HALOGEN MIGRATION IN THE REACTION OF DICHLOROALKANES WITH ALUMINUM CHLORIDE

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Abstract—The same equilibrium mixture of dichloropropanes is obtained when either 1,1-, 1,2-, or 1,3-dichloropropane is treated with aluminum chloride. 1,2- and 1,3-Dichlorobutane undergo very rapid interconversion under comparable conditions. *No trace* of any other isomer is detectable. The 2,3-dichlorobutanes undergo diastereomeric equilibration accompanied by about 3% 2,2-dichlorobutane. 1,4-Dichlorobutane can be partially isomerized to a mixture of 1,2- and 1,3-dichlorobutane. Analogous results are obtained with the dichloropentanes. Thus, both 2,3- and 2,4-dichloropentane diastereomers undergo rapid equilibration. 1,2-Dichloropentane forms predominantly 1,3- and 1,4-dichloropentane.

INTRODUCTION

SEVERAL reports[1] describe the rearrangement of dihaloalkanes during Friedel–Crafts alkylations and related reactions. However, only a few instances report the rearrangement of halocarbons with Lewis acids. Nenitzescu and Dinulescu[2] isolated crystalline *trans*-1,4-dibromocyclohexane from the reaction products of *trans*-1,2-dibromocyclohexane with aluminum bromide. Recently, Nozaki, *et al.*,[3] isomerized *trans*-1,2-dichlorocyclohexane with aluminum chloride in carbon disulfide to give the equilibrium mixture of dichlorocyclohexanes. Sommer[4] has reported that all the dibromobutanes are produced when any isomer is treated with aluminum bromide in carbon disulfide.

This paper describes the equilibration of the isomeric dichloropropanes, dichlorobutanes and dichloropentanes[5] with aluminum chloride. In most instances carbon disulfide was used as solvent.

RESULTS AND DISCUSSION

Dichloropropanes. Treatment of either 1,2-dichloropropane, 1,3-dichloropropane or 1,1-dichloropropane with 10 mole% aluminum chloride gives an equilibrium mixture of the four possible isomers (Table 1). The total time required for equilibration is about 4 hr. However, it is noteworthy that when the starting dichloride is 1,1-dichloropropane then >90% conversion to 1,2-dichloropropane is observed within 2 min. 2,2-Dichloropropane gives only partial isomerization before catalyst deactivation. This reluctance to isomerize is presumably due to the stability of the t-chlorodimethylcarbonium ion. Indeed, the great stability of such a species is clearly demonstrated by the fact that they are directly observable by NMR spectroscopy in

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highly acidic media.[6] Taft, *et al.*[7] have reached the same conclusion concerning the ability of chlorine to stabilize a cationic center.

TABLE 1. EQUILIBRATION OF DICHLOROPROPANES AT 25°

| | % Composition of dichloropropanes | | | |
	1,3-	1,2-	1,1-	2,2-
1,3-Dichloropropane	8·5	90·0	1·2	0·3
1,2-Dichloropropane	7·3	91·0	1·1	0·3
1,1-Dichloropropane	10·3	87·6	1·7	0·4

The most striking feature of this isomerization is the migration of the chlorine to a primary carbon in the apparent conversion of 1,2-dichloropropane to 1,3-dichloropropane, although such a rearrangement is not without precedent. Frigerio and Shaw,[8] have very recently reported the aluminum chloride-catalyzed interconversion of n-propyl and isopropyl chloride. Furthermore, these workers showed that no halogen exchange occurred between the catalyst and alkyl halide. These results must indicate considerable specificity in these rearrangements.

Deno and Lincoln[9] have shown that the catalytic bromination of cyclopropane leads to 1,1- and 1,2-dibromopropane in addition to the expected 1,3-dibromopropane. These results were explained on the basis of intermediate equilibrating protonated cyclopropanes. Since this system parallels that of Deno's then it seems likely that protonated cyclopropane intermediates may be important here also. Karabatsos *et al.* [10] have proved the existence of such intermediates in the aluminum bromide catalyzed conversion of n-propyl bromide to isopropyl bromide.

