manner that 80–90% of the calciferol was in the precipitate and the rest in the washings. The pyridine calciferyl sulfate precipitate was found to be slightly soluble in petroleum ether by employing the above criteria in subsequent experiments. These experiments were confirmed by employing 50 mg. of calciferol and weighing the amount of calciferol in the petroleum ether washings which were washed free of any traces of pyridine sulfur trioxide by water. The precipitate was treated with potassium hydroxide in water (using 4–6 moles of the base for each mole of sulfur trioxide employed in the original reaction) and extracted repeatedly with petroleum ether. The petroleum ether fraction was washed free of potassium hydroxide and taken to dryness. There was no potassium or sulfate in the residue, which was found to contain all the calciferol as shown by the mercuric acetate test and later by gravimetric procedure. These relations were also established by the animal experiments using the technique previously outlined [Natelson and Sobel, above].

Thus, it appears that the potassium hydroxide hydrolyzes the pyridine calciferyl salt whereas in the ergosteryl and cholesteryl salts the pyridine is displaced by potassium in a double decomposition and the extremely insoluble potassium sulfate derivative is formed. The reaction for calciferol may be illustrated

$$StOH + SO_3C_5H_5N \xrightarrow{C_5H_5N} StOSO_3OHC_5H_5N$$

$$StOSO_3OHC_5H_5N + 2KOH \longrightarrow StOH + C_5H_5N + K_2SO_4$$

The reaction was next applied to cod liver oil concentrate. Two grams of the concentrate (containing 73.333 I. U. per g. obtained through the courtesy of the National Oil Products Co.) was dissolved in 4 cc. of pyridine and followed by the addition of 1 g. of pyridine sulfur trioxide, heated at 46° for one hour and 50 cc. of petroleum ether added, and then allowed to stand for three days in an ice-box. A yellowish white precipitate settled which was washed with cold petroleum ether. The precipitate was then treated with potassium hydroxide in the presence of petroleum ether. Two fractions of sterols were obtained, one the insoluble potassium steryl sulfates and the other the petroleum ether soluble fraction. The latter was evaporated down to dryness in the presence of maize oil and used for bio-assay. A vitamin bio-assay was run comparing the activity of this fraction against the original material, the unreacted fraction of the concentrate and the insoluble potassium steryl sulfate. It was found by this criterion that approximately 60% of the original vitamin D content precipitated and was found later in the petroleum ether fraction while the insoluble potassium sulfate does not contain any vitamin D. Thus a simple method for obtaining a high concentration of natural vitamin D was obtained. Further work is in progress at present to isolate a pure vitamin D from natural sources.

PEDIATRIC RESEARCH LABORATORY
THE JEWISH HOSPITAL OF BROOKLYN
BROOKLYN, N. Y. RECEIVED MAY 18, 1936

COMMUNICATIONS TO THE EDITOR

SURFACE IONIZATION OF CESIUM ON TUNGSTEN

Sir:

Alterum, Krebs and Rompe [*Z. Physik*, **92**, 1 (1934)], in an article on the surface ionization of cesium on a tungsten filament, have reported obtaining values of 0.21 at 1520°K. and 0.29 at 1830°K. for its degree of ionization. These values are considerably lower than the ones predicted by theory for these temperatures; they also show an increase in the degree of ionization occurring with rising temperature, whereas theory predicts a decrease. The apparatus used by Alterum, Krebs and Rompe was one in which the ionization unit was surrounded by the saturated vapor of cesium. Taylor and Langmuir [*Phys. Rev.*, **44**, 423 (1933)], using the same type of apparatus, previously had obtained values approximating 100% ionization at temperatures as high as 1500°K. Above this temperature the onset of a very large photoelectric current from plate to filament, caused by the action of the light from the filament on an adsorbed layer of cesium on the

plate prevented them from extending their measurements further.

In view of these contradictory reports, it was decided to investigate the surface ionization of cesium by a different method. Copley and Phipps [*Phys. Rev.*, **45,** 344 (1934); **48,** 960 (1935)] found that the use of an atomic ray instead of saturated vapor almost entirely eliminated the photoelectric current in the case of potassium, and they were able to determine its degree of ionization up to a temperature of 2800°K. An apparatus similar to the one described by Copley and Phipps was constructed, its furnace was filled with carefully purified cesium, and the measurements were taken in the same manner as was described in the case of potassium.

