

27.2 g. (b. p. 102–118° at 21 mm., mainly at 105–110°) consisting of a mixture of phenyl propionate and ethyl α -isopropyl propionylacetate. An ether solution (150 cc.) of this mixture was shaken with ten 50-cc. portions of 10% sodium hydroxide solution, the ether solution dried, and distilled. The residue on fractionation through a twelve-inch Vigreux column yielded 18.3 g. (58% yield based on the sodium triphenylmethyl) of ethyl α -isopropyl propionylacetate, b. p. 107–109° at 21 mm. (b. p. reported in the literature, 107–108° at 21 mm.¹¹). An analysis (calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 68.24; H, 8.12) indicated that the β -keto ester was still contaminated with phenyl propionate. The product (10.6 g.) was hydrolyzed by refluxing for eight hours with a mixture of 30 cc. of glacial acetic acid, 3 cc. of concentrated sulfuric acid and 3 cc. of water. There was obtained 3.3 g. (50% yield) of ethyl isobutyl ketone, b. p. 133–135°¹⁶ (semicarbazone, m. p. 128–129°¹⁶).

t-Butyl Cyanoacetate with Ethylmagnesium Bromide.—*t*-Butyl cyanoacetate was prepared¹⁷ in 32% yield from *t*-butyl α -bromoacetate and potassium cyanide in methanol solution.

*Anal.*¹⁴ Calcd. for $C_7H_{11}O_2N$: N, 9.92. Found: N, 9.67.

t-Butyl α -bromoacetate was obtained in 70% yield by treating *t*-butyl alcohol with α -bromoacetyl bromide in the presence of dimethylaniline.¹⁸

Sixteen grams (0.11 mole) of *t*-butyl cyanoacetate (b. p. 107–108° at 23 mm.) dissolved in 25 cc. of dry ether was added, with stirring, during one hour to 0.25 mole of cold (0°) ethylmagnesium bromide solution. At first, addition of the nitrile caused the formation of a precipitate and the evolution of gas. The mixture was stirred at room temperature and then allowed to stand for twelve hours. On working up the reaction mixture, the products obtained consisted of a mixture boiling over a very wide range with considerable tarry material.

(16) Douris, *Compt. rend.*, **157**, 57 (1913).

(17) The procedure was similar to that used by Noyes for the preparation of ethyl cyanoacetate, *THIS JOURNAL*, **26**, 1545 (1904).

(18) For the preparation of *t*-butyl acetate by this method, see Norris and Rigby, *THIS JOURNAL*, **54**, 2097 (1932).

Methyl Ethyl Ketone with Ethyl Carbonate.—Methyl ethyl ketone (14.4 g., 0.2 mole) (b. p. 80°) was added to 0.2 mole of sodium triphenylmethyl solution cooled in a bath at -5° . The color changed immediately to a light orange. After twenty seconds 23.5 g. (0.2 mole) of ethyl carbonate (b. p. 125.5–126°) was introduced. The bottle containing the mixture was shaken vigorously and allowed to stand in the cold bath, after which it was allowed to warm up (1 hour) to room temperature (30°). The reaction mixture was worked up in the usual manner, and upon fractionation of the products, first at atmospheric pressure and then *in vacuo*, there was obtained 2.4 g. of unreacted ketone (b. p. 75–85°), 11.7 g. (50% recovery) of ethyl carbonate (b. p. 122–127°) and 3.9 g. of 3-methyl heptene-3-one-5, b. p. 60–75° at 20 mm., mainly at 65–70° (reported b. p. 66–68° at 20 mm.).¹⁹ The ketone was converted into the semicarbazone, m. p. 113–114°; reported m. p. 114–115°.¹⁹ The 65–70° fraction on redistillation gave a small fraction which gave a positive ferric chloride test indicating the presence of some β -keto ester.

Summary

1. A study has been made of the use of phenyl esters as reagents for the acylation of the anions of certain alkyl esters.

2. Ethyl propionylacetate has been prepared by the acylation of the anion of ethyl acetate with *p*-diphenylpropionate.

3. *n*-Amyl propionylacetate and ethyl α -isopropyl propionylacetate have been prepared from phenyl propionate and the anions of *n*-amyl acetate and of ethyl isovalerate, respectively.

4. Unsuccessful attempts were made to prepare *t*-butyl propionylacetate from *t*-butyl cyanoacetate and ethylmagnesium bromide, and ethyl propionylacetate from the sodium enolate of methyl ethyl ketone and ethyl carbonate.

(19) Bodroux and Taboury, *Compt. rend.*, [11] **149**, 422 (1909).

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Chemical Constitution and the Tanning Effect. I. Simple Esters and Polyesters of Gallic Acid

BY ALFRED RUSSELL AND W. G. TEBBENS, JR.

