Summary and Conclusions

1. A study has been made of the methane fermentation of 45 substances, including carbohydrates, alcohols, acids, aldehydes, ketones, etc. For this work approximately 1900 separate feedings, 700 gas analyses and 800 analyses of culture medium were made.

2. It has been shown that the fermentation is an anaerobic oxidation-reduction reaction involving water and catalyzed by bacteria. Carbon dioxide and hydrogen appear to be primary products, the hydrogen combining with a portion of the carbon dioxide to give methane and water. Organic acids are indicated to be intermediates in the reaction.

3. This reaction follows a simple equation in which the number of molecules of water necessary for the reaction and the amounts of carbon dioxide and methane produced bear a mathematical relation to the formula of the compound undergoing fermentation.

4. Thermodynamic calculations show that if water is the only source of oxygen beside that in the compound undergoing fermentation, carbon dioxide and methane are the end-products that might be expected since the greatest decrease in free energy occurs with their formation.

5. The reaction proceeds in the same manner at both mesophilic (33–35°) and thermophilic (58–60°) temperatures.

URBANA, ILLINOIS

RECEIVED OCTOBER 17, 1932
PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DELAWARE]

The Condensation of Oxalic Esters with Benzyl Cyanide

BY GLENN S. SKINNER

Recently the methyl ester of phenylcyanopyruvic acid was prepared by the action of dimethyl oxalate on benzyl cyanide using sodium in absolute ether as the condensing agent. This compound had previously been made by Bougault[1] using a different procedure but no analysis was reported. Also in view of the fact that it melts 15° lower than the well-known ethyl ester it was examined with the result that the analysis, molecular weight and chemical behavior definitely show it to be the compound indicated. Preparation of the higher homologs including the *n*-octyl ester now reveals the fact that the esters with alkyl groups containing an even number of carbon atoms invariably melt higher than the preceding or succeeding member.

The condensation of methyl oxalate with sodium in absolute ether proceeds so slowly that approximately three weeks are required for the reaction to go to completion. The reaction of the higher homologs, however, proceeds so rapidly that the reaction mixture must be efficiently cooled. It was observed that the crude odd alkyl phenylcyanopyruvic

---

[1] Bougault, *J. Pharm. Chim.*, **10**, 309 (1914).

esters are less intensely colored than those with an even number of carbon atoms in the alkyl groups. The last trace of color can be removed by distillation and subsequent crystallization.

TABLE I

PHYSICAL PROPERTIES OF PHENYLCYANOPYRUVIC ESTERS

Ester	M. p., °C.	Difference	Yield, %	Nitrogen, % Found	Nitrogen, % Calcd.	B. p., °C.	Mm.
C_1	115		90	6.94	6.90	152–154	3
C_2	130	15	78			158–160	4
C_3	93	−37	65	6.02	6.06	161–163	3
C_4	95	2	55	5.68	5.71	167–169	3
C_5	88	−7	72	5.45	5.41	173–175	3
C_6	94	6	69	5.19	5.13	181–183	4
C_7	91.5	−2.5	48	4.72	4.81	200–205	8
C_8	97.5	6.0	51	4.54	4.59	195–197	2

This difference in reactivity of methyl oxalate is undoubtedly due in part to the greater insolubility of the resulting sodium derivative in ether. A crust of solid forms on the surface of the sodium in this case and at the completion of the reaction the product is fully precipitated. The surface of the sodium remains clean as it reacts with the esters of higher molecular weight. This view is further supported by the fact that the condensation of the methyl ester proceeds normally with sodium methoxide in methyl alcohol wherein there is no separation of the sodium salt.

In view of the incompleteness of the data in the literature samples of the corresponding oxalic esters were prepared and their physical constants determined as shown in Table II. It is evident that here the odd alkyl esters uniformly tend to melt higher than would be expected. The C_7 member melts higher than the C_6 or C_8 member. The melting point aberrations are therefore precisely opposite in the two series. The odd alkyl esters of succinic acid show an even greater tendency to melt higher than the even alkyl esters.[2] From other available data also it appears that the melting point variation of esters of monobasic paraffin acids is the

