205.1 (s, 11-C), 215.6 (s, 1-C); IR (KBr) 3510, 3460, 1725, 1701, 1690, 988, 919; MS (CI; NH$_3$; 40 eV) *m/z* 384 (M$^+$ + 18, 0.92), 368 (M$^+$ + 2, 12), 367 (M$^+$ + 1, 100), 349 (14), 331 (46), 288 (55), 271 (8), 156 (7), 94 (6). Anal. Calcd for C$_{20}$H$_{30}$O$_6$: C, 65.55; H, 8.25. Found: C, 65.65; H, 8.20.

8,13-Epoxy-6β-(benzoyloxy)-7β,9α-dihydroxylabd-14-ene-1,11-dione (6-Benzoyl-7-desacetyl-1-deoxy-1-oxoforskolin, 5). Trimethyl orthobenzoate (1.6 mL), 3 mg of benzoic acid and 48 mg of **3** were stirred at 105–110 °C for 3 h. Excess trimethyl orthobenzoate and methyl benzoate formed during the reaction were removed under vacuum (80 °C). The yellow-orange oily residue thus obtained (i.e., **4**) was immediately dissolved in 1.5 mL of THF and 0.5 mL of water treated with 6 drops of glacial acetic acid and 2 drops of concentrated HCl. After 22 h at room temperature, the reaction mixture was added to 10 mL of water and extracted three times with 15-mL portions of EtOAc. The combined organic layers were washed with water (2 × 10 mL) and were evaporated to dryness in vacuo, yielding 58 mg of 6-mono-benzoate **5** (94% yield): mp 243–245 °C (hexanes/EtOAc); [α]^{25}$_D$ +36.6° (*c* 0.791, CHCl$_3$); ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.16, 1.18, 1.42, 1.66, 2.04 (all s, 3 H), 1.62 (m, 1 H, 3β-H), 1.76 (ddd, 1 H, *J* = 13.7, 5.5, 3.9 Hz, 3α-H), 2.12 (d, 1 H, *J* = 3.0 Hz, 7-OH), 2.25 (ddd, 1 H, *J* = 13.7, 3.9, 3.9 Hz, 2β-H), 2.42 (d, 1 H, *J* = 15.2 Hz, 12α-H), 2.52 (d, 1 H, *J* = 2.6 Hz, 5-H), 3.13 (ddd, 1 H, *J* = 13.7, 13.7, 5.5 Hz, 2α-H), 3.51 (d, 1 H, *J* = 15.2 Hz, 12β-H), 4.09 (s, 1 H, 9-OH), 4.36 (dd, 1 H, *J* = 4.4, 3.0 Hz, 7-H), 5.02 (dd, 1 H, *J* = 10.7, 0.7 Hz, 15-H), 5.22 (dd, 1 H, *J* = 17.2, 0.7 Hz, 15-H), 6.07 (dd, 1 H, *J* = 17.2, 10.7 Hz, 14-H), 6.14 (dd, 1 H, *J* = 4.4, 2.6 Hz, 6-H), 7.49 (dd, 2 H, *J* = 7.7, 7.7 Hz, Ar-H), 7.61 (tt, 1 H, *J* = 7.7, 1.4 Hz, Ar-H), 8.03 (dd, 2 H, *J* = 7.7, 1.4 Hz, Ar-H); ^{13}C NMR (90.56 MHz, CDCl$_3$) δ 18.1 (q), 21.9 (q), 23.5 (q), 30.1 (q), 31.8 (q), 34.0 (s, 4-C), 35.4 (t, 2-C), 43.5 (t, 3-C), 49.1 (d, 5-C), 49.6 (t, 12-C), 56.5 (s, 10-C), 72.3 (d, 6-C), 74.1 (d, 7-C), 77.3 (s, 13-C), 81.0 and 82.8 (both s, 8- and 9-C), 110.5 (t, 15-C), 128.7, 129.7, and 129.9 (all d, Ar-C), 133.3 (s, Ar-C), 146.0 (d, 14-C), 166.6 (s, ArCOO), 205.3 (s, 11-C), 214.0 (s, 1-C); IR (KBr) 3512, 1723, 1684, 1641, 994, 925 cm^{-1}; MS (CI; NH$_3$; 40 eV) *m/z* 488 (M$^+$ + 18, 16), 472 (M$^+$ + 2, 29), 471 (M$^+$ + 1, 100), 470 (M$^+$, 35), 453 (18), 436 (18), 435 (60), 393 (14), 392 (63), 348 (20), 331 (25), 285 (11), 226 (10), 156 (18), 139 (18), 139 (22), 105 (16), 94 (26). Anal. Calcd for C$_{27}$H$_{34}$O$_7$: C, 68.92; H, 7.28. Found: C, 68.83; H, 7.19.

