NOTES

New Types of Racemization Reactions

By Ernst Bergmann and Alfred Bondi

To the number of racemization reactions which obviously are of fundamental importance for our knowledge of the stability of spacial configurations, three new types have recently been added: (a) the racemization of methylalkyliodomethanes by interaction with iodide ions,[1] (b) the racemization of 2-bromohexane during its conversion into the Grignard compound,[2] and (c) the racemization occurring during the interaction between active ethyl propylmethylacetate and phenylmagnesium bromide.[3] Only the first of these three types has so far a theoretical and experimental treatment.

For case (b) one would perhaps be inclined to assume that racemization is due to electrolytic dissociation of the Grignard compound. But this assumption seems inadmissible, since negative carbonium ions seem to be sufficiently stable,[4] while positive ions of carbon are unstable.[5] Therefore one has probably to conclude that the racemization belongs to type (a): the bromide is racemized by bromide ions, which are formed by the ordinary equilibrium reaction $2RMgBr \rightleftharpoons R_2Mg + MgBr_2$. The case, therefore, is analogous to the racemization of phenylmethylchloromethane by interaction with magnesium or sodium metal.[1,6]

For case (c) the following suggestion has been advanced by Bergmann and Hartrott.[3] The ester does not undergo racemization—it is unstable only in alkaline solution[7]—but the carbinol is subjected to an equilibrium $(Me)(Pr\text{-}\alpha)CH\text{-}C(OH)Ph_2 \rightleftharpoons H_2O + (Me)(Pr\text{-}\alpha)C{=}CPh_2$, whereby the asymmetry is destroyed. It is well known that diphenylalkylcarbinols are easily dehydrated. If this explanation is correct, ethyl propylmethylacetate should give optically active carbinols with simple aliphatic alkylmagnesium halides, since compounds like (2-pentyl)-diethylcarbinol, $(Me)(Pr\text{-}\alpha)CHC(OH)Et_2$, do not lose water so easily. The conclusion has been confirmed by experiment. Into a solution of ethylmagnesium bromide (from 2.5 g. of magnesium and 11 g. of ethyl bromide), active methyl propylmethylacetate (4 g., rotation in acetone, $l = 1$, $c = 2.70$, α_D $-0.19°$; hence $[\alpha]_D$ $-7.04°$) was introduced. The rather violent reaction was completed by boiling for thirty minutes, then the mixture was decomposed with ice and ammonium chloride and the ethereal layer dried with anhydrous sodium sulfate and evaporated. The (2-pentyl)-diethylcarbinol boiled at 92–93° (32 mm.); yield 2.9 g. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 75.8, 75.4; H, 14.4, 14.1. Rotation in acetone: $l = 1$, $c = 2.80$, α^{22}_D $-0.365°$; hence $[\alpha]^{22}_D$ $-13.04°$.

The Daniel Sieff Research Institute
Rehovoth, Palestine

Received April 9, 1936

---

[1] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **20B**, 161 (1933); *Trans. Faraday Soc.*, **32**, 843 (1936).

[2] Porter, This Journal, **57**, 1436 (1935).

[3] Bergmann and Hartrott, *J. Chem. Soc.*, 1218 (1935).

[4] Wallis and Adams, This Journal, **54**, 4753 (1932); **55**, 3838 (1933).

[5] Bergmann and Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

[6] Ott. *Ber.*, **61**, 2124 (1926).

[7] Menon and Peacock, *J. Ind. Chem. Soc.*, **12**, 268 (1935).

The Preparation of Pure Apocodeine and its Hydrochloride

By Karl Folkers

Early preparations of apocodeine were complex mixtures.[1] Knorr obtained "pseudoapocodeine"[2] by melting codeine with oxalic acid, and later he showed[3] that his apocodeine was identical with the monomethylation product of apomorphine; although this latter product had been reported earlier by Pschorr,[4] but with widely different physical properties. Later methods[5] of making apocodeine from codeine with zinc and sodium chlorides still introduced apomorphine impurities, which necessitated the use of a troublesome perchlorate, chromate or phosphate salt for purification.

Nevertheless, a certain confusion exists in the

---

[1] Small, "Chemistry of the Opium Alkaloids," Supp. No. 103, Public Health Reports, 1932, pp. 183, 362.

[2] Knorr and Roth, *Ber.*, **40**, 3355 (1907). The name pseudoapocodeine was introduced by Knorr as he believed pseudocodeine to be an intermediate in the transformation of the morphine nucleus to the aporphine nucleus. Apocodeine is the generally accepted name, and it suggests the same relationship to codeine that apomorphine has to morphine.

