

74.92; H, 10.94; OCH₃, 9.20. The Zerewitinoff test showed 5.38% OH; calcd. for C₂₁H₃₀O₈, 5.06.

Saponification with 0.1 *N* sodium hydroxide in alcoholic solution for four hours at reflux temperature: Calcd.: 4.34 cc. of 0.1 *N* sodium hydroxide; found, 0.23 cc.

One gram of the methyl ester distilled at 175–180° at 2 mm. Found: C, 75.06; H, 10.92; OCH₃, 9.16.

Fusion of Lactonized Dihydroabiatic Acid with Potassium Hydroxide.—Four grams of 88% potassium hydroxide was melted and heated to 200° in a nickel crucible. To this one gram of lactonized dihydroabiatic acid was added. The mixture was stirred and the heating was continued for fifteen minutes. As the reaction proceeded the insoluble potassium salt separated as a white powder that floated on the surface of the caustic. The fusion mass was cooled and dissolved in 200 cc. of water and shaken with ether to remove any unchanged lactone. The alkaline solution was made acid to litmus with 10% acetic acid. The tetrahydrohydroxyabiatic acid that separated as pearly plates was filtered and washed with water. When dried in vacuum the acid melted at 164–165° with effervescence and showed no depression with tetrahydro-

hydroxyabiatic acid prepared by the *n*-butyl alcoholic hydrolysis. When the melted acid was allowed to cool and crystallize, it remelted at 130–131°.

Summary

Dihydro-*l*-pimaric acid and dihydro-*l*-abiatic acid, [α]_D +108°, have been lactonized to form lactones identical with lactonized dihydroabiatic acid.

Formulations for these dihydro compounds have been advanced to show how they may all yield the same lactone.

Oxidation and acylation experiments have been shown to indicate the C-13 position as a more probable point of lactonization than C-10.

A rapid method for hydrolysis of lactonized dihydroabiatic acid by caustic fusion has been developed.

WASHINGTON, D. C.

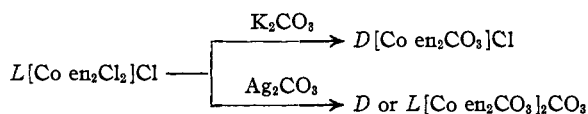
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. V. The Reaction of Carbonates with Dichloro-dipropylenediamine Cobaltic Chloride. A New Method of Determining Relative Configurations

BY JOHN C. BAILAR, JR., AND J. P. McREYNOLDS¹

The reaction of dichloro-diethylenediamine cobaltic chloride with potassium and silver carbonates yielded the first example of the Walden inversion in the field of optically active inorganic complex compounds.² Bailar, Jonelis and Huffman³ found that either enantiomorph of the re-



sulting carbonato compound could be produced by the action of silver carbonate, depending upon the conditions under which the reaction took place.

Mathieu⁴ checked the Walden inversion reaction of Bailar and Auten² and from circular dichroism measurements came to the conclusion that the carbonato diethylenediamine cobaltic salt resulting from the use of potassium carbonate was the non-inverted form.

It was thought that the use of rotatory dis-

persion curves for closely related compounds might lead to valuable information in respect to this reaction. Lowry, Pickard and Kenyon⁵ found that the rotatory dispersion curves for a series of secondary alcohols showed similarities as to dispersion ratios. The rotatory dispersion curves for a large number of diethylenediamine cobaltic complexes are given by Mathieu.⁶ A comparison of these curves with those of analogous members of the di-*levo*-propylenediamine (*l*-pn) cobaltic series was undertaken as a method of attacking the Walden inversion problem.

Evidence has been presented to show that cobaltic complexes containing optically active diamines do not exist in all of the possible stereochemical forms, but only in certain preferred configurations. Hürlimann,⁷ working with dinitrodipropylenediamine cobaltic compounds, could isolate only half of the calculated number of *cis* forms. Jaeger,⁸ using active cyclopentylendiamine, observed the same result. He assigned

(1) Taken from a portion of the doctorate thesis of J. P. McReynolds, 1938. Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) Bailar and Auten, *THIS JOURNAL*, **56**, 774 (1934).

