glass wool and evaporation yielded the ether-soluble rubber. The portion insoluble in ether was similarly treated with 100 ml. of chloroform for four hours and the residue from that treatment was extracted with 100 ml. of benzene for four hours.

Phenylsodium and Rubber.—Phenylsodium was made from 2.5 g. (0.022 mole) of chlorobenzene and sodium sand in a total volume of 160 ml. of thiophene-free benzene in the usual way. The mixture was forced by nitrogen pressure into a solution of 1.5 g. of rubber in 100 ml. of thiophene-free benzene. The viscous mixture was allowed to stand for the period given in Table II, after which it was forced onto solid carbon dioxide. Subsequent recoveries of rubber were as described in the previous section. The operations with stirring were in general the same as when the mixture was allowed to stand. Other conditions and results are given in Table II.

Amylsodium and Rubber.—The quantities of amyl chloride and sodium used for preparing amylsodium were such as to give 0.044 mole in each experiment based on an 80% yield. If isopropyl alcohol was added to this mixture in order to form the isopropoxide, enough additional amylsodium was prepared to allow for this consumption. Rubber, 1.5 g., was shredded and added to the reaction mixture. For the reaction at 20° the solvent was pentane; for the higher temperatures it was cyclohexane. The products were handled as before. The results are given in Table III.

Pentenylsodium and Rubber.—The preparation of amylsodium was carried out in the usual manner but with 1-pentene as a solvent.[4] Isopropoxide was obtained when desired by addition of the requisite quantity of isopropyl alcohol to 1-pentenylsodium. Rubber was added and the products separated as described in the previous section. The results are given in Table IV. The gel, swelling volume (S. V.) and intrinsic viscosity were determined by standard methods.

Alkali Metals and Rubber.—Sodium (5 g.) was shaken in 100 ml. of hot sulfur-free toluene. Rubber (1.5 g.) was then added and dissolved in 60°. An atmosphere of nitrogen was maintained. After removal of as much of the toluene as possible by use of an aspirator, the remainder was removed under a molecular still. Heat and vacuum was applied as described in Table VI. Carbon dioxide was then admitted, the reaction mixture cooled, and treated with solid carbon dioxide. The rubber was washed and fractionated as described below. The results are given in Table VI.

Reaction of Metals with Hydrocarbons.—The hydrocarbon in the quantities specified in Tables VII and VIII was dissolved in 40 ml. of benzene or xylene. Sodium was cut into small pieces and added. Alcohol was added as specified; the mixture was refluxed under an atmosphere of dry nitrogen. After the period of time specified in the table the mixture was carbonated by forcing it onto solid carbon dioxide. Alcohol, 100 ml., was added to destroy the sodium. Water, 13 ml., was then added and the solution heated on a water-bath to evaporate the alcohol. The aqueous solution was extracted with petroleum ether and with benzene and was then acidified with hydrochloric acid. The acid solution was then extracted with three 100-ml. portions of benzene and with three 100-ml. portions of ether.

The procedure was, in general, the same when the mixtures were stirred instead of refluxed. Usually the carboxylic acid precipitated upon the addition of hydrochloric acid and a single crystallization gave fairly good material. Triphenylacetic acid, recrystallized once from benzene, melted at 256.5–258.5° (the recorded[12] value is 264–265° dec.), fluorene-9-carboxylic acid, recrystallized once from alcohol, melted at 216–218° (a recorded[13] value is 220–222°), and phenylacetic acid, as obtained by evaporation of the ether extract, melted at 70–72° (recorded[14] value 76.7°).

Summary

When metalating agents act on natural or Alfin rubber, gel is formed. The amount of gel increases with the activity of the metalating agent and the severity of the conditions under which it is used.

Metallic sodium or potassium does not cause gel to form in natural rubber. Under very severe conditions these metals will metalate the highly active hydrocarbons, fluorene, triphenylmethane and diphenylmethane, in fair to poor amount, depending on the hydrocarbon, but they metalate toluene only slightly, even under highly favorable conditions.

[12] Schmidlin, *Ber.*, **39**, 636 (1906).

[13] Friedländer, *ibid.*, **10**, 536 (1877).

[14] Huntress and Mulliken, "Identification of Pure Organic Compounds Order I," John Wiley and Sons, New York, N. Y., 1941.

CAMBRIDGE, MASS. RECEIVED JULY 15, 1947

NOTES

The Preparation of Methyl Esters

BY R. O. CLINTON AND S. C. LASKOWSKI

There appears to be no description in the literature of an easily applicable general method for the preparation of the methyl esters of aliphatic and aromatic acids, especially for large-scale preparations. A large number of individual preparations have been described, involving in most cases the use of methanol–sulfuric acid or the Fischer methanol–hydrogen chloride method. In certain cases either of these methods gives excellent results; usually, however, the yields are of the order of 60–80%. The Fischer method generally gives the better yield, but is not easily adaptable to large-scale preparations. Other methods involving fractional distillation, such as the method of Weissberger and Kibler[1] require elaborate equipment and considerable manipulation. Baker[2] has described a procedure of apparently wide adaptability for small scale preparations, in which a mixture of the acid, methanol, chloroform (or benzene) and sulfuric acid is refluxed under a Soxhlet apparatus containing anhydrous magnesium sulfate. Baker[2b] states that continuous

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[1] Weissberger and Kibler, "Organic Syntheses," **24**, 72 (1944).

[2] (a) Baker, THIS JOURNAL, **65**, 1577 (1943); (b) Baker, Querry, Safir and Bernstein, *J. Org. Chem.*, **12**, 144 (1947).

drying of this type is essential for high yields. The limiting factors in this method are the large amounts of anhydrous magnesium sulfate required, the necessity for inclusion of a Soxhlet-type apparatus in the condensate path, and in some cases the time required for complete distillation of the water formed in the reaction, due to low concentration in the vapor phase.

A method in use in these Laboratories for some years appears to be of general applicability, and in ease of manipulation offers very evident advantages. We have found that the use of either methylene dichloride or ethylene dichloride as solvent removes the necessity for continuous drying and gives very high yields of methyl esters. The choice of solvent depends to some extent upon the boiling point of the required methyl ester; in general ethylene dichloride is the preferred solvent. A generalized procedure is as follows:

For *each mole* of aliphatic carboxyl group there are used 96 g. (3 moles) of commercial methanol, 300 ml. of ethylene dichloride, and 3 ml. of concentrated sulfuric acid. If the acid is aromatic, the amount of sulfuric acid is increased to 15 ml. per mole of carboxyl group.

The mixture is refluxed for from six to fifteen hours.[3] Progress of esterification is usually, but not invariably, indicated by the development of cloudiness and the separation of an upper layer containing water, methanol and sulfuric acid. The cooled reaction mixture is washed successively with water, sodium bicarbonate solution[4] and again with water. The ethylene dichloride layer is then distilled at atmospheric pressure or *in vacuo*, and the residual methyl ester processed by distillation or crystallization.

The procedure is not limited to insensitive acids; substitution of a milder catalyst such as ethanesulfonic acid (0.5 to 1.0 ml. per mole of carboxyl group) for the sulfuric acid allows the preparation of, *e. g.*, methyl pyruvate with no difficulty.

Table I includes a few examples to indicate the versatility of the method.

TABLE I

METHYL ESTERS[a]

Acid	Size of experiment, moles	Yield,[b] %	Properties of methyl ester[c]
Cyclohexylacetic[d,e]	20	93	B. p. 64–65° (18 mm.), $n^{25}D$ 1.4450
Adipic[f]	14	87	B. p. 113–113.5° (13 mm.), $n^{25}D$ 1.4265
Benzoic	2	95	B. p. 80–80.5°, $n^{25}D$ 1.5155
Coumarin-3-carboxylic	2	98	M. p. 114–115°
Salicylic[g]	1	92	B. p. 104–105° (14 mm.), $n^{25}D$ 1.5360
2,4-Dinitrophenylacetic[h]	1	91	M. p. 82–83°
Pyruvic[i]	1	73	B. p. 136–140°, $n^{25}D$ 1.4046

[a] The general procedure, with ethylene dichloride as solvent, was used unless otherwise specified. [b] The yields given are for material with the properties indicated. [c] These properties agree well with those recorded in the literature for the pure compounds. [d] Preparation by Dr. E. D. Homiller. [e] Using methylene dichloride as solvent, a 95% yield of pure ester was obtained after seven hours of reflux. [f] Preparation by Dr. Bill Elpern. [g] Methylene dichloride as solvent, forty-eight hours reflux period. [h] Methylene dichloride as solvent, fifteen hours reflux period. Time for complete solution of the acid was seven hours. [i] Fifteen hours reflux period, substituting 0.5 ml. of ethanesulfonic acid for the sulfuric acid. No tar formation was noted. Extension of the reflux period to forty-eight hours gave the same yield.

