chloride at 80° for several hours yielded the corresponding hydroxy compound, m. p. 141.5–142.5°.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.2; H, 9.68. Found: C, 79.7; H, 9.89.

This hydroxy ketone was further characterized by the orange colored 2,4-dinitrophenylhydrazone, m. p. 230–232°, which it formed.

Anal. Calcd. for $C_{25}H_{32}N_4O_5$: C, 64.0; H, 6.89. Found: C, 63.2; H, 6.99.

Androstenedione.—To a solution of 2.5 g. of $\Delta^{4,5}$-androstenol-17 in 200 cc. of acetic acid was added at 35–45° and with stirring a solution of 3 g. of chromic acid in 50 cc. of 90% acetic acid. The addition required one-half hour and the solution was then kept at 45° for one-half hour. The solution was poured into water and the product was extracted with ether. The ether solution was washed well with sodium carbonate solution and water and concentrated to a small volume. On cooling this solution for some time crystals formed and were filtered. They were recrystallized from ether to yield androstenedione, m. p. 168–170°, identical with the known product.

Summary

Cholestene dibromide was oxidized to $\Delta^{5,6}$-androstenone-17 which was converted to desoxotestosterone acetate and $\Delta^{4,5}$-androstenone-17. These new compounds on oxidation were converted to testosterone acetate and androstenedione. An isomeric 7-keto-$\Delta^{5,6}$-androstenol-17 was also obtained.

STATE COLLEGE, PENNA.
DETROIT, MICH.

RECEIVED DECEMBER 1, 1939

NOTES

An Attempted Synthesis of Morphenol

BY ALFRED BURGER AND S. AVAKIAN

A recent announcement by Gilman and Cheney[1] that these authors are studying the closure of a six-membered ring between positions 1 and 9 in dibenzofuran types prompts us to report unsuccessful attempts to synthesize methylmorphenol through 6-methoxy-9-hydroxy-phenanthrylene oxide and subsequent selective reduction of the 9-hydroxy group. 4-Methoxy-dibenzofuran-1-acetic acid was treated with (a) concentrated sulfuric acid, (b) 85% sulfuric acid, (c) anhydrous hydrogen fluoride at room temperature,[2] and (d) stannic chloride in the cold, and at the boiling point of the condensing agent. The acid chloride was treated with aluminum chloride in ice-cold benzene (e), and the acid bromide with aluminum chloride in nitrobenzene solution at room temperature (f), and with boiling stannic chloride (g), but none of these reactions yielded phenanthrene derivatives. It is possible that Gilman and his coworkers will achieve ring closure by using compounds containing strongly *para*-orienting groups in position 6 of the dibenzofuran system.[1]

Since the distance between sulfur and carbon atoms is greater than that between oxygen and carbon atoms, the positions 1 and 9 in dibenzothiophene should be closer to each other than in dibenzofuran, and ring closure should be easier in the dibenzothiophene series. In investigating the effect of substituting sulfur atoms for —CH=CH— groups in polycyclic aromatic systems we are now studying the intramolecular dehydration and decarboxylation of 1-carboxy-dibenzothiophene-9-acetic acid, which should lead to derivatives of 4,5-phenanthrylene sulfide, a possible isoester of pyrene.

Experimental

4-Methoxydibenzofuran-1-carboxylic acid[3] was converted into the chloride by the action of thionyl chloride. The acid chloride crystallized from benzene–ligroin as colorless needles, m. p. 162.5–163.5°. The yield was 93%.

Anal. Calcd. for $C_{14}H_9ClO_3$: C, 64.48; H, 3.48. Found: C, 64.22; H, 3.62.

The acid chloride was stirred with an ethereal solution of diazomethane for sixteen hours. The diazo ketone crystallized out. Recrystallization from benzene–petroleum ether rendered yellow crystals, m. p. 150–151° (dec.). The yield was 86%.

Anal. Calcd. for $C_{15}H_{11}N_2O_3$: C, 67.39; H, 4.15. Found: C, 67.50; H, 4.00.

The diazo ketone was treated with ammonium hydroxide in dioxane solution according to Arndt and Eistert.[3,4] 4-Methoxydibenzofuran-1-acetamide crystallized from ethanol as colorless needles, m. p. 203°. The yield was 75%.

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.56; H, 5.14 Found: C, 70.93; H, 5.34.

(1) Gilman and Cheney, THIS JOURNAL, **61**, 3149 (1939).
(2) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939).
(3) Gilman, Parker, Bailie and Brown, *ibid.*, **61**, 2836 (1939).
(4) Arndt and Eistert, *Ber.*, **68**, 200 (1935).

