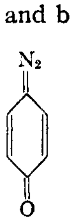
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

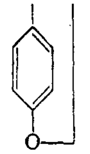
The Structure of Some Diazophenols

BY LEIGH C. ANDERSON AND MILTON J. ROEDEL[1]

Para- and ortho-diazophenols are stable, colored and soluble in non-polar solvents. In books which have been published in recent years, the structure of these compounds has been accepted as quinonoid, I, by Sidgwick[2] and as cyclic, II, by Heilbron[3] and by Saunders.[4] Hodgson and Marsden[5] have postulated quinonoid forms where possible for these compounds and ionic structures where quinonoid are not permissible. The purpose of the present investigation was to attempt to show by means of absorption spectra whether the predominant structure of the 1,4- and 1,2-diazophenols in non-polar solvents is cyclic or quinonoid by comparing the absorption spectra of the diazophenols with the absorption spectra of compounds of known cyclic and of known quinonoid structure. The only previous absorption spectrum work in this field was carried out by Hantzsch and Lifschitz[6] in 1912 when they compared the qualitative absorption spectra of diazo-acetic ester and p-diazophenol and drew the conclusion that the structure of the latter was quinonoid.



I



II

The quantitative absorption spectra curves of ether solutions of 1,4-diazonaphthol and p-diazophenol are compared with those of the corresponding quinones in Fig. 1. The curve for p-benzoquinone was reproduced from previous work by Anderson and Geiger.[7] The two characteristic absorption bands of 1,4-quinones are the quinonoid band which occurs in the region $\bar{\nu} = 2300$ (the main band as a whole is discussed although it frequently may consist of several small bands) and the ketonic band which occurs in the region $\bar{\nu} = 3000$. (In the case of p-benzoquinone this latter band is shifted more toward the ultraviolet than is usually the case and overlaps the bands which occur at higher frequencies.) The substitution of a diazide group for a carbonyl oxygen in the 1,4-quinones has shifted the ketone band toward the infrared, increased the intensity of absorption, caused a new band to appear in the region $\bar{\nu} = 3600$ and decreased the selectivity of the quinonoid band. The similarity of the curves of ether solutions of the diazo compounds to the corresponding quinones indicates that both types of compounds have the same structure predominating in such a solvent.

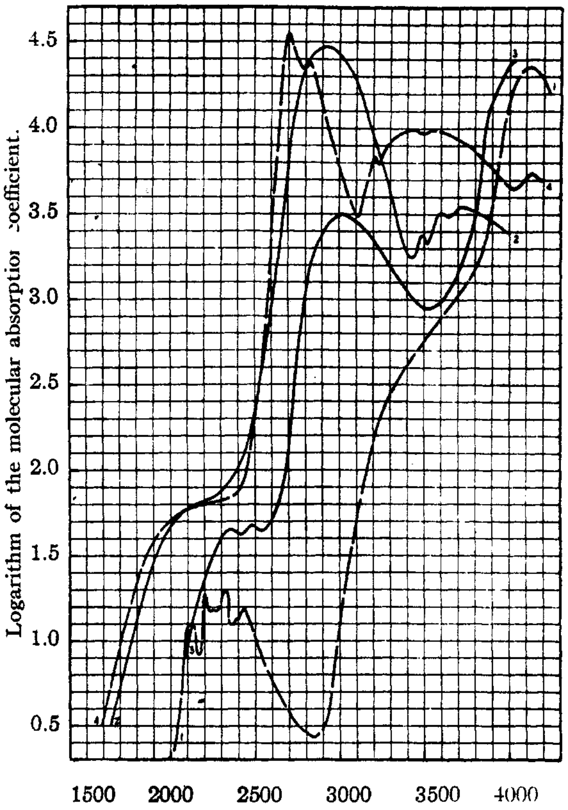


Fig. 1.—(1) p-Benzoquinone; (2) p-diazophenol; (3) 1,4-naphthoquinone; (4) 1,4-diazonaphthol.

