ground spruce wood that went into solution was unknown. For this reason, a method was developed to dissolve the wood entirely by stirring fuming hydrochloric acid into finely milled wood that had been moistened with an ethanol solution of resorcinol. In 10 minutes, a purple solution with only a slight haze was obtained. The maximum absorption then occurred at 588 mμ. . The solution probably was colloidal in nature, however, and, because the cellulose still was present, the situation actually may not have differed much from that with the wood sections.

The resorcinol staining of "native lignin" in the solid state was investigated as another approach to the problem. To a suspension of spruce "native lignin" in a benzene solution of resorcinol was added hydrogen chloride to develop the color. The stained lignin was filtered off and made into a paste with tricresyl phosphate. A maximum absorption of 587 mμ was obtained. When a transparent film of the "native lignin" containing resorcinol was stained with hydrogen chloride gas to produce a color, a maximum absorption of 585 mμ resulted. In both experiments, the colored material was dissolved in a mixture of 1 volume of concd. hydrochloric acid and 2 volumes of ethanol. The resulting solutions had normal maxima at 579 mμ. On the other hand, when "native lignin" suspended in concd. hydrochloric acid was stained with resorcinol, the maximum in the solid state was practically at the same wave length (591 mμ) as that of the material subsequently put into solution. This indicated that some secondary condensation may have occurred.

The color produced by strong acid alone on spruce wood was also reinvestigated. Solutions in which the first color produced (yellow) was partially leached from the milled wood had a maximum absorption in ethanolic hydrogen chloride of 453 mμ, as contrasted to 449 mμ for coniferylaldehyde solutions and 463 mμ for wood sections. A solution of the milled wood in fuming hydrochloric acid became emerald green on standing, and the blue component of this color had a maximum absorption at 628 mμ, exactly the same as that obtained with wood sections.

These data indicate that, in spite of the excellent correlation obtained with absorption spectra in previous work[1,2] further confirmation is required of the type of substitution in the coniferylaldehyde groups responsible for the color reactions of lignin in spruce wood.

Experimental

Measurement of the Coniferylaldehyde-Resorcinol Color on Filter Paper.—A mixture of 0.5 ml. of a 0.01 molar solution of coniferylaldehyde in ethanol, 0.5 ml. of a 0.01 solution of resorcinol in ethanol and 1 ml. of a 38% ethanolic solution of hydrogen chloride was allowed to stand 5 minutes to develop the purple color. After 0.75 ml. of water was added, filter paper was dipped in the solution and air-dried. A portion of the stained paper was mounted in tricresyl phosphate, and, using a similarly mounted piece of unstained paper as a reference, the absorption spectrum was measured as in previous work.[1]

Measurement of Resorcinol Color Partially Extracted from Wood.—Resin-free spruce wood meal was dried over anhydrous magnesium perchlorate and then ground 1 hour in a vibratory ball mill.[4] To 0.03 g. of the resulting powder was added 0.5 ml. of 0.01 molar solution of resor-

cinol in aqueous ethanol, 2.5 ml. of a 38% ethanolic solution of hydrogen chloride, and 2.5 ml. of concd. hydrochloric acid. The mixture was stirred at room temperature for 15 minutes, 2 ml. of water added, and the mixture diluted to 15 ml. with ethanol and filtered with suction on an asbestos mat. The absorption spectrum was measured on the filtrate at 2°.

Measurement of Resorcinol Color Produced with Wood in Solution.—A portion of the powdered spruce wood weighing 0.012 g. was moistened with 0.3 ml. of a 0.001 molar ethanol solution of resorcinol and 5 ml. of fuming hydrochloric acid added with stirring. After standing 10 minutes with occasional stirring, the solution was diluted to 15 ml. with concd. hydrochloric acid, and the color measured as with the extracted resorcinol color.

Resorcinol Staining of "Native Lignin" in the Solid State.—Spruce "native lignin" (0.05 g.) was suspended in 5 ml. of benzene containing 0.005 g. of resorcinol in solution, and a stream of hydrogen chloride was bubbled through the mixture for 5 minutes. The mixture was allowed to stand an additional 5 minutes before the lignin was filtered on a fritted glass crucible. The benzene was then allowed to evaporate from the filtrate, and a portion of the stained powder residue was rubbed up with tricresyl phosphate. A film of this paste was spread on a glass slide for measurement of the absorption spectrum. When the reaction was conducted in hydrochloric acid suspension, the same amount of "native lignin" was stirred into a solution of 0.005 g. of resorcinol in 1 ml. of concd. hydrochloric acid. After the solution stood for 5 minutes, the lignin was filtered off, air-dried, and made into a paste as before.

