by the dipole moment method [2]. For 1, 4-dithiin itself, the boat conformation has been shown by the X-ray method [3].

We have also carried out a spectroscopic study of III. The PMR spectrum of III in carbon disulfide contains two signals: 6.50 ppm and 7.20 ppm (with tetramethylsilane as standard). In the PMR spectrum of 2, 5-diphenyl-1, 4-dithiin [4] there is also a signal at 6.5 ppm and a group of lines in the 7.2–7.7 ppm region.

The UV spectrum of III in methanol consists of two absorption bands with λ_{max}, nm (log ε): 240 (4.30) and 342.5 (4.28). The energy of the $\pi \rightarrow \pi^*$ electronic transition calculated from the position of the first absorption band is 119.2 kcal/mole. The excitation energy of the p-electrons of selenium is 83.9 kcal/mole, calculated from the position of the second absorption band.

The IR spectra contain the following most characteristic absorption bands (cm^{-1}): 3050, C—H stretching vibrations; 1650, C=C vibrations in a heterocycle; 1585, 1560, 1495, 1450, stretching vibrations of conjugated C=C bonds; 895, 825, deformation vibrations of C—H in a ring, and in addition there are strong bands with frequencies of 775, 755, 690, and 510 cm^{-1}.

EXPERIMENTAL

A mixture of 19 g (0.24 g-atom) of red selenium and 24 g (0.24 mole) of phenylacetylene was heated in the presence of an equimolar amount of sodium ethoxide in 20 ml of boiling dioxane for 8 hr. The dioxane was then distilled off, the solid product was washed free of catalyst with water, and was recrystallized from benzene with the addition of petroleum ether. After repeated recrystallization, 9 g of 2, 5-diphenyl-1, 4-diselenacyclohexa-1, 5-diene with mp 135.5°–136° C was obtained. Found, %: C 53.17; H 3.20; Se 43.31; M 366.50. Calculated for $C_{16}H_{12}Se_2$, %: C 53.06; H 3.34; Se 43.60; M 362.18.

The measurement (in dioxane) and calculation of the dipole moment was carried out as described previously [5]. The PMR spectrum was measured on a RYa-2303 instrument constructed by SKB AP AN SSSR [Special Design Bureau for Analytical Instruments of the Academy of Sciences of the USSR]. The UV spectrum was measured on a SF-4 spectrophotometer. The IR spectrum of III was recorded in KBr tablets on a UR-10 spectrometer.

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SYNTHESIS OF 2, 2, 5, 5-TETRAMETHYLTETRAHYDROTHIOPHENE

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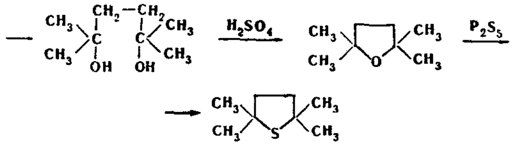
Under the conditions of the Grignard reaction, 2, 5-dimethyl-2, 5-hexanediol has been obtained from diethyl succinate. Under the action of sulfuric acid, the latter has been cyclized to 2, 2, 5, 5-tetramethyltetrahydrofuran which, in its turn, by treatment with phosphorus pentasulfide, has given 2, 2, 5, 5-tetramethyltetrahydrothiophene. Its reaction with methyl iodide has given 2, 2, 5, 5-tetramethyltetrahydrothiophene methiodide.

The method of synthesizing tetrahydrothiophene from 1, 4-dihalobutanes and sodium sulfide is well known. In an attempt to synthesize 2, 2, 5, 5-tetramethyltetrahydrothiophene (I) from 2, 5-dibromo-2, 5-dimethylhexane and sodium sulfide, a mixture of products difficult to separate and containing only a small amount of I was obtained. The treatment of 2, 5-dimethyl-2, 5-hexanediol with phosphorus pentasulfide gave only traces of I. Thus, it is found to be completely analogous to 2, 2, 6, 6-tetramethyltetrahydrothiopyran [1], the synthesis of which could be effected only by treating 2, 2, 6, 6-tetramethyltetrahydropyran with phosphorus pentasulfide.

On this basis, the synthesis of I was carried out by the following route.



Naylor [1] has reported that 2, 2, 6, 6-tetramethyltetrahydrothiopyran methiodide is formed only when the initial reactants are allowed to stand cold for a long time; performing the reaction at 100° C leads to the production of trimethylsulfonium iodide as the main product. A similar phenomenon was found in our case, although I proved to be somewhat more stable and did not require cooling during the reaction with methyl iodide.

