4,6-Dimethyltetrahydro-2-pyrone (β,δ-Dimethyl-δ-valerolactone).—A solution of 6.2 g. (0.05 mole) of 4,6-dimethyl-2-pyrone in 100 ml. of diethyl ether with 1.0 g. of catalyst absorbed two molar equivalents of hydrogen in 75 minutes. Fractionation gave 5.3 g., 83%, of the product, b.p. 69–70° (1 mm.), $n^{30}D$ 1.4427; reported[5] b.p. 83–86° (3 mm.), $n^{30}D$ 1.4437.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.54; H, 9.42.

4,6-Dimethyl-5-carbethoxytetrahydro-2-pyrone (Ethyl Tetrahydroisodehydroacetate).—A solution of 39.2 g. (0.2 mole) of ethyl isodehydroacetate in 150 ml. of diethyl ether with 3.0 g. of catalyst absorbed two molar equivalents of hydrogen in 2.5 hours. Fractionation gave 34.0 g., 85% of the product, b.p. 160–3° (5 mm.); refractionated material b.p. 160–161° (5 mm.), $n^{29.5}D$ 1.4564, was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.54; H, 8.01.

4,6-Dimethyltetrahydro-2-pyrone-5-carboxylic Acid (Tetrahydroisodehydroacetic Acid).—A solution of 16.8 g. (0.1 mole) of isodehydroacetic acid in 300 ml. of diethyl ether with 3.0 g. of catalyst absorbed two molar equivalents of hydrogen in 5.5 hours. The solid residue remaining after evaporation of the filtered reaction mixture was recrystallized from toluene to give 6.3 g., 37%, of a white crystalline solid, m.p. 108–118°. After three additional recrystallizations from toluene the product melted at 121–126°. The material probably consists of a mixture of stereoisomers.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03; neut. equiv., 172. Found: C, 56.00; H, 7.02; neut. equiv., 169.

Tetrahydro-2-pyrone-5-carboxylic Acid (Tetrahydrocoumalic Acid).—A solution of 14.0 g. (0.1 mole) of purified coumalic acid in 300 ml. of methanol with 1.0 g. of catalyst absorbed 1.24 molar equivalents of hydrogen in 45 minutes. Most of the hydrogen was absorbed in the first 15 minutes. The semi-solid residue remaining on evaporation of the filtered reaction mixture was recrystallized alternately from benzene–petroleum ether and diethyl ether–petroleum ether mixtures five times to give β-methylglutaric acid, m.p. 74–75°, reported[1] m.p. 77°; dianilide m.p. 174–176°, reported[1] 179–180°. The neutral equivalent of the acid (75.7) agreed with theory (73.1).

The residue remaining after the benzene extractions was fractionated to give 8.2 g. of a product, b.p. 169–180° (2 mm.), which solidified on cooling. Repeated recrystallization from toluene and benzene gave white crystals, m.p. 124–129°.

Anal. Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.60. Found: C, 49.86; H, 5.56.

6-Carbomethoxytetrahydro-2-pyrone.—A solution of 4.9 g. (0.032 mole) of methyl 2-pyrone-6-carboxylate in 150 ml. of methanol with 1.0 g. of catalyst absorbed two molar equivalents of hydrogen in 70 minutes. Fractionation gave 4.1 g., 82%, of a very hygroscopic product, b.p. 145–147° (3 mm.), $n^{30}D$ 1.4615. The material is soluble in water and acidic to moist test paper. Titration shows a slowly drifting end-point with gradual and continued uptake of alkali.

Anal. Calcd. for $C_7H_{10}O_4 \cdot H_2O$: C, 47.72; H, 6.87. Found: C, 47.54; H, 6.94.

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[5] F. G. Young, THIS JOURNAL, **71**, 1346 (1946).

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A New Method for the Conversion of Optically Active Alcohols to Halides with Inversion of Configuration

BY CALVIN L. STEVENS, DUANE MORROW[1] AND JOHN LAWSON[1]

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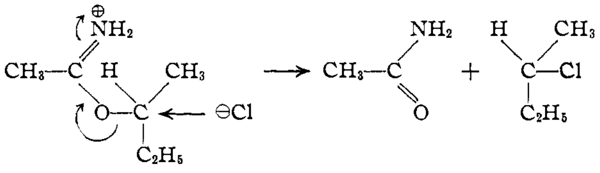
Iminoester hydrochlorides have been used for many years as intermediates for the conversion in good yields of nitriles to amides by pyrolysis, to esters by hydrolysis and to orthoesters by alcoholysis. However, little attention has been devoted to the alkyl halide produced concurrently in the amide pyrolysis. The purpose of this Note is to point out that iminoester hydrochlorides also may be used as intermediates in the conversion in high yields of optically active alcohols to the corresponding chlorides with inversion of configuration at the optically active center.