According to statistical mechanics, the degree of ionization of cesium on tungsten is given by the expression

$$\frac{1}{1 + 2 \exp [(I - \phi)\epsilon/kT]} \qquad (1)$$

where ϕ is the work function of tungsten at the temperature T, and I is the ionization potential of cesium. Curve A in Fig. 1 was obtained by

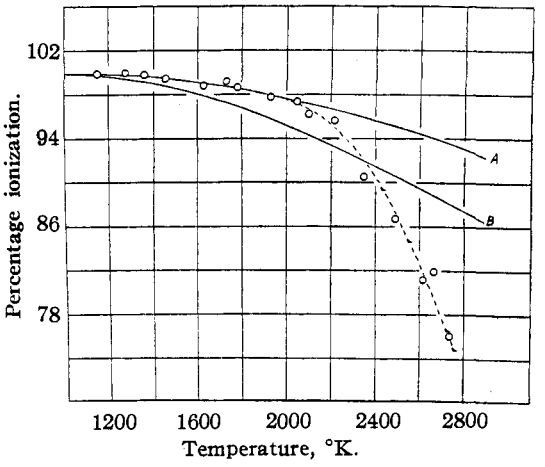


Fig. 1.—The percentage ionization of cesium on tungsten *versus* temperature.

plotting Eq. 1 with ϕ replaced by $\phi_0 + \alpha T$ where ϕ_0 is the work function at absolute zero and α is its temperature coefficient. The numerical values used for these constants (4.514 v. e. for ϕ_0 and 5.6×10^{-5} v. deg.$^{-1}$ for α) are the same as those which were found necessary to account for the results obtained with potassium. It is evident that the experimental values for the degree of ionization of cesium below 2000°K. are in satisfactory agreement with curve A. Furthermore, our results confirm those found in the low temperature range by Taylor and Langmuir. Curve B, which is shown for comparison, was obtained by plotting Eq. 1 assuming a negligible temperature coefficient of the work function.

Above 2000°K. the experimental values for the degree of ionization fell off too rapidly to agree with curve A. This behavior may be accounted for in part by experimental error caused by a photoelectric current, which, in spite of the use of the atomic ray, was present in this range of temperature. A similar rapid falling off of the ionization of potassium at temperatures above 2000°K. has been observed. This phenomenon is being further investigated by using atomic rays of potassium and sodium. Since these metals have higher ionization potentials than cesium, their surface ionization in the high temperature range may be more accurately measured.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
M. J. COPLEY
JULIAN GLASSER

RECEIVED APRIL 17, 1936

KINETICS OF THERMAL CIS-TRANS ISOMERIZATIONS

Sir:

Kistiakowsky and Smith [THIS JOURNAL, **58,** 766 (1936)] have shown that the *cis–trans* isomerization of butene-2 appears to be of approximately first order during a run but of second order with respect to initial pressure. The purpose of this communication is to point out that when the equilibrium constant is approximately 1 as in this reaction, the rate in a given run for a bimolecular reaction would be indistinguishable from that calculated for a first order reaction.

If x is the concentration of the *trans* isomer, the net rate for a bimolecular reaction may be expressed by the equation $-dx/dt = Kx^2 - (1 - x)^2 = (K - 1)x^2 + 2x - 1$ where K equals K_1/K_2, the ratio of the rate constants for the forward and reverse reactions. If the equilibrium corresponds to $x = 0.5$, then $K = 1$ and $-dx/dt = +2(x - 0.5)$, which is the expression for a first order reaction. The deviations from this result are considerable for equilibrium mixtures differing only slightly from 50%, so it is desirable to make a calculation for the experimental value of $x = 0.528$ at equilibrium. This rate is given by $-dx/dt = -0.20x^2 + 2x - 1 = (x - 0.528)(-0.20x + 1.894)$. The first order rate would be proportional to $(x - 0.528)$ so the variations in

the second term correspond to the deviations from the first order rate. For example, if a velocity constant for a first order reaction were calculated for $x = 1$, the observed rate would be about 11% high when $x = 0$.

Since 11% is not more than the experimental error in Kistiakowsky and Smith's velocity constants, it seems that all of their results, with the exception of the two runs at 1440 mm., are consistent with the hypothesis of a bimolecular mechanism for the isomerization. Probably the simplest way to test this hypothesis would be to investigate the effects of inert gases but negative results would be inconclusive because collisions of butene with inert molecules would not necessarily have the same effect as collisions with molecules of their own kind.

