this heterocycle with those of its sulfur and selenium analogs, as well as identifying similarities and differences from the properties of other types of tellurium heterocycle, namely, the tricyclic systems telluroxanthene [3] and phenotellurazine [4], studied by us previously.

The tellurochromene (I) system possesses several reaction centers, namely the tellurium atom, and the double bond and the methylene group. In principle, reactions are possible involving electrophilic substitution fo the hydrogen atoms of the annelated benzene ring. However, in view of the ease of fission of the $Te—C_{sp^3}$ bond on treatment with electrophiles and the conversion of the tellurium thereby into the tetracoordinated state, which deactivates the benzene ring [5], reactions of this type may be regarded as highly unlikely for tellurochromene.

The presence in the tellurochromene molecule of a dicoordinated tellurium atom implies (unlike its sulfur analog [6], but like other dicoordinated tellurium compounds [3-5]) that it will readily undergo reactions resulting in an increase in the coordination number of the tellurium to 4 or 3. These reactions give the tetracoordinated derivaties of (I) (σ-

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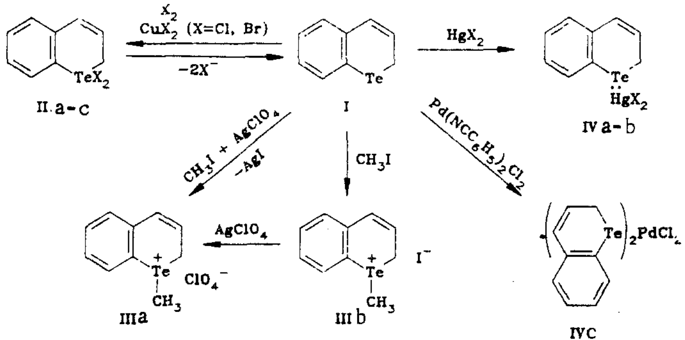
telluranes), tricoordinated compounds (telluronium salts), and molecular complexes of (I) with metal salts.



II a IVa X=Cl; b X=Br; II c X=I

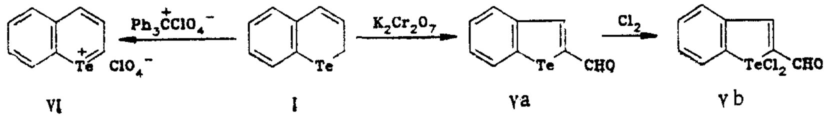
Tellurochromene reacts with halogens or sulfuryl chloride in inert solvents to give the corresponding σ-telluranes (1,1-dihalotellurochromenes (IIa-c)) in near-quantitative yields. On treatment with a variety of reducing agents (Na_2SO_3, $Na_2S_2O_5$, and zinc dust in ethanol), these compounds readily regenerate tellurochromene, and can therefore be used for its purification. The PMR spectra of the σ-telluranes (IIa-c) are reminiscent of that of tellurochromene, but differ in that the signals for the methylene and olefinic protons are shifted to lower field, owing to the strong electron-acceptor influence of the TeX_2 group [7]. It is interesting that even when an excess of halogen is used at high temperatures, no addition of halogen to the double bond occurs. It is likely that the σ-tellurane TeX_2 groups formed in the first stage of the reaction deactivate the double bond towards electrophilic addition of halogens.

The conditions required for the conversion of dicoordinated tellurium compounds into telluronium salts are governed by their structures. Although dialkyl and aryl alkyl tellurides readily give telluronium salts on treatment with activated or unactivated alkyl bromides and iodides, the tricyclic tellurium systems telluroxanthene [3] and phenotellurazine [4], in which the nucleophilicity of the tellurium atom is reduced by the annealated benzene rings, are converted into telluronium salts only on treatment with alkyl iodides in the presence of silver perchlorate or fluoroborate. Tellurochromene, like the heterocycles mentioned above, gives 1-methyltelluroniochromene perchlorate (IIIa) on treatment with methyl iodide in the presence of an equivalent amount of silver perchlorate. Unlike these compounds, however, tellurochromene, being a cyclic aryl alkyl telluride, is converted in high yield into 1-methyltelluroniochromene iodide (IIIb) on reaction with methyl iodide in the absence of a solvent. On treatment with silver perchlorate, (IIIb) is converted in quantitative yield into the perchlorate (IIIa).

