FORCE FIELD	Coefficients						
$t_1 = r_1 \sin \alpha_6/q_1$	$s_1 = (r_4 - r_1 \cos \alpha_6)/q_1$						
$t_2 = r_4 \sin \alpha_6/q_1$	$s_2 = (r_1 - r_4 \cos \alpha_6)/q_1$						
$t_3 = r_2 \sin \alpha_1/q_2$	$s_3 = (r_1 - r_2 \cos \alpha_1)/q_2$						
$t_4 = r_1 \sin \alpha_1/q_2$	$s_4 = (r_2 - r_1 \cos \alpha_1)/q_2$						
$t_5 = r_3 \sin \alpha_3/q_3$	$s_5 = (r_1 - r_3 \cos \alpha_3)/q_3$						
$t_6 = r_1 \sin \alpha_3/q_3$	$s_6 = (r_3 - r_1 \cos \alpha_3)/q_3$						
$t_7 = r_2 \sin \alpha_2/q_4$	$s_7 = (r_3 - r_2 \cos \alpha_2)/q_4$						
$t_8 = r_3 \sin \alpha_2/q_4$	$s_8 = (r_2 - r_3 \cos \alpha_2)/q_4$						
$t_9 = r_5 \sin \alpha_5/q_6$	$s_9 = (r_2 - r_5 \cos \alpha_5)/q_6$						
$t_{10} = r_2 \sin \alpha_5/q_6$	$s_{10} = (r_5 - r_2 \cos \alpha_5)/q_6$						
$t_{11} = r_2 \sin \alpha_4/q_5$	$s_{11} = (r_2 - r_2 \cos \alpha_4)/q_5$						
$q_1^2 = r_4^2 + r_1^2 - 2r_4r_1 \cos \alpha_6$	$q_4{}^2 = r_2{}^2 + r_3{}^2 - 2r_2r_3\cos\alpha_2$						
$q_2^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos \alpha_1$	$q_5^2 = r_2^2 + r_2^2 - 2r_2r_2 \cos \alpha_4$						
$q_{3}^{2} = r_{1}^{2} + r_{3}^{2} - 2r_{1}r_{3}\cos\alpha_{3}$	$q_6^2 = r_2^2 + r_5^2 - 2r_2r_5 \cos \alpha_5$						
$q_1 = q_{\mathrm{C}} \dots \mathbf{s}$ $q_2 = q_{\mathrm{C}}' \dots \mathbf{s}$ $q_3 = q_{\mathrm{R}} \dots \mathbf{s}$							
$q_4 = q_{\rm C}' \dots {}_{\rm R}, q_5 = q_6$	$\mathbf{cc}, q_6 = q_{\mathbf{C}\mathbf{H}}$						

TABLE X

observed possibly arise from changes in methyl group environment in the different lattices.

The results of the normal-coordinate analysis are consistent with the absence of iron-sulfur bonding shown by X-ray diffraction studies.

An opportunity to apply the normal-coordinate treatment developed for DTAA⁺ to another compound possibly of identical structure was provided by the recent synthesis of salts of the 3,5-dimethyl-1,2-diselenolylium ion hereafter denoted as DSeAA⁺. After carbon-selenium and selenium-selenium bond lengths for this cation were estimated, bond angles for a planar five-membered diselenide ring were adjusted by reference to molecular parameters of DTAA⁺ which were common to DSeAA⁺. Except for K(C-Se) and K(Se-Se), which were varied to obtain a best fit between observed and calculated frequencies, the force constants used were transferred from the disulfide cation. Assignments based on potential energy dis-

tributions which appear in Table VIII were supported by calculation of Jacobian terms. Based on the model adopted good agreement was obtained between calculated and observed frequencies as recorded in Table VII.

The weak band near 600 cm^{-1} was assigned to the carbon-selenium stretching vibration. It was of interest to note the corresponding force constant, 2.80 mdyn/Å, almost equals 2.78 mdyn/Å, which is the value for K(C-Se) in the metal chelates of diethyldiselenocarbamic acid.²² Although a pure seleniumselenium stretching vibration was not predicted, an absorption band close to 320 cm^{-1} and one predicted near 290 cm⁻¹ were assigned to coupled modes which contain that vibration. In the series of seleniumselenium bonded compounds-dimethyl selenide, Se42+, and Se₂—the intermediate value, 2.20 mdyn/Å, for $\mathrm{Se_4^{2+}}$ has been considered²³ to indicate the existence of a degree of multiple bonding. Since the corresponding force constant is 2.00 mdyn/Å for the diselenide ion, the selenium double-bond character of the two ions is probably similar.

The carbon-selenium stretching force constant in the diselenolylium ion is less than the carbon-sulfur constant in the dithiolylium ion. Similar decreases were observed in the pairs of compounds selenourea, thiourea and selenoacetamide, thioacetamide.²⁴ These trends conform to the usual expectation for differences in selenium and sulfur bond energies.

