An Improved Synthesis of 2-Methylpyrrole

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The elegant new synthesis of 2-formylpyrrole described by Silverstein, *et al.*[1] makes possible a convenient method for the ready preparation of pure 2-methylpyrrole. Early syntheses of 2-methylpyrrole[2–5] are cumbersome and indirect, and in some cases lead to mixtures of isomers which are not easily separated. More recently, the catalytic vapor phase conversion of alkylfurans to the corresponding pyrroles has proved fruitful, although highly specialized equipment is required, and even in the best process[6] conversion of only 28% of 2-methylfuran to 2-methylpyrrole is realized.

Our synthesis, which involves simply the pyrolysis of a mixture of 2-formylpyrrole semicarbazone with potassium hydroxide in a stream of dry nitrogen, is based on a somewhat analogous reaction of Shepard[7] in the thiophene series. It is simple and direct and leads to the production of pure 2-methylpyrrole in 67% yield starting with pyrrole.

EXPERIMENTAL

2-Formylpyrrole semicarbazone. A solution of 60.0 g. of 2-formylpyrrole, prepared by the method of Silverstein,[1] in 500 ml. of 50% aqueous ethanol was added to a 1-l., 3-necked, round-bottomed flask fitted with a mechanical stirrer, a dropping-funnel equipped with a nitrogen inlet, and a reflux condenser. A solution of 90 g. of sodium acetate in 200 ml. of water was added rapidly with stirring under a nitrogen atmosphere. Then a solution of 60.0 g. of semicarbazide hydrochloride in 200 ml. of water was added dropwise. The mixture was heated on a steam-bath with stirring for five minutes whereupon precipitation of the semicarbazone began. Filtration of the ice-chilled mixture afforded a quantitative yield (96.0 g.) of 2-formylpyrrole semicarbazone, m.p. 181–183° with decomposition.

2-Methylpyrrole. A finely ground, intimate mixture of 96.0 g. of 2-formylpyrrole semicarbazone and 100 g. of potassium hydroxide was placed in a 1-l. modified Claisen flask provided with a gas inlet tube for purified nitrogen, an efficient condenser, and an ice-cooled receiver. Then 20 ml. of water was added and the entire mass was stirred to effect thorough mixing. The flask then was heated cautiously with a free flame until no more liquid distilled. The distillate was transferred to a separatory-funnel, the oil layer was removed, the water layer was extracted with four 50-ml. portions of ether, and the combined extracts were dried over Drierite. After removal of the ether, the residue was distilled to give 38.2 g., 74.7%, of pure 2-methylpyrrole, b.p. 147–148° at 740 mm.

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[1] Silverstein, Ryskiewecz, and Chaiken, *J. Am. Chem. Soc.*, **76**, 4485 (1954).

[2] Pictet, *Ber.*, **37**, 2792 (1904).

[3] Harries, *Ber.*, **31**, 44 (1898).

[4] Benary, *Ber.*, **44**, 493 (1911).

[5] Andrews and McElvain, *J. Am. Chem. Soc.*, **51**, 888 (1929).

[6] Bordner, U. S. Patent 2,600,289 (1952).

[7] Shepard, *J. Am. Chem. Soc.*, **54**, 2951 (1932).

A New Primary Resin Acid from *Pinus Caribaea*

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It was observed in this laboratory that, in the course of precipitating the resin acids from the naturally occurring oleoresin by means of their cyclohexylamine salts,[1] higher yields of the amine salts were obtained from the oleoresin of longleaf than from the oleoresin of slash pine.

By evaporating the mother liquor from the amine salt precipitation to a small volume *in vacuo*, dissolving in ether, and extracting with 1% sodium hydroxide an acidic fraction was obtained which contained a residual amount of known resin acids which were removed by dissolving this acidic fraction in acetone and precipitating them as their insoluble butanolamine salts. The acidic material recovered from the mother liquor was further purified by dissolving in a large volume of pentane, shaking with fullers earth, filtering, and recovering. This fraction is amorphous and when obtained from fresh slash gum has a neutralization equivalent of 318 indicating the presence of one atom of oxygen. The carbon and hydrogen analysis also is correct for a molecular weight of 318, $C_{20}H_{30}O_3$. By observing the infrared spectra and running the usual chemical tests, we have not been able to confirm the presence of an oxygen atom, leading us to suspect it could be present as an ether linkage if present at all. The ultraviolet absorption curve showed a single maximum at 233 mμ. The specific absorption coefficient was 50.

