temperature and pouring the mixture into 200 cc. of water an oil separated which soon crystallized. Recrystallizing the dried crystals from 50 cc. of ligroin (b. p. 75–115°) with the addition of 1.0 g. of Norit, white triphenylchloroethylene was obtained. The combined first and second crops gave, recrystallized from 12 parts of ethanol, 8.5 g. of m. p. 117.5–118° (65%). This material gave no depression with that obtained above.

Triphenylchloromethoxyethane (V).—One gram of triphenyldichloroethane was refluxed with 15 cc. of methanol for two hours. The mixture was cooled and the crystals which separated were collected. The mother liquors gave some additional material. In all, 0.85 g. of material of m. p. 117.5–118° was obtained. Mixed with triphenylchloroethylene a depression in m. p. was observed.

Anal. Calcd. for $C_{21}H_{19}OCl$: C, 78.13; H, 5.93; Cl, 10.98. Found: C, 77.94; H, 5.96; Cl, 11.21.

Summary

1. A simple method for the preparation of triphenylchloroethylene, giving excellent yields, is described. Bergmann and Bondi's method is discussed.
2. 1,1,2-Triphenyl-1,2-dichloroethane and a triphenylmethoxychloroethane are described.

RAHWAY, N. J. RECEIVED MARCH 5, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Action of Organic Nitrogen Bases on Cornstalk Lignin*

BY ELTON FISHER AND R. S. BOWER

The commercial availability of monoethanolamine has led to studies of its action on plant tissues. This manuscript reports the action of other commercially available organic nitrogen bases on cornstalk lignin.

Action of Bases on Cornstalk.—Ten-gram samples of air dried ground cornstalks were digested with 110 ml. of anhydrous ethanolamines and N-substituted morpholines for six hours at elevated temperatures. Each sample was then diluted with an equal volume of hot water, filtered and washed with hot water until the filtrate was free of base. The air dried pulp was analyzed for lignin by the cold sulfuric acid method.[1] Table I gives the results obtained.

TABLE I

Base	Temp., °C.	Weight of pulp, g.	Lignin removed, %
Monoethanolamine	100	4.63	93.9
Diethanolamine	100	4.89	75.6
Triethanolamine	100	6.15	42.6
	130	5.56	53.6
	160	4.80	81.2
Morpholine-ethanol	100	6.61	25.6
N-Phenylmorpholine	100	7.83	23.8

The values given in Fig. 1 except those for Curve H were obtained in a similar manner from 10-g. samples of cornstalks autoclaved with aqueous solutions of the bases for three hours at 20 pounds pressure. Curve H represents the results obtained in a corresponding manner from similar samples digested for six hours at 100° with aqueous solutions of morpholine-ethanol.

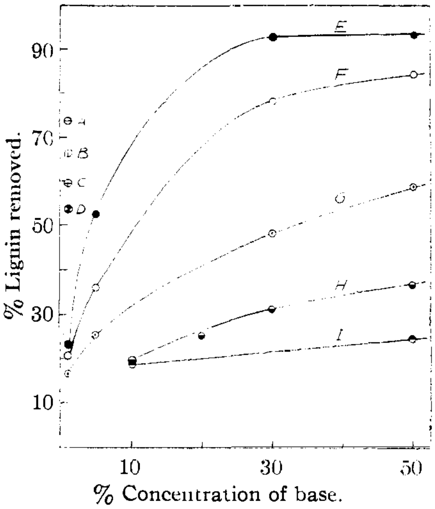

Fig. 1.—A, sodium hydroxide + monoethanolamine; B, sodium hydroxide; C, sodium hydroxide + diethanolamine; D, sodium hydroxide + triethanolamine; E, monoethanolamine; F, diethanolamine; G, triethanolamine; H, morpholine-ethanol at 100°; I, morpholine-ethanol at 20 pounds pressure.

Recovery of Lignins.—The filtrates from the basic extractions were concentrated to 150 ml.; the pentosans were precipitated with 3 volumes of alcohol, filtered and washed with alcohol. After evaporating the alcohol the filtrates were acidified with an excess of dilute sulfuric acid; this caused the lignins to precipitate. The precipitated lignins were filtered, washed and purified by redissolving in the base, precipitating with

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* Supported in part by a grant from the Industrial Science Research funds of the Iowa State College for the study of lignin.

(1) Peterson, Walde and Hixon, *Ind. Eng. Chem., Anal. Ed.*, **4**, 216 (1932).

acid, filtering and washing. No appreciable lignin was recovered from filtrates of the anhydrous bases except in the case of triethanolamine. The purified lignins were analyzed for methoxyl[2] and nitrogen[3] after drying over phosphoric anhydride in a vacuum desiccator.

Lignin was isolated by the sulfuric acid method[1] from 10-g. samples of some of the pulps prepared by the basic digestions. These lignins were dried and analyzed as above.