Dichlorobutanes. When either 1,2-dichlorobutane or 1,3-dichlorobutane is treated with a catalytic amount (10 mole %) of aluminum chloride an equilibrium mixture of the two compounds is rapidly obtained which consists of about 92% 1,3-dichlorobutane and 8% 1,2-dichlorobutane. Although these reactions are heterogeneous, analysis of both phases after separation gave essentially the same mixture of dichlorides. Curiously, *no trace* of any other isomer is detectable by GLPC. 1,4-Dichlorobutane can be partially isomerized to a mixture of the 1,2-and 1,3-isomers; however, catalyst deactivation is observed prior to complete equilibration. This premature catalyst deactivation may result from the formation of stable allylic cations.
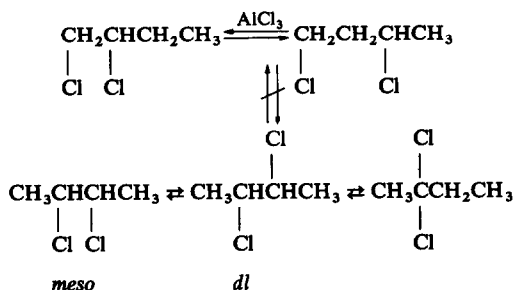
Under comparable conditions both 2,3-dichlorobutane diastereomers undergo partial diastereomeric equilibration accompanied by 2,2-dichlorobutane formation. Again no trace of any other isomer is detectable. When the aluminum chloride concentration is increased to 25 mole % and carbon disulfide used as solvent the same equilibrium ($\sim$1:1) can be obtained from each isomer.
Table 2 shows the equilibrium values for the various isomers.

TABLE 2. EQUILIBRATION OF DICHLOROBUTANES AT 25°[a]

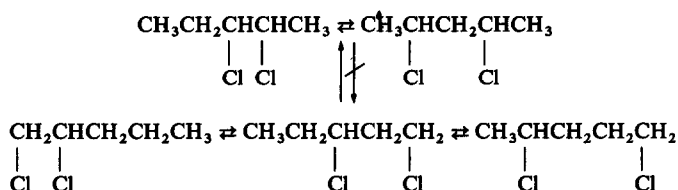| | % Composition of dichlorobutanes | | | | | |
	1,2-	1,3-	2,2-	meso 2,3-	dl 2,3-	1,4-
1,2-Dichlorobutane	8·3	91·7	—	—	—	—
1,3-Dichlorobutane	7·9	92·1	—	—	—	—
meso-2,3-Dichlorobutane	—	—	3·1	46·9	50·0	—
dl-2,3-Dichlorobutane	—	—	2·9	47·1	50·0	—

[a] CS$_2$ solvent.

The "partial equilibria" established in these equilibrations are puzzling in view of Sommer's[4] results which show that all the dibromobutanes are produced under comparable reaction conditions with aluminum bromide.

Two mechanisms are envisioned for these chlorine migrations in longer chain dichlorides. One which was invoked previously for the dichloropropanes involves protonation of the dichloroalkane, closure to a protonated cyclopropane, isomerization by migration of H$^+$ or Cl$^+$ bridges, and reopening. This was discarded because such a mechanism should have caused formation of appreciable amounts of products with a branched carbon chain. The preferred mechanism involves intermediate chloronium ions of the type long accepted as intermediates in the addition of halogens to alkenes. The existence of such ions has very recently been conclusively shown by direct NMR observation.[6, 11]

It should be pointed out that 1,3-dichlorobutane has been prepared in large quantities in >70% yield from the readily available 1,2-dichlorobutane. For large runs the yields are higher if the temperature is kept below 10°. Hence, this synthesis represents a convenient method for the preparation of 1,3-dichlorobutane and its derivatives, i.e., the diamine, dimercaptan, diol, etc.

Dichloropentanes. Closely related observations are made when the dichloropentanes are equilibrated. When either 2,4-dichloropentane or 2,3-dichloropentane is equilibrated a mixture of the four diastereomers is obtained. Table 3 shows the equilibrium distribution of the various isomers and diastereomers. Equilibrium is rapidly obtained at 25° (within 0·5 hr) although the mixture is nearly at equilibrium much sooner. 1,2-Dichloropentane gives predominantly a mixture of 1,3- and 1,4-dichloropentane; however, about 5% of the mixture is composed of the four possible 2,3- and 2,4-dichloropentane diastereomers. No geminal isomers are detectable in any instance. The formation of the 2,3- and 2,4-dichloropentanes is puzzling in view of the results obtained with 1,2- and 1,3-dichlorobutane. These systems may well involve

long-range chlorine participation since the existence of 5-membered chloronium ions has been conclusively shown.[12]

$$CH_3CH_2CHCHCH_3 \rightleftarrows CH_3CHCH_2CHCH_3$$
$$\overset{|}{Cl}\ \overset{|}{Cl} \qquad \overset{|}{Cl} \qquad \overset{|}{Cl}$$

$$CH_2CHCH_2CH_2CH_3 \rightleftarrows CH_3CH_2CHCH_2CH_2 \rightleftarrows CH_3CHCH_2CH_2CH_2$$
$$\overset{|}{Cl}\ \overset{|}{Cl} \qquad\qquad \overset{|}{Cl}\ \overset{|}{Cl} \qquad\qquad \overset{|}{Cl} \qquad\qquad \overset{|}{Cl}$$

