

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.

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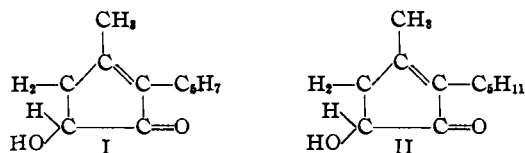
RECEIVED MAY 13, 1936

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

Sir:

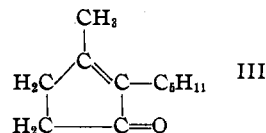
In article IV of this series [*J. Org. Chem.*, **1**, 38 (1936)] we have reported that the semicarbazones of pyrethrolone and tetrahydropyrethrolone contain two less hydrogen atoms than are required by their accepted formulas. Pyrethrolone semicarbazone corresponds to the formula $C_{12}H_{17}O_2N_3$ 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.



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 dihydrojasmonone, 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)].



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

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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)] $R = 1.315 \times 10^{-13} \sqrt{\text{at. wt.}}$. 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^+ group to form He^+ .

TABLE I
THE EMISSION OF POSITRONS AND ELECTRONS

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

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

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

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

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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.