

Order of reflection		1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
4-Substituted p.a.	I_c	275	0	15	12	2	2	7	0	2	4
4-Keto-p.a.	I_0	st	...	wk ⁺	wk ⁺	wk ⁻	vwk	wk ⁺	vwk	vwk	wk
4-Hydroxy-p.a.	I_0	st	...	wk ⁺	m	wk ⁻	wk	m	vwk	wk	wk ⁺
11-Substituted p.a.	I_c	94	7	87	2	2	0	3	13	1	3
11-Keto-p.a.	I_0	m ⁻	vwk	m ⁺	...	vwk	...	vwk	wk ⁺	...	vwk
11-Hydroxy-p.a.	I_0	m ⁻	wk	st	wk	wk	vwk	wk ⁻	m ⁺	wk	wk ⁺
12-Substituted p.a.	I_c	80	2	87	8	10	0	0	2	2	13
12-Keto-p.a.	I_0	m ⁺	...	st	m ⁻	m	wk	wk	m
12-Hydroxy-p.a.	I_0	wk ⁺	vwk	m	wk	wk	wk ⁻	wk ⁻	wk

p.a. = palmitic acid, st = strong, m = medium, wk = weak, v = very, I_c = calculated intensity, I_0 = observed intensity.

being produced by the "guest" molecules behaving as a one-dimensional crystal along the channel direction of the "host" structure, and the molecular length is readily calculated from the line positions.¹

We have now examined the intensity sequence at the centers (corresponding to $(00l)$ -reflections) of such lines, produced by a series of compounds where the chain length is held constant and the position of a substituent on the chain is varied. In general, a unique pattern of intensities was found for each position isomer, suggesting the possibility of determining the position of substituents on a hydrocarbon chain. For all of the substituted palmitic acids examined (twelve keto-acids and six hydroxy-acids) very good agreement was obtained between the calculated and the observed intensities of the lines, three examples of each series of which are listed. The same calculated values apply to methyl substituted acids.

In such a one-dimensional problem the calculation of relative intensities $I_c(00l)$ can be done by the formula

$$I_c(00l) = C_\theta \cdot |F_{(00l)}|^2$$

where

$$C_\theta = (1 + \cos^2 2\theta) / \sin 2\theta$$

and

$$F_{(00l)} = \sum_{n=1}^N f_n (\cos 2\pi lz_n + i \sin 2\pi lz_n)$$

or

$$|F_{(00l)}|^2 = 2 \sum_{n=1}^{N/2} f_n \cos 2\pi lz_n$$

for the general and the centrosymmetrical cases, respectively. The function C_θ of the diffraction angle θ corrects for the Lorentz factor and the polarization factor. In the formula for the structure factor $F_{(00l)}$, f_n is the atomic scattering factor and z_n the coordinate in the chain direction of the n^{th} atom, taking the period length of the adducted compound (repeat distance) as unity, whereas l is the Laue index of the reflection order. The summation is taken over all N atoms of a repeat unit, or if the origin is put on a center of symmetry, over all $N/2$ centrosymmetrical pairs of atoms.

For the palmitic acid dimer, $c = 45.1 \text{ \AA}$. Since the hydrocarbon chains are nearly stretched out in the urea channels, the coordinates z_n were computed assuming 1.26 \AA . and 3.74 \AA . for the c -projection of the C-C single bond length and of the van der Waals distance between two neighboring methyl end groups, respectively. For simplicity,

(1) N. Nicolaides and F. Laves, *THIS JOURNAL*, **76**, 2596 (1954); other references found there.

a uniform atomic scattering factor, f_n , was introduced for all carbon and oxygen atoms; this is justified, since carbon on the average is connected to two hydrogen atoms thus having the same number of electrons as oxygen has. The good agreement between calculated and observed intensities shows that calculations based upon such a simplified model are adequate for identification purposes.

More details and applications will appear in *Zeitschrift für Kristallographie*.

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(2) Department of Medicine, The University of Chicago, Chicago 37, Illinois. Guggenheim Fellow for the year 1955-56.

