The production of salted-out films may thus prove to be a rapid and convenient microtechnique for purifying small amounts of various proteins. By the choice of the proper salt and concentration it should be possible to separate proteins from one another and to measure the amounts.

Summary

When a glass or metal plate is dipped into a protein solution, then into a concentrated solution of a salt such as ammonium, sodium or magnesium sulfate, or sodium chloride, a compact film of protein often 200–1000 Å. thick is salted out onto the plate. This can be fixed by 1% tannic acid and can then be washed with water without loss. After it has dried the thickness can be determined optically by interference colors. Insulin films, formed by using 1% sodium chloride solution, need no tannic acid treatment.

Salted-out protein films, in some cases up to 7000 Å. in thickness, are formed on the surface of salt solutions by applying a few drops of the protein solution. These can be deposited as hydrous B-films or as lifted A_L films onto plates or small pieces of metal foil, and they can thus be transferred to clean water surfaces where the amount of the protein can be measured from the area of the monolayer produced, or they can be fixed by tannic acid, washed and dried and the amount of protein per sq. cm. determined optically.

The refractive index of dried salted-out films of crystalline egg albumin was found to be 1.48. This low value and the power of the film to absorb hydrocarbon vapors indicate that the dried film has a skeleton-like structure.

The formation of these films at the surface of the solution or on a plate is aided by the concentration gradient in the salt solution. This carrying effect is analogous to the Ludwig–Soret phenomenon by which a solute originally uniformly distributed through a solution tends to concentrate in a portion of the solution which is cooled.

SCHENECTADY, N. Y. RECEIVED AUGUST 12, 1938

NOTES

Esters of Chlorosulfonic Acid[1]

BY W. W. BINKLEY WITH ED. F. DEGERING

While the lower alkyl esters of chlorosulfonic acid have been prepared, they have not been purified by redistillation and there is some disagreement in the values of the physical constants which have been reported.[2] We have therefore again prepared these substances and have purified them by careful rectification using a modified Podbielniak column and have redetermined with care certain of their physical constants.

The esters were prepared by adding dropwise one-fifth mole of the absolute alcohol to one-fifth mole of sulfuryl chloride contained in a test-tube 20 cm. long immersed in an ice-bath, the sulfuryl chloride being agitated by a brisk current of dry air drawn through it. A rough separation of the alkyl chlorosulfonate from the dialkyl sulfate was first accomplished by distillation under diminished pressure at the lowest possible temperature. The distillate was then rectified under diminished pressure in a jacketed electrically heated column which has a continuous nichrome wire gage No. 18 for packing.[3] An average yield of 50% based on the alcohol was obtained. The characteristic physical constants for these esters and other analyses are collected in Table I.

The chlorine content was estimated by a modified Fajans method[4] after the ester was allowed to decompose in a pressure bottle containing calcium carbonate. Sulfur was determined by the method of Carius.

All the lower normal esters of this series are lachrymators. The tear-producing effect decreases as the length of carbon chain is increased.

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[1] Abstracted from a portion of a thesis submitted by W. W. Binkley in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1939.

[2] Bushong, *Am. Chem. J.*, **30**, 212 (1903).

[3] Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 119 (1933).

[4] Mellon, "Methods of Quantitative Chemical Analysis," The Macmillan Co., New York, 1937, p. 297.

TABLE I

	Methyl	Ethyl	*n*-Propyl	*n*-Butyl
Sp. gr. at 25°	1.48	1.35	1.28	1.23
Ref. index 20°	1.414	1.416	1.422	1.427
B. p., °C.	48.1 at 29 mm.	42.3 at 10 mm.	53.2 at 10 mm.	69 at 10 mm.
% S, calcd.	24.53	22.18	20.18	18.65
% S, found	24.8 ± 0.2	22.0 ± 0.2	20.4 ± 0.2	18.3 ± 0.2
% Cl, calcd.	27.13	24.54	22.38	20.56
% Cl, found	27.0 ± 0.1	24.5 ± 0.1	22.2 ± 0.1	20.5 ± 0.1

They are colorless liquids, insoluble in water, but quite soluble in the common organic solvents.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
RECEIVED JULY 11, 1938

Nitrogen-Terminated Conjugated Systems and Maleic Anhydride

BY FELIX BERGMANN

The ability of 9-vinylphenanthrenes to condense with maleic anhydride[1] induced us to investigate whether conjugated systems consisting of a cyclic C–N double bond and an exocyclic ethylenic linkage would add maleic anhydride. 2-Styrylquinoline gave a well-defined reaction product, which, however, besides the components, contained one molecule of water, and therefore was styrylquinolinium maleate. This became obvious in its reaction with diazomethane, yielding dimethylpyrazoline-4,5-dicarboxylate.[2] Analogous observations have been made recently by La Parola[3] in the case of antipyrine and pyramidone. For comparison purposes, we studied the interaction between maleic anhydride and cinnamylidene-aniline, which contains the nitrogen-terminated conjugated system entirely in an open chain. Here, too, the reaction involves one molecule of water (from the air), but the maleate, presumably formed as above, is unstable and decomposes spontaneously into cinnamic aldehyde and maleanilic acid, HOOCCH=CHCONNH-C_6H_5.

Experimental

2-Styrylquinoline[4] (1.2 g.) and **maleic anhydride** (0.5 g.) were heated on the water-bath or in xylene solution for some minutes. The mixture turned yellow at once and deposited on cooling yellow crystals, which were recrystallized from xylene or butyl acetate. 2-Styrylquinolinium maleate formed long, silky needles, m. p. 165–167°. *Anal.* Calcd. for $C_{21}H_{17}O_4N$: C, 72.6; H, 4.9. Found: C, 72.8; H, 5.3. The salt was kept in contact with an excess of ethereal diazomethane solution; on evaporation a crystalline mass was obtained which was triturated with light petroleum (b. p. 80–100°) and recrystallized from the same solvent. Dimethyl pyrazoline-4,5-dicarboxylate was obtained in the form of leaflets, m. p. 103–105°. *Anal.* Calcd. for $C_7H_{10}O_4N_2$: C, 45.2; H, 5.4; N, 15.1. Found: C, 44.8; H, 5.5; N, 15.6.

Cinnamylidene-aniline[5] (1 g.) and **maleic anhydride** (0.5 g.) were heated together on the water-bath; the mixture turned brown, then red and an intense odor of cinnamic aldehyde developed. After fifteen minutes, benzene was added, whereupon maleanilic acid crystallized, yield 300 mg.; from butyl acetate as rhombohedra, m. p. 210°.[6] *Anal.* Calcd. for $C_{10}H_9O_3N$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.5; H, 4.5; N, 7.7. Diazomethane gave as above the expected methyl ester-anilide of pyrazoline-4,5-dicarboxylic acid, from xylene or butyl acetate; crystals, m. p. 175° (dec.). *Anal.* Calcd. for $C_{12}H_{13}O_3N_3$: N, 17.0. Found: N, 17.4.

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[1] E. Bergmann and F. Bergmann, THIS JOURNAL, **59**, 1443 (1937).

