SYNTHESIS OF PHENOXATELLURINE DERIVATIVES

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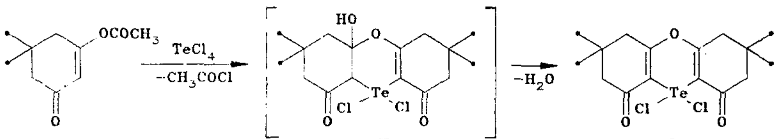
The reaction of dimedon enol acetate with tellurium tetrachloride gives derivatives of octahydrophenoxatellurine. The reaction of cyclohexanone enol acetate and methyl ethyl ketone with tellurium tetrachloride or aryltellurium trichloride gives the respective organotellurium trichloride and diorganotellurium dichloride.

The synthesis and reactivity of phenoxatellurine and its derivatives (mainly 2,8-disubstituted) have been studied quite thoroughly [1-12]. But so far no information has been published on the hydrogenated derivatives of phenoxatellurine.

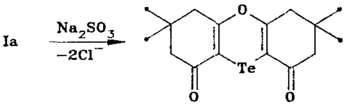
In studying a new synthesis of σ-telluranes containing β-keto groups based on the reaction of ketone enol acetates with tellurium tetrachloride or aryltellurium trichloride, we have found a new reaction that gives hitherto unknown octahydro derivatives of phenoxatellurine. When dimedon enol acetate reacts with tellurium tetrachloride in glacial acetic acid, 1,2,3,4,6,7,8,9-octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine 10,10-dichloride (Ia) is formed in 55-60% yield. By analogy with the data of [13] pertaining to the properties of bis(cyclohexan-1,3-dion-2-yl)methanes we can presume that the reaction goes through the intermediate formation of bis(5,5-dimethylcyclohexan-1,3-dion-2-yl)tellurium dichloride, which is in equilibrium with its cyclic polyketal form II. In acid medium the latter splits out a molecule of water to form Ia:



II

Ia

The tellurium dichloride Ia, like other σ-telluranes [14], is reduced in high yield by sodium sulfite to the respective tellurine, viz., 1,2,3,4,6,7,8,9-octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine (III):



III

The structure is demonstrated by elemental analysis, and IR, PMR, and mass spectroscopy. The IR spectrum of III shows an absorption band at 1620 cm^{-1} that corresponds to the vibrations of a carbonyl conjugated with a double bond. The mass spectrum contains an intense molecular peak with m/z 388 that corresponds to the structure of III. The PMR spectrum shows signals at 1.07 (s, 12H, CH_3); 2.32 (s, 4H, protons at 4,6 positions) and 2.42 ppm (s, 4H, protons at 2,8 positions) (in deuterochloroform). Since the methyl groups in III are isochronous (at ordinary temperature they give a common signal), this is evidence of a rapid low-barrier inverstion of the cyclohexene rings in this compound.

Compound III has the typical properties of diorganotellurides [14]. It is easily oxidized by halogens (chlorine, bromine, iodine) to the respective σ-telluranes Ia-c (X = Cl, Br, I) in quantitative yield. The same σ-telluranes were obtained [15-17] by a method developed for the synthesis of similar compounds based on the reaction of the telluronium ylid IV (obtained according to [18] from Ia and dimedone in the presence of triethylamine) with hydrohalic acid. The PMR spectrum of IV shows the signals of three nonequivalent pairs

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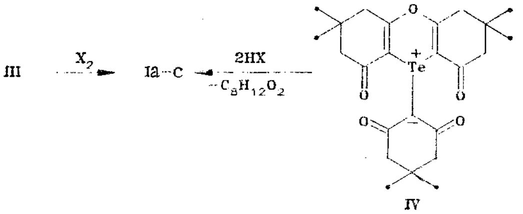
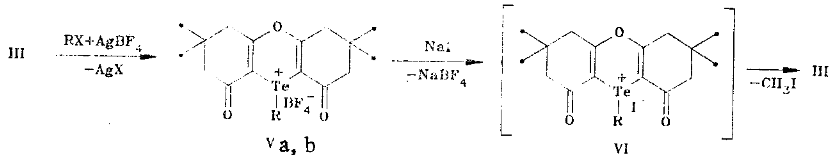
of methyl groups; these are due to the pyramidal structure of the tricoordinated tellurium, which causes the methyls of the cyclohexene segment to be diastereotopic.



