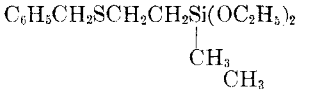
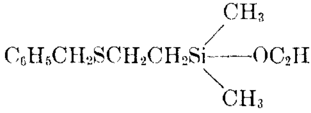
TABLE I

Preparation of New Silane Sulfides

Formula	Reaction Conditions Temp.	Hours	B.p., °C.	Mm.	Yield, %	Analysis Carbon Calc'd	Found	Hydrogen Calc'd	Found	Sulfur Calc'd	Found
$C_6H_5SCH_2CH_2Si(OC_2H_5)_3$	80–100	6	130	0.8	75	55.96	56.07	8.05	8.19	10.67	10.46
$C_6H_5CH_2SCH_2CH_2Si(OC_2H_5)_3$	100–120	4	125–126	0.3–0.4	34	57.28	57.19	8.33	8.40	10.20	10.34
 $C_6H_5CH_2SCH_2CH_2\underset{CH_3}{Si}(OC_2H_5)_2$	110–130	8	114	0.2	36	59.15	59.41	8.45	8.33	11.27	11.18
 $C_6H_5CH_2SCH_2CH_2Si(CH_3)_2OC_2H_5$	125–130	10	107	0.5	26	61.42	61.60	8.66	8.60	12.60	12.41

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Department of Chemistry
Polytechnic Institute of Brooklyn
Brooklyn 1, New York

The Electrolysis of (+)-2-Methylbutanoic Acid[1a]

Joseph Brenner[1b] and Kurt Mislow

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It has long been suspected that the Kolbe electrolysis of carboxylic acids and the decomposition of diacyl peroxides proceed by way of a common intermediate.[2–4] This hypothesis has been reinforced by the similarity of the products isolated in both reactions.[3,4] In addition the nature of the products has suggested free radical mechanisms for both reactions.[3–7] The isolation of optically active hydrocarbon,[8] alcohol[8] and ester[8,9] of retained configuration from the decomposition of optically active diacyl peroxides has led us to inquire into the stereochemical nature of the products of the electrolysis of an optically acid. We now report the results of such an investigation.

Electrolysis of (+)-2-methylbutanoic acid gave, directly, inactive 2-butanol, identified as the α-naphthylurethan, and the (±)-2-butyl ester of (+)-2-methylbutanoic acid, identified by comparison with a synthetic product and by saponification to inactive 2-butanol and optically active (+)-2-methylbutanoic acid.

Since Wallis and Adams have reported[10] the isolation of inactive 2,3-dimethylhexane from the electrolysis of (+)-2-methylbutanoic acid, it can now be concluded that the products of the Kolbe electrolysis of carboxylic acids and those of the decomposition of diacyl peroxides, although chemically similar, are formed by stereochemically different paths. In explanation of this discrepancy, the view may be taken that radicals are formed in both reactions but that their subsequent fate is a function of the particular mode of generation and the environment into which they are produced. Alternatively, it is to be noted that in the case of the decomposition of diacyl peroxides, recombination of radicals within the solvent cage or internal rearrangement *via* cyclic transition states[8] are possibilities which appear rather less likely in the course of the electrolysis reaction.

EXPERIMENTAL

(+)-2-Methylbutanoic acid. The acid, α^{27}_D +17.85° (*l*, 1, neat), was prepared in 70% yield by permanganate oxidation[11] of 99% optically pure (−)-2-methyl-1-butanol, α^{20}_D −4.80° (*l*, 1, neat), obtained by fractionation of commercial fusel oil[12] through a Podbielniak Hyper-Cal column.

Electrolysis of (+)-2-methylbutanoic acid. The cathode consisted of a perforated platinum foil cylinder, 1.3 cm. in diameter and 5 cm. high, mounted on a stout platinum wire; the anode was a platinum wire 0.038 cm. in diameter with a surface area of 2.26 cm.^{2} The current during the

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[1b] Present address: U. S. Forest Products Laboratory, Madison, Wisconsin.

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reaction varied from 2.8 to 3.5 amp. and the voltage remained at 19 to 20 V. The reaction was carried out in an ice-water cooled three-neck flask, equipped with a condenser leading to a Dry Ice trap, a Tru-Bore stirrer, and the electrodes. To the flask was added 30 g. of (+)-2-methylbutanoic acid and 9 g. of KOH dissolved in 30 ml. of water. After 193 minutes of current passage another 20 g. of (+)-2-methylbutanoic acid was added and electrolysis was continued for 145 minutes; total 67,000 coulombs or 0.64 Faraday. The light yellow upper layer after separation and drying (sodium sulfate) weighed 11.0 g. One gram of residue was obtained when the 9 g. of liquid in the Dry Ice trap was permitted to warm up to room temperature. The combined fractions were distilled twice, the second time through a small Podbielniak column, and the following principal fractions were obtained:

1. b.p. 96.6-98.0°; 1.09 g.; n_{D}^{25} 1.3977; α_{D}^{27} 0.00° (l, 0.5, neat)
2. b.p. 151.0-161.5°; 1.51 g.; n_{D}^{25} 1.4036; α_{D}^{27} 5.44° (l, 0.5, neat)
3. b.p. 161.5-162.1°; 1.25 g.; n_{D}^{25} 1.4031; α_{D}^{27} 6.31° (*l*, 0.5, neat)

The α-naphthylurethan of fraction 1, after one crystallization from cyclohexane, had m.p. 95.5-96°, undepressed by admixture of the α-naphthylurethan of authentic (±)-2-butanol. Fractions 2 and 3 analyzed for slightly impure butyl methylbutanoate.

