TABLE X
FORCE FIELD COEFFICIENTS

$$\begin{aligned}
t_1 &= r_1 \sin \alpha_6/q_1 & s_1 &= (r_4 - r_1 \cos \alpha_6)/q_1 \\
t_2 &= r_4 \sin \alpha_6/q_1 & s_2 &= (r_1 - r_4 \cos \alpha_6)/q_1 \\
t_3 &= r_2 \sin \alpha_1/q_2 & s_3 &= (r_1 - r_2 \cos \alpha_1)/q_2 \\
t_4 &= r_1 \sin \alpha_1/q_2 & s_4 &= (r_2 - r_1 \cos \alpha_1)/q_2 \\
t_5 &= r_3 \sin \alpha_3/q_3 & s_5 &= (r_1 - r_3 \cos \alpha_3)/q_3 \\
t_6 &= r_1 \sin \alpha_3/q_3 & s_6 &= (r_3 - r_1 \cos \alpha_3)/q_3 \\
t_7 &= r_2 \sin \alpha_2/q_4 & s_7 &= (r_3 - r_2 \cos \alpha_2)/q_4 \\
t_8 &= r_3 \sin \alpha_2/q_4 & s_8 &= (r_2 - r_3 \cos \alpha_2)/q_4 \\
t_9 &= r_5 \sin \alpha_5/q_6 & s_9 &= (r_2 - r_5 \cos \alpha_5)/q_6 \\
t_{10} &= r_2 \sin \alpha_5/q_6 & s_{10} &= (r_5 - r_2 \cos \alpha_5)/q_6 \\
t_{11} &= r_2 \sin \alpha_4/q_5 & s_{11} &= (r_2 - r_2 \cos \alpha_4)/q_5 \\
q_1^2 &= r_4^2 + r_1^2 - 2r_4r_1 \cos \alpha_6 & q_4^2 &= r_2^2 + r_3^2 - 2r_2r_3 \cos \alpha_2 \\
q_2^2 &= r_1^2 + r_2^2 - 2r_1r_2 \cos \alpha_1 & q_5^2 &= r_2^2 + r_2^2 - 2r_2r_2 \cos \alpha_4 \\
q_3^2 &= r_1^2 + r_3^2 - 2r_1r_3 \cos \alpha_3 & q_6^2 &= r_2^2 + r_5^2 - 2r_2r_5 \cos \alpha_5
\end{aligned}$$

$$q_1 = q_{\mathrm{C}\cdots\mathrm{S}} \quad q_2 = q_{\mathrm{C}'\cdots\mathrm{S}} \quad q_3 = q_{\mathrm{R}\cdots\mathrm{S}}$$

$$q_4 = q_{\mathrm{C}'\cdots\mathrm{R}}, \quad q_5 = q_{\mathrm{C}\cdots\mathrm{C}}, \quad q_6 = q_{\mathrm{C}\cdots\mathrm{H}}$$

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 distributions 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 selenium–selenium 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 selenium–selenium bonded compounds—dimethyl selenide, Se_4^{2+}, and Se_2—the intermediate value, 2.20 mdyn/Å, for Se_4^{2+} has been considered[23] 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 ^{19}F and ^{1}H 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, Sheppard[2] has demonstrated the stability of organosulfur tri- and pentafluorides. In a continuing study of organoselenium halides[3] we have found further evidence for the 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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[2] W. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

[3] (a) K. J. Wynne and J. W. George, *ibid.*, **91**, 1649 (1969); (b) *ibid.*, **87**, 4750 (1965).

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TABLE I

DIALKYL- AND DIARYLSELENIUM DIFLUORIDES

Compound	Amt of selenide, mol	Amt of AgF_2, mol	Yield, %	Bp, °C (0.01 mm)	Mp, °C (uncor)	Mol wt	Analyses, %	C	H	Se	F
$(CH_3)_2SeF_2$	0.13	0.27	22	40	12	Calcd 147	Calcd	16.3	4.10	53.7	25.8
						Found 156	Found	16.6	4.22	55.3	23.6
$(C_2H_5)_2SeF_2$	0.13	0.27	29	49	*Ca.* −45[a]	Calcd 175	Calcd	27.4	5.72	45.2	21.7
						Found 181	Found	27.4	5.70	45.5	21.6
$(n\text{-}C_3H_7)_2SeF_2$	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]	...
$(i\text{-}C_3H_7)_2SeF_2$	0.08	0.16	57	60	*Ca.* −10	Calcd 203	Calcd	35.5	6.95	38.9	18.71
						Found 201	Found	...	6.29	37.0[b]	...
$(C_6H_5)_2SeF_2$	0.06	0.13	60	...	50–51	Calcd 271	Calcd	53.14	3.72	29.12	14.05
						Found 312	Found	52.49	4.13	...	14.08
$(CH_2)_4SeF_2$	0.11	0.22	22	...	91–92	Calcd 173	Calcd	27.8	4.67	45.62	21.96
						Found 168	Found	27.7	4.94	...	...