It is believed that the assumption of a bimolecular mechanism eliminates some of the difficulties involved in explaining the low energy of activation and in postulating a chain mechanism of unknown nature.

RESEARCH LABORATORY ROY W. HARKNESS
SUN OIL COMPANY
NORWOOD, PENNSYLVANIA

RECEIVED MAY 21, 1936

THE N-ALKYL GROUP OF ACONINE (ACONITINE)

Sir:

Since the first applications of the Herzig-Meyer method for N-alkyl determinations to aconine [H. Schulze, *Arch. Pharm.*, **244,** 165 (1906)], it has been commonly assumed that aconitine (aconine) possesses an N-methyl group. This has apparently not been questioned in the interpretations given by a number of workers to the results obtained in alkyl determinations on aconitine, aconine, etc. [among others, R. Majima and S. Morio, *Ann.*, **476,** 194 (1929); A. Lawson, *J. Chem. Soc.*, 80 (1936); although Henry and Sharp, *J. Chem. Soc.*, 581 (1931) considered the possibility of the presence of an N-ethyl group but rejected it as unprecedented].

In the course of work which is now in progress in this Laboratory on the structure of the aconite alkaloids, we have found that when aconine hydrochloride is fused with potassium hydroxide in an atmosphere of hydrogen, the principal volatile amine formed is ethylamine, which was readily identified as the *picrate*, m. p. 166° [*Anal.* Calcd. for $C_8H_{10}O_7N_4$: C, 35.02; H, 3.59. Found: C, 35.43; H, 3.46], and as the *ethyl phenyl thiourea*, m. p. 100–100.5° [*Anal.* Calcd. for $C_9H_{12}N_2S$: C, 59.93; H, 6.72. Found: C, 59.93; H, 6.58]. Since this result appeared to contradict the long-standing statement of Ehrenberg and Purfürst [*J. prakt. Chem.* [2], **45,** 604 (1892)] that dimethylamine results on fusion of aconine with barium hydroxide, we have also repeated this experiment. Here again only ethylamine could be identified as before. The so-called dimethylamine derivative of Ehrenberg and Purfürst was unquestionably a double platinum salt of ethylamine. These results therefore strongly indicate the presence of an N-ethyl group in aconine and its parent alkaloid, aconitine.

This conclusion was confirmed by a study of the products of the decomposition of aconine hydrochloride with hydriodic acid under the conditions of the usual alkyl determination. After removal of the methyl iodide which comes from the methoxyl groups, the succeeding iodide originating from the N-alkyl group was shown to be ethyl iodide by identification as *ethyl trimethyl ammonium iodide* [R. Willstätter and M. Utzinger, *Ann.*, **382,** 148 (1911)]. *Anal.* Calcd. for $C_5H_{14}NI$: C, 27.91; H, 6.56; I, 59.02. Found: C, 28.42; H, 6.49; I, 58.48. It is not likely that the ethyl iodide could have had another origin, *e. g.*, in a larger grouping to which the cyclic N atom is attached.

Further, in the similar study of oxonitine, which different workers have examined for N-methyl with unconvincing indications, our own determinations have been negative. It is to be concluded that in the transformation of aconitine into oxonitine by oxidation the reaction involves in some way the N-ethyl group which is thus removed. Possibly the acetaldehyde which has been previously reported as a by-product of the reaction may have its origin in this group. Oxonitine may be of betaine or lactam character.

Finally, in the preparation of oxonitine a second, possibly isomeric substance of m. p. 261°, with decomposition, and $[\alpha]^{26}D$ −98° in chloroform has been isolated as a by-product. *Anal.* Found: C, 61.40, 61.45; H, 6.69, 6.75; N, 2.57, 2.42; OCH_3, 19.18, 19.07; $N(CH_3)$, trace.

THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
NEW YORK, N. Y.
WALTER A. JACOBS
ROBERT C. ELDERFIELD

RECEIVED MAY 21, 1936

THE KINETICS OF CYCLOPENTADIENE

Sir:

In a recent letter in *Nature*, **137**, 496–7 (1936), Wasserman and Khambata discuss the rates of polymerization of cyclopentadiene and of the depolymerization of dicyclopentadiene in solution. Since we have studied these reactions for some time, we wish to report our results which, in several instances, are more extensive than those of Wasserman. In the gas phase the reactions were found to be of the second and of the first order, respectively. Their velocity constants are given by

$$\text{Polymerization } k = 6.5 \times 10^{6}\, e^{-12{,}700/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

$$\text{Depolymerization } k = 10^{13}\, e^{-23{,}700/RT} \text{ sec.}^{-1}$$

While the constants in these expressions differ somewhat from those given by Wasserman and Khambata, the absolute rates are nearly the same, indicating that the differences are mostly to be attributed to experimental errors in determining the temperature coefficients of the rates. We have also studied the association reaction in tetrahydronaphthalene as solvent, and find, as did Wasserman, that the reaction is of the second order.

