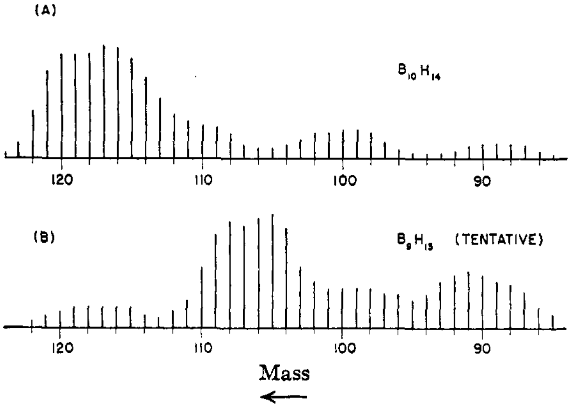


Fig. 1.

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 co-workers 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 co-workers 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 $\Delta H_{\mathrm{R}} = -1653.83 \pm 0.32$ 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

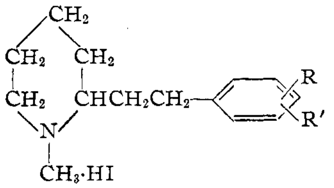
Recently the author has reported the preparation of a series of 2- and 4-stilbazole methiodides.[1] It was considered that powerful pharmacological activities could reasonably be anticipated in the stilbazoline hydrogenation products of these stilbazoles by virtue of their relationship to such alkaloidal 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.

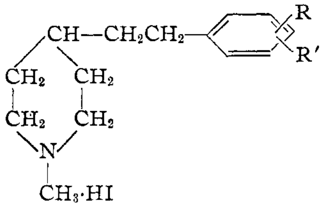
The desired compounds, salts of 1-methyl-2- or 4-substituted phenethylpiperidines, were readily obtained by the catalytic hydrogenation of the corresponding 2- or 4-stilbazole methiodides using Adams catalyst in methanol solution. In general