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The Preparation and Properties of Diorganoselenium Difluorides

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The synthesis of a number of alkyl- and aryldiorganoselenium difluorides is reported from the reaction of silver(II) fluoride with diorganoselenides. Diorganoselenium difluorides are liquids or low-melting solids which are monomers in benzene solution. Infrared and ¹⁹F and ¹H nmr data are presented and discussed with regard to bonding and fluorine exchange in these compounds.

Some years ago it was suggested that higher organochalcogen fluorides were unstable.¹ However, Sheppard² has demonstrated the stability of organosulfur tri- and pentafluorides. In a continuing study of organoselenium halides³ we have found further evidence for the

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(2) W. Sheppard, J. Am. Chem. Soc., 84, 3058 (1962).

stability of organochalcogen fluorides. We have communicated the synthesis of the first reported example of a diorganoselenium difluoride, dimethylselenium difluoride,⁴ from the reaction of dimethyl selenide with

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(4) K. J. Wynne and J. Puckett, Chem. Commun., 1532 (1968).

			D	IALKYL- A	nd Diaryls	ELENIUM DIFL	UORIDES				
	Amt of	Amt of	Amt of Vield,	Bp, ℃	Mp, °C	Analyses, %					
Compound	selenide, mol	AgF ₂ , mol	%	(0.01 mm)	(uncor)	←Mol wt→		С	н	Se	\mathbf{F}
						Calcd 147	Caled	16.3	4.10	53.7	25.8
$(CH_3)_2SeF_2$	0.13	0.27	22	40	12	Found 156	Found	16.6	4.22	55.3	23.6
						Calcd 175	Calcd	27.4	5.72	45.2	21.7
$(C_2H_5)_2SeF_2$	0.13	0.27	29	49	Ca. -45^{a}	Found 181	Found	27.4	5.70	45.5	21.6
$(n-C_3H_7)_2SeF_2$	0.095	0.20	87	66	< -30	Calcd 203	Calcd	35.5	6.95	38.9	18.71
						Found 182	Found		7.15	37.6^{b}	
						Calcd 203	Calcd	35.5	6.95	38.9	18.71
$(i-C_3H_7)_2$ SeF ₂	0.08	0.16	57	60	Ca10	Found 201	Found		6.29	37.0^{b}	
						Calcd 271	Calcd	53.14	3.72	29.12	14.05
$(C_6H_5)_2SeF_2$	0.06	0.13	60		50 - 51	Found 312	Found	52.49	4.13		14.08
						Caled 173	Calcd	27.8	4.67	45.62	21.96
$(CH_2)_4SeF_2$	0.11	0.22	22		91 - 92	Found 168	Found	27.7	4.94		

TABLE I

^a Determined by extreme broadening of the proton nmr signal at this temperature. ^b The analytical laboratories obtained eratic Cl and Se analyses on these two compounds. We obtained satisfactory results by analyzing for Se gravimetrically.³

silver(II) fluoride. The study reported below was undertaken to establish the general applicability of this synthetic route. Also, our goal was to prepare a number of diorganoselenium difluorides in order to observe the effect of differing organo groups on fluorine exchange through nuclear magnetic resonance studies.

Experimental Section

General Information.—The sensitivity of compounds prepared in this study to atmospheric moisture required the use of nitrogen-filled glove bags and a standard high-vacuum line. Except as otherwise noted, diorganoselenium diffuorides were handled in standard borosilicate glassware, with which reaction was noted to occur at slow to moderate rates.

Spectra.—Infrared spectra were obtained using a Beckman IR-11 spectrometer. Samples were run as 5–10% solutions in benzene using 0.5-mm polyethylene liquid cells. Proton magnetic resonance spectra were obtained using Perkin-Elmer Hitachi Model R-20 and Varian HA-100 spectrometers. Teflon inserts (NMR Specialties) were employed so as to avoid or limit sample contact with glass.

Materials.—Silver(II) fluoride was used as obtained from Harshaw Chemical Co., while diphenyl selenide was purchased from Eastman Organic Chemicals. Dialkyl selenides were prepared from the parent iodides (or diiodide for tetramethylene selenide) by the method of Bird and Challanger.⁵ 1,1,2-Trichlorotrifluoroethane (Freon 113) was obtained frm the Matheson Co. and was dried over 5-Å molecular sieves.

Molecular Weights.—Preliminary results indicated that diorganoselenium difluorides reacted with glass at a sufficiently rapid rate at the freezing point of benzene so as to give unreliable molecular weight results. We therefore devised a nonglass apparatus consisting of a polyethylene test tube, Teflon stir bar, and a Beckmann thermometer. The latter had the portion which dipped into the solution coated with spray-on Teflon lubricant. Samples were weighed directly into the polyethylene test tube. Heat transfer through polyethylene was slow enough to eliminate the need for an insulating jacket. The cooling bath temperature was kept at about 4°. Stirring of both sample and cooling bath was accomplished magnetically.