Anal. Calc'd for $C_9H_{18}O_2$: C, 68.3; H, 11.4. Found (fraction 2): C, 69.3; H, 11.8. Found (fraction 3): C, 70.5; H, 11.1.

Fractions 2 and 3 were combined and saponified according to the method of Kharasch, *et al.*,[9] by using aqueous KOH in diethylene glycol and heating at 155° for one hour. The reaction mixture was steam-distilled directly. The distillate on thorough drying with sodium sulfate had n_{D}^{25} 1.3953 and α_{D}^{28} 0.00° (*l*, 0.5, neat). The α-naphthylurethan had m.p. 95-96° and did not depress the melting point of the α-naphthylurethan of authentic (±)-2-butanol. Acidification of the residue and steam-distillation gave crude (+)-2-methylbutanoic acid with a rotation of α_{D}^{27} 5.0° (*l*, 0.5, neat).

From the aqueous phase of the electrolysis mixture it was possible to recover 4.4 g. of unchanged (+)-2-methylbutanoic acid, b.p. 93-95° (38 mm.), α_{D}^{27} 8.91° (*l*, 0.5, neat).

(±)-2-Butyl ester of (+)-2-methylbutanoic acid. A mixture of 5.1 g. of (+)-2-methylbutanoic acid, 44 g. of (±)-2-butanol, and 1.0 g. of sulfuric acid was refluxed for 41 hours. Distillation after workup afforded a 57% yield of ester, b.p. 160-163°. Redistillation through a small Podbielniak column afforded a middle cut with n_{D}^{25} 1.4035 and α_{D}^{27} +6.60° (*l*, 0.5, neat).

WM. H. NICHOLS CHEMICAL LABORATORY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.

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The Boron Fluoride Catalyzed Condensation of Pyridine-2-Aldehyde[1]

C. S. MARVEL AND J. K. STILLE

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In an attempt to prepare 2-pyridalacetone by the condensation of pyridine-2-aldehyde and acetone in the presence of boron trifluoride we found that the reaction product was composed of 2-pyridoin and 2-pyridil. The same products were obtained from pyridine-2-aldehyde without the addition of acetone. Hensel[2] has shown that 2-pyridoin can be obtained by the action of acetic acid on pyridine-2-aldehyde. The infrared spectrum of his 2-pyridoin showed weak bands at 1700 and 1710 cm.$^{-1}$ which indicates that he too had obtained some 2-pyridil. Apparently boron fluoride serves as a benzoin reaction catalyst with pyridine-2-aldehyde. The 2-pyridil probably is formed by air oxidation of the pyridoin although the amount of this product formed in the reaction was not increased by passing air through the reaction mixture.

No similar condensation of pyridine-3-aldehyde or pyridine-4-aldehyde with boron fluoride was obtained.

EXPERIMENTAL

In a 500-ml. three-necked round-bottomed flask equipped with a mercury sealed stirrer, a delivery tube, and a drying outlet tube, was added 44 g. (0.4 mole) of freshly distilled pyridine-2-aldehyde. The aldehyde was chilled and saturated with BF_3 by the method of Breslow and Hauser.[3] The red color which quickly formed, turned dark red, and the mixture thickened to a syrupy consistency. The saturation was usually complete after two hours. At the end of this period, the mixture was allowed to come to room temperature and to it was added 46.4 g. of acetone. The reaction mixture retained the deep red color, and upon the addition of an aqueous sodium acetate solution, a bright orange precipitate formed which was removed by filtration, (14.6 g., 34.1%). The same product was obtained with the omission of the acetone, and the yield was not dependent on the sodium acetate solution for hydrolysis, as an aqueous sodium carbonate solution served as well. The product could be recrystallized from alcohol-water or cyclohexane. The final purification step consisted of crystallization from water by dissolving the product in a slightly acidic solution at 90°, and neutralization with base. M.p. 153° (lit. 156°).[2]

Anal. Calc'd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.29; H, 4.78; N, 12.93.

The structure was consistent with that described by other investigators[4,5] and showed infrared bands previously reported.[2,6] However, the broad band from the highly bonded alcohol appeared at 2670 cm.$^{-1}$ Characteristic absorption maxima at 1592 and 1275 cm.$^{-1}$ were also observed.

The filtrate from the 2-pyridoin was extracted with ethyl ether until the extracts no longer contained a yellow coloration. The extracts were combined, dried over magnesium sulfate, and the ether was stripped under reduced pressure. The product was recrystallized from absolute ethanol, yielding 3 g. (7.1%) of light lemon-yellow crystals (m.p. 154°). This material gave double 1,2-dicarbonyl peaks at 1700 and 1710 cm.$^{-1}$, which were present in Hensel's spectrum.[2,3]

Anal. Calc'd for $C_{12}H_8N_2O_2$: C, 67.91; H, 3.80; N, 13.20. Found: C, 67.69; H, 4.07; N, 13.10.

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