8,13-Epoxy-6β,7β-bis(benzoyloxy)-9α-hydroxylabd-14-ene-1,11-dione (6,7-Dibenzoyl-7-desacetyl-1-deoxy-1-oxo-forskolin, 6). To 15 mg of **5** and 6 mg of 4-(dimethylamino)-pyridine in 1 mL of pyridine was added 65 mg of benzoic anhydride at room temperature. After being stirred at room temperature overnight, the solution was treated with 1 mL of methanol. The resulting mixture was dried in vacuo and partitioned between 15-mL portions of EtOAc and 10% aqueous HCl. The organic layer was washed with 15-mL volumes of 10% aqueous NaHCO$_3$ and water and was taken to dryness in vacuo. Preparative HPLC (hexanes/EtOAc, 10/1) of the product yielded 15 mg of dibenzoate **6** (82% yield): mp 118–120 °C (hexanes/EtOAc); [α]^{24}$_D$ +61.9° (*c* 0.832, CHCl$_3$); ^{1}H NMR (360 MHz, CDCl$_3$) δ 1.15, 1.20, 1.32, 1.81, 2.12 (all s, 3 H), 1.67 (ddd, 1 H, *J* = 13.7, 13.6, 4.1 Hz, 3β-H), 1.78 (ddd, 1 H, *J* = 13.7, 5.4, 4.6 Hz, 3α-H), 2.30 (ddd, 1 H, *J* = 13.9, 4.6, 4.1 Hz, 2β-H), 2.41 (d, 1 H, *J* = 14.6 Hz, 12α-H) 2.71 (d, 1 H, *J* = 2.6 Hz, 5-H), 3.08 (ddd, 1 H, *J* = 13.9, 13.6, 5.4 Hz, 2α-H), 3.56 (d, 1 H, *J* = 14.6 Hz, 12β-H), 4.03 (s, 1 H, 9-OH), 4.95 (dd, 1 H, *J* = 17.1, 1.0 Hz, 15-H), 5.26 (dd, 1 H, *J* = 10.6, 1.0 Hz, 15-H), 5.79 (d, 1 H, *J* = 4.5 Hz, 7-H), 5.89 (dd, 1 H, *J* = 17.1, 10.6 Hz, 14-H), 6.22 (dd, 1 H, *J* = 4.5, 2.6 Hz, 6-H), 7.31 (dd, 2 H, *J* = 8.1, 8.1 Hz, Ar-H), 7.48 (dd, 2 H, *J* = 7.8, 7.8 Hz, Ar-H), 7.50 (tt, 1 H, *J* = 8.1, 1.2 Hz, Ar-H), 7.62 (tt, 1 H, *J* = 7.8, 1.2 Hz, Ar-H), 7.85 (dd, 2 H, *J* = 8.1, 1.2 Hz, Ar-H), 7.90 (dd, 2 H, *J* = 7.8, 1.2 Hz, Ar-H); ^{13}C NMR (90.56 MHz, CDCl$_3$) δ 18.1 (q), 22.4 (q), 23.7 (q), 30.3 (q), 31.7 (q), 33.9 (s, 4-C), 35.3 (t, 2-C), 42.7 (t, 3-C), 48.4 (d, 5-C), 49.8 (t, 12-C), 56.3 (s, 10-C), 70.7 (d, 6-C), 74.7 (d, 7-C), 77.7 (s, 13-C), 81.2 and 82.1 (both s, 8- and 9-C), 110.5 (t, 15-C), 128.2, 128.7, 129.5, 129.6, 129.7, and 130.0 (all d, Ar-C), 132.8 and 133.3 (both s, Ar-C), 145.4 (d, 14-C), 165.7 and 166.3 (both s, ArCOO), 206.0 (s, 11-C), 212.6 (s, 1-C); IR (KBr) 3508, 1725, 1643, 987, 924 cm^{-1}; MS (CI; NH$_3$; 40 eV) *m/z* 593 (M$^+$ + 19, 13), 592 (M$^+$ + 18, 39), 576 (M$^+$ + 2, 32), 575 (M$^+$ + 1, 100), 557 (29), 529 (12), 497 (14), 496 (49), 436 (13), 435 (36), 313 (6), 285 (5), 245 (6). Anal. Calcd for C$_{34}$H$_{38}$O$_8$:

