carbon dioxide gives, in addition to the expected carboxylic acids, significant quantities of the malonic acids. The malonic acids probably owe their formation largely to a secondary metalation reaction of the active methylene group by the unused RM compound present in slow carbonation. The typical transformations may be illustrated by the studies of Ivanoff and Spassoff[3] with benzylmagnesium chloride.

$$C_6H_5CH_2MgCl + CO_2 \longrightarrow C_6H_5CH_2CO_2MgCl$$

$$C_6H_5CH_2CO_2MgCl + C_6H_5CH_2MgCl \longrightarrow [C_6H_5CHCO_2MgCl][MgCl] + C_6H_5CH_3$$

$$[C_6H_5CHCO_2MgCl][MgCl] + CO_2 \xrightarrow{[H_2O]} C_6H_5CH(CO_2H)_2$$

Our carbonation experiments with benzylalkali types[2] raise a question concerning benzylidene-dialkali compounds like $C_6H_5CHM_2$. If such compounds are formed in one way or another incidental to the several procedures[2] for the preparation of benzylalkali compounds, then it is possible, but somewhat unlikely, that they are not carbonated by solid carbon dioxide. We are at present of the opinion that they are either not formed or are formed to a subordinate extent, incidental to the preparation of benzylalkali types.

Of more immediate interest are the aliphatic types, $RCHM_2$, like amylidene-disodium.[4] From the experiments now reported, we find that the organosodium compound or compounds formed by interaction of *n*-amyl chloride and sodium give largely caproic acid with very little *n*-butylmalonic acid when carbonation is effected by solid carbon dioxide; and a mixture of caproic acid with large amounts of *n*-butylmalonic acid when gaseous carbon dioxide is used. Additional experiments may provide an answer to the question as to whether secondary metalations or other transformations, some of which have been reported,[4] are responsible for the reactions of compounds of benzylidene-dimetallic and amylidene-dimetallic types.

Experimental Part

In a typical experiment, a solution of 16.5 g. (0.155 mole) of freshly distilled *n*-amyl chloride (b. p., 107–108°) in 15 cc. of petroleum ether (b. p. 85–100°) was added dropwise over a one-hour period to 8.75 g. (0.38 g. atom) of sodium sand in 75 cc. of petroleum ether. The mixture was stirred at room temperature for four hours, after which it was carbonated by pouring jet-wise on solid carbon dioxide, the addition being completed within ten seconds. The products obtained (by isolation and weighing) were 6.9 g. or 38.5% of caproic acid and less than 1% of impure *n*-butylmalonic acid. In a check experiment on this carbonation by solid carbon dioxide the yield of *n*-caproic acid was 7.3 g. or 40.8%; and the yield of impure *n*-butylmalonic acid was again less than 1%. In a parallel experiment in which carbonation was effected by admitting gaseous carbon dioxide to the surface of the reaction mixture over a five-hour period at 27–28° and with stirring, the yield of *n*-caproic acid was 2.72 g. or 15.2%; and the yield of *n*-butylmalonic acid was 2.1 g. or 16.9%.

Again using the same quantities of reagents, two parallel experiments were carried out by first stirring at 27–28° for one hour and then at 42° for two hours. Rapid carbonation (solid carbon dioxide, ten seconds) yielded 6.52 g. or 36.4% of *n*-caproic acid, and less than 1% of impure *n*-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, five hours) yielded 3.53 g. or 19.5% of *n*-caproic acid, and 1.83 g. or 14.8% of *n*-butylmalonic acid.

Acting on the suggestion that low boiling petroleum ether might give different results, parallel experiments were carried out with purified petroleum ether distilling over the range 28–38°. Rapid carbonation (solid carbon dioxide, five to ten seconds) yielded 51.5% of caproic acid and less than 2% of *n*-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, four hours) yielded 17.3% of caproic acid and 31.4% of *n*-butylmalonic acid.

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Agaric Acid and the Donnan Theory of Membrane Equilibrium

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The electromotive force of the following cell was measured at 25°.

Calomel electrode	Satd. KCl	Outside solution: dilute HCl	"Parlodion" membrane	Inside solution: agaric acid, 1.25%; $Ca(OH)_2$ or HCl, in varying quantities	Satd. KCl	Calomel electrode

The agaric acid was prepared by electrodialyzing "Noble Difco" agar agar for twenty-four hours under a potential of 110 volts according to the procedure of Hoffman and Gortner.[2] The procedure followed in making the electromotive force measurements was essentially the same as that used by Loeb.[3] After about twenty-four hours a true membrane equilibrium was established as

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[3] Ivanoff and Spassoff, *Bull. soc. chim.*, **49**, 19 (1931). See, also, Morton, Fallwell and Palmer, This Journal, **60**, 1426 (1938), for the carbonation of benzylsodium.