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[3] It is usually convenient to reflux overnight. The lower time limit varies for each compound, and may be as short as one-half hour. In certain cases where the initial acid is quite insoluble in the mixture the full time specified may be required.

[4] In large-scale preparations it is more convenient to dilute with water, siphon the upper layer, and stir the lower layer with excess solid sodium bicarbonate.

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK
RECEIVED MARCH 16, 1948

Condensation of Thiophene and Certain Derivatives with Chloral[1]

BY JAMES F. FEEMAN,[2] JOHN R. DOVE AND E. D. AMSTUTZ

The recent appearance of several papers[3,4] on the condensation of thiophene and several of its derivatives with chloral prompts us to report work which has been carried out along the same lines in this Laboratory.

Peter[5] in 1884 found that thiophene reacts with chloral in acetic acid solution in the presence of sulfuric acid giving "at most a 30% yield of the desired product which melted at 76°." Recent investigators[3,4] have in general employed the same reaction conditions with corresponding results. In the present work we have made use of aqueous sulfuric acid of varying concentrations which, in two cases at least, appears to make possible better yields than those previously reported.

In search of new insecticidal materials, we have prepared five dithienyltrichloroethanes, listed in Table I, analogous to DDT and related compounds. Two of these are new compounds while the other three have been reported by the investigators mentioned above.[3,4,5]

TABLE I

SUBSTITUTED DITHIENYL-TRICHLOROETHANES, R_2—CH—CCl_3

Compound	R =	M. p., °C.	Yield, %	Sulfur, % Calcd.	Sulfur, % Found
I	C_4H_3S—	77.5–78.0	73.2	21.54	21.63
II	5-Cl-C_4H_2S—	64–64.5	62.0	17.49	17.86
III	5-Br-C_4H_2S—	92.5–93.0	35.1	14.08	14.31
IV	2,5-di-Cl-C_4HS—	109.5–109.7	66.1	14.74	14.44
V	5-*t*-C_4H_9-C_4H_2S—	90.5–91.0	13.9	15.65	15.41

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[1] Taken in part from the senior research thesis of John R. Dove, June, 1947.

[2] Lehigh Institute of Research Fellow in Organic Chemistry, 1947.

[3] Metcalf and Gunther, THIS JOURNAL, **69**, 2579 (1947).

[4] Truitt, Mattison and Richardson, *ibid.*, **70**, 79 (1948).

[5] Peter, *Ber.*, **17**, 1341 (1884).

Metcalf and Gunther[3] have shown, by oxidation of the dehydrochlorinated dithienyltrichloroethane to the corresponding 2,2′-dithienyl ketone, that condensation in this case takes place in the expected 2 position of thiophene, and have substantiated this with evidence of failure of the indophenine test on the condensation products of the 2-substituted thiophenes, while the parent compound gave a positive test.

We have obtained evidence which indicates the above conclusions are correct, *i. e.*, that the 2-substituted thiophenes condense with chloral at the reactive 5 position. It is well known that mercuration of thiophene and its derivatives takes place first at an open α-position. By mercuration of 2,2-bis-(2-thienyl)-1,1,1-trichloroethane (I) with mercuric acetate in ethanol and acetic acid, and subsequent bromination of the di-mercurated product we obtained a compound (III) which proved to be identical with the product of condensation of 2-bromothiophene and chloral.

All attempts to condense 2-*t*-octyl-thiophene, 2,5-di-*t*-butyl-thiophene, 2-benzoyl-thiophene and 2,3,5-trichloro-thiophene with chloral by this method failed.

Acknowledgments.—The authors express their thanks to the Lehigh Institute of Research for funds which permitted carrying out this investigation, to the Michigan Chemical Corp. for the sample of 2-bromothiophene used in some of the work, and to the Research and Development Department of the Socony–Vacuum Oil Co., Inc., Paulsboro, N. J., for generous samples of the remainder of the thiophene derivatives used in this study.

Experimental[6]

In general the procedure followed for the condensations involved mixing sulfuric acid of the proper concentration with the calculated quantity of chloral hydrate in a three-necked flask fitted with mechanical stirrer and dropping funnel, and cooled by means of an ice-bath. The thiophene derivative (calculated amount) was then added at once with stirring, and a second quantity of sulfuric acid dropped into the reaction mixture over a period of one hour. Stirring was then continued for five hours, when the mixture was poured into ice-water, and the crude product either filtered off or the acid solution decanted. The crude material was washed with water, 10% bicarbonate solution, and water again, and then dried over phosphorus pentoxide overnight in a vacuum desiccator. Purification was effected by several recrystallizations from ethanol, including treatment with active charcoal.

2,2-bis-(2-Thienyl)-1,1,1-trichloroethane (I).—Thiophene (16.8 g., 0.2 mole), chloral hydrate (16.6 g., 0.1 mole), 20 ml. of sulfuric acid and 20 ml. of water were allowed to react as above. Concentrated sulfuric acid (50 ml.) was dropped in during one hour.

2,2-bis-(5-Chloro-2-thienyl)-1,1,1-trichloroethane (II).—Chloral hydrate (34.0 g., 0.22 mole), and 2-chlorothiophene (50.0 g., 0.44 mole) were condensed in the presence of 50 ml. concd. sulfuric acid; yield, 50.0 g. of a colorless crystalline substance with a fruity odor.

2,2-bis-(5-Bromo-2-thienyl)-1,1,1-trichloroethane (III).—2-Bromothiophene (81.5 g., 0.5 mole) was condensed with 41.4 g. (0.25 mole) of chloral hydrate in the presence of 200 ml. of concd. sulfuric acid; yield, 40.0 g. of colorless crystals with a slight fruity odor.

2,2-bis-(2,5-Dichloro-3-thienyl)-1,1,1-trichloroethane (IV).—Chloral hydrate (41.4 g., 0.25 mole) and 78.0 g. (0.52 mole) of 2,5-dichlorothiophene were condensed in the presence of half of a solution of 100 g. of concd. sulfuric acid and 200 g. of oleum (15% sulfur trioxide). The remainder of the acid was dropped in during one hour. The crude product weighed 99 g. (90.9%) (m. p. 93–104°). Two recrystallizations from ethanol gave colorless crystals.

2,2-bis-(2,5-Dichloro-3-thienyl)-1,1-dichloroethylene.—(2,2-bis-(2,5-Dichloro-3-thienyl)-1,1,1-trichloroethane (17.4 g., 0.04 mole) was refluxed with 200 ml. of 7.5% ethanolic potassium hydroxide for one hour. The solution was poured into 500 ml. of cold water, and the oil which separated was taken up in ether, the extracts dried over calcium chloride, and the ether evaporated. The oil solidified upon standing in the cold, and two recrystallizations from methanol gave colorless prisms, 11.1 g. (69.5%), m. p. 64.5–65.5°.

Anal. Calcd. for $C_{10}H_5S_2Cl_6$: S, 16.07. Found: S, 16.06.

Attempted Oxidations.—Several attempts were made to oxidize the above ethylene derivative with chromic anhydride in glacial acetic acid to the corresponding dithienyl ketone. These gave only yellow oils which could not be crystallized. Similar oxidations of the oil formed by alkaline hydrolysis of 2,2-bis-(5-*t*-butyl-2-thienyl)-1,1,1-trichloroethane produced only yellow oils which could not be crystallized nor distilled (1 mm. pressure).

2,2-bis-(5-*t*-Butyl-2-thienyl)-1,1,1-trichloroethane (V).—2-*t*-Butylthiophene (70.0 g., 0.50 mole) and 41.4 g. (0.25 mole) of chloral hydrate were condensed in a similar manner to that for 2,5-dichlorothiophene. The product was a yellow resinous material which was triturated with cold ethanol, leaving the desired product undissolved. Three recrystallizations from ethanol gave colorless crystals.

