TABLE II

MELTING POINTS AND ANALYSES OF THE *p*-NITROBENZOATES

Ester	M. p., °C. (cor.)	Nitrogen, % Calcd.	Found
Methyl	95.1[a]	7.73	8.03
Ethyl	56.3	7.18	7.14
n-Propyl	34.0	6.70	7.12
i-Propyl	108.3	6.70	6.71
n-Butyl	35.3	6.28	6.56
i-Butyl	69.5	6.28	6.58
s-Butyl	25.0	..	..
Amyl	11.2	5.91	6.09
Hexyl	6.7	5.59	5.78
Heptyl	7.9	5.28	5.36
Octyl	16.6	5.02	5.10
Nonyl	18.7	4.78	4.87
Decyl	29.8[b]	4.56	4.52
Undecyl	29.2	4.36	4.86
Dodecyl	41.9	4.18	4.17
Tridecyl	37.4	4.01	3.97
Tetradecyl	51.2	3.86	4.06
Pentadecyl	45.8	3.71	3.75
Hexadecyl	58.4	3.58	3.79
Heptadecyl	53.8	3.46	3.40
Octadecyl	64.3	3.36	3.46
Nonadecyl	58.9	3.23	3.29
Eicosyl	69.4	3.15	3.20

[a] Henstock, *J. Chem. Soc.*, 216 (1933), gave melting points for the following esters: methyl 96°, ethyl 57°, *n*-propyl 32°, *i*-propyl 55.5°, *n*-butyl 35°, *i*-butyl 67°, amyl 54°; Wilbrand and Beilstein, *Ann.*, 128, 262-263 (1863), gave the same values as Henstock for methyl and ethyl; *Chem. Zentr.* **80**, (II) 1025 (1909), gave 35° for propyl; R. Kuhn, *et al.*, *Ber.*, **75B**, 711-719 (1942), gave butyl 34-35°, dodecyl 43-44° and hexadecyl 53-55°. [b] Komppa and Talvitie, *J. prakt. Chem.*, **135**, 193 (1932), gave 30.2° for decyl.

completion. The alcohols from decyl through octadecyl were from those prepared by Meyer and Reid.[3] Thanks are also due Hooker Electrochemical Company for furnishing the *p*-nitrobenzoyl chloride.

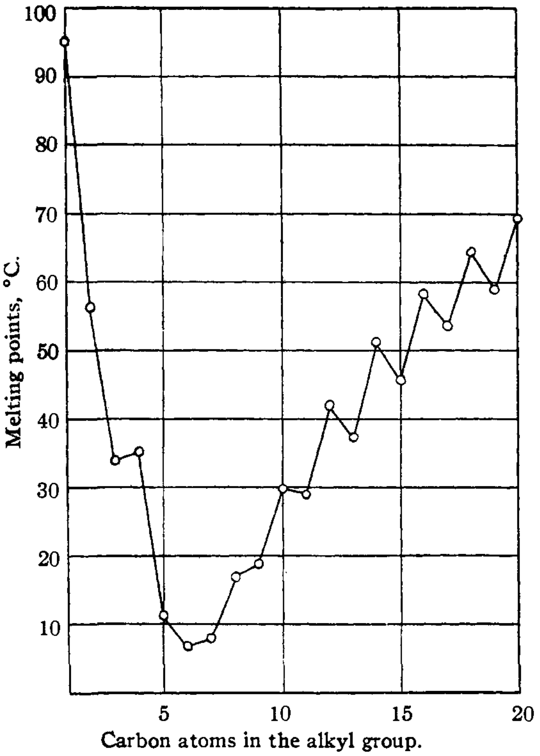

Fig. 1.—Melting points of the alkyl *p*-nitrobenzoates.

Summary

The alkyl esters, through eicosyl, of *p*-nitrobenzoic acid have been prepared and some of their properties determined. A curve is shown for the melting points, which exhibits regular alternation above the hexyl ester. Fifteen of the twenty-three derivatives are new compounds.

COLUMBIA, SOUTH CAROLINA RECEIVED AUGUST 7, 1943

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[3] Meyer and Reid, THIS JOURNAL, **55**, 1574-1584 (1933).

NOTES

The Dissociation of Dimethyl Ether-Boron Trifluoride at Low Temperatures

BY HERBERT C. BROWN AND[1a] RICHARD M. ADAMS

There has appeared recently an electron diffraction study of dimethyl ether-boron trifluoride,[1] the results of which are of considerable importance to chemists interested in the properties of addition compounds. Before the interpretation of the electron diffraction photographs is accepted, however, one doubtful point should be clarified. In the article cited, the authors state that the dissociation of dimethyl ether-boron trifluoride in the vapor phase at 40° is less than 10%, and may be neglected in the interpretation of the diffraction patterns. There is, however, good reason to believe that the dissociation of the complex is much greater than the figure given. This opinion is based upon the following evidence.

Two independent studies of the vapor phase dissociation of dimethyl ether-boron trifluoride are now available. One by Laubengayer and Finlay[2] was published simultaneously with the

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[1a] Present address: Department of Chemistry, Wayne University, Detroit, Michigan.