C, 71.06; H, 6.66. Found: C, 70.94; H, 6.57. CD (MeOH/dioxane, 9/1): Δε$_{239}$ +15.18, Δε$_{227}$ 0, Δε$_{221}$ −2.43.

# Pyrolysis of β-Chlorine-Containing Esters, Vinyl Ether, and Alkene[1]

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Introduction

The synthetic utility of the pyrolysis reaction of acetates has been recognized for many years. This reaction proceeds via a cyclic, quasi-six-membered transition state, in which atoms A and C are oxygens, and the reaction is generally believed to be concerted. Several comprehensive review articles have been published.[2,3]
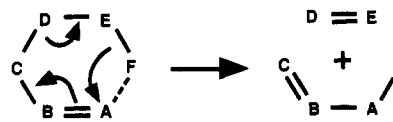
Over the years we, and others, were interested in finding out what other atoms would allow the six-membered cyclic process to operate. This led to pyrolysis of lactones,[4] esters in general,[5,6] vinyl ethers,[7] ketones,[8] olefins,[9] allyl sulfides,[10] β-hydroxy olefins,[11] β-hydroxy esters,[12] β-hydroxy ketones,[13] allylamines,[14] and carbamates.[15] In all of the compounds pyrolyzed, atoms A, B, C, D, or E were either carbon, sulfur, oxygen, or nitrogen. Atom F has always been the hydrogen atom.

White et al.[16] proposed a mechanism for the Claisen rearrangement involving a quasi-radical bond formation and bond cleavage in the transition state. It was reasoned that if the cyclic pyrolysis mechanism involved some radical character, either through an uncoupling of the electrons in the allylic bond or some n→π* or π→π* transition, then other atoms, including halogens should be capable of migration (atom F).

Yano and Bailey tested the above hypothesis by pyrolyzing 2,2,2-trichloroethyl vinyl ether and 2,2,2-trifluoro-ethyl vinyl ether to vinylidene chloride and vinylidene fluoride, respectively.[17] The pyrolysis of 2-chloroethyl vinyl ether was also briefly investigated, following the course of reaction by the amount of ethylene produced (33–80%).[17] The lowest yield of ethylene (33%), the statistical amount expected from a cyclic process, was obtained at low temperatures (<530 °C), but no mechanistic studies were carried out. We became interested in the pyrolysis of halogen-containing compounds to determine

Table I. Pyrolysis of Some Halogen-Containing Compounds[a]

| run	substrate	temp, °C	temp, °C for 50% conv[b]	olefinic products, % yield	% conv
1	AcOEt	550	550	CH_2=CH_2 (92)	49
2	AcOCH$_2$CH$_2$Cl	530	556	CH_2CH_3 (18), CH_2=CHCl (70)	18
3	AcOCH$_2$CHCl$_2$	520	560	CH_2CHCl (64), CH_2=CCl$_2$ (29)	12
4	AcOCH$_2$CCl$_3$	540	564	CH_2=CCl$_2$ (89)	36
5	AcOCH$_2$CH$_2$F	610	625	CH_2CH_3 (11), CH_2=CHF (73)	20
6	AcOCH$_2$CF$_3$	650	690	CH_2=CF$_3$ (91)	8
7	CH_2=CHOCH$_2$CH$_2$Cl	500	495	CH_2=CH_2 (26), CH_2=CHCl (60) ClCH$_2$CH=O (30), CH$_3$CH=O (55)	45
8	CH_2=CHOCH$_2$CCl$_3$	530	520	CH_2=CCl$_2$ (87)	53
9	CH_2=CH(CH$_2$)$_3$Cl	650	648	CH$_3$CH=CH$_2$ (29), CH_2=CHCH$_2$Cl (64) CH_2=CHCl (36), CH_2=CH_2 (56)	49

