cellent paper on cocarboxylase has appeared. In that paper it was suggested that the use of silver might be avoided.

Acknowledgments.—I wish to express my appreciation to Dr. R. T. Major and Dr. J. R. Stevens for advice and interest; to Mr. Harold Levy for general assistance. The analytical work was carried out by Messrs. D. F. Hayman, W. Reiss and Harold Levy.

Summary

An improved process for the synthesis of cocarboxylase chloride has been presented as well as evidence indicating that cocarboxylase is stable under normal conditions except slight loss of water of crystallization.

RAHWAY, N. J. RECEIVED JANUARY 28, 1941

NOTES

Polymorphic Forms of Substituted Phenols

BY RICHARD T. ARNOLD, HAROLD KLUG, JOSEPH SPRUNG AND HAROLD ZAUGG

In connection with the research on another problem, we prepared 6-hydroxytetralin (β-tetralol) by fusion of the sodium sulfonate with alkali according to Schroeter.[1] This sample of tetralol melted at 53–54° in contrast to the reported value of 62°. It formed transparent, huskily built crystals when precipitated from low-boiling ligroin.

Another sample of β-tetralol from the decomposition of 6-tetralin diazonium chloride melted at 62° and formed opaque needles from low-boiling ligroin.

If a large crystal of the form melting at 54° was brought into contact with one fine needle of the 62° modification, it turned opaque at the point of contact and this opaque boundary passed across the crystal so that in about five minutes the transformation was complete. The resulting melting point of the big crystal was then 62°.

Using a Buerger[2] precision powder camera of 57.3 mm. radius, powder photographs were taken at room temperature using Fe K_α radiation. The powder samples were extruded rods of powder crystals prepared in the device described by Lukesh[3] using LePage's glue as a binder. The following photographs were taken: (a) 54° form, (b) 62°—from 54° by contact with 62° form, (c) 62° form. Both (b) and (c) were identical and different from (a).

In a similar manner 4-hydroxyhydrindene has been obtained in two crystalline forms. The first, m. p. 39.5–40°, was produced by alkali fusion of the sodium sulfonate and precipitated from ligroin in needles.

From the 4-hydrindenediazonium chloride we obtained 4-hydrindenol melting at 49–50° as described by Linder.[4]

Powder photographs of these two forms showed them to be entirely different. The melting point of the low-melting form (39.5–40°) was raised to 49–50° by contact with the 49–50° modification.

(1) Schroeter, *Ann.*, **426**, 120 (1922).
(2) Buerger, *Am. Mineral.*, **21**, 11–17 (1936).
(3) Lukesh, *Rev. Sci. Instruments*, **11**, 200 (1940).
(4) Linder, *Monatsh.*, **72**, 219 (1939).

UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 11, 1941

p-(*p*-Aminophenyl)-benzenesulfonamide

BY CONARD K. DONNELL, JAMES H. DIETZ AND WILLIAM T. CALDWELL

Recently Van Meter, Bianculli and Lowy[1] reported the preparation of *p*-(*p*-aminophenyl)-benzenesulfonamide from *p*-aminobiphenyl. We, too, had prepared this compound in the same way with results essentially like theirs; however, we determined the orientation of the sulfonamide group differently by means of an independent synthesis from *p*-nitrobiphenyl, a synthesis which is, of course, equally applicable to the preparation of other N′-substituted sulfanilamides. The structure of the requisite intermediate *p*-(*p*-nitrophenyl)-benzenesulfonic acid was proved by Gabriel and Dambergis,[2] by showing that the same product is obtained upon sulfonation of *p*-nitrobiphenyl as upon nitration of *p*-phenyl-

(1) Van Meter, Bianculli and Lowy, THIS JOURNAL, **62**, 3146 (1940).
(2) Gabriel and Dambergis, *Ber.*, **13**, 1410 (1880).

benzenesulfonic acid; accordingly, since the *p*-(*p*-aminophenyl)-benzenesulfonamide prepared from this was identical with that obtained from *p*-aminobiphenyl, the structure of the latter was established.