Leather is the imputrescible substance that is obtained through treatment of easily putrescible animal protein by various materials. The tanning effect of certain metallic salts (chromium, iron, zirconium, etc.), of aldehydes (chiefly formaldehyde), of various drying oils and, most important of all, natural organic tanning materials, is well established. However, up to the present, no serious attempt has been made to relate the

characteristic leather forming properties of any of these with their chemical constitution. It is now proposed to investigate the relation between chemical constitution and the tanning effect of the natural organic tannins through the preparation of relatively simple compounds of known constitution that have tanning properties and produce leather similar to "vegetable" leather in quality. "Vegetable" leather is very distinctive in charac-

sulfate. After filtering, the solution was taken to dryness on a steam-bath under reduced pressure and the residue was taken up in anhydrous acetone, filtered, and again reduced to dryness. The tan friable solid which weighed 57.4 g. (93%) was finally dried in an Abderhalden pistol at 57° over phosphorus pentoxide and paraffin at 1 mm. pressure for five days, m. p. 72° (sintered). The acetyl compound was tasteless and odorless. It gave no color with ferric alum solution and was insoluble in water. *Anal.* Calcd. for $C_{70}H_{62}O_{40}$: C, 54.5; H, 4.05. Found: C, 54.4; H, 4.08.

***d*-Arabitol Pentagallate.**—30.8 g. of penta-(triacetyl-galloyl)-*d*-arabitol was taken up in 60 cc. of acetone and an oxygen-free stream of nitrogen passed into the solution while 330 cc. of 1 *N* sodium hydroxide solution was added with mechanical stirring at such a rate that the reaction temperature was maintained at 0° (ice-salt-bath). The gummy mass which separated was brought into solution by the addition of 100 cc. of acetone. Stirring was continued under a nitrogen atmosphere for two and one-half hours at 0°, 330 cc. of cold 1 *N* sulfuric acid was added, and the acetone was removed from the solution under reduced pressure. The residual solution was extracted with neutral ethyl acetate and the solvent layer dried over sodium sulfate, filtered, and concentrated to dryness under reduced pressure. The golden colored, friable hygroscopic glass produced was suspended in chloroform and then filtered. Repetition of this suspension gave 20 g. of a water soluble product. After drying at 57° over phosphorus pentoxide and paraffin at 1 mm. pressure for five days the color was a very pale tan, m. p. 83° (sintered). This product gave a blue-black color with dilute ferric alum solution. *Anal.* Calcd. for $C_{40}H_{32}O_{26}$: C, 52.6; H, 3.53. Found: C, 52.5; H, 3.52.

Hexa-(triacetylgalloyl)-sorbitol.—The method employed by Fischer¹ for the corresponding mannitol derivative was applied to sorbitol. The white, odorless tasteless product

gave no coloration with ferric alum, m. p. 106° (sintered). After drying in an Abderhalden pistol as described for the derivative of *d*-arabitol it was converted to the gallic ester.

Sorbitol Hexagallate.—18.5 g. of hexa-(triacetyl-galloyl)-sorbitol was treated by the method employed by Fischer¹ for the production of mannitol hexagallate to give 8.6 g. of gritty, white solid which was dried in a pistol as indicated above (m. p. 76° sint.). It has an astringent taste, was soluble in water and in neutral ethyl acetate, but was insoluble in petroleum ether. It gave a blue color with ferric alum. *Anal.* Calcd. for $C_{48}H_{38}O_{30}$: C, 52.5; H, 3.49. Found: C, 52.6; H, 3.51.

The experimental tannages were carried out on pickled calf-skin using the following standard procedure. A piece of selected pickled calfskin (8" × 4", wt. 25-35 g.), covered with three times its weight of 4% aqueous sodium chloride was treated with 25% of its weight of the material to be tested and the whole was rotated slowly in a bottle for from twenty-four to forty-eight hours. The piece of skin was now washed with water to a pH of 4.5, dried and compared as to color, feel, texture, flexibility and fullness with a similar piece tanned with gallotannin.

Summary

A number of simple esters and polyesters of gallic acid have been prepared and tested for leather forming properties. None of the simple esters showed any such properties. However, leather forming properties were shown by the polyesters of gallic acid with various polyhydric alcohols. The leather forming properties of the members of the latter series were poor but definite, and seemed to improve on ascending the series.

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The Catalytic Properties of Charcoal. IV. Factors Influencing the Indophenol Reaction^{1,2}

By CLAUDE SCHWOB, WITH JOHN E. BIEGNER, KENNETH J. CARSON AND GEORGE V. SCOTT

The indophenol reaction has been used in this Laboratory to investigate the oxidase and peroxidase action of charcoal.^{3,4} In this reaction indophenol is formed by the oxidation of a mixture of *p*-phenylenediamine and α -naphthol by oxygen or hydrogen peroxide in the presence of charcoal. It was found that when equimolar amounts of *p*-phenylenediamine and α -naphthol are used, the yield of indophenol diminishes after the first

minute. Moreover, in later work, considerable difficulty was encountered in duplicating results.

In an attempt to clear up these points, and in order to gain further knowledge of the mechanism of the reaction, four modes of attack were employed: (a) variation in the concentrations of the individual reagents, (b) study of the pH during the course of the reaction, (c) effect of catalyst poisons and (d) study of the factors affecting the recovery of indophenol.

1. **Reagent Concentrations.**—Previous evidence⁴ indicated that excess reagents are responsible for the drop in the yield of indophenol after

(1) Paper III, *THIS JOURNAL*, **60**, 2483 (1938).

(2) Presented in part at the 102nd meeting of the American Chemical Society, Atlantic City, N. J., September, 1941.

(3) Schwob, *THIS JOURNAL*, **68**, 1115 (1936).

(4) O'Brien, Tkac and Schwob, *ibid.*, **60**, 2480 (1938).