[1] Bauer, Finlay and Laubengayer, THIS JOURNAL, **65**, 889 (1943).

[2] Laubengayer and Finlay, *ibid.*, **65**, 887 (1943).

electron diffraction study; another by the present authors,[3] appeared some six months earlier. In the latter paper the dissociation constants of the complex over the temperature range from 66 to 99° are given. These constants were satisfactorily represented by the equation

$$\text{Log } K_p = -2904/T + 7.049 \qquad (1)$$

The heat of dissociation, calculated from the variation of the dissociation constant with temperature, was 13.3 kcal.

Laubengayer and Finlay list two series of measurements, one covering the temperature range from 90 to 130°, and the other the range from 50 to 100°. Their heat of dissociation, calculated from the dissociation constants in the range from 100 to 130°, was 13 kcal., in excellent agreement with the one found by the present authors. Moreover, the dissociation constants in the range from 100 to 130° agree satisfactorily with the ones calculated for the same temperatures by means of our equation (1) (Table I). On the other hand, Laubengayer and Finlay's measurements at lower temperatures are in marked disagreement with our experimental values in the same temperature range. Moreover, their results are not self-consistent—for example, their recorded values for the dissociation constants at 80, 90 and 100° are 0.107, 0.055 and 0.180, respectively (Table I); and their value for 50°, 0.002, is obviously far too low. The difficulty of reconciling these measurements at lower temperatures either with their own results at the higher temperatures or with our data is well brought out by Fig. 1. It therefore appears reasonable to discard the few erratic values (90, 80, 50°) in calculating the value of the dissociation constant at 40°, and to rely for this purpose primarily on equation (1), which fits the data quite satisfactorily from 130 to 66°.

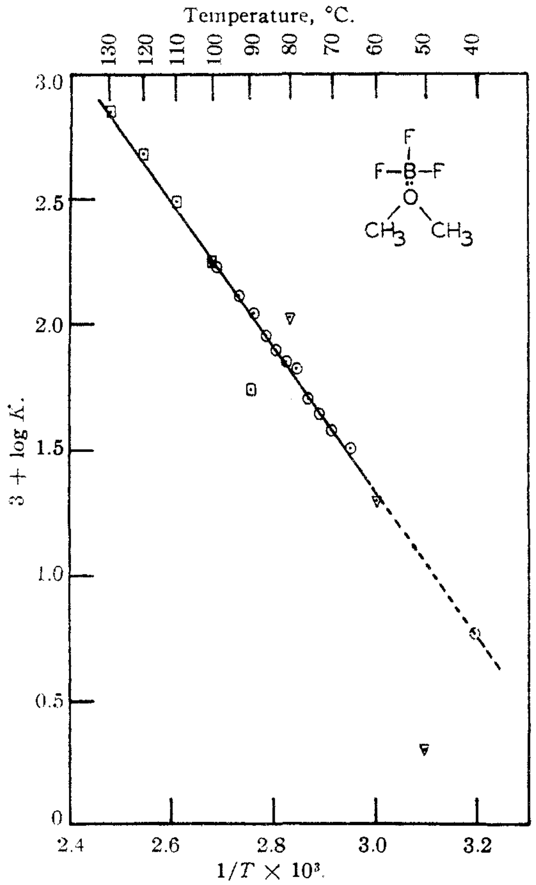

Fig. 1.—Dissociation data of dimethyl ether-boron fluoride: □, data of L. and F.[2] (sample 1); ▽, data of L. and F.[2] (sample 2); ○, data of B. and A.[3]

TABLE I

DISSOCIATION DATA FOR DIMETHYL ETHER-BORON TRIFLUORIDE

Source of data	Temp., °C.	Dissociation constant, $K_{(\text{atm.})}$ Found	Calcd.
B. and A.[3]	66	0.032	0.030
	70	.038	.038
	73	.044	.045
	75.5	.051	.052
	78.5	.067	.061
	81	.071	.070
	83.5	.079	.080
	86	.091	.091
	89	.111	.107
	93	.131	.130
	99	.171	.175
L. and F.[2]	90	.055	.112
(Sample No. 1)	100	.180	.183
	110	.312	.293
	120	.483	.458
	130	.701	.699
L. and F.[2]	50	.002	.011
(Sample No. 2)	60	.020	.021
	80	.107	.066
	100	.180	.183

Bauer, Finlay and Laubengayer[1] do not report the basis of their conclusion that the dissociation of dimethyl ether-boron trifluoride is less than 10% at 40°. The dissociation constant at 40°, calculated by equation (1), is 0.0059; at this temperature and at the saturation pressure, 9.5 mm., the complex is 57% dissociated. At pressures below the saturation pressure, the degree of dissociation is, of course, even greater. The conclusions drawn from the electron diffraction photographs should be reconsidered in the light of these facts.[4]

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RECEIVED JUNE 22, 1943

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[3] Brown and Adams, THIS JOURNAL, **64**, 2559 (1942).

