calcd for $C_7H_8N_6O$ 192.0759, obsd 192.0753.

Conversion of 5b to 5c. A solution of 25 mg (0.11 mmol) of **5b** in 8 mL absolute MeOH was treated with 0.5 mL of a 10% solution of picric acid in MeOH, and the resulting mixture was allowed to stand at room temperature for 30 min. The precipitate was filtered and dried under vacuum to afford 39 mg (85%) of a yellow solid which was shown to be identical with **5c**, prepared as described above, by TLC and "mixed" ^{1}H NMR.

1,*N*^{2}-Ethenoguanine (5,9-Dihydro-9-oxoimidazo[1,2-*a*]purine) (3). A solution of the bisimidazole hydrochloride **5b** (250 mg, 1.1 mmol) in 25 mL of 1 M NaOH was heated to gentle reflux with stirring under N_2 for 1 h. The solution was adjusted to pH 7 with glacial acetic acid, and the resulting mixture was cooled at 5 °C for 1 h. The precipitate was collected by filtration, washed with hot 1-propanol, and dried overnight under vacuum at 120 °C to yield 160 mg (84% based on unhydrated free base) of an off-white solid: mp >300 °C. This material was compared with an authentic sample of the product obtained by HI reduction of the guanine–glyoxal adduct[6] and was found to be identical by TLC in two systems (R_f 0.47, solvent A; 0.68, solvent B), mass spectrometry, UV, and "mixed" ^{1}H NMR (HI salts).

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Registry No. 3, 56287-13-9; **5a**, 73971-13-8; **5b**, 73971-14-9; **5c**, 73971-15-0; **7**, 10333-88-7; **8**, 73971-16-1; **9**, 73971-17-2; aminoacetaldehyde diethyl acetal, 645-36-3; picric acid, 88-89-1.

2,2,4,4-Tetrakis(trifluoromethyl)- and 2,4-Bis(hexafluoroisopropylidene)-1,3-diselenetane

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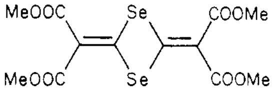
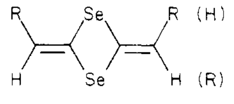
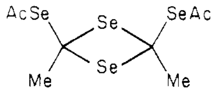
The nine known 1,3-diselenetanes (1,3-diselenacyclobutanes) have been synthesized by a variety of approaches.[2] Polymerization of selenocarbonyl fluoride followed by cracking of the polymer yields tetrafluoro-1,3-diselenetane.[3] Treatment of this compound with boron trichloride and with boron tribromide provides tetrachloro- and tetrabromo-1,3-diselenetane, respectively.[3b] Tetraacetyl-1,3-diselenetane has been made by the reaction of acetylacetone with selenium tetrachloride,[4] and 1 results from the reaction of carbon diselenide with the anion of dimethyl malonate.[5] Thermal decomposition of 1,2,3-selenadiazoles produces 2.[6] Compound 3 is obtained from acetyl chloride and hydrogen selenide in the presence of aluminum chloride.[7]



1

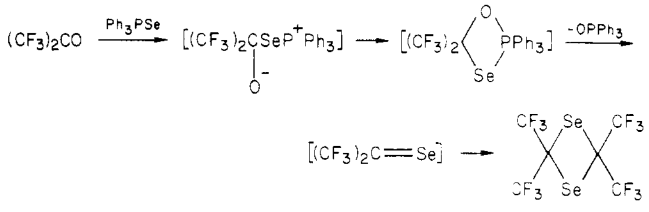


2, R = H, Me, *t*-Bu



3

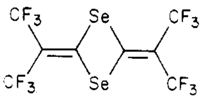
Tetrakis(trifluoromethyl)-1,3-diselenetane (4) has now been readily made in 73% yield by heating hexafluoroacetone and triphenylphosphine selenide at 150 °C for 5 h. Presumably, the oxygen–selenium exchange takes place through a cyclic four-membered intermediate. The mass spectrum of 4 is in agreement with the structure and provides no evidence indicative of the 1,2-diselenetane isomer.



4

This diselenetane was reported[8] in 6.4% yield as one of the products from the reaction of hexafluoropropene with selenium in the presence of antimony pentafluoride, but no melting point or characterization other than the mass spectrum was given.

Similarly, bis(trifluoromethyl)ketene and triphenylphosphine selenide provide 2,4-bis(hexafluoroisopropylidene)-1,3-diselenetane 5 in 16% yield. The ^{19}F NMR singlet for 5 eliminates the isomeric 1,2-diselenetane structure. This synthesis is less successful than the reaction of the ketene with triphenylphosphine sulfide which gives the sulfur analogue of 5 in 60% yield.[9]



5

Experimental Section

The ^{19}F NMR spectra were measured with a Varian XL-100 instrument with CCl_3F as internal standard. A Du Pont 900 differential thermal analyzer was used for thermal analysis.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-diselenetane (4). Triphenylphosphine selenide[10] was made by heating a stirred mixture of triphenylphosphine and selenium powder in a flask in an oil bath at 190 °C for 2.5 h and recrystallizing the product from ethanol, mp 188–189 °C.

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(1) Contribution no. 2764.

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Hexafluoroacetone (12 g, 0.072 mol) and 20.4 g (0.06 mol) of triphenylphosphine selenide were sealed in a glass tube and heated at 150 °C for 5 h. The mixture was steam distilled and the pale yellow diselenetane was filtered from the distillate and recrystallized from pentane to give 10.0 g (73%): mp 59.2-60 °C; mp 60 °C, bp 138 °C, by differential thermal analysis; ^{19}F NMR (CCl_4) -70.5 ppm (s); mass spectrum, *m/z* 459.8142 (parent), other peaks corresponding to $C_6F_{11}Se_2$, $C_5F_9Se_2$, C_3F_6Se, C_3F_5Se, C_2F_3Se, C_2F_2Se, CF_3. The compound is very volatile, and some escapes with boiling pentane.