Like other dicoordinated tellurium compounds [3-5], tellurochromene readily forms molecular complexes with metal salts. Reaction with mercury salts gives the weakly-colored 1:1 complexes (IVa, b), and the benzonitrile complex of palladium(II) chloride, the dark red compound (IVc), in which each $PdCl_2$ molecule is accompanied by two molecules of tellurochromene. All the tellurochromene complexes are sparingly soluble in organic solvents.

As with telluroxanthene [3] and N-alkylpenotellurazines [4], reaction of tellurochromene (I) with copper dihalides affords the oxidation products of (I), the 1,1-dihalotellurochromenes (IIa, b), rather than the complexes.

The methylene group in telluroxanthene is readily oxidized to carbonyl by treatment with potassium dichromate in glacial acetic acid [3]. It might be expected that a similar reaction with tellurochromene would give, as in the oxidation of 2H-thio- and 2H-selenochromene with CrO_3 in pyridine [8], tellurochromen-2-one, obtained recently by Renson by a two-step synthesis from o-methyltellurobenzaldehyde [9]. However, the principal product from the reaction was 2-formylbenzo[b]tellurophene (Va). The identity and structure of this compound were shown by its elemental analysis (see Experimental) and its coversion into 1,1-dichlorobenzo[b]tellurophene (Vb), the analytical and spectral characteristics of which were in accordance with the proposed structure. Telurochromene, therefore, is oxidized by potassium dichromate in the same way as with SeO_2 [2] to give (V).



The second type of reaction involving the methylene group in tellurochromene is conversion into tellurochromylium perchlorate (VI). This reaction is carried out as for the preparation of telluroxanthylium perchlorate [10], by reaction of tellurochromene with trityl perchlroate in trifluoroacetic acid [11]. Attempts to effect the disproportionation of tellurochromene into tellurochromane by reaction with $HClO_4$ in ether, as for thiochromenes [6], gave mixtures of products, from which individual compounds could not be isolated.

EXPERIMENTAL

IR spectra were obtained on a UR-20 instrument in Vaseline oil, and UV spectra on a Specord M-40. PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) with HMDS as internal standard.

Tellurochromene (I) was obtained as described in [1].

1,1-Dichlorotellurochromene (IIa). A. A rapid stream of dry chlorine was passed through a solution of 1.22 g (5 mmole) of (I) in 20 ml of benzene with ice-water cooling for 15 min. The solid which separated was filtered off, washed with hexane, and dried to give 1.50 g (96%) of (IIa) as yellow crystals, mp 187°C (decomp., from chlorobenzene). PMR spectrum ($DMSO-D_6$): 4.40 (2H, d, J_{23} = 2.5 Hz, CH_2); 6.20 (1H, d. t, 3–H); 7.00 (1H, d, J_{34} = 5.5 Hz, 4–H); 7.25... 8.70 ppm (4H, 4, 5-, 6-, 7-, and $8–H_4$). Found: C 34.1; H 2.2%. $C_9H_8Cl_2Te$. Calculated: C 34.2; H 2.5%.

B. To a solution of 2.44 g (10 mmole) of tellurochromene (I) in 50 ml of acetone was added with stirring a solution of 2.80 g (21 mmole of $CuCl_2$ in a mixture of 25 ml of water and 25 ml of acetone. After boiling for 30 min, the solution was cooled, filtered from copper (I) chloride, and the filtrate poured into water. The solid (IIa) which separated was filtered off, washed with water, and dried. Recrystallization from chlorobenzene gave 2.61 g (83%) of (IIa), mp 187°C (decomp.).

1,1-Dibromotellurochromene (IIb). A. To a solution of 1.22 g (5 mmole) of tellurochromene in 20 ml of benzene was added with stirring and ice-water cooling a solution of 0.8 g (5 mmole) of bromine in 5 ml of benzene. The solid which separated was filtered off, washed with hexane, and dried to give 1.93 g (96%) of (IIb) as yellow crystals, mp 197°C (decomp., from chlorobenzene). PMR spectrum ($DMSO-D_6$): 4.30 (2H, d, J_{23} = 2.5 Hz, CH_2); 6.10 (1H, d.t, 3–H); 6.90 (1H, d, J_{34} = 5.5 Hz, 4–H); 7.21...8.64 ppm (4H, m, 5-, 6-, 7-, and $8–H_4$). Found: C 26.2; H 2.3%. $C_9H_8Br_2Te$. Calculated: C 26.7; H 2.0%.