[2] Von Pechmann, *Ber.*, **27**, 1888 (1894); v. Pechmann and Burkard, *ibid.*, **33**, 3590 (1900).

[3] La Parola, *Gazz. chim. ital.*, **67**, 645 (1937).

[4] Skraup and Boehm, *Ber.*, **59**, 1013 (1927).

[5] Doebner and v. Miller, *ibid.*, **16**, 1665 (1883).

[6] The highest m. p. recorded before is 198° [Auwers and Schleicher, *Ann.*, **309**, 347 (1899)]. A preparation made according to Anschütz [*Ber.*, **20**, 3214 (1897)] showed m. p. 210°, after recrystallization from butyl acetate or butyl alcohol.

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
RECEIVED JULY 12, 1938

The Calculation of the Dissociation Constant of Weak Acids in H_2O–D_2O Mixtures

BY FRANK BRESCIA

From the exchange equilibria

$$2DCl + QH_2 = 2HCl + QD_2 \qquad K_1 = 14.64 \qquad (1)$$

$$QH_2 + D_2O = QD_2 + H_2O \qquad K_2 = 0.96 \qquad (2)$$

$$H_2O + D_2O = 2HDO \qquad K_3 = 3.27 \qquad (3)$$

Korman and La Mer[1] have calculated the equilibrium constant for the process, $D^+ + H_2O = H^+ + HDO$, to be $K_4 = 7.1$. Their derived equation for the calculation of dissociation constants of weak acids in H_2O–D_2O mixtures

$$K_M = K_D \left[1 + 7.1 \frac{C_{H_2O}}{C_{HDO}} \Big/ 1 + 7.1 \left(\frac{K_D}{K_H}\right) \frac{C_{H_2O}}{C_{HDO}}\right] \quad (5)$$

contains, therefore, the factor 7.1. K_M is the dissociation constant of the acid in the mixtures of H_2O–D_2O, K_D is the dissociation constant of

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[1] Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).

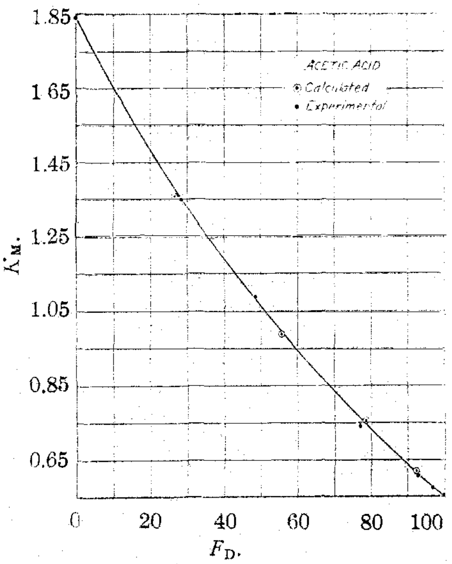

Fig. 1.—Acetic acid: ◉, calculated; ●, experimental.

the heavy acid, and K_H is the dissociation constant of the light acid. This equation, tested by Chittum and La Mer,[2] does not give the same K_M constants as those calculated from the conductance data. The sag of the experimental curve for acetic acid is opposite from that predicted by equation (5).

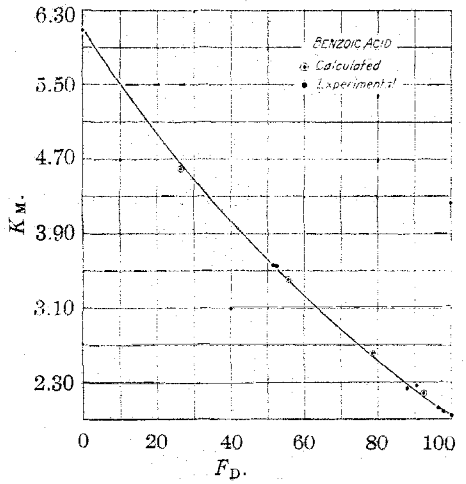

Fig. 2.—Benzoic acid: ◉, calculated; ●, experimental.

The value of K_4 can now be arrived at by an independent method. K_4 (column 4, Table I) has been calculated from the customary K_3 = 3.27[3] and from the values of C_{H^+} and C_{D^+} (columns 2 and 3, Table I), obtained through kinetic measurements of a specific hydrogen-ion catalyzed reaction: hydrolysis of ethyl orthoformate in mixtures of H_2O–D_2O.[5] The average value thus obtained, 3.76, is much smaller than the previous value, 7.1. Equation (5) is, therefore, corrected to

TABLE 1

(1) F_D	(2) $C_{H^+} \times 10^7$	(3) $C_{D^+} \times 10^7$	(4) K_4
26.40	3.68	0.624	3.99
55.60	1.93	1.16	3.72
78.49	0.827	1.49	3.46
92.51[4]	0.303	1.65	3.86

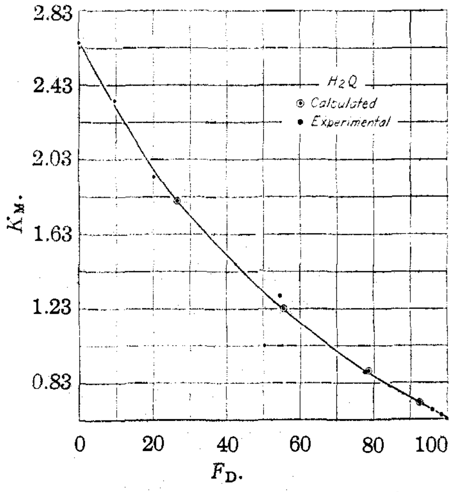

Fig. 3.—H_2Q: ◉, calculated; ●, experimental.

$$K_M = K_D \left[1 + 3.76\,\frac{C_{H_2O}}{C_{HDO}} \Big/ 1 + 3.76 \left(\frac{K_D}{K_H}\right) \frac{C_{H_2O}}{C_{HDO}}\right] \quad (6)$$

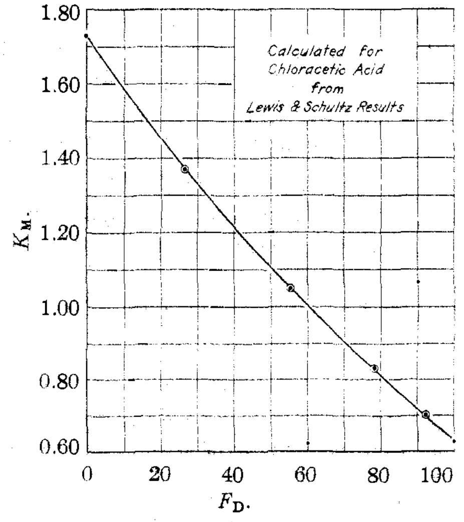

Fig. 4.—Calculated for chloroacetic acid from the results of Lewis and Schultz.

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(2) Chittum and La Mer, THIS JOURNAL, **59**, 2425 (1937).

(3) Topley and Eyring, *J. Chem. Phys.*, **2**, 217 (1934).