2,2-bis-(5-Acetoxymercuri-2-thienyl)-1,1,1-trichloroethane.—To a solution of 10 g. (0.03 mole) of dithienyltrichloroethane in 100 ml. of ethanol at 70° in a 500-ml. flask fitted with a reflux condenser was added a solution of 19.2 g. (0.06 mole) of mercuric acetate in 100 ml. of ethanol and 10 ml. of acetic acid. After fifteen minutes refluxing a white precipitate began forming. At the end of an hour it was filtered off, washed twice with 25-ml. portions of ethanol, and dried at 110° in the oven, giving 23.5 g. (94.0%) of fine white powder, m. p. 192–193°, dec.

Anal. Calcd. for $C_{14}H_{11}O_4S_2Cl_3Hg_2$: Hg, 49.23. Found:[7] Hg, 48.27, 48.10.

Bromination of Dichloromercuri-Dithienyl Trichloroethane.—The diacetoxymercuri-dithienyl-trichloroethane (15.5 g., 0.019 mole) was suspended with stirring in a saturated solution of 25 g. of sodium chloride for a half-hour at 40–50°. The white product was then filtered off, washed well with water and dried in the 110° oven, giving 14.6 g. of fine white powder, m. p. 188–190° dec. A solution of 7.7 g. (0.01 mole) of 2,2-bis-(5-chloromercuri-2-thienyl)-1,1,1-trichloroethane in 150 ml. of carbon tetrachloride was placed in a 300-ml. three-necked flask, fitted

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(6) All melting points have been corrected for thermometer stem-emergence unless otherwise noted.

(7) Analyses for mercury were carried out gravimetrically by decomposition with fuming nitric acid in a sealed tube, and quantitative precipitation in the form of the complex $[HgI_4][Cu\ en_2]$ from the neutralized solution (ammonia) according to the method of Spacu and Suciu, *Z. anal. Chem.*, **92**, 247 (1933). Rauscher's method (Rauscher. *Ind. Eng. Chem., Anal. Ed.*, **10**, 331 (1938)) for determination of mercury was attempted but the presence of sulfur interfered with the reduction.

with a dropping funnel, stirrer and thermometer, and cooled with an ice–salt-bath. Bromine (3.2 g., 0.02 mole) was then dropped in with stirring over a period of one-half hour. The solution was filtered and the carbon tetrachloride removed under reduced pressure. There remained a dark-colored oil which solidified to a brown solid (crude yield, 4.9 g.). Several recrystallizations from ethanol with activated charcoal treatment afforded 3.7 g. of colorless crystals with a fruity odor, m. p. 92–93°. A mixed melting point with the product of condensation of chloral and 2-bromothiophene gave no depression.

Anal. Calcd. for $C_{10}H_5S_2Br_2Cl_3$: S, 14.08. Found: S, 14.15.

Attempted Condensations.—Attempts were made to condense 2-*t*-octylthiophene, 2,5-*t*-butylthiophene, 2,3,5-trichlorothiophene and 2-benzoylthiophene with chloral using conditions reported above for the successful condensations and also using acetic acid as solvent in the reaction. 2-Benzoylthiophene was unaffected by these reaction conditions, being isolated quantitatively unchanged, while the other thiophene derivatives gave dark oils which we were not able to crystallize or to distill under reduced pressure (1 mm.).

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RECEIVED MARCH 30, 1948

2-Ethylpyridine and Derivatives

BY EARL C. GREGG, JR., AND DAVID CRAIG

2-Ethylpyridine has been prepared in this Laboratory by two independent methods; the hydrogenation of 2-vinylpyridine and the reaction of methyl iodide with α-picolyl lithium. Nevertheless, derivatives (picrate[1] and mercuric chloride[2]) reported by others for 2-ethylpyridine do not agree in their properties with our derivatives.

Since our methods of preparation appear unequivocal, we believe that previously recorded preparations of this compound have been impure or unauthentic.

Experimental

2-Vinylpyridine[3] was hydrogenated at 60 lb. hydrogen pressure at room temperature over old Raney nickel. One-tenth mole of hydrogen was absorbed by one-tenth mole of 2-vinylpyridine in 35 ml. of alcohol. The hydrogenation product distilled at 70–73° at 50 mm. or 144° at atmospheric pressure, $n^{20}D$ 1.4978. The picrate melted at 108.5–110° (uncor.) when crystallized from alcohol instead of 187° (uncor.) reported by Bergstrom.[1] It was established that no other picrate forming substance was present.

Analytical

Calculated picric acid content for $C_5H_4O_7N_3 \cdot C_7H_9N$ is 68.1%. Picric acid found by polarographic analysis in 0.1 *N* hydrochloric acid solution is 68.1 ± 0.3%.

The chloroplatinic acid derivative melted at 165–166° (uncor.) as reported by Ladenburg.[2] However, the mercuric chloride derivative melted at 113–114° (uncor.) instead of 103–106° (uncor.) reported by Ladenburg.[2] α-Picolyl lithium was prepared according to Walter.[4]

Dry methyl iodide was added dropwise to the α-picolyl lithium in the reaction flask which was immersed in ice. The resulting ether mixture was extracted with water to remove lithium iodide and some of the unreacted α-picoline. The ether layer was extracted with dilute hydrochloric acid to remove the 2-ethylpyridine and remaining unreacted α-picoline. The hydrochloric acid layer was neutralized and the resulting 2-ethylpyridine was drawn off and steam distilled. The 2-ethylpyridine was dried over anhydrous sodium sulfate and fractionated to remove α-picoline at 77–79° at 80 mm. The picrate from the higher boiling (70–73° 50 mm.) fraction melted at 108.5–110° (uncor.). The mixed melting point of the picrates prepared by the two methods was 108.5–110° (uncor.).

The ultraviolet absorption spectrum of the 2-ethylpyridine prepared above was characteristic of a monoalkyl pyridine.

We wish to acknowledge the measurement and interpretation of the ultraviolet absorption spectrum of 2-ethylpyridine by Laura Schaefgen.

A CONTRIBUTION FROM THE
RESEARCH CENTER OF THE
B. F. GOODRICH CO.
BRECKSVILLE, OHIO

RECEIVED APRIL 15, 1948

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[1] Bergstrom and McAllister, THIS JOURNAL, **52**, 2848 (1930).

[2] A. Ladenburg, *Ber.*, **32**, 44 (1899).

[3] Supplied by the Reilly Coal Tar and Chemical Company.

[4] Walter, "Organic Syntheses," Vol. XXIII, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 83.

Small Angle X-Ray Scattering of Various Cellulose Fibers

BY A. N. J. HEYN

The study of diffraction and scattering of X-rays at small angles by various substances has been undertaken only very recently and may be considered negligible in comparison with the studies at larger angles.

Small angles studies of fibrous material have been mainly confined to proteins[1–7] which give *discontinuous* scattering indicating the presence of a large (super-identity) period, inside the large molecules.

Only very preliminary work has been done on scattering of cellulose fibers, although it has been long known that ramie fiber gives a *continuous* small angle scattering.[2,8] Kratky and collaborators (1938–1942)[9,10] recently ventured a quantitative evaluation of the scattering in this material and related the identity period calculated to the size and distance of the cellulose micelles, which they found to be 50–60 Å. Besides ramie they also studied a special regenerated cellulose product derived from viscose. (Other authors[11–14]

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[1] J. D. Bernal and D. Crowfoot, *Nature*, **133**, 794 (1934).

[2] R. B. Corey and R. W. G. Wyckoff, *J. Biol. Chem.*, **114**, 407 (1936).

[3] W. T. Astbury and W. A. Sisson, *Proc. Roy. Soc.* (London), **A150**, 533 (1935).

[4] J. D. Bernal and I. Fankuchen, *J. Gen. Physiol.*, **25**, 111 (1941).

[5] R. S. Bear, THIS JOURNAL, **66**, 1297 and 2043 (1944).

[6] I. MacArthur, *Nature*, **152**, 38 (1943).

[7] I. Fankuchen, *J. Biol. Chem.*, **150**, 57 (1943).

[8] H. Mark, "Physik und Chemie de Cellulose," Berlin, 1932, quotes a description by R. O. Herzog, H. Mark and J. Henstenberg.

