



Fig. 2.

apparently represents a constant value. The acid groups open up slightly more until 11.7% of a monobasic acid is available. While it is of

course impossible to evaluate the dissociation constants of lecithin with such data, they do indicate that the lecithin-cephalin mixture has a somewhat more acid than basic reaction which is in keeping with the electrophoretic measurement of an isoelectric point of 3.73.

Summary

1. Lecithin-cephalin mixtures have been prepared from eggs.
2. The importance of the effect of cephalin upon the isoelectric point has been emphasized and the isoelectric point has been plotted as a function of the amino nitrogen content. The curve has been extrapolated to zero amino nitrogen content and yields an isoelectric point of 6.4 for lecithin.
3. The change of the isoelectric point with time has been studied.
4. Titration curves for lecithin suspensions are reported.

ST. PAUL, MINNESOTA RECEIVED DECEMBER 30, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WESLEYAN AND HARVARD UNIVERSITIES]

Semicarbazones of Certain Ketones

BY HERBERT S. RHINESMITH

Certain ketones of the ethyl, methyl and propyl series have been prepared in order that the melting points of their semicarbazones might serve to identify certain degradation products obtained during work now under way in the Hall Laboratory.

Experimental

5-Carbomethoxyheptanone-2.—Thirty-four grams of ethyl ethylmalonate was dissolved in 50 ml. of absolute ethyl alcohol and mixed with 12.0 g. of methyl vinyl ketone.¹ Addition of 5 drops of 10% sodium ethoxide caused a vigorous reaction, and after standing one hour at room temperature the solution was acidified and extracted with ether. The latter, dried over sodium sulfate and distilled, yielded 18.5 g. of the dibasic ester, 5,5-dicarbomethoxyheptanone-2.

Anal. Calcd. for $C_{13}H_{22}O_5$: C, 60.5; H, 8.5. Found: C, 60.8; H, 8.8.

Anal. Semicarbazone. Calcd. for $C_{14}H_{25}O_5N_3$: C, 53.3; H, 7.9. Found: C, 52.9; H, 8.2.

This ester upon saponification with cold, dilute alcoholic potassium hydroxide yielded the acid ester, 5-carboxy-5-carbomethoxyheptanone-2, as a colorless oil.

(1) Obtained through the courtesy of W. H. Carothers, du Pont Experimental Station, Wilmington, Delaware.

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.4; H, 7.8. Found: C, 57.4; H, 8.2.

Anal. Semicarbazone. Calcd. for $C_{12}H_{21}O_5N_3$: C, 50.2; H, 7.3. Found: C, 50.2; H, 7.6.

On treating the dibasic ester with hot, concentrated alcoholic potassium hydroxide, the potassium salt of the dibasic acid separated in tiny white flakes. Subsequent acidification and extraction with ether yielded a pale yellow oil which in turn evolved carbon dioxide at 130°, to form the monobasic acid, 5-carboxyheptanone-2.

Anal. Calcd. for $C_9H_{16}O_5$: C, 60.8; H, 8.9. Found: C, 60.5; H, 9.3.

Anal. Semicarbazone. Calcd. for $C_9H_{17}O_5N_3$: C, 50.2; H, 7.9. Found: C, 50.2; H, 8.4.

This acid readily formed the desired methyl ester upon standing for four hours at 0° in a solution of absolute methyl alcohol saturated with dry hydrogen chloride.

Anal. Calcd. for $C_9H_{16}O_5$: C, 62.8; H, 9.3. Found: C, 63.0; H, 9.6.

Anal. Semicarbazone. Calcd. for $C_{10}H_{20}O_5N_3$: C, 52.4; H, 8.3. Found: C, 52.5; H, 8.9.

5-Ethylheptanone-3.—Phosphorous tribromide (51 g.) was added dropwise to 57 g. of 2-ethylbutanol-1 and the solution was warmed for one hour. The oil layer on exhaustive fractional distillation yielded 52 g. of crude 1-bromo-2-ethylbutane, b. p. 144–145° and n_D^{20} 1.4498. Of this, 47 g. refluxed for twelve hours with 42 g. of sodium

cyanide in 45 ml. of 50% alcohol yielded 8.0 g. of crude 2-ethylbutyl nitrile, b. p. 164–166°. This was refluxed for three hours with 20 g. of ethylmagnesium bromide in an atmosphere of nitrogen. The reaction mixture, decomposed with ice water, strongly acidified with sulfuric acid and steam distilled, gave 4.5 g. of an oil, b. p. 98–100° at 50 mm. and 171–173° at 74.5 mm., characterized by its semicarbazone.

Anal. Calcd. for $C_{10}H_{21}ON_3$: C, 60.3; H, 10.5. Found: C, 60.5; H, 10.2.

The ketone from hydrolysis of the semicarbazone was distilled: n_D^{20} 1.4237.

Anal. Calcd. for $C_8H_{17}O$: C, 76.1; H, 12.7. Found: C, 75.8; H, 13.0.

5-Methylhexanone-3.—This ketone was prepared by adding 25 g. of isovaleraldehyde to 39 g. of ethylmagnesium bromide and oxidizing the resulting secondary alcohol (10 g.) with chromic acid solution. Semicarbazone: plates from methyl alcohol.

