

Acetone precipitation was most satisfactory for the preparation of concentrates. The fraction soluble at 50% but insoluble in 55% aqueous acetone was redissolved in water. This solution had a "Kat. f." of 1800, representing a threefold concentration of the original activity. Stern has used acetone in the preparation of liver catalase concentrates.<sup>7</sup>

A cottonseed extract (pH 6.4) was only slightly affected by heating at 50° for thirty minutes. At 60° the catalase was destroyed completely in fifteen minutes, and at 70° no activity remained after five minutes. However, dry ether-extracted cottonseed meats could be heated at 105° for several hours without destruction of the enzyme. Commercial cottonseed meal contained no catalase; this material is generally subjected to a

(7) K. J. Stern, *J. Biol. Chem.*, **112**, 661 (1935-36).

steaming process for twenty to forty minutes prior to the pressing operation.

The activity of concentrates was almost entirely repressed in 0.02 *N* sodium cyanide solution.

During the first forty-eight hours of germination, the catalase concentration of whole seeds increased from 120 to 140% of the original content.

The characteristics of this enzyme are not essentially different from those of other plant catalases.<sup>3</sup> The availability of a plant source of somewhat greater original catalase content should facilitate its further investigation.

### Summary

Cottonseeds contain appreciably more catalase than do a number of other seeds examined. Some properties of the enzyme have been described.

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[CONTRIBUTION FROM THE BAILEY CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

## Reduction of Diazonium Salts to Hydrocarbons with Alkaline Formaldehyde

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It is well known that the classical method<sup>1</sup> for the reduction of a diazonium salt such as phenyldiazonium chloride or sulfate to a hydrocarbon by reaction with an alcohol produces an ether as well as the hydrocarbon. In most cases the ether is the major product. An experiment by Hantzsch and Jochem,<sup>2</sup> which is typical of many recorded in the literature, produced 1.6 g. of benzene and 34.1 g. of phenetole from the reaction of ethyl alcohol upon 64 g. of phenyldiazonium chloride. Similar results with varying proportions in the yield of hydrocarbon (hydrogen reaction, I) and ether (alkoxy reaction, II) have been obtained by a large number of investigators.<sup>3</sup> The extent to which the reaction between any given diazonium salt and an alcohol will follow one course or the other depends upon the character of the radical (R) and upon the nature of the alcohol. In general the yield of hydrocarbon increases with the



substitution of a carboxyl, halogen or nitro group

ortho to the diazonium radical, and the hydrogen reaction becomes quite predominant in the case of 2,4,6-tribromophenyldiazonium sulfate where the yield of tribromobenzene<sup>4</sup> is 75-78% of the theoretical quantity. The alcohols used most commonly are methyl and ethyl, of which the latter usually gives the better yield of hydrocarbon. Some experiments using other alcohols are to be found in the literature and they are being extended in this Laboratory.

In the deamination of certain aminodiphenyl ether derivatives in which we were interested, the alkoxy reaction occurred almost exclusively and it was necessary to devise some other method for replacement of the amino group by hydrogen. Inasmuch as the hydrogen reaction involves a reduction of the carbon atom to which the diazonium salt is joined, it would seem that a reducing agent considerably stronger than an alcohol should be used. Such reducing agents as sodium alcoholate,<sup>5</sup> stannous chloride<sup>6</sup> and hypophosphorous acid<sup>7</sup> in certain cases have increased somewhat the yield of the hydrocarbon but it would seem that the more effective reducing action of an

(1) Griess, *Ann.*, **137**, 69 (1866).

(2) Hantzsch and Jochem, *Ber.*, **34**, 3340 (1901).

(3) A. W. Hofmann, *Ber.*, **17**, 1919 (1884); Remsen and Orndorff, *Am. Chem. J.*, **9**, 387 (1887); Cameron, *ibid.*, **20**, 229 (1898); Franklin, *ibid.*, **20**, 455 (1898), and many others.

(4) *Org. Syntheses*, **13**, 96 (1933).

(5) Beeson, *Am. Chem. J.*, **16**, 250 (1894).

(6) Friedländer, *Ber.*, **22**, 587 (1889).

(7) Mai, *ibid.*, **35**, 163 (1902).

alkaline solution of formaldehyde should give a greater increase in the yield of hydrocarbon. This expectation was realized and the following table shows that quite a wide variety of compounds have been deaminated in yields of 50–80%. Some substances such as 2,5-dichloroaniline and anthranilic acid, which are deaminated in the poorest yields by this method, are the ones which succeed best by the time-honored alcohol method. Thus the two processes supplement each other. A typical experiment is described and the table shows the yields obtained with other compounds by using the same procedure.