MINERALOGISCHES INSTITUT
EIDG. TECHN. HOCHSCHULE
ZÜRICH, SWITZERLAND

N. NICOLAIDES²
F. LAVES
A. NIGGLI

RECEIVED NOVEMBER 2, 1956

FORMATION OF AN ORGANO BORON PEROXIDE BY REACTION OF OXYGEN AND TRIMETHYLBORANE¹

Sir:

The reaction of trimethylborane with oxygen at pressures below the explosion limit produces a 1:1 reaction product as previously reported by Bamford and Newitt² and observed by Coleman.³ However, we have found that this product is not

Molar flow ratio $O_2:B(CH_3)_3$	% $B(CH_3)_3$ reacted	Molar product ^a $O_2:B(CH_3)_3$	Milliequivalents ^b oxidizing power per g.
0.8:1	63	0.91:1	...
1.0:1	73	0.95:1	...
1.2:1	92	0.91:1	...
1.4:1	95	1.03:1	...
1.5:1	96	0.98:1	...
2.0:1	99	0.96:1 ^c	11.02 ± 0.05
2.3:1	99	0.93:1 ^c	11.15 ± .05
2.0:1	99	...	11.00 ± .02

^a Calculated from the weight of product and the amount of $B(CH_3)_3$ consumed in the reaction. ^b One gram $(CH_3)_2BOOCH_3$ is equivalent to 11.38 millimoles. Reported values are the means of six determinations in each case. Neither $B(CH_3)_3$ nor $CH_3B(OCH_3)_2$ liberate iodine by the procedure employed. ^c Molecular weight determinations on product from these preparations gave $M = 88.5$ and 87.4 .

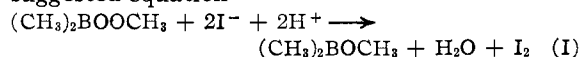
(1) This work was supported in part by the Ohio State University Research Foundation.

(2) C. H. Bamford and D. M. Newitt, *J. Chem. Soc.*, 695 (1946).

(3) J. E. Coleman, J. A. Lovinger, R. C. Petry and F. H. Verhoek, Final Report OSU Research Foundation Project 116-C, June 16, 1955.

the ester,^{4,5} dimethoxymethylborane, $\text{CH}_3\text{B}(\text{OCH}_3)_2$, (II), but is instead dimethylborylmethylperoxide, $(\text{CH}_3)_2\text{BOOCH}_3$, (I).

(I) was prepared by reaction of oxygen and trimethylborane in a flow system at room temperature and 10–15 mm. pressure and a 2–3 minute contact time. At molar flow ratios of oxygen to trimethylborane of 2:1, the reaction is quantitative (Table I). The peroxide, which appears to be the only product of this reaction, is a colorless liquid of negligible vapor pressure at -118° . Its vapor pressure curve lies between those of the esters methoxydimethylborane and dimethoxymethylborane. The peroxide liberates iodine quantitatively from a degassed sodium iodide-isopropyl alcohol solution acidified with glacial acetic acid, by the suggested equation



Supporting evidence for equation (I) is obtained from the reaction of the peroxide with two equivalents of anhydrous hydrogen iodide at -78° . Methoxydimethylborane, identified by its vapor pressure curve⁶ and mass spectrum, was isolated from the reaction mixture in 80% yield together with substantial amounts of water and iodine. However, there is some indication that the primary products of this reaction are methanol and hydroxydimethylborane, and that the products isolated result from an esterification reaction during fractionation of the reaction mixture.

The peroxide (I) rearranges in a sealed tube in the liquid phase and in the gas phase (air absent) at room temperature to give approximately 90% of a compound of identical molecular weight. Preliminary results show that the rearrangement in the gas phase and in benzene solution follows first order kinetics; the half-life in the gas phase is approximately 60 days at room temperature. The rearranged product is dimethoxymethylborane (II), and shows the same mass spectrum, vapor pressure curve, and molecular weight as samples of II (b.p. 52.5° , 747 mm.) prepared by the reaction of trimethylborate and methyl Grignard reagent.

The peroxide (I) forms crystalline addition compounds when allowed to react with an equivalent amount of ammonia or pyridine. This reaction produces no substances not condensed at liquid nitrogen temperature, and preliminary results indicate no appreciable destruction of the peroxide bond by adduct formation. The ester (II) forms no adduct with pyridine.

