with ice-cold H_2O, and sucked dry, 1.9 g (58%): mp 101–103.5° dec;[14] ir (mull) 3110 (m), 1765 (m), 1710 (s), 1635 (m), 1320 (s), 1270 (s), 865 (m), 850 (m) cm^{-1}.

2*H*-1,3(3*H*)-Oxazine-2,6-dione (1a). To a stirred dispersion of *N*-chloromaleimide (250 mg, 1.9 mmol) in 10 ml of H_2O at 0° was added dropwise over a period of 0.25 hr a solution of $NaHCO_3$ (180 mg, 2.1 mmol) in 5.0 ml of H_2O. The solid dissolved during the above addition to yield a clear solution. After neutralization with cold dilute H_2SO_4, the solution was saturated with NaCl and the oxazinedione **1a** isolated by ethyl acetate extraction. It was identical with that prepared as described above.

Registry No.—**1a,** 24314-63-1; **1b,** 51440-82-5; **1d,** 53907-40-7; **1e,** 53907-41-8; **1f,** 53907-42-9; **1g,** 53907-43-0; **4a,** 53907-44-1; **4b,** 53907-45-2; **6,** 45514-70-3; maleic anhydride, 108-31-6; trimethylsilyl azide, 4648-54-8; citraconic anhydride, 616-02-4; fluoromaleic anhydride, 2714-23-0; dichloromaleic anhydride, 1122-17-4; bromomaleic anhydride, 5926-51-2.

References and Notes

(1) This research was supported by Grant No. CA-13120-03 from the National Cancer Institute and Contract No. DAMD 17-74-C-4100 from the U.S. Army Medical Research and Development Command. This is Contribution No. 1303 to the Army Research Program on Malaria.

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(11) Although acyl azides are known to react with silylamines to generate silyl azides, e.g., $Me_3SiNHBu + PhCON_3 + \text{cat. } AlCl_3 \rightarrow Me_3SiN_3 + PhCONHBu$ [K. Rühlmann, A. Reiche, and M. Becker, *Chem. Ber.*, **98,** 1814 (1965)], acyloxysilanes do not react with acyl azides, e.g., $BuCO_2SiMe_3 + BuCON_3 \nrightarrow (BuCO)_2O + Me_3SiN_3$ [S. S. Washburne and W. R. Peterson, Jr., *Synth. Commun.*, **2,** 227 (1972)].

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The Synthesis of 1,3-Diselenole-2-selones and -2-thiones

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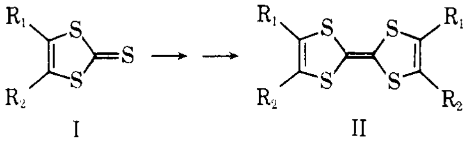
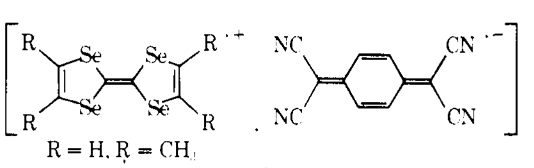
The synthesis and some physical and chemical properties of 1,3-diselenole-2-selones and -2-thiones are reported. The compounds were prepared in a three-step synthesis from *N,N*-pentamethylenediselenocarbamate and appropriate α-halo ketones.

In recent years 1,3-dithiole-2-thiones (I) have gained interest as intermediates in the synthesis of tetrathiafulvalenes (II), which have been used as the donor in several highly conducting organic "metals."[2,3]



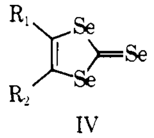
I II

As a part of a systematic study of organic conducting solids,[4] we have been interested in substituting sulfur with selenium in order to increase electronic interactions in the donor stacks of the organic "metals." So far the selenium-containing fulvalenes have shown very promising properties in salts of the general type III.[5,6]

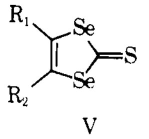


III

In order to obtain the tetraselenafulvalenes in question, we have developed a general synthetic route to mono- and disubstituted 1,3-diselenole-2-selones (IV) and -2-thiones (V), which by dechalkogenizing reagents can be coupled to tetraselenafulvalenes.[5,6] Reaction sequences similar to those outlined in Scheme I have been reported for sulfur analogs of some of the compounds described in this paper.[7,8]



IV



V

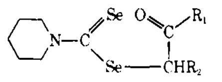
Recently Engler and Patel[5,9] have prepared 1,3-diselenole-2-selone (IV, $R_1 = R_2 = H$) from sodium acetylide, selenium, and carbon diselenide, utilizing a modified procedure originally developed to prepare 1,3-dithiole-2-thiones.[10,11] Engler and Patel also prepared several thiaselenoles.[9]

Results and Discussion

The compounds in question were all prepared by the general route outlined in Scheme I.