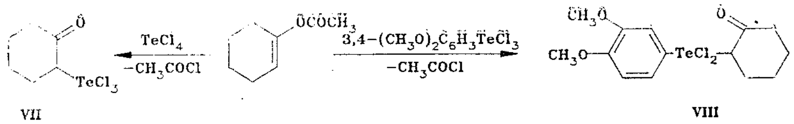
I a X=Cl; b X=Br; c X=I

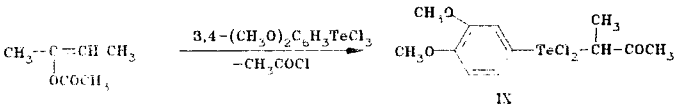
Due to the substantial weakening of the nucleophilic properties of tellurium in III under the influence of carbonyl, as in other tricyclic tellurium systems (telluroxanthene [16], 10 alkylphenotellurazines [17]), III can be alkylated by alkyl halides only in the presence of silver fluoborate. It is of interest that in contrast to the reactions of other triorganotellurium salts containing weakly nucleophilic aniona [14], the reaction of fluoborate Va with sodium iodide at room temperature gives not triorganotellurium iodide VI, but the starting heterocycle III. Evidently under the influence of the electron acceptor C=O group, VI eliminates methyl iodide even at room temperature, whereas with most other telluronium salts this process occurs only upon heating:



$R=CH_3$, $X=I$; $R=C_6H_5CH_2$, $X=Cl$; Va, VI $R=CH_3$; V b $R=C_6H_5CH_2$

Thus the reaction of dimedon enol acetate with tellurium tetrachloride is quite specific and gives heterocycle Ia. The reactions of some other ketone enol acetates (cyclohexanone, methyl ethyl ketone) give acyclic products, the structure of which depends on the nature of the substrate. Thus cyclohexanone enol acetate reacts with both tellurium tetrachloride and aryltellurium chlorides to give the σ-telluranes VII and VIII. At the same time methyl ethyl ketone enol acetate reacts with 3,4-dimethoxyphenyltellurium trichloride to give σ-tellurane IX, whereas in the case of tellurium tetrachloride the latter is reduced to tellurium metal.





EXPERIMENTAL

IR spectra were recorded in mineral oil on a UR-20 spectrometer. PMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz).

The enol acetates were synthesized by the procedure of [19]; 3,4-dimethoxyphenyltellurium trichloride was obtained by the procedure of [20].

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine 10,10-Dichloride (Ia). To a solution of 40 g (0.149 mole) of tellurium tetrachloride in 200 ml of glacial acetic acid was added 55 g (0.30 mole) of dimedon enol acetate in one proton. The mixture, which turned orange-red, was heated at 100°C for 30 min and cooled to 40-50°. The very small amount of tellurium metal was filtered off and the transparent dark red filtrate was allowed to stand at 5° for 2 days. The voluminous precipitate was filtered off, washed with ether, and dried. Yield 41 g (60%). For purification the reaction product was dissolved in a minimal amount of chloroform and filtered; to the hot filtrate was added hot carbon tetrachloride until crystallization began. Colorless fine crystals, mp 227-228.5°. IR spectrum: 1645, 1618, 1573, 1345, 1312, 1285, 1266, 1232, 1180, 1155, 805, 785 cm^{-1}. PMR spectrum ($CDCl_3$):

1.03 (s, 12H, CH_3); 2.40 (s, 4H, protons in 4,6 positions); 2.67 ppm (s, 4H, protons in 2,8 positions). Found: C 42.1 H 4.6%. $C_{16}H_{20}Cl_2O_3Te$. Calculated: C 41.9 H 4.4%.

1,2,3,4,6,7,8,9-Octhydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine (III). A solution of 15 g (32.7 mmole) of Ia dichloride in 60 ml of chloroform was mixed in a separatory funnel with a solution of 8.8 g (0.07 mole) of Na_2SO_3 in, 100 ml of water and carefully shaken for 10-15 min. The chloroform layer changed from colorless to orange. The orange layer was washed with two 100-ml portions of water, dried over Na_2SO_4, and evaporated in air. Yield, 11.7 g (92%). Long thin light-orange needles, mp 183-184° (from benzene–ethanol mixture). IR spectrum: 1622, 1587, 1415, 1350, 1335, 1300, 1255, 1187, 1155, 1135, 1020, 1005, 930, 895, 880 cm^{-1}. PMR spectrum ($CDCL_3$): 1.07 (s, 12H, CH_3); 2.32 (s, 4H, protons in 4,6-positions); 2.42 ppm (s, 4H, protons in 2,8 positions). Found: C 49.9 H 5.4%. $C_{16}H_{20}O_3Te$. Calculated: C 49.5; H 5.2%.