Preliminary partition chromatography using an amine as the mobile phase indicated the fraction to be impure. This could be expected since it could neither be crystallized nor distilled. The principal fraction from the chromatographic column could not be crystallized.[2]

All the known resin acids from *P. palustris* and *P. caribaea* have identical infrared absorptions at 5.92 μ and 7.85 μ due to the carboxylic acid group.

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[1] G. E. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 334 (1948).

[2] Further study of this material, including the use of partition chromatography, will emanate from the U. S. Department of Agriculture Laboratory at Olustee, Florida.

In addition each acid has its own characteristic absorption which aids in identifying it. This new acid which we have named caribeic (I), has the common absorptions of a resin acid. Its own strong characteristic absorptions are at 6.1 μ indicating terminal methylenic unsaturation, and at 11.25 μ, apparently due to the presence of an isopropenyl group. A weaker typical absorption is at 10.16 μ. The typical resin acid carbonyl absorption found at 7.85 μ has shifted somewhat in I to 7.9 μ, possibly due to an oxygen linkage.

Ozonolysis of I yielded formaldehyde proving the presence of a terminal methylene group. On hydrogenation at atmospheric pressure one mole of hydrogen was very rapidly absorbed removing the infrared absorption at 10.16 μ. A second mole of hydrogen was more slowly absorbed removing the absorption at 11.25 μ. The possibility remains that there are two terminal methylene groups present. This view is partially supported by the fact that after one mole of hydrogen is absorbed, the absorption at 6.1 μ is reduced proportionately and after two moles are taken up this absorption disappears.

On dehydrogenation with palladinized charcoal at 310° an oil was obtained, the spectra of which was identical with pimanthrene or retene. However, the thought must not be excluded that the original acid contains only two rings, fusing occurring to yield the phenanthrene nucleus on heating with palladium-charcoal.

On heat-treating this acid at 280° a high-melting insoluble material was formed. We believe the presence of caribeic acid in gum rosin contributes generously in making certain commercial derivatives of gum rosin so different from those of wood and tall oil rosins.

The infrared spectra of the mixed rosin acids, precipitated from slash and longleaf gums by means of their cyclohexylamine salts were identical in every respect. However, a comparison of the spectra of the total resin acids present showed the presence of significant amounts of caribeic acid in the slash acids, but none in the longleaf.

It seems evident that caribeic acid is present in the original slash gum in sufficient quantity (*ca.* 3%) to aid in retarding the crystallizing tendency of the gum.

Caribeic acid could represent an additional link between the southern pine and pines from remote parts of the world.

EXPERIMENTAL

Separation of crystalline from non-crystalline acids via amine salts. A. Fresh slash gum (1500 g.) was dissolved in 7 liters of heptane and the solution was filtered, heated to 40°, and 338 g. of cyclohexylamine in 350 ml. of heptane was slowly added with good stirring. The precipitated salts were filtered, washed with solvent, and air-dried. The yield was 1185 g. or 89% of resin acids calculated to be present by titration of an aliquot. The mother liquor was evaporated to a low volume at 50° under a vacuum. The residue was shaken with ether and then the acids were liberated with boric acid. The recovered acidic fraction was taken up in ether, washed with water, and dried over sodium sulfate. After removing the last traces of ether, 110 g. of recovered acid fraction was obtained. Of this fraction 108 g. was dissolved in 450 ml. of acetone and 32 g. of butanolamine (2-amino-2-methyl-1-propanol) in 40 ml. of acetone was added at 40°. Crystals formed at once, but in order to ensure complete removal of the crystalline resin acids, the solution was allowed to stand in the ice-box for several days, when it was filtered and washed with cold acetone; yield 31 g. of salts. The ultraviolet absorption spectrum of the salts indicated the presence of a mixture of abietic and neoabietic acids.

After evaporating the mother liquor from the butanolamine precipitation to a small volume, there was no further precipitation and the acidic material was recovered from the acetone mother liquor with boric acid and ether as described above. The yield of non-crystalline acid was 76 g. The acid number was 170 and the specific rotation was +15° (2% ethanol). Attempts were made to form amine salts that could be crystallized, but all such salts prepared were amorphous and very soluble. All attempts to crystallize the acid were unsuccessful. Finally, the acid was further purified by dissolving it in 64 ml. of heptane and diluting to 1 liter with heptane. A precipitate resulted from which the clear solution was decanted and then shaken with fullers earth. The process was repeated using pentane. From 64 g. of crude acid there was obtained 25 g. of light straw-colored product (I), caribeic acid, which has a specific rotation of +32° (2% in ethanol).