[9] O. Kratky, *Naturwiss.*, **26**, 94 (1938); **30**, 542 (1942).

[10] O. Kratky, A. Sekora and R. Treer, *Z. Elektrochem.*, **48**, 587 (1942).

[11] A. Guinier, *C. R. acad. Sci. Paris*, **204**, 1115 (1937); Thesis, Paris, 1939.

[12] R. Hosemann, *Z. Physik*, **113**, 751 (1939); **114**, 133 (1939).

[13] B. E. Warren, *J. Chem. Phys.*, **2**, 551 (1934); *Phys. Rev.*, **49**, 885 (1936).

[14] J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942).

used different principles for the evaluation of scattering in other materials.)

The investigation of small angle scattering of many different cellulose fibers by the writer showed the following new facts:

1. Different Angle of Scattering in Different Cellulose Fibers.—The angle of scattering of various cellulose fibers proved to vary considerably. In all cases—with the exposure time used—the scattering was very intense within a small angle from the primary beam, causing almost complete blackening of the film, and decreasing quickly within a short distance at the end of the spot (compare photographs). Therefore the extent of the scattering was sufficiently well defined to be easily measured. For illustration, the angle of intense scattering of some of the fibers investigated is given in the order of smaller angles.

Fiber	Hemp	Flax	Jute	Ramie	Viscose	Merc. Cotton	Cotton
Maximum scattering angle	2°	1°42′	1°35′	1°18′	1°9′	51′	36′
Smallest period in Å.	22	26	27	34	38	51, 5	73
Average period in Å. as calculated from mid-point of scattering	44	51, 5	55	68	73	95	146

Accepting Kratky's assumption regarding the validity of the principle of Bragg's law on scattering of compact structures, the angles given would be related with the minimum size and intermicellar distance of the micelles in these fibers. As a preliminary approximation of the *average* size, the identity period is also calculated from the angle at the midpoint of the scattering zone.

Anyway on the basis of this or other principles[11–14] and in connection with other considerations, the data obtained can be explained by the presence of smaller micelles and probably smaller intermicellar distances in hemp, flax and jute, larger micelles and small distances in ramie and cotton and probably small micelles and large intermicellar distances in viscose (faint scattering).

2. Relation with Orientation of Micelles.—The present studies were carried out by using a pin-hole beam instead of a slit, as used in most of the low angle studies by others. This resulted in a scattering image consisting of a horizontal line on the equator of a definite length on both sides of the primary beam in the case of hemp, jute and flax, the line having the same width over its total length, tapering only somewhat at the end. This can be explained by an orientation of the micelles completely parallel to the long axis of these fibers.

In addition fibers were studied where the fibrils and the micellar axis form an angle with the long axis of the fiber. Fibers were selected with decreasing pitch of the fibrils, namely, of *Sanseviera guinensis*, *Agave heterocantha*, and *Cocos nucifera* (and others). The interesting fact was observed that in all these cases the low angle picture consisted of two lines intersecting at the center of the diagram (primary beam), forming a "*cross*" at an angle, presumably identical with the double angle between the micellar and fiber axis. In *Sanseviera* the angle was about 20°, in *Agave* 45° and in *Cocos* (coir, in which the fibrils make an angle of 45° with the long axis) the two scattering lines intersect at exactly 90° (compare photographs).

This fact is the more remarkable as the "*wide*" angle diffraction pattern in these cases shows a *continuous* 002 arc of increasing extent, without any complete interruption. The low angle picture does not show any such smooth transition or continuity between the intersecting lines of the "cross" and appears to represent only the angle formed by opposite parts of the fibrillar spiral at points where the radius is parallel to the X-ray beam.

Therefore, such small angle studies allow a *direct* clear measurement of micellar orientation in fibers. A full explanation of the phenomenon of "cross formation," as described above, might lead moreover to a deeper insight of the micellar structure of fibers.

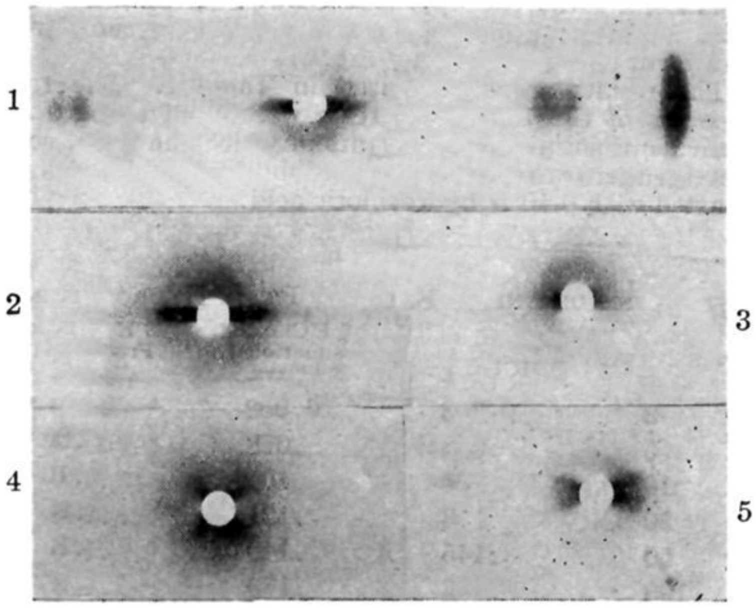

Fig. 1.—Small angle scattering and equatorial wide angle interferences of (1) ramie; (2) jute; (3) mercerized cotton; (4) coir; (5) *Agave heterocantha*. Exposure time, amount of material and distance are the same for all samples.

SCHOOL OF TEXTILES
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RECEIVED JULY 21, 1948

Hydrolysis Regeneration of an Anion Exchange Resin

BY HUGO P. KORTSCHAK AND JOHN H. PAYNE

No quantitative examination of the regeneration of anion exchange resins by water without the use of the usual alkaline regenerating agents has appeared in the literature, although it has been mentioned[1,2] that some hydrolysis occurs.

In the course of investigations on the sodium hydroxide regeneration of Amberlite IR-4B, in which the resin was exhausted with hydrochloric acid, then rinsed and backwashed with a total of 24 volumes of water, it was found that the hydrolysis was by no means negligible, amounting to 20% of the total capacity. This was therefore studied more closely.

Experimental

A sample of Amberlite IR-4B was freed of particles smaller than 30 mesh by wet screening, and placed in a $^1/_2$ in. o. d. pyrex tube, supported on a platinum screen. Regenerated, backwashed, settled and drained, the volume of resin was 105 ml. This had been exhausted with hydrochloric acid and regenerated with sodium hydroxide about 25 times before the test run.

Hydrochloric acid, 0.100 *N*, was run through the resin until the effluent concentration was also 0.100 *N*. Water was then run at 25 ml./min., the first 100 ml. being discarded as representing the volume of liquid in the column. The water was purified by ion exchange, and had a *p*H of 6.5. The effluent was collected in convenient increments, and titrated against 0.10 *N* sodium hydroxide, with phenolphthalein indicator. The run was continued until the titration values were found to approach that of the blank, 0.08 ml./100 ml.

This volume of water was not run without interruption. It was found, however, that standing overnight did not increase the acid concentration measurably, if this concentration was below 0.01 *N*. This indicates that under the conditions used, the approach to equilibrium was very close, and interruption of the flow would cause no significant error (compare Kunin,[3] Fig. 6).

The results are summarized in Table I. The total capacity of the 105 ml. of resin was found to be 0.270 equivalents in other experiments in which the resin, completely regenerated by 0.25 *N* sodium hydroxide, was exhausted with 0.10 *N* hydrochloric acid.

TABLE I

HYDROLYSIS OF ANION EXCHANGE RESIN HYDROCHLORIDE

Volume water, liters	Σ HCl removed, equivs.	Σ HCl calcd. Equation 1, equivs.	Σ HCl calcd. Freundlich, equivs.
2	0.053	0.052	0.019
5	.075	.078	.069
10	.095	.100	.100
20	.118	.121	.126
50	.145	.149	.155
100	.168	.170	.173
200	.189	.191	.188

Discussion

Table I gives the total volume of water used, *V*, in column 1, and the amount of hydrochloric acid removed from the resin, Σ HCl, in column 2. The third column was calculated from the empirical equation

$$\Sigma \text{HCl} = 0.07 \log V + 0.03 \qquad (1)$$

Column 4 was calculated from the Freundlich adsorption isotherm. The result agrees with the conclusion of Kunin and Myers in their study of acid adsorption[1,3] that the Freundlich equation can be applied at acid concentrations below 0.01 *N*. The data of Table I cannot be described in terms of the Donnan equilibrium, lending support to the hypothesis that the mechanism of acid removal by this resin is one of adsorption, and not of ion exchange.