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine 10,10-Dibromide (Ib). To a solution of 2.0 g (5.16 mmole) of III in 15 ml of chloroform was added a solution of 0.83 g (5.16 mmole) of bromine in 10 ml of chloroform dropwise with stirring. The color of the solution changed from orange to yellow. The solution was evaporated to dryness to yield 2.8 g (100%) of Ib. Yellow needles, mp 202-204° (from dioxane–hexane mixture). Found: C 34.8; H 3.5%. $C_{16}H_{20}Br_2O_3Te$. Calculated: C 35.1; H 3.7%.

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurine 10,10-Diiodide (Ic). To a solution of 2.0 g (5.16 mmole) of phenoxatellurine III in 15 ml of chloroform was added a solution of 1.31 g (5.16 mmole) of iodine in 25 ml of chloroform dropwise with stirring. The solution was evaporated in air to dryness to give 3.29 g (100%) of Ic. Red crystals, mp 193-195° (from benzene–hexane mixture). Found: C 29.8; H 3.3%. $C_{16}H_{20}I_2O_3Te$. Calculated: C 30.0; H 3.1%.

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7-tetramethyl-1,9-dioxophenoxatellurinium Dimedonylid (IV). In a separatory funnel was placed 10 g (21.8 mmole) of dichloride Ia and 3.06 g (21.8 mmole) of dimedon in 150 ml of chloroform. To the clear colorless solution was added 6.3 ml (45 mmole) of triethylamine dropwise with stirring. The mixture immediately turned yellow. It was shaken for 20 min at room temperature and washed with three 150-ml portions of water. The chloroform layer was dried with Na_2SO_4 and concentrated on a water bath to 30 ml. From the dark yellow solution, 8.70 g (76%) of ylid IV was precipitated with diethyl ether. It was dissolved in 30 ml of chloroform and the solution was filtered. To the hot filtrate was added ether until crystallization began. Fine pale-yellow crystals, mp 198-200° (with decomposition). IR spectrum: 1628, 1585, 1538, 1315, 1285, 1270, 1215, 1180, 1155, 1030 cm^{-1}. PMR spectrum ($CDCl_3$): 0.80 (s, 6H); 0.91 (s, 6H); 1.05 (s, 6H); 2.08 (s, 4H); 2.33 (s, 4H); 2.67 (s, 4H). Found: C 54.6 H 5.6%. $C_{24}H_{30}O_5Te$. Calculated: C 54.8; H 5.8%.

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7,10-pentamethyl-1,9-dioxophenoxatellurinium Fluoborate (Va). To a solution of 6.5 g (16.8 mmole) of phenoxatellurine III and 3 ml (excess) of methyl iodide in 50 ml of acetone was added a solution of 3.30 g (17 mmole) of silver fluoborate in 30 ml of acetone with stirring. The solution changed from orange to colorless and silver iodide precipitated. The mixture was boiled for 1 h, the precipitate was filtered off, and the filtrate was evaporated to dryness in air. There was obtained 7.9% g (96%) of Va. Recrystallization from a minimal amount of acetone gave coarse colorless crystals, mp 219°. Found: C 41.5; H 4.9%. $C_{17}H_{23}BF_4O_3Te$. Calculated: C 41.7; H 4.8%.

1,2,3,4,6,7,8,9-Octahydro-3,3,7,7-tetramethyl-10-benzyl-1,9-dioxophenoxatellurinium fluoborate (Vb) was obtained analogously. Yield 82%. Colorless lustrous plates, mp 202° (from acetone–hexane mixture). Found: C 48.0; H 5.0%. $C_{23}H_{27}BF_4O_3Te$. Calculated: C 48.8; H 4.8%.

Reaction of Fluoborate Va with Sodium Iodide. To a solution of 1 g (2.04 mmole) of Va in 20 ml of acetone was added a solution of 0.4 g (2.15 mmole) of $NaI \cdot 2H_2O$ in 10 ml of acetone. The mixture turned orange at once. Then 80 ml of benzene and 80 ml of water were added, the mixture was shaken, and the benzene layer was separated, dried by azeotropic distillation, and evaporated in air. There was obtained 0.77 g (97%) of orange needles of heterocycle III.