The acid amide was boiled under reflux with thirty parts of a 20% alcoholic solution of potassium hydroxide for three hours. The alcohol was replaced by water and evaporated, and the 4-methoxydibenzofuran-1-acetic acid was precipitated from the filtered solution. It was recrystallized from ethanol and appeared as colorless needles, m. p. 223–224°. The yield was 90%.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.28; H, 4.73. Found: C, 70.31; H, 4.43.

UNIVERSITY, VIRGINIA RECEIVED NOVEMBER 21, 1939

The Preparation of Acetyl Bromide*

BY THEODORE M. BURTON WITH ED. F. DEGERING

Acetyl bromide was prepared as early as 1863 by distilling it as formed from a mixture of glacial acetic acid, bromine and phosphorus.[1]

Investigations have shown, however, that acetyl bromide undergoes substitution with bromine to form bromo-acetyl bromides with decrease in the yield of acetyl bromide. Further improvements designed to increase the yield of acetyl bromide have also resulted in increased bromination in the nucleus.[2]

By the elimination of free bromine it was thought possible to increase the yield of acetyl bromide according to the reaction

$$3CH_3CO_2H + PBr_3 \longrightarrow 3CH_3COBr + P(OH)_3$$

Phosphorus tribromide (b. p. 169–170° at 740 mm.) can be prepared readily in 99.5% yield by slowly adding dried bromine from a dropping funnel into a slight excess of freshly washed and dried red phosphorus placed in a round-bottomed flask equipped with a mechanical stirrer and a reflux condenser.

The acetyl bromide was prepared by adding slowly through the dropping funnel, with stirring, a slight excess of 99.5% glacial acetic acid (3.075 moles of CH_3COOH per mole of phosphorus tribromide) to the cold phosphorus tribromide. The mixture separated into two layers which were distilled separately into a common receiver packed in ice. The crude acetyl bromide was rectified in a modified Podbielniak column to produce a water-white fraction boiling from 73–76° at 740 mm. The yield varied from 71.4 to 73.4% of the theoretical.

In other experiments the phosphorus tribromide was purified before use, but yields were increased only by a slight amount to 74.9% of the theoretical. In an effort to test the effect of temperature, the acetyl bromide was distilled from the reaction mixture at room temperature under reduced pressure. The product was collected in a gas bottle immersed in a bath cooled with solid carbon dioxide. No change, however, was observed in the yield. In all cases large amounts of hydrogen bromide were liberated so that the reaction probably does not proceed as indicated in the above equation.

It was found possible to prepare acetyl bromide without the formation of hydrogen bromide by adding phosphorus tribromide slowly, with stirring, to an excess of boiling acetic anhydride. The boiling point dropped as acetyl bromide was formed and when the addition of phosphorus tribromide was completed, the acetyl bromide was distilled from the mixture and rectified as before. The yield was 81.7% of the theoretical.

By using the readily prepared phosphorus tribromide, instead of free bromine with glacial acetic acid, substitution reactions are avoided and the yield of acetyl bromide can be increased to about 80% of the theoretical.

CHEMICAL LABORATORY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA RECEIVED AUGUST 3, 1939

Hydrogen Bonds Involving the C–H Link. IX.[1] Nitriles and Dinitriles as Solvents for Hydrogen Containing Halogenated Methanes

BY M. J. COPLEY, G. F. ZELLHOEFER AND C. S. MARVEL

Nitriles should be capable of bonding with hydrogen in halogenated methanes of the CH_2X_2 and CHX_3 types and hence should be good solvents for these products. Work reported earlier[1] shows that valeronitrile and benzonitrile do dissolve methylene chloride and monochlorodifluoromethane in excess of the amount calculated from Raoult's law. It is interesting to find that the aliphatic dinitriles, succinonitrile and glutaronitrile, dissolve less than the calculated amounts of these two halogenated methanes. Adiponitrile dissolves almost the exact calculated amount and sebaconitrile takes up more than the calculated amount. These results are interesting when considered with the boiling points of the dinitriles.

*Presented before the Indiana Academy of Science at Terre Haute, Indiana, November, 1939.

(1) H. Gal, *Ann.*, **129**, 53 (1863); M. Hanriot, *Ann. chim. phys.*, [5] **17**, 83 (1879).

(2) H. Gal, *Compt. rend.*, **56**, 1258 (1863); F. Urech, *Ber.*, **13**, 1687 (1880); J. Volhard, *Ann.*, **242**, 144 (1887); C. Hell, *Ber.*, **21**, 1726 (1888); C. F. Ward, *J. Chem. Soc.*, **123**, 2207–2213 (1923); H. B. Watson, *ibid.*, **127**, 2067–2082 (1925); Bernard Gwynn and Ed. F. Degering, *Proc. Indiana Acad. Sci.*, **87** (1939).

(1) For the eighth communication in this series see THIS JOURNAL, **61**, 3550 (1939).