[a] Reaction conditions: sample size, 1–20 μL; diluents, benzene or toluene, 5–10/1, ArH/substrate, g/g. [b] 20% diluent as internal standard. [c] By GLC, average of at least two runs, based on reacted substrate.

whether a competition between a halogen and a hydrogen atom in the cyclic transition state was operative, and to determine reaction conditions needed for such transformation.

Results and Discussion

The pyrolysis of esters is a well-established convenient method for the preparation of alkenes. The products are those predicted for β-elimination, and usually the products undergo minimal secondary reactions.[2,3] In this regard, pyrolysis of ethyl acetate at 550–600 °C gave a high yield of ethylene (exp 1, Table I). When the pyrolysis of 2-chloroethyl acetate was carried out neat, under comparable conditions, the product was complex. Besides the expected ethylene and vinyl chloride, substantial amounts of carbon dioxide and methyl chloride were formed, along with smaller amounts of propyl chloride, ethane, and several unidentified components. While the formation of vinyl chloride appeared to be a straight-forward ester pyrolysis, the mechanism of formation of ethylene was not immediately obvious since involvement of two electronegative groups (Cl, O) in the cyclic transition state could be expected to hinder such transformation. In order to simplify the products, conditions were chosen which would suppress secondary reactions. This was accomplished by carrying out reactions in toluene or benzene solvent at the lowest practical temperature and accepting a lower conversion. Thus, pyrolysis of 2-chloroethyl acetate in toluene (530 °C;

6/1, CH$_3$Ph/ester, g/g, exp 2) gave vinyl chloride and ethylene (molar ratio 80/20) in good yield at 18% conversion. Under such conditions, the formation of carbon
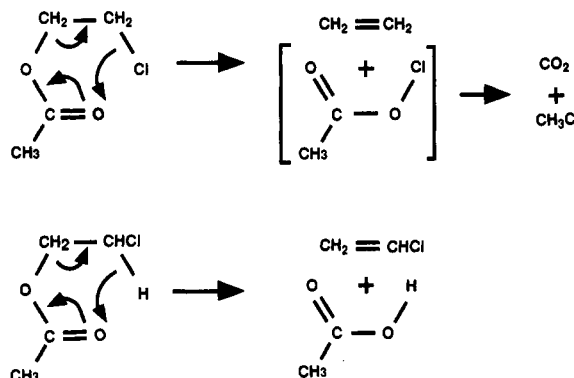
dioxide and methyl chloride were completely eliminated, and minor products were greatly suppressed. Pyrolysis of 2,2-dichloroethyl acetate, under similar conditions, gave vinyl chloride and vinylidene chloride (molar ratio 69:31, exp 3), while 2,2,2-trichloroethyl acetate was converted exclusively to vinylidene chloride (exp 4). We believe that the use of toluene to lessen the vapor pressure of the ester and the low temperature both served to suppress secondary radical reactions, and that the products we were observing are those arising from the cyclic mechanism. Toluene has been frequently used for inhibition in the gas-phase pyrolyses,[3] but dibenzyl, the coupling product of benzyl radicals, has not been detected in our pyrolysis products. Dilution effects have also been known to suppress rival radical reactions.[18]

If ethylene is formed by a mechanism involving chlorine atom in the cyclic transition state, the corresponding acyl hypochlorite should be eliminated, instead of acetic acid, which should be susceptible to trapping. Thus, when the pyrolysate from 2,2,2-trichloroethyl acetate containing acyl hypochlorite, or acyl hypochlorite independently prepared,[19] was reacted with cyclohexene at reflux, trans-2-chlorocyclohexyl acetate was formed via an ionic addition. In the presence of peroxide, a mixture of cis- and trans-2-chlorocyclohexyl acetates was formed in 20–30% yield. In a control reaction, heating a mixture of 2,2,2-trichloroethyl acetate, acetic acid, cyclohexene, and benzoyl peroxide gave 3- and 4-chlorocyclohexenes, but no 2-chlorocyclohexyl acetate isomers. The literature reports that acyl hypochlorite is a powerful oxidizing agent, it should not be purified, and its stability in solutions has been questioned.[19] In view of high oxidation potency of