(4) The rate constant used to calculate this value of C_{H^+} and C_{D^+} was taken from the experimental curve in preference to the slightly lower determined value since the calculation in this region of F_D is very sensitive to small changes in the rateconstant. $F_D = \Delta S(100)/0.1079$ = fraction of deuterium in the solvent.

(5) Brescia and La Mer, THIS JOURNAL, **60**, 1962 (1938).

TABLE II

SUMMARY OF CALCULATED VALUES USING EQUATION (6) AND OF EXPERIMENTAL DATA

	$K_M \times 10^5$ HAc		$K_M \times 10^5$ HB		$K_M \times 10^{11}$ H_2Q		$K_M \times 10^3$ ClHAc	
F_D	Exptl.[6]	Calcd.	Exptl.[7]	Calcd.	Exptl.[7]	Calcd.	Exptl.[8]	Calcd.
0.0	1.84	(1.84)	6.09	(6.09)	2.66	(2.66)	1.73	(1.73)
9.61					2.35			
25.18					1.94			
26.40		1.36		4.60		1.81		1.37
28.4	1.352							
48.4	1.088							
51.45			3.56					
52.42			3.55					
54.69					1.30			
55.60		0.988		3.41		1.23		1.05
77.1	0.741							
77.49					0.889			
78.49		.756		2.61		0.895		0.827
87.99			2.23					
92.51		.622		2.18		.722		.700
93.0	.608							
96.00					(.684)			
96.51			2.03					
97.0	.575							
97.87			1.99					
98.67					.657			
100	(.555)	(.555)	(1.95)	(1.95)	(.639)	(.639)	(0.631)	(.631)

The K_M values, calculated from the revised equation (6), are now in very good agreement with the experimental results. These are summarized in Table II and plotted in Figs. 1, 2, and 3. The predicted slope for chloroacetic acid is given in Fig. 4; no experimental data for comparison are available. The value of K_D for salicylic acid is extrapolated with equation (6) from the average value $K_M = 0.24 \times 10^{-3}$, a. d. 12%, at $F_D = 91.7$, and from the average $K_H = 0.98 \times 10^{-3}$, a. d. 2%, determined by Korman and La Mer.[1] The K_D thus calculated is 0.21×10^{-3} which also has not yet been determined experimentally.

It is apparent that true values of hydrogen and deuterium ion concentrations are obtainable from kinetic data when tested by means of acid dissociation constants.

(6) (Acetic acid) Chittum and La Mer, THIS JOURNAL, 59, 2524 (1937).

(7) (Benzoic acid and hydroquinone) Rule and La Mer, *ibid.*, 60, 1974 (1938).

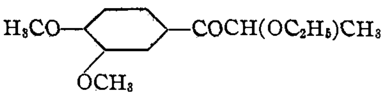
(8) (Chloroacetic acid) Lewis and Schultz, *ibid.*, 56, 1913 (1934).

DEPARTMENT OF CHEMISTRY
THE CITY COLLEGE
THE COLLEGE OF THE CITY OF NEW YORK
NEW YORK, N. Y. RECEIVED AUGUST 25, 1938

The Structure of Lignin

BY A. B. CRAMER, M. J. HUNTER AND HAROLD HIBBERT

In a recent note[1] the isolation of a new aromatic ketone ($C_{13}H_{18}O_4$) was described. This has now been identified (by direct synthesis and mixed melting point determination) as α-ethoxypropioveratrone



The synthesis (after numerous unsuccessful attempts, and using a variety of methods) was accomplished as follows:

$$\begin{tikzcd}
\text{Veratrole + propionyl chloride} \arrow[r] & \text{Propioveratrone} \arrow[dl] \\
\alpha\text{-Brompropioveratrone} \arrow[r] & \text{Acetate of } \alpha\text{-hydroxypropioveratrone} \arrow[dl] \arrow[d] \\
\alpha\text{-Hydroxypropioveratrone} \arrow[r] & \alpha\text{-Ethoxypropioveratrone}
\end{tikzcd}$$

The synthetic compound melted at 81–82°; a mixed melting point with natural compound gave no depression. The melting point of the 2,4-dinitrophenylhydrazone of the natural compound is 134–136°; synthetic compound, 134–136°; the mixed melting point also showed no depression.

DIVISION OF INDUSTRIAL
AND CELLULOSE CHEMISTRY
McGILL UNIVERSITY
MONTREAL, CANADA RECEIVED OCTOBER 18, 1938

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(1) Cramer, Hunter and Hibbert, THIS JOURNAL, 60, 2274 (1938).

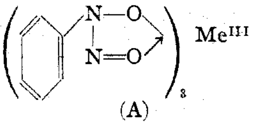
The Classification of Chelating Groups

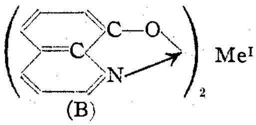
BY HELMUT M. HAENDLER AND BRADFORD P. GEYER

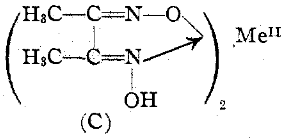
In the course of preliminary work on organic analytical reagents which form inner complex compounds with metal ions, it was found advisable to devise a system for the classification of chelating groups present in various organic compounds to serve as a basis of comparison. The available classifications, in particular that of Diehl,[1] are too unwieldy for rapid grouping and comparison. In addition to classifying the organic compounds now known, any system should also present information concerning possible reagents. The common method of indicating the number of members in the completed chelate ring is too cumbersome, in view of the recent increases in both number and variety of compounds possessing groups capable of chelation.

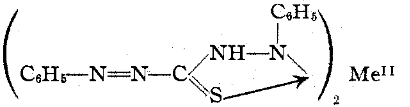
TABLE I

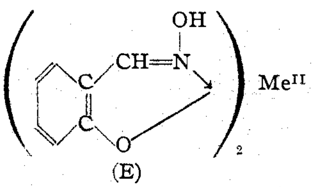
Group designation	Representative compound
C–N, SH	Mercaptobenzothiazole
C–NH, SH	Rubianic acid
C–NOH, OH	Benzohydroxamic acid
N–NONH$_4$, O	Cupferron (A)
C,C–N, NOH	Phenyl α-pyridyl ketoxime
C,C–N, OH	8-Quinolinol (B)
C,C–N, SH	8-Quinolinethiol
C,C–NH, SH	Thionalide
C,C–NH$_2$, OH	Glycocoll
C,C–NOH, NOH	Dimethylglyoxime (C)
C,C–NOH, O	α-Nitroso-β-naphthol
C,C–O, OH	Oxalic acid
C,C–O, SH	Thioglycolic acid
C,C–OH, OH	Catechol
C,C–OH, S	Thiohydantoic acid
C,N–NH, NOH	Nitrosoguanidine
C,N–NH$_2$, OH	Hydrazinecarboxylic acid
C,N–NH$_2$, SH	Dithizone (D)
C,C,C–N, NH	Chlorophyll type
C,C,C–NOH, OH	Salicylaldoxime (E)
C,C,C–O, OH	Alizarin
C,C,N–N, NH	Phthalocyanine
C,C,N–NH, NH	Biguanidine
C,C,N–NH, NH$_2$	Biuret
C,C,N–NH, O	Dicyandiamidine (F)

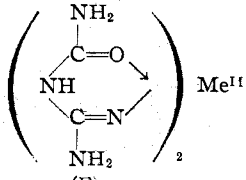

(A)


(B)


(C)


(D)


(E)


(F)

In this classification the two functioning groups, which supply the primary and secondary valences involved in the general formation of a chelate ring, and the atom or atoms linking these two groups form the basis of the system. Compounds with identical chelating groups have the same group designation, regardless of the structure of the remainder of the molecule. The group designation is derived as follows: (*a*) The atom or atoms connecting the two functional groups are expressed by their conventional symbols, arranged alphabetically. (*b*) The functioning groups are given by their symbolic representations in alphabetical order of the atoms by which they are attached to the original compound before chelation.