TABLE I

SOLUBILITY OF HALOGENATED METHANES IN NITRILES

Theoretical solubility	Formula	B. p., °C.	CH_2Cl_2 G./g.	CH_2Cl_2 M. F., 0.311	$CHCl_2F$ G./g.	$CHCl_2F$ M. F., 0.381
Caprylonitrile	$CH_3(CH_2)_6CN$	198–200	0.462	0.405	0.875	0.420
Benzonitrile	C_6H_5CN	190.7	.463	.359	See Ref. 1	
Succinonitrile	$CN(CH_2)_2CN$	265–267	.199	.158	.231	.152
Glutaronitrile	$CN(CH_2)_3CN$	285–287	.319	.261	.457	.294
Adiponitrile	$CN(CH_2)_4CN$	295	.364	.316	.560	.428
Sebaconitrile	$CN(CH_2)_8CN$	199–200 (15 mm.)	.425	.435	.730	.522

It is obvious that succinonitrile and glutaronitrile are associated to a considerable extent; this undoubtedly is due to bonding between hydrogens of the methylene groups and the nitrogen atom of the nitrile groups. In succinonitrile the $-CH_2-$ group is alpha to one nitrile residue and beta to another and the cumulative effect is sufficient to give labile hydrogen atoms. In glutaronitrile the further separation of the nitrile groups makes their cumulative effect less on each $-CH_2-$ group. In adiponitrile this effect is fairly well overcome by the distance between the nitrile groups. In sebaconitrile the solubility goes above the calculated value but not as much as might have been expected from the solubility of the mononitriles. This evidence for hydrogen bond association in the dinitriles is of interest in view of the recent estimation that hydrogen cyanide is similarly associated to the extent of 3% at the boiling point.[2]

The solubility determinations were made at 32.2° as described earlier[3] and are reported in the table.

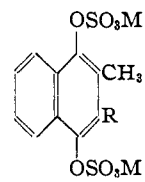
(2) Giauque and Ruehrwein, THIS JOURNAL, **61**, 2626 (1939).
(3) Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).

NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
WILLIAMS OIL-O-MATIC HEATING CORPORATION, BLOOMINGTON, ILLINOIS
RECEIVED DECEMBER 1, 1939

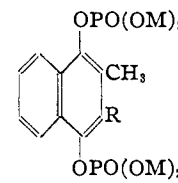
Water-Soluble Antihemorrhagic Esters

BY LOUIS F. FIESER AND EDWARD M. FRY

As a possible means of providing antihemorrhagic compounds which can be administered parenterally in a small volume of aqueous solution, we have prepared a series of water-soluble sulfuric and phosphoric acid ester derivatives of vitamin K_1 and of other quinones of established vitamin K activity. In chick assays conducted by Dr. W. L. Sampson potassium vitamin K_1 hydroquinone disulfate (I, R = phytyl, M = K) was found inactive at a dosage of 500 γ, an observation which perhaps finds a counterpart in the great loss of biological activity attending the conversion of oestrone into oestrone sulfate.[1] Similarly sodium 2,3-dimethyl-1,4-naphthohydroquinone disulfate was inactive at the same high dosage, in contrast to the corresponding quinone which is active at 50 γ. On the other hand, vitamin K_1 hydro-



I



II

quinone diphosphoric acid II (R = phytyl, M = H) shows activity at dosages down to 25 γ, but not at 10 γ, and thus does not fall greatly short of vitamin K_1, which gives a response at 1.5–2 γ by the same procedure. Still more potent is the sodium salt of 2-methyl-1,4-naphthohydroquinone disulfuric acid (I, R = H, M = Na), which shows antihemorrhagic activity at a level of 2 γ (assays at lower dosages are still to be made). The substance crystallizes as a dihydrate, and if the administered material undergoes hydrolysis it could give rise to only 52% of its weight of 2-methyl-1,4-naphthoquinone.

Of the water-soluble substances previously suggested for use in vitamin K therapy, phthiocol[2] suffers from being only weakly active, and free naphthohydroquinone and aminonaphthol derivatives[3] are highly sensitive to oxidation. The above active ester derivatives are colorless solids which are stable in aqueous solution and not sensitive to air or light. Furthermore, 2-methyl-3-phytyl-1,4-naphthohydroquinone diphosphoric acid can be described as a water-soluble form of vitamin K_1.

In a clinical trial conducted by Drs. H. A. Frank, A. Hurwitz and A. M. Seligman at the

(1) Butenandt and Hofstetter, *Z. physiol. Chem.*, **259**, 222 (1939).
(2) Almquist and Klose, THIS JOURNAL, **61**, 1923 (1939).
(3) Doisy, *et al.*, *ibid.*, **61**, 1932, 2563 (1939).