***p*-(*p*-Nitrophenyl)-benzenesulfonyl Chloride.**—This compound was prepared by the method of Gabriel and Dambergis[2] and also by adding, with good stirring, *p*-nitrobiphenyl to two and one-half moles of chlorosulfonic acid at a temperature below 15°, then allowing the temperature to rise to that of the room and finally to 60° for two hours. The dark, sirupy liquid was then poured, with vigorous stirring, into a slush of ice. After filtering, pressing out on a porous plate and recrystallizing from acetic acid, the yellow crystals melted at 178°, the melting point given by Gabriel and Dambergis,[2] yield 94%.

***p*-(*p*-Aminophenyl)-benzenesulfonamide.**—To 10 g. of *p*-(*p*-nitrophenyl)-benzenesulfonamide[2] dissolved in 200 cc. of ethanol, were added 8 g. of tin and 50 cc. of concd. hydrochloric acid. After heating for one and one-half hours, the material was neutralized with sodium hydroxide, diluted to a volume of 600 cc. and acidified with 15 cc. of concd. hydrochloric acid. The tin sulfide precipitated by hydrogen sulfide was removed by filtration, the filtrate made alkaline with ammonium hydroxide and the product so obtained was purified by recrystallization from ethanol; m. p. 263° (cor.), unchanged when mixed with product prepared from *p*-aminobiphenyl, yield, 3.1 g.

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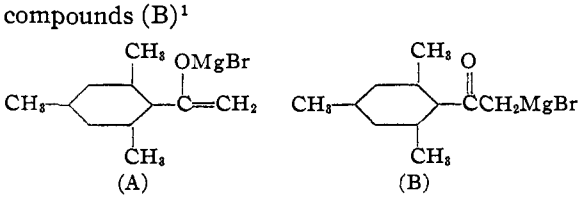
PHILADELPHIA, PENNSYLVANIA

RECEIVED DECEMBER 18, 1940

Metallic Derivatives of Acetomesitylene

BY HENRY GILMAN AND R. G. JONES

Bromomagnesium derivatives of sterically hindered ketones, like acetomesitylene, give enolates (A) which behave like true organomagnesium compounds (B)[1]



(A) (B)

In view of the extensive studies by Fuson and co-workers and Kohler and co-workers[1b] on the reaction of these bromomagnesium types with the carbonyl group, one might have predicted a positive Michler ketone color test.[2a] We have found that the bromomagnesium derivative of acetomesitylene does give this color test. The bromomagnesium compound was prepared from phenylmagnesium bromide and an excess of acetomesitylene. Phenylmagnesium bromide was selected in preference to an alkylmagnesium halide because the recently described[2b] Color Test III differentiates between reactive *aryl*metallic compounds and *alkyl*metallic types. In this manner, any uncertainty concerning the influence of phenylmagnesium bromide is ruled out, for the negative test with triphenylbismuth dichloride (Color Test III) showed the absence of phenylmagnesium bromide in the bromomagnesium compound prepared from it and acetomesitylene.

Of greater interest are the metallic derivatives prepared from RLi and RNa compounds. If acetomesitylene is an equilibrium mixture of the keto and enol forms, the more reactive organolithium[2c] and organosodium[2d] compounds might be expected to add appreciably to the carbonyl group. The large quantities of acetomesitylene recovered subsequent to hydrolysis belied any significant addition.[3] Furthermore, acetomesitylene with excess methyllithium evolved essentially the theoretical volume of methane.

Both the lithium and sodium derivatives of acetomesitylene gave a positive Michler ketone test. Unlike the bromomagnesium salt, the lithium compound is completely soluble in ether.

If a formula like (B) is correct for the lithium and sodium derivatives of acetomesitylene, it is not novel to find within a molecule a carbonyl group and a reactive C-M linkage for C-Li linkages have been prepared recently in molecules containing reactive anil and carbonyl groups.[4a] It is improbable that coördinate compounds are formed in the Michler ketone color tests with the lithium and sodium derivatives.[4b]

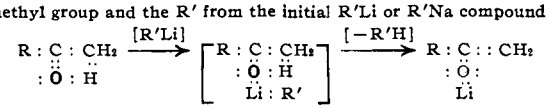
Experimental Part

Phenylmagnesium Bromide.—A solution of 4.87 g. (0.030 mole) of acetomesitylene in 25 cc. of ether was added to 10 cc. of 2.40 molar phenylmagnesium bromide. After refluxing for one hour the mixture was allowed to cool. Both the white crystalline solid and the clear supernatant

(1) (a) Malmgren, *Ber.*, **36**, 2608 (1903). (b) Fuson, Fugate and Fisher, THIS JOURNAL, **61**, 2362 (1939). This article contains references to earlier work, particularly by Kohler and co-workers and Fuson and co-workers.

