time as butyrophenone (14),[9] and several minor peaks of intensity of 10–20%. The nmr spectra of various fractions were also similar, showing the characteristic pentet at δ 1.65, triplet at δ 1.80, and ortho aromatic protons at δ 7.85 of butyrophenone together with variable strong absorptions in the aromatic (δ 7.0–7.4), aliphatic (δ 0.8–1.4), and vinyl (δ 5–6.3) regions. The clean-looking vpc trace yet a somewhat messy nmr could possibly be explained by the existence of polymeric products which might arise during reaction, distillation, and/or chromatography. The starting alcohol **13** is fairly susceptible to dehydration and polymerization, as we found out in some of our preparations. The butyllithium could promote a base-catalyzed elimination of water and polymerization of **13**.

The reaction was repeated as before except the TMEDA was left out and THF was added in its place, so that the solvent system consisted of a mixture of hexane and THF. Analysis of the crude product by vpc (SE 30) showed, again, only one outstanding peak of retention time identical with that of authentic butyrophenone. However, the nmr of the crude product showed by overlapping comparisons to authentic samples that it was about a 1:1 mixture of alcohol **13** (which was not showing up to any great extent on the vpc possibly due to polymerization on the column) and ketone **14**, together with additional aromatic and aliphatic signals.

Registry No.—**9**, 6051-52-1; **10** (R = *n*-Bu), 53109-16-3; **10** (R = *t*-Bu), 37887-25-5; **11** (R = *n*-Bu), 53109-17-4; **11** (R = *t*-Bu), 37887-26-6; *cis*-**12**, 768-00-3; *trans*-**12**, 767-99-7; **13**, 3347-57-7; **14**, 495-40-9.

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(1) To whom correspondence should be addressed at the Synthetics Department, Research Center, Hercules, Inc., Wilmington, Del. 19899.
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(4) Samples of these compounds were kindly supplied to us by Dr. M. A. McKinney (Marquette University). The olefins were prepared by dehydration of 2-phenyl-2-butanol according to the procedure of J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969). The olefins, present in a 3:1 ratio, were separated by preparative vpc from the terminal olefin. The major olefin is reported to be the cis isomer: J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York, N.Y., 1970, p 365. The major olefin possessed an ir spectrum identical with that of *cis*-2-phenyl-2-butene (Sadler, Vol. I, 1619).[5] The minor olefin possessed an ir spectrum identical with that of *trans*-2-phenyl-2-butene (Sadler, Vol. I, 1618).[5]
(5) Spectral data given in Table I.
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Zinc Chloride Catalysis in the Reaction of Thionyl Halides with Aliphatic Alcohols

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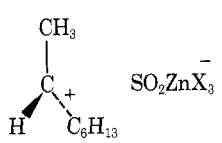
Since our report[2] that zinc chloride–thionyl chloride (**1**) easily converts 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**2**) to 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**3**), we have extended the use of reagent **1** to aliphatic systems. Since rapid, easy, high-yield, and high-purity synthesis of **3** was a significant breakthrough for carbohydrate chemists, we have documented the effectiveness of **1** with representative alcohols. We report here (1) clear proof that zinc chloride catalyzes the reaction of thionyl chloride with alcohols (Table I), (2) comparison of zinc chloride with pyridine as a catalyst, and (3) the yield and stereochemical result of converting optically active 2-octanol (**4**) to its chloride and bromide with the appropriate thionyl halide (Table II).

In addition to **4**, the reagent **1** was allowed to react with the following alcohols: 1-butanol (**5**), 2-butanol (**6**), 2-methyl-2-propanol (**7**), and cyclohexanol (**8**). In Table I we show that reagent **1** readily converts each of these alcohols to product, under conditions where thionyl chloride alone gives little or no substitution. These data also document the synthetic utility of reagent **1** (runs 5, 8, 11, and 14). The yields of isolated products are acceptable, and no effort was made to optimize them.

The 2-chlorobutane produced from **5** (runs 4 and 5) is a primary reaction product, for 1-chlorobutane does not isomerize when treated with **1** for 2 days. This product mixture from **5** has been previously reported,[3] and led us to seek a catalyst to suppress the formation of the rearrangement product, 2-chlorobutane. Since pyridine has been widely used as a catalyst with thionyl chloride,[4] we investigated it with alcohols **5** and **6**. With **5**, pyridine was superior to zinc chloride; no rearrangement was detected by vpc (although 55% product formed in 2 days). With alcohol **6**, pyridine gave lower initial and overall conversion than was attained with reagent **1**. Attempts to combine zinc chloride and pyridine as a mixed catalyst were unsuccessful; lower conversion to product was generally observed than with either catalyst used alone.