In the film experiment, one or two drops of a solution of 0.1 g. of "native lignin" and 0.01 g. of resorcinol in a mixture of 1 ml. of ethanol and 1 ml. of Cellosolve were placed on a glass slide, and the solvent was allowed to evaporate. The color was developed by placing the slide in an atmosphere of hydrogen chloride for a few minutes.

Colors Produced by Action of Acid on Spruce Wood.—Powdered spruce wood (0.03 g.) was moistened with 2 drops of ethanol, the mixture cooled to −30°, and 4 drops of cold fuming hydrochloric acid were stirred into the moistened powdered wood. The resulting yellow gel was diluted to 10 ml. with a 38% ethanolic solution of hydrogen chloride. Glass beads were added, and the mixture was shaken for 5 minutes, allowed to stand for an additional 5 minutes, and filtered by gravity on a fritted glass crucible. All these operations were carried out at −30°. The absorption spectrum of the clear yellow solution was determined at −10°.

To produce an emerald-green solution of the wood, 0.03 g. of the powdered substance was moistened with 0.2 ml. of ethanol, 9.8 ml. of fuming hydrochloric acid stirred in, and the mixture allowed to stand for 10 minutes. The operation was carried out at −30°. To develop the green color, this yellow solution was warmed to 2° and maintained at that temperature for 2 hours.

FOREST PRODUCTS LABORATORY, FOREST SERVICE
U. S. DEPARTMENT OF AGRICULTURE
UNIVERSITY OF WISCONSIN
MADISON 5, WISCONSIN

The Stereochemistry of the 3-Carboxycyclohexane-acetic Acids

BY FAUSTO RAMIREZ AND JOHN W. SARGENT[1]

Only one diastereoisomeric form of 3-carboxy-cyclohexaneacetic acid, of unknown configuration, has been reported.[2] This substance, m.p. 156–158°, was obtained by Komppa[3] from the catalytic

(1) From part of the Ph.D. thesis of J. W. Sargent.

(2) Both *cis*- and *trans*-2-carboxycyclohexaneacetic acids, of known configurations have been prepared (E. G. Davis, Ph.D. dissertation (1942) in "Summaries of Theses," Harvard Graduate School (1946)). Only one form of 4-carboxycyclohexaneacetic acid appears to be known; G. Komppa (*Ber.*, **68B**, 1267 (1935)) assigned to this substance, which formed no anhydride, the *trans* configuration.

(3) G. Komppa, T. Hirn, W. Rohrmann and S. Beckmann, *Ann.*, **521**, 242 (1936).

hydrogenation of homoisophthalic acid (3-carboxy-phenylacetic acid). In connection with other work we have prepared both diastereoisomeric 3-carboxycyclohexaneacetic acids by methods which disclose their configurations; the melting points of the cis (IVa) and trans (IVb) isomers were found to be 158.5–159.1° and 132.8–134.1°, respectively. It seems therefore that the substance obtained by Komppa[3] and regarded as the trans isomer has actually the cis- configuration.

cis- and trans-3-carbomethoxycyclohexanecarboxylic acids (IIa and IIb, respectively) were submitted to the sequence of steps of the Arndt–Eistert synthesis, following the modification recently introduced by Newman and Beal.[4] Hydrolysis of the resulting dimethyl esters (IIIa and IIIb, respectively) gave the stereoisomeric acids IVa and IVb. In view of the relatively low yields of pure IVa and IVb obtained in these hydrolyses the possibility of some epimerization is not excluded, although the melting point–composition diagram for IVa–IVb substantiates the homogeneity of the isolated acids. IIIa was also obtained by rearrangement of the corresponding diazoketone in methanol solution in the usual manner.[5] In agreement with previous observations the cis isomers melted higher than the trans isomers in this series of compounds.[6]

Although instances of extensive racemization during the rearrangement of some optically active diazoketones having α-hydrogen are known in the Arndt–Eistert reaction,[7] the work of Davies[2] and of Bachmann and Controulis[8] have demonstrated the applicability of this method to the determination of configuration of cyclohexane derivatives.