[4] Before this Note was submitted to the JOURNAL, a copy was sent to Drs. Laubengayer and Bauer. Dr. Bauer has informed us that a reëxamination of the electron diffraction study will be made in order to determine the effect of the high dissociation of the complex on the interpretation of the diffraction photographs.

The Reaction of Chloral with Cyclohexylmagnesium Bromide

By Vaughn W. Floutz

The action of chloral with various organomagnesium halides gives a number of reaction products depending principally upon the nature of the organomagnesium halide employed. Secondary alcohols which contain the trichloromethyl and alkyl groups have been prepared by several investigators.[1,2,3] In some instances the reported yields of such alcohols have been low,[2] and in one case[4] leading to the synthesis of trichloroisopropanol, trichloroethanol was formed in isolable quantity. A recent study[5] of the interaction of chloral and ethylmagnesium halides has shown that trichloroethanol is produced in yields up to 65%, but that no significant quantities of secondary alcohol are formed. Secondary alcohols containing the trichloromethyl group together with an aryl group are formed readily in good yield by the Grignard reaction.[6,7] Unpublished research by the author has shown that trichloromethylphenylcarbinol and trichloromethyl-*o*-tolylcarbinol can be prepared in yields as high as 70%. With the exception of trichloromethylbenzylcarbinol described first by Howard,[2] and more recently by Gilman and Abbott,[5] attempts to prepare secondary alcohols from chloral and phenyl substituted alkylmagnesium halides have proved unsuccessful. In this connection Dean and Wolf[8] have shown that β-phenylethylmagnesium bromide, γ-phenylpropylmagnesium bromide, and δ-phenylbutylmagnesium bromide react with chloral to give trichloroethanol, styrene and its homologs, and 1,4-diphenylbutane and its homologs, but no detectable secondary alcohol.

The object of this study was to investigate the behavior of cyclohexylmagnesium bromide with chloral.

Procedure.—The Grignard reagent was prepared by adding a 0.2-mole portion of cyclohexyl bromide dissolved in a like volume of anhydrous ether to 0.2 g.-atom of magnesium turnings in 200 ml. of anhydrous ether under an atmosphere of nitrogen. In the normal addition, 0.2 mole of freshly distilled chloral dissolved in a like volume of anhydrous ether was added slowly to the Grignard reagent and the mixture finally refluxed for one-half hour. In the inverse addition the Grignard reagent was removed and slowly added to 0.2 mole of freshly distilled chloral dissolved in 75 ml. of anhydrous ether. In both types of addition very little solid separated in the course of the reaction. The reaction mixture was treated with 1 *N* hydrochloric acid and the ether layer was separated and washed in turn with sodium bicarbonate solution, sodium bisulfite solution, and water, then dried over anhydrous sodium sulfate.

The dried ether was removed by distillation and the residue was heated in an oil-bath to a bath temperature of 110°. This gave a distillate which was found to be principally cyclohexene. The hydrocarbon was identified by its conversion to 1,2-dibromocyclohexane, boiling point 116–118° at 29 mm. In determinations carried out subsequent to the identification of cyclohexene, it was found advisable to add the cyclohexene distillate to the ether first removed by distillation, and treat the resulting ether solution with a slight excess of bromine. Following this the ether solution was washed with sodium bicarbonate solution and water. The dried ether was removed by distillation and the residue subjected to fractional distillation under diminished pressure to obtain the 1,2-dibromocyclohexane.

The residue from the removal of the cyclohexene was fractionated under diminished pressure. The first fraction collected gave upon redistillation an oily liquid distilling at 66–69° at 25 mm. This product was identified as trichloroethanol through the preparation of the *m*-nitrobenzoate, melting point 75°, and the α-naphthyl urethan, melting point 119°. Dicyclohexyl, boiling point 122–125° at 20 mm., was isolated from a higher boiling fraction.

From a number of determinations the average yields of trichloroethanol, 1,2-dibromocyclohexane, and dicyclohexyl were, where normal addition was followed, 12.5 g., 14.5 g. and 1 g.; where inverse addition was followed, 15.5 g., 21 g. and 2 g., respectively.

This investigation shows that the interaction of cyclohexylmagnesium bromide and chloral produces no secondary alcohol. Cyclohexene, trichloroethanol, and dicyclohexyl are formed in the reaction. Inverse addition gives in general better yields, but does not change the nature of the reaction products.

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Received July 23, 1943

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[1] Henry, *Compt. rend.*, **138**, 205 (1904).

[2] Howard, This Journal, **48**, 774 (1926).

[3] Howard, *ibid.*, **49**, 1068 (1927).

[4] Kharasch, Kleiger, Martin and Mayo, *ibid.*, **63**, 2305 (1941).

[5] Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1943).

[6] Savarian, *Compt. rend.*, **146**, 297 (1908).

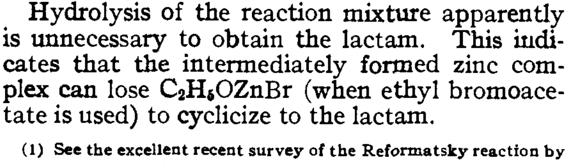
[7] Fritzman, *J. Russ. Phys.-Chem. Soc.*, **7**, 1046–1048 (1906).