Although the pyrolysis of iminoester hydrochlorides to amides and alkyl chlorides has been used in organic synthesis since the work of Pinner[2] in 1877, no detailed investigation of the reaction has been reported until recently. Cloke and Hartigan,[3] in 1945, determined a constant which they termed the mean temperature of pyrolysis for twenty-five different crystalline iminoesters. However, the difference between the mean temperatures of pyrolysis for various iminoester hydrochlorides was too small to give important information about the mechanism of the reaction. The most significant investigation of the pyrolysis was reported by McElvain and Tate,[4] who presented data to support a bimolecular displacement reaction for pyrolyses conducted in chloroform or *t*-butyl alcohol solution. A consequence of such a reaction mechanism would be inversion of the ester alkyl group as indicated in I.



I

Although pyrolysis of a crystalline iminoester hydrochloride need not proceed by the same mechanism as pyrolysis in solution, evidence that inversion would occur was available in a report of McCasland and Smith[5] that pyrolysis of a crystalline oxazoline hydrochloride (an N-alkyl iminoester hydrochloride) in the cyclohexane series proceeded with inversion to form a chloramide.

In this Laboratory an iminoester hydrochloride made from optically active *sec*-butyl alcohol was used as an intermediate in the conversion of an optically active alcohol to the corresponding chloride with inversion. The positive rotating enantiomorph was allowed to react with acetonitrile and dry hydrogen chloride to give the iminoester hydrochloride (I) in 60–65% yield. Pyrolysis of the iminoester hydrochloride gave the optically active *sec*-butyl chloride in 65–80% yield. From (+)-2-butanol,[6] $[\alpha]^{20}D$ +13.9°, was obtained (−)-2-butyl chloride, $[\alpha]^{20}D$ −31.2°. Previously, Lane and Ulrich[7] have converted 2-butanol, $[\alpha]^{25}D$ −5.54°,

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[1] Undergraduate Research Students.

[2] A. Pinner and F. Klein, *Ber.*, **10**, 1889 (1877).

[3] R. H. Hartigan and J. B. Cloke, THIS JOURNAL, **67**, 709 (1945).

[4] S. M. McElvain and B. E. Tate, *ibid.*, **73**, 2233 (1951); *cf.* S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950).

[5] G. E. McCasland and D. A. Smith, *ibid.*, **72**, 2190 (1950). E. E. van Tamelen (*ibid.*, **74**, 2074 (1952)) also reported such a transformation in dioxane solution.

[6] The highest value recorded in the literature is by R. H. Pickard and J. Kenyon (*J. Chem. Soc.*, **99**, 45 (1911)) who also reported $[\alpha]^{20}D$ +13.9°.

[7] J. F. Lane and S. E. Ulrich, THIS JOURNAL, **72**, 5132 (1950).

to 2-chlorobutane, $[\alpha]^{25}_D + 13.70°$. Further, Letsinger[8] recently calculated from these data and his work on the displacement of *sec*-butyl chloride with benzylsodium that the optical rotation for a pure enantiomorph must lie between $[\alpha]^{25}_D$ 33.8° and $[\alpha]^{25}_D$ 38.4°.

Since it has been shown that the (+)*sec*-butyl chloride has the same configuration as the (+)*sec*-butyl alcohol,[9] evidence presented here indicates that inversion has occurred in the pyrolysis and corroborates that provided by McElvain for a bimolecular mechanism of pyrolysis.

The high rotation of the chloride indicates that a minimum of racemization has occurred; thus this sequence of reactions involving the iminoester hydrochloride provides an excellent method for the preparation in good yield, and under mild reaction conditions, of optically active chloride with high optical purity.

Experimental

Optically active 2-butanol was prepared according to the procedure of Kantor and Hauser[10] with the following modification. In order to reduce the volume of water, the saponification of the brucine salt was carried out in diethylene glycol. From 87.2 g. of pure brucine salt, m.p. 158–159°, was obtained 7.4 g. (79%) of (+)-2-butanol, $[\alpha]^{20}_D$+13.9°.

One difficulty encountered in the isolation of the active alcohol resulted from the formation of the water–alcohol azeotrope. Pure alcohol was recovered from the azeotrope in this work by the use of calcium hydride, which reacted rapidly with the water but left the alcohol unchanged.

***sec*-Butyl Iminoacetate Hydrochloride.**—Preliminary experiments were performed with the *dl*-2-butanol. A mixture of 2.35 g. (0.057 mole) of acetonitrile and 4.70 g. (0.063 mole) of 2-butanol was cooled to 0° and dry hydrogen chloride bubbled into the reaction mixture until 2.29 g. (0.063 mole) was dissolved. The flask was kept at 0° for 7 days after which time an equal volume of ether was added and the salt filtered, washed with ether and dried. The yield was 5.8 g. (70%), m.p. 118° dec. The salt contained 23.44% chlorine ion (calcd. 23.38%).