TABLE II

PHYSICAL PROPERTIES OF NEUTRAL OXALIC ESTERS

Ester	M. p., °C.	Difference	B. p., °C. (mm).	n_D^{20}	n_D^{25}	d^{20}	d^{25}	η_0	η_{20}
C_2	−40.2	−94.5		1.4101	1.4078	1.0790	1.0711	0.0287	0.0204
C_3	−46.3	− 5.1	78–80 (3)	1.4169	1.4150	1.0211	1.0125	.0465	.0279
C_4	−30	15.3	95–97 (2)	1.4234	1.4211	0.9888	0.9821	.0583	.0340
C_5	−12.8	18.2	131–132 (5)	1.4302	1.4281	.9722	.9659	.0857	.0437
C_6	− 9.0	3.8	135–136 (2.5)	1.4331	1.4312	.9523	.9457	.1303	.0576
C_7	12.5	21.5	142–144 (2)	1.4372	1.4352	.9393	.9352		
C_8	11.2	− 1.3	167–169 (3)	1.4404	1.4389	.9293	.9254		

Acknowledgment is made to Mr. R. B. Gibney for assistance in securing these data. The toluene thermometer was checked against the melting point of ice, carbon tetrachloride (−22.9°), and chlorobenzene (−45.2°).

---

(2) Coutzen-Crowet, *Bull. soc. chim. Belg.*, **35**, 165–196 (1926); Timmermans, *ibid.*, **36**, 502–518 (1927).

reverse of that for esters of paraffin dibasic acids. The phenylcyanopyruvic esters offer no exception to this relationship.

The experience gained in preparing a variety of oxalic esters has shown that a modification of Cahours' method[3] of heating oxalic acid with primary and secondary alcohols may give yields as high as 95 and 85%, respectively. Using *n*-butyl and higher boiling alcohols the reaction is suitably conducted under diminished pressure such that the temperature of the reaction mixture is 70–90° while the water distils through a fractionating column. Nearly all of the alcohol is thereby returned avoiding the use of a very large excess otherwise necessary to carry the reaction to completion.

Experimental

***n*-Propyl Oxalate.**—This ester was made by a slight modification of the procedure employed by Jewell and Butts for the ethyl ester. The mixture was heated three hours, allowing the temperature to rise gradually from 90 to 105°. The yield was 91% of the theoretical. The sample used showed a constant melting point of −46.3°. Very careful fractionation was necessary to remove small amounts of both lower and higher boiling impurities.

***n*-Butyl Oxalate.**—One liter of *n*-butyl alcohol and 500 g. of hydrated oxalic acid were heated in an oil-bath four hours allowing the temperature to rise slowly from 90 to 105°. The mixture was then distilled under slightly reduced pressure through a fractionating column with the bath at 50–60°. The distillation was interrupted after 150–175 cc. of distillate had been obtained and the residue was heated for two hours. It was again distilled as long as water separated in the distillate. *n*-Butyl alcohol (500 cc.) was added to the residue which was heated for three hours and distilled as before. The yield of butyl oxalate boiling at 95–100° (2 mm.) was 762 g. or 95% of the theoretical. The melting point of the sample used in the experiments changed 0.1° when fractionally frozen.

***n*-Hexyl Oxalate.**—Sixty-three grams (0.50 mole) of hydrated oxalic acid and 123 g. (1.20 moles) of *n*-hexyl alcohol were heated under diminished pressure in a flask provided with a good column. Water distilled rapidly under a pressure of 65 mm. with the temperature of the bath initially at 70°. After heating for one-half hour, all of the oxalic acid had dissolved while the bath temperature had been allowed to rise to 75° and the pressure to 90 mm. by means of a capillary T in the vacuum line. The mixture was heated for one and one-half hours longer under these conditions, one-half hour at 100° under atmospheric pressure, and finally at 100° (30 mm.) until no more hexyl alcohol distilled. The yield of *n*-hexyl oxalate, b. p. 135–137° (2.5 mm.) was 116 g. or 90% of the theoretical. The *n*-hexyl alcohol recovered amounted to 18 g. The ester melted constantly at −9.0°.

***n*-Pentyl, *n*-Heptyl and *n*-Octyl Oxalates.**—These esters were prepared by the method described for *n*-hexyl oxalate, the pressure being regulated so that the reaction proceeded smoothly to completion at a temperature of 70–80°. The yields were, respectively, 89, 86 and 81% of the theoretical. The samples taken for observations were fractionally frozen until the m. p. changed not more than 0.1° (Table II).