The first step involves nucleophilic substitution of a halogen with the *N,N*-pentamethylenediselenocarbamate anion. The substitution proceeds rapidly, but the solution was usually left 2–4 hr at room temperature to assure complete reaction. In addition to piperidinium *N,N*-pentamethylenediselenocarbamate,[12] we have used the morpholine and pyrrolidine analogs which react as well, but since piperidinium *N,N*-pentamethylenediselenocarbamate is

Table I (2-Oxoalkyl)-*N,N*-pentamethylenediselenocarbamates

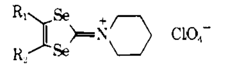


VI

Symbol	R_1	R2	Mp, °C	Yield, %	Nmr[a] δ, ppm (rel to TMS) R_1	R_2, –Se–CH–	–N(CH₂–)₂	H₂C(CH₂–)₂
VIa	CH_3	H	45–46	83	2.40 (3 H)	4.45 (2 H)	3.9 and 4.45 (4 H)	1.69 (6 H)
VIb	CH_3	CH_3	43–44	79	2.31 (3 H)	J = 7 Hz 1.47 (3 H), 4.94 (1 H)	4.07 (4 H)	1.69 (6 H)
VIc	Ph	H	99–102	95	7.4–8.25 (5 H)	5.06 (2 H)	3.9 and 4.45 (4 H)	1.75 (6 H)
VId	Ph	Ph		15	b	b	b	b

[a] $CDCl_3$. [b] Not recorded.

Table II 2-*N,N*-Pentamethylenimino-1,3-diselenolium Perchlorates

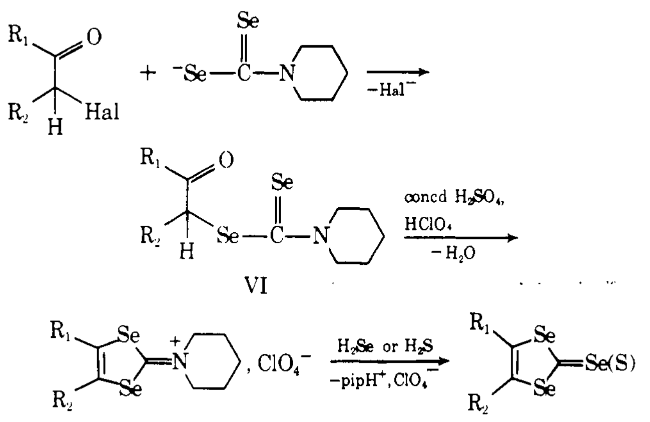


VII

Symbol	R_1	R_2	Yield, %	Nmr, δ (rel to TMS) R_1	R_2	=N⁺(CH₂–)₂	–CH₂CH₂CH₂–
VIIa	H	CH_3	87	J = 1.5 Hz 7.83 (1 H),	2.54 (3 H)[a]	3.97 (4 H)	1.8–2.15 (6 H)
VIIb	CH_3	CH_3	91	2.66 (6 H)[b]		3.66 (4 H)	1.7–2.1
VIIc	H	Ph	91	7.89 (1 H),	7.59 (5 H)[c]	3.90 (4 H)	1.8–2.15 (6 H)
VIId	Ph	Ph	90				

[a] $(CD_3)_2CO$. [b] CD_3CN. [c] CF_3COOH.

Scheme I



readily obtained[13] and relatively stable, it was generally preferred.

The resulting oxo esters (VI) obtained are crystalline, colorless solids, and can be recrystallized from nonpolar solvents. Results are summarized in Table I.

The ring closure of the oxo esters was found to proceed smoothly in concentrated sulfuric acid. The hydrosulfates obtained were converted to perchlorates or fluoroborates by treating the reaction mixture with excess perchloric or fluoroboric acid. Various other procedures, including treatment of the esters with acetic anhydride containing fluoroboric or perchloric acid, were tested, but all tended to give lower yields due to decomposition.

