Products VIa, VIc, and VId were obtained by analogy (Table 2).

<u>Tetrathiafulvalenecarboxylic Acid (III)</u>. A solution of 1.2 g NaOH in 90 ml water was added to a solution of 3 g (0.01 mole) IVb in 60 ml ethanol. The mixture was heated at 40-50°C in an inert argon atmosphere for 2-3 h and then acidified with hydrochloric acid. The red crystalline precipitate was filtered off, dried in vacuum, and recrystallized from benzene-hexane to give 1.6 g (66%) acid III, mp 183-184°C (dec.) (mp 182-184°C [3]). IR spectrum: 1655 (C=0), 1558, 1534 cm<sup>-1</sup> (C=C). UV spectrum in acetonitrile ( $\lambda_{max}$  (log  $\varepsilon$ )): 288 (4.08), 302 (4.14), 313 (4.15), 431 nm (3.30). PMR spectrum (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>, ppm): 6.33 s (2H, 6-H, 7-H), 7.27 s (1H, 3-H), 10.3 br. s (OH).

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REACTIONS OF 1,5-DIKETONES WITH HYDROGEN SELENIDE IN THE PRESENCE OF

TRIFLUOROACETIC ACID

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Two competing pathways were found in the transformations of 1,5-diketones and the 4H-selenopyrans formed from these diketones upon reaction with  $CF_3CO_2H$  in the presence of hydrogen selenide entailing disproportionation and the electrophilic addition of hydrogen selenide.

In our previous work [1, 2], we found that 1,5-diketones react with hydrogen selenide and hydrogen chloride in acetic acid in an inert atmosphere to give the corresponding 4Hselenopyrans or 2,6-di(hydroseleno)-1-selenocyclohexanes, depending on the structure of the starting diketones. A complex mixture of products, from which separated selenopyridilium salts in 13-30% yield, was obtained under the same conditions but in the presence of oxygen.

In order to elucidate the probable mechanism for the formation of 2,6-di(hydroseleno)-1selenocyclohexanes (IIa and IIb), we studied the reaction of 1,5-diketones with hydrogen selenide in trifluoroacetic acid. The reaction of 1,5-diketones with hydrogen sulfide in the presence of acids gives the corresponding 4H-thiopyrans [4] or the products of their disproportionation into thiapyrilium salts and thiacyclohexanes. Trifluoroacetic acid facilitates the disproportionation reaction [5, 6]. We might have expected that the reaction of 1,3,5triphenyl-1,5-pentanediode (Ia) with hydrogen selenide in trifluoroacetic acid would yield 2,4,6-triphenylselenopyrilium salt (IVa) and 2,4,6-triphenyl-1-selenocyclohexane (IIIa). However, in addition to expected IIIa and IVa, 2,4,6-triphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIa) gives the corresponding 2,6-diphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIb), in addition to the products of the disproportionation of 4H-selenopyrans IIIb and IVb. The poor solubility of IIa and IIIb in  $CF_3CO_2H$  likely plays a significant role in the formation of these compounds as they are removed from the reaction medium.

We have found that 2,4,6-triphenyl-4H-selenopyran (V) may disproportionate in the presence of  $CF_3CO_2H$  to form IIIa and IVa. It was important to learn whether 4H-selenopyrans in addition to the disproportionation products are capable of forming 2,6-di(hydroseleno)-l-

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1345

TABLE 1. Products of the Reaction of Ia and Ib with  $\rm H_2Se$  and  $\rm CF_3CO_2H$ 

Starting compound	Solvent	Reaction time, days	Yield of final products, %
I a	$\begin{array}{c} CF_3COOH/Et_2O, \ 5:2\\ CF_3COOH\\ CF_3COOH\\ CF_3COOH\\ CF_3COOH\\ CF_3COOH/Et_2O, \ 5:2\\ CF_3COOH/Et_2O, \ 5:2 \end{array}$	2	56 (IIa), 8 (IVc), 3,5 (IIIa)
la		2	50 (IIa), 12 (IVc), 6,5 (IIIa)
Ib		11	21 (IIb), 31 (IVd), 18 (IIIb)
Ib		2	28 (IIb), 65 (Ib)
Ib		2	37 (IIb), 59 (Ib)
V		0,25	51 (IIa), 12 (IVc), 8 (IIIa)

selenocyclohexanes by the addition of hydrogen selenide or whether these cyclohexanes arise only directly from 1,5-diketones. To answer this question, we studied the ratio of selenopyran V to trifluoroacetic acid in the presence of hydrogen selenide. The reaction is complicated by the poor solubility of V in  $CF_3CO_2H$ . Thus, ether was added to the reaction mixture. The addition of ether did not have a significant effect on the direction of the reactions of Ia and Ib and selenopyran V reacts under these conditions to form IIIa, IVa, and IIa (see Table 1).