We also find, however, that with pure liquid cyclopentadiene the order decreases, a reaction of nearly first order obtaining while the activation energy (17,300 kcal.) is still practically identical with that found by Wasserman.

TABLE I

DIMERIZATION OF PURE LIQUID CYCLOPENTADIENE, 58.4°

Time, sec.	Mole % cyclopentadiene	k (1st order)	k (2nd order)
0	98.9		
1215	87.4	9.8×10^{-5}	1.09×10^{-7}
4830	61.3	9.8	1.34
12640	28.8	9.6	2.43

Earlier work on this reaction and our own experiments definitely show that no chains are involved and thus the change of the reaction order must be attributed to other causes. While their discussion is reserved for the more detailed publication soon to follow, we wish to point out that this finding may have a very important bearing on the kinetics of other, more complex, polymerization reactions in pure liquids. Rideal and Gee [*Trans. Faraday Soc.*, **31**, 969 (1935)] and Mark and Dostal [*Z. physik. Chem.*, **29B**, 299 (1935)] recently have discussed the mechanism of such reactions, deriving kinetic expressions which account for the first order in terms of the chain mechanism. If, as we now find, the first order is due not to the intervention of the chains but to the changing environment during the progress of the reaction, these kinetics interpretations, when applied to pure liquid reactants, should be considerably revised.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY G. B. KISTIAKOWSKY
CAMBRIDGE, MASSACHUSETTS WHITNEY H. MEARS

RECEIVED MAY 15, 1936

THE LUCIFERIN–OXYLUCIFERIN SYSTEM

Sir:

By connecting solutions of a series of partially reduced oxidation–reduction indicators with crude extracts of oxyluciferin, both the solutions and extracts being oxygen-free and buffered at the same *p*H, through platinum electrodes and a salt-bridge, I have found that the oxidation–reduction potential of luciferin-oxyluciferin lies in the neighborhood of the quinhydrone system. (The oxyluciferin was obtained by extracting powdered Cypridina with the phosphate buffer, filtering and allowing to stand until all luminescence had ceased due to complete oxidation of the luciferin. Reduction of the oxyluciferin to luciferin was indicated by appearance of luminescence when air was passed through the extract.) Although it has hitherto been thought that there is a gap of about 0.5 v. in oxidation–reduction potential between the systems which reduce oxyluciferin and those which oxidize luciferin upon mixing (quinhydrone representing the level at which (luciferin is oxidized) I have now found, in addition to the above evidence, that the system is reversible, since if a luciferin extract is connected in the above manner with an oxyluciferin extract, some of the latter is reduced to luciferin. The amount of reduction in all cases was, however, small, due to the instability of oxyluciferin, as shown by Harvey and by Anderson.

To the facts that (1) luciferin is slowly autoxidized in the physiological *p*H range, that (2) its oxidation by oxygen is catalyzed by an enzyme (luciferase) and that (3) the oxidant is unstable, may now be added the facts that (4) the system is at least partially reversible, (5) is active at an electrode and (6) has, for a biological compound, an unusually positive oxidation–reduction potential. It is noteworthy that these characteristics are similar to those of a group of substances in which certain special derivatives of ortho- and

para-hydroxybenzenes are the reductants and some representatives of which have been investigated by Ball and Chen, *e. g.*, epinephrine, catechol, pyrogallol and gallic acid.

I should like, also, to suggest, from a consideration of the available facts, that luciferase serves the same oxidative function with regard to luciferin as oxidases such as catechol oxidase, laccase, and polyphenolase do, to their respective substrates.

THE PHYSIOLOGICAL LABORATORY IRVIN M. KORR
PRINCETON UNIVERSITY
PRINCETON, N. J.