[3] Knorr and Raabe, *ibid.*, **41**, 3050 (1908).

[4] Pschorr, Jaeckel and Fecht, *ibid.*, **35**, 4377 (1902).

[5] German Patent 489,185, *Frdl.*, **16**, 2485.

literature[6] concerning the chemical properties of pure apocodeine.

The herein described method is an improvement of the Knorr reaction, and a confirmation of Knorr's properties of apocodeine with ethanol of crystallization. The pure anhydrous base and hydrochloride have not been described previously.

Apocodeine.—Twenty grams of anhydrous codeine and 60 g. of anhydrous oxalic acid,[7] were heated for one and one-half hours at 150–155° bath temperature with very slow stirring. The melt was cooled and diluted with 250 ml. of water. After complete solution, it was further diluted to 600 ml. in a separatory funnel, shaken with 300 ml. of ether, and the bases precipitated with addition of concentrated ammonia solution. Too slow operation caused troublesome crystallization of ammonium oxalate. The ether layer was separated, filtered and distilled *in vacuo*. A residue of 5.8 g. remained, which was dissolved in 15 ml. of absolute ethanol. Nearly pure apocodeine with a molecule of ethanol crystallized on standing at 10°; yield 2.7–2.8 g. (12.8%). One crystallization gave pure white products of m. p. 104.5–106.5° with gas evolution $[\alpha]^{23}D$ −90.0, *C*, 0.533, abs. ethanol, $l = 1$. Further crystallization did not change the melting point or optical rotation.

Anal. Calcd. for $C_{18}H_{19}O_2N \cdot C_2H_5OH$: C, 73.35; H, 7.70; C_2H_5OH, 14.06. Found: C, 72.99, 73.01; H, 7.57, 7.76; C_2H_5OH, 13.76.

The base was best purified by recrystallization from absolute ethanol. The use of the hydriodide as Knorr suggested resulted in partial oxidation. The crystals showed no ready tendency to oxidize, unless they were finely pulverized. The ethanol was lost very slowly at 25° (2 mm.), but readily at 78° (2 mm.). The anhydrous base showed m. p. 122.5–124.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.82; H, 6.81. Found: C, 76.63, 76.80; H, 7.02, 7.06.

As Knorr described, there were ether and water insoluble bases present. It was found, however, that nearly all the apocodeine was extracted by the ether. In one experiment very little more was obtained by redissolving the insoluble bases with acid, reprecipitating, extracting etc. A third repetition of this process yielded no more apocodeine. Thus it was not necessary to bring all the precipitated bases into ether solution as Knorr described. In fact, the moderate insolubility of pseudocodeine[8] and the amorphous products in ether make the first extraction one of considerable purification.

Apocodeine Hydrochloride.—To a solution of the base in absolute ethanol was added the calculated amount of dry hydrogen chloride in absolute ethanol and, while hot, absolute ether was added until crystallization started. The yield of pure white salt was quantitative; m. p. softening started at 140°, dec. at 260–263°; $[\alpha]^{22}D$ −41.3 to 43.3°; *c*, 0.508; H_2O, $l = 1$. Recrystallization from 95% ethanol and ether did not alter the physical constants. The salt was practically anhydrous.

Anal. Calcd. for $C_{18}H_{19}O_2N \cdot HCl$: C, 68.00; H, 6.35. Found: C, 68.26, 67.92; H, 6.35, 6.22.

RESEARCH AND DEVELOPMENT
MERCK & CO., INC.
RAHWAY, N. J.

RECEIVED JULY 3, 1936

The Thermal Decomposition of Acetone

BY JOHN R. HUFFMAN[1]

The present experiments were undertaken to discover whether the unimolecular rate constant for the thermal decomposition of acetone fell off at low pressures and in such a case to apply the theories of Rice and Ramsperger and of Kassel.[2] Recently Winkler and Hinshelwood[3] working at 875°K. and pressures down to 2.5 mm. reported that this decrease of rate constant started at 100 mm.

