Preparation of the Crystalline Reineckate of the Antibiotic.—This salt was precipitated by addition of a saturated aqueous solution of freshly recrystallized ammonium reineckate to a neutral aqueous solution of the antibiotic. After crystallizations from 95% ethanol and 50% aqueous acetone, red needles were obtained which gave no characteristic melting point. Assay: 15,000 units/mg. *vs. B. subtilis*.[4,5] *Anal.*[9] Calcd. for $C_{29}H_{42}N_9O_7S_4Cr$: C, 43.05; H, 5.24; N, 15.58; S, 15.85; ash (Cr_2O_3), 9.40. Found: C, 43.17, 43.27; H, 5.24, 5.33; N, 15.36; S, 15.62; ash, 10.77.

Acknowledgment.—The authors are indebted to Dr. John Ehrlich and Mr. Robert M. Smith who supplied the crude cultures used in this work; to Mr. Dwight A. Joslyn, Mrs. F. E. Guest, and Mrs. Margaret Galbraith for performing the numerous assays required; to Dr. John M. Vandenbelt for the ultraviolet absorption measurements; to Dr. O. M. Gruhzit for the toxicity studies; and to Mr. Quinten W. Martin and Mr. Anthony B. Sakoski for technical assistance in working up the culture beers.

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(9) Microanalyses were performed by C. W. Beazley.

RESEARCH LABORATORIES
PARKE, DAVIS & COMPANY
DETROIT 32, MICHIGAN

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The Decarboxylation of Simple Fatty Acids

BY THOMAS S. OAKWOOD AND MAXINE R. MILLER

Although textbooks almost universally state that fusion of the fatty acid salts with sodium hydroxide yields hydrocarbons according to the equation: $RCO_2Na + NaOH \rightarrow RH + Na_2CO_3$, it is difficult to support this statement with evidence. Berthelot[1] reported in 1866 that this reaction was not general.

We have heated the sodium salts of acetic, propionic, butyric and caproic acids with equimolar quantities of sodium hydroxide, and separated the gaseous products. An examination of the data in Table I shows that the decomposition of sodium acetate alone gives products in accord with the above equation.

TABLE I

Sodium salt (0.05 mole)	Acetate	Propionate	Butyrate	Caproate
Reaction temp., °C.	371–376	370–380	360–365	355–360
Gas liberated, mole	0.045	0.044	0.07	0.056
	Composition of gas, %			
H_2	0.5	33	31	38
CH_4	98.9	20	39	37.6
C_2H_6	..	44	7	1.4
C_3H_8	..	..	17	1.3
C_4H_{10}	..	..	..	3.8
C_5H_{12}	..	..	..	12.1
Unsaturates	..	0.3	5.7	2.5

It is noted that these decompositions all occur in the same temperature range. The reaction is exothermic and the major portion of the gas is liberated in a few minutes. Analysis of the water-soluble residues showed that in all cases the amount of sodium carbonate formed was above 90% of the theoretical.

Berthelot considered that the formation of methane, hydrogen, etc., from sodium propionate was caused by the thermal decomposition of the ethane first formed. Although this explanation may, in part, account for these products, the thermal stability of ethane and propane at such temperatures[2] and the rapidity of the reaction suggest that the primary pyrolytic products are complex. In any case the method is not suitable for the preparation of the simple paraffin hydrocarbons.

Experimental

The sodium salts, excepting the acetate, were prepared from aqueous sodium hydroxide and an excess of the acid, followed by evaporation to dryness. After washing with ether, the salts were recrystallized from water and dried *in vacuo* to constant weight over phosphorus pentoxide.

By calculation from the analyses for sodium, all the salts were better than 98% pure.

The apparatus for the fusion consisted of a side-arm test-tube (35 mm. o.d.) placed inside a jacket wound with a heating element, and insulated. The test-tube was closed with a rubber stopper carrying a thermocouple well and connected through a condenser to a gas collecting bottle.

A mixture of the dried sodium salt (0.05 mole) and sodium hydroxide (0.05 mole), powdered in a "dry box," was placed in the test-tube and the system flushed with dry nitrogen. The mixture was heated to the decomposition temperature, when the internal temperature increased and gas was rapidly evolved; most of the gas was evolved in about five minutes.

The gases were separated by a cryostat, using isothermal distillations at successive temperatures.[3,4] The gas fractions were identified by combustion analyses. The data are shown in Table I.

The carbonate in the residues was determined by standard procedures.

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(1) Berthelot, *Ann. chim. phys.*, [4] **9**, 444 (1866).

(2) Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, p. 99 *et seq.*, p. 119 *et seq.*

(3) Allman, Ph.D. Thesis, The Pennsylvania State College, 1938.

(4) We are indebted to Dr. H. D. Zook and Mr. W. J. McAleer for these analyses.

THE WHITMORE LABORATORIES
SCHOOL OF CHEMISTRY AND PHYSICS
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Mass Spectrometric Evidence for a New Boron Hydride

BY FRANCIS J. NORTON

In examining with the mass spectrometer the residues from pure B_5H_{11} which had been stored at −78° for a long time, there was detected a small amount of $B_{10}H_{14}$, B_6H_{10} and B_5H_9 with the B_5H_{11}. In addition, a group of hitherto unobserved peaks, dominant peak mass 105, was found. It is believed they represent a new boron hydride, B_9H_{13}.