[4] Morton and Richardson, *ibid.*, **62**, 129 (1940). Earlier references are to be had from this most recent article.

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[1] This paper is constructed from a dissertation presented by Joseph Elliott Weber to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Hoffman and Gortner, *J. Biol. Chem.*, **65**, 371 (1925).

[3] J. Loeb, "Proteins and the Theory of Colloidal Behavior," Chapter XI, McGraw-Hill Book Co., New York, N. Y., 1924, p. 177.

TABLE I

MEMBRANE AND HYDROGEN ELECTRODE POTENTIALS FOR THE SYSTEM, AGARIC ACID/HYDROCHLORIC ACID

N $Ca(OH)_2$ in 50 ml. of agaric acid solution, ml.	Milliequivalents HCl in 50 ml. of agaric acid solution	Original *p*H	Final *p*H outside	Final *p*H inside	*p*H Out − *p*H In	H_2 elect. potential, mv.	Measured potential, mv.
50.0	..	3.95	4.00	3.93	0.07	4.1	3.85
25.0	..	3.64	3.73	3.64	.09	5.3	5.24
10.0	..	3.28	3.38	3.28	.10	5.9	6.00
6.0	..	3.13	3.26	3.14	.12	7.1	6.85
4.0	..	3.06	3.20	3.06	.14	8.3	8.59
3.0	..	3.02	3.19	3.03	.16	9.5	8.92
2.0	..	2.97	3.00	2.91	.09	5.3	4.82
1.0	..	2.70	2.71	2.68	.03	1.8	2.09
0.5	..	2.66	2.69	2.67	.02	1.2	1.16
..	0.0	2.48	2.48	2.47	.01	0.6	0.92
..	0.5	1.79	1.80	1.78	.02	1.2	.88
..	1.0	1.42	1.47	1.41	.06	3.6	1.19
..	2.0	1.20	1.23	1.20	.03	1.8	1.59
..	3.0	1.09	1.10	1.04	.06	3.6	2.85
..	4.0	1.01	1.02	0.94	.08	4.7	4.85
..	5.0	0.98	0.99	.91	.08	4.7	4.15
..	6.0	.94	.95	.90	.05	3.0	2.99
..	10.0	.72	.73	.71	.02	1.2	1.05
..	12.0	.71	.72	.70	.02	1.2	1.07

is shown in Table I where the observed P. D. (Measured Potential) is found to be in reasonably good agreement with the hydrogen electrode potential calculated from the *p*H values of the two solutions (measured at the end of the experiment). The membrane potential thus obtained arises from the unequal distribution of H^+ and Cl^- on opposite sides of the membrane. Tests of the hydrogen chloride solution revealed that neither Ca^{++} nor agarate ions passed through the membrane in detectable quantities.

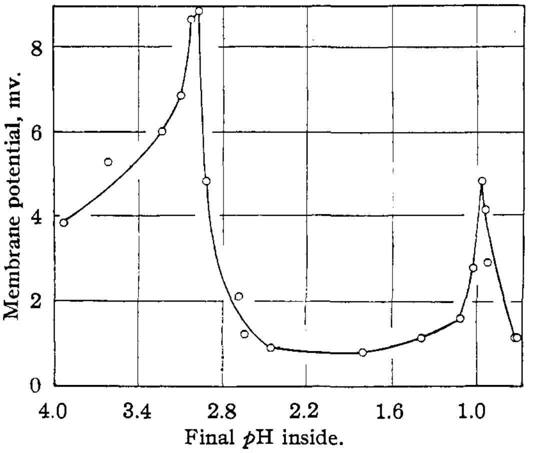

Fig. 1.—Relationship between *p*H and membrane potential.

When the final *p*H inside is plotted against the measured membrane potential, two maxima are found at *p*H values of approximately 3.0 and 1.0 (see Fig. 1). The second maximum is attributed to the hydrolytic decomposition of the agar. Since the membrane potential of such systems is a colligative property depending upon the number of discrete discontinuities of the dissolved constituent present, it is to be expected that the membrane potential will vary as a function of the concentration of the osmotically active particles. Agaric acid, a polyuronide, yields uronic acid units and reducing sugars.[4] Therefore, a second equilibrium is to be expected at *p*H values of approximately 1.0 where the agar complex is known to hydrolyze into simpler units.

(4) A. G. Norman, "The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Oxford University Press, Oxford, England, 1937.

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Melting Points of the *p*-Bromoanilides of Solid Fatty Acids[1]

BY DAVID F. HOUSTON

The melting points of the *p*-bromoanilides of certain solid fatty acids recently prepared in this Laboratory differ greatly from those in the literature.[1a] Several of our results agree with those previously ascribed to higher homologs. A graph of our values has the general form of the melting-point curves of aliphatic series; that of

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(1) Not subject to copyright.

(1a) P. W. Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).