Anal. Calcd for $C_6F_{12}Se_2$: C, 15.73; Se, 34.47; M_r, 458. Found: C, 15.67; Se, 34.24; M_r 467 (cryoscopic in benzene).

2,4-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-diselenetane (5). Bis(trifluoromethyl)ketene[11] (14 g, 0.08 mol), 24 g (0.07 mol) of triphenylphosphine selenide, and 20 mL of dichloromethane were heated in a sealed glass tube at 100 °C for 15 h. The product was steam distilled and taken up in additional dichloromethane. After being dried ($MgSO_4$), the solution was concentrated to crystallization and 2.67 g (15.8%) of the diselenetane was filtered off: mp 88-89 °C; mp 89 °C, bp 186 °C, by differential thermal analysis; IR 1595, 1626 (d, C=C) cm^{-1}; ^{19}F NMR (CCl_4) -59.6 ppm (s).

Anal. Calcd for $C_8F_{12}Se_2$: C, 19.93; Se, 32.77; M_r 482. Found: C, 20.25; Se, 32.22; M_r 490 (cryoscopic in benzene).

The yields were about the same when the reaction was carried out in benzene at 150 °C and without solvent at 200 °C.

Registry No. 4, 36827-57-3; **5**, 74036-94-5; triphenylphosphine selenide, 3878-44-2; hexafluoroacetone, 684-16-2; bis(trifluoromethyl)ketene, 684-22-0.

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Dissymmetric Chromophores. 5.[1] Synthesis and Circular Dichroism of Chiral 3-Methylenebicyclo[2.2.1]heptan-2-ones

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Chiral α,β-unsaturated ketones which exhibit skew-dependent Cotton effects[2,3] in their optical rotatory dispersion spectra were classified in 1962[2] as inherently dissymmetric chromophores.[4] Subsequently, there appeared various empirically derived modified octant[5] and chirality rules[5,6] which attempted to provide predictive correlations between Cotton effect (CE) signs associated with the erstwhile $\pi-\pi^*$ and n–π^* (K and R band) electronic transitions and relevant aspects of molecular geometry.[7,8] Thus, the CE sign of the long wavelength n–π^* (R band) transition is thought to be determined largely by the inherent chirality of the skewed enone chromophore,[7,9] but the sign-determining criteria for the short wavelength CEs are less well understood. It was first postulated that the $\pi-\pi^*$ (K band) transition CE was determined by the inherent chirality of a transoid enone.[2] That notion was marshalled later[7,9] and extended to cisoid enones.[7,10] Simultaneously it was shown that allylic and homoallylic axial bond contributions can control the CE sign of the short wavelength transition;[6,8,10] however, the relative importance of those contributions depends critically on whether the enone assumes a transoid or a cisoid configuration.[7,8,11] Only a small number of cisoid α,β-unsaturated ketones have been studied, and those are limited to steroids[5-8,12] with only a few exceptions, e.g., (+)-methylenecamphor[10,13,14] and 3-ethylidenecamphor.[10] The latter compounds are of special interest because they appear to have an essentially planar enone chromophore. We surmise, therefore, that they should be good systems to aid in educing the nature and importance of allylic and homoallylic bond chirality effects on the sign and magnitude of the CE. In this work we present the syntheses and circular dichroism (CD) data for simple, structurally rigid cisoid α,β-unsaturated ketones: (1*R*)-3-methylenenorcamphor (**1**), (1*R*)-3-methylene-α-fenchocamphorone (**2**), (1*R*)-3-methylenecamphor (**3**), (1*R*)-2-methyleneepicamphor (**4**), and (1*R*)-3-isopropylidenecamphor (**9**).

Synthesis and Stereochemistry. The synthesis of **1** proceeded smoothly in two steps from the known,[15] chiral (−)-(1*R*)-bicyclo[2.2.1]heptan-2-one (**5**) [44.5% enantiomeric excess (e.e.)] by the method of Adams and Vaughan,[16] who reacted (±)-norcamphor with formaldehyde/piperidine hydrochloride and then pyrolyzed the resultant 3-(piperidinomethyl)norcamphor hydrochloride. The enone (**1**) produced presumably retains the same (44.5%) e.e. as its precursor **5**. Enone **2** was prepared by reaction of α-fenchocamphorone[17] (**6**) with lithium diisopropylamide and treatment of the resulting lithium enolate with chloromethyl ether followed by base-catalyzed elimination of methoxide. Since **6** was prepared stereospecifically from (+)-camphor (**7**), we assume it has the same (100%) e.e. The synthesis of **3** or **4** could be achieved from **7** or **8**, respectively, in the same manner as the conversion of **6** to **2**. Alternatively, **3** was prepared from the 3-hydroxymethylene derivative of **7**, and **8** was prepared by SeO_2 oxidation of the methylene Wittig product of **7**. Isopropylidene derivative **9** was prepared first by quenching camphor zinc enolate with acetone followed by $SOCl_2$–pyridine catalyzed elimination of the alcohol. Since **3**, **4**, and **9** originate from (100% e.e.) **7**, we assume that they too have the same (100%) e.e.

Molecular Structure, Nuclear Magnetic Resonance, and Circular Dichroism Spectra. The ^{13}C NMR spectra of α,β-unsaturated ketones **1-4**, **9**, and pulegone and those of the parent bicyclic ketones (**5-8**) and

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