Action of Bases on Sulfuric Acid Lignin.—One-gram samples of sulfuric acid lignin[1] from untreated cornstalks were autoclaved for three hours at 20 pounds pressure with 200 ml. of 50% aqueous solutions of mono-, di-, and tri- ethanolamines, filtered and precipitated with dilute sulfuric acid. The recovered lignins were dried and analyzed as above.

TABLE II

Source of Lignin	Weight of lignin, g.	Recovered, %	CH_3O, %	N, %
Recovered from filtrate of:				
50% Aqueous monoethanolamine[b]	0.38	25[a]	15.6	2.42
50% Aqueous diethanolamine[b]	.70	50[a]	15.0	2.37
50% Aqueous triethanolamine[b]	.51	53[a]	13.6	2.42
Anhydrous triethanolamine[c]	.16	12[a]	10.5	1.97
30% Aqueous morpholine-ethanol[d]	.30	59[a]	7.3	3.12
Sulfuric acid lignin from pulp of:				
50% Aqueous monoethanolamine	.25	100	5.1	1.05
50% Aqueous diethanolamine	.53	100	9.6	1.35
50% Aqueous triethanolamine	1.24	100	13.6	1.03
30% Aqueous morpholine-ethanol	1.76	100	14.2	1.22
Sulfuric acid lignin digested with:				
50% Aqueous monoethanolamine[b]	0.55	55	12.4	2.44
50% Aqueous diethanolamine[b]	.62	62	12.8	1.82
50% Aqueous triethanolamine[b]	.71	71	13.2	1.23
30% Aqueous morpholine-ethanol[d]	.25 .60[e]	25 60[e]	5.8 12.1[e]	2.65 1.98[e]
Sulfuric acid lignin (untreated)	..	..	12.5	1.06

[a] Calculated to show % recovery of extracted lignin. [b] Autoclaved for three hours at 20 pounds pressure. [c] Heated six hours at 160°. [d] Heated six hours at 100°. [e] Portion insoluble in hot 30% morpholine-ethanol.

A similar sample of sulfuric acid lignin[1] was treated at 100° for six hours with 100 ml. of 30% aqueous morpholine-ethanol. Only part of the lignin dissolved; after digestion the sample was filtered and washed with hot water. The soluble lignin was precipitated with sulfuric acid; both fractions were dried and analyzed as above.

Purification of Pentosans.—The precipitated pentosans were purified by extracting with alcohol. The pentosans obtained from mono- and di-ethanolamines, in yields of 1.2 g. and 1.0 g., respectively, from the 50% aqueous amines, were lighter colored than those from the other bases.

The Basic Strength of the Nitrogen Bases.—The ionization constants were determined by the method of Carothers, Bickford and Hurwitz[4] modified by using a glass electrode to determine the *p*H of half-neutralized aqueous solutions of the specially purified bases. The values obtained were: monoethanolamine $K_B = 3.0 \times 10^{-5}$; diethanolamine $K_B = 7.3 \times 10^{-6}$; triethanolamine $K_B = 6.1 \times 10^{-7}$; and morpholine-ethanol $K_B = 9.0 \times 10^{-8}$. The value for monoethanolamine is in reasonable agreement with the more accurate value of Sivertz, Reitmeier and Tartar.[5]

It appears with the limited data available that the amount of lignin removed from plant tissue by organic nitrogen bases depends upon the basic strength of the extracting agent. This seems to hold for both the anhydrous bases and their aqueous solutions. This tentative conclusion does not preclude the possibility that anhydrous bases can remove lignin from plant tissues by organic solvent action rather than by their basic strength.

The more highly methylated fraction of lignin was isolated from the extracting liquors when cornstalks were autoclaved with 50% aqueous solutions of mono- and di-ethanolamines. Demethylation was not observed in any of the lignins treated with aqueous ethanolamines. The low percentage of methoxyl in the lignin extracted from cornstalks with anhydrous triethanolamine indicates demethylation, but the yield of recovered lignin was not sufficient to give definite proof that this was not merely fractionation. Demethylation was observed in lignin extracted

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(2) Roth and Daw, "Quantitative Organic Microanalysis of Fritz Pregl," P. Blakiston's Son and Co., Inc., Philadelphia, Pa., 1937, p. 179.

(3) Joseph B. Niederl and Victor Niederl, "Micromethods of Quantitative Organic Elementary Analysis," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 54.

(4) Carothers, Bickford and Hurwitz, THIS JOURNAL, **49**, 2908 (1927).

(5) Sivertz, Reitmeier and Tartar, *ibid.*, **62**, 1379 (1940).

from cornstalks by 30% aqueous morpholine-ethanol and in the sulfuric acid lignin digested with a 30% aqueous solution of this base.