In salicylaldoxime, for example, the functional groups are linked by three carbon atoms, and these functional groups are the oxime and hydroxyl radicals. Consequently, the classification is C,C,C–NOH, OH.

The accompanying list gives in order of increasing complexity the designations of the more common chelating groups and the names of representative compounds containing such groupings. For the sake of clarity, structural formulas illustrating some of the inner complexes formed are also given. It is evident that exact knowledge of the structure of the chelate compound formed is not essential for this method, insofar as the primary and secondary valence connections are concerned. No attempt is made to designate these linkages as to type, and compounds are arranged solely on the basis of general structure.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

RECEIVED JULY 29, 1938

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[1] H. Diehl, *Chem. Rev.*, **21**, 39–111 (1937).

Dynamic Isomerism of Acetaldehyde 2,4-Dinitrophenylhydrazone

BY W. M. D. BRYANT

In earlier papers the writer[1,2] presented conclusive evidence based on optical crystallographic measurements that there are at least two distinct crystalline modifications of acetaldehyde 2,4-

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[1] Bryant, THIS JOURNAL, **55**, 3201 (1933).

[2] *Ibid.*, **58**, 2335 (1936).

dinitrophenylhydrazone, and refuted the contention of Campbell[3] that the second modification is merely a product contaminated with the dinitrophenylhydrazone of another carbonyl compound. On the basis of the evidence then available the relationship between these two crystal modifications was assumed to be one of polymorphism. However, a new melting point study using a Kofler and Hilbck micro heating stage[4] has been completed and the results indicate dynamic isomerism rather than polymorphism as the true relationship. This explanation was proposed by Allen and Richmond[5] on the basis of some work by Bredereck[6] with substituted furfural derivatives, and is in accord with the new experimental results.

Experimental

The new melting point observations were made using a Kofler and Hilbck micro heating stage[7] mounted on the object stage of a chemical microscope equipped with a 10X Reichert heat resisting objective. By this means thermal changes in individual crystals could be followed and the temperatures read by means of a calibrated thermocouple. Melting points by this method were found accurate to ±2° and precise to ±0.5°. The samples of acetaldehyde 2,4-dinitrophenylhydrazone employed were prepared during the two earlier investigations.

Acetaldehyde 2,4-dinitrophenylhydrazone I (previously called the "stable form") recrystallized five times from 95% ethanol[1] was found to melt sharply without transition at 168–170° in agreement with 168.5° obtained previously by the more precise macro method. Above 115° in the initial heating a slight sublimate of orange lozenge-shaped crystals appeared and was recognized as the II modification (previously designated as "metastable"). These crystals melted at 156–157°. A few of these crystals in contact with modification I began melting at slightly lower temperature. The resulting liquid noticeably eroded plates of the I form below their regular melting temperature. In another experiment the sublimate was the I form (plates) and melted at the higher temperature (168–170°). On slowly cooling the liquid phase after complete fusion, the II form often reappeared first, usually at 130–140°; on reheating, this form was in equilibrium with the liquid at 148°, a slight change of temperature being sufficient to induce either growth or solution. In cases where the I form reappears first, the fusion or solution process begins at 150–155° and complete solution occurs between 155 and 160°. The above behavior is typical of a system in which the two compounds are, strictly speaking, different chemical entities but mutually convertible one into the other.

A sample of derivative recrystallized once from benzene[2] had an initial melting point of 148–151°. Crystals (mainly the II modification) reappeared at 131° and were completely fused (or dissolved) at 149.5°. After several repetitions the fusion temperature was lowered to 142°.

The above observations indicate that acetaldehyde 2,4-dinitrophenylhydrazone exists in two chemically different forms (dynamic isomers), the ordinary form (I) melting sharply near 169° and a form (II) obtained by sublimation melting at 157°. Crystallization of the melt produces a mixture (probably an equilibrium mixture) melting near 148°. The derivative recrystallized from benzene although optically identical with the I modification melts near 149° as does the "equilibrium mixture," hence must contain traces of a catalyst (possibly sulfuric acid) capable of inducing a rapid isomerization. This accounts for the low melting points sometimes observed.[2] In the writer's earlier experiments[1] slow isomerization was mistaken for a more fundamental thermal breakdown and hence not given the attention it deserved.

AMMONIA DEPARTMENT
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON, DELAWARE
RECEIVED OCTOBER 3, 1938

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[3] Campbell, *Analyst*, **61**, 391 (1936).

[4] Kofler and Hilbck, *Mikrochemie*, **9**, 38 (1931).

[5] Allen and Richmond, *J. Org. Chem.*, **2**, 222 (1937).

[6] Bredereck, *Ber.*, **65**, 1833 (1932).

[7] This instrument manufactured by the optical firm of C. Reichert, Vienna, was obtained from Pfaltz and Bauer, Inc., Empire State Building, New York City.

Structure of Lignin

BY M. J. HUNTER, A. B. CRAMER AND HAROLD HIBBERT

In a recent note[1] the isolation of an aromatic ketone, $C_{13}H_{18}O_4$, from spruce wood by organic solvent extraction was reported and the additional presence of derivatives containing the syringyl group from hard woods noted.

Using maple wood and similar organic solvent extraction, there is obtained a mixture of two ketones, having in the pure state the empirical formulas $C_{12}H_{16}O_4$ and $C_{13}H_{18}O_5$, respectively, which can be readily separated by conversion into their *p*-nitrobenzoates.

One of these corresponds to the ester from the ketone previously reported, while the new crystalline *p*-nitrobenzoate is derived from the second ketone, the latter being related to the former by possessing an additional methoxyl group. They are apparently present in approximately equal amounts.

The theoretical conclusion drawn previously that hard woods differ from soft in having present in the building unit not only the guaiacyl but also the syringyl radical has thus been substantiated.

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[1] THIS JOURNAL, **60**, 2274 (1938).

The compound containing the syringyl radical was characterized as follows: melting point, 141–142.5°. *Analysis* of the *p*-nitrobenzoate. Calcd. for $C_{20}H_{21}NO_8$: C, 59.5; H, 5.3; N, 3.47; OCH_3, 23.1. Found: C, 59.5; H, 5.28; N, 3.5; alkoxyl as OCH_3, 23.0.