(2) (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925). (b) Gilman and Yablunky, *ibid.*, **63**, 839 (1941). (c) Gilman and Kirby, *ibid.*, **55**, 1265 (1933). (d) Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

(3) It is possible that the lithium and sodium atoms first added to the oxygen of the carbonyl form; then the enolate developed with the accompanying formation of R'H, the hydrogen coming from the methyl group and the R' from the initial R'Li or R'Na compound



(4) (a) Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940). (b) Gilman and Jones, *ibid.*, **62**, 1243 (1940).

ether gave positive Michler ketone tests. Tests with triphenylbismuth dichloride were negative.[2b]

Organolithium Compounds.—A solution of 8.2 g. (0.05 mole) of acetomesitylene in 25 cc. of ether was added dropwise to a refluxing ether solution of 0.061 mole of methyllithium. The evolved gas (methane by combustion) was 97% of the theoretical quantity. Hydrolysis of the clear ethereal solution yielded 85.5% of acetomesitylene. This experiment was checked.

From a related experiment using 8.0 g. (0.049 mole) of acetomesitylene and 0.10 mole of phenyllithium in 85 cc. of ether, there was recovered 7.8 g. or a 97% yield of acetomesitylene.

The lithium derivative prepared from 2.43 g. (0.015 mole) of acetomesitylene in 10 cc. of ether and 0.013 mole (15 cc. of 0.88 molar ether solution) of *n*-butyllithium or phenyllithium gave a weak but definite Michler ketone color test.

Phenylsodium.—To phenylsodium, prepared by stirring a mixture of 5.7 g. (0.25 g. atom) of sodium sand, 11.2 g. (0.10 mole) of chlorobenzene and 100 cc. of dry benzene for six hours at 35–40°, was added dropwise 24.3 g. (0.15 mole) of acetomesitylene in 25 cc. of benzene. The reaction was highly exothermic. After standing for twelve hours, samples gave good positive tests with Michler ketone. Hydrolysis, by the cautious addition of water, gave 20.9 g. or an 86% yield of acetomesitylene. No other identifiable products were isolated.

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RECEIVED JANUARY 13, 1941

The Antioxidant Properties of Antihemorrhagic Compounds

BY CALVIN GOLUMBIC

Many quinols possess the property of delaying the oxidative deterioration of fats and oils.[1,2,3] The antioxygenic capacity of the corresponding quinones is less than that of the quinols. However, the widespread occurrence of quinones in nature and the presence of vitamin K in alfalfa[4] and in soybean oil[5] prompted an investigation of the antioxygenic properties of these compounds,[6] particularly of those exhibiting vitamin K activity. The oxygen absorption method[7] was used to measure the induction period of the substrates with and without added stabilizers; lard, the ethyl esters of lard fatty acids, and purified fatty acids were used.

Effective antioxidants are found among the antihemorrhagic α-naphthols, α-naphthoquinones and *p*-benzoquinones and corresponding quinols (Table I). α-Naphthol and its homologs are by far the most active. The methyl α-naphthols are less effective than the parent compound and their action varies with the position of the methyl substituent. Similarly, the 2-methyl homolog of α-naphthohydroquinone exhibits diminished antioxygenic activity and the corresponding quinone, 2-methyl-1,4-naphthoquinone, is inactive. Similar relations between structure and antioxygenic activity have previously been observed in the benzene series.[2,3] Duroquinone and α-tocoquinone, reported to show slight vitamin K activity,[8,9] do not stabilize lard.[3]