The mass spectrum of the peroxide (I) is in agreement with the proposed structure and is inconsistent with the alternative hydroperoxide $(\text{CH}_3)_2\text{BCH}_2\text{OOH}$. Similarly, the hydroperoxide is excluded by consideration of the high vapor pressure of I as compared to that of hydroperoxides, the ease of rearrangement to the ester (II) and the nature of the reduction products.

Three explosions have been encountered thus far in the course of this investigation: two occurred

(4) J. R. Johnson and M. G. Van Campen, Jr., *THIS JOURNAL*, **60**, 121 (1938).

(5) E. Frankland, *J. Chem. Soc.*, **15**, 363 (1862).

(6) A. B. Burg and R. I. Wagner, *THIS JOURNAL*, **75**, 3872 (1953).

during transfers of the peroxide in vacuo and a third during a peroxide preparation. The compound should be handled cautiously.

Acknowledgment.—We wish to express our appreciation to John W. Kraus for the determinations of the mass spectra and to Dr. Earl W. Malmberg for his counsel.

THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

ROBERT C. PETRY
FRANK H. VERHOEK

RECEIVED NOVEMBER 12, 1956

THE C-3 CONFIGURATION OF CERTAIN INDOLE ALKALOIDS¹

Sir:

In connection with studies on the stereochemistry of indole alkaloids containing the ring system of yohimbine, ajmalicine, or corynantheine, we have had occasion to inspect the infrared spectra of chloroform solutions of various pairs of C-3 epimers. It became apparent that the 3.4–3.7 μ region of the C–H stretching vibration can be used to identify unmistakably the stereo-configuration of the hydrogen atom at C-3 of the alkaloids or their derivatives. Thus, all compounds possessing an α -hydrogen at C-3, *i.e.*, *normal* and *allo* products such as yohimbine² (IA), *d,l*-alloyohimbane² (IIA), and ajmalicine^{2,3} (IIIA) (illustrated in the Figure below), exhibit two or more distinct and characteristic peaks of medium intensity on the high-wave length side of the major 3.46 μ band. However, those compounds containing a C₃-H β -orientation, *i.e.*, *pseudo* or *epiallo* products such as ψ -yohimbine² (IB), *d,l*-epialloyohimbane² (IIB), and 3-iso-ajmalicine (IIIB), m.p. 193 – 194° (found: C, 71.39; H, 6.96; N, 7.79), prepared by a zinc-acetic acid reduction⁴ of 3-dehydroajmalicine,⁵ show merely shoulders on the high-wave length side of the main peak.⁵

On the basis of the above spectrophotometric

(1) This work was supported in part by a research grant (M 1301) from the National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare.

(2) For a recent review of the stereochemistry of this compound and related derivatives, cf. J. E. Saxton, *Quart. Revs.*, **10**, 108 (1956).

(3) E. Wenkert and D. K. Roychaudhuri, *J. Org. Chem.*, in press.

(4) F. L. Weisenborn and P. A. Diassi, *THIS JOURNAL*, **78**, 2022 (1956).

(5) *Epiallo* compounds containing 18-aryloxy groups, *e.g.*, reserpine, show a fully developed extra peak instead of one of the shoulders.

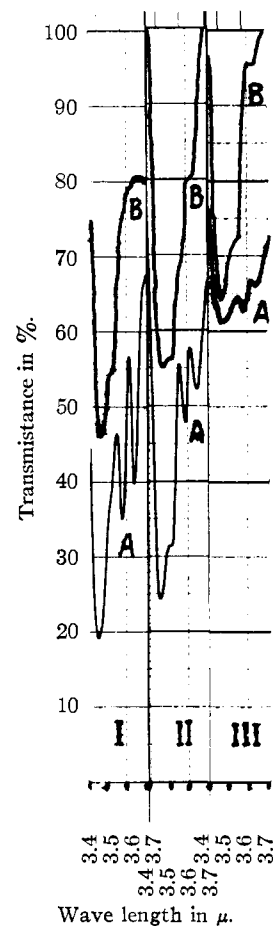


Fig. 1.