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

TABLE I

2- AND 4-STILBAZOLINES

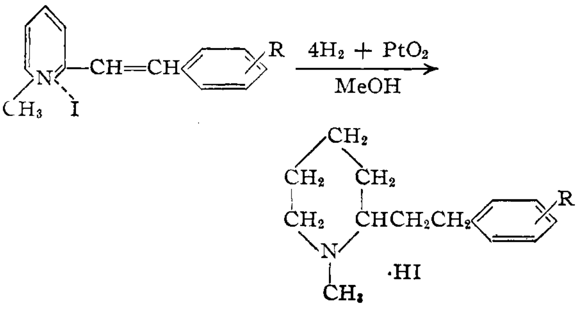




Substituents on phenyl	Cryst. solvent[a]	Yield, %	M. p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
		A.	-2-Stilbazolines				
None	A. Æ. E.	95	114–115	50.72	50.72	6.70	6.72
2-HO	A. Æ. E.	87	159–160	48.39	48.19	6.39	6.34
3-HO	M. Æ. E.	100	120	48.39	48.63	6.39	6.14
4-HO	A. Æ. E.	98	162–163	48.39	48.44	6.39	6.40
2-CH_3O	A. Æ. E.	92	146–147	49.83	50.10	6.70	6.59
4-CH_3O	Æ.	100	113–114	49.83	49.91	6.70	6.65
3,4-CH_2O_2	A. Æ. E.	100	100–101	47.97	48.26	5.92	6.16
2-HO-3-CH_3O	A. Æ.	98	165–166	47.72	47.71	6.42	6.34
2-HO-3-C_2H_5O	A. Æ.	98	179–180	49.08	49.29	6.70	6.91
3-CH_3O-4-HO	A. Æ. E.	98	151–152	47.72	47.88	6.42	6.48
3-C_2H_5O-4-HO	A. E.	95	128–129	49.08	49.32	6.70	6.83
2,5-$(CH_3O)_2$	M. Æ. E.	100	141–142	49.08	49.38	6.70	6.82
3,4-$(CH_3O)_2$	A. E.	100	141–142	49.08	49.24	6.70	6.69
4-$(CH_3)_2N$	M. Æ.	100	187–188	51.31	51.42	7.27	7.53
3-Br-4-$(CH_3)_2N$	Ac. E.	90	104–105	42.37	42.08	5.78	5.75
4-$(C_2H_5)_2N$	A. E.	98	134–135	53.70	53.46	7.76	7.53
		B.	-4-Stilbazolines				
None	A. Æ. E.	85	153–154	50.72	50.44	6.70	6.49
2-HO	A. Æ. E.	90	167–168	48.39	48.50	6.39	6.50
3-HO	A. Æ. E.	100	141–142	48.39	48.51	6.39	6.30
4-HO	A. Æ. E.	95	174–175	48.39	48.42	6.39	6.24
2-CH_3O	A. Æ. E.	96	128–129	49.83	50.11	6.70	6.51
4-CH_3O	A. Æ. E.	93	104–105	49.83	50.11	6.70	6.67
3,4-CH_2O_2	A. Æ. E.	93	129–130	47.97	48.12	5.92	6.05
2-HO-3-CH_3O	A. Æ. E.	100	119–120	47.72	47.98	6.42	6.42
2-HO-3-C_2H_5O	A. Æ.	100	135–136	49.08	49.21	6.70	6.59
3-CH_3O-4-HO	A. Æ. E.	100	141–142	47.72	47.87	6.42	6.37
3-C_2H_5O-4-HO	A. E.	100	152–153	49.08	49.30	6.70	6.71
2,5-$(CH_3O)_2$	M. Æ. E.	100	161–162	49.08	48.83	6.70	6.72
3,4-$(CH_3O)_2$	M. Æ. E.	99	171–172	49.08	49.28	6.70	6.74
4-$(CH_3)_2N$	A. Æ. E.	98	107–108	51.31	51.49	7.27	7.43
4-$(C_2H_5)_2N$[b]	A. Æ. E.	100	207–208	62.19	61.94	9.30	9.30

[a] A. = ethanol; Ac. = acetone; Æ. = ethyl acetate; E. = ether; M. = methanol. [b] This compound was isolated as the dihydrochloride.

the reductions proceeded rapidly to completion giving yields usually in excess of 90%.



In the case of 2-(3′-bromo-4′-dimethylaminostyryl)-pyridine methiodide it was interesting that the 3′-bromo was retained during the complete hydrogenation of the pyridine ring and of the side chain double bond.

There was no evidence of poisoning of Adams catalyst by the iodide ion during the reduction of these iodides. In contrast, palladized charcoal catalyst was completely and irreversibly poisoned by small amounts of iodide ion, the adverse effect not being removed by repeated washing of the catalyst.[2]

The original intense orange-red color of the

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[2] Baltzly and Phillips, THIS JOURNAL, 68, 261 (1946).

dialkylaminostilbazole methiodides, which reduce to colorless products, persisted during the hydrogenation until the hydrogen uptake was practically complete. This was taken to mean that some of the unreacted material was still present right up to the end. From this it was inferred that once reduction of a particular molecule had started it was carried to completion before another of the colored molecules was attacked. For if either the pyridine ring alone *or* the ethylenic side chain alone had been saturated the resulting molecule would be colorless. If either all pyridine rings or all side chains were preferentially hydrogenated then the reaction mixture should become practically colorless by the time three-fourths of the total hydrogen uptake had been accomplished in the first case or by the time one-fourth had been done in the second. As high color persisted significantly beyond the three quarters point both of these latter possibilities seem to be eliminated. In contrast, the ethylenic side chain of 2- or 4-stilbazole hydrochloride was reduced preferentially, under the same conditions, and the reduction could be stopped conveniently at that stage to yield the 2- or 4-phenethylpyridines.[3]

Experimental

Hydrogenation of the Stilbazole Methiodides.—The pure stilbazole methiodide (0.02–0.05 *M*) was dissolved or suspended in absolute methanol (50–100 cc.), approximately 0.2 g. of Adams catalyst was added, and the hydrogenation was carried out in a Burgess–Parr catalytic hydrogenation apparatus with shaking at two to three atmospheres overpressure of hydrogen. Hydrogen uptake proceeded rapidly (usually complete in one to two hours) and came to a stop at or near the calculated value. Platinum was removed by filtration, washed with methanol, and the methanol filtrates were evaporated to dryness. The residue stirred up with ether gave usually a white crystalline product, which was recrystallized from combinations of alcohol, ethyl acetate and ether. For details see Table I.

