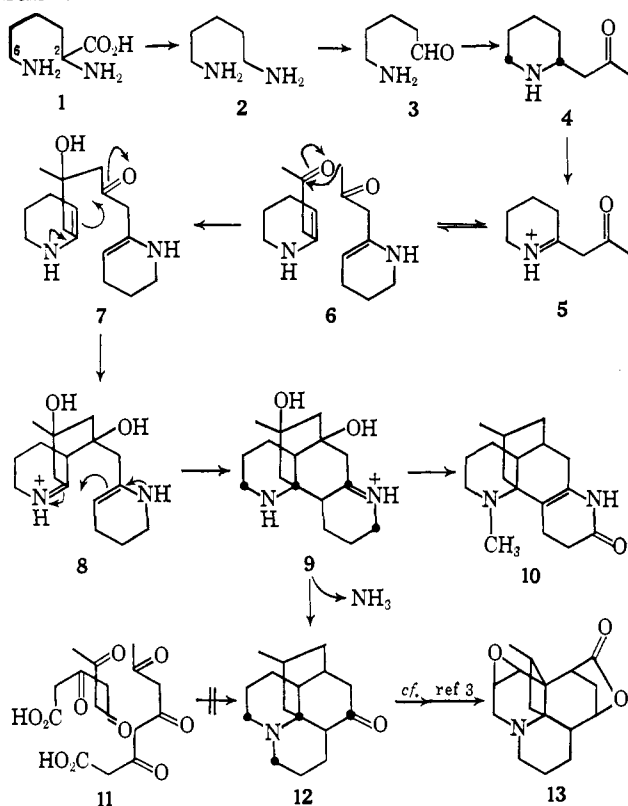


Scheme I



labeled lysine. The observed loss of 22% is in accord with this prediction.

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### Diastereomeric Equilibration of the Dichloropentanes. A Model System for Polyvinyl Chloride

Sir:

Stereochemical equilibrium in chain molecules possessing two or more asymmetric centers is of considerable interest. Flory<sup>1</sup> has recently developed an excellent statistical mechanical theory capable of predicting the stereochemical equilibrium of such molecules. Since the same factors that determine the frequency of incidence of the conformations of a chain molecule also determine the diastereomeric equilibrium distribution of its lower homologs, it becomes of immediate interest to find suitable methods for equilibrating such species.<sup>2</sup>

The importance of the 2,4-dichloropentane system as a model for the structure of polyvinyl chloride has been recognized by other workers,<sup>3</sup> who have given conclusive evidence for the most stable conformers of each of the *meso* or *dl* varieties. What is lacking is the experimental verification of the relative stabilities of the *meso* and *dl* diastereomers, such as has been reported for the 2,4-diphenylpentanes.<sup>2</sup> In connection with our research

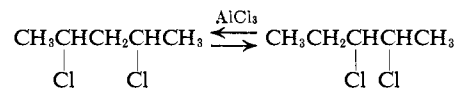
(1) P. J. Flory, *J. Am. Chem. Soc.*, **89**, 1798 (1967).

(2) While this manuscript was in preparation the epimerization of 2,4-diphenylpentane was reported: A. D. Williams, J. I. Brauman, N. J. Nelson, and P. J. Flory, *ibid.*, **89**, 4807 (1967).

(3) T. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, **17**, 755 (1961).

program<sup>4</sup> on the isomerization of chloro- and dichloroparaffins with Friedel-Crafts catalysts we had the occasion to observe the facile equilibration of the dichloropentanes, thus providing a simple experimental tool for determining the relative stabilities of the 2,4-dichloropentane diastereomers.<sup>5</sup>

A suspension of aluminum chloride in carbon disulfide was used for equilibration.<sup>6</sup> *A priori*, one would also expect the 2,3-dichloropentane diastereomers to be produced in the equilibration, and this turns out to be the case. The same equilibrium mixture can be obtained starting with either the 2,3-dichloropentane or 2,4-dichloropentane diastereomers.<sup>7</sup> Table I shows the



equilibrium distribution of the various diastereomers.<sup>8</sup> Equilibrium was rapidly attained (usually within 0.5 hr).