Presence of the carbonyl group was confirmed by preparing the 2,4-dinitrophenylhydrazone of the ester. Calcd. for $C_{26}H_{25}N_5O_{11}$: N, 12.0. Found: N, 11.9.

These two products undoubtedly are to be regarded as important constituents of the building unit of the lignin molecule.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
MCGILL UNIVERSITY
MONTREAL, P. Q., CANADA
RECEIVED OCTOBER 3, 1938

The Dimerization of 3-Phenylindene

BY C. S. MARVEL AND H. A. PACEVITZ

Blum-Bergmann has reported[1,2] a dimer of 3-phenylindene (m. p. 207–209°) as a by-product in a reaction in which 3-phenylindene was treated with lithium. No exact method of producing or isolating the dimer was described. We have tried to obtain the same compound for comparison with an isomeric hydrocarbon melting at 210–211°.[3] Various combinations of conditions have been used but none yielded the dimer reported. A different dimer melting at 157° has, however, been obtained.

Dimer of 3-Phenylindene.—A mixture of 30 cc. of 47% hydrogen iodide solution and 2 g. of 3-phenylindene was shaken for sixteen hours. A dark brown solid separated out. This was separated and dissolved in about 400 cc. of low-boiling petroleum ether (b. p. 40–60°). The ether solution was concentrated to about 100 cc., at which point some crystals separated. The product was twice recrystallized from petroleum ether. The yield was 1.9 g. of a product melting at 156–157°.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.6; H, 6.4; mol. wt., 384. Found: C, 93.55, 93.48; H, 6.36, 6.45; mol. wt. (Rast), 357, 359.

In a similar manner 2 g. of 3-phenylindene and 25 cc. of fuming stannic chloride gave 1.7 g. of dimer melting at 156–157°.

Heating 3-phenylindene with equal parts of sirupy phosphoric acid and water, with glacial acetic acid, with concentrated sulfuric acid or a mixture of sulfuric acid and hydrochloric acid did not cause it to dimerize.

Treating a benzene solution of 3-phenylindene with metallic lithium in an atmosphere of nitrogen for several days did not produce a dimer.

Heating the dimer to 350° caused some charring but no 3-phenylindene was found in the distillate.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
RECEIVED JULY 15, 1938

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(1) Blum-Bergmann, *Ann.*, **484**, 26 (1930).

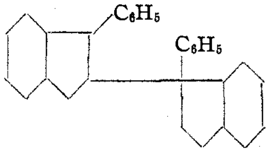
(2) Through the kindness of Dr. E. Bergmann we have obtained a sample of the dimer of 3-phenylindene melting at 210–211°. This product proved to be a different hydrocarbon from the hydrocarbon of the same composition and melting point reported by Farley and Marvel,[3] since a mixture of the two melted at 185–190°.

(3) Farley and Marvel, THIS JOURNAL, **58**, 32 (1936).

The Dimerization of 3-Phenylindene

BY E. BERGMANN

The preceding Note by Marvel and Pacevitz has been made accessible to me through the courtesy of the Editor. The dimeric 3-phenylindene had only occasionally been obtained and its structure therefore had not been elucidated. Although the mechanism by which indene is dimerized[1] would lead only to one dimer of 3-phenylindene, there may be other ways, too, of dimerization. An experiment has shown that the two substances, m. p. 210–211° and 156–157°, respectively, are not allyl isomeric forms, as they are not interconvertible by means of sodium ethylate solution.



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(1) E. Bergmann and Taubadel, *Ber.*, **65**, 463 (1932).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
RECEIVED AUGUST 30, 1938

β,β',β''-Trichlorotriethylamine

BY J. PHILIP MASON AND DALE J. GASCH

In the course of some other work, we had occasion to make trichlorotriethylamine and its hydrochloride. By a slight modification of the procedure used by Ward,[1] we were able to increase the yield of the hydrochloride from 70 to 92%.

Two moles (238 g.) of thionyl chloride dissolved in 150 ml. of benzene was added to 0.5 mole (92.7 g.) of triethanolamine hydrochloride in a 1-liter round-bottomed flask equipped with a reflux condenser and a gas absorption trap. The mixture was heated to 55° and kept at that temperature for three hours. The benzene and excess thionyl chloride were distilled under diminished pressure at 50°. In order to decompose the last portion of thionyl chloride, about 50 ml. of ethyl alcohol was added. The mixture was warmed for

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(1) Ward, THIS JOURNAL, **57**, 914 (1935).

ten to fifteen minutes and then the alcohol was distilled. This step was found desirable because otherwise charring occurred when acetone was added to recrystallize the product. The residue was recrystallized from boiling acetone; yield, 106.3 g. (88%). By concentrating the acetone filtrate, a second crop of crystals (4.5 g.) was obtained, bringing the total yield up to 92%. McCombie and Purdie[2] made trichlorotriethylamine hydrochloride directly from triethanolamine and thionyl chloride, using chloroform as a solvent, and obtained a yield of 73.8%.

The free trichlorotriethylamine, obtained in the usual way from the hydrochloride, had a b. p. of 143–144° at 15 mm., which is 6° higher than that reported by McCombie and Purdie[2] at the same pressure.

Anal. Calcd. for $C_6H_{12}Cl_3N$: Cl, 52.1; mol. wt., 204.5. Found: Cl, 51.6, 51.8; mol. wt. (benzene), 205.9.

The amine was almost colorless when freshly distilled, but turned to a light brown color on standing for sixty hours. The color darkened on longer standing. Crystals, which were not identified, appeared in the liquid after standing for a month. Ether solutions of the amine darkened more slowly and no crystals were observed. Instead, a small amount of dark brown material was deposited from an ether solution which had been kept for two months. No attempt was made to identify this material.

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[2] McCombie and Purdie, *J. Chem. Soc.*, 1217 (1935).

CHEMISTRY LABORATORY
BOSTON UNIVERSITY
BOSTON, MASS.

RECEIVED SEPTEMBER 3, 1938

The Catalytic Reaction between Sodium Nitrite and Dichlorodiethylenediamine Cobaltic Chloride

BY J. P. MCREYNOLDS AND JOHN C. BAILAR, JR.

In the course of stereochemical studies on the complex inorganic compounds, it was observed that racemic dichlorodiethylenediamine cobaltic chloride reacts almost instantaneously with sodium nitrite according to the equation $[Coen_2Cl_2]^+ + 2NaNO_2 \longrightarrow [Coen_2(NO_2)_2]^+ + 2NaCl$[1] but that the material which has been resolved into its optical antipodes reacts very slowly. This resolution is carried out through the α-bromocamphor-π-sulfonate, which is reconverted to the chloride by means of hydrochloric acid in alcohol and ether. The active product is then washed with alcohol and ether.[2] It was found that washing the racemic material with alcohol and ether caused it to lose its reactivity toward sodium nitrite. The washings contained cobaltous ion. That cobaltous ion catalyzes the reaction in question was demonstrated easily.[3]

Werner has noted[4] briefly that traces of acids catalyze this reaction but no other example of such catalytic substitution has been reported for compounds of this type. A study was therefore made to determine the mechanism of the reaction. Two compounds which seemed possible intermediates are sodium cobaltinitrite, $Na_3Co(NO_2)_6$, and sodium cobaltonitrite, $Na_2Co(NO_2)_4$. Sodium cobaltinitrite was found to have no catalytic effect in this reaction. On the other hand, the cobaltonitrite ion could be precipitated (as the potassium salt) from mixtures which had been catalyzed artificially by addition of cobaltous ion. This seems to point to the intermediate formation of sodium cobaltonitrite.

