TABLE III

IONIZATION CONSTANTS OF PICRIC ACID IN SOLVENTS OF THE TYPES R-CO-CH_3 AND RCN

Solvent	Dielectric constant, 20°	Specific conductance at 25° × 10^7	Electron-sharing ability of R, (3)	$K \times 10^4$ of picric acid
Methyl ethyl ketone	17.8	1.65	−1.45	1.98
Acetone	21.5	1.46	−1.40	1.38
Acetophenone	18.1	0.97	+4.2	0.15
Propionitrile	27.0	3.00	−1.45	4.25
Benzonitrile	26.5	0.66	+4.2	1.02

On the other hand, in both types of solvent as the electron-sharing ability of the radical increases the ionizing power decreases. The order of magnitude of the constants found in the nitriles is the same as that for those found in the ketones. This is to be expected from the fact that the ability of the —CN group to associate with active hydrogens is about the same as that of the carbonyl group.

Summary

The conductances and the ionization constants of picric acid in acetone, methyl ethyl ketone, acetophenone, propionitrile and benzonitrile have been determined. The ionization constants depend on the electron-sharing ability of the radicals in the solvent molecule rather than on the dielectric constant of the solvent.

AMES, IOWA RECEIVED AUGUST 20, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Electrolytic Preparation of Ethyl Glyoxylate[1]

BY WILLIAM OROSHNIK AND PAUL E. SPOERRI

During the course of investigations concerning the synthesis of amino-heterocyclics a ready source of pure ethyl glyoxylate became necessary. The literature revealed only one preparation with a reported yield, that of Traube,[2] who reduced ethyl oxalate with sodium amalgam in absolute ethanol obtaining 20% yields of the alcoholate of ethyl glyoxylate. Since a German patent[3] claims "very good" yields of glyoxylic esters are obtained by the electrolytic reduction of oxalic esters in aqueous sulfuric acid, it was decided to investigate the electrolytic method as a source of ethyl glyoxylate.

Ethyl oxalate was reduced to ethyl glyoxylate in ethanol, ethanol–water, and water media at mercury, lead, and lead amalgam cathodes, using sulfuric acid as the electrolyte. The best yields, 53 and 50%, were obtained in ethanol solution at lead amalgam and mercury cathodes. When aqueous alcohol was used the yield dropped in proportion to the amount of water present, and the poorest yields were obtained in purely aqueous solution.

The ethyl glyoxylate was obtained as the alcoholate. This was converted into the free aldehyde in 98% yields, by means of phosphorus pentoxide by modifying the method of Traube.[2]

Experimental

Apparatus.—Two types of cells were used. The first cell consisted of a mercury cathode, porous porcelain diaphragm, and a circular lead anode in the porcelain cup. The second cell varied only in that the cathode was a circular strip of lead which surrounded the porous cup. C. P. mercury and C. P. lead (National Lead Company) were used as cathodes. The lead amalgam cathode was made by allowing a clean lead cathode to stand in a saturated mercuric chloride solution for an hour, washing it free of solution, and drying and polishing with a dry cloth.

Electrolysis.—The current used in this work was 110 d. c. After the apparatus was assembled and placed in an ice–salt-bath, the catholyte was put in and the anode chamber was filled with 30% aqueous sulfuric acid to the same level. With the catholyte at 10°, the current was turned on, and on becoming constant, was adjusted to the desired value. The voltage drop across the cell was adjusted by varying the distance between anode cup and cathode. The temperature of the catholyte was kept at 10–15° in all experiments.

In using the lead amalgam and mercury cathodes, and with ethanol solutions, there was no escape of hydrogen until about three-quarters of the theoretical amount of current was consumed. With the lead cathode there was a constant escape of hydrogen.

Electroendosmosis was prevalent in all cases, a total of 60 cc. of anolyte migrating to catholyte every four hours.

(a) Isolation of Product from an Alcohol Solution.—The reduction mixture, neutralized with an excess of sodium bicarbonate, was filtered free of solids and made acid to litmus with oxalic acid. (When alcoholic sodium hydroxide or sodium ethoxide are used to neutralize the sulfuric acid the resulting sodium sulfate is very slimy and extremely difficult to filter off). Benzene equal in volume to half the solution was added and the solution was frac-

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[1] This paper was presented at the Baltimore meeting of the American Chemical Society, April, 1939. Original manuscript received April 9, 1940.

[2] Traube, *Ber.*, **40**, 4953 (1907).