Beth Israel Hospital, Boston, sodium 2-methyl-1,4-naphthohydroquinone disulfate was given to a patient having a complete biliary fistula. A solution of 10 mg. of the salt in 10 cc. of 0.9% salt solution remained clear after autoclaving at 250°F. and when given intravenously reduced the prothrombin clotting time from 54 seconds to 28.5 seconds in four hours; the lowest level reached was 25 seconds in about twelve hours (normal, 15 seconds).

Experimental Part[4]

Potassium Vitamin K_1 Hydroquinone Disulfate.—A cooled suspension prepared by slowly adding 0.6 cc. of chlorosulfonic acid to 2 cc. of pyridine and 5 cc. of carbon tetrachloride was treated with 0.48 g. of vitamin K_1 hydroquinone. On manipulating the mixture with a stirring rod and boiling for ten minutes, the pyridine salt separated as a viscous mass which went to a sticky solid on cooling and diluting with ether. The liquor and washings afforded 0.17 g. of oil giving no color test with alcoholic alkali. The solid was treated while cooling with sufficient 10 *N* sodium hydroxide to produce a red color, ether was added to dissolve the liberated pyridine, and the sodium disulfate ester was separated by centrifugation as a dark red oil. This was stirred with excess 25% absolute alcoholic potassium hydroxide to effect conversion to the potassium salt, which separated as a light brown crystalline solid after dilution with absolute alcohol. Crystallization from 95% alcohol (Norite) gave colorless plates. The salt gives a clear solution in water. The sample was dried at 80° and 18 mm.

Anal. Calcd. for $C_{31}H_{46}O_8S_2K_2$: C, 54.04; H, 6.73; K, 11.35. Found: C, 54.54; H, 6.71; K, 10.67.

Sodium 2-Methyl-1,4-naphthohydroquinone Disulfate.—A mixture of 0.5 g. of 2-methyl-1,4-naphthohydroquinone with a cooled suspension from 1 cc. of pyridine, 10 cc. of carbon tetrachloride and 0.5 cc. of chlorosulfonic acid was heated for ten minutes on the steam-bath, cooled, and the solvent decanted from the oily yellow pyridine salt. This was treated with a slight excess of 10 *N* alkali, the mixture was extracted with ether, and the residual red oil taken up in a little hot water. Alcohol added in portions precipitated first inorganic material, which was removed, and then the ester salt as tan crystals (0.58 g., 0.27 g. more from the mother liquor). Crystallization from water gave 0.4 g. of colorless product free from inorganic salts, and this was further purified by dissolving it in water and adding alcohol. The air dried material proved to be a dihydrate.

Anal. Calcd. for $C_{11}H_8O_8S_2Na_2 \cdot 2H_2O$: C, 31.89; H, 2.92; Na, 11.10; H_2O, 8.70. Found: C, 31.82; H, 3.20; Na, 11.21; H_2O, 8.29.

Sodium 2,3-dimethyl-1,4-naphthohydroquinone disulfate was prepared as above from 0.5 g. of the hydroquinone. The pyridine salt was obtained on cooling as a highly hygroscopic solid. The sodium salt was crystallized once from water (0.8 g.) and then from water diluted with alcohol, giving colorless plates (air dried).

Anal. Calcd. for $C_{12}H_{10}O_8S_2Na_2 \cdot 2H_2O$: C, 33.64; H, 3.29; Na, 10.74; H_2O, 8.41. Found: C, 33.47; H, 3.49; Na, 10.97; H_2O, 9.00.

Sodium 2-Methyl-1,4-naphthohydroquinone Diphosphate (Normal Salt; II, M = Na).—A solution of 0.3 g. of the hydroquinone in 0.8 cc. of pyridine was added by drops with ice cooling to a suspension prepared by adding 0.5 cc. of phosphorus oxychloride with cooling to 1 cc. of pyridine. At the end the mixture was allowed to warm up until the exothermic reaction was over. The white suspension was then treated with 6 cc. of water, added cautiously at first with ice cooling and later heating to dissolve the product. Solid sodium carbonate was added until alkaline to litmus and the pyridine layer which separated was removed. The solution of sodium salts was stirred with absolute alcohol and the solvent decanted, leaving an aqueous solution of greatly diminished volume. The remainder of the water can be removed by stirring either with fresh portions of alcohol or with smaller portions of pyridine, leaving the sodium salt as a gum. Inorganic salts can be largely eliminated by dissolving in the least amount of hot water, cooling in ice, centrifuging and decanting from the crystallizate. Alternately, the gum is treated in the cold with methanol and enough water to bring the oily salt into solution; by adjusting the proportions inorganic salts are left undissolved and are removed by filtration. For crystallization of the product such a methanol–water filtrate was concentrated and cooled, oily salt was brought into solution with a little water, pyridine was added by drops until the solution became cloudy, and on warming on the steam-bath the sodium diphosphate separated as an oil which then crystallized (it is less soluble hot than cold). The colorless crystals were washed with methanol and dried; yield 0.68 g. The substance is very hygroscopic and liquefies on exposure to moist air. The sample for analysis was dried at 150° and 2 mm.