Acetone was decomposed in a 200-cc. silica bulb in a furnace automatically controlled to

TABLE I

Run	P_0, mm.	$k \times 10^4$	Run	P_0, mm.	$k \times 10^4$
59	128.6	10.86	46	56.2	9.70
65	127.2	11.39	63	55.9	9.85
64	124.3	11.17	42	53.5	9.41
69	120.4	10.72	22	47.8	9.38
71	115.5	11.42	37	45.9	8.80
58	112.6	11.33	35	41.6	8.68
73	107.0	10.96	24	34.9	9.05
72	101.2	10.32	75	35.2	8.50
57	100.2	10.69	76	35.1	8.66
61	100.2	11.31	36	27.8	8.12
66	99.0	11.27	32	27.8	7.98
70	98.6	11.35	45	25.6	8.18
60	86.7	10.78	31	22.9	7.65
68	83.4	10.42	23	21.5	8.07
74	80.4	10.60	52	21.85	8.36
50	78.8	10.93	34	18.54	7.43
40	78.3	10.75	29	17.86	7.68
51	78.2	10.48	27	17.08	7.43
55	74.3	10.79	44	16.60	7.48
62	79.1	10.32	43	16.53	7.37
56	76.3	10.13	25	15.53	6.83
49	72.5	10.53	33	12.80	6.86
39	72.9	10.60	30	9.71	5.92
41	66.0	9.79	28	7.51	5.51
48	62.1	10.08	26	7.49	5.40
38	60.7	9.54	54	5.65	5.06
47	57.7	9.90	53	4.68	4.50
67	58.5	9.88			

---

[6] For example, see Krayer, *Arch. exptl. Path. Pharm.*, **111**, 60 (1920). Schwartze, *Arch. intern. pharmacodynamie*, **41**, 461 (1931).

[7] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 415.

[8] Lutz and Small, THIS JOURNAL, **54**, 4723 (1932).

[1] Sterling Research Fellow in Chemistry, Yale University, 1933–1934.

[2] For a detailed discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," A. C. S. Monograph No. 57, Chemical Catalog Company, New York, 1932.

[3] Winkler and Hinshelwood, *Proc. Roy. Soc.* (London), **A149**, 340 (1935).

±0.2°. Pressures were read either on a mercury or a bromonaphthalene–mercury manometer. Experimental errors were smoothed out by a process of graphical differentiation and re-integration.[4] To correct for dead space (1.7%) the rate constants were calculated by the method suggested by Allen.[5] These constants fell off during a run due to the second step in the decomposition and consequently were extrapolated to zero time. The results, corrected slightly to 826°K., are presented in Table I.

A second series of runs was made to determine the temperature effect of the high pressure reaction. This is expressed by the equation

$$\ln k_\infty = 34.52 - 68120/RT$$

and is shown in Table II.

TABLE II

T.,°K.	817	826	836	845.5	854
$k_\infty \times 10^4$	5.85	9.3	15.41	24.18	34.88

A plot of k *versus* P_0 (k_∞ = 0.001125 at 826°K.) establishes 100 mm. as the pressure where the reaction commences to fall off, checking the results of previous workers. A plot of $1/k$ versus $1/P_0$ indicates a break at 40 mm. pressure suggesting a second mode of activation.

Application of Hinshelwood's simple theory gives 22 active degrees of freedom. Using O. K. Rice's classical theory, 8 degrees of freedom and a molecular diameter of 28.3×10^{-8} cm. appear to be the best values to use. Kassel's quantum theory gives curves that fit the experimental results the best. The most reasonable values in this case appear to be 8 degrees of freedom, 22 quanta, and a diameter of 45×10^{-8} cm. This gives a frequency in the infra-red and a vibrational specific heat contribution of 12 cal./g. The results of Winkler and Hinshelwood at 875°K. are satisfied by 8 degrees of freedom, 22 quanta and 35×10^{-8} cm. Table III gives a comparison of the experimental and calculated results.

TABLE III

	826°K.		875°K.[a]	
P_0, mm.	k/k_∞ exptl.	k/k_∞ calcd.	k/k_∞ exptl.	k/k_∞ calcd.
200		0.916		0.855
100	1.000	.864	1.000	.780
50	0.865	.791	0.708	.685
20	.675	.664	.540	.540
10	.537	.555	.437	.427
5	.426	.439	.344	.320

[a] From the work of Winkler and Hinshelwood.

It was impossible to obtain a fit of theory to experiment throughout the whole pressure range. The calculated results fit within the experimental error from about 50 mm. pressure down. The rate constant falls off with decreasing pressure rather abruptly in comparison with other unimolecular reactions in such a manner as to indicate a free radical chain mechanism as proposed by F. O. Rice and Herzfeld.[6] This is further substantiated by the recent publication of A. O. Allen.[7]

---

(4) Nybölle, *Nordisk Statistisk Tidskrift*, **8**, 103 (1929), Stockholm Aftonbladets Tr.

(5) Allen, THIS JOURNAL, **56**, 2053 (1934).

(6) F. O. Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

(7) Allen, *ibid.*, **58**, 1052 (1936).