Anal. Calc'd for $C_{20}H_{30}O_3$: C, 75.44; H, 9.49; Neut. equiv., 318.4. Found: C, 75.40: H, 9.58; Neut. equiv., 317.5.

The ultraviolet absorption coefficient, $[\alpha = [\frac{\text{g./l.}}{\text{1cm}}]$ was 50, with a maximum at 233 mμ. Its infrared spectrum was similar to that of the other resin acids and with its own typical absorption at 11.25 mμ described above.

B. Longleaf oleoresin was treated as described in *A* with a yield of resin acid salts of 97% of theory. From the non-crystalline residue no material with an ultraviolet absorption maximum of 233 mμ could be isolated.

Quantitative hydrogenation of I at atmospheric pressure. Compound I (3 g.) was dissolved in 30 ml. of absolute ethanol and 0.1 g. of platinum oxide was added. The apparatus[3] used allowed small quantities of hydrogen to be measured over water at atmospheric pressure. The initial absorption of hydrogen was very rapid, 232 cc. (corr.) (1.04 moles) being absorbed in 15 minutes. At the end of this initial period absorption was slow and at the end of 4 hours 412 cc. (corr.) (1.96 moles) of hydrogen had been absorbed. Under the same conditions abietic acid absorbed 1.06 moles of hydrogen.

After one mole of hydrogen had been absorbed, the infrared absorption at 10.16 μ had disappeared and while the absorption at 6.1 μ was reduced that at 11.25 μ was little effected. After two moles of hydrogen had been absorbed, the absorptions at 6.1 μ and 11.25 μ had disappeared. N.E. 324.

Dehydrogenation of the hydrogenated resin acid (II). The hydrogenated acid (II) (2 moles hydrogen) (3.5 g.) was mixed well with 3.5 g. of 5% palladium-carbon catalyst and heated at 310–320° for four hours. The recovered oils show typical pimanthrene or retene absorptions in the ultraviolet regions.

Ozonization of caribeic acid. The ozonization was carried out as described by Harris and Sanderson.[4] Caribeic acid

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(3) Gatterman and Wieland, *Laboratory Methods of Organic Chemistry*, The MacMillan Company, New York, New York, 1932, page 367.

(4) G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 2080 (1948).

(1.2 g.) was dissolved in 60 ml. of dry ethyl chloride and treated at −60° for two hours with a stream of oxygen containing about 3% of ozone. The ethyl chloride was evaporated over water at room temperature. The ozonide was decomposed in boiling water and the escaping gasses were passed into an aqueous alcohol solution of "dimedon" (5,5-dimethyl-1,3-cyclohexanedione). After standing, needles of the dimedon derivatives of formaldehyde precipitated, m.p. 190.5–191.50°. A mixture melting point showed no depression.

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The Halodecarboxylation of Cyanoacetic Acid

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The current interest in halodecarboxylation[1] reactions is reflected in the number of relevant papers in recent journals.[2] A novel example of this type reaction occurs when cyanoacetic acid (or its potassium salt) is treated with an N-halosuccinimide in water. Dihaloacetonitriles are formed in good yield in an extremely facile manner. This is believed to be the simplest route to these halonitriles.[3,4a,b,c]

Cyanoacetic acid and the N-halosuccinimide are mixed in a molar ratio of 1:2[5] in water (about 100 ml. per 0.1 mole of reactants). Upon stirring for a short time at room temperature, a mildly exothermic reaction ensues with evolution of carbon dioxide. In 10–15 minutes, the clear solution is completely free of solid and has a bottom phase of the dihaloacetonitrile, which may be either separated or extracted from the aqueous phase, dried, and distilled.

In this manner, dibromoacetonitrile and dichloroacetonitrile were obtained from the corresponding N-halosuccinimide in 75% and 60% yields, respectively.