Acknowledgment.—The author wishes to thank Mr. Samuel W. Blackman for the microanalytical results included here.

(3) Phillips, *J. Org. Chem.*, **13**, 622 (1948).

WELLCOME RESEARCH LABORATORIES
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RECEIVED NOVEMBER 18, 1949

The Alpha Phase of Sodium Dodecyl Sulfate

BY FLOYD RAWLINGS, JR.,[1] AND E. C. LINGAFELTER

We have thought it of interest to compare the solid phases of the sodium alkyl sulfates with those of the sodium alkane sulfonates which have been under investigation in this Laboratory for some time.[1a,2,3,4] We have accordingly started an X-ray crystallographic investigation of the series, sodium hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl and octadecyl sulfates.

From a solution of sodium dodecyl sulfate in 95% ethanol, slow evaporation at room temperature yielded a crop of well-formed crystals, some of which were used for X-ray investigation. The crystals are very similar in habit to the alpha phase of the sodium alkane sulfonates.[1a] They are quite thin, tabular on (001), and elongated parallel to the *a* axis. In most cases the tablet is outlined by (01*l*) and (11*l*).

X-Ray diffraction data were obtained from rotation, Weissenberg, and precession photographs using copper radiation. Table I contains the constants of the monoclinic unit cell, and the data for two sodium 1-alkane sulfonates for comparison.

TABLE I

	a_0, Å.	b_0, Å.	c_0, Å.	β
$C_{12}H_{25}SO_4Na \cdot xH_2O$	16.47	10.35	77.70	93° 18′
$C_{13}H_{27}SO_3Na \cdot {}^1/_8H_2O$[4]	16.76	10.04	78.21	91° 40′
$C_{12}H_{25}SO_3Na \cdot {}^1/_8H_2O$[1a]	16.80	10.14	76.07	92° 3′

The space group (Aa or A2/a) and the number of molecules in the unit cell (32) is the same for all three of the substances. The amount of hydration of the sodium dodecyl sulfate has not yet been determined. However, the assumption of $^1/_8$ H_2O gives a calculated density of 1.166 g./cc. (observed by flotation method, 1.165 g./cc.).

The sodium dodecyl sulfate differs from the sodium tridecane sulfonate by the substitution of an oxygen atom for a methylene group. Taking the covalent radii to be 0.66 and 0.77 Å., respectively,[5] and assuming the angle of tilt of the chains from the normal to (001), one calculates an expected decrease in d_{001} of 0.68 Å. compared with the observed decrease of 0.51 Å. There is also a small, but real, decrease in a_0 and increase in b_0.

Two other solid phases of sodium dodecyl sulfate have been found, one from 95% alcohol at 25–26° and one from water at 25–26°, both of which are also similar in habit to known phases of the sodium alkane sulfonates. We are continuing the investigation of these phases and others which may be discovered for the long-chain sodium alkyl sulfates.

(1) Procter and Gamble Research Fellow, 1949–1950.

(1a) Jensen and Lingafelter, THIS JOURNAL, **66**, 1946 (1944).

(2) Jensen and Lingafelter, *ibid.*, **68**, 1729, 2730 (1946).

(3) Lingafelter and Jensen, *Am. Mineral.*, **32**, 691 (1947).

(4) Wilcox and Lingafelter, to be published.

(5) Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1948, p. 164.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON
RECEIVED NOVEMBER 28, 1949

Synthesis of 2-(4′-Diethylamino-1′-methylbutylamino)-4-phenylquinoline and a 6-Chloro Derivative

BY GEORGE A. REYNOLDS AND CHARLES R. HAUSER

The recent synthesis of 4-phenyl-2-chloroquinoline (I, X = H)[1] from aniline and ethyl benzoylacetate followed by treatment with phosphorous oxychloride has made possible the convenient

(1) Hauser and Reynolds, THIS JOURNAL, **70**, 2402 (1948).