ductive fragmentation with lithium aluminum hydride in ether to give a mixture of exo and endo alcohols **5**. Hydrogenation and hydrogenolysis to alcohol **6** is routine and oxidation gives the desired ketone **1**.

A problem we encountered in the synthesis was the conversion of enol acetate **3** into cyclopropyl acetate **4**. Kraus stated that chloroform and 50% aqueous sodium hydroxide with catalytic amounts of benzyltriethylammonium chloride according to Makosza's procedure[8] gave a 67% yield of adduct **4**. He also mentioned that enol acetate **3** does not react with dihalocarbenes if they are generated from potassium *tert*-butoxide and trihalomethanes or from sodium trihaloacetates. This is probably due to the electron-deficient nature of the carbon–carbon double bond of **3**.

We have been unable to reproduce the addition of dichlorocarbene to acetate **3** by this procedure. Only nonvolatile products were obtained. However, use of Seyferth's reagent, (bromodichloromethyl)phenylmercury ($PhHgCCl_2Br$),[9] has been known for some time to be a mild method of generating dichlorocarbene.[10,11] Excess acetate **3** heated with this reagent in refluxing benzene for 4 h gives cyclopropyl adduct **4** in 57% yield and some **3**, easily separable by vacuum distillation, for a total recovery of 90%. The recovered enol acetate can be reused in the same reaction. The necessity of using excess **3** was not investigated, but a 1:1 stoichiometry has been found to be satisfactory for all but the least reactive olefins.[10] This change in the method of generating the dichlorocarbene makes bicyclo[4.2.1]nonan-2-one readily available through large-scale preparation.

Experimental Section

Melting and boiling points are uncorrected. Gas chromatography was performed on an SE-30 column at 190 °C.

3,3-Dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl Acetate (4). Bicyclo[3.2.1]oct-2-en-2-yl acetate (**3**, 90% pure by GC, 24.39 g, 0.147 mol) and (bromodichloromethyl)phenylmercury (32.41 g, 0.0735 mol) were magnetically stirred and refluxed for 4 h with dry benzene (150 mL) under nitrogen. After the mixture was cooled, the phenylmercuric bromide (mp 275–280 °C, lit.[11] mp 283–285 °C) was suction filtered and washed with petroleum ether (bp 30–60 °C, 100 mL). The solvents were rotary evaporated and the yellow oil was vacuum distilled. The first fraction had bp 50–90 °C (0.12–0.18 mm) and was identified as enol acetate **3** (15.02 g, 0.0905 mol). The second fraction distilled as a colorless liquid with bp 93–108 °C (0.15–0.20 mm) and was found to be 3,3-dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl acetate [**4**, 10.37 g, 0.0416 mol, 57%, lit.[6] bp 96 °C (0.5 mm)]: IR (neat) 3070 (cyclopropyl C–H), 2990 and 2930 (C–H), 1765 (C=O), 1445 (CH_2), 1355, 1200 (C–O), 1150, 1120 (C–O), 1015, 810 cm^{-1} (C–Cl); NMR (CCl_4) δ 3.0–3.2 (m, 1, $CHCCl_2$), 2.03 (s, 3, CH_3COO), 1.0–2.4 (m, 10). The starting material **3** plus product **4** represents a total recovery of 90%.

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Registry No.—**1**, 3850-55-3; **3**, 37678-33-4; **4**, 37678-34-5; $PhHgCCl_2Br$, 3294-58-4.

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Synthesis of the Torsionally Strained Monocyclic Polythiaether 1,4,7-Trithiacyclononane

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In a previous paper, we had reported convenient synthetic methods[1] for macrocyclic polythiaether ligands, which were subsequently exploited in our continuing investigation of macrocyclic polythiaether coordination chemistry with copper and mercury.[2] In the course of current crystallographic studies of the metal complexes as a function of ring size and sulfur atom donor number, we required the 1,4,7-trithiacyclononane **2** ligand. Whereas the oxa, aza, and the mixed oxa–aza–thia nine-membered cyclic ligand syntheses have been reported[3] by methods analogous to those illustrated in Scheme I, often in excellent yields, the corresponding trithia ligand **2** in our hands proved to be frustratingly inaccessible.