The discussion of mechanism for this transformation is at present somewhat speculative, but some relevant facts are known: the reaction also proceeds essentially as described with potassium cyanoacetate,[6] but fails to occur under these conditions with chloroacetonitrile, and α-cyanopropionic acid or its anion. Such results indicate: (1) that the reaction may proceed *via* the acid anion, the route generally believed taken in similar decarboxylations;[7] (2) that the presumed first intermediate, monohalocyanoacetic acid, does not decarboxylate to a monohaloacetonitrile *prior* to further halogenation;[8] and (3) that α-hydrogen atoms reduced in lability are unreactive in such halodecarboxylations.[9]

The following mechanism is in accordance with such facts.

$$\mathrm{NCCH_2CO_2H} \rightleftharpoons \mathrm{NCCH_2CO_2^{\ominus}} + \mathrm{H^{\oplus}}$$

$$\mathrm{NCCH_2CO_2^{\ominus}} + 2\ \mathrm{X{-}N}\Big\langle \longrightarrow [\mathrm{NCCX_2CO_2^{\ominus}}] + 2\ \mathrm{H{-}N}\Big\langle$$

$$[\mathrm{NCCX_2CO_2^{\ominus}}] \longrightarrow [\mathrm{NCCX_2}]^{\ominus} + \mathrm{CO_2}$$

$$[\mathrm{NCCX_2}]^{\ominus} + \mathrm{H_2O} \longrightarrow \mathrm{NCCHX_2} + \mathrm{OH^{\ominus}}$$

$$\mathrm{H^{\oplus}} + \mathrm{OH^{\ominus}} \longrightarrow \mathrm{H_2O}$$

In an alkaline medium, the carbon dioxide is retained as bicarbonate ion.

EXPERIMENTAL[10]

Materials. The *cyanoacetic acid* and *N-halosuccinimides* were commercial products used as received. *Chloroaceto-*

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[1] This name for the reaction also known as "halogenative decarboxylation" is in accordance with suggestions for nomenclature reported by Patterson, *Chem. Eng. News*, **32**, 4019 (1954).

[2] *Inter alia*, see Grovenstein, Jr., and Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); Grovenstein, Jr., and Theophilou, *J. Am. Chem. Soc.*, **77**, 3795 (1955); Grovenstein, Jr., and Henderson, Jr., *J. Am. Chem. Soc.*, **78**, 569 (1956); Price and Berman, *Am. Chem. Soc. Abst.*, Cincinnati Meeting, March, 1955, p. 12N; Wilt, *J. Am. Chem. Soc.*, **77**, 6397 (1955).

[3] van't Hoff, *Ber.*, **7**, 1382, 1571 (1874), reported the production of dibromoacetonitrile by the action of bromine on cyanoacetic acid. He listed the nitrile as a solid, m.p. 142°. Steinkopf (*loc. cit.*) repeated the work and showed van't Hoff's nitrile to be impure dibromoacetamide, m.p. 153°.

[4] The dihalonitriles have customarily been prepared by a dehydration of the corresponding amide, essentially as described by (a) Bisschopinck, *Ber.*, **6**, 731 (1873); (b) Steinkopf, *Ber.*, **38**, 2695 (1905); **41**, 2541 (1908); and (c) Steinkopf and Bohrmann, *Ber.*, **40**, 1638 (1907). This reaction is troublesome and the yield of pure material in these cases is generally only 25–40%.

[5] The *same* reaction occurs (though in lower yield) when a molar ratio of 1:1 is used. This fact has mechanistic importance (*cf.* footnote 8).

[6] Potassium bicarbonate, rather than carbon dioxide, is produced in this case and the reaction mixture colors considerably.

[7] *Cf.* Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 283–284 and the references cited therein. A *general mechanism* involving cyanoacetate ion is therefore favored by precedent over *separate mechanisms* for the acid and anion, although presumably both undissociated acid and acid anion are present in the systems used here. Separate mechanisms for each case are therefore not precluded.

[8] The production of *dihalo-* and not *trihalo-* acetonitriles when a 1:1 molar ratio of acid and N-haloimide is used also indicates that monohaloacetonitriles are not intermediates. For the existence of such a reaction path would imply that monohaloacetonitriles are halogenated faster than dihaloacetonitriles. Such a rate order is the reverse of that observed in similar reactions such as the haloform reaction or the halogenation of ketones. *Cf.* Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 240–241.

[9] Correspondingly, when activation is present, the reaction is facilitated. Thus malonic acid has recently been converted in 78% yield to dichloroacetic acid *via* the reaction described here (work performed by Mr. A. Danielzadeh and the author).

[10] All melting points and boiling points are uncorrected. Analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.