The nitrogen content of the isolated lignins (1.97–3.12%) was not significantly greater than that reported by Walde and Hixon[6] as due to contamination in oat hull lignins. These investigators[6] found that caustic alkali lignin contained 1.9% nitrogen and ammonia lignin analyzed 3.04% nitrogen. The increased nitrogen content of sulfuric acid lignin digested with the aqueous bases cannot be due to protein contamination, nor can it be entirely due to a fractionation of contaminating protein material. From these facts it must be concluded that the organic nitrogen bases form nitrogenous compounds with lignin.

Summary

1. The action of a series of commercially available organic nitrogen bases on lignin has been studied; cornstalk tissues and isolated lignin (72% sulfuric acid) were used as substrates.

2. It appears that the amount of lignin extracted depends upon the basic strength of the extracting liquors for both the aqueous and anhydrous nitrogen bases. This does not preclude the possibility that anhydrous bases may remove lignin by organic solvent action.

3. Evidence indicating that the aqueous bases form nitrogenous compounds with lignin is presented.

Ames, Iowa

Received January 13, 1941

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[6] Walde and Hixon, This Journal, **56**, 2656 (1934).

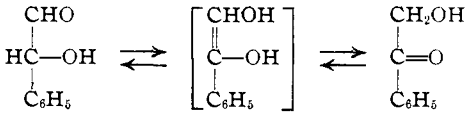
[Contribution from the Chemical Laboratory of The Ohio State University]

The Preparation of Glycerophenylose Enedioldiacetate*

By Wm. G. Dauben, Wm. Lloyd Evans and Robert I. Meltzer

Many of the results obtained in a study of the chemical behavior of reducing sugars in alkaline solutions have been best understood by assuming as the first step in reaction the intermediate formation of the aldehydo[1] structure which is then converted into a series of enediols. The existence of these enediols was postulated by Fischer, Wohl and Neuberg, and Nef, but their synthesis has not been hitherto achieved.[2] Ascorbic acid, dihydroxymaleic acid and the Redukton of Euler and Martius are some of the well known examples of compounds which contain the enediolic functional group, $\left[\mathrm{HO{-}\overset{|}{C}{=}\overset{|}{C}{-}OH}\right]$.

The following experiments deal with the first synthesis of a sugar enediol derivative. Benzoylcarbinol (C_6H_5-CO-CH_2OH) is related to mandelic aldehyde (C_6H_5-CHOH-CHO) as a ketose is to an aldose, respectively. Adapting the nomenclature suggested by Votoček[3] for the methyloses, mandelic aldehyde may be designated as *aldo*-glycerophenylose and benzoylcarbinol as *keto*-glycerophenylose. These two phenyloses should give the same enediol, *i. e.*, glycerophenylose enediol



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HC{-}OH}\\ |\\ \mathrm{C_6H_5}\end{array} \rightleftharpoons \left[\begin{array}{c}\mathrm{CHOH}\\ \|\\ \mathrm{C{-}OH}\\ |\\ \mathrm{C_6H_5}\end{array}\right] \rightleftharpoons \begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{C_6H_5}\end{array}$$

(*aldo*-glycerophenylose) (glycerophenylose enediol) (*keto*-glycerophenylose)

The experiments of Gomberg, Fuson, Thompson, and Barnes and Tulane[4] suggest methods of approach to the synthesis of the sugar enediols.

The diacetate of glycerophenylose enediol (I) was prepared by the techniques of Barnes and Tulane, through refluxing a mixture of ω-bromoacetophenone, freshly fused potassium acetate and acetic anhydride for three hours. This compound reacted as expected of the enediol as shown by the following: (a) on partial deacetylation with potassium acetate and glacial acetic acid, the reaction mixture yielded keto-glycerophenylose monoacetate (II) (m. p. 49°)[5]; (b) when completely hydrolyzed with water in the presence of $CaCO_3$, keto-glycerophenylose (III) (m. p. 86.5°)

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* Presented at the Meeting of the American Chemical Society, St. Louis, Missouri, April 10, 1941.

[1] (a) M. L. Wolfrom, This Journal, **51**, 2188 (1929); (b) M. L. Wolfrom, *ibid.*, **52**, 2464 (1930).

[2] (a) E. Fischer, *Ber.*, **28**, 1149 (1895). (b) Wohl and Neuberg, *ibid.*, **33**, 3099 (1900). (c) Nef, *Ann.*, **335**, 191 (1904).

[3] E. Votoček, *Bull. Soc. Chim.*, [4] **43**, 1 (1928).

[4] (a) M. Gomberg and W. E. Bachmann, This Journal, **49**, 236 (1927); (b) R. C. Fuson and J. Corse, *ibid.*, **61**, 975 (1939); (c) R. B. Thompson, *ibid.*, **61**, 1281 (1939); (d) R. P. Barnes and V. S. Tulane, *ibid.*, **62**, 894 (1940).

[5] (a) Th. Zincke, *Ann.*, **216**, 306 (1883); (b) ref. 4d; (c) R. P. Barnes and V. J. Tulane, This Journal, **63** 867 (1941).