[8] Dean and Wolf, This Journal, **58**, 332 (1936).

The Reformatsky Reaction with Benzalaniline

By Henry Gilman and Merrill Speeter

There appears to be no report on a Reformatsky reaction with an anil linkage.[1] We have observed that a mixture of ethyl bromoacetate and zinc adds to the anil linkage of benzalaniline to give a 56% yield of the β-lactam of β-anilino-β-phenylpropionic acid [A]



$$\overset{\text{H}}{\text{C}_6\text{H}_5\text{C}}{=}\text{NC}_6\text{H}_5 + \text{BrCH}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{Zn} \longrightarrow$$

$$\underset{\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5}{\overset{\text{H}}{\text{C}_6\text{H}_5\text{C}}}\text{—}\underset{\text{ZnBr}}{\text{NC}_6\text{H}_5} \xrightarrow{-\text{C}_2\text{H}_5\text{OZnBr}} \begin{array}{c}\text{C}_6\text{H}_5\text{—}\overset{\text{H}}{\text{C}}\text{—NC}_6\text{H}_5\\ \vert \qquad \vert\\ \text{CH}_2\text{—C}{=}\text{O}\end{array}$$

A

The structure of the lactam was established by the method of mixed melting points with a sample prepared by adding ketene to benzalaniline.[2]

Hydrolysis of the reaction mixture apparently is unnecessary to obtain the lactam. This indicates that the intermediately formed zinc complex can lose C_2H_5OZnBr (when ethyl bromoacetate is used) to cyclicize to the lactam.

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[1] See the excellent recent survey of the Reformatsky reaction by Shriner in Adams, "Organic Reactions," John Wiley and Sons, New York, N. Y., 1942, Vol. I, pp. 1–37.

[2] Staudinger, *Ber.*, **50**, 1037 (1917).

The extent of addition to the anil linkage is significantly increased when ethyl α-bromopropionate is used. In this case there is obtained an 85% yield of the β-lactam of α-methyl-β-anilino-β-phenylpropionic acid. The Reformatsky reaction with anils appears to be broad in scope, and more complete details will be published later.

Experimental

β-Lactam of β-Anilino-β-phenylpropionic Acid.—A solution of 36.2 g. (0.2 mole) of benzalaniline in 200 cc. of sodium-dried toluene was heated to boiling with 13.5 g. (0.21 g. atom) of sandpapered zinc foil and a crystal of iodine. Three cc. of ethyl α-bromoacetate was added and on stirring an exothermic reaction set in. Twenty more cc. (a total of 0.21 mole) of the bromo-ester was now added at such a rate as to maintain gentle refluxing. When the addition was completed, the mixture was boiled gently for one-half hour. Hydrolysis was effected with 200 cc. of concd. ammonium hydroxide. The toluene layer was then washed with water, dilute hydrochloric acid, sodium bisulfite solution, and again with water. After distillation of the solvent, and two recrystallizations from methanol, a 56% yield of lactam melting at 153–154° was obtained.

Ketene[3] was treated with 0.1 mole of benzalaniline following the directions of Staudinger.[2] After a number of recrystallizations from methanol, the product melted at Staudinger's value of 153–154°. A mixed melting point determination showed the compounds to be identical.

Reaction without Hydrolysis.—A mixture of 11.1 cc. (0.1 mole) of ethyl α-bromoacetate and 18.1 g. (0.1 mole) of benzalaniline in 100 cc. of toluene reacted with 6.6 g. (0.1 g. atom) of zinc. After the reaction, the mixture was diluted with 500 cc. of dry ether. The precipitate was allowed to settle and the supernatant liquid then decanted. After distillation of the solvent, the residue was twice recrystallized from anhydrous methanol. The melting point of the product was 154°, and there was no depression when this compound was mixed with lactam prepared from ketene.

β-Lactam of α-Methyl β-Anilino-β-phenylpropionic Acid.—Using the same general procedure as in the first reaction, but substituting 0.21 mole of ethyl α-bromopropionate for the ethyl α-bromoacetate, an 85% yield of lactam melting at 109–110° was obtained. Crystallization was from methanol.

Reaction with Benzyl α-Bromoacetate.—A solution of 18.1 g. of benzalaniline (0.1 mole) in 100 cc. of toluene reacted with 6.6 g. of zinc (0.1 g. atom) and 23 g. (0.1 mole) of benzyl α-bromoacetate. The product was isolated and purified by the procedure of the first reaction. A 40% yield of lactam melting at 153–154° was obtained. This compound was identified by a mixed melting point determination with the lactam obtained from ketene.

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(3) Hurd, "Organic Syntheses," **4**, 39 (1925).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED AUGUST 16, 1943

4-Phenylphenyl Iodoacetate

BY LEE C. HENSLEY AND STEWART E. HAZLET

Bromine previously[1] has been shown to convert 4-phenylphenyl chloroacetate to 4-phenylphenyl bromoacetate by a reaction in specially prepared acetic acid in the presence of a trace of iron. We have now prepared the corresponding iodoacetate by the reaction of potassium iodide with the chloro or bromo compound.