HAWAIIAN SUGAR PLANTERS' ASSOCIATION AND
THE PACIFIC CHEMICAL & FERTILIZER CO.
HONOLULU, HAWAII
RECEIVED MARCH 19, 1948

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[1] R. Kunin and R. J. Myers, THIS JOURNAL, **69**, 2874 (1947).

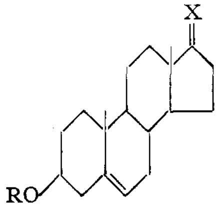
[2] P. Smit, U. S. Patent Application No. 359,575 (Oct. 3, 1940).

[3] R. Kunin and R. J. Myers, *J. Phys. Chem.*, **51**, 1111 (1947).

Dimercaptols of Dehydroisoandrosterone

BY ROBERT H. LEVIN AND J. L. THOMPSON

A recent publication[1] reports the reaction of dehydroisoandrosterone acetate (I) with benzylmercaptan and ethylmercaptan to give the corresponding dimercaptols (II, III). Saponification of II led to the hydroxy compound IV.



I R = CH_3CO, X = O
II R = CH_3CO, X = $(SCH_2C_6H_5)_2$
III R = CH_3CO, X = $(SCH_2CH_3)_2$
IV R = H, X = $(SCH_2C_6H_5)_2$
V R = H, X = $(SCH_2CO_2H)_2$

We had independently prepared the dibenzylmercaptol (IV) in 65% yield by directly condensing dehydroisoandrosterone with benzylmercaptan in the presence of zinc chloride and sodium acetate. Acetylation with acetic anhydride in pyridine at room temperature gave the acetate (II) of dehydroisoandrosterone dibenzylmercaptol in 94% yield.

In the same manner dehydroisoandrosterone has been condensed with thioglycolic acid to give the dimercaptol (V) in 73% yield. The sodium salt of this interesting compound is water soluble.

Experimental

Dibenzylmercaptol of Dehydroisoandrosterone (IV).—To a mixture of 2.8 g. of freshly fused and pulverized zinc chloride, 5 g. of anhydrous sodium sulfate, and 2.88 g. (0.01 mole) of dehydroisoandrosterone was added 25 ml. of benzyl mercaptan. After standing at room temperature for fifteen minutes the mixture was placed in the refrigerator for twenty hours, then allowed to warm up to room temperature and poured into 500 ml. of ice-water. The mixture was extracted with three 125-ml. portions of ether and the ether washed with 5% sodium hydroxide solution and with water and dried over anhydrous sodium sulfate. The ether solution was concentrated on the steam-bath and the excess benzyl mercaptan distilled at 1–5 mm. The residue was crystallized from hexane, giving 4.09 g. (79%) of product, m. p. 150–154°. which, after several recrystallizations from hexane, melted at 184–186°. The yield of pure material was 65% of the theoretical.

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[1] Norymberska, Norymberski and Olalde, THIS JOURNAL, **70**, 1256 (1948).

Anal. Calcd. for $C_{33}H_{42}OS_2$: C, 76.40; H, 8.16; S, 12.4. Found: C, 76.18; H, 8.53; S, 12.5.

Acetylation of IV (1 g.) in 5 ml. of acetic anhydride and 10 ml. of pyridine at room temperature for twenty hours and crystallization from acetone–water gave 1.02 g. (94%) of colorless needles, m. p. 150–152°, of the **dibenzylmercaptol of dehydroisoandrosterone acetate.**

Anal. Calcd. for $C_{35}H_{44}O_2S$: S, 11.4. Found: S, 11.4.

Dimercaptol of Dehydroisoandrosterone and Thioglycolic Acid (V).—In an analogous manner 2.88 g. (0.01 mole) of dehydroisoandrosterone, 2.8 g. of zinc chloride, and 5 g. of sodium sulfate were mixed and treated with 10 ml. of thioglycolic acid. The reaction mixture was poured into 500 ml. of water, giving a precipitate which was separated by filtration. Crystallization of the dimercaptol (V) from 100 ml. of acetone and 10 ml. of water gave 3.35 g. (73%) of material, m. p. 130–155°. Several recrystallizations from ethyl acetate gave colorless needles, m. p. 177–179°.

Anal. Calcd. for $C_{23}H_{34}O_5S_2$: S, 14.1. Found: S, 14.3.

Hydrolysis of the dimercaptol (V) in refluxing aqueous alcoholic hydrochloric acid gave dehydroisoandrosterone, m. p. 140–142°.

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RECEIVED APRIL 20, 1948

A General Relation Among the Various Additive–Constitutive Physical Properties

BY FAUSTO W. LIMA

There have been found linear relations among some physical properties, like the one of R. T. Lagemann[1] between molecular refraction and Souder's viscosity constant, the numerical coefficients of which are obtained by the method of least squares.

Lagemann and Dunbar[2] showed also that molecular refraction, parachor, Souder's viscosity constant, van der Waals' *b* and molecular magnetic rotation are related to the molecular sound velocity[3] by linear relation; consequently, between any two of these properties there will also be linear relations.

We can show that there is a way of generalizing such relations and of obtaining new ones and, at the same time, of justifying them theoretically.

Let us consider the members of an homologous series of organic compounds; one can say that an additive–constitutive property *F* (like parachor, molecular refraction, Souder's viscosity constant, etc.) can be taken as *n* times the contributions of the CH_2 groups (where *n* are the number of CH_2 groups of the member of the homologous series) plus the contributions of any special characteristic of the series, like double bonds, triple bonds, carbonyls, carboxyls, or rings, etc.; one must include also the contributions of the hydrogen atoms that remain after putting CH_2 in evidence. We have then

$$F = nF_{CH_2} + F_1 \qquad (1)$$

where F_{CH_2} is the contribution of the group CH_2 and F_1 the contributions of the structural characteristic of the series plus the contribution of the hydrogen atoms that remain after putting CH_2 in evidence.

For another additive-constitutive property *G* one can write for the same series that

$$G = nG_{CH_2} + G_1 \qquad (2)$$

where the symbols have the same meaning as before but with regard to the *G* property.

By eliminating *n* between (1) and (2) we have

$$F = GF_{CH_2}/G_{CH_2} - G_1F_{CH_2}/G_{CH_2} + F_1 \qquad (3)$$

which is a linear relation

$$F = aG + b$$

The relation (3) shows why the slope F_{CH_2}/G_{CH_2} is the same for the components of any homologous series, as Lagemann[1] observed.

The equation (3) was tested for the relation Souder's viscosity constant (*I*)–parachor (*P*) and parachor (*P*)–molecular refraction (*R*) and the agreement between calculated and observed values was found to be less than 1%.

For the relation between *I* and *P*, $a = I_{CH_2}$ $P_{CH_2} = 55.6/40 = 1.4$, and *b* for the series studied is

Paraffins	−37.7
Alkyl bromides	−36.5
Alkyl chlorides	−35.9
Alkyl iodides	−34.9
Monohydric alcohols	− 3.8
Carboxyl acids (monobasics)	−19.7
Esters of acetic acid	−34.4
Esters of formic acid	−33.2
Esters of propionic acid	−39.8

LABORATORY OF PHYSICAL-CHEMISTRY AND
ELECTROCHEMISTRY OF "ESCOLA POLITÉCNICA DA
UNIVERSIDADE DE S. PAULO, BRAZIL,"
PÇA. CEL. FERNANDO PRESTES 174
S. PAULO, BRAZIL

RECEIVED APRIL 5, 1948

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(1) R. T. Lagemann, THIS JOURNAL, **67**, 498 (1945).

(2) R. T. Lagemann and Dunbar, *J. Phys. Chem.*, **49**, 428 (1945).

(3) M. R. Rao, *J. Chem. Phys.*, **9**, 682 (1941).