[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 difluorides 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 difluorides 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 difluorides 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 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 round-bottom flask. A solution of dimethyl selenide (14 g, 0.13 mol) in 20 ml of Freon 113 was added slowly to the AgF_2 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 AgF_2 turned yellow as the reaction proceeded, while with *n*-propyl and isopropyl selenides it turned red-brown.

1,1-Difluoroselenacyclopentane.—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 AgF_2 (19.1 g, 0.13 mol), $(C_6H_5)_2Se$ (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 $(C_6H_5)_2SeF_2$. 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

$$2AgF_2 + R_2Se \longrightarrow R_2SeF_2 + 2AgF$$

The melting points of diorganoselenium difluorides 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 $(CH_3)_2SeF_2$, $(CH_3)_2AsF_3$ (unlike $(C_6H_5)_2AsF_3$), shows evidence of association.[6]

The infrared and nmr data presented below for

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TABLE II

PROTON AND FLUORINE NMR PARAMETERS FOR DIORGANOSELENIUM DIFLUORIDES

Compound	^{19}F chem shift,[a] ppm	^{1}H chem shift,[b] ppm	$J_{^1H-^{19}F}$, Hz	$J_{^{19}F-^{77}Se}$, Hz
$(CH_3)_2SeF_2$[c]	Septet, +66.6	Triplet, 3.13	9.0	650.2
$(C_2H_5)_2SeF_2$[c]	Single peak,	CH_3, triplet	...	...
	+87.8	CH_2, broad single peak		
$(i\text{-}C_3H_7)_2SeF_2$	Single peak,	CH_3, doublet, 1.45	...	...
	+107.5	CH, septet, 3.40		
$(n\text{-}C_3H_7)_2SeF_2$	Single peak,	CH_3, triplet, 1.08	...	...
	+84.0	CH_2 (β), multiplet, 1.90		
		CH_2 (α), triplet, 3.24		
$(CH_2)_4SeF_2$[d]	Quintet,	CH_2 (β) quintet, 2.38		688
	+84.5	CH_2 (α) 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		

[a] Fluorine chemical shifts were measured *vs.* internal fluorotrichloromethane. [b] Proton chemical shifts are *vs.* internal tetramethylsilane. [c] For $(CH_3)_2SeF_2$ and $(C_2H_5)_2SeF_2$ $J_{^1H-^{77}Se}$ = 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 ± 10 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 SeF_4 at 719 and 541 cm^{-1}.[7] It seems reasonable that the absorption at 541 cm^{-1} is due mainly to axial Se–F stretching and compares favorably with our value for R_2SeF_2 compounds (compare also absorptions at 664 and 605 cm^{-1} in $SeOF_2$[8]). The low Se–F stretching frequency in diorganoselenium difluorides suggests that these bonds are relatively weak.

In Table II are listed ^{19}F chemical shifts for the diorganoselenium difluorides prepared in this study. It is seen that the ^{19}F 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 SeF_4. If the proper conversions are made, the ^{19}F chemical shift of SeF_4 is found to be −64 ppm relative to $CFCl_3$,[9] but this is an average shift value for axial and equatorial fluorines. By analogy with SF_4 and RSF_3 compounds[6] this value may set an upper limit on the axial ^{19}F chemical shift. Reference to Table II shows that substitution of two alkyl or aryl groups for two equatorial fluorines in SeF_4 causes a shift upfield of at least *ca.* 100 ppm. The comparison suggests[10] that Se–F bonds are more ionic in diorganoselenium difluorides than the corresponding bonds in SeF_4. This trend is reasonable when one considers that replacing three fluorines with organo groups produces selenonium fluorides, $R_3Se^+F^-$.[1]

There is a signigficant upfield flurine chemical shift 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 ^{19}F chemical shifts for $(CH_2)_4SeF_2$ and $(C_2H_5)_2SeF_2$ are about the same would seem to eliminate a through-space effect as the cause of the observed shifts.

The ^{19}F nmr data for SeF_4 in propane showed fluorine exchange occurs even at −200°.[9] In contrast our ^{19}F–^{1}H coupling constants for R_2SeF_2 systems shown in Table II indicate that for dimethyl- and tetramethyleneselenium difluorides slow fluorine exchange occurs at 34°. The observation of a large ^{77}Se coupling constant also suggests slow exchange for $(C_6H_5)_2SeF_2$. 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 ^{77}Se–^{19}F 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 ^{19}F–^{77}Se coupling constants can be made until the temperature dependence of the nmr spectrum of each compound is known in detail.

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