Preparation of 4-Phenylphenyl Iodoacetate from 4-Phenylphenyl Bromoacetate.—Four and seventy-five hundredths grams of the bromoacetate was dissolved in 40 ml. of acetone. This solution was added in small portions to 275 ml. of acetone saturated with potassium iodide and containing an excess of 0.5 g. of undissolved potassium iodide. At first a cloudiness appeared but, as more of the solution containing the ester was added, small granules formed and precipitated. The mixture was set aside at room temperature for thirty-six hours; Norite was added and the mixture was then allowed to stand for an additional six hours. Boiling, filtering, and removing about one-half of the acetone on the steam-bath followed. The remaining solution was poured into 600 ml. of water, and a flocculent precipitate was formed. This product represented a 77.8% yield of 4-phenylphenyl iodoacetate; m. p. 113–114°. Two recrystallizations from methanol followed by two from 70–90° ligroin raised the melting point to 113.5–114.3°.

Anal. Calcd. for $C_{14}H_{11}O_2I$: I, 37.53. Found: I, 37.76.

Preparation of 4-Phenylphenyl Iodoacetate from 4-Phenylphenyl Chloroacetate.—The same procedure, applied to the bromoacetate, gave 18.3% yield of the iodo product.

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(1) Hazlet, Hensley and Jass, THIS JOURNAL, **64**, 2449 (1942).

DEPARTMENT OF CHEMISTRY
STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON

RECEIVED AUGUST 9, 1943

[BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
AGRICULTURAL RESEARCH ADMINISTRATION, UNITED
STATES DEPARTMENT OF AGRICULTURE]

The Hydrolysis of Nicotinonitrile by Ammonia

BY CHARLES F. KREWSON AND JAMES F. COUCH

It is well known that the action of potassium or sodium hydroxide on nitriles leads directly to the formation of the corresponding acids.[1] The amides, postulated as intermediate products in this reaction, are obtained when hydrogen peroxide is added to the mixture.[2]

The action of ammonium hydroxide has not been extensively studied. Schlieper reported that it did not react with valeronitrile. The idea that ammonium hydroxide reacts with nitriles to form amidines possibly stems from Bernthsen's[3] discovery that amine hydrochlorides react with certain nitriles to form amidine hydrochlorides. Ammonium chloride, however, did not react in this way. We have found that ammonium hydroxide reacts with nicotinonitrile to form nicotinamide.

Procedure.—A mixture of nicotinonitrile (20 g.) prepared either by the Woodward, Badgett and Willaman process[4] or from nicotinamide by the method of LaForge,[5] and 120 ml. (9 moles) of concentrated ammonium hydroxide solution in a cylindrical glass bulb made of 60-mm. Pyrex glass tubing, to one end of which is sealed a short piece of 10-mm. tubing, is cooled in ice, and the small tube drawn down to a spiral capillary. The bulb is then placed in a 500-cc. steel bomb along with 100 cc. of concen-

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(1) (a) A. Schlieper, *Ann. Chem. Pharm.*, **59**, 1–23 (1846); (b) E. Frankland and H. Kolbe, *ibid.*, **65**, 288–304 (1848).

(2) (a) Br. Radziszewski, *Ber.*, **17**, 1289–1290 (1884); **18**, 355–356 (1885); (b) L. McMaster and F. B. Langreck, THIS JOURNAL, **39**, 103–109 (1917); (c) L. McMaster and C. R. Noller, *J. Indian Chem. Soc.*, **12**, 652–653 (1935); *C. A.*, **30**, 1736 (1936).

(3) A. Bernthsen, *Ann. Chem. Pharm.*, **184**, 321–370 (1876); **192**, 1–60 (1878); *Ber.*, **10**, 1235 (1877).

(4) In course of publication.

(5) F. B. LaForge, THIS JOURNAL, **50**, 2477 (1928).

trated ammonium hydroxide. The bomb is then closed and heated at 107–109° for twelve hours, cooled, and the reaction mixture transferred to a desiccator and evaporated. The non-volatile product, 21.2 g., m. p. 114–122°, contains 80.5% of nicotinamide,[6] the remainder being nicotinic acid.[7] The yield of amide is 72.66%. After two recrystallizations from ethyl acetate, the amide melts at 129–130°, and the mixed melting point with pure nicotinamide shows no depression.

Anal. Calcd. for $C_6H_6ON_2$: C, 59.01; H, 4.95; N, 22.94. Found:[8] C, 58.97, 59.06; H, 4.9, 5.11; N, 22.80, 22.82.

The amide may, however, be extracted directly in the reaction mixture in very pure condition by ethyl acetate. Using this procedure, we have obtained a product containing 98.93% of amide and melting at 129–130°.

Addition of sodium hydroxide to the reaction mixture results in markedly speeding up the reaction, with an increased production of nicotinic acid and a corresponding decrease in the yield of amide.

Hydrogen peroxide (3.5 moles in 30% solution) added to the ammonium hydroxide (2 moles) and nitrile (1 mole) shortens the reaction time and gives increased yields (94 and 96%). The product, however, contains more nicotinic acid and melts over a wide range of temperature.