We have characterized the 2-immonio-1,3-diselenoles as their prechlorates (VII) since these salts are the ones most readily isolated. *However, an evident detonation of 1,3-dithiolylium perchlorate has recently been reported,* and although we have not so far observed any spontaneous detonation of VII it might be advisable to handle these substances with care only in small quantities.

Compounds obtained are colorless crystalline solids, but may be pink due to a small amount of free selenium, which can be removed by dissolving the salts in acetonitrile, filtering, and precipitating with ether. Results are summarized in Table II.

Cleavage of VII with excess H_2Se or H_2S was achieved in methanol or methanol–water mixtures. The slightly soluble perchlorates (VIIc and VIId) were suspended in methanol and an equimolar amount of pyridine added as a catalyst. Compounds VIIa and VIIb were treated with excess H_2Se or H_2S in 70% methanol–water without catalyst, since pyridine or $NaHCO_3$ tended to produce polymeric tars instead of the desired selones or thiones.

The 1,3-diselenole-2-selones (IVa–d) are red crystalline solids, whereas the -2-thiones (Va and b) are yellow.

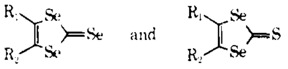
Ir spectroscopy is a convenient tool for the identification of compounds IV and V since they both exhibit a very characteristic pattern of two strong (absorption) bands in the 700–1100-cm^{-1} region which arise from the Se–CSe–Se or Se–CS–Se grouping. The high-frequency bands are found at 880–920 cm^{-1} for IV and at 920–1020 cm^{-1} for V and have been approximately ascribed to C=Se or C=S stretching vibrations, respectively.[14] The low-frequency band is found at 750–780 cm^{-1} for both compounds and is approximately described as a C—Se stretching band.[14]

Uv–Visible Spectra. 1,3-Diselenole-2-selone[5] was reported to have a maximum at 555 nm. Aliphatic substitution has only a minor effect, whereas the aryl-substituted compounds as expected exhibit a shift to higher energy (see Table III). The two analogous 2-thiones exhibit a band at approximately 450 nm.

Nmr spectral data are summarized in Table III.

Chemical Properties. Preliminary investigations of the chemical properties of IV and V have given the following

Table III
1,3-Diselenole-2-selones and -2-thiones[a]



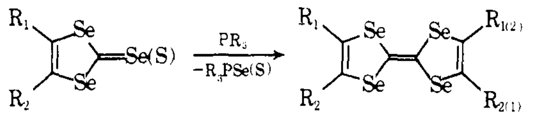
IV V

Symbol	R_1	R_2	Yield, %	Mp, °C	ir, cm^{-1} [b]	Uv-vis, nm (ε)[c]	Nmr,[e] δ, ppm
IVa	CH_3	H	66	80–81	890, 880, and 700	558 (197), 417 (15,500) 318 (870), 266 (7300)	2.42 (3 H), 7.42 (1 H), $J = 1.5$ Hz
IVb	CH_3	CH_3	60	149–150	890, -, and 762	555 (224), 424 (14,800) 328 (730), 266 (6200)	2.25
IVc	Ph	H	86	121–122	902, 885, and 732	524 (296), 431 (16,800)	7.36 (5 H), 7.87 (1 H)
IVd	Ph	Ph	55	161–163	902, 889, and 750	528[d] (291), 434 (19,300)	7.15
Va	CH_3	H	90	81–81.5	1020, 990, and 752	460 (sh), 382 (15,000) 295 (1400), 255 (9800)	2.42 (3 H), 7.23 (1 H), $J = 1.5$ Hz
Vb	CH_3	CH_3	87	101–102	1020, -, and 772	453 (53), 385 (13,800) 304 (1000), 276 (2400) 254 (8300)	2.19

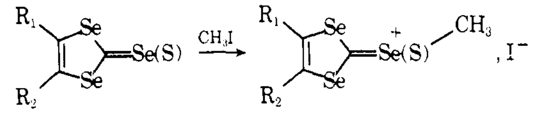
[a] Satisfactory analytical data (±0.3 for C, H) were obtained for all compounds listed in the table. [b] KBr. [c] Hexane. [d] CH_2Cl_2. [e] $CDCl_3$ relative to TMS.