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.

RECEIVED MARCH 11, 1936

Semiquinones of Neutral Red and Safranines

BY LEONOR MICHAELIS

Many derivatives of phenazine have been shown to form semiquinones on partial reduction, all of green color in compounds containing only benzene and no naphthalene rings. The separation of the two steps of reduction is more distinct as the acidity of the solvent increases. The degree of acidity at which a distinct separation of the steps becomes easily recognizable varies from dye to dye. So far, no semiquinone has been observed in a number of those phenazine or phenazonium compounds containing amino groups as side chains. However, even in these compounds a semiquinone will be demonstrated by the following experiment, in which the conditions of reduction are slightly changed. One simply has to work in extremely acid solution. The experiment can be performed with neutral red, phenosafranine or the commercial "safranine."

Dissolve a small amount of the dye in concentrated hydrochloric acid. The color will be, according to the dye, blue to green. Dilute with water just enough to make it blue, with a shade of violet. Add some particles of solid chromous chloride and stir. The color will change first to an intense green, then to the almost colorless condition of the leuco dye. On reoxidizing, say by adding a crystal of potassium persulfate, the twofold change of color will be reversed. Zinc dust may also be used as reductant.

Since the color of the oxidized form of the dye in utmost acid solution (especially in concentrated sulfuric acid) itself is green, the acidity has to be lowered just to such an extent as to make it blue-violet before adding the reductant. Otherwise there is no visible change on reducing the dye to the semiquinone state.

FROM THE LABORATORIES OF
THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED JUNE 18, 1936

Polymolecular Films

BY WILLIAM D. HARKINS AND ROBERT J. MYERS

Surface films which spread over water are supposed to be monomolecular. However, Harkins and Morgan[1] were able to produce solid, partly crystalline films with a mean thickness much greater than this. Thus to a spreading substance whose organic molecules contain a polar group (stearic acid, etc.) they added a thickening or nonpolar substance (phenanthrene). In the present work polymolecular liquid films were produced by thickening the films with a liquid paraffin oil (nujol) of low volatility.

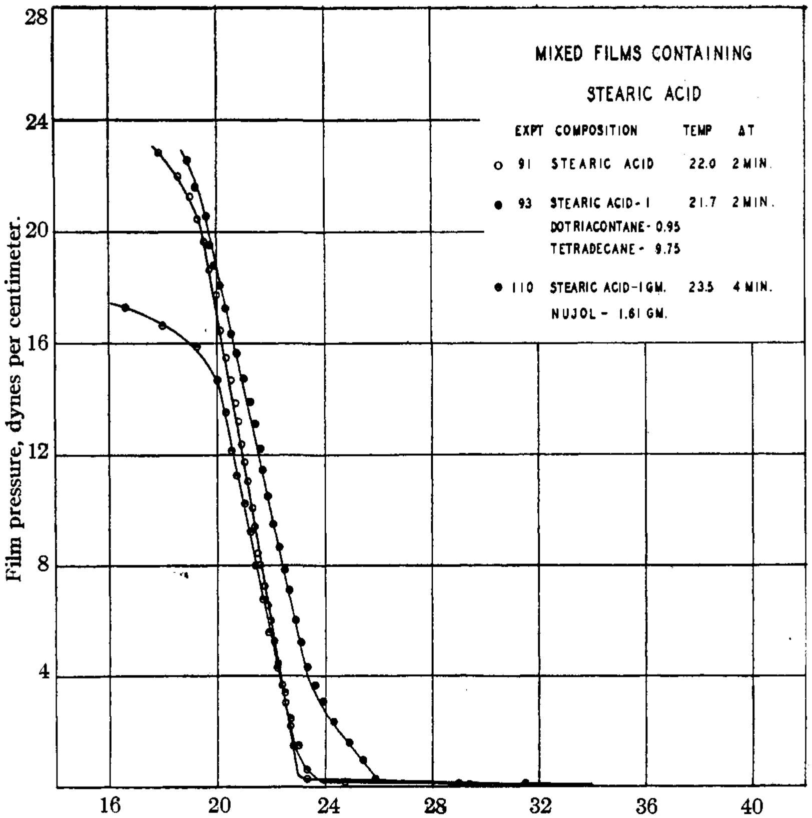

Fig. 1.—Poly- and mono-molecular films with stearic acid.

1. Condensed Films.—Films of pure stearic acid form condensed films on 0.01 N hydrochloric acid at room temperature except at pressures below about 0.2 dyne per cm. The addition of 1.61 g. of nujol to 1 g. of stearic acid in the film forming substances does not seem to increase the area of the condensed film (Fig. 1, expts. 91 and 110), but only weakens it at high pressures.