Triethylenetetranitramine

BY G. N. R. SMART AND GEORGE F WRIGHT

The nitration of dialkylchloramines[1] and of monoalkyldichloramines[2] has recently been reported. It seemed of interest to inquire whether nitration would be successful in cases where these two types of chloramine linkage were incorporated into the same molecule. Triethylenetetramine was chosen as a type, and was N-chlorinated[3] to give N-hexachlorotriethylenetetramine, I.

We were unable to isolate the chloramine as a chemical individual. At best it decomposed slowly during evaporation of the solvent in which it was prepared; in the dry state it often decomposed explosively. However, a slight decomposition ought to be inconsequential since the more

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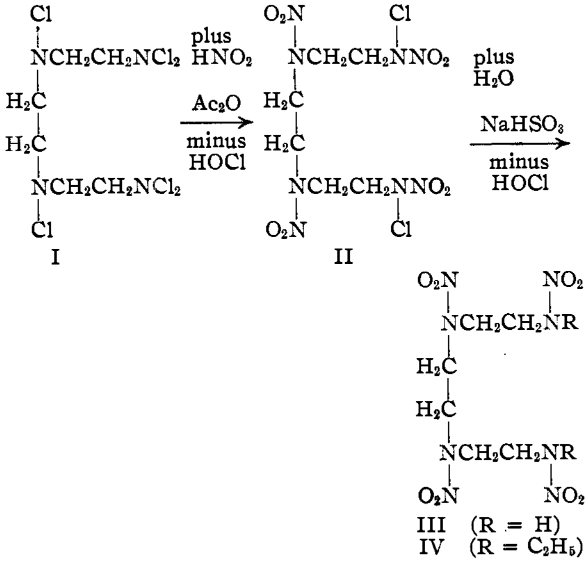
(1) G. S. Myers and G. F Wright, *Can. J. Res.*, **26B**, 257 (1948).

(2) G. N. R. Smart and G. F Wright, *ibid.*, **26B**, 284 (1948).

(3) L. K. Jackson, G. N. R. Smart and G. F Wright, THIS JOURNAL, **69**, 1539 (1947).

sensitive linkage ($RNClR > RNCl_2$) is known to decompose largely to the amine hydrochloride. The amine hydrochloride linkage has been found to revert to the chloramine in the presence of nitric acid in acetic anhydride.[1]

No attempt was made therefore to isolate the N-hexachlorotriethylenetetramine, I, from the chloroform solution in which it was prepared. Direct nitration in acetic anhydride solution yielded N^1,N^4-dichlorotriethylenetetranitramine, II, in fair yield, and this was converted readily to triethylenetetranitramine by means of aqueous sodium sulfite.



I II

III (R = H)
IV ($R = C_2H_5$)

The alkali soluble III was characterized by conversion to N^1,N^4-diethyltriethylenetetranitramine, IV, with diazoethane.

Experimental[4]

Chlorination of Triethylenetetramine.—A solution of 49 g. (0.3 mole) of triethylenetetramine and 252 g. (3.0 moles) of sodium bicarbonate in 1500 cc. of water was combined with 100 cc. of chloroform and treated at 25° with a rapid stream of chlorine for ten hours. The chloroform layer was separated and dried with calcium chloride. This chloroform solution was used for the nitration described subsequently. Analysis showed that it contained five-sixths of the expected electropositive chlorine.

Dichlorotetranitrotriethylenetetramine.—One-half of the chloroform solution (assumed to be 0.15 mole of N-hexachlorotriethylenetetramine) was added proportionately with 36.3 ml. (0.9 mole) of 98% nitric acid to 143 ml. (1.5 mole) of acetic anhydride over one hour. The temperature was maintained at 40° during addition and subsequently for one hour. After the mixture was chilled to 0° for nine hours it was filtered to remove 25 g. of material melting roughly at 114–116°. This crude product when analyzed for electropositive chlorine seemed to be a mixture of N^1-chloro and N^1,N^4-dichlorotriethylenetetranitramine. If it were the latter compound the yield would be 42% of theoretical.

Triethylenetetranitramine.—When the crude reaction product (25 g.) was suspended in 250 cc. of cold stirred half-saturated sodium sulfite solution for nine hours the electropositive chlorine was consumed. The suspension was then filtered to remove 17.5 g. (36% yield from triethylenetetramine), melting at 159–160°. This material was dissolved in alkali (*p*H 8) and filtered. It was reprecipitated (m. p. 168°) by acidification to *p*H 4 with dilute hydrochloric acid. Final purification (m. p. 174.1°) was effected by two crystallizations from hot nitromethane (10 cc. per g.). The compound gave a positive Franchimont test for a nitramine. It formed an insoluble silver salt and a relatively insoluble pyridine salt.

Anal. Calcd. for $C_6H_{14}N_8O_8$: C, 22.1; H, 4.30; N, 34.4. Found: C, 22.4; H, 4.25; N, 33.9.

N^1,N^4-Diethyltriethylenetetranitramine.—A suspension of 0.5 g. of triethylenetetranitramine in an ether solution containing 0.25 g. of diazoethane evolved gas rapidly. Evaporation of the ether left a sirup which gradually solidified during four days. It was crystallized from ethanol to melt at 68–70° (yield 50% of theoretical). A recrystallization raised this melting point to 96.5–96.8°. The compound was insoluble in alkali, and it gave a positive Franchimont test for a nitramine.

Anal. Calcd. for $C_{10}H_{22}N_8O_8$: C, 31.5; H, 5.82; N, 29.3. Found: C, 31.9; H, 5.85; N, 29.1.

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[4] All melting points have been corrected against known standards.

The Rare Earth Metals and their Compounds. VIII. An Improved Method for the Synthesis of Some Rare Earth Acetylacetonates[1a]

BY JOSEPH G. STITES, C. N. MCCARTY AND LAURENCE L. QUILL

Methods reported in the literature[1-7] for the preparation of the acetylacetonates of the rare earths involve, for the most part, the addition of a solution of sodium or ammonium acetylacetonate to a dilute acid solution of the rare earth nitrate. The yields are either unreported or are low.

This study was undertaken to observe the effect of changing the acidity on the formation of the rare earth acetylacetonates since (a) acetylacetone is a weak acid and (b) completeness of precipitation of many rare earth compounds is *p*H dependent. Also, since acetylacetone is so easily oxidized it was thought that part of the lower yield resulting when the nitrates of the rare earths are used was due to an oxidation effect and, consequently, that the chlorides might give better results.

Experimental

A weighed quantity of rare earth oxide was dissolved in the minimum amount of dilute hydrochloric acid and the *p*H of the solution adjusted by the addition of dilute ammonium hydroxide to a value of approximately 5.0 as measured by the glass electrode. A solution of ammonium acetylacetonate was prepared by adding concen-

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[1a] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting April 1948.

[1] W. Biltz, *Ann.*, **331**, 334 (1904).

[2] G. Jantsch and E. Meyer, *Ber.*, **53B**, 1577–1587 (1920).

[3] G. Urbain, *Bull. soc. chim.*, [3] **15**, 338–347 (1896).

[4] G. Urbain, *Ann. chim. phys.*, [7] **19**, 223 (1900).

[5] R. C. Young and J. Kovitz, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, 1947, p. 123.

[6] R. A. Staniforth, L. L. Quill and J. P. McReynolds, Thesis, Ohio State University, 1943, unpublished.

[7] J. K. Marsh, *J. Chem. Soc.*, 1084 (1947).