For stereochemical studies (Table II), commercial 2-octanol (**4**) was resolved and purified according to the method of Kenyon.[5] Zinc chloride with either thionyl chloride or bromide in benzene or dioxane solution was an effective catalyst. At the concentration employed here, thionyl bromide slowly converts **4** to 2-bromooctane, but even this relatively easy reaction was greatly aided by zinc chloride. In every case where zinc chloride was used as a catalyst, the product was less optically pure than the starting **4** (*e.g.*, runs 15 and 16). This fact, along with the rearrangement product observed when reacting **5** with the reagent **1**, suggests that, at some time during the reaction, at least partial symmetry is attained by the cation. Boozer and Lewis appear to be the first to propose that ions are involved in the mechanism of transforming alcohols to alkyl chlorides.[6] We find their mechanism compatible with our data, by assuming that zinc chloride complexes at one or more stages of the reaction, makes some reaction species more ionic, and in this manner speeds the reaction. The structure **9** is a representation of a possible intermediate



9, X = Cl or Br

when **1** converts **4** to the chloride. Solvation of such an intermediate could explain the effect of dioxane on the reaction of **1** with optically active **4**. We can neither support nor reject the "ion pair" hypothesis of Sneen for solvolytic reactions.[7]

In conclusion, we have demonstrated that zinc chloride catalysis can be of value in converting alcohols to the corresponding chloride or bromide. As in the previously cited example of the conversion of **2** → **3**,[2] this can be especially important when low acidity, mild temperature reaction conditions are desired.

Experimental Section

General Procedures. All boiling points are uncorrected. All reagents were the best commercial grade available, dried and/or distilled before use, and stored appropriately so as to prevent contamination. Reaction analysis was done on the Varian 90P-3 gas chromatograph (vpc) with the Model 244 disk-chart integrator for

Table I
Reaction of Selected Alcohols with Thionyl Chloride[a]

Run	Alcohol (mmol)	Equivalents of thionyl chloride	Mmol of zinc chloride	Hours to half-conversion	Maximum % conversion	Total hr for reaction
1	4 (22.0)	3.45	0		15[c]	161
2	4 (15.4)	3.25	1.8	~0.25[b]	100[b]	1.0
3	5 (55.0)	1.0	0		0	48
4	5 (55.0)	2.0	7.3		49[d]	48
5	5 (547)[e]	1.2	18.0	~2[b]	73[c,f]	30
6	6 (11.0)	1.0	0		~1	48
7	6 (11.0)	1.0	0.37	0.5	94	24
8	6 (437)[g]	1.2	14.5	~0.5[b]	73[c]	2.5
9	7 (2.7)	1.0	0	38	64	72
10	7 (2.7)	1.0	0.37	0.4	90	30
11	7 (533)[h]	1.2	18.0	~2[b]	78[c]	12
12	8 (9.5)	1.5	0		0	116
13	8 (9.5)	1.5	0.37	0.35	100	1.0
14	8 (473)[i]	1.2	18	~0.5[b]	75[c]	1.5

[a] All reactions were conducted under anhydrous conditions, at room temperature, and, except as noted, in 50 ml of benzene solvent. See Experimental Section for other details. [b] Estimated from vpc by disappearance of the starting alcohol. [c] Isolated by distillation. [d] Total chloride produced; 67% 1-chlorobutane and 33% 2-chlorobutane, by vpc on column B. [e] 100 ml of decane as solvent. [f] 73% 1-chlorobutane and 27% 2-chlorobutane by vpc on column B. [g] 180 ml of decane as solvent. [h] 250 ml of toluene as solvent. [i] 250 ml of benzene as solvent.

Table II
Reaction of *d*- or *l*-2-Octanol with Thionyl Halides

Run	$[\alpha]_D$ alcohol	Solvent (50 ml)	Mmol of alcohol	Mmol of thionyl chloride	Mmol of thionyl bromide	Mmol of zinc chloride	Reaction time, hr	Yield	$[\alpha]_D$ halide[a]	Stereochemical result,[b] %
15	+5.9	Benzene	22.0	76.0		0	161	15	−20.0	93 inversion
16	+5.9	Benzene	15.4	50.0		1.8	1.0	100	−10.3	48 inversion
17	−8.75	Dioxane	23.0	60.0		0	42	100	−25.7	82 retention
18	+5.9	Dioxane	15.4	50.0		1.8	1.0	100	− 0.4	98 racemization (2 inversion)
19	+5.9	Benzene	23.0		51.0	0	20	89	−13.5	64 inversion
20	−8.75	Benzene	11.4		36.6	1.8	1.0	100[c]	+17.7	59 inversion
21	+6.3	Dioxane	15.4		50.0	0	110	100	+10.0	48 retention
22	−8.75	Dioxane	11.4		36.6	1.8	1.0	100[c]	+ 4.90	84 racemization (16 inversion)