Synthesis.—The preparation of diorganoselenium diffuorides was effected by slowly adding a Freon 113 solution of the appropriate selenide to a suspension of AgF_2 in the same solvent. With the exception of diphenyl selenide, each addition of selenide solution resulted in a vigorously exothermic reaction. The compounds synthesized, some of their properties, and analytical results are listed in Table I. Diorganoselenium diffuorides were stored at -20° in glass containers. Those compounds which were solids at this temperature exhibited little reaction with glass, while those that were liquids underwent considerable

(5) M. L. Bird and F. Challanger, J. Chem. Soc., 570 (1942).

reaction over the course of a few months. The details of typical preparations are given below.

Dimethylselenium Difluoride.—Silver difluoride (40 g, 0.27 mol) and 125 ml of Freon 113 were added to a 250-ml roundbottom flask. A solution of dimethyl selenide (14 g, 0.13 mol) in 20 ml of Freon 113 was added slowly to the AgF₂ over a 1-hr period. The resulting mixture was filtered and solvent was removed. Vacuum distillation yielded 0.031 mol of colorless $(CH_3)_2SeF_2$ (22% yield). In this reaction and that with diethyl selenide the brown-black AgF₂ turned yellow as the reaction proceeded, while with *n*-propyl and isopropyl selenides it turned red-brown.

1,1-Diffuoroselenacyclopentane.—This reaction was carried out as that for $(CH_3)_2SeF_2$. However, after filtration the solution was cooled to -20° overnight. Colorless crystals of $(CH_2)_4SeF_2$ formed and were filtered. Additional product was obtained by concentration of the filtrate. The product could be recrystallized from Freon 113 but oiled out of methylene chloride-hexane and 1,1,2,2-tetrachloroethane solutions.

Diphenylselenium Difluoride.—A mixture of AgF₂ (19.1 g, 0.13 mol), (C₆H₅)₂Se (13.6 g, 0.06 mol), and 50 ml of Freon 113 was refluxed overnight. A slow stream of dry nitrogen was passed over the top of the condenser during this time. The warm solution was filtered and cooled to -20° yielding 6.5 g (0.24 mol, 40% yield) of colorless, crystalline (C₆H₅)₂SeF₂. Concentration of the filtrate gave an additional 20% yield of product. Diphenylselenium difluoride was recrystallized from hexane.

Results and Discussion

The results in Table I show that a variety of selenides react with AgF_2 to give diorganoselenium difluorides presumably *via* the general reaction

$2\mathrm{AgF}_2 + \mathrm{R}_2\mathrm{Se} \longrightarrow \mathrm{R}_2\mathrm{SeF}_2 + 2\mathrm{AgF}$

The melting points of diorganoselenium diffuorides show a marked dependence on the symmetry of the organo substituent. This is shown dramatically by the melting points of $(C_2H_5)_2SeF_2$ (-45°) and $(CH_2)_4SeF_2$ (91-92°).

The diaryl- and dialkylselenium difluorides prepared in this study are monomeric in benzene solution. In addition, those compounds which are not solids at room temperature are mobile liquids suggesting little if any association. In contrast the arsenic analog of $(CH_3)_2$ -SeF₂, $(CH_3)_2AsF_3$ (unlike $(C_6H_5)_2AsF_3$), shows evidence of association.⁶

The infrared and nmr data presented below for (6) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

Compound	¹⁹ F chem shift, ^a ppm	¹ H chem shift, ^b ppm	$J_{{}^{1}\!{ m H}-{}^{19}{ m F}}$, Hz	J ¹⁹ F- ⁷⁷ Se, Hz				
$(CH_3)_2SeF_2^{c}$	Septet, +66.6	Triplet, 3.13	9.0	650.2				
$(C_2H_5)_2SeF_2^{\circ}$	Single peak,	CH ₃ , triplet		• • •				
	+87.8	CH ₂ , broad single peak						
$(i-C_3H_7)_2SeF_2$	Single peak,	CH_{δ} , doublet, 1.45						
	+107.5	CH, septet, 3.40						
$(n-C_3H_7)_2SeF_2$	Single peak,	CH ₈ , triplet, 1.08						
	+84.0	CH_2 (β), multiplet, 1.90						
		$CH_2(\alpha)$, triplet, 3.24						
$(CH_2)_4 SeF_2^d$	Quintet,	CH_2 (β) quintet, 2.38		688				
	+84.5	$CH_2(\alpha)$ broad multiplet, 3.37	12.1					
$(C_6H_5)_2SeF_2{}^d$	+65.4	ortho, multiplet, 7.88		312.6				
•		meta, para, multiplet, 7.39						

TABLE II PROTON AND FLUORINE 'NMR PARAMETERS FOR DIORGANOSELENIUM DIFLUORIDES

^a Fluorine chemical shifts were measured vs. internal fluorotrichloromethane. ^b Proton chemical shifts are vs. internal tetramethylsilane. ^c For $(CH_3)_2SeF_2$ and $(C_2H_5)_2SeF_2 J_{1H_n}n_{S6} = 9.5$ and 10.5 Hz, respectively. ^d Methylene chloride solution.