Hydrogen peroxide (3.5 moles in 30% solution), sodium hydroxide (0.3 mole), and the nitrile (1 mole) heated for six hours at 50° gives yields of 89 and 93%. The product is discolored and is less easily purified than the product obtained by the use of ammonia alone.

The observation that ammonium hydroxide may hydrolyze nitriles to the corresponding amide without the use of hydrogen peroxide may make it possible to obtain amides from nitriles oxidized or polymerized by the peroxide.

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(6) C. F. Krewson, *Am. J. Pharm.*, **115**, 122–125 (1943).

(7) The evaporation of solutions of nicotinic acid in ammonia results in dissociation of any ammonium nicotinate present and leaves a residue of nicotinic acid free from ammonia.

(8) C and H determined by D. M. Mortimore; N by C. L. Ogg.

EASTERN REGIONAL RESEARCH LABORATORY
PHILADELPHIA, PA. RECEIVED APRIL 2, 1943

The Stereochemistry of Coördination Number Eight. Isomers for the Trigonal Prism with Symmetry C_2^v

BY LOUIS E. MARCHI

In a previous paper[1] four likely configurations for compounds of elements exhibiting coördination number eight were considered. In the light of one referee's comments about the radius ratio the trigonal prism considered in that paper seems to be a very unlikely configuration for coördination number eight.[2] The trigonal prism with two extra bonds along the normals to two of the rectangular faces and with symmetry C_2^v, Fig. 1, previously suggested by Hoard and Nordsieck, and Kimball,[3] is now considered.

The possible isomers for all classes containing only monodentate groups are given in Table I.

TABLE I

ISOMERS FOR MONODENTATE GROUPS

	Configuration, *T*	Optically active	Optically inactive	Total
8a	M	0	1	1
7ab	M	2	2	4
6a2b	M	12	4	16
6abc	M	26	2	28
5a3b	M	22	6	28
5a2bc		78	6	84
5abcd		168	0	168
4a4b	M	32	6	38
4a3bc		134	6	140
4a2b2c		204	12	216
4a2bcd		414	6	420
4abcde		840	0	840
3a3b2c		268	12	280
3a2bcd		560	0	560
3a2b3cd		828	12	840
3a2bcde		1,680	0	1,680
3abcdef		3,360	0	3,360
2a2b2c2d		1,252	22	1,274
2a2b2cde		2,508	12	2,520
2a2bcdef		5,040	0	5,040
2abcdefg		10,080	0	10,080
abcdefgh		20,160	0	20,160

M indicates that the isomer count was also determined by the construction of models and it was found in agreement with the number obtained by the use of Lunn and Senior's method.[4]

TABLE II

SPECIAL CLASSES OF BIDENTATE GROUPS

AA6b	6	3	9
AB6c	16	1	17
2AA4b	38	6	42
3AA2b	50	5	55
4'.A	10	1	11

For the bidentate groups the same restrictions were imposed as with the other configurations. The isomer numbers for the limited number of classes containing bidentate groups, which were considered, are given in Table II. (The classes 2AB 4C, 3AB 2C and 4AB have not been considered because a preliminary study of these classes has shown that the isomer count is probably greater than for the corresponding classes in the other configurations).

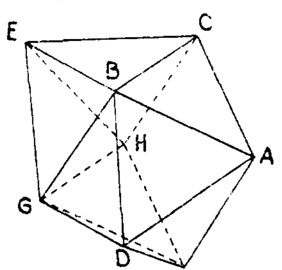

Fig. 1.—The trigonal prism is outlined by ABCFGH; D and E are the two extra bonds.

It is apparent that the number of isomers for class 4AA of this trigonal prism and of the dodecahedron, is exactly the same. Consequently

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(1) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, THIS JOURNAL, **65**, 329 (1943).

(2) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, *ibid.*, ref. 5 d.

(3) Marchi, Fernelius and McReynolds, *ibid.*, ref. 5.

(4) Lunn and Senior, *J. Phys. Chem.*, **33**, 1027 (1929).

the conclusions arrived at for the resolution of the $[Co(C_2O_4)_3]^{\equiv}$ ion must be altered to include this trigonal prism as well. It is obvious also that it is not possible to distinguish between these two configurations on the basis of chemical methods alone.

Marchi and McReynolds, This Journal, **65**, 333 (1943).

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

RECEIVED JULY 26, 1943

[CONTRIBUTION FROM THE CARNEGIE INSTITUTION OF WASHINGTON, DIVISION OF PLANT BIOLOGY]

A Unique Polyene Pigment of the Marine Diatom *Navicula Torquatum*

BY HAROLD H. STRAIN AND WINSTON M. MANNING

Among the pigments of the colonial pennate diatom *Navicula torquatum*, we have discovered a hitherto undescribed, yellow, polyene compound. This new pigment exhibits properties characteristic of the polyene hydrocarbons or carotenes. Isomerization reactions of this pigment indicate that its chromophoric polyene group occurs in the stable or *trans* form. Its spectral absorption properties resemble those of the violaxanthins and of neoxanthin[1]; hence, all these compounds probably contain similar chromophoric structures.