Compound **2** had been reported in 1920 by Ray as a by-product from the synthesis of ethanedithiol by the reaction of ethylene bromide in alcoholic potassium hydrogen sulfide.[4] We have reinvestigated this reaction and found that the main cyclic product is *p*-dithiane **1**, without the slightest trace of **2** being detectable by analytical high-pressure liquid chromatography.

We had previously reported the absence of **2** from the cyclization of sodium mercaptides of either 3-thiapentane-1,5-dithiol with ethylene bromide or 1,2-ethanedithiol with 1,5-dichloro-3-thiapentane in butanol media at 60 °C.[1] Rather, in both of these reactions, the major direct cyclization product was the hexathia macrocycle **4** along with *p*-dithiane **1** and the tetrathia macrocycle **3**, both of the latter being formed by intrachain cyclization. The absence of **2** was reasonably rationalized by the prohibitive torsional ring strain of the cyclononane structure.[5] Analysis of the structure with CPK space-filling models reveals that the most stable conformation of **2** requires nearly completely eclipsed conformations of the ethylene bridges.

However, when we reacted the sodium dimercaptide of 3-thiapentane-1,5-dithiol with ethylene chloride in ethanol media below 5 °C, the desired product **2** was isolated in 0.04% yield from a preparative scale reaction. This low yield was not

Scheme I

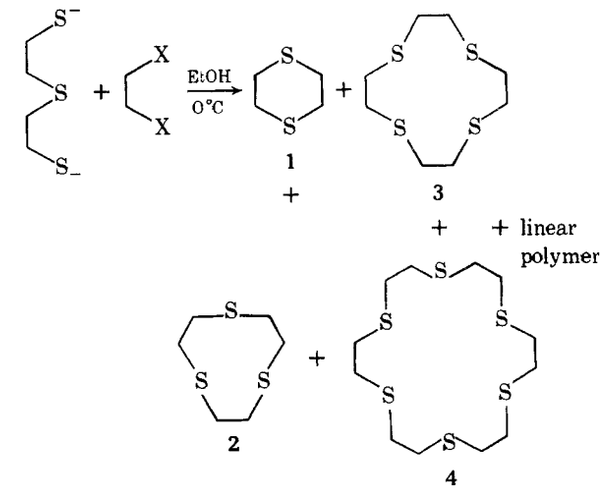

Table I. Product Yields and Direct vs. Intrachain Cyclization Ratios

Leaving group X	Yield % product[a] 1	2	3	4	Ratio (1 + 3/2 + 4)
Br	14.83	0	3.09	2.42	7.46
Cl	7.92	Trace	0.88	4.31	2.05

[a] Based on direct addition of 0.5 M ethylene halide–ethanol solution to 0.5 M 3-thiapentane-1,5-dimercaptide–ethanol solution under nitrogen. Reactants maintained below 5 °C for reaction duration; column chromatographic isolation.[1]

conveniently improved by use of high dilution conditions, which were investigated over a 50-fold dilution range.

The change in reaction course from a slight modification of reactants and conditions is consistent with our earlier observations[1] that leaving group, solvent polarity, and temperature could have a critical effect on intrachain cyclization, by which **1** and **3** arise, in competition with direct cyclization leading to the intended products **2** and **4**. The results in Table I illustrate the effect of leaving group on cyclization. The intrachain cyclization process is enhanced by better leaving group, by virtue of lower nucleophilicity of the chain-interior thia function relative to the ω-mercaptide function which affords direct cyclization. Thus the lesser polarizability of chloro relative to bromo leaving group could represent the boundary at which the enthalpy of nucleophilic displacement by mercaptide and thia functions, respectively, is sufficiently differentiated as to significantly diminish the difference in total enthalpy for formation of the six- and nine-membered ring systems.

However, two additional observations suggest that formation of **2** might in fact be due to a fortuitous solvation effect of ethanol media at a particular stage in the two-step cyclization process. The reaction of 1,5-dichloro-3-thiapentane with the dimercaptide of ethanedithiol should give rise to the same intermediate, and therefore **2**, as could be postulated in the present experimental design. As previously noted, **2** was not observed from these reactants in butanol media,[1] nor when subsequently investigated in ethanol media. Secondly, the use of less polar butanol media was found in all previous cases to inhibit intrachain cyclization and enhance direct cyclization relative to linear polymerization with better leaving groups than chloride. This observation also held true when chloride was displaced from 1,11-dichloro-3,6,9-trithiaundecane by 3-thiapentane-1,5-dimercaptide to yield macrocycle **4**.[1] Thus the results in Table I are anomalous with respect to the usual solvent effect.