According to the data given, two competing pathways exist for stabilization of the carbocations upon the action of hydrogen selenide and protic acids in an inert atmosphere: a) addition of SeH, and b) intermolecular hydride ion transfer upon disproportionation.

We should note that IIa was isolated in 32% yield upon carrying out the reaction of diketone Ia with hydrogen selenide and hydrogen chloride in acetic acid similarly to our previous procedure [2] but with subsequent maintenance of the reaction mixture for ten days.

2,6-Di(hydroseleno)-l-selenocyclohexane IIa is capable of conversion to a mixture of selenopyrilium salts IVa or IVd, selenocyclohexane IIIa and elemental selenium upon reaction with acids ( $CF_3CO_2H$  or  $BF_3\cdot Et_2O$ ) in benzene solution in the presence of atmospheric oxygen.

Completion of this reaction requires a significantly longer reaction time (about nine days) than in the case of the disproportionation of V under analogous conditions (about 3 h). Hence, we may assume that the conversion of IIa to the corresponding selenopyrilium salt and selenocyclohexane proceeds through the formation of selenopyran V and that IIa and V in the presence of hydrogen selenide are capable of interconversion.

The possibility of the formation of 2,6-di(hydroseleno)-l-selenocyclohexanes IIa and IIb directly from Ia and Ib according to the following scheme is not excluded in the reaction of 1,5-diketones with hydrogen selenide in the presence of protic acids:



Com- pound	Мр, °С	Found, %		Chemical	Calculated, %	
		с	н	formula	с	н
IIa IIb IIIa	110—111 125,5—126,5 143—144 (dec)	73,5 67,8 51,7	6,2 6,5 4,1	C <sub>23</sub> H <sub>22</sub> Se C <sub>17</sub> H <sub>18</sub> Se C <sub>23</sub> H <sub>22</sub> Se <sub>3</sub>	73,2 67,8 51,6	5,9 6,0 4,1
ШΦ	145-146	44,0	4,0	C <sub>17</sub> H <sub>18</sub> Se <sub>3</sub>	44,4	4,0
IVe	(dec.) 172—173	60,4	4,0	C <sub>23</sub> H <sub>17</sub> BF <sub>4</sub> Se	60,2	3,7

TABLE 2. Characteristics of Organoselenium Compounds IIa, IIb, IIIa, IIIb, and IVe

TABLE 3. PMR Spectra of Organoselenium Compounds IIa, IIb, and  ${\tt V}$ 

Com- pound	Solvent	Chemical shifts, δ, ppm
IIa	CDC1 <sub>3</sub>	7,02–7,42 (m 15H, arom.) $4,46$ (t, 2H, $\alpha$ -H)
НЬ	CCl <sub>4</sub> (C <sub>6</sub> D <sub>6</sub> )	$(2,56 \text{ (m, 5H, }\beta+\gamma-H))$ 7,07-7,32 (m 10H, arom.) 4,19 (q, 2H, $\alpha$ -H)
v	CCl <sub>4</sub> (C <sub>6</sub> D <sub>6</sub> )	2,03-2,36 (m 6H, $\beta + \gamma \cdot H$ ) 7,05-7,52 (m 15H, arom.) 6,12 (d, 2H, $\alpha \cdot H$ ) 4,19 (t, 1H, $\gamma \cdot H$ )

The compositions and structures of the compounds obtained were supported by elemental analysis and IR and PMR spectroscopy (Tables 2 and 3). The IR spectra of IIa and IIb contain bands for the SeH group at 2275 cm<sup>-1</sup> and lack bands for the selenopyran ring at 1620-1700 cm<sup>-1</sup>. The PMR spectra of selenopyrilium salts IVc and IVe in  $CF_3CO_2H$  are in accord with the data given by Tolmachev et al. [7] for IVc.

## EXPERIMENTAL

The reaction course and purity of the products were monitored by thin-layer chromatography on Silufol-254 plates using 3:1:1 hexane-ether-chloroform and 6:1 hexane-ether as eluents. The IR spectra were taken on a UR-20 spectrophotometer in vaseline oil and hexachlorobutadiene. The PMR spectra were taken on a Varian 80 MT spectrometer with HMDS as the internal standard.

A sample of 2,4,6-triphenyl-4H-selenopyran (V) was obtained according to our previous procedure [2] and its melting point was in accord with our previous data.