The areas given in the figures of this paper represent the area per molecule of the more polar constituent (stearic acid, etc.).

2. Expanded Films of Oleic Acid.—The effects are, however, markedly different in cases in which the acid when alone forms an "expanded" film, as in the case of oleic acid (Fig. 2). Here the mixed film contains 1.66 parts by weight of the paraffin oil to 1 part of oleic acid. The effect of the paraffin oil is very great, since it raises the surface pressure greatly at large areas, and decreases it very markedly at low areas. At 36.4 sq. Å. per molecule of oleic acid the pressures are the same for the pure acid and the mixture.

3. Expanded Films of Myristic Acid.—At 22.8° films of pure myristic acid exhibit a kink in the curve at an area of 25.45 sq. Å. and a pressure of 17.25 dynes per cm. The addition of 1.67 parts

---

[1] Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 631 (1925).

by weight of nujol to 1 part of myristic acid removes the kink and increases the film pressure at any given area. The increase is particularly great at the lower pressures (larger areas). With a greater proportion of nujol (9.08 parts) the phenomenon encountered with oleic acid is found, that is, the paraffin oil increases the pressure at large molecular areas and decreases it at the lower areas. The decrease in surface pressure at the lower areas becomes much more marked as the amount of paraffin oil is increased (expt. 104, Fig. 3).

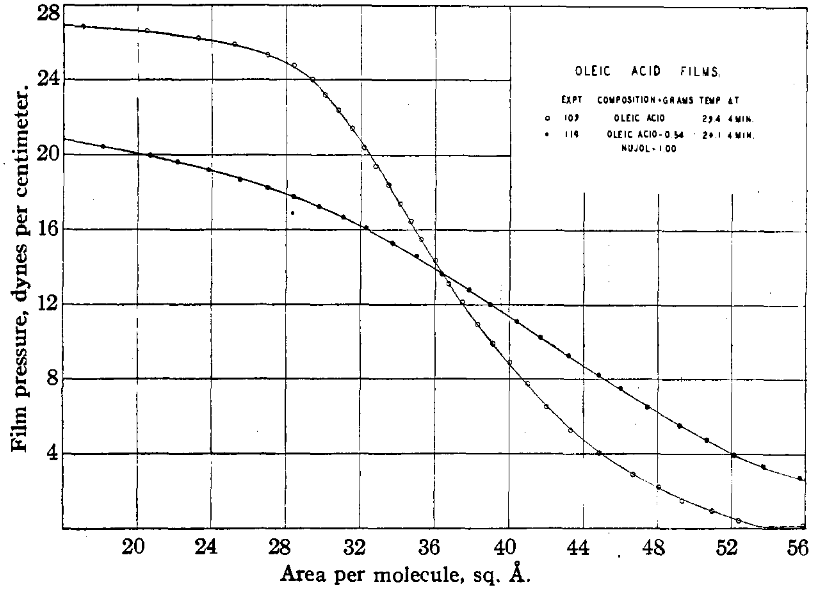

Fig. 2.—Poly- and mono-molecular films with oleic acid.

4. **Films of Pentadecylic Acid (Fig. 4).**—The addition of 1.5 g. of the paraffin oil to 1 g. of pentadecylic acid increases the film pressure very greatly, both above and below the kink in the curve. However, at about 20 sq. Å. per molecule the two sets of curves cross. The curve for experiment 97 indicates that the tetradecane has evaporated.

5. **Surface Potentials of Polymolecular Films.**—Figure 5 exhibits interesting relations and shows that there is a kink in the potential area curves of both the pure acid and the mixture.