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Table II. NMR Spectral Data of 7-Chlorospiro[4.5]dec-6-yl Acetate

assignment	intensity	δ (ppm)	J (Hz)	mult
		Cis		
H_a	1	4.94	2.5	d
H_b	1	4.04	2.6	d
		4.00	2.2	t
		3.96	2.6	d
H_c, H_d	2	1.72–1.86		m
CH_2	12	1.07–1.67		m
CH_3	3	2.03		s
		Trans		
H_a	1	4.83	10.3	d
H_b	1	3.78	6.0	d
		3.74	2.0, 6.0	dd
		3.70	6.0	d
H_c, H_d	2	1.70–1.82		m
CH_2	12	1.05–1.69		m
CH_3	3	2.01		s

acyl hypochlorite, it is remarkable that even modest amounts of acyl hypochlorite were isolated by trapping experiments.
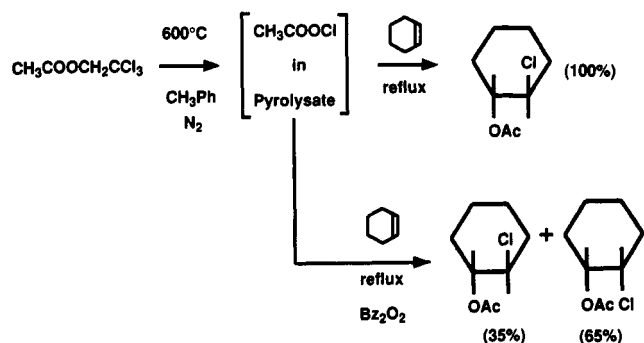

The pyrolysis of several bromo and iodo acetates proved to be problematic as these were more sensitive to changes in concentration than the chloro compounds, and they formed coke and dehydrohalogenation products more easily. Thus, in the pyrolysis of 2,2,2-tribromoethyl acetate at 540 °C, for example, the major product isolated was 2,2-dibromovinyl acetate. Surprisingly, the more stable fluorine-containing esters—2-fluoroethyl and 2,2,2-trifluoroethyl acetates—gave very simple pyrolysis products (exp 5, 6). In this respect, pyrolysis of 2,2,2-trifluoroethyl acetate is of interest, since this reaction may potentially be developed as an alternate method for preparing acyl hypofluorite.[20]

We also extended the scope of reaction to include 2-chloroethyl vinyl ether (exp 7) and 5-chloro-1-pentene (exp 9). A mechanism similar to that of 2-chloroethyl acetate pyrolysis can be written for the above two substrates.

In order to establish the steric requirements of the reaction, we have studied the pyrolysis of cis- and trans-2-chlorocyclohexyl acetates and vinyl ethers, systems which have been previously studied to establish the syn nature of these pyrolytic eliminations.[15,21,22] The former compounds are known;[23] the latter compounds were prepared via mercuric acetate catalyzed transetherification of cis- or trans-2-chlorocyclohexanol with ethyl vinyl ether.[24] The pyrolyses were carried out in toluene to inhibit de-