Methyl Phenylcyanopyruvate.—To 14 g. of sodium wire covered with 300 cc. of absolute ether was added a mixture of 65.0 g. of benzyl cyanide and 64.7 g. of dimethyl oxalate. No apparent reaction took place after the mixture had stood for several days. One cc. of methyl alcohol was added, whereupon a yellow crust formed very slowly on the sodium. After standing for three weeks the reaction was complete. The salt was de-

---

[3] Cahours, *Compt. rend.*, **83**, 693 (1876); Jewell and Butts, THIS JOURNAL, **53**, 3560 (1931).

composed with cold dilute sulfuric acid. The yield of the crude yellow crystalline product was 101.5 g. or 90% of the theoretical. The separation of the colored compound is effected by extraction of the ester with hot ligroin. The weight of this impurity was 2 g. If the snow-white product is desired the material is distilled *in vacuo* and crystallized from ligroin, benzene, or methyl alcohol; m. p. 115° (corr.).

Molecular weight. (Benzene, b. p. method) 213. Calcd.: 203. *Anal.* Calcd. for $C_{11}H_9O_3N$: C, 65.00; H, 4.46; N, 6.90. Found: C, 65.07; H, 4.67; N, 6.94.

To a solution of 32.3 g. of methyl oxalate in 33.2 g. of benzyl cyanide was added a hot solution of 15.0 g. of sodium methoxide in 70 cc. of absolute methyl alcohol with stirring. After standing overnight the alcohol was evaporated and the residue was treated with ice-cold dilute sulfuric acid in a manner to secure quick mixing. The crude crystalline product separating from hot ligroin amounted to 38.5 g. or 69% of the theoretical.

The pure substance was characterized by the spontaneous decomposition of its aqueous alkaline solution to benzyl cyanide and sodium acid oxalate, the latter being identified by analysis for sodium and water of crystallization. Five grams of the substance refluxed for ten hours with 85 cc. of 10% sulfuric acid yielded 1.7 g. of pure phenylpyruvic acid (from benzene). It was also converted to the ethyl ester by refluxing with one equivalent of sodium hydroxide in absolute ethyl alcohol followed by an excess of hydrogen chloride.

Homologous Phenylcyanopyruvic Esters.—These esters were made according to a modification of the procedures for the preparation of the ethyl ester.[4]

The details for the *n*-propyl, *n*-butyl, *n*-hexyl, *n*-heptyl and *n*-octyl esters are essentially as described for the *n*-amyl ester. Benzyl cyanide (0.278 mole) was dissolved in *n*-amyl oxalate (0.274 mole). Approximately ten grams of the solution was mixed with 150 cc. of absolute ether which covered 6.5 g. (0.282 at.) of sodium ribbon. The ether soon assumed a golden-yellow color and usually within a half hour the reaction was proceeding freely. The flask was fitted to a reflux condenser protected from moisture and was cooled with finely crushed ice. The remainder of the solution was added slowly through a dropping funnel. After all had been added and the sodium was dissolved the contents of the flask were thoroughly mixed if necessary and allowed to stand two days at room temperature. The reaction mixture was cooled in ice and thoroughly shaken with dilute sulfuric acid. After drying with anhydrous sodium sulfate, most of the ether was removed on the water-bath. The remainder together with amyl alcohol, unreacted benzyl cyanide, and amyl oxalate was removed rapidly under diminished pressure. The residual heavy oil was transferred to a beaker while hot, stirred as it solidified, filtered with suction to remove any adhering oil and crystallized from hot ligroin.

A product possessing the proper melting point may be obtained in this manner, but if a snow-white product is desired it is necessary to continue the distillation under greatly reduced pressure and then recrystallize. Usually two crystallizations from hot ligroin are sufficient if the product is carefully washed with petroleum ether. It is better to isolate the crude heptyl and octyl derivatives before distilling them to avoid undue decomposition.

Summary

The preparation and properties of the C_1–C_8 *n*-alkyl esters of oxalic and phenylcyanopyruvic acid have been studied. It is shown that the alternate effect of even and odd alkyls upon the melting temperature is reversed in the two series.

NEWARK, DELAWARE

RECEIVED OCTOBER 19, 1932
PUBLISHED MAY 6, 1933

---

[4] Erlenmeyer, Jr., *Ann.*, **271**, 172 (1892); Hessler, *Am. Chem. J.*, **39**, 78 (1908).