In Fig. 2, the quantitative absorption spectra curves of ether solutions of 1,2- and 2,1-diazonaphthols are compared with that of 1,2-naphthoquinone. 1,2-Naphthoquinone, similar to the 1,4-quinones, shows a relatively low quinonoid band but it has two strong ketonic bands. In the spectra of the 1,2- and 2,1-diazonaphthols, the ketonic band appears with increased intensity ($\bar{\nu} = 2600$), a band occurs at $\bar{\nu} = 3700$ and there is only a large slope in the curves in the quinonoid region. Although this comparison might indicate that these diazo compounds are not quinonoid since the quinonoid band is not apparent, there is the possibility that the quinonoid band has been damped out, a phenomenon which is known to happen in a few other cases, *e. g.*, p-benzoquinonedioxime.[7]

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[1] The material presented in this paper constitutes a portion of a dissertation submitted by Milton John Roedel to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, June, 1940.

[2] Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 422.

[3] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1938, Vol. 3, p. 25.

[4] Saunders, "The Aromatic Diazo Compounds," Arnold and Co., London, 1936, p. 181.

[5] Hodgson and Marsden, *J. Soc. Dyers Colourists*, **59**, 271 (1943).

[6] Hantzsch and Lifschitz, *Ber.*, **45**, 3011 (1912).

[7] Anderson and Geiger, THIS JOURNAL, **54**, 3064 (1932).

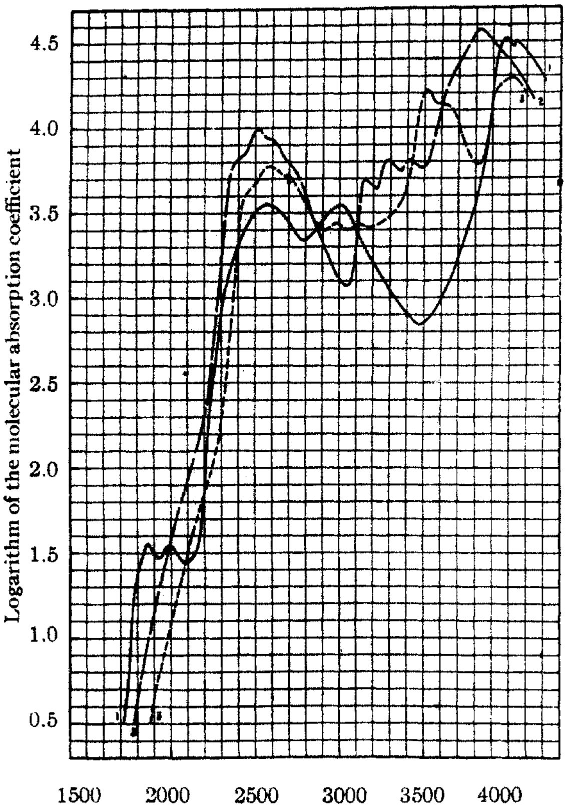

Fig. 2.—(1) 1,2-Naphthoquinone; (2) 2-diazonaphthol-1; (3) 1-diazonaphthol-2.