Anal. Calcd. for $C_8H_{17}ON_3$: C, 56.1; H, 9.9. Found: C, 55.9; H, 10.0.

3-Methylhexanone-2.—For preparation of this ketone see Clarke² and Jones.³ Semicarbazone: plates from petroleum ether.

Anal. Calcd. for $C_8H_{17}ON_3$: C, 56.1; H, 9.9. Found: C, 55.9; H, 10.2.

4-Methylhexanone-2.—For preparation of this ketone see Kohler⁴ and Clarke.⁵ Semicarbazone: white needles from water.

Anal. Calcd. for $C_8H_{17}ON_3$: C, 56.1; H, 9.9. Found: C, 56.2; H, 10.0.

Semicarbazone of 5-Methylhexanone-2.—This semicarbazone crystallizes from ether in leaflets, m. p. 146–147° rather than 141°.⁶

(2) Clarke, *THIS JOURNAL*, **33**, 529 (1911).

(3) Jones, *Ann.*, **226**, 293 (1884).

(4) Kohler, *J. Chem. Soc.*, **38**, 526 (1911).

(5) Clarke, *THIS JOURNAL*, **30**, 1150 (1908).

(6) Darzens, *Compt. rend.*, **140**, 153 (1905); Freylon, *Ann. chim.*, [8] **19**, 559 (1910); Fournier, *Bull. soc. chim.*, [4] **7**, 838 (1910).

Anal. Calcd. for $C_8H_{17}ON_3$: C, 56.1; H, 9.9. Found: C, 56.2; H, 9.8.

6-Methyloctanone-4.—*dl-s*-Butylcarbinol (30 g.), prepared by the action of formaldehyde on *s*-butylmagnesium iodide, reacted with phosphorus and iodine to yield 44.0 g. of the corresponding iodide, b. p. 137–140°. This in turn reacted with 4.8 g. of magnesium to form a Grignard reagent. Addition of 15 g. of *n*-butylaldehyde and subsequent purification of the reaction product gave 8.0 g. of propyl-*dl-s*-butylcarbinol, b. p. 157–163°. Chromic acid oxidation of this carbinol yielded 2.0 g. of the corresponding ketone which was characterized through its semicarbazone.

Anal. Calcd. for $C_{10}H_{21}ON_3$: C, 60.3; H, 10.6. Found: C, 60.6; H, 10.3.

Preparation of Semicarbazones.—The following procedure was followed in all preparations: 0.2 g. of the ketone was suspended in 5 ml. of water and enough ethyl alcohol added to produce homogeneity. A solution of 1.0 g. of semicarbazide hydrochloride and 2.0 g. of potassium acetate in 10 ml. of water was then added and, after standing several hours at room temperature, the mixture was refrigerated until crystallization occurred.

TABLE I

Ketone	B. p.		Semicarbazone m. p., °C.
	°C.	Mm.	
1 5,5-Dicarbethoxyheptanone-2	136–138	2	116.5–117.5
2 5-Carboxy, 5-carbethoxyheptanone-2	71–73	2	114–115
3 5-Carboxyheptanone-2	135–137	2	127–129
4 5-Carbomethoxyheptanone-2	75	2	108
5 5-Ethylheptanone-3	171–173	760	133–134
6 5-Methylhexanone-3	135–137	760	149–150
7 3-Methylhexanone-2	136–139	760	69–70
8 4-Methylhexanone-2	137–139	760	127–128
9 5-Methylhexanone-2	143–144	760	146–147
10 6-Methyloctanone-4	75

Conclusion

Several new ketones have been prepared and characterized through their semicarbazones.

MIDDLETOWN, CONN.

RECEIVED JANUARY 13, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

The Preparation and Hydrolysis of Some Polyhydroxyanthraquinone Glucosides^{1,2}

BY HARLAN FOSTER WITH JOHN H. GARDNER

Since it has been known for a long time that barbaloin on hydrolysis in acid solution gives a complex mixture from which aloë-emodin (1,8-dihydroxyanthraquinone-3-carbinol, Formula I) and *d*-arabinose are the only constituents which have as yet been identified, that substance has

(1) No. X in this series of Anthracene Studies: IX, *THIS JOURNAL*, **57**, 1074 (1935).

(2) Based upon a dissertation submitted by Harlan Foster in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

been regarded as either an arabinoside or an arabinose ether of aloë-emodin.³ More recently, it has been found that barbaloin, on hydrolysis with an aqueous solution of borax, gives an aloë-emodin-anthrone (1,8-dihydroxy-9,10-dihydro-9-ketoanthracene-3-carbinol, Formula II).⁴ Because of this, barbaloin has been formulated as an

(3) Leger, *Ann. chim.*, [9] **6**, 318 (1916).

(4) (a) Hauser, *Pharm. Acta Helv.*, **6**, 79 (1931); (b) Rosenthaler, *ibid.*, **9**, 9 (1934); (c) McDonnell and Gardner, *THIS JOURNAL*, **56**, 1246 (1934).