composition of acyl hypochlorite to carbon dioxide and methyl chloride, which apparently occurs via a free-radical mechanism.[20] The results of our studies are summarized below. The cis isomers gave cyclohexene, but no 1-chlorocyclohexene, while the trans isomers gave 1-chlorocyclohexene, but no cyclohexene, indicative of syn elimination. Accompanying the above products was 3-chlorocyclohexene which was not stable under pyrolysis conditions and gave varying amounts of 1,3-cyclohexadiene. All attempts to suppress dehydrochlorination reaction were not successful. In all cases, however, the ratio of cyclohexene or 1-chlorocyclohexene to that of 3-chlorocyclohexene and 1,3-cyclohexadiene combined remained constant.
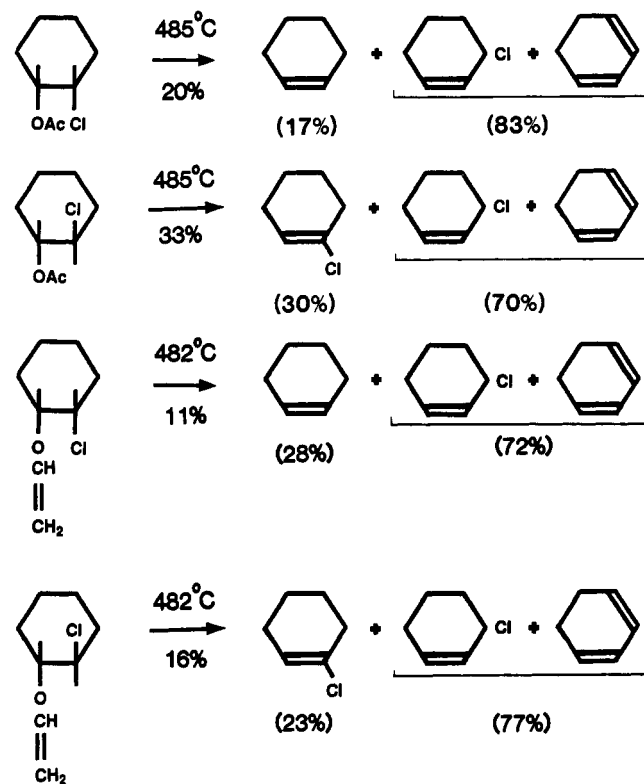
In view of the complication encountered with stability of 3-chlorocyclohexene above, a spirodecane model system was designed. In essence, the spirodecane system is analogous to the cyclohexane system, except that the α-position has been blocked with a tetramethylene functionality to allow only one direction of elimination. The compounds of interest were prepared from a known 7-chlorospiro[4.5]decan-6-one[25] via Meerwein–Pondorff–Verley reduction[26] to give a mixture of cis- and trans-7-chlorospiro[4.5]decan-6-ols (70:30), which were separated by column chromatography,[27] acetylated, and analyzed by NMR (Table II).

cis   trans
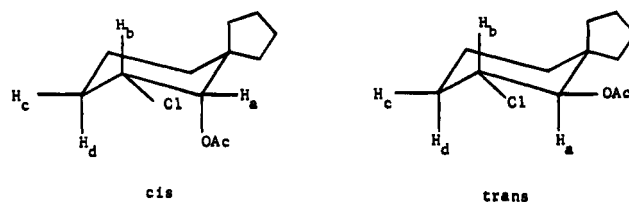
Subjecting cis-7-chlorospiro[4.5]dec-6-yl acetate to pyrolysis was expected to afford spiro[4.5]dec-6-ene, while

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the corresponding trans isomer was expected to give 7-chlorospiro[4.5]dec-6-ene, providing a clear evidence for the syn elimination of chloro esters. The predicted results were verified experimentally and are summarized below.

540°C → 25%   (96%)

OAc Cl

540°C → 30%   (98%) Cl

Cl
OAc
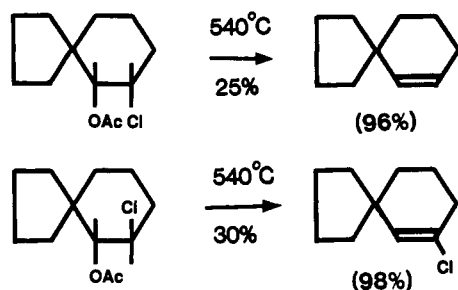
Conclusion

The pyrolysis of simple β-chlorine-containing compounds—2-chloro-, 2,2-dichloro-, and 2,2,2-trichloroethyl acetates, 2-chloro- and 2,2,2-trichloroethyl vinyl ethers, and 5-chloro-1-pentene—was studied. The major products were explained by a syn elimination mechanism, well established for the normal esters, and the chlorine atom in this mechanism performs the same role as is common for a β-hydrogen. Stereochemical studies using the cyclohexane ring system and trapping of acyl hypochlorite coproduct with cyclohexene are consistent with our proposal. The molar ratio of elimination of chlorine atom over the hydrogen atom was 1:1 for 2-chloroethyl vinyl ether, 1:2 for 2-chloroethyl acetate, and 1:0.25 for 5-chloro-1-pentene.