COOR
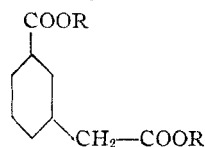
IIIa, R = CH₃ (cis)
IIIb, R = CH₃ (trans)
IVa, R = H (cis)
IVb, R = H (trans)

CH₂—COOR

Experimental[9]

cis- and trans-Hexahydroisophthalic Acids (Ia and Ib).—Saponification of the mixture of esters resulting from the hydrogenation of dimethyl isophthalate[10] in acetic acid solution at 3 atmospheres using a platinum oxide catalyst (Baker and Co., Inc., Newark, N. J.), gave 82% (based on dimethyl isophthalate) of a mixture of Ia and Ib, m.p. 155–160°. Epimerization and separation of the isomers as described[11a] gave 53% of pure Ia, m.p. 166.0–166.5° (from

(4) M. S. Newman and P. F. Beal, III, THIS JOURNAL, 72, 5163 (1950).

(5) W. E. Bachmann and W. S. Struve in R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(6) The opposite relationship is observed among similar isomers in the 1,2- and 1,4-series. See: ref. 11; E. G. Davis, footnote 2; R. Malachowski, J. J. Wasowska, S. Jozkiewicz, J. Adamiczka and G. F. Pasternack, Ber., 71B, 759 (1938); W. Hückel and H. Friedrich, Ann., 451, 132 (1926).

(7) J. F. Lane and E. S. Wallis, J. Org. Chem., 6, 443 (1941). See however G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 519.

(8) W. E. Bachmann and J. Controulis, THIS JOURNAL, 73, 2636 (1951).

(9) Microanalyses by Micro-Tech Laboratories, Skokie, Ill. All melting points are corrected.

(10) P. G. Scheurer and G. M. LeFeve, THIS JOURNAL, 72, 3308 (1950). We thank Dr. R. H. Kimball of the Hooker Electrochemical Co., Niagara Falls, N. Y. for a gift of m-bis-(trifluoromethyl)-benzene.

(11) (a) A. Skita and R. Rossler, Ber., 72, 265 (1939); (b) cf. H. Smith and F. P. Byrne, THIS JOURNAL, 72, 4406 (1950).

water) and 20% of product melting at 135–140°, from which 6% of Ib, m.p. 149.0–150.5°, was obtained after four recrystallizations from water and one from ethyl acetate–benzene; reported[11b] for Ia, m.p. 167.0–167.8°; for Ib, m.p. 150.5–150.7°.

cis-3-Carbomethoxycyclohexanecarboxylic Acid (IIa).—IIa, m.p. 62–66°, was prepared from Ia in 58% over-all yield, via the solid cis-anhydride, m.p. 185–188° (from benzene–hexane), as described by Smith and Byrne.[11b] The analytical sample melted at 66.0–66.8° (from petroleum ether b.p. 30–60°); reported[11b] m.p. 56.6–57.4°. Anal. Calcd. for C₉H₁₄O₄: C, 58.1; H, 7.6. Found: C, 58.1; H, 7.6.

The monoanilide[12] recrystallized twice from aqueous ethanol and four times from hexane, was obtained as fine colorless needles, m.p. 122.8–123.6°. Anal. Calcd. for C₁₅H₁₉O₃N: C, 68.9; H, 7.3; N, 5.4. Found: C, 69.0; H, 7.3; N, 5.6.

Dimethyl Ester of cis-3-Carboxycyclohexaneacetic Acid (IIIa). (a).—To a chilled solution of diazomethane (from 15 g. of N-nitrosomethylurea) in 100 ml. of anhydrous ether was added an ether solution (50 ml.) of the ester acid chloride prepared as described[13] from 8.70 g. of IIa. The temperature was kept at 50° or below throughout the reaction. The oily diazoketone which remained after removal of the ether was dissolved in 100 ml. of anhydrous methanol and the solution treated with dry silver benzoate (2.0 g.) dissolved in freshly distilled triethylamine (20 ml.). The mixture was refluxed for two hours and filtered; the filtrate was evaporated under reduced pressure and the residue taken up in ether. After the organic layer had been washed with 5% sodium bicarbonate, 5% hydrochloric acid and water, the ether was removed and the residue distilled at 139–143° (20 mm.); yield 4.12 g., $n^{22}D$ 1.4562. For analysis a sample was distilled at 98–101° (0.8 mm.), $n^{25}D$ 1.4564, d^{25}_{25} 1.0848, M_D 53.72. Anal. Calcd. for C₁₁H₁₈O₄: C, 61.6; H, 8.5. Found: C, 61.4; H, 8.5.