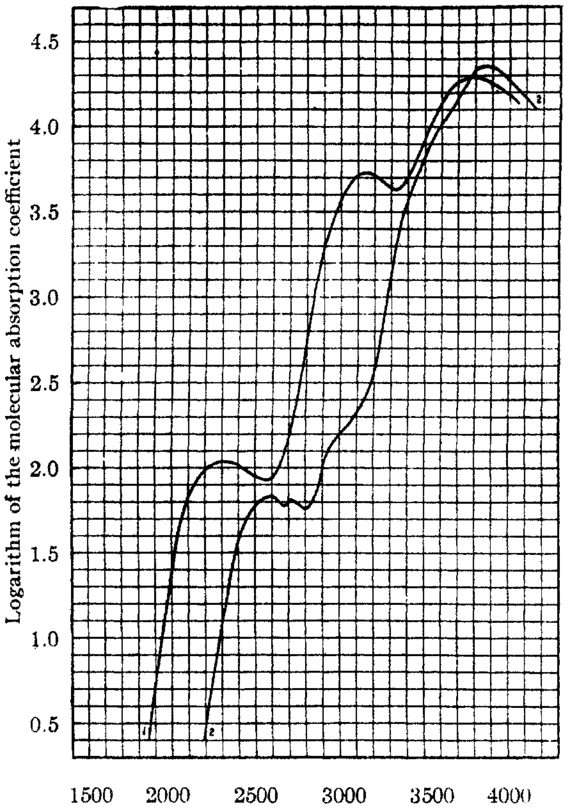

Fig. 3.—(1) Azibenzil; (2) benzil

In Fig. 3, the quantitative absorption spectrum curve of an ether solution of azibenzil may be compared with that of a corresponding solution of benzil for which a diketonic structure is generally accepted. The similarity of these curves leaves little doubt that azibenzil possesses the diketonic structure, a conclusion which is in accord with the accepted structure of the aliphatic diazoketones in general. The failure of the aliphatic 1,2-diazoketones to give a ring structure is very strong evidence against assigning a cyclic structure to the 1,2-diazonaphthols.

The absorption spectra of known cyclic compounds were ascertained and compared with the curves of the 1,2- and 2,1-diazonaphthols under investigation. Behaghel and Schneider[8] published the absorption spectrum curves for the cyclic series consisting of 2-methylbenzoxazole, 2-methylbenzthiazole and 2-methylbenziminazole. Their data show that when the oxygen atom in such cyclic compounds is replaced by a sulfur atom or an imino group, the absorption remains fundamentally the same. The absorption spectrum of the sulfur compound is nearest the infrared and the least intense, that for the oxygen compound nearest the ultraviolet and more intense, that for the imino compound in between the other two as regards frequency and the most intense. In Fig. 4 the curves are given for the quantitative absorption spectra of ether solutions of 2,1-diazonaphthol, 5,4-(1′,2′-naphtho)-1,2,3-thiadiazole and 5,-4-(1′,2′-naphtho)-1,2,3-triazole. According to the literature, the latter two compounds have a cyclic structure.[18,19,20] Examination of the curves shows that the sulfur and imino compounds compare to each other as would be expected, that is, the sulfur compound is less intense and nearer the infrared than the imino compound. However, the curve for the diazonaphthol fails to fall in place. It is shifted markedly toward the infrared instead of being the nearest to the ultraviolet and the band nearest the infrared is broader, more intense and fails to show the selectivity of the sulfur and imino compounds as would be expected if it were the cyclic analog of the sulfur and imino compounds. The curves for the 1,2- and 2,1-diazonaphthols, except for the absence of a definite band in the quinonoid region, are similar to the curves for quinonoid compounds and are very unlike those of cyclic compounds. The data indicate, therefore, that in ether solution, the structure of these ortho-diazonaphthols is not cyclic and a quinonoid structure is probably indicated.

The principal argument in favor of the cyclic structure cited by previous writers is the state-

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(8) Behaghel and Schneider, *Ber.*, **69**, 88 (1936).

ment by Morgan and Porter[9] that peridiazonaphthol resembles the diazophenols and that it is impossible to write a quinonoid structure for the peri-compound. However, when an attempt was made in the present investigation to obtain this compound so that its absorption spectrum could be ascertained, no mention of its preparation could be found in the literature. The references which Morgan and Porter give are to the preparation of peri-aminonaphthol or substituted peri-aminonaphthols. Apparently peridiazonaphthol has never been made despite repeated references to it as evidence for the cyclic structure. Our attempts at its preparation from peri-aminonaphthol gave no typical diazonaphthol but only, besides decomposition products, a compound which apparently was a coupled product of the 1-hydroxynaphthalene diazonium compound. The properties of the product are those of an inner salt; that is, it is only soluble in polar solvents and it decomposes at 250° without melting. When the diazonium group is replaced by a hydrogen atom or a hydroxyl group the salt-like characteristics disappear. This evidence leads to the conclusion that if the peri-diazonaphthol could be prepared it would possess the ionic inner salt structure and not the oxadiazole structure.