B. To a solution of 2.44 g (10 mmole) of (I) in 50 ml of acetone was added with stirring a soluton of 4.48 g (10 mmole) of $CuBr_2$ in a mixture of 25 ml of water and 25 ml of acetone. After boiling for 30 min, the solution was cooled, filtered from CuBr, and the filtrate poured into water. The precipitated dibromotellurochromene was filtered off, washed with water, and dried. Recrystallization from chlorobenzene gave 3.31 g (82%) of (IIb), mp 197°C (decomp.).

1,1-Diiodotellurochromene (IIc). To a solution of 1.22 g (5 mmole) of tellurochromene in 20 ml of chloroform was added with stirring and ice-water cooling a solution of 1.27 g (5 mmole) of iodine in 15 ml of chloroform. After stirring for 10 min at this temperature, the solvent was evaporated in air to 1.04 g (99%) of the diiode (IIc) as dark reddish-brown crystals, mp 211°C (decomp., from chloroform). Found: C 21.4; H 1.5%. $C_9H_8I_2Te$. Calculated: C 21.6; H 1.6%.

1-Methyltelluroniochromene Perchlorate (IIIa). To a solution of 1.22 g (5 mmole) of tellurochromene and 0.71 g (5 mmole) of iodomethane in 30 ml of acetonitrile was added with stirring at room temperature a solution of 1.04 g (5 mmole) of silver perchlorate in 10 ml of acetonitrile. After stirring for 30 min at this temperature, the solution was filtered from precipitated AgI (1.17 g, 100%). The solvent was evaporated in air to give 1.52 g (85%) of (IIIa) as large, colorless crystals, mp 170°C (decomp., from acetonitrile-benzene). Found: C 31.2; H 3.3%. $C_{10}H_{11}ClO_4Te$. Calculated: C 31.0; H 3.2%.

1-Methyltelluroniochromene Iodide (IIIb). To 1.22 g (5 mmole) of tellurochromene was added 3 ml (46 mmole) of methyl iodide. An exothermic reaction set in, with the separation of a yellowish, crystalline solid. Excess methyl iodide was decanted off, and the crystals washed throughly on the filter with hexane. After drying, there was obtained 1.73 g (90%) of (IIIb) as pale yellow crystals, mp 104-105°C (decomp., from benzene-hexane). PMR spectrum ($DMSO-D_6$): 2.50 (3H, s, CH_3); 4.00 (2H, d, J_{23} = 2.5 Hz, CH_2); 6.10 (1H, d.t, 3-H); 7.00 (1H, d, J_{34} = 5.5 Hz, 4-H); 7.10...8.5 ppm (4H, m, 5-, 6-, 7-, and 8-H_4). Found: C 30.9; H 2.7%. $C_{10}H_{11}ITe$. Calculated: C 31.1; H 2.8%.

Dichloro(tellurochromene)mercury (IVa). To a solution of 1.22 g (5 mmole) of (I) in 15 ml of benzene was added with stirring a solution of 1.36 g (5 mmole) of $HgCl_2$ in 5 ml of alcohol, and the mixture boiled for 10 min. It was then cooled, and the crystals of (IV) which separated were filtered off, washed with ether, and dried to give light reddish-brown crystals, mp 188°C (decomp.). Found: C 21.3; H 1.3%. $C_9H_8Cl_2HgTe$. Calculated: C 20.0; H 1.5%.

Dibromo(tellurochromene)mercury (IVb). Obtained by the preceding method. Yield 96%. Yellowish crystals, mp 192°C (decomp.). Found: C 17.9; H 1.6%. $C_9H_8Br_2HgTe$. Calculated: C 17.8; 1.3%.

Dichlorobis(tellurochromene)palladium (IVc). To a solution of 1.22 g (5 mmole) of tellurochromene in 10 ml of acetone was added with stirring a solution of 0.96 g (2.5 mmole) of dichlorobis(benzonitrile)palladium [12] in 10 ml of acetone. After 15 min of boiling, the darkly cherry-colored solid was filtered off, washed with acetone, and dried. 1.57 g (95%) of (IVc), mp 163°C (decomp.), was obtained. Found: C 32.9; H 2.6%. $C_{18}H_{16}Cl_2PdTe$. Calculated: C 32.5; H 2.4%.