 R_2SeF_2 compounds are interpreted in terms of a trigonal-bipyramidal structure in which the electronegative fluorines occupy the apical positions. This view is based on X-ray data on diorganoselenium dichlorides and dibromides which have shown these compounds uniformly display trigonal-bipyrimidal geometry. Our data do not uniquely distinguish this structure from a square-pyramidal arrangement.

Each diorganoselenium difluoride exhibited a strong absorption at $470 \pm 10 \text{ cm}^{-1}$. This absorption is assigned to a combination of symmetric and asymmetric Se–F stretching modes. Two strong absorptions were observed in the Raman spectrum of SeF₄ at 719 and $541 \text{ cm}^{-1.7}$ It seems reasonable that the absorption at $541 \text{ cm}^{-1.1}$ is due mainly to axial Se–F stretching and compares favorably with our value for R₂SeF₂ compounds (compare also absorptions at 664 and 605 cm⁻¹ in SeOF₂⁸). The low Se–F stretching frequency in diorganoselenium difluorides suggests that these bonds are relatively weak.

In Table II are listed ¹⁹F chemical shifts for the diorganoselenium difluorides prepared in this study. It is seen that the ¹⁹F shifts fall over the rather wide range of 43 ppm. It is of interest to compare the chemical shifts for diorganoselenium difluorides with those found for the axial fluorines in SeF4. If the proper conversions are made, the ¹⁹F chemical shift of SeF₄ is found to be -64 ppm relative to CFCl₃,⁹ but this is an average shift value for axial and equatorial fluorines. By analogy with SF4 and RSF3 compounds⁶ this value may set an upper limit on the axial ¹⁹F chemical shift. Reference to Table II shows that substitution of two alkyl or aryl groups for two equatorial fluorines in SeF₄ causes a shift upfield of at least ca. 100 ppm. The comparison suggests¹⁰ that Se-F bonds are more ionic in diorganoselenium difluorides than the corresponding bonds in SeF₄. This trend is reasonable when one considers that replacing three fluorines with organo groups produces selenonium fluorides, R₃Se⁺F^{-.1}

There is a significant upfield flurine chemical shift (7) J. A. Rolfe, L. A. Woodward, and D. A. Long, *Trans. Faraday Soc.*, 49, 1388 (1953).

(8) J. A. Rolfe and L. A. Woodward, *ibid.*, **51**, 779 (1955).

(9) E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 81, 1084 (1959).

in the order methyl < ethyl ~ *n*-propyl ~ tetramethylene < isopropyl. A similar trend (methyl < ethyl ~ *n*-butyl) was found in studies on triorganodifluorophosphoranes.¹¹ The shift is in the direction expected based on simple inductive effects, but the magnitude of the shift seems out of proportion. That ¹⁹F chemical shifts for $(CH_2)_4SeF_2$ and $(C_2H_5)_2SeF_2$ are about the same would seem to eliminate a throughspace effect as the cause of the observed shifts.

The ¹⁹F nmr data for SeF₄ in propane showed fluorine exchange occurs even at $-200^{\circ.9}$ In contrast our ¹⁹F-¹H coupling constants for R₂SeF₂ systems shown in Table II indicate that for dimethyl- and tetramethyleneselenium difluorides slow fluorine exchange occurs at 34°. The observation of a large ⁷⁷Se coupling constant also suggests slow exchange for $(C_6H_5)_2$ SeF₂. Quite broad peaks were found for α protons in diethyl-, di-n-propyl-, and diisopropylselenium difluorides. The varying rates of fluorine exchange with changing organo substituent clearly have an important consequence on the choice of a mechanism for the exchange reaction. Unfortunately in preliminary studies on the temperature dependence of the proton nmr spectra we have found that small amounts of impurity or contact with glass increases the exchange rate drastically. Therefore the relative exchange rates presented above are not certain, and the ⁷⁷Se-¹⁹F coupling constants recorded in Table II must be considered lower limits. We are currently devising a system to study ultrapure samples in an effort to establish unambiguously relative rates of fluorine exchange and ultimately the mechanism of the exchange process. It is clear that no meaningful discussion of the ¹⁹F-⁷⁷Se coupling constants can be made until the temperature dependence of the nmr spectrum of each compound is known in detail.

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