[a] Optically pure 2-chlorooctane has a rotation of 35.8°; 2-bromooctane, 34.2°. [b] Calculated relative to the optical purity of the starting alcohol. [c] Vpc analysis on column A showed no 2-chlorooctane, where the detection limit was 0.5 ± 0.5% (see Experimental Section).

the Varian Model 20 recorder. The columns used were A, 0.25 in. by 5 ft 20% SE-30 in 60–80 Chromosorb W; and, B, 0.25 in. by 10 ft 20% Apiezon-L on 45–60 mesh Chromosorb P. The column was operated between 80 and 145°, with 45–60 ml/min helium gas flow, and thermal conductivity detection. All products were identified by vpc comparison to authentic material and by comparing ir spectra on the Beckman IR 5-A.

The yields in Table I were determined, except as noted, on column B by the vpc method of internal standard.[8] In the runs without a standard solvent (**1**, **2**, **5**, **8**, **11**, and 14), the reactions were terminated when the vpc showed either complete consumption of alcohol, or no further change. Column A was used for 1 and 2; column B, the others.

The resolved 2-octanol[5] for the experiments of Table II was considered acceptable if greater than 50% optically pure. Yields were determined by noting the vpc disappearance of the alcohol (column A). Optical rotations were measured in ethanol solution at 22°. The measurements were made with ~0.4 *M* solutions, on a Rudolph polarimeter with a sodium D lamp.

Typical Procedure for the Reactions Reported in Table I (Run 7). A 100-ml flask was fitted with a calcium chloride drying tube and a magnetic stirrer. A 50-ml pipet of standard solvent[8] (primarily benzene) was transferred into it, followed by 0.05 g (0.37 mmol) of zinc chloride, 1.00 ml (11 mmol) of **6**, and finally 0.80 ml (11 mmol) of freshly distilled thionyl chloride. The time of reaction was measured from the time of $SOCl_2$ addition. The reaction was monitored by quenching small aliquots in saturated sodium bicarbonate and then comparing the vpc area (column B) of the 2-butyl chloride peak with the internal standard. All reactions were conducted in duplicate, and all aliquots were analyzed at least three times. Runs 1 and 2 were similar, except that after quenching with saturated $NaHCO_3$, the chloride was additionally purified by filtration through silica gel.

Preparation of 2-Butyl Chloride (Run 8). A three-neck flask was protected from moisture, stirred magnetically, and equipped with a condenser and dropping funnel. The decane solvent (180 ml), 40 ml (0.437 mole) of **6**, and 2.0 g (14.5 mmol) of $ZnCl_2$ were added. Into this mixture was dropped 38 ml (0.524 mol) of $SOCl_2$, at a slow enough rate to keep the temperature below 30°. The reaction was stirred an additional 2.5 hr, following $SOCl_2$ addition, and then quenched carefully with 400 ml of saturated $NaHCO_3$. The organic layer was washed with 50 ml of water and dried over $MgSO_4$. The product was distilled through a short column and weighed 29.6 g (73%). Runs 5, 11, and 14 were done in a similar manner. All were analyzed on column B.

General Procedure for Preparation of 2-Octyl Halide from Optically Active 4. The optically active **4** was reacted with either $SOCl_2$ or $SOBr_2$ in the same manner as for run 7. The yields were determined by analysis of an aliquot on column A. The reactions were quenched with saturated $NaHCO_3$ and the product layers were separated (or extracted with benzene when dioxane was the solvent) and dried over $MgSO_4$. After distillation (and/or purification through Woelm Silica Gel), the 2-octyl halide was >98% pure (column A).

Control Experiments. In order to confirm that the 2-octyl halide did not react further after initial formation, a control was run with each experiment. A sample of *l*-4-bromide was treated with 40 ml of dioxane, 200 mg of $ZnCl_2$, and 1.0 ml of thionyl bromide.

After 22.5 hr, the recovered product was unchanged in optical rotation. Similarly, with *l*-4-chloride, the rotation was constant over 5 hr.