Using the same procedure with 2.64 g. of (+)-2-butanol, $[\alpha]^{20}_D$ 13.9°, 5.1 g. (59%) of the iminoester hydrochloride was isolated which melted with decomposition at 125°. (+)-2-Butyl iminoacetate hydrochloride from a similar run contained 23.09% chloride ion (calcd. 23.38%).

Pyrolysis of the Iminoester Hydrochloride.—The dry *dl*-iminoester hydrochloride (11.7 g., 0.078 mole) was placed in a 50-ml. distilling flask and heated to about 130°, at which temperature the pyrolysis took place smoothly to give 5.69 g. (80%) of *sec*-butyl chloride. The chloride was purified by distillation; essentially all of the material distilled at 67.5–68°, n^{28}_D 1.3936, d^{28}_4 0.5678. The solid remaining in the distillation flask was identified as acetamide by mixture m.p. determination.

The 5.1 g. of iminoester hydrochloride prepared from (+)-2-butanol ($[\alpha]^{20}_D$ 13.9°) was subjected to the same pyrolysis procedure to give 2.42 g. (78%) of (−)-2-butyl chloride, n^{25}_D 1.3941, $[\alpha]^{20}_D$ 31.2°.

All of the optical rotation readings were taken on the pure liquids.

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[8] R. L. Letsinger, L. G. Maury and R. L. Burwell, THIS JOURNAL, **73**, 2373 (1951).

[9] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, **59**, 1266 (1937); *J. Chem. Soc.*, 1252 (1937). For a discussion of the relationship of configuration and sign of rotation also see: H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 278; and Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 386.

[10] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **75**, 1744 (1953).

The Proximity Effect in the Alkaline Rearrangement of 1,2-Diketones. I. The Migratory Aptitudes in the Rearrangement of *o*-Chlorobenzil and 1-Chlorophenanthraquinone[1,2]

BY GRANT GILL SMITH AND DONALD G. OTT[3]

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It has been reported that the alkaline rearrangement of *m*- and *p*-chlorobenzil[4] and 2- and 3-chlorophenanthraquinone[5] results in the preferential migration of the *substituted* rings. This investigation has revealed the preferential migration of the *unsubstituted* rings in *o*-chlorobenzil and 1-chlorophenanthraquinone. Anomalies of this type have been observed with many reactions in which substituents are present in the aromatic ring *ortho* to the reacting group, and this effect has been termed an *ortho effect* or a *proximity effect*.[6] The larger migratory preference of the chloro substituted ring of *o*-chlorobenzil as compared to 1-chlorophenanthraquinone, may be attributed to the relative accessibility to hydroxide ion attack at the carbonyl groups adjacent to the substituted rings. With the quinone, if the hydroxide ion is to attack at this position, it must approach relatively close to the (electronegative) chlorine substituent. This hindrance is not so great in the case of the benzil, which is not restricted by the biphenylene linkage, and hydroxide ion can more readily approach the carbonyl group. Migratory preferences are reported in Table I.

The mechanism proposed for the rearrangement would predict that the chloro substituent would tend to lower the electron density at the adjacent carbonyl group which would favor preferential migration of the substituted ring. The proximity effect of the *o*-chloro group, however, overshadows the electronic effects transmitted within the molecule, and the hydroxide ion attacks more readily at the carbonyl group adjacent to the unsubstituted ring. In order to study the proximity effect further, other substituted aromatic 1,2-diketones are being studied.

Experimental[7]

***o*-Chlorophenylacetic acid-carboxyl-C^{14}** (I) was obtained from *o*-chlorobenzyl chloride by a method described for the preparation of 2-phenyl-5-chloro-α-toluic acid-carboxyl-C^{14}.[5] A 68.7% yield of the acid was obtained; m.p. 94.5–95.5°.

Anal. Calcd. for $C_8H_7O_2Cl$: C, 56.33; H, 4.34; Cl, 20.78. Found: C, 56.20; H, 4.14; Cl, 20.67.

***o*-Chlorodesoxybenzoin** (II).—Compound I was converted

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[2] Abstracted in part from a thesis presented to the Graduate Faculty of the State College of Washington by Donald G. Ott in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1953. Supported in part by a grant from the State College of Washington Isotopes Research Fund.

[3] Atomic Energy Commission Predoctoral Fellow, 1951–1953.

[4] M. T. Clark, E. C. Hendley and O. K. Neville, THIS JOURNAL, in press.

[5] Donald G. Ott and Grant G. Smith, *ibid.*, **76**, 2325 (1954).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 204.

[7] All melting points are corrected. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn. The yields given for the carbon-14 compounds are comparable to those obtained with non-labeled analogs.