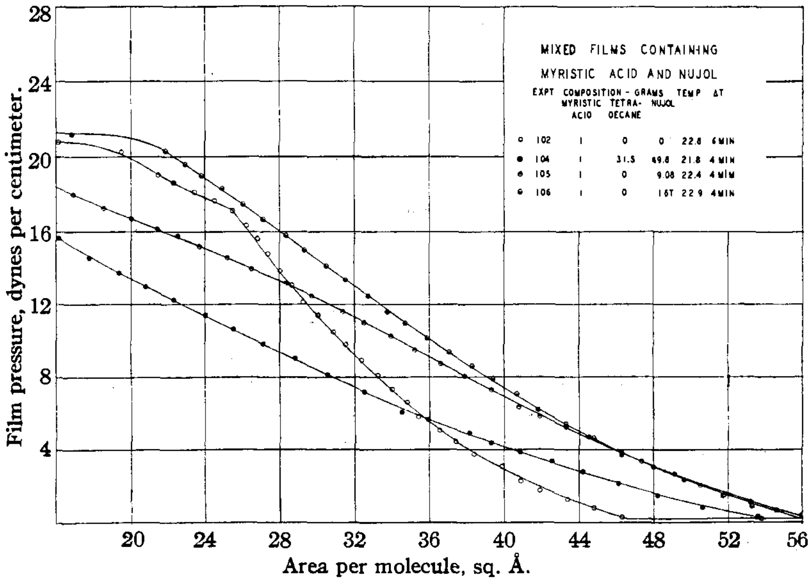

Fig. 3.—Poly- and mono-molecular films with myristic acid.

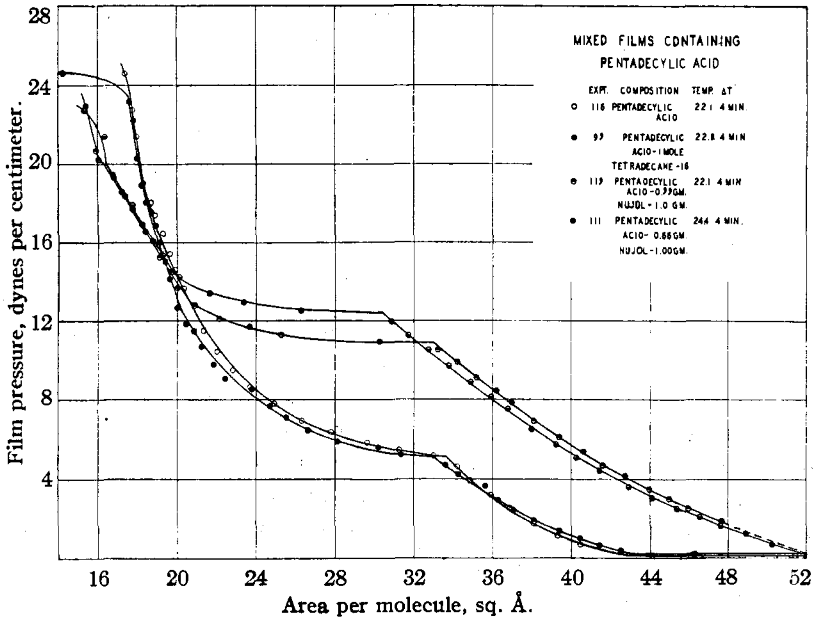

Fig. 4.—Poly- and mono-molecular films with pentadecylic acid.

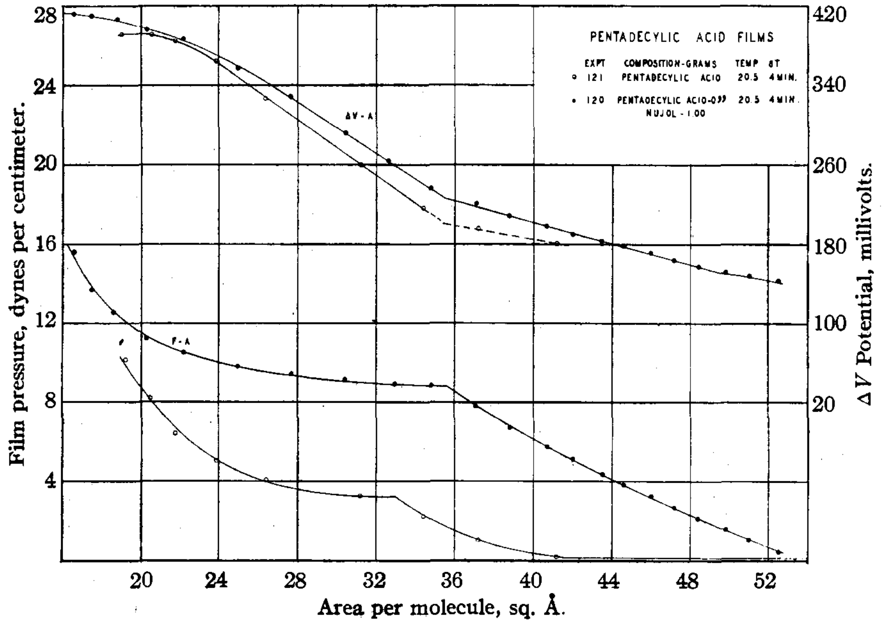

Fig. 5.—Surface potentials and areas of poly- and mono-molecular films of pentadecylic acid.