The spectrum of pure $B_{10}H_{14}$ is given in Fig. 1 (A), from mass 85 to 124, the parent peak. This was obtained with mass spectrometer operating conditions already described.[1] Peaks of double ionization for $B_{10}H_{14}$ were observed in the region 55–59.

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(1) F. J. Norton, THIS JOURNAL, **71**, 3488 (1949)

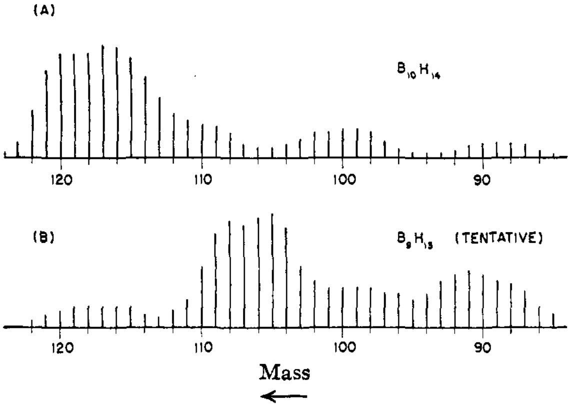

Fig. 1.

Wiberg[2] has proposed the type formula B_nH_{n+4} which includes the more stable known hydrides: B_2H_6, B_5H_9, B_6H_{10} and $B_{10}H_{14}$. The less stable B_4H_{10} and B_5H_{11} belong to the series B_nH_{n+6}. The composition B_9H_{13} fits into the more stable series formula. However, the composition B_9H_{15} is not excluded by the mass spectrum observed.

The group of peaks in Fig. 1(B) centering about masses 105 to 108 is obviously from some new material in addition to the $B_{10}H_{14}$ present. The position and distribution of these new peaks are not inconsistent with the spectrum which such a material as B_9H_{13} would be apt to furnish. Peaks of double ionization also were observed in the region 50–53, which indicates resemblance to $B_{10}H_{14}$ in its ionization characteristics, and the volatility of these two materials is of the same order.

Higher boron hydrides (above $B_{10}H_{14}$) were sought up to mass 400 but none was found of sufficient volatility to enter the mass spectrometer.

[2] E. Wiberg, *Ber.*, **69B**, 2816 (1936).

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK RECEIVED NOVEMBER 22, 1949

Redetermination of the Heat of Combustion of Diphenylmethane

BY GEORGE S. PARKS AND JOHN R. MOSLEY

Parks and co-workers[1] reported 9822.2 cal./g. for the heat of combustion of diphenylmethane under the conditions of their calorimetric bomb process. They ascribed their value to the liquid state, as they had been able to undercool the liquid, in a test-tube, several degrees below 25.1°, m. p. of crystalline diphenylmethane. Recently, however, we have tried to burn undercooled liquid cyclohexanol (m. p. 25.2°) in our bomb in an analogous fashion, but this material, although liquid at 23° in a small glass bulb exposed to atmospheric pressure, invariably crystallized within the bomb on the imposition of 30 atm. pressure at 24°. Such an experience led to doubt concerning the state of diphenylmethane in the previous work and accordingly we have now made a redetermination of the heat of combustion under unambiguous conditions.

Our material was an Eastman sample which was further purified by nine fractional crystallizations to a final m. p. of 25.1°. It was utilized in the present study immediately after preparation, whereas the sample employed by Parks and coworkers had stood in a bottle of transparent glass for almost two months prior to their combustions.

In our study three combustion determinations were first made upon crystalline diphenylmethane, obtained by cooling to 0°. The resulting mean was 9799.9 ± 1.0 cal./g. for the bomb process. Then three crystallization tests, all negative, were made by exposing liquid samples at 23° to a pressure of more than 30 atm. within the bomb. Thereupon we proceeded to combustion measurements on this liquid with a mean result of 9825.8 ± 1.1 cal./g. from five determinations.

These data demonstrate that Parks and coworkers were previously dealing with liquid diphenylmethane. However, their material had probably deteriorated with time in the manner described by De Vries and Strow[2] and thus produced a result about 0.04% lower than our present one.

Our new, and more reliable, value yields $\Delta H_R = -1653.83 \pm 0.32$ kcal. for the molal heat of combustion of the liquid at 25° and 1 atm. constant pressure. The corresponding heat of formation from the elements is $\Delta H_f^0 = 21.25$ kcal.

[1] G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, THIS JOURNAL, **68**, 2524 (1946).

[2] T. De Vries and H. A. Strow, THIS JOURNAL, **61**, 1796 (1939).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA RECEIVED NOVEMBER 18, 1949

Catalytic Hydrogenation of Some 2- and 4-Stilbazole Methiodides

BY ARTHUR P. PHILLIPS

Recently the author has reported the preparation of a series of 2- and 4-stilbazole methiodides.[1] It was considered that powerful pharmacological activities could reasonably be anticipated in the stilbazoline hydrogenation products of these stilbazoles by virtue of their relationship to such alkaloidal types as coniine, lobeline and laudanosine. Spasmolytic, analgesic or curare-like activities were specifically sought. This paper deals solely with the chemical aspects of these substances.

The desired compounds, salts of 1-methyl-2- or 4-substituted phenethylpiperidines, were readily obtained by the catalytic hydrogenation of the corresponding 2- or 4-stilbazole methiodides using Adams catalyst in methanol solution. In general

[1] Phillips, *J. Org. Chem.*, **12**, 333 (1947); **14**, 302 (1949).