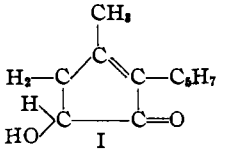
RECEIVED MAY 13, 1936

CONSTITUENTS OF PYRETHRUM FLOWERS. V. CONCERNING THE STRUCTURE OF PYRETHROLONE

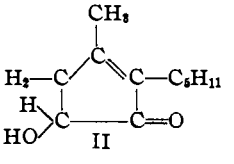
Sir:

In article IV of this series [*J. Org. Chem.*, **1**, 38 (1936)] we have reported that the semicarbazones of pyrethrolone and tetrahydropyrethrolone contain two less hydrogen atoms than are required by their accepted formulas. Pyrethrolone semicarbazone corresponds to the formula $C_{12}H_{17}O_2N_3$ and tetrahydropyrethrolone semicarbazone to $C_{12}H_{21}O_2N_3$. The formulas for pyrethrolone and tetrahydropyrethrolone would therefore be represented by $C_{11}H_{14}O_2$ and $C_{11}H_{18}O_2$, respectively. These formulas have now been confirmed by analyses of the free ketones and some of their derivatives.

The establishment of the new empirical formulas for pyrethrolone and tetrahydropyrethrolone necessitates a revision of their structural formulas, and we suggest that formulas I and II be assigned to pyrethrolone and tetrahydropyrethrolone, respectively.

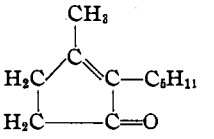


I



II

Tetrahydropyrethrolone, having a saturated side chain, is better suited for study of the nuclear reactions than is pyrethrolone. The hydroxyl group is readily replaced by chlorine, and the resulting chloro derivative yields on reduction an optically inactive ketone of probable structure III. This formula, on the basis of degradation and synthesis, has been assigned to dihydrojasmone, the semicarbazone of which melts at 175°. The semicarbazone of our reduced compound melts at 176°. While it has not been possible to make a mixed melting point, the two values are so close as to indicate identity [Treff and Werner, *Ber.*, **66**, 1521 (1933); Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 257 (1924)].



III

With the assumption that tetrahydropyrethrolone corresponds to formula II, its recorded characteristic reactions also are readily explained.

DIVISION OF INSECTICIDE INVESTIGATIONS
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE F. B. LAFORGE
WASHINGTON, D. C. H. L. HALLER

RECEIVED MAY 21, 1936

THE CONSTANCY OF NUCLEAR BOND ENERGIES

Sir:

Recent accurate determinations of the masses of the lighter elements [Oliphant, *Nature*, **137**, 396 (1936)] permit a further check on the assumption [Latimer and Libby, *J. Chem. Phys.*, **1**, 133 (1933)] that the energies of nuclear reactions can be calculated as the sum of changes in the energies of the nuclear bonds and the coulombic fields. As an approximation for the latter, Latimer and Libby used the classical expression $M_F = 2Z^2/3R$, where Z is the charge and R the radius. Experimental values for the nuclear radii agree very well with the equation [Dunning, *Phys. Rev.*, **45**, 587 (1934)] $R = 1.315 \times 10^{-13} \sqrt[3]{\text{at. wt.}}$ Using these values for the radii we may calculate M_F for each nucleus and the ΔM_F for nuclear reactions. The difference between the experimental change in mass, ΔM, and the ΔM_F then constitutes a measure of the change in the nuclear bond energies.

In Table I the data expressed in atomic weight units are summarized for reactions involving the emission of positrons and electrons. For the positron reactions the bond calculated is remarkably constant and appears to be simply the energy of the reaction: neutron plus positron to give a proton. For the five electron reactions, however, the energy for the conversion of a neutron to a proton is considerably smaller than the energies of the other four reactions, so that the bond energy must represent the expulsion of an electron from a H^4 group to form He^4.

TABLE I

THE EMISSION OF POSITRONS AND ELECTRONS

	$\Delta M_{Expt.}$[a]	ΔM_F	Bond
$^+H^1 = n^1 + e^+$	0.0021	−0.0002	0.0023
$^+He^3 = H^3 + e^+$	.0011	− .0011	.0022
$^+B^9 = Be^9 + e^+$	− .0003	− .0027	.0024
$^+C^{11} = B^{11} + e^+$	− .0013	− .0033	.0020
$^+N^{13} = C^{13} + e^+$	− .0015	− .0037	.0022
$^+O^{15} = N^{15} + e^+$	− .0021	− .0043	.0022
$^+F^{17} = O^{17} + e^+$	− .0025	− .0047	.0022
$Li^8 = {}^+Be^8 + e^-$	− .0112	.0031	− .0143
$B^{12} = {}^+C^{12} + e^-$	− .0117	.0043	− .0160
$N^{16} = {}^+O^{16} + e^-$	− .0070	.0052	− .0122
$F^{20} = {}^+Ne^{20} + e^-$	− .0064	.0059	− .0123
$n^1 = {}^+H^1 + e^-$	− .0010	.0012	− .0022

[a] Fowler, Delsasso and Lauritsen, *Phys. Rev.*, **49**, 561 (1936). The ΔM for the non-radioactive reactions are from Ref. 1. The masses of e^+ and e^- have been included in ΔM_F.