### Experimental Part

**Deamination of *p*-Toluidine to Toluene.**—A solution of 0.5 mole (53.5 g.) of *p*-toluidine in 150 cc. of concentrated hydrochloric acid and 400 cc. of water was chilled by the addition of 400 g. of ice and diazotized in the usual manner with 36 g. of sodium nitrite. A solution of 100 g. of commercial sodium hydroxide in 600 cc. of water was then prepared and placed with 500 g. of shaved ice into a 5-liter flask which was fitted with a mechanical stirrer. The stirrer was started and 75 cc. of formalin (37% formaldehyde) added. The solution of *p*-tolylidiazonium chloride was then poured in a slow stream into the rapidly stirred alkaline solution of formaldehyde. The rapid escape of nitrogen caused considerable frothing. After all of the diazonium chloride solution had been added the stirring was continued for two to three minutes, after which the stirrer was removed, the mouth of the flask covered with a

watch glass and the reaction mixture allowed to stand with occasional shaking for thirty to forty minutes. The toluene in the upper oily layer was then removed by distillation in steam, separated from the water, dried and distilled. The yield of toluene, b. p. 108–111°, was 36–38 g. (78–82%).

**Discussion.**—The addition of the diazonium salt to the alkaline formaldehyde may produce both the *syn* and *anti* diazotates, the former of which might be reduced more rapidly than the latter. However, after the reduction had proceeded for five minutes, reacidification of the solution and again making it alkaline did not increase the yield. Neither was the yield of toluene increased by addition of sodium stannite, zinc dust or ferrous sulfate to the alkaline solution of formaldehyde. The use of alkaline pyrogallol in place of alkaline formaldehyde gave a little toluene but chiefly an azo dye (coupling reaction) with excessive frothing. Since no alcohol is used in the method, the formation of an ether is avoided. The loss of material in each experiment was accounted for by the formation of tarry substances which were chiefly polymers of the aromatic radical and remained in the flask after steam distillation. Replacement of *p*-tolylidiazonium chloride by the sulfate reduced the yield of toluene from 80 to 75% and an increase in the concentration of the sulfate ion by the addition of 1 g. mole of sodium sulfate further reduced the yield of toluene to 55%. The low yield of nitrobenzene from the three nitroanilines is explained by the fact that the nitro group is largely reduced by the alkaline formaldehyde to a mixture of azo compounds. The reaction of phenyldiazonium chloride with alkaline acetaldehyde in place of formaldehyde gave a red dye as reported by Bamberger and Müller.<sup>8</sup> In our experiments the yield of benzene by this reaction was less than 5%.

TABLE I

YIELD OF DEAMINATED PRODUCTS FROM DIAZONIUM SALTS

Amino compound	Product and % yield	
Aniline	Benzene	60
<i>o</i> -Toluidine	Toluene	80
<i>p</i> -Toluidine	Toluene	80
<i>o</i> -Anisidine	Anisole	75
<i>p</i> -Anisidine	Anisole	72
<i>o</i> -Phenetidine	Phenetole	75
<i>p</i> -Phenetidine	Phenetole	65
2,4-Dimethylaminobenzene	<i>m</i> -Xylene	80
<i>p</i> -Chloroaniline	Chlorobenzene	50
<i>o</i> -Chloroaniline	Chlorobenzene	55
4-Aminodiphenyl ether	Diphenyl ether	60
2-Aminodiphenyl ether	Diphenyl ether	60
2-Amino-4'-methyl-diphenyl ether	4-Methyl diphenyl ether	50
4-Amino-4'-methyl-diphenyl ether	4-Methyl diphenyl ether	50
2,5-Dichloroaniline	<i>p</i> -Dichlorobenzene	10
Anthranilic acid	Benzoic acid	25
<i>o</i> -Nitraniline	Nitrobenzene	20
<i>m</i> -Nitraniline	Nitrobenzene	10
<i>p</i> -Nitraniline	Nitrobenzene	10

### Summary

The reduction of a number of diazonium salts with alkaline formaldehyde has been found to produce good yields of hydrocarbons. This procedure often gave the best yields of hydrocarbons in cases where the classical reduction with alcohol gave the poorest yields and vice versa. Hence the two methods supplement each other.

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(8) Bamberger and Müller, *J. prakt. Chem.*, [2] **64**, 199 (1901).