Stability of diastereomers. Finally, it is of interest to compare the stabilities of diastereomers, since relatively little experimental work is available on this subject.[13] In general, the free energies of acyclic diastereomers do not differ by much. The *meso* form is usually thought to be more stable than *dl* pairs and *erythro* isomers are likely to be more stable than *threo* isomers for compounds whose asymmetric centers are adjacent. These assumptions are made on the basis that no bonded interactions are present and that the largest source of energy difference is steric (non-bonded interactions). Based on these principles one might predict that *meso*-2,3-dichlorobutane is more stable than *dl*-2,3-dichlorobutane. However, the data, although somewhat tenuous, due to competing condensation reactions suggest that the diastereomers are of about equal stability.

It is also of interest to compare the stabilities of the dichloropentane diastereomers. Although the small amount of 2,3-dichloropentane (~10%) in equilibrium with the 2,4-dichloropentane diastereomers does not allow an accurate calculation of ΔG, the data roughly suggest the diastereomers do not differ in free energy by more than a few calories.

TABLE 3. EQUILIBRATION OF DICHLOROPENTANES AT 25°[a]

| | | | % Composition of dichloropentanes | | | | |
| | *dl-* | *meso-* | *erythro-* | *threo-* | | | |
	2,4-	2,4-	2,3-	2,3-	1,2-	1,3-	1,4-
2,4-Dichloropentane[b]	64·3	26·1	5·0	4·6	—	—	—
2,3-Dichloropentane[c]	64·2	25·9	4·4	5·5	—	—	—
1,2-Dichloropentane	5·2		0·3		6·5	23·9	64·1

[a] CS$_2$ solvent.   [b] 49% *dl*, 51% *meso*.   [c] 52% *erythro*, 48% *threo*.

A priori, one would expect *dl*-2,4-dichloropentane to be considerably more stable than *meso*-2,4-dichloropentane. This energy difference has been shown by both NMR interpreted in terms of coupling constants and detailed calculations assuming interactions characterized by Lennard-Jones type potentials between nonbonded atoms and groups.[14] Our *dl/meso* ratio (2·46) completely corroborate these calculations.

EXPERIMENTAL

Materials. 1,2-Dichloropropane (Union Carbide) and 1,3-dichloropropane (Eastman Organic Chemicals) were redistilled and shown to be homogeneous by GLPC. 2,2-Dichloropropane (Columbia

Organics) was obtained in 98% purity after distillation. 1,1-Dichloropropane was prepared from propionaldehyde and PCl₅ in 99% purity. 1,2-Dichlorobutane and 1,3-dichlorobutane were obtained from Aldrich Chemical Company and used without further purification. 1,4-Dichlorobutane was obtained from Eastman Organic Chemicals and shown to be pure by GLPC. *meso* and *dl*-2,3-Dichlorobutanes were prepared from *trans* and *cis*-2-butene, respectively.[15] 2,3-Dichloropentane (mixture of diastereomers) was prepared by the ionic chlorination of mixed 2-pentene isomers using the general procedure described by Poutsma[15] for the butenes. The 2,4-dichloropentane diastereomers were prepared in 99·5% purity by the method of Pritchard and Vollmer.[16] Anhydrous purified aluminum chloride (Matheson Coleman and Bell) was used throughout.

*Analysis procedure.*A variety of columns were used for GLPC analyses. The dichlorobutanes were analyzed using a 6 ft × 0·25 in column packed with Se–30 silicone rubber on 80–100S. The dichloropropanes were separated using a 6 ft × 0·25 in column packed with FFAP (Varian) packing on 80–100 mesh Chromosorb W. Capillary GC was necessary for complete resolution of all the dichloropentane diastereomers. A 150 ft × 0·01 in. i.d. column coated with DC–550 silicone oil and operated at 25–150° at 2·5°/min and 50 psi (Helium) was used.

Isomerization Equilibrations were run by adding 0·10 mole of the dichloride to 0·01 mole of anhyds AlCl₃. In most instances the dichloride was dissolved in 25 ml of dry CS₂. The mixture was stirred for the appropriate time (usually 0·5 hr) under a N₂ purge and then quenched in ice water. The organic layer was dried over Na₂SO₄ and analyzed directly by gas chromatography.

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