In *Navicula torquatum*, this new carotenoid comprises about one-fourth to one-third of the total carotenes. It was not found in several other diatoms nor in brown algae.

Experimental

Filamentous masses of the diatom *Navicula torquatum* were collected near Half Moon Bay, California, where they were found growing epiphytically on several species of large brown algae, the common kelps of the Pacific Coast. Pigments extracted from the diatoms with alcohol were transferred to petroleum ether and adsorbed upon a column prepared from a mixture of equal parts of Micron Brand magnesium oxide No. 2641 and heat-treated siliceous earth (Filter Aid 501).[1,2] Under these conditions, the new carotenoid formed a lemon-yellow band below the orange band of β-carotene. Between these two pigment zones there appeared a small yellow zone containing an isomer of the new carotenoid. Concentration of the elutriate from the lowest yellow band yielded golden-orange crystals of the new pigment.

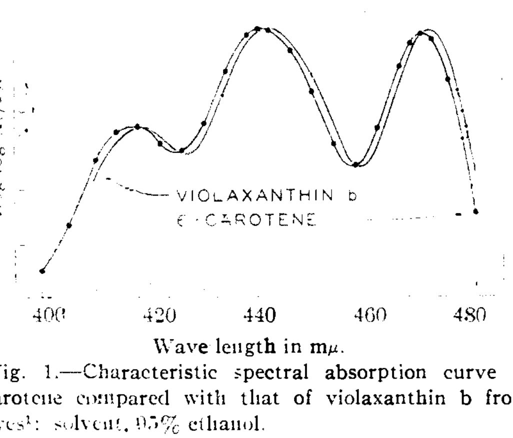

Fig. 1.—Characteristic spectral absorption curve of ε-carotene compared with that of violaxanthin b from leaves[1]; solvent, 95% ethanol.

The pigment from *Navicula* exhibited color reactions typical of polyene compounds. Crystals of this substance were turned deep blue by concentrated sulfuric acid. This acid removed the pigment from solution in chloroform and the acid layer became blue. A solution of the pigment in chloroform was also turned blue by antimony trichloride.

In respect to its solubility, adsorbability and chemical reactions, the pigment from *Navicula* behaved like a polyene hydrocarbon or carotene rather than like an ester or ether of a xanthophyll. It was but slightly soluble in methanol, yielding a pale yellow solution. It was more soluble in ethanol and quite soluble in ether and petroleum ether. Upon partition between petroleum ether and 95% methanol all but traces of the pigment dissolved in the petroleum ether layer. Treatment of the pigment with alcoholic potassium hydroxide did not alter its spectral properties, adsorbability or solubility. An ether solution of the pigment yielded no trace of blue color when treated for a week with an equal volume of concentrated hydrochloric acid. Mixed with α-carotene and adsorbed upon a column of magnesia from solution in petroleum ether, the polyene from *Navicula* formed the lower or least adsorbed band. It moved through the column about three times as fast as the α-carotene. This new pigment was not extractable from solution in petroleum ether with 85% phosphoric acid,[3] whereas all the xanthophylls and xanthophyll esters which were available for examination and which included cryptoxanthin and its *p*-nitrobenzoate were partially or wholly extractable.

When heated in *n*-propanol at 100° for three hours or when treated with iodine dissolved in petroleum ether containing pyridine, the new carotenoid yielded small quantities of a more adsorbed pigment. This product resembled the second yellow pigment observed in the extracts of the diatom. Spectral absorption curves of these pigment preparations exhibited maxima and minima which were less pronounced than those of the unheated pigment and which occurred about 5 mμ nearer the violet region of the spectrum. All these facts indicate that the new carotenoid is the stable isomer of a polyene hydrocarbon, probably a carotene, for which we suggest the provisional name ε-carotene.

When dissolved in the same solvents, the *Navicula* carotenoid exhibited spectral absorption maxima at wave lengths almost identical with those reported for violaxanthin b.[1, p. 73] Characteristic spectral absorption curves of these two pigments in ethanol, Fig. 1, are nearly identical in shape. They are also nearly identical in shape with the curve reported for neoxanthin,[1] although the latter is shifted about 4 mμ toward the violet region of the spectrum.

This unusual coincidence in shape of absorption curves which have absorption maxima at different wave lengths appears to be the exception rather than the rule among polyene compounds.[4] It has prompted us to compare the spectral absorption curves of the flavoxanthins of leaves[1] with the spectral curve of a "flavoxanthin-like" polyene pigment of carrots. To this end, the "flavoxanthin-like carotene," provisionally called ζ-carotene, was again prepared from carrots,[5] and its spectral absorption curve was determined in ethanol. Maxima and minima occurred at wave lengths about 22.5 mμ nearer the violet region of the spectrum than those of the flavoxanthins from leaves; yet the shapes of the curves were remarkably similar. An even closer correspondence in shape between the two curves was

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(1) H. H. Strain, "Leaf Xanthophylls," Carnegie Institution of Washington Publication No. 490, 1938.