(3) Bailar, Jonelis and Huffman, *THIS JOURNAL*, **58**, 2224 (1936).

(4) Mathieu, *Bull. soc. chim.*, [5] **3**, 497 (1936).

(5) Lowry, Pickard and Kenyon, *J. Chem. Soc.*, **105**, 94–102 (1914).

(6) Mathieu, *Bull. soc. chim.*, [5] **3**, 463–475 (1936).

(7) Hürlimann, Dissertation, Zurich, 1918.

(8) Jaeger, *Rec. trav. chim.*, **38**, 170 (1919).

the structures $[\text{Co}_D(l\text{-cptd})_2\text{X}_2]^+$ and $[\text{Co}_L(d\text{-cptd})_2\text{X}_2]^+$ to the two isomers stable enough to be isolated. It was supposed from this that $[\text{Co}(l\text{-pn})_2\text{Cl}_2]^+$ and $[\text{Co}(l\text{-pn})_2\text{CO}_3]^+$ would each exist in only one form, so that the conversion of the former into the latter could not produce a Walden inversion. It has been found, however, that the carbonato salt can exist in both possible configurations. One of these is much more stable than the other, however, so the principle involved evidently can be used to determine configurations.

Upon comparison of the rotatory dispersion curves of *cis*-dichloro-diethylenediamine cobaltic chloride⁵ and *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride it was found that the general shape of the curves, the maxima, the minima and the points of zero rotation were essentially the same (Fig. 1). The absorption curves for the two

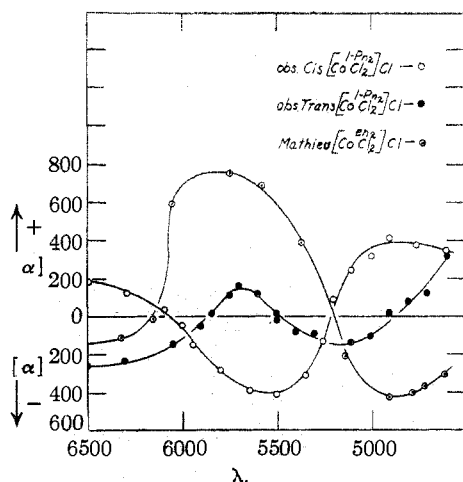


Fig. 1.

compounds (not shown here) were also found to be almost identical. Comparison of the rotatory dispersion curve for carbonato diethylenediamine cobaltic chloride⁶ with those for the two diastereoisomeric forms of carbonato di-*l*-propylenediamine cobaltic carbonate shows one of these forms to give a curve very similar to that of the diethylenediamine compound while the other form shows a curve of markedly different characteristics (Fig. 2). The form of the carbonato di-*l*-propylenediamine complex which showed the marked dissimilarity as to dispersion characteristics was easily converted to the other diastereoisomeric form by heating in solution. Using Jaeger's convention⁸ for the stable form, the starting material is assigned the structure $[\text{Co}_D(l\text{-pn})_2$

$\text{Cl}_2]^+$, the more stable product $[\text{Co}_D(l\text{-pn})_2\text{CO}_3]^+$ and the less stable form $[\text{Co}_L(l\text{-pn})_2\text{CO}_3]^+$.