TABLE II

THREE TYPES OF NUCLEAR REACTIONS

	$\Delta M_{Expt.}$	ΔM_F	Bond
$H^3 + H^1 = He^4$	−0.0213	0.0006	0.0219
$Li^7 + H^1 = Be^8$	− .0183	.0016	.0199
$B^{11} + H^1 = C^{12}$	− .0173	.0025	.0198
$N^{15} + H^1 = O^{16}$	− .0129	.0036	.0165
$F^{19} + H^1 = Ne^{20}$	− .0140	.0043	.0183
$He^3 + n^1 = He^4$	− .0223	− .0002	.0221
$C^{11} + n^1 = C^{12}$	− .0198	− .0004	.0194
$C^{12} + H^1 = N^{13}$	− .0021	.0031	.0052
$O^{16} + H^1 = F^{17}$	− .0008	.0040	.0048
$C^{12} + n^1 = C^{13}$	− .0054	− .0003	.0051
$O^{16} + n^1 = O^{17}$	− .0045	− .0004	.0041
$H^2 + H^2 = He^4$	− .0255	.0007	.0262
$Li^6 + H^2 = Be^8$	− .0236	.0015	.0251
$B^{10} + H^2 = C^{12}$	− .0275	.0026	.0301
$N^{14} + H^2 = O^{16}$	− .0220	.0034	.0254

TABLE III

THE FORMATION OF $4n$ NUCLEI FROM He^4

	$\Delta M_{Expt.}$	ΔM_F	Bond: Calcd.	Bond: Model
$2He^4 = Be^8$	−0.000	+0.0024	0.0024	0.005
$3He^4 = C^{12}$	− .081	.0065	.0146	.015
$4He^4 = O^{16}$	− .156	.0121	.0277	.030
$5He^4 = Ne^{20}$	− .021	.0191	.0402	.042
$7He^4 = Si^{28}$	− .041	.037	.078	.083

Three types of reactions are given in Table II: (1) the addition of a mass particle, proton or neutron, to a $4n + 3$ nucleus, (2) the addition of a mass particle to a $4n$ nucleus and (3) the addition of H^2 to a $4n + 2$ nucleus. With few exceptions the bond energies for each group are constant within the experimental error. Many other examples may be given showing the same general constancy.

Latimer and Libby (Ref. 1) calculated the mass defect for a number of the heavier nuclei using Latimer's nuclear model, but the present accepted mass of He^4 necessitates a revision of those calculations and, in fact, requires the use of the experimental values of the radii instead of the somewhat smaller values which they used. A summary of the calculated bond energies and the comparison with the values predicted by the model for the lighter elements is given in Table III. The bond energies used are 0.005 for the bond between two mass particles and 0.017 between three particles. It should be emphasized that these values in terms of the model are not entirely arbitrary, the first is taken as $1/6$ of the total experimental bond energy of He^4, 0.031 M units, since in a tetrahedron there are six pairs of interactions, and the second is approximately $1/2$ the He^4 value.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.
WENDELL M. LATIMER

RECEIVED MAY 14, 1936

TRANS- AND CIS-AS-OCTAHYDROPHENANTHRENE

Sir:

The hydrocarbon skeleton of morphine (or more correctly that of dihydromorphine) consists principally of a 1,2,3,4,9,10,11,12-octahydrophenanthrene (*as*-octahydrophenanthrene) nucleus, and therefore the preparation of derivatives of this hydrocarbon carrying functional groups of the morphine molecule has been undertaken. Amino alcohols derived from symmetric octahydrophenanthrene were described in a recent communication [van de Kamp and Mosettig, THIS JOURNAL, **57**, 1107 (1935)].