The mechanism postulated for this catalysis must explain the very rapid replacement of chloro by nitro groups and the apparent absence of oxygen to cobalt linkages at any step in the reaction. This latter requirement is evidenced by the fact that at no time is there any indication of a red coloration such as is found in nitrito cobalt compounds. The isolated intermediate and the almost instantaneously formed product both have the yellow color characteristic of the nitrogen to cobalt bond. Further, nitrite complexes of trivalent cobalt have been prepared and characterized. They are stable in solution for a considerable period, changing to nitro complexes quite slowly.

The explanation offered here involves a shift of the electrons upon the nitrogen to allow it to form a coördinate bond to both trivalent and bivalent cobalt. This is a very unstable arrangement and is broken up immediately, leaving the nitrogen attached to the trivalent cobalt. This latter step seems quite logical since the trivalent cobalt complexes are very much more stable than those of bivalent cobalt. It must be assumed that

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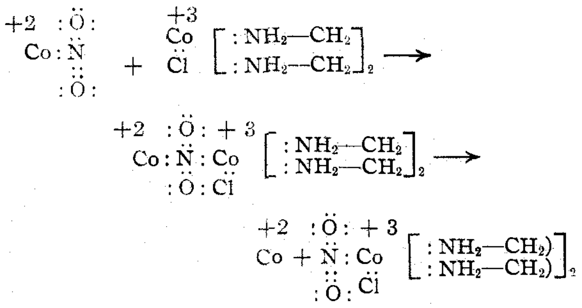
[1] The symbol "en" represents ethylenediamine.

[2] Bailar and Auten, THIS JOURNAL, **56**, 774 (1934).

[3] The traces of cobaltous ion present in the racemic material evidently are produced during the conversion of the *trans* form of the complex to the *cis* form by evaporation of the solution and subsequent heating of the residue in the oven. A dry sample of optically active material unreactive to sodium nitrite became reactive after several hours of such heating. It lost a large part of its optical activity during the heating.

[4] Werner, *Ber.*, **34**, 1734 (1901).

one chloride group ionizes from the cobaltic complex momentarily or that the coördination number of the cobaltic ion may exceed six, at least for an instant. On the first assumption, the mechanism of the catalytic reaction may be as follows



It is possible that the familiar coördination compounds of metal ions with ethylene compounds and with azo compounds are formed in the same way—by the shift of a pair of electrons from the double bond to an adjacent atom.

The catalyzed reaction, when applied to optically active starting material, lends further evidence in favor of such a mechanism since the product always has a much lower activity than that formed through the uncatalyzed reaction.

A further investigation was carried out to determine the possibilities of extending this type of catalysis to other substitutions. All attempts to catalyze the substitution of oxalate or thiocyanate groups for chloro groups by the addition of metallic ions failed to show positive results. The ions used were nickelous, ferric, aluminum, stannous and cobaltous, all of which tend to form unstable complex ions. This study showed that cobaltous ion is unique among those tried in producing the catalytic substitution of the nitro group.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
RECEIVED JULY 25, 1938

Ammonium Chloride–Sodium Sulfide Solutions for Organic Nitro Reductions and for Inorganic Qualitative Analysis

BY M. J. MURRAY AND D. E. WATERS[1]

Two disadvantages in the use of ammonium sulfide as reducing agent for organic nitro compounds have been: (1) the length of time consumed in saturating the ammonium hydroxide with hydrogen sulfide, and (2) the indefinite amounts of materials used. Both of these disadvantages are overcome by preparing a solution containing equivalent amounts of ammonium chloride and crystalline sodium sulfide ($Na_2S \cdot 9H_2O$). This solution is added to the nitro compound dissolved in ammonium hydroxide or alcohol and ammonium hydroxide. The mixture can be heated at once until excess hydrogen sulfide has escaped, and from this point the isolation of the reduction product is the same as in standard procedures.

The reagent was tested most thoroughly on the reduction of *p*-nitrobenzoic acid. The yields were consistently higher than on parallel runs using hydrogen sulfide and ammonium hydroxide. The melting point and the neutralization equivalent showed the product to be one of high purity. Reduction by sodium polysulfide, sodium sulfide alone, and sodium hydrogen sulfide gave yields inferior as to both quality and quantity. Other compounds reduced by the sodium sulfide–ammonium chloride reagent were: *p*-nitrophenylacetic acid,[2] 3-nitrophthalhydrazide,[3] and *m*-dinitrobenzene.[4] In each case the yield equaled or exceeded that reported in the reference given.

A second use of this rapid method for the preparation of ammonium sulfide is in the making up of solutions of ammonium polysulfide for inorganic qualitative analysis. A solution of approximately known strength can be prepared in a few minutes as follows: equivalent amounts of ammonium chloride and crystalline sodium sulfide ($Na_2S \cdot 9H_2O$) are dissolved in a small volume of water, powdered sulfur is added, and the mixture warmed to promote solution. Then ammonium hydroxide is added and the solution diluted to the desired strength. Concentrations are not given here because textbooks do not agree as to the optimum strength.[5] Attention should also be directed to the fact that few laboratory assistants make up the ammonium polysulfide solutions as strong as called for because of the difficulty of completely saturating the ammonium hydroxide with hydrogen sulfide. For this reason solutions prepared by the short method just described will be, in general, considerably more concentrated than ordinarily

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(1) Present address. Transylvania College, Lexington, Ky.

(2) "Organic Syntheses," Coll. Vol. I, 1932, p. 44.

(3) Huntress, Stanley and Parker, *J. Chem. Ed.*, **11**, 143 (1934).

(4) Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," 22nd edition, The Macmillan Co., New York, N. Y., 1932, p. 162.

(5) Curtman and Lehrman, *J. Chem. Ed.*, **6**, 2203 (1929), recommend a definite strength but it is doubtful whether such a high concentration is advisable in all procedures.

made up, and it may be advisable to redetermine which strength is best for the particular scheme of analysis being used.

Ammonium polysulfide prepared by the rapid method has been used successfully in this Laboratory over a period of three years for the separation of Divisions A and B in Group II.

DEPARTMENT OF CHEMISTRY
LYNCHBURG COLLEGE
LYNCHBURG, VA.

RECEIVED AUGUST 26, 1938

The Interaction between Methylene Radicals and Hydrogen

BY CHARLES ROSENBLUM

The photolysis of ketene in the presence of hydrogen points to a reaction between methylene radicals and hydrogen, in contrast with the relative stability[1] of methylene toward ketene itself and toward ether vapor. The reactants, 100 mm. of ketene and 225 mm. of hydrogen, were irradiated in a cylindrical quartz vessel (volume 130 cc.) by a "hot" mercury arc for about forty-five minutes, and the resultant gas mixture analyzed. Although a constricted arc was used throughout, a hydrogen–mercury vapor filter[2] for resonance radiation was interposed as an added precaution against the lamp as a source of hydrogen atoms. A mixture of ethylene and hydrogen did not react when exposed to the arc under these conditions.