Table I. Equilibration of the Dichloropentanes at 25°

	% composition of dichloropentanes			
	<i>dl</i> -2,4-	<i>meso</i> -2,4-	2,3- <i>erythro</i> -	2,3- <i>threo</i> -
2,4-Dichloropentane <sup>a</sup>	64.3	26.1	5.0	4.6
2,3-Dichloropentane <sup>b</sup>	64.2	25.9	4.4	5.5

<sup>a</sup> 49% *dl*, 51% *meso*. <sup>b</sup> 52% *erythro*, 48% *threo*.

Capillary gas chromatography was necessary for complete resolution of all the diastereomers.<sup>9</sup> Since calibration samples prepared by mixing the appropriate amounts of the 2,3-dichloropentanes and 2,4-dichloropentanes confirmed that the response of the flame ionization detector was proportional to the concentration of the isomers, it was assumed the various diastereomers had nearly identical response factors.

In rationalizing the relative stabilities of the diastereomers it becomes necessary first to determine the stable rotational conformers. This has been studied by both infrared<sup>3</sup> and high-resolution nuclear magnetic reso-

(4) Unpublished work.

(5) An examination of the literature reveals that relatively little experimental information is available on the relative stabilities of diastereomers. For example, see L. I. Peterson, *J. Am. Chem. Soc.*, **89**, 2677 (1966), and references therein. See also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 138-139.

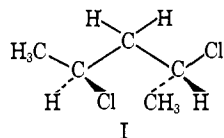
(6) H. Nozaki, M. Kawanisi, M. Okazaki, M. Yamae, Y. Nisikawa, T. Hisida, and K. Sisido, *J. Org. Chem.*, **30**, 1303 (1965), have equilibrated the dichlorocyclohexanes with aluminum chloride.

(7) 2,3-Dichloropentane (mixture of diastereomers) was prepared by the ionic chlorination of mixed 2-pentene isomers using the general procedure described by Poutsma for the chlorination of the butenes. See M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965). *threo*-2,3-Dichloropentane was prepared by the chlorination of pure *cis*-2-pentene. The 2,4-dichloropentane diastereomers were prepared by the method of J. G. Pritchard and R. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

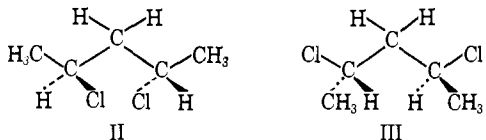
(8) Equilibrations were run by adding 0.10 mole of the dichloride to 25 ml of CS<sub>2</sub> containing 0.01 mole of anhydrous aluminum chloride. The mixture was stirred for the appropriate time under a nitrogen purge and quenched in ice water. The organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The carbon disulfide solution was analyzed directly by gas chromatography. In general, polymerization to the extent of some 20-30% accompanies this isomerization-equilibration; however, we feel certain that polymerization does not affect the relative proportions of isomers since we approach the same equilibrium composition "from both sides;" *i.e.*, the rate of equilibration is greater than the rate of polymerization.

(9) Perkin-Elmer Model 226 with flame ionization detector. 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.

nance spectroscopy<sup>10</sup> in the case of the 2,4-dichloropentanes. Both methods show that the only eligible conformer for the *meso* isomer is structure I, *i.e.*, the *trans,gauche* structure and its analog, the *gauche,trans* form. The possible conformers for the *dl* form are



structures II and III. However, the conformer repre-



sented by III appears to be absent since it could not be detected by infrared even at elevated temperatures.<sup>3</sup> This large energy difference was also confirmed 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.<sup>10</sup> The conformer represented by II is favored over III by the factor  $\eta^2 = 22.4$  using the equation<sup>2</sup> developed from statistical mechanical considerations. This high value of  $\eta$  certainly emphasizes the insignificance of III as a contributing conformer for the racemic diastereomer. As pointed out by Flory,<sup>2</sup> in the case of the diphenylpentanes the equilibration of the 2,4,6-trisubstituted heptane would be required for interpretation of the stereochemical equilibrium and distribution among conformers for higher homologs.