In the preparation of *as*-octahydrophenanthrene according to the synthetic methods known so far, either the *cis*- or the *trans*-form, or more likely a mixture of the two, can be expected. As far as we know no statements concerning the configuration of this hydrocarbon have been made previously. We prepared the *as*-octahydrophenanthrene by effecting the dehydration and the isomerization of 1-β-phenylethylcyclohexanol [prepared according to Cook and Hewett (*J. Chem. Soc.* 1098 (1933)] with phosphorus pentoxide in one step. The yield in this last step calculated on the carbinol, was 90%. Phosphorus pentoxide has already been employed by Bardhan and Sengupta [*J. Chem. Soc.*, 2520 (1932)] in the ring closure of 2-β-phenylethylcyclohexanol.

The product thus obtained, after refluxing with sodium and distilling off, was fractionated, using a Widmer fractionating column.

By repeated fractionation (until constancy of physical data was reached) the *as*-octahydrophenanthrene was separated into two main fractions, A and B, and a relatively small mixed fraction.

TABLE I

Fraction		A (20%)	B (70%)
B. p.,	°C.	135.5–135.7	142.6–142.8
	Mm.	10.5–10.8	9.2
Refr. index		$n^{15}D$ 1.5460	$n^{10.6}D$ 1.5592
d^{25}_4		0.9828	1.0053

From a comparison of the above data with those of *trans*- and *cis*-decahydronaphthalene [Hückel, *Ann.*, **441**, 42 (1925)], we assign by analogy to the hydrocarbon A the *trans*-configuration and to the hydrocarbon B the *cis*-configuration.

A. *d,l-Trans*- B. *d,l-Cis*-

as-Octahydrophenanthrenes

It is possible that on repeating this separation on a larger scale, we will obtain slightly different and better physical data on the isomeric *as*-octahydrophenanthrenes. Furthermore, the possibility that one of the fractions may be a constant boiling mixture, still remains. We have prepared from each of the isomers a methyl ketone, its semicarbazone, and the carboxylic acid by oxidation of the methyl ketone.

TABLE II

DERIVATIVES OF

trans- AND *cis*-*as*-OCTAHYDROPHENANTHRENE

	Trans-, m. p., °C.	*Cis*-, m. p., °C.
—$COCH_3$	94–94.5	Oily
———semicarbazone	230–231.5	211–213
mixed m. p.	192–203	
—COOH	226–228	230–232
mixed m. p.	180–190	

We wish to mention the remote possibility that the acetyl group and consequently the carboxyl group are attached in different positions in the two hydrocarbons. Furthermore, it has to be taken into account that, in the Friedel–Crafts reaction, partial isomerization may have taken place through the action of the aluminum chloride [*cf.* Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1299 (1932)].

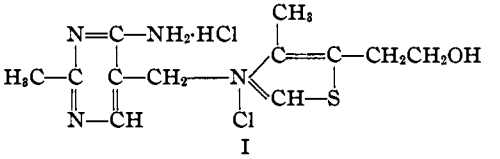
COBB CHEMICAL LABORATORY JACOB VAN DE KAMP
UNIVERSITY, VIRGINIA ERICH MOSETTIG

RECEIVED MAY 13, 1936

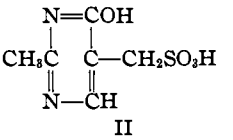
STRUCTURE OF VITAMIN B_1

Sir:

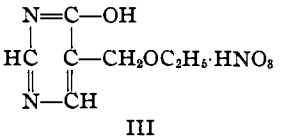
Certain provisional features of the structure previously proposed [THIS JOURNAL, **57**, 229 (1935)] require revision. We now feel justified in proposing Structure I for the vitamin.



I



II



III

We obtained by liquid ammonia cleavage of the vitamin a free base, $C_6H_{10}N_4$, which gives a double banded absorption quite different from the single bands of 2,6, 4,6 or 5,6-diaminopyrimidines but closely akin to those of 5-alkyl 6-amino pyrimidines. (Alkyl groups in position 5 have a profound influence on absorption of 6-amino pyrimidines; alkyls in other positions have minor effects.) The ultraviolet absorption of an extended series of pyrimidines provided convincing evidence that the second amino group of the base, $C_6H_{10}N_4$, is in a side chain. This base forms a dipicrate, m. p. 225°, presumably identical with the picrate of Windaus [*Z. physiol. Chem.*, **237**, 100 (1935)].