Irradiation of ketene alone[3] results in an increase in volume due to the formation of carbon monoxide and ethylene as the sole gaseous products, this increase falling below the theoretical value after longer exposures because attendant polymerization creates a gaseous hydrocarbon deficiency. The reaction which occurs in the presence of hydrogen differs markedly from the above in that it is characterized by a volume decrease. This can be accounted for only if the gaseous hydrocarbon is saturated and some saturated liquid (or solid) hydrocarbons of low vapor pressure are formed, which implies a disappearance of hydrogen.

Analysis confirmed these expectations fully. Of the ketene decomposed in the presence of hydrogen at 35°, 1% yielded methane, 74% was recovered as a gas with an average composition[4] $C_{2.56}H_{7.12}$, and 25% yielded a residue of low volatility. At 200° the methane content corresponded to 9.6% of the decomposed ketene, the gaseous fraction with a mean composition[4] $C_{2.68}H_{7.36}$ represented 69%, and the residue accounted for 21% of the ketene present originally. In both cases, the average composition of the residual polymeric product was C_4H_{10}. The mean composition and quantity of this polymer were deduced from the carbon and hydrogen deficiencies in the balance sheet of initial and final gaseous components of the reaction system. The amounts of condensed product calculated in this manner agreed well with the observed volume decreases.

The experiments indicate that the direct association of methylene radicals and molecular hydrogen to form methane is inappreciable. The profound change in the nature of the products when hydrogen is present suggests that the interaction in question is

$$CH_2' + H_2 = CH_3 + H$$

Such a reaction yielding methyl radicals and atomic hydrogen would account for the formation of saturated and higher molecular weight hydrocarbons.[5] The methylene radical has been represented as energy rich (CH_2') since present accepted views as to bond energies would suggest that the reaction of a normal methylene radical with hydrogen would be endothermic. The energy of the radical must arise from the photoenergy absorbed during the dissociation process.

A secondary source of methyl radicals might be a reaction between methylene radicals and methane already formed

$$CH_2 + CH_4 = 2CH_3$$

This would be less endothermic than the reaction with hydrogen. The low yields of methane, increasing at higher temperatures, do not appear to support this view.

The source of methane is probably an interaction of methyl radicals with hydrogen[6] or hydrocarbons[7] which is known to take place readily at or above 150–160°. The recombination of methyl radicals to form ethane would account for the

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(1) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

(2) Morikawa, Benedict and Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

(3) Norris, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

(4) Shown by cracking over a nickel catalyst in an excess of hydrogen.

(5) Summarized in Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Dresden-Blasewitz, Germany, 1933, p. 264; also Jungers and Taylor, *J. Chem. Phys.*, **6**, 325 (1938).

(6) Cunningham and Taylor, *J. Chem. Phys.*, **6**, 359 (1938); Taylor and Rosenblum, *ibid.*, **6**, 119 (1938).

(7) Unpublished work of J. O. Smith, Princeton, 1938.

prominence of this constituent in the gaseous product.

Details of the temperature effect, which so far indicates a very small temperature coefficient for the photo-decomposition of ketene in hydrogen,[8] as well as the influence of varying concentrations of reactants and the addition of hydrocarbons, are being investigated.

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[8] See also Ross and Kistiakowsky[3] in the absence of hydrogen.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

RECEIVED AUGUST 22, 1938

Potassium Acid Phthalate as a Buffer for Use with the Hydrogen Electrode

BY JOHN RUSSELL AND R. ELIOT STAUFFER

Several investigators[1] have reported in the literature that accurate measurements on 0.05 molar potassium acid phthalate cannot be made with the hydrogen electrode. On the other hand, Clark[2] states that repeated experiments have shown measurements on phthalate buffers to be reliable. Recently, MacInnes and co-workers[3] again have intimated that phthalate solution is unstable and cannot be measured satisfactorily with the hydrogen electrode, especially at 38°.

Our experience in this connection definitely supports Clark's statement, and, since the 0.05 M phthalate is so convenient a buffer for use in pH standardization, we are submitting the following data as evidence for the stability and reproducibility of hydrogen electrode potentials observed in it. We have used the following type of cell for pH measurements in these Laboratories (Pt) H_2; Solution X: 3.5 N KCl: 3.5 N KCl, satd. Hg_2Cl_2; Hg_2Cl_2; Hg, with 0.05 M phthalate as solution X in this cell both at 25 and 40°.

An essential feature in the design of the cell, which we hope to describe in detail later in connection with other studies, is the possibility of creating a very reproducible and constant junction between the potassium chloride bridge solution and solution X. Equally important in the obtaining of consistent and accurate measurements is the elimination of rubber connections in contact with the hydrogen supply or solution X, and the use of hydrogen prepared electrolytically in glass and passed over a hot platinum gauze catalyst in a fused silica tube. As a result, the cell in question has yielded highly reproducible and constant e. m. f. values with phthalate and other buffers. A few of these for phthalate at 40° are given in Table I.

TABLE I

ELECTROMOTIVE FORCE MEASUREMENTS OF POTASSIUM ACID PHTHALATE (0.05 M) WITH THE HYDROGEN ELECTRODE AT 40°

Reference half-cell	Phthalate soln.	E. m. f., v.	Date
A	1 X	0.49500	8-28-36
B	2 Y	.49504	9-21-36
B	2 Y	.49503	9-24-36
B	2 Y	.49496	9-28-36
B	3 X	.49503	9-25-36
B	3 X	.49501	9-28-36
C	4 Z	.49494	1-20-37
D	5 X	.49502	5- 5-37
	Average	.49500	

These measurements cover a period of about nine months during which four different calomel half-elements and bridging solutions were prepared, and five different phthalate solutions from three commercial sources of potassium acid phthalate were used. Each value in the table represents an average of values obtained by two or more platinum electrodes whose differences were rarely more than a few hundredths of a millivolt. Table II taken from a typical page of data shows that the e. m f. of the cell using phthalate as solution X remains substantially constant for periods as long as four hours after creating the liquid junction. The junction was formed as soon as the solution reached the temperature of the thermostat (*ca.* fifteen minutes).

TABLE II

CONSTANCY OF HYDROGEN ELECTRODE AND JUNCTION POTENTIALS WITH 0.05 M PHTHALATE BUFFER AT 40°

Hours after formation of junction	E. m. f., v.
0	0.49495
0.5	.49501
1	.49504
2	.49505
4	.49506

These data indicate that in our experience 0.05 M potassium acid phthalate can be used very satisfactorily as a buffer with the hydrogen elec-

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[1] I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim. Pays-Bas.*, **46**, 39 (1927); E. T. Oakes and H. M. Salisbury, THIS JOURNAL, **44**, 948 (1922); C. Z. Draves and H. V. Tartar, *ibid.*, **47**, 1226 (1925).