TABLE I

THE ANTIOXYGENIC ACTION OF NAPHTHOLS, QUINONES AND QUINOLS ON LARD AND ON ETHYL ESTERS OF LARD FATTY ACIDS

Substrate	% Inhibitor added	Antioxygenic index at 75°[a]
Ethyl esters of lard fatty acids	0.02 α-naphthol	30
	.02 2-methyl-1-naphthol	24
	.02 3-methyl-1-naphthol	16
Lard	.10 α-naphthoquinone	1.5
	.04 α-naphthohydroquinone	7
	.10 2-methyl-1,4-naphthohydroquinone	1.5
Lard	.10 *p*-xyloquinone	1.5
	.04 *p*-xylohydroquinone	5
Lard	.02 β-naphthoquinone	8
	.10 β-lapachone	2.5
	.02 dehydro-iso-β-lapachone	2
	.02 pyrano-*o*-quinone (from α-tocopherol)	2

[a] The antioxygenic index is the ratio of the induction period in hours of the protected fat to that of the unprotected.

The effectiveness of benzenoid inhibitors is increased by the presence of additional hydroxyl groups[1]; this effect was not observed among the naphthenoid compounds. Thus, phthiocol and its corresponding quinol are not stabilizers. Other 2,3-disubstituted α-naphthoquinones, lomatiol, lapachol and the cyclic derivatives, α-lapachone and isopropylfuran α-naphthoquinone, are also inactive under the conditions used.

(1) H. A. Mattill, *J. Biol. Chem.*, **90**, 141 (1931).
(2) H. S. Olcott, THIS JOURNAL, **56**, 2492 (1934).
(3) C. Golumbic, *ibid.*, **63**, 1143 (1941).
(4) S. B. Binkley, D. W. MacCorquodale, S. A. Thayer and E. A. Doisy, *J. Biol. Chem.*, **130**, 219 (1939).
(5) H. J. Almquist and A. A. Klose, THIS JOURNAL, **61**, 1610 (1939).
(6) Grateful acknowledgment is extended to Dr. L. F. Fieser, Harvard University, for generous samples of lomatiol, lapachol and their cyclic derivatives. Samples of the methyl α-naphthols were kindly furnished by Dr. M. Tishler, Merck and Company, Rahway, N. J.
(7) R. B. French, H. S. Olcott and H. A. Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).
(8) R. Kuhn, K. Wallenfels, F. Weygand, Th. Moll and L. Hepding, *Naturwissenschaften*, **27**, 518 (1939).
(9) H. Dam, J. Glavind and P. Karrer, *Helv. Chim. Acta*, **23**, 224 (1940).

As was to be expected[1,2] compounds in the β-naphthoquinone series possess greater antioxygenic activity than the analogous α-naphthoquinones but they are less active than corresponding benzoquinones. Thus, β-lapachone is only about one-fifth as effective as the pyrano-*o*-quinone derived from α-tocopherol. Since β-lapachone is much less effective than α-naphthoquinone, it is doubtful that the chroman ring of the former contributes to its antioxygenic action; in the benzene series the presence of a chroman ring markedly increases antioxygenic activity.

Obviously, no relation exists between antihemorrhagic and antioxygenic activity.

The author is indebted to Lever Brothers Company, Cambridge, Mass., for a grant in support of this work and to Dr. H. A. Mattill for his advice and encouragement.

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IOWA CITY, IOWA RECEIVED DECEMBER 16, 1940

Some Addition Compounds of Morpholine

BY HELMUT M. HAENDLER AND GEORGE MCP. SMITH

During an investigation of dithiane addition compounds of various inorganic substances,[1] it was suggested that morpholine, C_4H_9NO, might form similar complexes. Consequently, several representative addition compounds of zinc, cadmium and mercuric halides have been prepared. These compounds are white, crystalline, soluble in *aqua regia* with decomposition and slowly soluble in water, also with decomposition. In all compounds prepared, there are two moles of morpholine per mole of halide, in contrast to dioxane compounds, reported first by Rheinboldt, Luyken and Schmittmann,[2] of which only the zinc compounds are analogous, and to dithiane complexes.[1]

The addition compounds were prepared by direct reaction between the halide and excess morpholine at the boiling point of the latter. After cooling, the crystals were centrifuged rapidly, washed with absolute alcohol and ether and dried in a vacuum desiccator. In some cases, the inorganic halide was dissolved in absolute alcohol and then added to the morpholine. Addition compounds of morpholine and cupric halides are extremely sensitive to moisture, decomposing rapidly. Morpholine also appears to react with cobalt and cupric chloride in hydrochloric acid solution.