results. (1) Both selones and thiones can, in analogy with previous reports,[5,6] be coupled (by treatment with triphenylphosphine or trialkyl phosphites) to give tetraselenafulvalenes in 30–60% yield (Scheme II). (2) Treatment of IV or V with excess methyl iodide gives methiodides[15] (Scheme III). (3) 1,3-Dithiolium salts can be prepared by peracid oxidation of 1,3-dithiole-2-thiones.[1,16] Several attempts to prepare the hitherto unknown 1,3-diselenolium salts (VIII) by this method (Scheme IV) were unsuccessful, probably due to oxidation of the selenium atoms in the ring.[5]

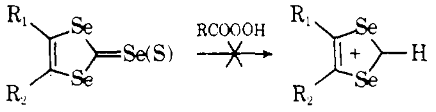
Scheme II



Scheme III



Scheme IV



VIII

Summary

The synthetic route described above provides a pathway to mono- and disubstituted 1,3-diselenole-2-selones and -2-thiones. When compared to Engler and Patel's procedures,[5,9] the advantage of the present method is that 4,5-disubstituted 1,3-diselenoles are obtainable, since no acetylenic hydrogen is required.

Experimental Section

(2-Oxoalkyl)-*N*,*N*-pentamethylenediselenocarbamates. VIb. Piperidinium *N*,*N*-pentamethylenediselenocarbamate (0.03 mol) dissolved in 60 ml of dry CH_2Cl_2 was added, under argon, to a stirred solution of 3-bromo-2-butanone (0.04 mol) in 200 ml of dry CH_2Cl_2. After the addition was completed, the solution was left with stirring at room temperature for 4 hr, and then washed with five 100-ml portions of water and dried over $MgSO_4$, and the solvent evaporated *in vacuo*. The resulting yellow oil was recrystallized from hexane to yield slightly yellow crystals of VIb. VIa was prepared in the same manner as VIb from chloroacetone. VIc and VId were prepared from phenacyl bromide and 2-bromo-1,2-diphenylethanone, respectively. Both recrystallized from cyclohexane.

2-(*N*,*N*-pentamethylenimino)-1,3-diselenolium Salts. VIIb. VIb (0.003 mol) was dissolved slowly in 3 g of concentrated H_2SO_4. After standing 0.5 hr at room temperature enough EtOAc was added cautiously to cause starting precipitation of the hydrosulfate. The solution was then filtered into a mixture of 1–2 ml of 70% $HClO_4$ and 50 ml of absolute EtOH, and 300–500 ml of ether was added. The resulting white solid was filtered off, washed with ether, and dried *in vacuo*. VIIa, VIIc, and VIId were prepared in the same manner as VIIb.

1,3-Diselenole-2-selones or -2-thiones. IVb. VIIb (0.0025 mol) was dissolved in 60 ml of 70% MeOH–water cooled to −10°, and the stirred solution, which was kept under argon, treated with a sixfold excess of H_2Se.[17] A red solid was slowly formed and the solution was allowed to warm to 0° over 2–3 hr. Water (40 ml) was added and the solid filtered off and dried in a desiccator over P_2O_5. Recrystallization from heptane yielded bright red plates of IVb. IVa was prepared in the same manner as IVb.

IVc and IVd. Since VIIc and VIId are rather insoluble, they were suspended in absolute MeOH, and an equimolar amount of pyridine was added as a catalyst. Both products were recrystallized from absolute EtOH. Va and Vb were prepared by essentially the same procedure as IVb. Due to its lower reactivity, however, H_2S was passed through the stirred solution at room temperature for 4–6 hr.

Acknowledgment. The present work was supported by Materials Science Office, Advanced Research Projects Agency, Department of Defense. K.B. wishes to thank Statens Naturvidenskabelige Forskningsraad for a travel grant.

Registry No.—IVa, 53808-61-0; IVb, 53808-62-1; IVc, 53808-63-2; IVd, 53808-64-3; Va, 53808-65-4; Vb, 53808-66-5; VIa, 53808-67-6; VIb, 53808-68-7; VIc, 53808-69-8; VId, 53808-70-1; VIIa, 53808-72-3; VIIb, 53808-74-5; VIIc, 53808-76-7; VIId, 53808-78-9; piperidinium *N*,*N*-pentamethylenediselenocarbamate, 30611-91-7; 3-bromo-2-butanone, 814-75-5; chloroacetone, 78-95-5; phenacyl bromide, 70-11-1; 2-bromo-1,2-diphenylethanone, 1484-50-0.