Anal. Calcd. for $C_{11}H_8O_8P_2Na_4 \cdot 2H_2O$: C, 28.83; H, 2.64. Found: C, 28.36; H, 2.21.

Vitamin K_1 Hydroquinone Diphosphoric Acid.—A solution of 0.48 g. of vitamin K_1 hydroquinone in 10 cc. of pyridine was cooled and added to an iced mixture of 1 cc. of phosphorus oxychloride and 5 cc. of pyridine (temperature rise to 15°). The solvent was largely removed in vacuum at 45° and the residue treated with 10 cc. of water and extracted with ether. The ethereal extract was shaken with a slight excess of 1 *N* sodium hydroxide and the alkaline layer separated and acidified with hydrochloric acid, when the diphosphoric acid precipitated. Collected by extraction with ether, the substance was obtained as a light tan amorphous solid (0.4 g.). Repetition of the process of purification by extraction from ether with alkali and precipitation with acid gave a somewhat waxy, nearly colorless solid. It gives a gel with a small amount of water and a clear solution with an adequate quantity. The sample was dried at 100° and 1 mm. (oil).

Anal. Calcd. for $C_{31}H_{50}O_8P_2$: C, 60.76; H, 8.28. Found: C, 60.92; H, 8.20.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS. RECEIVED DECEMBER 18, 1939

(4) Microanalyses by Lyon Southworth.

The Preparation of Pure Stearic Acid

BY J. P. KASS AND L. S. KEYSER

The preparation of pure stearic acid is complicated by the difficulty of removing final traces of the contaminating palmitic acid, since the separation by physical means is tedious and never unquestionably complete. In a recent study, Guy and Smith[1] considered it necessary to subject "pure" stearic acid to twenty-four recrystallizations from various solvents and to three fractional distillations to obtain a 3.8% yield of final product, m. p. 69.62°, the homogeneity of which was still not beyond question. During the course of our investigations of the chemistry of the fatty acids, we have found it convenient to prepare pure stearic acid totally free from palmitic acid by the catalytic reduction of the readily purifiable octadecenoic acids. Elaidic acid,[2] and especially the α- or β-eleostearic acids,[3] are easily available and may be brought to a high state of purity by a few recrystallizations of the free acids, while pure linoleic acid[4] of theoretical iodine value may be obtained from the crystallizable α-tetrabromostearic acid.[5] Quantitative reduction was effected by shaking the acetic acid solutions of the unsaturated acids for three hours in an atmosphere of hydrogen at room temperature and 45 lb. (3 atm.) pressure in the presence of platinum oxide catalyst. One recrystallization of the product from acetic acid or 85% alcohol yielded a stearic acid melting in a capillary tube at 69.6–70.2° (corr.) and dissolving in concentrated sulfuric acid at 70° without discoloration. A similar procedure was used by Francis, Collins and Piper[6] for the preparation of behenic acid from erucic acid.

(1) Guy and Smith, *J. Chem. Soc.*, 616 (1939).
(2) Rankoff, *Ber.*, **64**, 619 (1931); Smith, *J. Chem. Soc.*, 976 (1939).
(3) Wan and Chen, THIS JOURNAL, **61**, 2283 (1939).
(4) Rollet, *Z. physiol. Chem.*, **62**, 410 (1909).
(5) McCutcheon, *Can. J. Research*, **16**, 158 (1938).
(6) Francis, Collins and Piper, *Proc. Roy. Soc.* (London), **A158**, 707 (1937).

HORMEL FOUNDATION
DEPARTMENTS OF BOTANY AND CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN. RECEIVED NOVEMBER 17, 1939

The Preparation of *m*-Halogenophenols

BY HERBERT H. HODGSON

The author's attention has been drawn to a recent paper by S. Natelson and S. P. Gottfried[1] in which the preparation of *m*-bromophenol is described in language which implies originality, *viz.*: "Since this paper[1] was written, Smith and Haller[2] have published a method for obtaining *m*-bromophenol in good yield .... Their over-all yield is not as good as that obtained from the procedure described herein[1] nor is their procedure as simple."

It is of interest to note that from January to May of this present year (1939) the preparation of *m*-bromophenol has been described no fewer than three times,[1,2,3] and in only one of them[3] has the work of the present writer been mentioned.

The method apparently claimed as new by Natelson and Gottfried[1] was patented by the author[4] in 1923, and C. F. Koelsch[3] has stated recently that this patent of seventeen years ago is substantially true and that yields of 75–80% may be obtained thereby. Similar confirmations of the patent claim, however, have already been made to the writer by numerous chemists during the past seventeen years, who have found yields of the order of 80–90%.