Polymolecular films exhibit many interesting relations, and many of these are under investigation in this Laboratory. At constant pressure many polymolecular, as well as monomolecular, films shrink with time. This shrinkage is very marked with pentadecylic acid at areas just below and pressures just above that of the kink in the curve.

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED JUNE 22, 1936

Micro Determination of Active Hydrogen with Deuterium Oxide

BY ROGER J. WILLIAMS

The usual methods of determining active hydrogen involving the use of a Grignard reagent, cannot be applied to highly water soluble materials which do not dissolve in ethers or other organic solvents.

We early suggested[1] the determination of active hydrogen by dissolving the unknown in deuterium oxide followed by a determination of the changed density of the water distilled off. Others[2,3] have independently made use of the principle.

An experimentally simple embodiment of the same principle has now occurred to us which consists merely in dissolving the substance to be analyzed in deuterium oxide, evaporating to dryness and determining the increase in weight due to the replacement of active hydrogen by deuterium. This method has been applied to two known substances and the results are given in the following table. Other experimental work along similar lines which need not be detailed here has convinced us of the applicability of the method. The substances in small weighing bottles were simply dissolved in 0.25 ml. of 99.5% deuterium oxide and then carefully evaporated and dried to constant weight in vacuum desiccators, and weighed again.

Substance analyzed	Hydroxyproline			Urea		
Sample, mg.	8.386			5.749		
After treatment, mg.	8.592			6.121		
Incr. after subtr. 5 γ blank	0.201			0.367		
Calcd. increases	2H	3H	4H	3H	4H	5H
	0.128	0.192	0.256	0.297	0.383	0.479

The theoretical increases were calculated on the basis of complete replacement by deuterium. This assumption would introduce practically no error in the first determination and a very slight error in the second. A small increase in weight, about 5 γ, is noted when a glass weighing bottle itself is treated with heavy water.

The method need not be limited to water soluble substances since interchange should occur in ether or pyridine solution. In case of compounds which do not dry readily, appropriate means will have to be taken to bring the material to the same degree of dryness before and after treatment with deuterium oxide. Since the principle is so simple and the manipulation involves nothing beyond drying and weighing, it appears that no serious difficulty should be involved in applying the method. We hope other investigators to whom this type of work is less incidental, will perfect and extend the method which has been experimented with in our laboratory only in a preliminary way.

CHEMISTRY DEPARTMENT
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MARCH 24, 1936

---

[1] Roger J. Williams, "Introduction to Organic Chemistry," third edition, D. Van Nostrand Co., New York, 1935, p. 576.

[2] Bonhoeffer and Brown, *Z. physik. Chem.*, **B23**, 172 (1933).

[3] Hamill and Freudenberg, THIS JOURNAL, **57**, 1427 (1935).

Some Bismuth Derivatives of Diphenyl

BY DAVID E. WORRALL

Since the number of known organic compounds of bismuth is meager, previous work on diphenyl derivatives of the arsenic group has been extended to include this element.[1] Arylation was accomplished through the organo magnesium compound, for the Wurtz–Fittig method employing sodium, used so successfully with other members of the group, failed with bismuth.

Experimental

Tri-biphenylbismuth.—One hundred grams of *p*-bromodiphenyl was changed into the magnesium compound according to the directions of Bent.[2] After dilution with several volumes of ether, 36 g. of powdered bismuth chloride was added directly (in small lots) with shaking and the mixture allowed to stand overnight. The ether was removed by decantation, after which the residue was decomposed as usual. A small amount of dilute acid was added to remove basic salts. The black precipitate was then filtered, dried and extracted successively with hot alcohol and chloroform. A small amount of dibiphenyl separated from the chloroform extract on cooling, after which the filtrate was concentrated to a small volume. On the addition of an equal volume of alcohol a crystalline product formed; yield approximately 43 g.

Anal. Calcd. for $C_{36}H_{27}Bi$: C, 64.7; H, 4.0. Found: C, 65.0; H, 4.3.

It is insoluble in alcohol, but dissolves readily in chloroform, separating in the form of tiny flat needles that melt at 182–183°.

Tri-biphenylbismuth Dichloride.—To the above substance dissolved in carbon tetrachloride was added chlorine dissolved in the same solvent; yield nearly quantitative. The product was recrystallized from chloroform–alcohol mixture, from which it separated as small plates melting with decomposition at 198–200°, if heated slowly.

Anal. Calcd. for $C_{36}H_{27}BiCl_2$: Cl, 9.6. Found: Cl, 9.5.