[2] W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., The Williams and Wilkins Company, Baltimore, Md., 1928, p. 437.

[3] D. A. MacInnes, D. Belcher and T. Shedlovsky, THIS JOURNAL, **60**, 1099 (1938).

trode at temperatures as high as 40° for even the most precise work.

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.
RECEIVED AUGUST 24, 1938

The Preparation of *m*-Bromobenzaldehyde

BY FLOYD T. TYSON

For work in progress in this Laboratory it was necessary to prepare *m*-bromobenzalaminoacetal by the interaction of *m*-bromobenzaldehyde with aminoacetal. The *m*-bromobenzaldehyde was prepared by the reduction of *m*-nitrobenzaldehyde by stannous chloride and hydrochloric acid, followed by diazotization and conversion to bromobenzaldehyde by the Sandmeyer method as originally described by Einhorn and Gernsheim[1] and modified by Buck and Ide.[2] In these procedures, no attempt is made to isolate the intermediate *m*-aminobenzaldehyde from admixture with stannic chloride and hydrochloric acid.

Analysis of the *m*-bromobenzalaminoacetal yielded uniformly low results for halogen calculated as bromine and very high results for carbon and hydrogen. These analytical values were in accord with the assumption that much of the chloro compound was present with the bromo compound.

The *m*-bromobenzaldehyde used for the preparation of the impure *m*-bromobenzalaminoacetal was analyzed for halogen and the halogen calculated as bromine. The analytical values obtained were in agreement with the theoretical values for bromobenzaldehyde. However, analyses of the *m*-bromobenzaldehyde preparations for both chlorine and bromine proved the presence of both chlorine and bromine. The amounts of chlorine indicated a percentage of chlorobenzaldehyde ranging from 20 to 72 depending upon details of procedure.

Since *m*-nitrobenzaldehyde should be a convenient source for the preparation of pure *m*-bromobenzaldehyde, a procedure has been devised which will be published elsewhere, in which the presence of chlorides in the reaction mixture was avoided.

Experimental

The following table summarizes data obtained in the analysis of products resulting from the attempted preparation of pure *m*-bromobenzaldehyde from *m*-nitrobenzaldehyde as described in the literature. The preparations analyzed were fractionated; b. p. 92–97° (6 mm.).

TABLE I

Prepn.	Analyses, % Cl	Br	Calcd. % chlorobenzaldehyde present
1	18.17	11.86[3]	72.0
	18.31	11.57[4]	
2	5.11	34.50[3]	20.3
3	6.78	31.58[3]	26.9

Preparation No. 1 was made as described by Buck and Ide.[2] Preparation No. 2 was made as No. 1 except that the hydrobromic acid was added to the cuprous bromide mixture before mixing with the diazotized solution. Preparation No. 3 was made as described by Einhorn and Gernsheim.[1]

The analytical results reported in the following table were calculated on the erroneous assumption that the mixtures of silver chloride and bromide actually obtained in the analyses of preparations No. 1, 2 and 3 (Table I) were pure silver bromide. The satisfactory agreement with the values for *m*-bromobenzaldehyde may explain the fact that the preparations as recorded in the literature[1,2] were reported as essentially pure.

TABLE II

Prepn.	% Br found as assumed	% Br calcd. for *m*-bromobenzaldehyde
1	43.12	43.19
2	43.18	
3	43.25	

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[1] Einhorn and Gernsheim, *Ann.*, **284**, 141 (1894).

[2] Buck and Ide, *Org. Syntheses*, **13**, 30 (1933).

[3] Analyses made by the method of displacement of bromine from weighed silver chloride and bromide by chlorine as described in "Quantitative Analysis of Inorganic Materials," by N. Hackney, J. B. Lippincott, Philadelphia.

[4] Analysis made by the method of Baubigny [*Compt. rend.*, **136**, 1197 (1903)] as described by Hackney.[4]

DEPARTMENT OF CHEMISTRY
TEMPLE UNIVERSITY
PHILADELPHIA, PA.
RECEIVED JULY 6, 1938

The Optical Rotation of a Grignard Reagent

BY FRANK C. WHITMORE AND BENJAMIN R. HARRIMAN

Frequent use is made of the Grignard reaction in preparing optically active compounds from optically active halogen compounds, but not to our knowledge has the rotation of an optically active Grignard reagent been measured previously. Porter[1] observed a very small rotation in an ethereal solution of methyl-*n*-hexylmagnesium

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[1] Porter, THIS JOURNAL, **57**, 1436 (1935).

bromide which he had prepared from active methyl-*n*-hexyl bromide. He ascribed this activity to unchanged bromide.

Since the position of the functional halogen atom relative to the asymmetric carbon atom determines the degree to which the product is racemic, we sought a halide in which the halogen was on the carbon atom next to the asymmetric carbon atom. Optically active 1-bromo-2-methylbutane, "active amyl bromide," was selected because it was prepared easily from the readily available optically active 2-methyl-1-butanol, which J. H. Olewine of this Laboratory has obtained by the fractionation of fusel oil through a 100-plate column.[2] Since the conversion of this bromide to another compound through the intermediate Grignard reagent gives a product which is only partly racemic, it was thought that rotation measurements on Grignard reagents made from this and similar halides might throw light on the mechanism of such racemizations and on the structure of the Grignard reagent itself. With this in mind a manipulative procedure for measuring the rotation of the Grignard reagent was evolved.

Obviously it was necessary to be assured of the absence of any excess halide. This could be done either by using an excess of magnesium or by removing the excess halide after the Grignard reagent was made. Grignard reagents were made by the first method under the most careful conditions for the exclusion of air and moisture, and a special polarimeter tube with optical Pyrex sealed-in windows was made to hold the volatile ethereal solution. However, what appeared to be finely dispersed magnesium rendered the solutions too dark for measurement.

The alternative method of using an excess of the optically active halide produced clear Grignard reagent solutions. Di-*n*-butyl ether (b. p. 141°) was used as the solvent so that the excess active amyl bromide (b. p. 120°) could be removed by distillation under reduced pressure. The Grignard reagent solution freed from excess halide was then transferred with a pipet to an ordinary polarimeter tube, in which measurement of its optical rotation readily was made. Specific rotations were calculated from data obtained by titrating the Grignard reagent with standard hydrochloric acid. Molecular rotations are given below as being non-committal as to the structure of the Grignard reagent. It is significant that the molecular rotation of the Grignard reagent was slightly greater than that of the active amyl bromide from which it was prepared.

The following is a typical run. Active 1-bromo-2-methylbutane, $[M]^{25}_D$ +5.06°, was prepared with phosphorus tribromide from active 2-methyl-1-butanol $[M]^{25}_D - 4.35°$. Using an excess of this bromide with di-*n*-butyl ether as the solvent, the corresponding Grignard reagent was then prepared in the ordinary way. After distilling off the excess bromide under reduced pressure, a clear active Grignard reagent, $[M]^{25}_D$ +5.36°, was obtained.

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State College, Penna.
Received August 29, 1938

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[2] Olewine, This Journal, **60**, 2569 (1938).