Yields of over 90% of *m*-chlorophenol from *m*-chloroaniline have been obtained by the patented method[4] in large scale (kilo.) preparations. Subsequent work proved that excellent yields of *m*-fluorophenol[5] could also be obtained from *m*-fluoroaniline, while even the non-steam volatile *m*-hydroxybenzaldehyde[6] was prepared in excellent yield by the process.

The patented method[4] is substantially the same in detail as that described at length by Koelsch,[3] and is probably the best process yet devised for the preparation of steam-volatile phenols, since it is of universal application.

(1) Natelson and Gottfried, THIS JOURNAL, **61**, 1001 (1939).
(2) Smith and Haller, *ibid.*, **61**, 143 (1939).
(3) C. F. Koelsch, *ibid.*, **61**, 969 (1939).
(4) H. H. Hodgson and The British Dyestuffs Corporation, English Patent 200,714 (1923); *B. C. A.*, [i] 1005 (1923).
(5) H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, 1879 (1928).
(6) H. H. Hodgson and H. G. Beard, *J. Soc. Chem. Ind.*, **45**, 91T (1926).

DEPARTMENT OF CHEMISTRY
TECHNICAL COLLEGE
HUDDERSFIELD, ENGLAND RECEIVED JULY 29, 1939

The Freezing Points of Pure High Polymers

BY EDWIN L. LOVELL AND HAROLD HIBBERT

In a recent publication[1] it was shown that the setting points of the polymer-homologous series of polyoxyethylene glycols $HO(CH_2CH_2O)_pH$ followed very exactly the *empirical* equation

$$t_s = P/(a + bP) \qquad (1)$$

(1) Lovell and Hibbert, THIS JOURNAL, **61**, 1916 (1939).

where t_s is the setting point in °C., P the number of repeating units in the chain, and a and b constants. The experimental data covered molecules with from 54 to 558 atoms in the straight chain, a much wider range than has previously been available for pure compounds. At that time it was duly noted that this homologous series did *not* follow the logarithmic freezing point equation deduced from what might be termed "kinetic" considerations by Austin[2] but the authors could offer no explanation for the form of the equation actually obtained.

Very recently, however, a publication has appeared by Huggins[3] concerning the properties of long-chain compounds; it includes the derivation on purely thermodynamic grounds of a general law relating the freezing points in a polymer-homologous series to the number of atoms in the chain. This equation is

$$T_f = (A + Bn)/(C + Dn) \qquad (2)$$

where T_f is the absolute freezing point, n the number of atoms in the straight chain and the other symbols are constants. Inspection of the empirical relationship (1), and substituting for t_s its equivalent $T_f - 273$, reveals that this equation is identical in form with that of Huggins. This provides excellent support for the latter over a very wide range of chain lengths, many times greater than is possible in the n-alkane series, agreement for which (up to C_{70}) is shown by the previous work of Garner[4] and co-workers, who also have attempted to justify their results theoretically.[5] In both series the relation fails for chains of less than 20 atoms.

The agreement thus found between Huggins' thermodynamically derived freezing point equation and the freezing point data for the higher polyoxyethylene glycols is important additional evidence for the purity (uniformity of chain length) of this series of synthetic polymers.

(2) Austin, THIS JOURNAL, **52**, 1049 (1930).
(3) Huggins, *J. Phys. Chem.*, **43**, 1095 (1939).
(4) Garner, van Bibber and King, *J. Chem. Soc.*, 1533 (1931).
(5) Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926).

McGILL UNIVERSITY
MONTREAL, CANADA RECEIVED NOVEMBER 21, 1939

The Conversion of Chlorophyll to Pheophytin

BY G. MACKINNEY AND M. A. JOSLYN

In a previous paper[1] we presented evidence showing the rate of conversion of chlorophyll to pheophytin in 90% acetone was of first order with respect to acid concentration (normality) and possibly of second order with respect to chlorophyll. It was necessary to consider the two chlorophylls as a single component because we did not have the individual components separated. Evidence favored the assumption that the reaction was chiefly a conversion of chlorophyll a to pheophytin a, because the reaction was rarely carried to more than 80% completion. We have now separated sufficient quantities of chlorophylls a and b[2] to repeat previous experiments. Measurements were made at 5350 Å. for chlorophyll a, at 5280 Å. for chlorophyll b, where the respective pheophytin maxima occur.

Results are condensed in Table I. The first and second order rate constants, k_1 and k_2, have been calculated, and each value represents the average of 8–13 determinations over periods of time varying from two minutes to seven hours. The temperature was 28 ± 0.5°. The column Δ indicates the mean deviation of the arithmetic mean of the individual determinations. The values of k/N, whether k_1 or k_2 is taken, clearly show the reaction is of first order with respect to acid concentration, confirming our earlier work.