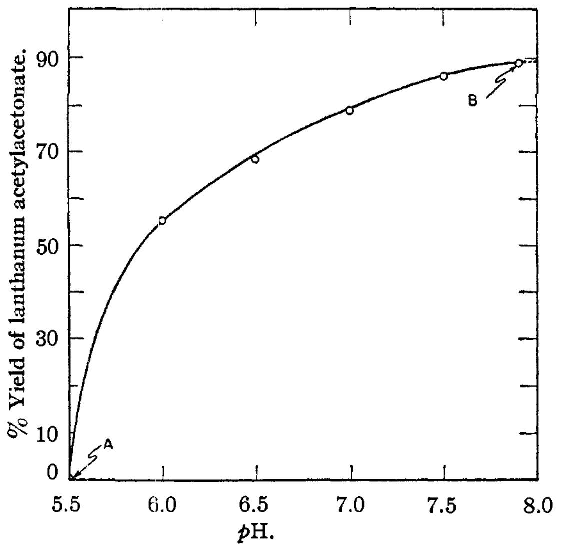

Fig. 1.—Point A represents pH of solution at first noticeable yield. Point B represents highest pH used for precipitation in order to prevent formation of lanthanum hydroxide.

trated ammonium hydroxide together with sufficient water for solution to an amount of freshly distilled acetylacetone which was 50% in excess of that required for complete reaction with the rare earth oxide. The solution of ammonium acetylacetonate was added slowly with stirring to the rare earth chloride solution. The pH of the reaction mixture was maintained at all times at a value just below that of the pH of precipitation of the corresponding rare early hydroxide[8] by the addition of either dilute ammonium hydroxide or hydrochloric acid as required. The mixture was stirred for twelve hours to insure conversion of any basic acetylacetonate to the normal compound and to allow for completeness of reaction. Crystalline precipitates of the rare earth acetylacetonates were obtained which were filtered, air dried for twenty-four hours, and then placed over magnesium perchlorate for four days. The precipitates were then weighed and their melting points obtained. For comparison of yields the same compounds were prepared using nitric acid in place of hydrochloric acid. The following table shows typical experimental data obtained from both nitrate and chloride solution.

TABLE I

Rare earth	Oxide taken, g.	pH	Yield, % Chlor.	Nit.	M. p., °C. obs.	lit.	
La	5.3	7.8	89	75	142–143	142–143[6]	
Ce	11.5[a]	6.9	83	74	146–147	145[1]	
Pr	5.47	6.5	90	65	143–144	146[1]	138–139[6]
Nd	5.47	6.5	96	67	144–145	144–146[1]	143–144[6]
Sm	5.68	6.5	96	88	144–145	146–147[1]	143–144[6]
Eu	2.85	6.5	98	90	144–145	144–145[6]	
Y	3.67	6.2	93	89	131–132	131[1]	129–130[6]

[a] Oxalate converted to chloride or nitrate.

The agreement of melting points obtained as compared to those recorded in the literature[1–7] even after purification indicates a product of high purity.

In preparing these acetylacetonates it was observed that if the solution was too acidic no precipitate was formed and if too basic a gelatinous product was obtained. Melting points of different samples of the gelatinous type of material were not consistent.

The variation in the yield of rare earth acetylacetonates with change in pH of the solution was determined by a series of experiments in which the amount of rare earth acetylacetonate formed in a solution of known pH was determined. Below is a typical curve drawn from data obtained in the preparation of lanthanum acetylacetonate.

It is obvious from the curve that the yield of the acetylacetonate is a function of the pH of the solution.

CONTRIBUTION FROM THE
KEDZIE CHEMICAL LABORATORY OF
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN
RECEIVED FEBRUARY 7, 1948

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[8] T. Moeller and H. E. Kremers, *Chem. Rev.*, **37**, I, 97–159 (1945).

Some Nuclear Halogenated Derivatives of α,α-Dihydroxymalonanilide

BY BENJAMIN WITTEN AND HAROLD H. ROSEN

Plowman and Whitely[1] have described the synthesis of α,α-dihydroxymalonanilide and 4,4′-dimethyl-α,α-dihydroxymalonanilide. We have extended the series to include three nuclear halogenated derivatives, the 4,4′-dichloro-, the 4,4′-dibromo- and the 2,2′,4,4′-tetrachloro-, α,α-dihydroxymalonanilides, following essentially the method of Plowman and Whitely.

Experimental

Nuclear Halogenated Malonanilide (I).—These compounds were prepared by the method of Chattaway and Mason.[2] The conversion of these compounds to the corresponding nuclear halogenated isonitroso N-ether and α,α-dihydroxymalonanilide was based on the method of Whitely,[3] and Plowman and Whitely.[1]

Nuclear Halogenated Isonitrosomalonanilide (II).—Into a 500-ml. three-necked flask equipped with a mechanical stirrer, gas inlet tube and thermometer was placed 0.05 mole of I suspended in 200 ml. of chloroform. The suspension was cooled to 0° and nitrosyl chloride (approximately 10 g.) was passed into the mixture until the color of the liquid became reddish-brown (about one hour). The white solid gave way to a yellow precipitate. It was filtered and crystallized from a 1:1 mixture of dioxane and alcohol. Yellow crystals of nuclear halogenated isonitrosomalonanilide were obtained.

The nitrosyl chloride used in the above synthesis was prepared by the method of Coleman, Lillis and Goheen.[4] This procedure was modified by using a 500-ml. three-necked flask and mechanical stirring in the preparation. The nitrosyl chloride was used without purification.

N-Methyl Ether of Nuclear Halogenated Isonitrosomalonanilide (III).—Into a 1-liter three-necked flask equipped with a mechanical stirrer, thermometer and dropping funnel was suspended 0.04 mole of II in 300 ml. of ether. The reaction was carried out at 0°. A solution of diazomethane, which was prepared from 13 g. of nitrosomethylurea[5] in 100 ml. of ether, was added dropwise. Nitrogen was evolved during the reaction. The mixture was allowed to warm up to room temperature. The yellow solid was filtered off and crystallized from absolute ethanol.

Nuclear Halogenated α,α-Dihydroxymalonanilide (IV).—Into a 500-ml. 3-necked flask, equipped with a mechanical stirrer and gas inlet tube, was suspended 0.02 mole of III in 150 ml. of chloroform. A stream of hydrogen chloride was allowed to pass first through glass wool saturated with water and then through the suspension. The

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[1] Plowman and Whitely, *J. Chem. Soc.*, **125**, 587 (1924).

[2] Chattaway and Mason, *ibid.*, **97**, 341 (1910).

[3] Whitely, *ibid.*, **83**, 34 (1903).

[4] H. S. Booth, Ed., "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

[5] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1937.

TABLE I

NUCLEAR HALOGENATED α,α-DIHYDROXYMALONANILIDE AND INTERMEDIATES

				Analyses, %					
				Carbon		Hydrogen		Nitrogen	
Derivative	Formula	M. p., °C.	Yield, %	Found	Calcd.	Found	Calcd.	Found	Calcd.
Nuclear Halogenated Isonitrosomalonanilide (II)									
4,4′-Dichloro	$C_{15}H_{11}N_3O_3Cl_2$	215	80	51.5	51.2	3.0	3.2	11.8	11.9
2,2′,4,4′-Tetrachloro	$C_{15}H_9N_3O_3Cl_4$	215	67	42.7	42.8	2.0	2.1	10.1	10.0
4,4′-Dibromo	$C_{15}H_{11}N_3O_3Br_2$	226	38	41.0	40.8	2.6	2.5	9.4	9.5
N-Methyl Ether of Nuclear Halogenated Isonitrosomalonanilide (III)									
4,4′-Dichloro	$C_{16}H_{13}N_3O_3Cl_2$	185	69	52.7	52.5	3.6	3.6	11.8	11.5
2,2′,4,4′-Tetrachloro	$C_{16}H_{11}N_3O_3Cl_4$	198	83	44.7	44.2	2.6	2.6	9.6	9.7
4,4′-Dibromo	$C_{16}H_{13}N_3O_3Br_2$	186	44	42.5	42.2	2.8	2.9	9.0	9.2
Nuclear Halogenated α,α-Dihydroxymalonanilide (IV)									
4,4′-Dichloro	$C_{15}H_{12}N_2O_4Cl_2$	208	21	51.0	50.7	3.2	3.4	8.2	7.9
2,2′,4,4′-Tetrachloro	$C_{16}H_{10}N_2O_4Cl_4$	190	19	42.7	42.5	2.2	2.4	6.7	6.6
4,4′-Dibromo	$C_{16}H_{12}N_2O_4Br_2$	166	50	40.6	40.5	2.6	2.7	6.4	6.3
O-Methyl Ether of 4,4′-Dibromo-isonitrosomalonanilide (V)									
	$C_{16}H_{13}N_3O_3Br_2$	219	10	42.3	42.2	3.1	2.9	8.8	9.2

hydrogen chloride was passed through for one hour. The yellow solid gave way to a white precipitate. The solid (IV) was filtered off and crystallized from glacial acetic acid. The chloroform filtrate contained an additional quantity of IV. This was recovered by removing the solvent under reduced pressure on the water-bath and crystallizing the residue from glacial acetic acid.