The experimental data are summarized in Table I. Zinc and cadmium were determined as anthranilate, mercury as $[Cu(en_2)]HgI_4$.

TABLE I

ADDITION COMPOUNDS OF MORPHOLINE

Formula	M. p., °C.	Metal analyses, % Calcd.	Found
$ZnCl_2 \cdot 2C_4H_9NO$[a]	Softens 200–210, then melts	21.1	21.0
$ZnBr_2 \cdot 2C_4H_9NO$[a]	Dec. 230–240	16.4	16.3
$CdCl_2 \cdot 2C_4H_9NO$[a]	...	31.4	32.2
$CdBr_2 \cdot 2C_4H_9NO$	Dec. 250–252	25.2	24.8
$CdI_2 \cdot 2C_4H_9NO$	Dec. 205–210	20.8	20.8
$HgCl_2 \cdot 2C_4H_9NO$	...	45.0	45.8
$HgBr_2 \cdot 2C_4H_9NO$	Dec. 131–135	37.5	37.4

[a] Inorganic halide dissolved in absolute alcohol.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON RECEIVED FEBRUARY 17, 1941

Investigations in the 1-Methylphenanthrene Series. I. The Conversion of Retene into 1-Methylphenanthrene

BY TORSTEN HASSELSTROM

A direct removal of the isopropyl group from the retene nucleus has been carried out successfully by refluxing retene with fuller's earth whereby 1-methylphenanthrene is obtained in satisfactory yields, together with propene. In this reaction a liquid hydrocarbon which was not investigated at this time is obtained as a by-product. The 1-methylphenanthrene was characterized through its picrate, quinone and phenazine prepared in the conventional manner. The melting points of the hydrocarbon and its derivatives agree, with exception of the phenazine, with those obtained by Pschorr[1] and Haworth[2] on the corresponding material obtained by complete synthesis.

The propene obtained in this reaction was absorbed in bromine and identified as propylene bromide.

Since retene is present in pine wood tar and can be obtained from abietic acid through dehydrogenation, 1-methylphenanthrene is easily produced from these natural products; it thus can

(1) Bouknight and Smith, THIS JOURNAL, **61**, 28 (1939).
(2) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **149**, 30 (1937).

(1) Pschorr, *Ber.*, **39**, 3111 (1908).
(2) Haworth, *J. Chem. Soc.*, 1125 (1932).

be readily used as a source for synthetic work in the phenanthrene and related series.[3]

Acknowledgment.—Thanks are due to the Southern Pine Chemical Company, Jacksonville, Florida, for a supply of retene used in this investigation.

Experimental

1-Methylphenanthrene.[4]—Two hundred and fifty grams of retene and 50 g. of dehydrated fuller's earth were refluxed for nine hours. The gas developed was passed over bromine and in time was transformed into a colorless liquid. After cooling the semisolid brownish reaction product containing fuller's earth was dissolved in hexane and filtered. The filtrate was evaporated to remove most of the solvent and residues left standing in the ice box overnight after which the separated brownish colored crude hydrocarbon was removed by filtration; yield of crude material 97 g. This was recrystallized from hexane as fine glistening scales, m. p. 122–122.5° (cor.).

Anal.[5] Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.55; H, 6.36.

The hexane solution from the above operation was evaporated and 118 g. of the residue was fractionated once in vacuum at 1 mm. pressure: I, 155–165°, 78 g. (solidified on standing); II, 165–175°, 20 g. (non-solidifying oil); III, 18 g. of residue. Only the first fraction was investigated at this time. It was recrystallized from hexane, m. p. 122–123° (cor.), and was found to be 1-methylphenanthrene since it did not depress the melting point of the analytical sample.

The 250 g. of retene yielded 62 g. of pure 1-methylphenanthrene.

