uct came over at 141–143° (15 mm.).[8] The yield was 16.2 g. (50%) of a colorless oil with a faint pleasant odor, having n^{25}_{D} 1.4318 and d^{25}_{4} 0.997.

Anal. Calcd. for $C_{11}H_{20}O_4Si$: C, 54.06; H, 8.25; Si, 11.5; mol. wt., 244; molecular refraction[9] 64.1. Found: C, 54.23; H, 8.65; Si, 11.0; mol. wt. 216; molecular refraction, 63.6; I, absent.

Symmetrical Bis-(2,2-dicarboxypropyl)-tetramethyldisiloxane (II).—To a solution of 3.0 g. of KOH in 50 ml. of ethanol was added 5.0 g. (0.020 mole) of compound I. The mixture was refluxed for two hours, during which time a white precipitate of the potassium salt of II formed. The precipitate was removed by filtration and the filtrate was discarded. The crude potassium salt was dissolved in 10 ml. of warm water and made just acid with HCl. The solution was extracted with four 30-ml. portions of diethyl ether, and the extracts were combined and dried over $MgSO_4$. The product was obtained by allowing the ether to evaporate, taking up the residue in ethyl acetate, and precipitating with petroleum ether. The yield was 2.2 g. (55%). After one more reprecipitation, the product was quite pure. (Analytical results were the same for material prepared in slightly different ways and crystallized from different solvents.)

Anal. Calcd. for $C_{14}H_{26}O_9Si_2$: C, 42.62; H, 6.64; neut. equiv., 98.6. Found: C, 42.79; H, 6.59; neut. equiv., 98.2.

The compound crystallized as small diamond-shaped prisms, soluble in water, alcohols, ethyl acetate and acetone, but only sparingly soluble in benzene and petroleum ether; m.p. 141–142° dec. When titrated with alkali, compound II gave a *p*H curve resembling that for a dibasic acid such as malonic acid. If the proposed structure is correct, the hydrogens must therefore ionize in pairs, presumably in a symmetrical fashion about the disiloxane group. The acidic dissociation constants were estimated to be $K_{\mathrm{I,II}} = 10^{-3}$ and $K_{\mathrm{III,IV}} = 5 \times 10^{-7}$ from the *p*H titration curve. The aqueous solution gave a white precipitate with Pb^{++}, but gave no precipitate with Na^+, K^+, Ag^+, Ca^{++} or Ba^{++}. The lead salt was filtered off, washed with water and dried at 120°.

Anal. Calcd. for $C_{14}H_{22}O_9Si_2Pb_2$: Pb, 51.5. Found: Pb, 51.9.

Decarboxylation of II.—In a typical experiment 0.2112 g. of II was heated to 160° for five minutes in a test-tube. The product, a viscous oil, was not purified. The yield was 0.156 g. The product had a neutralization equivalent of 150; that calculated for the diacid expected from the decarboxylation of II is 153.

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(8) 2-Ethylbutane-1,1-dicarboxylic acid diethyl ester, a carbon compound of similar molecular weight, has b.p. 130° at 13 mm.: F. Fichter, A. Kiefer and W. Bernoulli, *Ber.*, **42**, 4712 (1909).

(9) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

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2-Pyrones. XIV.[1] The Hydrogenation of 2-Pyrones

BY RICHARD H. WILEY AND ALBERT J. HART

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Although the hydrogenation and hydrogenolysis of unsaturated δ-lactones (2-pyrones) to saturated δ-lactones and open chain derivatives have been used as significant facets of the proof of structure of many naturally occurring and synthetic compounds,[2] there has been no reported study of the hydrogenation of the simple, readily available 2-pyrones. This is particularly striking in view of the variety of catalysts and conditions which have been used in structural studies and the apparent ease with which hydrogenolysis of certain structures occurs with some catalysts. The present study was undertaken to develop a satisfactory procedure for conversion of 2-pyrones to saturated δ-lactones and to provide additional information on this important reaction.