[3] German Patents 163,842, 210,693.

tionally distilled at 40–60 mm., using a one-meter column packed with glass helices and equipped with a dephlegmator. When this fractionation is carried out without first acidifying the solution or is carried out at atmospheric pressure, tarry resinous products result.

The residue from the benzene–alcohol distillation was taken up with dry ether, the ether evaporated and the crude ester fractionated at atmospheric pressure, collecting the fraction coming over at 134–138°.

The aldehyde was identified by its boiling point, 136°, its phenylhydrazone, m. p. 131°, and its semicarbazone, m. p. 218°.

(b) **From an Alcohol–Water or Water Solution.**—The solution was neutralized with sodium bicarbonate, and the alcohol removed under vacuum. The aqueous solution, saturated with sodium sulfate, was extracted ten times with ethyl acetate or formate. The rest of the procedure was similar to that under (a).

Summary of Results of Electrolysis.—(1) With a mercury cathode and a catholyte consisting of 300 ml. of 95% alcohol, 90 g. of sulfuric acid and 100 or 200 g. of ethyl oxalate, the yields varied between 38 and 50% using voltages between 9 and 13 and current densities between 7 and 12.1. (2) Using the same conditions but substituting 300 ml. of 50% solution of alcohol solution for the 95% alcohol, resulted in a drop in the yields to 33%. (3) If the alcohol is entirely omitted from the catholyte, the other conditions being varied as in part 1, the yields drop to 6 to 9%. (4) With a lead cathode and a catholyte consisting of 300 ml. of 95% alcohol, 90 g. of sulfuric acid and 100 g. of ethyl oxalate, the voltage being 7 and the current density 6.3, the yield was 35%. (5) Duplicating these conditions but substituting a lead amalgam cathode, the yields varied between 40 and 53%, the lower yield being obtained when 200 g. of ethyl oxalate was used and the higher yield when only 100 g. was used. In all cases the amount of current used was 10% in excess of theory.

De-alcoholation of the Hemi-acetal.—To 44 g. of ethyl glyoxylate alcoholate, cooled to 0°, was added under very good cooling and agitation, 14.2 g. of phosphorus pentoxide. The mixture, after coming to room temperature, was heated on a steam-bath until two liquid layers remained and no visible solid was present (three to four hours). The mixture was then distilled, the portion coming over up to 132° being collected. On redistillation 30 g. of material boiling at 129–130° was obtained (98%).

The free aldehyde was identified by its boiling point, 129–130°, its phenylhydrazone, m. p. 131°, and its semicarbazone, m. p. 218°.

Summary

1. A method for preparing ethyl glyoxylate alcoholate in good yields by the electrolytic reduction of ethyl oxalate in non-aqueous media has been developed.

2. Ethyl glyoxylate, free aldehyde, has been prepared in almost quantitative yields from its alcoholate by means of phosphorus pentoxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Reactions of β-Pinene. I. With Selenium Dioxide in Various Solvents[1]

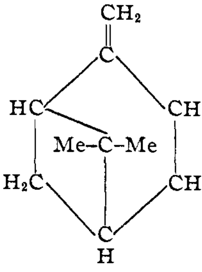
BY W. DAVID STALLCUP AND J. ERSKINE HAWKINS

The action of selenium dioxide on β-pinene was originally carried out by Dupont, Allard and Dulou[2] who identified the steam volatile oil as pinocarvone.

The present investigation was undertaken in order to conduct a more critical examination of the steam volatile products of the oxidation.

β-Pinene (I) was oxidized by selenium dioxide in eight solvents and in the absence of any solvent for periods of time varying from three to one hundred and sixty-eight hours and the resulting steam volatile oil was carefully examined.

The oil was found to consist of pinocarvone (II) and carvopinone (III) and was not pure pinocarvone as indicated by Dupont, Allard and Dulou.



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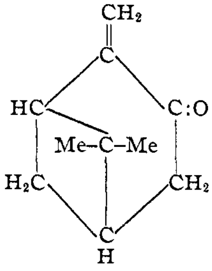

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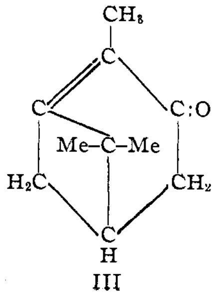

III

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[1] This material will be included in a thesis to be submitted to the Graduate Council of the University of Florida by W. David Stallcup in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Dupont, Allard and Dulou, *Bull. soc. chim.*, **53**, 599 (1933).