Experimental

p-Benzoquinonediazide.—Four grams of pure p-aminophenol hydrochloride was placed in 100 cc. of an absolute alcohol solution of hydrogen chloride and the mixture cooled to 0° with mechanical stirring. Four cc. of isoamyl nitrite was added and after the solution had been stirred for fifteen minutes, it was filtered by suction into 300 cc. of ether. The salt which precipitated was purified by dissolving it in cold absolute alcohol and reprecipitating it with cold ether. Clusters of small, colorless needles were obtained; yield, 75%.

p-Benzoquinonediazide has previously been prepared by Hantzsch and Davidson[10] in very poor yield by treating a saturated aqueous solution of the diazonium salt with silver oxide. We obtained much better yields by splitting off the hydrogen chloride in absolute alcohol, followed by precipitation of the diazide with cold ether.

The diazonium salt was dissolved in 100 cc. of absolute alcohol at 0°, a slight excess of silver oxide added and the mixture stirred mechanically for three hours at 0°, while protected from direct light. The silver chloride was then filtered off and the temperature kept at 0° while the alcoholic filtrate was concentrated to 25 cc. with a vigorous air blast. One hundred twenty-five cc. of ether was then added and the air blast continued until canary yellow needles precipitated out in clusters. The compound was quickly filtered off, redissolved in ether and reprecipitated by evaporation of the ether with the aid of the air blast. It was filtered by suction into a cold funnel and immediately placed in a dark bottle, previously cooled, and kept in a refrigerator. Even at 0° and in the absence of light there was noticeable decomposition after several weeks. The crystalline compound, according to Hantzsch and Davidson, contains four molecules of water; m. p. 38–39°.

1,4-Naphthoquinonediazide.—1,4-Aminonaphthol hydrochloride was made according to the directions in "Organic Syntheses"[11] by coupling α-naphthol with diazotized sulfanilic acid and reducing the azo compound with sodium hydrosulfite.

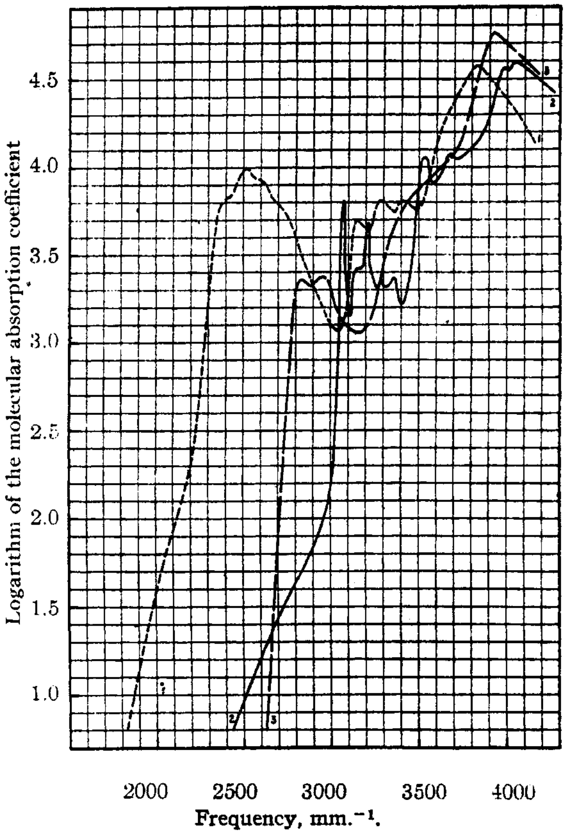

Fig. 4.—(1) 2-Diazonaphthol-1; (2) 5,4-(1',2'-naphtho)-1,2,3-triazole; (3) 5,4-(1',2'-naphtho)-1,2,3-thiadiazole.

Twelve grams of pure 1,4-aminonaphthol hydrochloride was made into a paste with 20 cc. of absolute alcohol and then 280 cc. of absolute alcohol containing dissolved hydrogen chloride added. The mixture was mechanically stirred and cooled to −5°, 8 cc. of isoamyl nitrite added and after five minutes the solution was filtered by suction into one liter of cold ether. The tan-colored diazonium salt thus obtained was filtered off and washed with ether; yield, 71%.

1,4-Naphthoquinonediazide was obtained by dissolving the diazonium salt in ice water, adding a slight excess of silver nitrate, filtering off the silver chloride and extracting the orange-colored solution with benzene. After the benzene was evaporated off at room temperature with an air blast, the residue was dissolved in a minimum amount of acetone and one and a half times its volume of petroleum ether (30–60°) was added. On standing at 0° dark orange octahedral crystals slowly formed; m. p. 123°.