The bromine absorption product was washed first with an aqueous sodium sulfite solution, then with a sodium carbonate solution and with water. The colorless liquid of propylene bromide was dried with anhydrous sodium sulfate and fractionated at ordinary pressure: b. p. 142–143° (uncor.); d_{20} 1.9297; $n^{20}D$ 1.52604.

Anal. Calcd. for: $C_3H_6Br_2$: Br, 79.16; Found: Br, 79.54.

Picrate of 1-Methylphenanthrene.—Brick red needles, recrystallized from alcohol, m. p. 139° (cor.).

Anal. Calcd. for: $C_{21}H_{15}O_7N_3$: N, 9.97. Found: N, 9.89.

The hydrocarbon recovered from the picrate melted at 122–122.5°.

1-Methylphenanthroquinone.—Dark reddish-brown needles, recrystallized from acetic acid, m. p. 192–193° decompn. (cor.).

Anal. Calcd. for: $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.10; H, 4.54.

In cold concentrated sulfuric acid it dissolved to a dark green solution, which color disappeared upon dilution.

Phenazine.—Fluffy slightly yellowish needles recrystallized from glacial acetic acid, m. p. 183.5° (cor.).

Anal. Calcd. for: $C_{21}H_{14}N_2$: N, 9.52. Found: N, 9.97.

In cold concentrated sulfuric acid solution the color was burgundy red, which was lost on dilution.

G. AND A. LABORATORIES
SAVANNAH, GEORGIA RECEIVED FEBRUARY 17, 1941

(3) Preliminary tests have shown, as expected, that 1-methylphenanthrene may be readily subjected to the Friedel-Crafts reactions, sulfonation, halogenation, etc.

(4) Subject matter for a U. S. Patent application.

(5) All analyses by Mr. S. Gottlieb, Columbia University, N. Y.

The Solubility of Carbon Dioxide in Aqueous Solutions of Sulfuric and Perchloric Acids at 25°

BY AARON E. MARKHAM AND KENNETH A. KOBE

The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions was recently reported by Markham and Kobe.[1] They found that the gas solubility isotherms could be fitted by an equation of the form

$$\frac{S}{S_0} = am + \frac{1}{1 + bm} \qquad (1)$$

in which S is the unit solubility, cc. gas (sc) dissolved by the amount of solution containing one gram of water, m is the salt molality, a and b are empirical constants derived from the data and specific for each curve. This equation fitted the isotherms within the limits of experimental error, about 0.2%, over the entire range of salt concentrations, up to 8 molal for sodium nitrate solutions.

It was the purpose of this work to determine the solubility of carbon dioxide in an aqueous solution of a strong electrolyte that is miscible in all proportions with water and whose gas solubility isotherm is not a continually decreasing function, as is the case with solutions of salts, and determine the range over which equation 1 can be fitted to the data.

Method and Results

Perchloric and sulfuric acids were Baker C. P. analyzed (A. C. S. specifications). The concentrated acid was standardized and diluted to give the desired solution, which was checked by a density determination.[2] The 100% sulfuric acid was made by adding fuming acid to the concentrated acid. The apparatus and technique were those described in the previous paper.[1] All measurements were made at a temperature of 25° and a partial gas pressure of 760 mm. The results are given in Table I. The Bunsen coefficient, α,

(1) Markham and Kobe, THIS JOURNAL, **63**, 449 (1941).

(2) For aqueous solutions of perchloric acid at 25°, see Markham, *ibid.*, **63**, 874 (1941).