(b) When the diazoketone was rearranged in the usual way[5] in methanol solution using Ag₂O, the yield of IIIa after distillation was 37%.

cis-3-Carboxycyclohexaneacetic Acid (IVa).—A solution containing 1.04 g. of IIIa, 5.5 ml. of methanol and 5.5 ml. of 10% aqueous sodium hydroxide solution was refluxed for two hours. The filtered solution was concentrated to one-half its original volume, allowed to cool and acidified with 5% hydrochloric acid. The dry residue which remained after removal of the solvents in a stream of air was extracted with ethyl acetate. Removal of the ethyl acetate gave 0.80 g. of crystalline product of wide melting range from which, after two recrystallizations from water (3.6 ml.), 0.34 g. (37%) of IVa, m.p. 153–156°, was obtained. The analytical sample was obtained as colorless prisms, m.p. 158.5–159.1°. Anal. Calcd. for C₉H₁₄O₄: C, 58.0; H, 7.6. Found: C, 57.9; H, 7.6.

The diamide melted at 284–286° (from methanol) with decomposition; reported[3] m.p. 277–278° (dec.).

trans-3-Carbomethoxycyclohexanecarboxylic Acid (IIb).—One equivalent of silver nitrate was added to a solution of 3.50 g. of Ib in 80 ml. of water containing one equivalent of sodium hydroxide. A mixture of the resulting dry silver salt (5.56 g.), 2.88 g. of methyl iodide and 100 ml. of benzene was refluxed for 11 hours and filtered. The residue remaining after removal of the benzene was separated into a neutral and an acidic fraction by means of aqueous sodium bicarbonate solution. From the neutral fraction 1.17 g. of oil (dimethyl ester derived from Ib) was obtained. Partial saponification of this material (2.5 hours reflux in methanol solution containing one equivalent of sodium hydroxide) gave 0.571 g. of crude monomethyl ester (IIb) which on evaporative distillation at 85° (0.02 mm.) yielded 0.204 g. of IIb, $n^{25}D$ 1.4705; calcd., neut. equiv., 186; found, 187.

The monoanilide[12] was obtained from IIb as colorless flakes, m.p. 117.5–118.2° (from hexane); mixed m.p. with cis-monoanilide, 87–99°. Anal. Calcd. for C₁₅H₁₉O₃N: C, 68.9; H, 7.3; N, 5.4. Found: C, 69.1; H, 7.3; N, 5.6.

From the bicarbonate solution obtained above, 1.27 g. of crude monoester IIb was obtained upon acidification.

(12) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158. The acid chloride was prepared at or below 50°.

(13) W. E. Bachmann, W. Cole and A. Wilds, THIS JOURNAL, 62, 834 (1940).

Evaporative distillation of this material at 65–85° (0.02 mm.) gave 0.703 g. of oil, whose neut. equiv. indicated about 80% of monoester. This fraction gave the same monoanilide, m.p. 117–118°, obtained above.

trans-3-Carboxycyclohexaneacetic Acid (IVb).—From 0.720 g. of IIb, 0.509 g. of crude dimethyl ester IIIb was obtained following procedure (a) above. Evaporative distillation at 70° (0.02 mm.) gave 0.427 g. (52%) of colorless oil, $n^{25}D$ 1.4593. The saponification of this material (0.383 g.) patterned after the procedure used with the *cis* isomer gave 0.235 g. of crystalline material of wide melting range from which 0.062 g. of pure IVb, m.p. 132.8–134.1°, was obtained as colorless plates after six recrystallizations from water. *Anal.* Calcd. for $C_6H_{14}O_4$: C, 58.1; H, 7.6. Found: C, 58.1; H, 7.6.

Mixtures of IVa and IVb of various compositions melted as follows.

% *cis* (IVa)	M.p., °C.
14.4	121–130
32.5	116–122
45.0	116–131
60.0	118–137
81.3	144–150

Acknowledgment.—A gift from Research Corporation in support of this work is gratefully acknowledged.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.


The Thermal Decomposition of Ethyl Chlorocarbonate[1,2]

BY LATHROP E. ROBERTS, ROBERT LASHBROOK, MARY J. TREAT AND WILLIAM YATES

Choppin, Frediani and Kirby[3] found that at temperatures of from 195 to 295° ethyl chlorocarbonate decomposed by a homogeneous unimolecular reaction, with ethyl chloride and carbon dioxide as the only products. We have found that at temperatures of from 280 to 330°, it decomposes by a more complex reaction into ethyl chloride, carbon dioxide, hydrogen chloride and ethylene. Ethylene and hydrogen chloride were formed in approximately equimolecular amounts, and the sum of the percentage of ethyl chloride and either ethylene or hydrogen chloride was approximately equal to that of the carbon dioxide. The reaction was conducted at constant volume and its course followed by recording changes in pressure. Runs made under apparently the same conditions frequently showed different pressure–time relations, although all runs proceeded smoothly. The reaction appears to be sensitive to surface conditions, and when a new reaction flask was used, concordant results could not be obtained until it was thoroughly seasoned. In a total of sixty runs, at temperatures of from 280 to 330°, the ratio of final to initial pressure varied from 2.27 to 2.59, with a mean value of 2.40 and an average deviation from

(1) From theses submitted by Robert Lashbrook, Mary J. Curry and William Yates in partial fulfillment of the requirements for the M.S. degree at the University of Arizona.