Finally, it is of interest to compare the stabilities of *erythro*- and *threo*-2,3-dichloropentanes. Usually, barring intramolecular interactions, the *erythro* diastereomer is expected to be slightly more stable.<sup>5</sup> Although the small amount of the 2,3 isomers ( $\sim 10\%$ ) in equilibrium with the 2,4-dichloropentane diastereomers does not allow an accurate calculation of  $\Delta G$ , the data roughly suggest that the diastereomers are of approximately equal stability.

**Acknowledgment.** The authors acknowledge the helpful discussion of this paper with Professor J. F. Bunnett. Thanks are also due to Mr. W. F. Tully for assistance with the gas chromatographic analyses.

(10) P. E. McMahon and W. C. Tincher, *J. Mol. Spectry.*, **15**, 180 (1965); P. E. McMahon, *ibid.*, **16**, 221 (1965).

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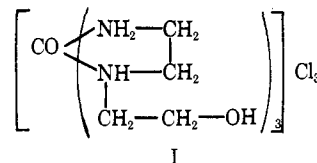
### Complexes of N-Hydroxyethylethylenediamine

Sir:

Several workers have investigated the cobalt(III) complexes with N-hydroxyethylethylenediamine,<sup>1</sup> but agreement on the nature of these substances has not

(1) 2-(2-Aminoethylamino)ethanol,  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$ , will be referred to as etolenH, where H is the hydroxy proton. Thus, etolen refers to  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{O}^-$ .

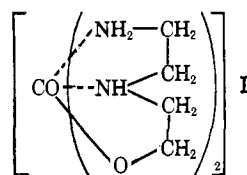
been reached. Keller and Edwards<sup>2</sup> reported the synthesis of  $[\text{Co}(\text{etolenH})_3]\text{Cl}_3$ , by the aerial oxidation of a mixture of cobalt(II) chloride (1 mole), etolenH (5 moles), and hydrochloric acid (0.5 mole) in aqueous solution, using active charcoal as a catalyst. The product was obtained as orange crystals, insoluble in ethanol. Keller and Edwards formulated this compound as



The uncoordinated hydroxy groups were reported to be unreactive toward several reagents which normally react with free hydroxyl groups. The Co(III) complex was reported to be stable in boiling concentrated acids, including aqua regia. Keller and Edwards also found that a solution of the compound turned purple on addition of caustic alkali.

Drinkard, Bauer, and Bailar<sup>3</sup> repeated this work during their investigation of the reactivity of organic hydroxy groups  $\beta$  to the coordination site in Co(III) complexes. The only product they could isolate from direct oxidation of a solution containing Co(II) and etolenH was proved to be tris(ethylenediamine)cobalt(III) chloride. Since their sample of purified etolenH was shown to contain no ethylenediamine, the latter must have resulted from a cleavage of a C-N bond of etolenH during the oxidation of Co(II). They showed that the reaction of 1 mole of hexaamminecobalt(III) chloride with 3 moles of etolenH in the presence of active charcoal gave a product which was extremely soluble in water and in ethanol. Analysis of their product, obtained as a red glass on dehydration over  $\text{P}_4\text{O}_{10}$ , agreed with the formula  $[\text{Co}(\text{etolenH})_3]\text{Cl}_3$  and was found to be inactive toward acetylation and benzoylation, like the product of Keller and Edwards. The red color is unusual for a complex containing six nitrogen atoms coordinated to Co(III), as in structure I, and was explained by an extensive effect of  $\text{OH}_2$  strongly hydrogen bonded to a hydrogen atom in an  $\text{NH}_2$  group. The hydrogen bonding supposedly also reduced the activity of the OH group.

Tennenhouse<sup>4</sup> reinvestigated the reaction of  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$  with etolenH. He found that the reaction of 2 moles of etolenH and 1 mole of complex in the presence of charcoal gave a purple solution which, upon the addition of sodium iodide in 50% ethanol solution, yielded a crystalline purple product. This gave an analysis corresponding to the formula  $[\text{Co}(\text{etolen})_2] \text{I}$  and was formulated as



(2) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952).

(3) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960).

(4) G. J. Tennenhouse, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.