that Dibepin and Dibepin-2 are only the first representatives of a new group of analytical reagents with a peculiar mechanism of their action.

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# THE REACTION OF SELENIUM WITH PHENYLACETYLENE

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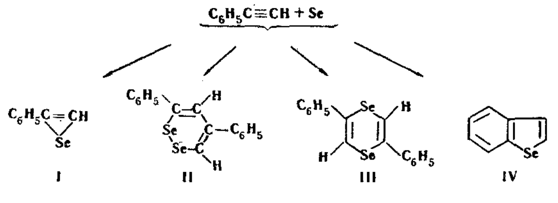
The reaction of selenium with phenylacetylene in the presence of sodium ethoxide in boiling dioxane has given 2,5-diphenyl-1,4-diselenacyclohexa-2,5-diene, whose molecules have the boat conformation.

Several variants have been proposed for the reaction of selenium with phenylacetylene in equimolar ratios, leading to the formation of different substances.

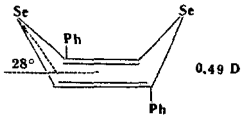


We have obtained a yellow crystalline substance with mp 136° C, the structure of which was to be established.

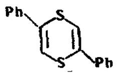
Structures I and IV cannot be accepted, since the molecular weight calculated for them (181.09) does not agree with that found experimentally, (366.5). Structure IV is also excluded because the benzoselenophene corresponding to it is a liquid with bp 150° C [1]. It remains only to make a choice between structures II and III, for which the calculated molecular weight (362.18) is in good agreement with the figure found experimentally. For this purpose, we used the dipole moment method.

The dipole moment calculated for the diselenide II is 1.81 D. A comparison of this value with the figure found experimentally of 0.45 D enables structure II to be excluded.

For the cyclic selenide III we calculated the dipole moments on the assumption of the chair conformation, 0.0 D and the boat conformation.



A comparison of these values with that found experimentally of 0.45 D shows that the product of the reaction of sulfur with phenylacetylene is 2,5-diphenyl-1,4-diselenacyclohexa-2,5-diene, the molecules of which have the boat conformation. We may note that the boat conformation has also been found for the corresponding sulfur analog, 2,5-diphenyl-1,4-dithiin



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 $\lambda_{max}$, 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.