My associate, Dr. J. K. Cline, was also able to obtain from the amino sulfonic acid [THIS JOURNAL, **57**, 1093 (1935)] by the action of sodium in liquid ammonia a small yield of a base, $C_6H_9N_3$, which was identified by mixed melting points of the picrates, 221°, as 2,5-dimethyl-6-aminopyrimidine which was synthesized for absorption studies. This is the first identified pyrimidine to be obtained from the vitamin. Its significance was greatly enhanced by subsequent synthesis of II which is undistinguishable by any known means from the oxy sulfonic acid of natural origin [Ref. 3].

We have synthesized five new ethoxy derivatives of 6-oxypyrimidine; others are described

in the literature. In general, when the ethoxy group is on a methylene group in position 2 or 4 or directly on the ring in position 5, these pyrimidines form nitrates which resemble the Windaus' oxidation product [*Z. physiol. Chem.*, **228,** 28 (1934)] $C_7H_{11}N_3O_5$, in absorption [Smakula, *ibid.*, **230,** 231 (1934)] and in solubilities. We infer that Windaus' product has the structure III but have not been able as yet to effect a synthesis for confirmation. Nitric acid is evidently not added across the double bond in positions 4–5 as in oxy-nitrothymin as such addition grossly modifies absorption.

We have long been delayed by misinterpretation of some earlier results. First, the formyl derivatives of 5,6-diaminopyrimidines exhibit absorption resembling that of the vitamin. This we now regard as fortuitous. Second, we obtained crystalline formamidine (hitherto unknown) by fusing the amino sulfonic acid with sodamide. Formamidine is apparently not derived from the ring as we once supposed but probably from the methylene bridge. At another time we obtained a cleavage product with absorption indicative of a 4,6-diaminopyrimidine, the second amino group, as we now see it, being introduced by reaction rather than preëxisting in the vitamin, Following these false leads, we have attempted the synthesis of various isomers of the vitamin with considerable success but with uniformly negative physiological results and are now engaged in devising a synthesis of structure I.

Abundant activity has been obtained in such a synthetic reaction mixture.

463 WEST ST. R. R. WILLIAMS
NEW YORK, N. Y.

RECEIVED MAY 23, 1936

NEW BOOKS

Dictionary of Organic Compounds. Volume II: Eccaine-Myrtillin Chloride. Edited by I. M. HEILBRON, D.S.O., D.Sc., Ph.D., F.I.C., F.R.S., Sir Samuel Hall Professor of Chemistry, University of Manchester, and H. M. Burnbury, M.S.C., A.I.C., Imperial Chemical Industries Ltd. Oxford University Press, 114 Fifth Avenue, New York, 1936. 846 pp. Price $30 or $75 for the set of three volumes.

The spontaneous and flattering reception accorded the initial volume of the "Dictionary of Organic Compounds" may be construed as a verdict that Heilbron's new contribution to the classification of carbon compounds will be ranked in importance along with Beilstein and Richter. That the authors are greatly encouraged "to maintain and even enhance the standard attained" in Volume I is attested by the fact that Volume II, which has just been issued by the Oxford University Press, "although originally intended to be of approximately the same size as Volume I, actually contains nearly 150 pages more."

Several outstanding features of the English work make a strong appeal: its relatively low cost; the alphabetical classification with the obvious advantage where ready reference is concerned; the inclusion under each compound listed of all descriptive data and functional derivatives ordinarily desired; the limited number of selected literature references which means a great saving in time where unessential detail is not demanded; and, finally, a review of the literature through the year prior to the date of publication of each volume.

Before the appearance of Heilbron, abstract journals were relied on in large part to supplement Beilstein in the preparation of up-to-date bibliographies. In this connection the following announcement in the Preface of the second volume is of interest: "No addendum has been found necessary, since the literature has been completely covered up to the end of 1934. Opportunity has been taken to add as many 1935 references as the exigencies of going to press would allow."

The benefits of an authoritative lexicon like Heilbron are well exemplified by the structural relationships of recent development among the coloring pigments in plant life. Here a mass of xanthones, flavones, flavonols and anthocyanidins have been isolated from natural sources and their complex structures established. A picture of the wonderful revelations in this important domain of organic chemistry is presented only when one can visualize the recently cleared-up substitutions and molecular rearrangements which are concerned in the metamorphosis of one product to another. What applies here is true all through Organic Chemistry; in the past few years many new fields have been explored and the accumulation of new facts has been so rapid that only the specialist in each particular domain can qualify as an authority in his realm.

Of necessity, in Heilbron, where will be crowded a vast subject matter into three volumes, will not be found thousands of known organic compounds. The only work which now embraces or probably ever will embrace an exhaustive survey is Beilstein. But here there exists at present a