The dibromide prepared in a similar manner formed pale yellow plates that melted indefinitely with decomposition when heated.

Anal. Calcd. for $C_{36}H_{27}BrBr_2$: Br, 19.3. Found: Br, 19.1.

Both halides dissolved in fuming nitric acid, forming nitro derivatives that deflagrated if heated quickly.

Di-biphenylbismuth Chloride.—This was prepared by the method of Challenger[3] using bismuth chloride with the

---

[1] Worrall, THIS JOURNAL, **52**, 664 and 2046 (1930).

[2] Bent, THIS JOURNAL, **54**, 1398 (1932).

[3] Challenger, *J. Chem. Soc.*, **107**, 19 (1915).

triarylbismuth derivative in dry ether. A bright yellow powder rapidly separated out. It melted indefinitely when heated and probably contained some dichloride.

Anal. Calcd. for $C_{24}H_{18}BiCl$: Cl, 6.5. Found: Cl, 7.0.

Tri-biphenylbismuth Dinitrate.—Alcoholic silver nitrate solution was added to an equivalent amount of tri-biphenylbismuth dichloride suspended in a large volume of acetone. On concentrating the filtrate after removal of insoluble material, small plates were obtained that decomposed at approximately 162°, but deflagrated if heated quickly.

Anal. Calcd. for $C_{36}H_{27}BiO_6N_3$: Bi, 26.4. Found: Bi, 26.6.

PEARSON MEMORIAL LABORATORY
TUFTS COLLEGE, MASS.
RECEIVED JULY 7, 1936

Chile Seed

BY W. A. BUSH

The seeds of the Chile pepper (sometimes called pimento) obtained from the pods of the Southern Pacific Coast cultural variety of *Capsicum Annuum* have received little mention in the literature from the point of view of their composition.

A representative sample of a quantity of sixteen tons of dried seeds accumulated during a year from pods mostly of Californian origin gave results differing somewhat from those obtained by Ebert and Bailey[1] from Southeastern seed.

Yields from the seed by drying and extraction were: oil, 26.10%; moisture, 6.25%; dried extracted meal, 67.65%. Analysis of the meal, free from oil and moisture, shows: protein (N × 6.25), 28.92%; fiber, 29.10%; ash, 5.61%; N-free extract (carbohydrates), 36.37%. The constants of the oil, obtained by hot pressing (100°) and then filtering are

Specific gravity, 24.5°/25°	0.918
Refractive index at 25°	1.4738
Color (2.54 cm. column, Lovibond)	100 yellow—46 red
Acid number	2.18
Iodine number, Hanus	133.5
Acetyl number	7.0
Saponification number	192.0
Unsaponifiable matter	1.7%
Melting pt. of separated fatty acids	21.2°

The resemblance to tomato seed oil is striking.[2] However, the presence of colored veins on the outer edges of the seeds imparts to the oil the deep color noted above and a characteristic burning taste and paprika-like aroma.

LOS ANGELES, CALIF.
RECEIVED JULY 6, 1936

---

[1] H. C. Ebert and H. S. Bailey, *Cotton Oil Press*, **7**, 35 (1924).

[2] Felice Sorgès, *Chim. Ind. Agr. Biol.*, **5**, 232 (1929); N. Barskii, *Masloboino-Zhirovoe Delo*, No. 6, 56 (1932).

COMMUNICATIONS TO THE EDITOR

MUREXIDE AND LEUCOMUREXIDE

Sir:

The recent publication of Kuhn and Lyman [*Ber.*, **69**, 1547 (1936)] concerning the oxidation-reduction potential of murexide prompts this report of results obtained in this field.

Preparation of Murexide.—The uncertainty in the preparation of murexide emphasized by previous writers including Kuhn and Lyman (who obtained only a 2% yield) has been removed by employing glacial acetic acid as the reaction medium. Furthermore, recrystallization has been effected without heating, by salting out at room temperature. Thus, 16.1 g. of finely powdered alloxantine suspended in 1600 cc. of boiling glacial acetic acid and treated with 80 g. of ammonium acetate with continued boiling for 1–2 minutes gave, on cooling, filtering, washing with acetic acid, alcohol and ether, and drying at 100°, 14.0 g. (calcd. 14.2 g.) of crude murexide. One gram of this dissolved in 900 cc. of water at 30° gave, on salting out the filtered solution with 60 g. of ammonium chloride, filtering, washing with 60% methanol and then with absolute methanol, and drying at 110°, about 75% of beautiful, reddish-brown crystals possessing a green reflex, which, on titration with sodium hydrosulfite, were found to be pure murexide.