2-Formylbenzo[b]tellurophene (Va). A soluton of 3 g (12.3 mmole) of tellurochromene and 5 g (17 mmole) of $K_2Cr_2O_7$ in 50 ml of acetic acid was boiled for 3 h, cooled, and poured into 150 ml of cold water. The solid which separated was filtered off, washed with water, and dried. The solid was extracted with hot benzene (5 × 15 ml), and the resulting red solution evaporated in air. Chromatography on alumina (eluent, benzene) and removal of the solvent gave 0.6 g (19%) of yellow crystals of (Va), mp 110°C (from CCl_4; according to [2], mp 108°C). PMR spectrum (CCl_4): 6.75-8.00 (4H, m, 4-, 5-, 6-, and 7-H_4); 8.40 (1H, s, 3-H); 9.70 ppm (1H, s, CHO). Found: C 41.8; H 3.2%. C_9H_6OTe. Calculated: C 41.7; H 3.1%.

1,1-Dichloro-2-formylbenzo[b]tellurophene (Vb). A stream of dry chlorine was passed for five minutes through a solution of 0.26 g (1 mmole) of (Va) in 5 ml of chloroform. Removal of the solvent gave 0.31 g (94%) of (Vb) as yellowish crystals, mp 240°C (decomp., from chlorobenzene). Found: C 33.1; H 2.6%. $C_9H_6Cl_2OTe$. Calculated: C 32.7; H 3.1%.

Tellurochromylium Perchlorate (VI). A mixture of 2.44 g (10 mmole) of tellurochromene and 3.43 g (170 mmole) of trityl perchlorate in 50 ml of anhydrous CF_3COOH was boiled for 30 min. The triphenylmethane which separated on cooling was filtered off, and the filtrate concentrated on the water bath to a volume of 10 ml. The solution was cooled, and the crystalline (VI) filtered off, washed with cold CF_3COOH (5 ml) followed by dry ether (3 × 10 ml), and dried to give 1.2 g (35%) of small deep violet crystals, mp 160-162°C (decomp.). IR spectrum: 1670, 1640, 1580, 1320, 1260, 1150, 1100, 760 cm^{-1}. UV spectrum in CF_3COOH, λ_{max} (log ε): 327 (3.99), 410 (3.31), 560 nm (2.58). Found: C 31.6; H 2.2%. $C_9H_7ClO_4Te$. Calculated: C 31.5; H 2.0%.

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REACTIONS OF PHTHALIMIDONITRENE WITH CONJUGATED ENAMINES. SYNTHESIS OF 1-AMINO-2-ETHYNYLAZIRIDINE

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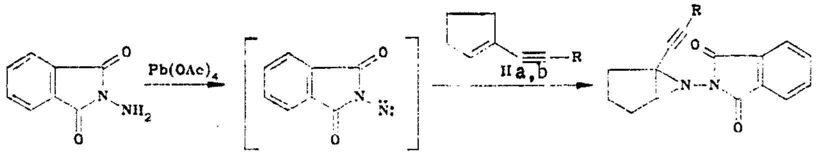
Addition of phthalimidonitrene to 1-(1-octynyl)- and 1-(phenylethynyl)-cyclopentene takes place exclusively at the double bond to give the bicyclic N-phthalimidoaziridines in ~40% yield.

Reaction of acylaminonitrenes, particularly the most thoroughly investigated phthalimidonitrene (I), with olefins provides a convenient method for the synthesis of N-aminoaziridines [1, 2]. Addition of acylaminonitrenes to conjugated dienes occurs smothly to give vinylaziridines, while acetylenes give small yields of 2-amino-2H-azirines, which are rearrangement products of the intermediate antiaromatic 1H-azirines [1, 3]. However, only one example has been reported of the reaction of the nitrene (I) with 2,5,5-trimethylhex-1-en-3-yne, a conjugated enyne system, which is present as an impurity in di-tert-butylacetylene, the reaction of which has been studied [3]. The sole addition products obtained in the latter case were the alkynylaziridines.

In order to study in greater depth the addition of acylaminonitrenes to conjugated enynes, we reacted the nitrene (I) with the alkynylcyclopentenes (II). The choice of substrates was made on the basis that the probable reaction products, namely the aziridines (III), are of considerable interest as synthons for the construction of prostanoid systems. In particular, their oxygen analogs (the corresponding epoxides) are not only used extensively in prostanoid synthesis, but have also been selected by computer as synthons for prostaglandins [4].

The reaction was carried out in the usual way [5], the nitrene (I) being generated by oxidation of N-aminophthalimide with lead tetraacetate in methylene chloride at 2-5°C in the presence of excess substrate (II). The products were isolated by column chromatography.



I

II, IIIa $R=C_6H_{13}$; b $R=C_6H_5$

IIIa,b

The bicyclic aziridines (III) were obtained in yields of around 40% as yellow, crystalline solids, readily soluble in chloroform. The PMR spectra of the adducts (III) showed a signal

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