2-Trichlorotellurocyclohexanone (VII). To a solution of 5.44 g (0.02 mole) of tellurium tetrachloride in 50 ml of ether was added 2.7 g (0.02 mole) of cyclohexanone enol acetate. The mixture became red, and after 10 min colorless plates of VII began to precipitate. The material was washed with ether and dried in vacuum. There were obtained 3.88 g (58%) of crystals, mp 109-110°. When stored the material gradually decomposed with separation of tellurium metal. Found: C 21.5; H 2.8%. $C_6H_9Cl_3OTe$. Calculated: C 21.8; H 2.7%.

3,4-Dimethoxyphenyl(2-cyclohexanonyl)tellurium Dichloride (VIII). To a solution of 3.7 g (0.01 mole) of 3,4-dimethoxyphenyltellurium trichloride in 50 ml of toluene was added 1.5 g (0.11 mole) of cyclohexanone enol acetate. The mixture was boiled for 30 min, then passed hot through a bed of aluminum oxide, and the filtrate was evaporated in air. There was obtained 2.58 (58%) of VIII. Colorless needles, mp 174° (from methanol). Found: C 38.6; H 4.2%. $C_{14}H_{18}Cl_2O_3Te$. Calculated: C 38.8; H 4.4%.

3,4-Dimethoxyphenyl(1-methylpropanon-2-yl)tellurium Dichloride (IX). To a solution of 3.7 g (0.01 mole) of 3,4-dimethoxyphenyltellurium trichloride in 20 ml of benzene was added 1.25 g (0.011 mole) of methyl ethyl ketone enol acetate. The solution was boiled for 6 h and passed through a bed of aluminum oxide, and the filtrate was evaporated in air. The residual oil solidified when triturated with hexane. Yield, 3.8 g (93%). Colorless needles, mp 105-107° (from methanol). Found: C 35.6; H 3.8%. $C_{12}H_{10}Cl_2O_3Te$. Calculated: C 35.4; H 4.0%.

LITERATURE CITED

1. H. D. K. Drew, J. Chem. Soc., 223 (1926).
2. H. D. K. Drew, J. Chem. Soc., 3054 (1926).
3. H. D. K. Drew and R. W. Thomason, J. Chem. Soc., 116 (1927).
4. H. D. K. Drew, J. Chem. Soc., 506 (1928).
5. H. D. K. Drew, J. Chem. Soc., 511 (1928).
6. I. G. M. Campbell, J. Chem. Soc., 37 (1938).
7. G. Vasiliu and A. Gioaba, Rev. Chim. (Bucharest), 19, 253 (1968).
8. G. Vasiliu and A. Gioaba, Rev. Chim. (Bucharest), 20, 357 (1969).
9. A. Gioaba and O. Maior, Rev. Chim. (Bucharest), 21, 613 (1970).
10. A. Gioaba and O. Maior, Ann. Univ. Bucuresti, 22, 111 (1973).
11. A. Gioaba, O. Maior, and M. Mitran, Rev. Roum. Chim., 21, 733 (1976).
12. A. Gioaba, M. Nedea, and O. Maior, Rev. Roum. Chim., 21, 739 (1976).
13. Ya. K. Lemba, É. V. Blums, and I. É. Lielbriedis, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 2, 207 (1976).
14. I. D. Sadekov, A. A. Maksimenko, and V. I. Minkin, The Chemistry of Organotellurium Compounds [in Russian], Rostov State University, Rostov-on-Don (1983).
15. I. D. Sadekov, A. I. Usachev, and V. I. Minkin, Zh. Obshch. Khim., 48, 475 (1978).
16. I. D. Sadekov, A. A. Ladatko, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 10, 1342 (1980).
17. I. D. Sadekov, G. M. Abakarov, V. B. Panov, L. Yu. Ukhin, A. D. Garnovskii, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 6, 757 (1985).
18. I. D. Sadekov, A. I. Usachev, V. A. Bren', M. S. Korobov, I. D. Tseimakh, and V. I. Minkin, Zh. Obshch. Khim., 47, 2232 (1977).
19. I. V. Machinskaya and V. A. Barkhash, Reactions and Method of Investigation of Organic Compounds [in Russian], Khimiya, Leningrad–Moscow (1964), p. 299.
20. I. D. Sadekov, L. M. Sayapina, A. Ya. Bushkov, and V. I. Minkin, Zh. Obshch. Khim., 41, 2713 (1971).