In the preparation of 4,4′-dibromo-α,α-dihydroxymalonanilide a second compound was isolated in 16% yield from the chloroform filtrate. After removing the solvent under reduced pressure on the water-bath, the residue was crystallized from alcohol. There was obtained as colorless crystals a compound melting at 219°. Its chemical composition indicated the conversion of some N-methyl ether to the O-methyl form (V). This conversion was similar to that reported by Plowman and Whitely[1] in the preparation of mesox p-toluidide.

CHEMICAL CORPS TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MD.

RECEIVED APRIL 14, 1948

Branched Structure of Guaran

BY ROY L. WHISTLER, TSIANG KWANG LI AND WILLIAM DVONCH

The principal polysaccharide of guar endosperm has been shown to be homogeneous[1] as to composition and to consist of anhydrogalactose and anhydromannose units in the ratio of one to two.[1,2] For convenience in designation, this particular polysaccharide has been given the name guaran.[1,3] Its triacetate can be formed into strong films which can be elongated 550% and thereby become birefringent, but they do not develop crystallinity which can be detected by X-ray examination. This has been taken to indicate the presence either of linear molecules in which a random distribution of anhydrogalactose and anhydromannose units occur or of a chain predominantly linear but with branches of very short length.[1] Recently Swanson[4] has shown that the galactose units occur principally as chain ends since from the methylated polysaccharide approximately 90% of the galactose can be recovered as 2,3,4,6-tetramethylgalactose. Consequently, one galactopyranoside end unit occurs for approximately two anhydromannose units. On oxidation of guaran with periodate Moe, Miller and Iwen[2] found that one mole of oxidant is consumed for each anhydrosugar unit present. This led them to conclude that the polysaccharide contained 1,4-glycosidic units although the possibility of branching was not eliminated.

The structure suggested by Swanson[4] is supported by work reported here on the periodate oxidation of guaran. In agreement with Moe, Miller and Iwen it is found that one mole of oxidant is consumed for each anhydrosugar unit present; but, in addition, it is found that by use of the oxidation method of Hirst, *et al.*,[5] one mole of formic acid is produced for approximately 2.7 anhydroglycosidic units. This indicates a large number of pyranosidic non-reducing end units or about one for two units of the main chain. Hence, one way to account for both the yield of formic acid and the fact that the polysaccharide consumes but one mole of oxidant for each anhydroglycosidic unit is to assume that guaran consists predominantly of a chain of anhydroglycosidic units one-half of which bear a glycopyranoside unit in conformity with the structure proposed by Swanson. Such a structure would require that on periodate oxidation the single unit side chains are split twice with the formation of one molecule of formic acid, that one-half of

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(1) E. Heyne and R. L. Whistler, THIS JOURNAL, **70**, 2249 (1948).

(2) O. A. Moe, S. E. Miller and M. H. Iwen, *ibid.*, **69**, 2621 (1947).

(3) R. L. Whistler, *Chem. Ind.*, **62**, 60 (1948).

(4) W. Swanson, paper presented before the Division of Sugar Chemistry and Technology at the 112th meeting of the American Chemical Society, New York, 1947.

(5) F. Brown, S. Dunstan, T. G. Halsall, E. L. Hirst and J. K. N. Jones, *Nature*, **156**, 785 (1945); T. G. Halsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1399 (1947); and private communication from Dr. E. L. Hirst.

the units of the main chain are split once, and that the other half of the units of the main chain, or those at the points of branching, are not split at all.

Experimental

Periodate Oxidation.—Following the method of Hirst, a 400-mg. sample of guaran was dissolved in 100 ml. of potassium chloride solution (5 g. of potassium chloride per 100 ml. of water) in a 500-ml. glass-stoppered bottle. Then 10 ml. of 0.3 M sodium periodate solution and 10 ml. of water were added and the mixture shaken at 25° for about one hundred hours. At this point the reaction was complete and ethylene glycol was added to consume the excess periodate. The formic acid present was titrated with 0.01 N barium hydroxide solution. One mole of formic acid was produced for 2.7 anhydrohexoside units. Samples of 200 mg. and 100 mg. gave similar values.

The presence of formic acid was confirmed by oxidation with mercuric chloride by the method of Auerbach and Zeglin.[6] Formic acid (*ca.* 40 mg.) formed from a 400-mg. sample of guaran was removed from the final reaction mixture by extraction with ether in a liquid–liquid extractor for ten days. A slight excess of sodium hydroxide was added to the ether extract and the mixture concentrated to about 5 ml. to remove ether and then was diluted to 60 ml. with water. After neutralization with 1 N hydrochloric acid, 1 ml. excess of acid and 3 g. of sodium acetate were added. The solution was filtered into an Erlenmeyer flask and 20 ml. of 5% mercuric chloride solution was added. The flask was covered with an inverted beaker and the mixture heated on a steam-bath for two hours. Precipitated mercurous chloride was filtered on a medium porosity sintered glass crucible, washed with hot water and ethanol, dried at 100°, and weighed. The weight of the precipitate corresponded to 103% of the formic acid determined by the above method of direct titration.

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(6) F. Auerbach and H. Zeglin, *Z. physik. Chem.*, **103**, 161 (1922).

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COMMUNICATIONS TO THE EDITOR

REVERSIBLE ACTION OF *macerans* AMYLASE[1]

Sir:

The action of *Bacillus macerans* amylase[2] on starch has been interpreted by Cori[3] as the exchange of a glycosidic bond in starch for a corresponding bond in a cyclic Schardinger dextrin (cycloamylose) molecule. In view of the small ΔF which would be expected for such an exchange, it might be expected that the reaction should be readily reversible. The reverse type reaction

$$\text{Cyclohexaamylose} + \text{Maltose} \xrightarrow{\textit{macerans}\ \text{amylase}} \text{Higher saccharides}$$

has been tested with crystalline substrates and verified; *macerans* amylase thus has a synthetic as well as degradative action.

Pure cyclohexaamylose,[4] 2.0 g., and C. P. maltose, 0.7 g., were dissolved in water, heated to complete mutarotation of the maltose, and treated with four units[2] of *macerans* amylase. The solution was made up to 100 ml. and the increase in rotation[5] was followed in the polarimeter: initial rotation, 7.87°; after two hours, 8.10°. At this point the enzyme was inactivated by boiling and the reaction products separated by fractional precipitation. The least soluble fraction, 0.14 g., sirupy, had $[\alpha]_D$ +163°; average chain length by alkaline ferricyanide,[6] 8.9 glucose units. These values indicate that the sample is probably a mixture of saccharides containing some non-carbohydrate impurities. It gave a slight deepening of the color of I_2–KI solution and no unchanged cyclohexaamylose could be detected by the Tilden micro test.[2] On treatment with *macerans* amylase the fraction was rapidly reconverted in part into cyclohexaamylose as indicated by the formation of the characteristic I_2–KI complex.

Results indicating a similar synthetic action of *macerans* amylase have been obtained from cyclohexaamylose with glucose, α-methylglucoside, sucrose, cellobiose or maltobionic acid as co-substrates; also from cycloheptaamylose[4] with maltose or glucose as co-substrates. These studies are being continued and will be reported in full at a later date.

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(1) Journal Paper No. J-1581 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 964.

(2) Tilden and Hudson, *J. Bact.*, **43**, 527 (1942).

(3) Cori, *Federation Proc.*, **4**, 226 (1945).

(4) French and Rundle, THIS JOURNAL, **64**, 1651 (1942).

(5) McClenahan, Tilden and Hudson, *ibid.*, **64**, 2139 (1942).

(6) Levine, Foster and Hixon, *ibid.*, **64**, 2331 (1942).

CHEMISTRY SECTION
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DEXTER FRENCH
JOHN PAZUR
MELVIN L. LEVINE
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RECEIVED AUGUST 10, 1948

FORMATION OF FLUORESCING SUBSTANCES FROM AMINO ACIDS

Sir:

Tauber[1] has reported recently on the formation of a fluorescing compound formed by the reaction of tryptophan with perchloric acid at room tem-

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(1) Tauber, THIS JOURNAL, **70**, 2615 (1948).