TABLE I

RATE CONSTANTS FOR CHLOROPHYLL, IN 90% ACETONE, WITH OXALIC ACID

Normality	k_1	Δ	k_2	Δ
	Chlorophyll *a*			
0.002	0.211	0.046	0.0069	0.0010
.004	.539	.072	.0189	.0099
.007	.907	.088	.0332	.0114
.01	1.39	.170	.0562	.0301
	Chlorophyll *b*			
0.01	0.148	0.021	0.0040	0.0007
.02	.328	.126	.0088	.0022
.05	.804	.180	.0271	.0049
.10	1.69	.216	.0580	.0148

We were previously at some loss to decide the order with respect to chlorophyll, because in most cases there was an apparent falling off in the calculated constants with time. The k_2 constants for oxalic acid were reasonably constant which led us to suggest a second order for chlorophyll. We knew only that pheophytin b contributed to the absorption at 5350 Å., but we could not then evaluate the extent of its absorption. Because the a and b mixture used was not highly purified, extensive recalculations are not deemed profit-

(1) Mackinney and Joslyn, THIS JOURNAL, **60**, 1132 (1938).
(2) Details will be published shortly.

able. Assuming, however, that with 0.002 N oxalic acid, for periods up to five hours, there is no conversion of chlorophyll b, we have recalculated some values on the basis of a 25% inert ingredient, *i. e.*, the chlorophyll b. Under these conditions, the oxalic results fall in line with the others, and we are given little preference between k_1 and k_2 for chlorophyll.

A limitation must be remembered, that with the visual B and L spectrophotometer, we cannot vary our chlorophyll concentrations within a wider range than 3 to 5 times without loss of accuracy. Initial concentrations of chlorophyll in the present experiments were 0.5×10^{-4} M, and the acid varied from 0.01 to 0.002 N for chlorophyll a and from 0.10 to 0.01 N for chlorophyll b.

The present values show no falling off with time, indicating there may be an error inherent in our earlier calculations as there could be no accurate compensation for the effect of chlorophyll b. The k_1/N values are in both cases more constant than those for k_2/N, and in two of the acid levels for chlorophyll b, and in three for a, the deviations are smaller for k_1 than for k_2. Furthermore, there is very little trend in the k_1 values, while in some cases there is a definite upward trend for k_2. We are therefore inclined to believe that the reaction is of first order with respect to both chlorophyll components.

An explanation is required for the fact that with 0.01 N oxalic acid, k_1/N for chlorophyll a has a value of 139, for chlorophyll b, 14.8. If the reactions are correctly interpreted on the basis of first order in both cases, the question arises as to the cause of this difference. We hope to throw further light on this in studies on the removal of magnesium from allomerized components, phytol-free derivatives, and the heats of activation.

Conclusions.—For the pure a and b chlorophyll components, it is confirmed that the reaction involving loss of magnesium is of first order with respect to acid. It is probably of the same order with respect to chlorophyll. The two hydrogens replacing the magnesium must therefore enter at different rates, and in all probability the entrance of the first hydrogen is the rate-governing step. This would materially weaken the remaining magnesium–nitrogen bond, in which respect it would then no longer be equivalent to the initial condition, presumably highly covalent in character.

The chlorophyll a reacts from seven to nine times more rapidly than chlorophyll b.

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The Synthesis of Amino Acids from Benzoylaminomalonic Ester

BY E. P. PAINTER

The use of benzoylaminodiethyl malonate in the synthesis of amino acids as recently reported by Redemann and Dunn[1] has been found to be superior in many respects to the malonic ester and phthalimido malonic ester methods.[2]

The ester alkylates in absolute alcohol with all alkyl halides tried. The ester or derivatives is readily hydrolyzed with constant boiling hydrochloric or hydrobromic acid. Glycine can be isolated in 85% yields by hydrolyzing the free ester with concentrated hydrobromic acid. To the list of amino acids prepared in good yields by Redemann and Dunn by the use of this reagent may be added norleucine, α-amino-γ-phenoxy-n-butyric acid and the lactone of α-amino-γ-hydroxy-n-butyric acid. These have been isolated after hydrolysis of the ester alkylated with n-butyl bromide, β-bromoethyl phenyl ether and ethylene bromohydrin.

In an attempt to prepare β- and γ-halogen amino acids benzoylaminomalonic ester has been alkylated with methylene dibromide, ethylene bromide and ethylene chloride. The products formed contain some halogen but always less than the theoretical amount and the desired amino acids have not been isolated after hydrolysis.

The aminomalonic ester was prepared by the method of Cerchez,[3] excepting the reduction was carried out in alkaline solution with aluminum amalgam made from aluminum turnings and the amino ester benzoylated in a suspension of sodium carbonate in ether saturated with water. By carrying the reaction straight through to the benzoyl compound without isolating the intermediary products, 40–45% over-all yields may be expected. Redemann and Dunn were able to obtain slightly better yields of benzoylaminomalonic ester, but their procedure is more expensive and not as convenient for many laboratories.