TABLE I

SOLUBILITY OF CARBON DIOXIDE IN ACID SOLUTIONS AT 25°

H_2SO_4, m	Mole %	α	S	$S_{calcd.}$
0.0	0	0.7565	0.7587	
0.5	0.8928	.6983	.7127	0.7183
1.0	1.7697	.6650	.6911	.6911
2.0	3.4779	.6132	.6610	.6642
3.0	5.1277	.5854	.6546	.6619
4.0	6.7220	.5740	.6659	.6757
6.0	9.7551	.5878	.7332	.7332
8.0	12.597	.6159	.8238	.8154
10.0	15.266	.6337	.9053	.9116
14.15	20.32	.6404	1.0372	1.1372
18.86	25.37	.6225	1.1453	
28.29	33.77	.5840	1.3386	
37.72	40.48	.5659	1.5573	
56.58	50.49	.5741	2.1232	
94.30	62.95	.645		
188.6	77.26	.753		
282.9	83.60	.813		
565.8	91.07	.880		
1131.6	95.32	.920		
	100	.960		
$HClO_4$				
0.0	0.0000	0.7565	0.7587	
.25	.4484	.753	.764	0.771
.50	.8928	.759	.778	.783
.75	1.3332	.765	.793	.796
1.00	1.7697	.772	.809	.809
1.50	2.6313	.785	.840	.835
2.00	3.4779	.798	.865	.861
4.00	6.7220	.835	.984	.973
6.00	9.7551	.863	1.091	1.091
10.00	15.266	.866	1.239	1.343
15.47	21.79	.762	1.264	
22.84	29.15	.718	1.426	

Constants for Equation 1

	a	b
H_2SO_4	0.0885	0.2159
$HClO_4$	.107	.04284

has been plotted against the weight and mole per cent. of acid in Fig. 1.

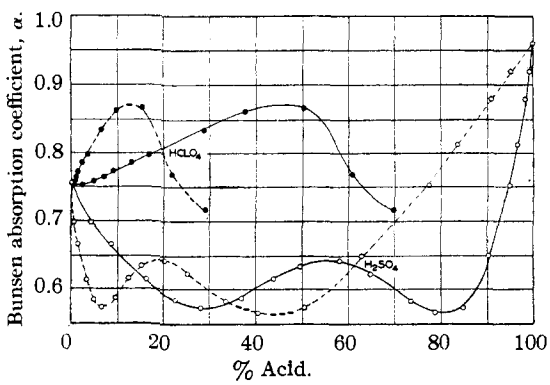

Fig. 1.—Bunsen coefficient for carbon dioxide in solutions of sulfuric and perchloric acids at 25°: ——, weight per cent.; – – –, mole per cent.

The solubility of carbon dioxide in concentrations of perchloric acid up to six molal, and in sulfuric acid up to ten molal, fits equation 1 with a maximum error of about 1%. The values calculated are given in Table I as $S_{calcd.}$. From the curves it is seen that the equation no longer fits the data after the solubility passes through the first maximum point, though the first minimum point in the sulfuric acid solution is fitted well by the calculated values. The maxima and minima in the gas solubility curves do not correspond to simple compounds of the acid with water.

Equation 1 represents a hyperbola which goes to positive infinity at $-1/b$ and becomes tangent to the line S_0am at the other extremity; the equation can account only for a minimum, as with sulfuric acid, but not for a maximum, in any actual isotherm.

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON RECEIVED DECEMBER 10, 1940

Recovery of the Cottonseed Allergenic Protein from its Picrate by Electrophoresis

BY JOSEPH R. SPIES

In a recent communication a chemical method for recovering the cottonseed allergenic protein CS-13A from its picrate was described.[1]

Incidental to a large scale electrophoretic separation of the allergenic fraction CS-1A it was found that the protein CS-13A could be recovered from its picrate by high voltage electrophoresis.[2,3,4] Advantage was taken of the fact that the protein picrate was soluble in 50% dioxane, in which the freed protein was insoluble. In this solution picric acid migrated toward the anode cell and the protein moved to the cathode cell where it precipitated.

Experimental

The electrophoresis apparatus used for the separation consisted of a series of six cells made from 125 ml. Erlenmeyer flasks with 10 mm. side tubes sealed on 25 mm. above the bottom. Cells were joined by 25 mm. lengths of heavy walled gum rubber tubing. Temperature was

(1) Spies, Coulson, Bernton and Stevens, THIS JOURNAL, **62**, 1420 (1940).

(2) The theory and an application of high-voltage electrophoresis have been described by R. J. Williams and J. H. Truesdail, *ibid.*, **53**, 4171 (1931). See also later papers by Williams and co-workers.