Experimental Section

General. Nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 NMR, Me_4Si as internal reference. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrometer. Molecular weights were determined with a Hitachi Perkin-Elmer 115 vapor pressure osmometer. Column chromatography was performed on Baker's Analyzed silica gel (60–200 mesh) and HPL chromatography was carried out with a Waters Associates 660 solvent programmable chromatograph. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. All other general experimental details were as reported earlier.[1]

1,4,7-Trithiacyclononane (2). To a sodium ethoxide solution generated and maintained under a nitrogen atmosphere by dissolving sodium (8.0 mol) in 4 L of ethanol was added all at once 605.2 g (3.93 mol) of 3-thiapentane-1,5-dithiol.[1] The solution was allowed to equilibrate for 1 h, then cooled and maintained below 5 °C for the duration of the reaction. To the mercaptide solution was added 385.1 g (3.93 mol) of ethylene chloride in dropwise fashion. After 3 days of efficient stirring, the reaction mixture was filtered cold and filtrate concentrated. The filter cake was air dried, powdered, loosely packed in a 8 × 30 cm column, and leached by elution of 5 L of hexane–ethyl acetate, 80:20 volume ratio solvent. The leaching concentrates and original reaction filtrate concentrates were combined as a 1-L solution of methylene chloride, washed with two 500-mL portions of 5% sodium hydroxide, dried with sodium sulfate, and reconcentrated to yield 87.5 g of white solid residue. TLC analysis by comparison to authentic samples on silica gel H with 4% ethyl acetate–hexane revealed in descending order *p*-dithiane **1**, traces of unreacted dithiol, substantial quantities of 1,4,7,10,13,16-hexathiacyclooctadecane (**4**), and finally higher polymers. The 1,4,7,10-tetrathiacyclododecane (**3**) is highly insoluble and may be leached directly from the filter cake as previously described.[1] Only at very high plate loading could an additional component be detected immediately following unreacted dithiol. The 87.5 g of residue was dispersed on 400 g of sand and loaded onto a 6 × 70 cm silica gel column. Elution with hexane yielded all of **1** and a portion of the unreacted dithiol in the first 2.6 L of eluent. The first traces of **4** did not appear until an additional 2.8 L of hexane was eluted. This void fraction was concentrated and yielded 0.630 g of oil. TLC analysis established the oil to be only unreacted dithiol and the presumed trithia macrocycle **2**. No additional **2** in the presence of **4** could be detected in further column aliquots. The 0.630 g oil residue was taken up in 150 mL of hexane and filtered hot with three consecutive 0.3-g portions of charcoal. Cooling overnight at −20 °C deposited 283 mg (0.04%) of fine white crystals, mp 81–82 °C.[6] Further recrystallizations from hexane had no effect on the melting point. The data obtained are consistent with the structure assigned **2**: NMR ($CDCl_3$) s, δ 3.08 (500-Hz sweep width) and in expansion mode m, $J \sim 0.2$ Hz (25-Hz sweep width); mol wt (in benzene), calcd 180.35, found 178 ± 1; IR (KBr) (s) 2922, (s) 2896, (w) 2805, (s) 1455, (m) 1408, (s) 1414, (s) 1420, (m) 1295, (s) 1283, (w) 1183, (s) 1135, (w) 1125, (m) 920, (s) 875, (m) 837, (s) 822, (w) 669, (w) 617, (w) 410.

Anal. Calcd for $C_6H_{12}S_3$: C, 39.95; H, 6.71; S, 53.33. Found: C, 39.60; H, 6.75; S, 53.55.

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Registry No.—**1**, 505-29-3; **2**, 6573-11-1; **3**, 25423-56-7; **4**, 296-41-3; 3-thiapentane-1,5-dithiol, 3570-55-6; ethylene chloride, 107-06-2; ethylene bromide, 106-93-4.

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Convenient and General Method for Aliphatic and Aromatic Selenonester and N-Mono- and N,N-Disubstituted Selenoamide Synthesis

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Selenonesters have been prepared by the treatment of arylethynylselenoate salts with alcohols,[1] or by addition of hydrogen selenide to imidoester or its hydrochloride,[2,3] or a less direct method.[4] These preparations are either not general, or require restrictive conditions or, in some cases, reagents that