(2) H. H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., 1942.

(3) Haagen-Smit, Jeffreys and Kirchner, *Ind. Eng. Chem., Anal. Ed.*, **15**, 179 (1943).

(4) Hausser, *Z. tech. Physik*, **15**, 10 (1934).

(5) Strain, *J. Biol. Chem.*, **127**, 191 (1939).

found when the values of log log (I_0/I) were plotted against the frequency or reciprocal wave length. Separate isomerization experiments indicated that the "flavoxanthin-like carotene," which apparently is not identical with a similar carotene of yellow corn,[6] contains the stable or *trans* form of the polyene chromophoric group.

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[6] White, Zscheile and Brunson, THIS JOURNAL, **64**, 2603 (1942).

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 10, 1943

COMMUNICATIONS TO THE EDITOR

α,β,γ,δ-TETRAPHENYLCHLORIN

Sir:

In 1939 Rothemund[1] described the preparation of tetraphenylporphin from pyrrole and benzaldehyde and claimed the separation of two isomers which he believed to be due to the two possible positions of the pyrrole acid hydrogen atoms. This work was continued by Aronoff and Calvin[2] in which a more complete separation was achieved by chromatographic adsorption. It was also shown that not only two but probably six different porphyrin-like substances were formed in the reaction.

Recently an examination of their spectra and a comparison with the spectra of naturally and synthetically derived porphyrins and chlorins[3] indicated that the spectra of the first two most abundant materials obtained in the tetraphenylporphin synthesis, called A (most abundant) and B (next most abundant) might be related as porphyrin to chlorin, respectively. If this be so it should be possible to convert B into A by oxidation and A into B by reduction. This we have succeeded in doing in the following manner. The spectrum of the Cu salt was used as identification since the difference there is greater and easier to observe than in the free base.

1. A sample A (several mg.) is dissolved in about 15 cc. of *n*-hexanol. Several crystals of cupric acetate are added and the solution is brought to a boil, cooled, and washed thoroughly with 6 *N* hydrochloric acid and then with water. The hexanol solution (after drying with sodium sulfate) then shows only the spectrum of the Cu salt of A, *i. e.*, a single intense band at 538 m.

2. Another sample (several mg.) of A is dissolved in 15 cc. of *n*-hexanol and several crystals (*ca.* ten-fold excess) of zinc acetate added and the solution brought to a boil. After cooling, the solution is washed with dilute acetic acid and with water and dried with sodium sulfate. This solution now shows the spectrum of the Zn salt of A which seems to consist of three bands in the following order of intensity: 555 $m\mu$, 596 $m\mu$ and 518 $m\mu$.

3. The solution of the A Zn salt is now boiled for two minutes and a piece of metallic sodium (5 mm.) dropped in and the boiling continued until all the sodium is dissolved or more sodium is added until the A Zn salt spectrum is completely replaced by a new one consisting of three bands 620 $m\mu$, 600 $m\mu$ and 559 $m\mu$. This solution shows a very powerful red fluorescence.

4. The solution from 3 is washed with water, then with 6 *N* hydrochloric acid which removes the Zn and converts the free base into the deep green hydrochloride (in the *n*-hexanol). This is then washed with water until all the hydrochloric acid is removed, leaving a solution of the free base (B) in the *n*-hexanol.

5. The solution from 4 is converted into Cu salt as described in 1 and shows two approximately equally intense bands 536 $m\mu$ and 615 $m\mu$ which is the spectrum of the B Cu salt. Operations 4 and 5 must be done as nearly in the absence of oxygen as possible.

6. Upon blowing oxygen through the solution obtained in 5 for several minutes and warming, the 615 $m\mu$ band disappears and, after a washing with water, the spectrum is that of the pure A Cu salt. The Cu salt of B obtained by chromatographing the original porphyrin preparation has also been oxidized by oxygen to give the A Cu salt.

Thus we have shown that A and B are related by oxidation and reduction and suggest that B is tetraphenylchlorin.

The work is being repeated quantitatively and will be so reported later, together with observations on the intermediate products in the oxidation and reduction.

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RECEIVED OCTOBER 13, 1943

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[1] Rothemund, THIS JOURNAL, **61**, 2912 (1939).

[2] Aronoff and Calvin, *J. Org. Chem.*, **8**, 205 (1943).

[3] Fischer-Orth, "Die Chemie des Pyrrols," Vol. 2, Part 2, 1940, Akademische Verlagsgesellschaft, Leipzig.

ROTENONE IN THE YAM BEAN (*PACHYRRHIZUS EROSUS*)

Sir:

The question of the possible occurrence of rotenone in the yam bean is of particular interest because this plant has recently been suggested[1] as a source of insecticidal material to supplement the usual rotenone-bearing insecticides. The seeds have long been known to be toxic to insects and fish, and Hwang[2] has reported the occurrence of

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[1] Hansberry and Lee, *J. Econ. Entomol.*, **36**, 351 (1943).

[2] Hwang, *Kwangsi Agr.*, **2**, 269 (1941) (in Chinese), summary in *Rev. Applied Entomol.*, **30A**, 418 (1942).