(3) V. du Vigneaud, G. W. Irving, H. Dyer and R. R. Sealock, *J. Biol. Chem.*, **123**, 45 (1938), have used high voltage electrophoresis in fractionating the posterior pituitary hormone.

(4) E. Gebauer-Fuelnegg and A. I. Kendall, *Ber.*, **64**, 1070 (1931), separated the strongly basic histamine from the dipicrate by electrodialysis using direct current at 110 v.

maintained below 35° by circulating water through a copper trough holding the apparatus.

To carry out the recovery of the protein, 1 g. of protein picrate (CS-5-7)[5] dissolved in 100 ml. of 50% dioxane, was placed in the third cell from the cathode and 100 ml. of 50% dioxane was placed in each of the other cells. Direct current at 1500–2500 volts was applied at the platinum electrodes in terminal cells for four hours, and the voltage was then increased to 4000 volts for sixty-eight hours. The initial current of 1.1 milliamperes gradually increased to 6.0 and then dropped to 2.9 where it remained constant. At the end of this operation the cathode cell contained a gummy precipitate and nearly colorless solution. The other cells contained picric acid as indicated by the yellow color which was progressively more intense toward the anode cell. The supernatant liquid in the cathode cell was decanted and the precipitate was dissolved in 30 ml. of water. This solution, decolorized by boiling with activated charcoal, was centrifuged and filtered through a Seitz sterilizing pad. The clear colorless filtrate was poured into 100 ml. of cold ethanol and precipitated by adjusting the *p*H to 6.3 with dilute acetic acid. A yield of 180 mg. of a white powder was recovered by centrifuging followed by drying in a vacuum over phosphorus pentoxide. The recovered solid contained 19.8% (ash-water free basis) nitrogen and gave protein color tests like CS-13A. The solid diluted to $1:10^6$ induced strongly positive cutaneous reactions on cottonseed sensitive patients.

(5) Spies, Bernton and Stevens, THIS JOURNAL, **62**, 2793 (1940).

ALLERGEN INVESTIGATIONS
BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C. RECEIVED JANUARY 24, 1941

COMMUNICATIONS TO THE EDITOR

ULTRAVIOLET ABSORPTION OF THE DIPHENIC ACIDS

Sir:

Recent studies have emphasized the fact that absorption in the ultraviolet is a measure of resonance or conjugation and that structure is indicated only incidentally as it contributes to this phenomenon. Recently in this Laboratory the absorption curves have been obtained for ortho-ortho′-, meta-meta′- and para-para′-diphenic acids. It is interesting to report the radically different behavior of these three compounds in respect to their ultraviolet absorption.

The *o-o′*-diphenic acid shows an absorption which differs but little from that of benzoic acid. Evidently the carboxyl groups in the *o*-position interfere to such an extent that the coplanar position is impossible and resonance between the rings completely disappears.

On the other hand, the *p-p′*-diphenic acid (in this case the methyl ester) shows a very great absorption with the maximum near 2800 Å. Here we have exact coplanarity with complete resonance throughout.

By far the most interesting of these compounds, however, is the *m-m′*-diphenic acid. While the absorption is much greater than that of the *o-o′*-compound, it is much less than that of the *p-p′*-acid and the maximum is shifted toward shorter wave lengths so that it lies beyond the range of the medium quartz spectrograph. It is clear that it is not possible for a structure to exist which involves double bonds between the rings and between the ring and the carbon of the carboxyl group at the same time and this is the important structure for total resonance. Hence competition between these structures results in a decreased amount of conjugation.

It is interesting to note that a similar situation arises in the case of diphenylmethane. *p*-Cresol shows a marked increase in absorption and a shift of the maximum toward longer wave lengths. On the other hand, *p*-hydroxydiphenylmethane shows little difference from the diphenylmethane. This is not difficult to understand when we recognize that the principal resonance structure which contributes to the absorption in diphenylmethane is one in which the *p*-carbon acquires a negative charge. This structure does not involve conjugation with the hydroxyl group.

The details of this research will be published later but meanwhile we wish to acknowledge our indebtedness to Dr. N. Kornblum and Messrs. L. Brooks and J. C. Robinson for the preparation of the several acids.

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