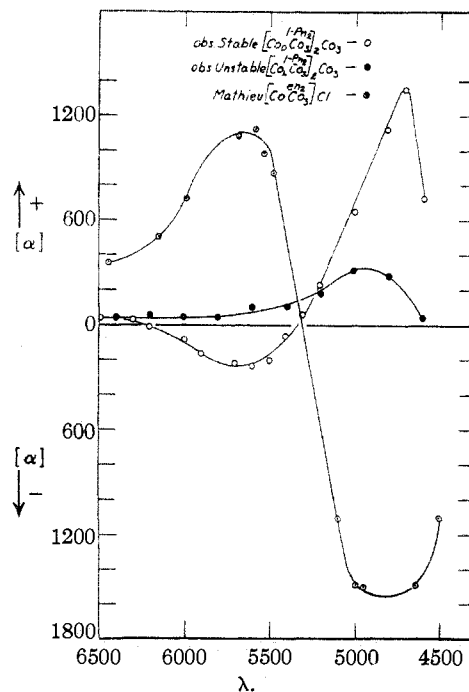


Fig. 2.

In the di-*l*-propylenediamine series the inversion can be brought about by either silver carbonate alone or potassium carbonate alone by varying the conditions under which the reaction is carried out. Under the conditions similar to those by which Bailar, Jonelis and Huffman⁸ produced the inversion with silver carbonate alone, analogous results are obtained. With potassium carbonate alone they were unable to produce an inversion in the diethylenediamine series. In the di-*l*-propylenediamine series such an inversion is produced easily. The stable diastereoisomeric form is produced by either reagent when conditions are favorable for a slow reaction. The assignment of inverted and non-inverted forms in the diethylenediamine series as made by analogy with the di-*l*-propylenediamine series agrees with that of Mathieu.⁴

In the course of the preparation of the diastereoisomeric carbonato di-*l*-propylenediamine complexes an explanation of the apparent effect of large excesses of insoluble silver carbonate was found. In every case in which the unstable diastereoisomer was produced, it was observed that the change from the purple dichloro starting material to the red carbonato compound was ex-

tremely rapid, while in the cases in which the stable diastereoisomer resulted the change was rather slow. The *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride undergoes aquation when allowed to stand in solution. This reaction proceeds at a fairly rapid rate, so that it seemed probable that the stable or non-inverted form resulted from a series of reactions. That this postulate was true was shown by allowing a solution of the dichloro-di-*l*-propylenediamine compound to stand until aquation was complete and then treating with silver carbonate. This procedure led to the production of the stable carbonato compound. The inverted form evidently is produced when conditions are such that the substitution of the carbonato group for the chloride ions in the complex proceeds directly, while the non-inverted form is produced by the stepwise displacement of chloride ions by water molecules and the subsequent displacement of the water molecules by the carbonato group.

Since this mechanism rests entirely upon the relative speeds of the aquation and the substitution reactions, the possibility of producing an inversion in the diethylenediamine series by the use of potassium carbonate alone was investigated further. It was found that the aquation rate in this series is more rapid than in the di-*l*-propylenediamine series and was markedly catalyzed by the addition of an alkaline reagent. To avoid the effect of an alkaline solution solid dichloro-diethylenediamine cobaltic chloride was ground with a large excess of dry potassium carbonate. After intimate grinding, water was added. The change to the carbonato compound was almost instantaneous and the product showed a rotation of opposite sign to that obtained by reaction with potassium carbonate in solution. This seems to substantiate the mechanism set up for the Walden inversion reactions discussed.

Experimental

Preparation of Compounds.—*l*-Propylenediamine was prepared by resolving commercial propylenediamine with tartaric acid by the method of Baumann⁹ as modified by Bailar, Stiegman, Balthis and Huffman.¹⁰ The dichloro-di-*l*-propylenediamine cobaltic chloride was prepared according to the directions of Bailar, Stiegman, Balthis and Huffman.¹⁰