Reaction of 1,3,5-Triphenyl-1,5-pentanedione (Ia) with Hydrogen Selenide and Trifluoroacetic Acid. A sample of 25 ml trifluoroacetic acid was saturated with hydrogen selenide in an argon atmosphere and then a mixture of 1.31 g (4 mmoles) diketone Ia and 10 ml abs. ether was added without stopping the hydrogen selenide flow. The mixture obtained was stirred at  $6^{\circ}C$  for 10 h. The H<sub>2</sub>Se stream was disconnected and the mixture was maintained at about 10°C until the starting diketone disappeared ( $^{4}$ 48 h). The precipitate formed was filtered off, washed with 5 ml acetic acid, and dried in vacuum to obtained 1.20 g 2,4,6-triphenyl-2,6-di-(hydroseleno)-1-selenocyclohexane, which was reprecipitated from benzene by the addition of ether. The mother liquor was washed with distilled water until the wash water was colorless. The wash water was poured into a flask with 15 ml 57% aq. HClO<sub>4</sub>. The precipitate formed was filtered off and dried to give 0.15 g 2,4,6-triphenylselenopyrilium perchlorate (IVc), mp 194-195°C (from acetic acid). The etheral solution was dried and evaporated. The residue was recrystallized from ethanol to give 0.05 g 2,4,6-triphenyl-1-selenocyclohexane (IIIa).

The reaction with 1,5-diphenyl-1,5-pentanedione (Ib) was carried out analogously. The data for these reactions and the products obtained are given in Tables 1 and 2.

Reaction of 2,4,6-Triphenyl-4H-selenopyran (V) with  $CF_3CO_2H$  and  $H_2Se$ . The reaction was carried out with 0.75 g (2 mmoles) V, 12.5 ml abs.  $CF_3CO_2H$ , and 5 ml abs. ether over 6 h as described for Ia to yield 0.54 g IIa, 0.11 g IVc, and 0.06 g IIIa.

<u>Reaction of Selenopyran V with  $CF_3CO_2H$ .</u> A. A mixture of 0.75 g (2 mmoles) V, 12.5 ml  $CF_3CO_2H$ , and 5 ml abs. ether was stirred for 12 h under argon. The reaction mixture was diluted with 100 ml ether and treated as described in the reaction of Ia to yield 0.55 g (58%) IVc and 0.2 g (27%) IIIa.

B. A sample of 2 ml abs.  $CF_3CO_2H$  was added to a solution of 0.6 g (1.6 mmole) V in 10 ml dry benzene. After 3 h, the reaction mixture was treated as in method A to give 0.43 g (57%) IVc and 0.15 g (25%) IIIa.

Reaction of 2,4,6-Triphenyl-2,6-di(hydroseleno)-1-selenocyclohexane (IIa) with  $CF_3CO_2H$ . A sample of 2 ml  $CF_3CO_2H$  was added to a solution of 0.89 g (1.6 mmole) IIa in 10 ml dry benzene. The mixture was maintained for nine days at 20°C, diluted with 100 ml ether, and treated as in the reaction of Ia to yield 0.38 g (50%) IVc, 0.17 g (28%) IIIa, and 0.22 g (87%) elemental selenium.

Reaction of IIa with Boron Trifluoride Etherate. A sample of 2 ml  $BF_3 \cdot Et_20$  was added to a solution of 0.89 g (1.6 mmole) IIa in 10 ml dry benzene. The mixture was maintained at 20°C for four days and then diluted with 100 ml ether to yield 0.43 g (59%) 2,4,6-triphenylselenopyrilium tetrafluoroborate (IVe), 0.16 g (27%) IIIa, and 0.235 g (93%) elemental selenium.

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MOLECULAR AND CRYSTAL STRUCTURE OF 2-PARA-TOLUIMIDO-4,4-DIMETHYL-

(4H)-1, 3-THIAZINE

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The imino structure of 2-p-toluimido-4,4-dimethyl-(4H)-1,3-thiazine (I) was demonstrated by x-ray diffraction structural analysis. Molecules of I in the crystal are linked by N-H···O hydrogen bonds in infinite chains. A shortened S···O intramolecular contact was found which corresponds to a secondary interaction. A mechanism was proposed for the thiazoline-thiazine rearrangement.

2-Acyliminothiazolines and 2-acyliminothiazines were obtained in the intramolecular cyclization of acylethynylthioureas and the possibility of the isomerization of the thiazoline to thiazines was discovered [1, 2]. The IR spectra of the compounds obtained show a shift to lower frequencies for the acyl substituent carbonyl group stretching vibrations. An attempt to relate this shift to intramolecular hydrogen bonding [2] did not account for the greater thermodynamic stability of the thiazine ring in comparison to the thiazoline ring upon isomerization. We carried out an x-ray diffraction structural analysis of 2-p-tolu-

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