Anal. Calcd. for $C_{10}H_6ON_2$: N, 16.5. Found: N, 16.5.

1,2-Naphthoquinonediazide-1.—2-Naphthol-1-diazonium chloride was prepared in the same manner as the 1,4-isomer by starting with β-naphthol instead of α-naphthol.

1,2-Naphthoquinonediazide-1 has been prepared previously by Bamberger[12] and others.[13] The following method in which an extraction is used is a modification of that used by Geigy and Co., who salted out the compound. The diazonium salt was dissolved in cold water, extracted with carbon tetrachloride and the extracts evaporated to dryness at room temperature with an air blast. The residue was dissolved in a minimum amount of ether and

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(9) Morgan and Porter, *J. Chem. Soc.*, **107**, 645 (1915).

(10) Hantzsch and Davidson, *Ber.*, **29**, 1522 (1896).

(11) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1937, Vol. 17, p. 9.

(12) Bamberger, *Ber.*, **27**, 680 (1894).

(13) Geigy and Co., German Patent 172,446; Vesely and Dvorak, *Bull. soc. chim.*, **33**, 319 (1923).

cooled to 0°. Dark red, octahedral crystals slowly formed; m. p. 95°.

1,2-Naphthoquinonediazide-2.—1,2-Chloronaphthylamine hydrochloride was prepared according to the directions of Morgan[14] by chlorinating aceto-β-naphthylamine and hydrolyzing off the acetyl group in alcoholic hydrogen chloride solution.

The following method for preparing 1,2-naphthoquinonediazide-2 is essentially the procedure used by Orton,[15] who, however, gave no specific instructions. Four grams of 1,2-chloronaphthylamine hydrochloride was added to 650 cc. of water containing 30 cc. of concentrated hydrochloric acid. The mixture was cooled to 0° with mechanical stirring and 1.4 g. of sodium nitrite dissolved in 50 cc. of water was added at once. The solution was stirred vigorously for one hour and filtered, after which 70 g. of sodium acetate was added and the solution kept in the dark at 0° for two days. The yellow needles, thus obtained, were filtered off in the absence of direct light and recrystallized from petroleum ether (30–60°). The diazide is stable at room temperature but is extremely sensitive to light; yield, 50%; m. p. 77°. When the corresponding 1-bromo-2-naphthalenediazonium chloride was treated with sodium acetate solution, the diazide precipitated out in a few minutes.

Azibenzil.—Benzil monohydrazone was prepared according to the directions of Ritter and Wiedeman[16] by treating benzil with 42% hydrazine hydrate; m. p. 151–152°. Azibenzil was then prepared according to the same authors by oxidizing the hydrazone with yellow mercuric oxide; m. p. 79°

1,2-Naphthoquinone.—This quinone was prepared according to the directions in "Organic Syntheses"[17] by oxidation of 1,2-amino-naphthol with ferric chloride; dec. 120°.

1,4-Naphthoquinone.—This compound was prepared according to the directions in "Organic Syntheses"[17] by oxidation of 1,4-amino-naphthol with chromic acid; m. p. 125°.

5,4-(1',2'-Naphtho)-1,2,3-thiadiazole.—This material was prepared according to the directions of Bamberger and Bocking[18] by heating a solid mixture of phosphorus pentasulfide with 1,2-naphthoquinonediazide-2; m. p. 89°; Bamberger and Bocking report 91–91.5° while Jacobson and Schwarz[19] report 89°.

5,4-(1',2'-Naphtho)-1,2,3-triazole.—This substance was prepared by a procedure similar to that of Diels.[20] Five grams of 1,2-diaminonaphthalene sulfate, prepared according to the directions of Bamberger and Schieffelin,[21] was decomposed with excess sodium carbonate solution and the 1,2-diamine filtered off and washed with water. The diamine was immediately transferred into a beaker with 40 cc. of water and 40 cc. of glacial acetic acid. The mixture was cooled to 0° and 1.5 g. of sodium nitrite dissolved in 20 cc. of water was added with vigorous stirring at the rate of one drop every five seconds. The triazole was filtered off, dissolved in dilute ammonia, filtered and the filtrate neutralized with dilute acetic acid. This mixture was boiled with a small amount of norite and after filtration and cooling, white needles precipitated out which, when dried, had a light gray appearance. The compound was obtained colorless by dissolving it in chloroform and precipitating it with petroleum ether (30–40°). After several recrystallizations from chloroform the compound melted at 185–186°. Diels reports 175–180°, while Fries, Walter and Schilling[22] report 188°.