(2) Presented before the Physical and Inorganic Division of the American Chemical Society, 117th Meeting, April 16–20, 1950, Detroit, Michigan.

(3) A. R. Choppin, H. A. Frediani and Q. F. Kirby, THIS JOURNAL, **61**, 3176 (1939).

the mean of 0.07. No systematic variation of this ratio with temperature was evident.

While the lack of agreement between runs made under the same conditions has made it impossible to determine mathematically the exact course of the reaction, certain conclusions may nevertheless be drawn. Ethyl chlorocarbonate, in the temperature range studied, does not decompose simply into ethyl chloride and carbon dioxide. The value of the ratio of final to initial pressure would, in itself, rule out such an interpretation. Nor does the ester decompose first into ethyl chloride and carbon dioxide, followed by partial decomposition of ethyl chloride into ethylene and hydrogen chloride. The complete stability of ethyl chloride under the conditions of these experiments, both alone and in the presence of the decomposition products, was shown independently, and is confirmed by the work of Nef.[4] Decomposition may occur by the two simultaneous reactions

(a)　$ClCOOC_2H_5 = C_2H_5Cl + CO_2$

(b)　$ClCOOC_2H_5 = C_2H_4 + HCl + CO_2$
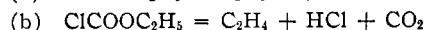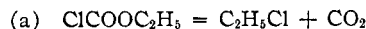
Such reactions would account for the values of the ratio P_f/P_i found, for the occurrence of ethylene and hydrogen chloride in approximately equimolecular quantities, and for the fact that the percentage of carbon dioxide is approximately equal to the sum of the percentage of ethyl chloride and either ethylene or hydrogen chloride.

However, the bimolecular reaction

$$2ClCOOC_2H_5 = 2CO_2 + HCl + C_2H_5Cl + C_2H_4$$
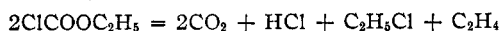
may also occur. It cannot be the only reaction, since it would demand a ratio P_f/P_i equal to 2.5.

Experimental

Ethyl chlorocarbonate from the Eastman Kodak Company was redistilled twice and the fraction boiling from 90.1 to 90.2° (700 mm.) was used. The reaction was carried out at constant volume in a Pyrex bulb of known volume, and pressures were read on a mercury manometer. The bulb was heated in a manually controlled electric furnace, with temperature control accurate to 0.1°. Prior to each run the heated bulb was exhausted for two hours with a mercury diffusion pump. Weighed amounts of ester were introduced for each run in sealed ampoules, which were broken with a solenoid hammer. Products were removed for analysis with a toepler pump.

Qualitative tests on the products showed the presence of carbon dioxide, hydrogen chloride and unsaturated hydrocarbon, and an inert residue which condensed as a colorless liquid at −72°. After removal of the carbon dioxide and hydrogen chloride, the residual gas absorbed bromine, forming a colorless liquid which melted at 9.3°, and had an index of refraction to sodium light of 1.5363 at 21°. It was evidently slightly impure ethylene bromide. After removal of the ethylene with fuming sulfuric acid, four micro-combustions on the residual gas showed a mean value of 2.0 gram-atoms of carbon for each mole of gas burned, and three determinations of chlorine showed a mean of 1.0 gram-atoms of chlorine per mole. Two determinations of molecular weight by direct weighing gave 67.2 and 66.4. It was concluded that the residual gas was ethyl chloride.

Experiments with mixtures of ethyl chloride, hydrogen chloride, ethylene and carbon dioxide showed that when ethyl chloride was condensed from the mixture, the other gases dissolved in it, hydrogen chloride being almost quantitatively removed from the gas phase. Hence, ethyl chloride could not be determined from the chlorine in the condensate.

The gas mixture was analyzed quantitatively as follows. Hydrogen chloride was absorbed in dilute sodium hydroxide

(4) U. Nef, *Ann.*, **318**, 14 (1901).