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Conformational Analysis of the Favorskii Rearrangement Using 3(a)-Chloro-3(e)-phenyl-*trans*-2-decalone and 3(e)-Chloro-3(a)-phenyl-*trans*-2-decalone[1a]

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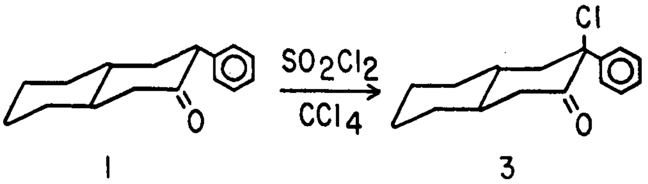
The starting material for the synthesis of the isomeric chloro ketones (3 and 4) was *trans*-2-decalone, which was converted to 3(e)-phenyl-*trans*-2-decalone (1) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2). Compound 1 was chlorinated by sulfuryl chloride in carbon tetrachloride to yield the axial chloro ketone 3, while compound 2 was chlorinated by thionyl chloride in carbon tetrachloride to yield the equatorial chloro ketone 4. Potassium *tert*-butoxide was used to effect the rearrangement both in ethanol (E) and 1,2-dimethoxyethane (D). The product from 3 when the rearrangement was performed in D included 2-phenylhexahydroindan-2-carboxylic acid [isolated as the methyl ester (5)] and 2-phenacyl-1-cyclohexaneacetic acid [isolated as the methyl ester (6)]. Rearrangement of 3 in E yielded 5, 6, and 1-ethoxy-3-phenyl-*trans*-2-decalone (7). Favorskii products were not evident when 4 was subjected to rearrangement conditions. It can be concluded that the axial conformation of the chlorine atom is more favorable for the Favorskii rearrangement. Compound 7 was apparently produced either from a cyclopropanone intermediate or an enol allylic chloride.

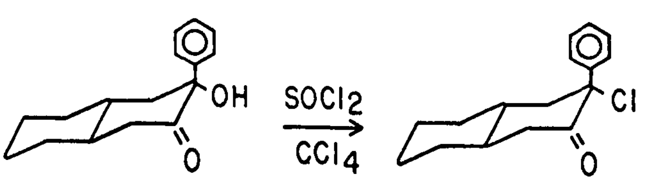
An attempt was made by Smissman et al.[2] to determine whether a cyclopropanone intermediate or a dipolar ion was operative in the Favorskii rearrangement of a pair of conformers, viz., 3(a)-bromo-*trans*-2-decalone (8) and 3(e)-bromo-*trans*-2-decalone (9). Since the axial compound gave no rearrangement product in either polar or nonpolar solvents whereas the equatorial compound rearranged in both solvent types, it was concluded that the results of this study disputed the role of the dipolar ion as an active participant in the Favorskii rearrangement. If this conclusion were valid, if not on a general basis, then at least for rigid systems such as the *trans*-decalones, it could be predicted that of the two conformers used in the present study, viz., 3(a)-chloro-3(e)-phenyl-*trans*-2-decalone and 3(e)-chloro-3(a)-phenyl-*trans*-2-decalone, the equatorial isomer would give the Favorskii product.

Results

The two chloro ketones 3 and 4 were synthesized by the chlorination of 3(e)-phenyl-*trans*-2-decalone (1) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2). Compounds 1 and 2 were synthesized by published methods.[3] Potassium *tert*-butoxide was used to effect the rearrangement both in the polar solvent ethanol and in the nonpolar solvent 1,2-dimethoxyethane. The products of the rearrangement were hydrolyzed and separated into an acidic fraction and a neutral fraction. The former was subjected to Fischer–Spier esterification prior to column chromatography on alumina. The components of the neutral fraction were separated by column chromatography on silica gel.



1 3



2 4

Rearrangement of the axial chloro ketone 3 in ethanol gave, after esterification, the methyl ester of 2-phenylhexahydroindan-2-carboxylic acid (5, 2% yield) and 2-phenacyl-1-cyclohexaneacetic acid (6, 2% yield). The neutral components included compounds 1-ethoxy-3-phenyl-*trans*-2-decalone (7, 2% yield) and 3(e)-hydroxy-3(a)-phenyl-*trans*-2-decalone (2, 42% yield). A polymeric material was also isolated.

The yield of 5 was similar (2%) when the rearrangement of 3 was performed in dimethoxyethane. Compound 6 was also isolated (<1% yield). Sublimation of the crude acid fraction prior to Fischer–Spier esterification yielded benzoic acid. The neutral components included polymeric material.