The addition of hydrogen to 2-pyrones is known to take place readily over platinum oxide or various palladium catalysts.[2] Experiments recorded here show that with a commercially available 5% palladium-on-charcoal catalyst, absorption of two moles of hydrogen per mole of 2-pyrone is complete within 45 minutes to 5 hours at 15 pounds pressure of hydrogen and in methanol or ether. Under these conditions coumalic acid reacted most rapidly absorbing in excess (122–129%) of two moles of hydrogen per mole of compound in less than 45 minutes. Isodehydroacetic acid absorbed two moles of hydrogen in five hours. The yields of isolated tetrahydro-2-pyrone varied from very low with coumalic acid to 37% for isodehydroacetic acid and to 82–85% with other 2-pyrones. The low yields were obtained in attempts to isolate pure solid products from the two acids—coumalic and isodehydroacetic. These isolations were difficult because the crude solid consists of mixtures of stereoisomers. The yields of the crude solid are considerably greater than those recorded for the recrystallized, analytical sample.

The hydrogenation of coumalic acid is not only more rapid than that of the other types but it is also accompanied by hydrogenolysis. α-Methylglutaric acid was identified as the chief constituent in a benzene-soluble fraction of the product, and tetrahydrocoumalic acid was separated in poor yield from the benzene-insoluble fraction. The formation of β-methylglutaric acid by hydrogenolysis of methyl coumalate has been noted before.[2] This behavior of coumalic acid and its ester is obviously exceptional and confirms previous observations[3] as to the anomalous character of coumalic acid and its derivatives.

The product from the reduction of methyl 2-pyrone-6-carboxylate is very soluble in water, is very hygroscopic, and is acidic to moist test paper. Ultimate analysis indicates the addition of a mole of water, presumably during isolation, as well as two moles of hydrogen, on which basis the compound is taken to be a hydrate. Its behavior toward alkali on titration indicates that the lactone structure is intact.

Acknowledgment.—The authors wish to thank the Damon Runyon Memorial Fund for a grant in support of this study.

Experimental[4]

All of the hydrogenations were run in a Parr hydrogenation apparatus under an initial hydrogen pressure of 50–60 lb. using 5% palladium-on-carbon catalyst.

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(1) Previous paper in this series; R. H. Wiley and L. H. Knabeschuh, THIS JOURNAL, **77**, 1615 (1955).

(2) M. Bergmann, L. Zervas and E. Silberkweit, *Ber.*, **64B**, 2428 (1931); T. W. Campbell, THIS JOURNAL, **73**, 4190 (1951); J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 577 (1941); R. Malachowski, *Bull. intern. acad. Polonaise*, 265A (1929); R. Malachowski and T. Wanzciera, *ibid.*, 547A (1933); J. Meinwald, THIS JOURNAL, **76,** 4571 (1954); E. B. Reid and J. R. Siegel, *ibid.*, **76**, 938 (1954); A. Stoll, A. Hofmann and N. Kreis, *Helv. Chim. Acta*, **17**, 1334 (1934); R. Tschesche and H. A. Offe, *Ber.*, **69B**, 2361 (1936); H. Wieland, G. Hesse and H. Meyer, *Ann.*, **493**, 272 (1932); F. G. Young, THIS JOURNAL, **71**, 1346 (1949).

(3) R. H. Wiley and L. H. Knabeschuh, *ibid.*, **77**, 1615 (1955).

(4) Analyses by Micro Tech Laboratories.

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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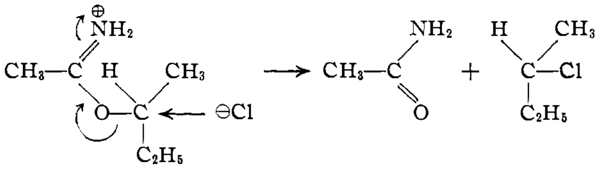
Iminoester hydrochlorides have been used for many years as intermediates for the conversion in good yields of nitriles to amides by pyrolysis, to esters by hydrolysis and to orthoesters by alcoholysis. However, little attention has been devoted to the alkyl halide produced concurrently in the amide pyrolysis. 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).