The stable diastereoisomeric form of carbonato di-*l*-propylenediamine cobaltic carbonate was prepared by

adding a 20% excess of silver carbonate to a solution of *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride and allowing the reaction to progress slowly until no purple color remained and no more silver chloride was formed. The solution was then filtered and evaporated until a red waxy mass remained. This mass was dried by extraction with a mixture of equal parts of absolute alcohol and absolute ether. The resultant product was crystalline but was too soluble in water to be purified by recrystallization. The same product was also obtained by allowing a solution of dichloro-di-*l*-propylenediamine cobaltic chloride to stand for twenty-four hours (to allow aquation to proceed to completion) and then adding an excess of silver carbonate. After silver chloride ceased to be precipitated, the product was isolated as before. The stable diastereoisomer could be obtained with potassium carbonate only when the amount of potassium carbonate added was much below the theoretical amount needed to produce the carbonato carbonate. Best results were obtained when an amount just in excess of the theoretical amount to produce carbonato chloride was added to the solution. This product was not isolated from solution due to the fact that its great solubility prevented a successful separation from the potassium salts. The solutions resulting from all three methods gave specific rotations of -170° when read in a 0.1% solution at the sodium D line.

The unstable diastereoisomeric form of the carbonato complex was prepared by adding the dry dichloro complex to a paste of silver carbonate with grinding. Best results were obtained by using an excess of at least five times the amount of silver carbonate necessary to produce the carbonato-carbonate and adding the dichloro compound in very small quantities over a period of an hour or more, with constant grinding. To isolate the compound it was necessary to filter out the silver chloride and evaporate the solution to a waxy mass at room temperature, since heating converts the product rapidly to the more stable form. The unstable form was prepared but not isolated by the action of an excess of potassium carbonate upon a solution of the dichloro complex.

Analyses for total carbon dioxide content were made upon the stable diastereoisomer obtained by the action of silver carbonate upon the fresh solution (no. 1), upon the stable diastereoisomer obtained by the action of silver carbonate upon the completely aquated solution (no. 2) and upon the stable diastereoisomer obtained by heating a solution of the unstable diastereoisomer (no. 3). These were carried out by displacing the carbonate radicals with hot sulfuric acid and absorbing the evolved carbon dioxide upon ascarite. Since the compounds could not be purified by recrystallization and the samples used were quite small, the checks obtained were not very satisfactory. For this reason the theoretical percentages for the other products which might reasonably be expected from such a reaction are included for comparison.

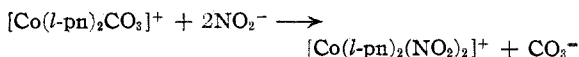
Anal. Found: CO₂, no. 1, 21.4; no. 2, 19.8; no. 3, 19.9. Calculated: [Co(*l*-pn)₂CO₂]₂CO₃, 22.2; [Co(*l*-pn)₂(OH)₂O]CO₃, 14.5; [Co(*l*-pn)₂(OH)₂]₂CO₃, 8.2; [Co(*l*-pn)₂(H₂O)₂]₂(CO)₃, 19.7.

It seems quite improbable that the diaquo salt could be formed under the conditions used, for it is **definitely acid**. To establish this point definitely, however, samples

(9) Baumann, *Ber.*, **26**, 1179 (1895).

(10) Bailar, Stiegman, Balthis and Huffman, *This Journal*, **61**, 2402 (1939).

of the stable isomer (prepared from the aquated dichloro salt and silver carbonate) and the unstable isomer, were analyzed for the ratio of ionic to non-ionic carbonate. Samples of about 0.5 g. were treated with calcium nitrite in excess. After standing for an hour the precipitated calcium carbonate was filtered out. The filtrate was heated on the steam-bath for several hours to effect the reaction



(which requires several weeks at room temperature), and the calcium carbonate was again filtered out. Making allowance for the slight amount of silver carbonate which goes into solution (determined by a blank) the ratios of ionic to non-ionic carbonate were found to be: stable isomer, 0.51; unstable isomer, 0.47; calculated, 0.50.

Rotatory Dispersion Curves.—The polarimeter readings for the rotatory dispersion curves were made with a Schmidt-Haensch polarimeter using an ordinary 1000-watt tungsten filament projection bulb as a light source. The wave lengths reported are not strictly monochromatic but represent an intensity average for a band of approximately 100 Å. obtained with a monochromator. All data represent an average of at least four readings and for the most part six or more readings were made. The polarimeter was scaled to read to 0.001° but the accuracy obtainable in this work was of the order of $\pm 0.01^\circ$ in the regions of high transparency and much less in the regions of high absorption.