Experimental Section

The infrared spectra were recorded on a Beckman IR-8 spectrometer. The chromatographic analyses were performed on Varian Aerograph 200 (TC) or Hewlett-Packard 5710A (TC) or 5880A (FID) chromatographs. The columns employed were 14 ft × 0.25 in. (glass), 30% cyanosilicone fluid on Chrom P, 20 in. × 0.125 in. 10% UCW on 80-100 WAW DUCS 885 support and temperature programming (50–200 °C, at 8 deg/min), and 75 ft, 2% OV-101, fused silica capillary (50–300 °C, at 8 deg/min). The ¹H NMR spectra were obtained on a Varian T60 or XL 200 spectrometers in CDCl₃ or CCl₄. The chemical shifts are in δ units (ppm), relative to Me₄Si (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). GC/MS data were obtained on a Finnigan 4510 system with an electron impact source at 70 eV.

Apparatus. The micropyrolyses were carried out through a 7 in. × ³/₈ in. i.d. Vycor tube, the middle section of which (4.5 in.) was packed with ¹/₁₆-in. Pyrex chips. The tube was placed vertically inside of an electrically heated microcombustion furnace (4 in. × 0.5 in. i.d.) and was connected to a chromatographic column. At the mid-point of the furnace, between the furnace wall and the pyrolysis tube, was placed the tip of the thermocouple for measuring the temperature. The temperature recorded was the outside temperature, with the temperature inside the tube being some 50–60 °C lower. The top of the pyrolysis tube was covered with a rubber serum cap through which samples could be injected using a Hamilton syringe. A side arm was provided near the top of the pyrolysis tube through which a steady flow of helium carrier gas was passed. The products of pyrolysis were identified by GLC by their retention times and confirmed by spiking with authentic samples using several columns.

For isolation of products, the same pyrolysis tube was used, except that it was connected to two "cold finger" condensers; experiments were carried out under a flow of nitrogen by injecting samples (20–50 μL) through the septum at a given temperature.

Pyrolysis of 2-Chloroethyl Acetate. The results of various pyrolyses are listed in Table I, but a typical micropyrolysis run is described for 2-chloroethyl acetate below. A sample of 2-chlorethyl acetate containing 20% toluene as internal standard was pyrolyzed by injecting 5-μL samples of the ester from 475 to 625 °C and plotting the amount of olefinic products formed

against the temperature. From the "S" shaped curve, a temperature of 556 °C was extrapolated for the pyrolysis to occur to the extent of 50%. The product mixture was complex. To simplify the products, the pyrolysis was carried out in toluene diluent (6:1, CH₃Ph/ester, g/g) by injecting 5–10 μL samples at 530 °C to suppress secondary pyrolysis.

trans-2-Chlorocyclohexyl Vinyl Ether. Obtained from *trans*-2-chlorocyclohexanol and ethyl vinyl ether in 17% yield,[24] bp 56–60 °C (3.8 mm). Analytical sample was collected off the GLC column. IR: 1610 (M), 1625 (M), 1175 (S) cm⁻¹ (vinyl ether). Anal. Calcd for C₈H₁₃ClO: C, 59.86; H, 8.16. Found: C, 59.95; H, 8.30.

cis-2-Chlorocyclohexyl Vinyl Ether. Obtained from *cis*-2-chlorocyclohexanol and ethyl vinyl ether in 14% yield,[24] bp 48–52 °C (1.7 mmHg). Analytical sample was collected off the GLC column. IR: 1610 (s), 1625 (s), 1180 (s) cm⁻¹ (vinyl ether). Anal. Calcd for C₈H₁₃ClO: C, 59.86; H, 8.16. Found: C, 59.86; H, 8.25.