EXPERIMENTAL

2, 5-Dimethyl-2, 5-hexanediol. From a dropping funnel, 59.2 g (0.34 mole) of diethyl succinate (bp 86° C, 6mm); d_4^{20} 1.040; n_D^{20} 1.4200, in 75 ml of ether was added to the cooled Grignard reagent prepared from 45 g (1.9 g-atom) of magnesium and 270 g (1.9 mole) of methyl iodide in 400 ml of ether.

Then the mixture was boiled for 2 hr and was left overnight. After this it was slowly poured into a previously-prepared solution of ammonium chloride (200 g in 700 ml of water) containing finely crushed ice (2000 g). The ethereal layer was separated off and the aqueous layer was carefully extracted with ether. The combined ethereal extracts were dried with magnesium sulfate. After the ether and volatile products had been distilled off in vacuum (1 mm), 18 g (36.5%) of a product with mp 92° C was obtained. According to the literature [2]: mp 90°-91° C.

2, 2, 5, 5-Tetramethyltetrahydrofuran. A flask fitted with a reflux condenser and a stirrer was charged with a mixture of 18 g (0.12 mole) of 2, 5-dimethyl-2, 5-hexanediol and 150 ml of 2 N sulfuric acid. Stirring and heating (100° C) was carried out for 2 hr. Then the organic layer was separated off and distilled. Colorless liquid with a characteristic odor, yield 7 g (45.5%), bp 115°-118° C, d_4^{20} 0.8336; n_D^{20} 1.4190. According to the literature [3], bp 116°-117° C.

2, 2, 5, 5-Tetramethyltetrahydrothiophene (I). A tube previously purged with nitrogen was charged with 7 g (55 mM) of 2, 2, 5, 5-tetramethyltetrahydrofuran and 24 g (0.11 mole) of phosphorus pentasulfide, sealed, and kept at 100° C for 6 hr. Then the mixture was treated with 30% aqueous alkali and twice extracted with ether. The ethereal extracts were dried with potassium carbonate. After the ether had been driven off, the residue was distilled in vacuum. Yield 4 g (51%).

Redistillation gave a colorless liquid with a sharp smell having bp 56° C (25 mm); d_4^{20} 0.8954; n_D^{20} 1.4670. Found, %: C 67.0; H 11.1; S 22.18; MR_D 44.63. Calculated for $C_8H_{16}S$, %; C 66.7; H 11.1; S 22.20; MR_D 44.44.

IR spectrum: 550 (w); 595 (s); 690 (m); 732 (m); 763 (m); 795 (m); 815 (w); 925 (w); 975 (m); 1013 (m); 1085 (s); 1120 (s); 1139 (v.s); 1185 (w); 1195 (m); 1312 (m); 1379 (s); 1385 (m); 1410 (m); 1460 (s).

Methiodide of I. A mixture of 1.44 g (0.01 mole) of I and 1.4 g (0.01 mole) of methyl iodide was kept at room temperature for 2 days. After recrystallization from ethanol–ether it formed light yellow crystals, mp 161° C (decomp.). The yield was quantitative. Found, %: I 44.76. Calculated for $C_9H_{19}SI$, %: I 44.45.

After I had been kept with an excess of methyl iodide at 80°-100° C for several hours, it was possible to isolate from the reaction mixture only trimethylsulfonium iodide (decomposing at 209° C; according to the literature [4]; decomp. 215° C). Yield 70%. Found, %: I 62.9 Calculated for C_3H_9SI, %: I 62.3.

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THE REACTION OF SODIUM SALTS OF URACILS WITH CHLORIDES OF ACIDS OF PHOSPHORUS. I

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The reaction of the sodium salts of 6-methyluracil (I) and 3, 6-dimethyluracil (II) with methyl and ethyl phosphorochloridates and phosphorochloridothioates give the corresponding N-methyl- and N-ethyluracils. The reaction of I with dimethyl phosphorochloridothioate has given a phosphorus-containing reaction product the structure of which has not been established.

The reaction of the Na salts of 6-methyluracil (I) and 3, 6-dimethyluracil (II) with dimethyl phosphorochloridothioate (III), diethyl phosphorochloridate, and ethyl ethylphosphonochloridothioate leads to the vigorous alkylation of the pyrimidine nucleus, particularly in the case of III. Thus, the reaction of III with I in dimethylformamide yielded 3, 6-dimethyluracil and 1, 3, 6-trimethyluracil, and the reaction of III with II yielded 1, 3, 6-trimethyluracil. The formation of these compounds can be represented by the following scheme.