TABLE I

cis-DICHLORO-DI-*l*-PROPYLENEDIAMINE COBALTIC CHLORIDE (FIG. 1)

The solution used contained 0.05 g. of complex in 100 cc. of water.

Wave length, Å.	Observed rotation, °	Specific rotation, °
6500	+0.09	+180
6300	+ .06	+120
6100	+ .02	+ 40
6000	- .02	- 40
5800	- .12	-240
5650	- .19	-380
5500	- .20	-400
5350	- .15	-300
5250	- .06	-120
5200	+ .05	+100
5100	+ .13	+260
5000	+ .16	+320
4900	+ .21	+420
4750	+ .19	+380
4600	+ .18	+360

Due to the rapid aquation of these compounds, it was found necessary to prepare a fresh solution for every four wave lengths, or at time intervals of about every thirty minutes. The readings above represent data taken upon at least two different solutions at each wave length.

In this series aquation did not affect the stability of the solution so that the same solution could be used for all the readings.

Extension of the Mechanism to Inversion of the Diethylenediamine Complex by Potassium Carbonate.—Forty

TABLE II

STABLE CARBONATO DI-*l*-PROPYLENEDIAMINE COBALTIC CARBONATE (FIG. 2)

Wave length, Å.	Observed rotation, °	Specific rotation, °
6500 ^a	+0.04	+ 40
6300 ^a	+ .02	+ 20
6200 ^a	- .02	- 20
6000 ^a	- .10	- 100
5900 ^a	- .18	- 180
5700 ^a	- .22	- 220
5600	- .12	- 240
5500	- .11	- 220
5400	- .04	- 80
5300	+ .03	+ 60
5200	+ .10	+ 200
5000	+ .32	+ 640
4800	+ .56	+1120
4700	+ .66	+1320
4600	+ .36	+ 720

^a These wave lengths were read upon a solution containing 0.1 g. of complex in 100 cc. of water, the remainder upon a solution containing 0.05 g. of complex in 100 cc. of water.

TABLE III

UNSTABLE CARBONATO DI-*l*-PROPYLENEDIAMINE COBALTIC CARBONATE (FIG. 2)

Wave length, Å.	Observed rotation, °	Specific rotation, °
6400 ^a	+0.04	+ 40
6200 ^a	+ .06	+ 60
6000 ^a	+ .04	+ 40
5800 ^a	+ .04	+ 40
5600 ^a	+ .10	+100
5400 ^a	+ .10	+100
5200	+ .09	+180
5000	+ .16	+320
4800	+ .14	+280
4600	+ .02	+ 40

^a These wave lengths were read upon a solution containing 0.1 g. of complex in 100 cc. of water. The other readings were made upon a solution containing 0.05 g. of complex in 100 cc. of water.

grams of potassium carbonate was ground with 0.2830 g. of dry *l-cis*-dichlorodiethylenediamine cobaltic chloride for one and one-half hours. Sufficient water was then added to give a solution containing 0.1% of the carbonate complex. An immediate reaction took place giving a product which showed a rotation of -0.03° . Normally the potassium carbonate reaction leads to a dextro product if allowed to proceed through the aquation intermediate. The levo rotation indicated that the inverted form was produced in excess. To check the effect of the presence of such large excesses of potassium carbonate upon the rotation of the carbonate complex, a 0.1% solution of carbonate diethylenediamine cobaltic carbonate was prepared having a rotation of -0.24° . To 20 cc. of this solution sufficient potassium carbonate was added to give the same concentration as was used above. The resultant solution had a volume of 22 cc. and a rotation of -0.21° . The effect of the large excess of potassium carbonate is evidently very slight.