The use of anhydrous reagents in alkylations should be emphasized.

(1) Redemann and Dunn, *J. Biol. Chem.*, **130**, 341–348 (1939).
(2) Painter, Ph.D. Thesis, U. of Minnesota, 1939.
(3) Cerchez, *Bull. soc. chim.*, [4] **47**, 1281 (1930).

From the author's experience and the paper by Redemann and Dunn it appears that benzoylaminomalonic ester should find general use in the synthesis of α-amino acids.

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The 3-Nitrophthalates of the Mono Ethers of Ethylene and Diethylene Glycol

BY A. J. VERAGUTH[1] AND HARVEY DIEHL

The problem of identifying the monoethyl ether of ethylene glycol (Cellosolve) arose here recently and was successfully solved by the use of the 3-nitrophthalic anhydride reagent proposed by Nicolet and Sachs[2] for the identification of alcohols. The work has now been extended to the other commercially available monoethers of ethylene glycol ("Cellosolve" series), and of diethylene glycol ("Carbitol" series).

The ethers were obtained from the Carbide and Carbon Chemicals Corporation, and were purified by fractional distillation. A constant boiling fraction was taken, the boiling points and refractive indices checking with recorded values.

The procedure followed for the preparation of the acid 3-nitrophthalate esters of these ether alcohols was essentially that recommended by Nicolet and Sachs.

The anhydride was heated with an excess of the ether alcohol at the boiling point of the latter until all of the anhydride had dissolved and then for fifteen minutes longer. In the cases of those liquids having boiling points above 150°, toluene was added to avoid higher temperatures which cause decomposition of the esters formed; the toluene was then removed by distillation under reduced pressure. The oily layer of ester was then extracted with hot water to remove the unreacted reagents. It was then treated with a hot mixture of water and the least amount of ethyl alcohol necessary to effect complete solution. This solution was allowed to cool slowly with frequent scratching to induce crystallization. The initial crystallization was generally very slow, periods of standing for several days in a refrigerator sometimes being required. Recrystallization was continued until a constant melting point was obtained, generally three to five recrystallizations. Toluene was found to be a better solvent for recrystallization of the monophenyl ether of ethylene glycol than the water–alcohol mixtures.

Molecular weights of the derivatives were determined by titrating, with standard alkali, a solution containing 0.5 g. of the ester in 50% alcohol, using phenolphthalein as indicator. The melting points were taken with standard Anschütz thermometers in a mechanically stirred bath.

White crystalline derivatives were obtained from the monomethyl, monoethyl, monobutyl and monophenyl ethers of ethylene glycol and from the monomethyl ether of diethylene glycol but not from the monobenzyl ether of ethylene glycol or from the monoethyl or monobutyl ethers of diethylene glycol.

The 3-nitrophthalates obtained from the monoethyl ether of ethylene glycol and from the monomethyl ether of diethylene glycol crystallize with one molecule of water. Their water of crystallization was determined by drying a weighed amount of the ester in a vacuum at 100° over anhydrous magnesium perchlorate (Fischer drying pistol). The percentages of water found were 5.89 and 5.83, the calculated values being 5.98 and 5.43, respectively.

TABLE I

3-NITROPHTHALATES OF MONO ALKYL ETHERS OF ETHYLENE GLYCOL

Alkyl	3-Nitrophalates M. P., °C.	Mol. wt. Calcd.	Found
Methyl	128.4–129.0	269	268 ± 1
Ethyl	118.0–118.6	283	284 ± 3
Ethyl (monohydrate)	94.2–94.5	301	302 ± 4
Butyl	121.0–120.6	311	311 ± 1
Phenyl	112.0–113.0	331	330 ± 2

The 3-nitrophthalate monohydrate of the monomethyl ether of diethylene glycol was also a white crystalline solid and melted at 87–90°. The anhydrous 3-nitrophthalate melted at 91.4–92.2° and was found to have a molecular weight of 313 ± 1, as compared with the calculated value of 313. All attempts to induce the liquid reaction products from the monobenzyl ether of ethylene glycol ("Benzyl Cellosolve") and the monoethyl and monobutyl ethers of diethylene glycol ("Carbitol" and "Butyl Carbitol," respectively) to crystallize failed.

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(1) Taken from a Thesis submitted to the Faculty of Purdue University by Mr. Veraguth in partial fulfilment of the requirements for the Degree of Master of Science.

(2) Nicolet and Sachs, THIS JOURNAL, **47**, 2348 (1925); see also the further work of Dickinson, Crosson and Copenhaver, *ibid.*, **59**, 1094 (1937).