cis- and *trans*-7-Chlorospiro[4.5]decan-6-ols. Obtained in 83% yield from 7-chlorospiro[4.5]decan-6-one[25] via the Meerwein–Pondorff–Verley reduction with a 3-fold excess of aluminum isopropoxide in 2-propanol[26] to give a mixture of cis/trans chlorohydrins (70/30), bp 84–90 °C (0.9 mm). Anal. Calcd for C₁₀H₁₇ClO: C, 63.60; H, 9.08; Cl, 18.80. Found: C, 63.57; H, 8.88; Cl, 18.70. The separation of cis/trans alcohols (3 g) was carried out on aluminum oxide column (150 g, Merck) by eluting with benzene/n-hexane mixtures.[27] The fractions containing *cis*-7-chlorospiro[4.5]decan-6-ol and *trans*-7-chlorospiro[4.5]decan-6-ol were each acetylated with acetyl chloride and analyzed.

cis-7-Chlorospiro[4.5]dec-6-yl acetate: IR 1735 (s), 1242 (s) cm⁻¹ (ester); mass spectrum, m/z (relative intensity) 230 (0) M⁺, 195 (1) (M − Cl)⁺, 194 (3) (M − HCl)⁺, 171 (1) (M − OAc)⁺, 170 (10) (M − HOAc)⁺, 153 (11), 152 (69), 136 (16), 135 (100), 134 (24), 121 (12), 111 (24), 108 (14), 107 (12), 97 (9), 95 (19), 94 (12), 93 (25) 91 (16), 81 (13), 79 (20), 70 (10), 67 (28), 43 (42); NMR, Table II.

trans-7-Chlorospiro[4.5]dec-6-yl acetate: IR 1735 (s), 1243 (s) cm⁻¹ (ester); mass spectrum, m/z (relative intensity) 230 (0) M⁺, 194 (1) (M − HCl)⁺, 171 (2) (M − OAc)⁺, 170 (12) (M − HOAc)⁺, 152 (36), 136 (14), 135 (100), 134 (23), 121 (10), 111 (18), 108 (12), 95 (16), 94 (10), 93 (20), 91 (13), 79 (16), 67 (23), 43 (27); NMR, Table II.

Pyrolysis of cis- and *trans*-7-Chlorospiro[4.5]dec-6-yl Acetates for Product Isolation. A mixture of chloro acetates (5 g, cis/trans, 70/30) was pyrolyzed by the dropwise addition of sample through the pyrolysis tube at 580 °C, under a flow of nitrogen, and collecting the products in a dry ice-acetone trap. The pyrolysate was allowed to come to room temperature, taken up in ethyl ether, washed several times with water, and dried (anhydrous MgSO₄), and the solvent was removed in vacuo. The expected products of pyrolysis—spiro[4.5]dec-6-ene and 7-chlorospiro[4.5]dec-6-ene—were isolated by collecting pure samples off the GLC column and analyzed.

Spiro[4.5]dec-6-ene: IR 1645 (w), 1690 (w), 3018 (s) cm⁻¹ (olefin); NMR 5.54 (s, 2 H, vinyl), 1.85 (m, 2 H, allylic), 1.55 (m, 12 H, methylene);[28] mass spectrum, m/z (relative intensity) 136 (30) M⁺, 121 (25), 108 (20), 107 (45), 95 (50), 94 (60), 93 (40), 80 (21), 79 (100), 67 (37), 59 (43), 57 (60), 56 (31).[29] Anal. Calcd for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 87.90; H, 11.60.

7-Chlorospiro[4.5]dec-6-ene: IR 1648 (w), 3018 (m) (olefin); 760 (s) cm⁻¹ (C–Cl); NMR 5.67 (s, 1 H, =CH), 2.07 (m, 2 H, =CClCH₂), 1.64 (m, 12 H, methylene); mass spectrum, m/z (relative intensity) 170 (13) M⁺, 141 (20), 135 (100), 130 (18), 128 (23), 107 (20), 105 (23), 93 (38), 92 (12), 91 (40), 79 (38), 77 (40), 67 (18), 65 (15). Anal. Calcd for C₁₀H₁₅Cl: Cl, 20.81. Found: Cl, 20.52.

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