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Registry No.—(+)-4, 5978-70-1; (−)-4, 6169-06-8; 5, 71-36-3; 6, 78-92-2; 7, 75-65-0; 8, 108-93-0; zinc chloride, 7646-85-7; thionyl chloride, 7719-09-7; thionyl bromide, 507-16-4.

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Oxymercuration of Nitrogen Heterocycles. II.[1] Syntheses of Novel Nitrogen Heterocycles and Cycloheptatriene Carboxaldehydes from *N*-Benzyldihydroazabullvalene and Dihydro-9-azabicyclo[4.2.2]deca-2,4,7-triene

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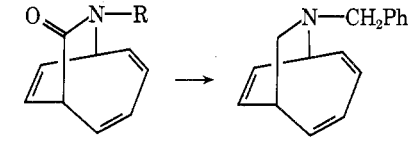
Solvomercuration–demercuration provides a convenient synthetic route for conversion of olefins into Markovnikov alcohols and ethers. An advantage of this synthetic approach is that additions generally occur without rearrangements.[2] However, there are a few alicyclic substrates which, because of their ground state strain or because they are precursors of stabilized carbonium ions, can rearrange either directly upon the addition of mercuric ions or following loss of free mercury from unstable hydroxymercurial ions. Most notably, rearranged oxymercurials are formed from bullvalene,[3,4] bicyclo[4.2.2]decatetraene,[4,5] and several 1-alkylidene-2-alkoxycyclopropanes,[6] while cyclobutene and 1-methylcyclobutene,[7] hexamethyl(Dewar benzene),[8] and cyclooctatetraene[9] undergo rearrangement with concomitant oxidative demercuration. Although mercuric acetate is capable of coordination with olefins in the presence of amines,[10,11] there have been no reports of rearrangements during the oxymercuration of heterocyclic structures. We here report two heterocyclic molecules **3** and **4** which can exhibit both of the above types of anomalous behavior during oxymercuation. In anhydrous media rearranged products of oxymercuration afford azabicyclic structures **5** and **6a** upon reduction, while in aqueous media, oxidative demercuration of hydroxymercurial product ions results in the synthesis of novel cycloheptatriene carboxaldehydes **7** and **8**.

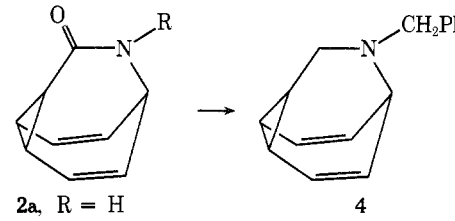
Discussion

The lactam **1a**[12] was benzylated with benzyl chloride–sodium hydride in dimethylformamide and the resulting *N*-benzyl lactam **1b** was treated with trimethyloxonium fluoroborate–sodium borohydride[13] to give amine **3**. Similar benzylation of lactam **2a** followed by aluminum hydride[14] reduction of **2b** afforded amine **4**. Detailed nmr analysis[15] of homotropilidene structure **4** has indicated the tautomeric structure is preferred in which nitrogen is not adjacent to cyclopropane.



1a, R = H
b, R = CH_2Ph

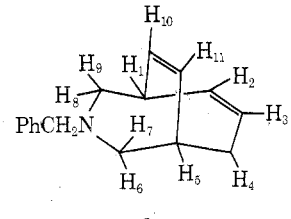
3



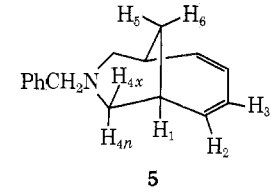
2a, R = H
b, R = CH_2Ph

4

Table I
Pmr Spectra of Azabicyclics 5 and 6a



6a



5

Proton	δ	Appearance, *J*, Hz	Proton	δ	Appearance, *J*, Hz
H_1	2.74	m, $J_{1,10}$ = 8.5	H_1	2.54	m, $J_{1,4x}$ = 3.5
H_2, H_3	5.72	m	H_{4x}	2.16	dd, $J_{4x,4n}$ = 11
H_4, H_5	2.26	br	H_{4n}	2.84	dd, $J_{1,4n}$ = 1.0
H_6, H_8	2.18, 2.30	d, $J_{8,9} = J_{6,7}$ = 11	H_5, H_6	1.80	br
H_7, H_9	2.60, 2.84	dd, $J_{5,7} = J_{1,9}$ = 4	H_2, H_3	5.86	br
H_{10}, H_{11}	5.90, 6.20	t, $J_{5,11}$ = 8.5			
CH_2Ph	3.60, 7.30	s, br	CH_2Ph	3.46, 7.20	s, s