Summary

1. Two diastereoisomeric forms of carbonato di-*l*-propylenediamine cobaltic carbonate have been prepared by a Walden inversion method. The inverted form is unstable in hot water, being converted to the more stable non-inverted form.

2. Rotatory dispersion curves have been made for *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride and for the two diastereoisomeric forms of carbonato di-*l*-propylenediamine cobaltic carbonate. By comparison of these curves with those for analogous compounds in the diethylenediamine series, it has been possible to determine which of the two carbonato forms is obtained by an inversion about the central cobalt atom in the latter case.

3. A mechanism for the production of the two

forms of the carbonato complex has been advanced. The non-inverted form is produced through the preliminary displacement of the chloride ions in the *cis*-dichloro-di-*l*-propylenediamine cobaltic chloride by water molecules, followed by the displacement of the water molecules by carbonato groups. The inverted form is produced by direct substitution of the carbonato group for the chloride ions within the complex. It was found possible by varying the reaction conditions on the basis of this mechanism to produce either form with either silver carbonate alone or potassium carbonate alone. Further it was found possible to produce the inverted form of carbonato diethylenediamine cobaltic carbonate with potassium carbonate for the first time.

URBANA, ILLINOIS

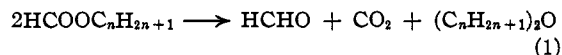
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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Kinetics of the Thermal Decomposition of Ethyl Formate

BY R. F. MAKENS¹ AND W. G. EVERSOLE

The vapor phase decomposition of ethyl formate in the absence of catalysts, other than the glass used as containers, has not been investigated extensively. Sabatier and Mailhe² found no appreciable decomposition when ethyl formate was passed through a glass tube at 400°. At 300° in a sealed flask the decomposition of this ester was reported by Engler and Grimm.³ Hurd⁴ states, "The esters with the general formula RCOOCH₂CH₂R should decompose into free acid and olefin." If this explanation is correct, ethyl formate should yield formic acid or its decomposition products and ethylene. The gases found by Engler and Grimm³ were in accord with this theory; however, the amounts of the various constituents which they found varied greatly from those required by the reaction. Sabatier and Mailhe,² Pearce and Wing⁵ and others have shown that this reaction does not predominate in the presence of any one of several different catalysts. Sabatier and Mailhe² found that the vapors of formic esters may decompose in two ways



This paper reports quantitative data on the thermal decomposition of ethyl formate. The data permit the calculation of the order of the principal primary reaction and its energy of activation. Evidence of the other associated reactions including those given above also is presented.

Experimental

Materials.—Ethyl formate (Eastman Kodak Co.) was dried and distilled in a packed column, and the resultant product was redistilled. It was found that the middle portion, which was the part used in the investigation, boiled at 54.20–54.26° (corr.). The density was d_{25}^4 0.9055 and the refractive index n_D^{25} 1.3582.

Apparatus and Procedure.—The apparatus, a modification of that used by Thompson and Frewing,⁶ was of the static type. The reaction vessel consisted of a 220-cc. Pyrex flask. For the rapid removal of gaseous decomposition products a large Toepler pump was provided. Liquid products were condensed by passing through a carbon dioxide-acetone trap and subsequently allowing the temperature to reach -10°. The resulting vapor was added to the main gas sample, while the remainder of the liquid was analyzed by micro-methods. A mercury vapor pump backed by a Hyvac oil pump comprised the evacuation equipment. Pressures in the system were reduced

(1) Present address: The Michigan College of Mining and Technology, Houghton, Michigan.

(2) Sabatier and Mailhe, *Compt. rend.*, **164**, 49–52 (1912).

(3) Engler and Grimm, *Ber.*, **30**, 2922 (1897).

(4) Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Company, New York, N. Y., 1929, p. 525.

(5) Pearce and Wing, *J. Phys. Chem.*, **36**, 709 (1932).

(6) Thompson and Frewing, *J. Chem. Soc.*, 1444 (1935).