Attempted Preparation of Peri-naphthoxadiazole.—Peri-aminonaphthol hydrochloride was prepared by modifying the procedure given in German Patent 62,289 taken out by Badische Anilin and Sodafabrik for the preparation of the sulfate. One hundred grams of peri-aminonaphthalenesulfonic acid was added slowly to a mixture of 150 g. of sodium hydroxide and 150 g. of potassium hydroxide at 200°. The mixture was heated for one hour at 200° and then for one hour at 250° with constant stirring. It was partially cooled and while still soft was transferred to a three-liter beaker. After the addition of 1000 g. of ice, 590 cc. of concentrated hydrochloric acid was added slowly and the mixture heated to boiling and filtered through a 1 cm. layer of norite. After cooling the filtrate, sodium carbonate was added in slight excess and the free base filtered by suction. This was treated with 40 cc. of concentrated hydrochloric acid and enough hot water to dissolve it, after which norite and 0.5 g. of stannous chloride were added and the hot mixture stirred and filtered. The resulting solution was cooled in an ice-bath and hydrogen chloride passed into it until precipitation was complete. The peri-aminonaphthol hydrochloride was filtered off, washed with a few cc. of cold hydrochloric acid and dried.

One gram of peri-aminonaphthol hydrochloride was placed in 100 cc. of an absolute alcohol solution of hydrogen chloride and cooled to 0°. One cc. of isoamyl nitrite was added and the solution stirred mechanically for thirty minutes, after which the mixture was filtered by suction into 600 cc. of ether. The dark gelatinous decomposition products were filtered off and the filtrate added to one liter of ether. The precipitate, thus obtained, was filtered and washed with ether. It had an orange color, gave no test for the chloride ion and charred at 250° without melting. It was insoluble in non-polar solvents and very soluble in polar solvents giving a dark red solution which turned yellow on addition of acids. The compound appeared to be a coupled product of peri-naphtholdiazonium compounds because neither α-naphthol nor peri-dihydroxynaphthalene could be isolated when the diazonium group was replaced with a hydrogen atom or a hydroxyl group but, instead, colored products were obtained which were soluble in non-polar solvents and decomposed above 200°. They melted when placed over a flame instead of charring like the original compound. In no experiment was the diazonium chloride obtained.

Summary

1. The quantitative absorption spectrum curves in the visible and ultraviolet region have been obtained for p-diazophenol, 1,4-diazonaphthol, 1,4-naphthoquinone, 1-diazonaphthol-2, 2-diazonaphthol-1, 1,2-naphthoquinone, 5,4-(1',2'-naphtho)-1,2,3-triazole, 5,4-(1',2'-naphtho)-1,2,3-thiadiazole, azibenzil and benzil.

2. The absorption spectra data indicate that in ether solution the para-diazophenols possess a quinonoid structure and that the ortho compounds are not cyclic and are probably quinonoid.

3. Substitution of a carbonyl oxygen in a quinone by a diazide group tends to give rise to four changes in the absorption spectrum: (a) a shift of the ketonic absorption toward the infrared; (b) an increase in intensity of absorption; (c) considerable loss in selectivity of the quinonoid band, especially in the case of the 1,2-naphthoquinonediazides; (d) a new band in the region $\bar{\nu} = 3600$.

4. Attempts to prepare peri-diazonaphthol were not successful.

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[14] Morgan, *J. Chem. Soc.*, **77**, 821 (1900).

[15] Orton, *Chem. News*, **87**, 21 (1903).

[16] Ritter and Wiedeman, THIS JOURNAL, **51**, 3584 (1929).

[17] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1937, Vol. 17, p. 69.

[18] Bamberger and Bocking, *J. prakt Chem.*, **105**, 260 (1923).

[19] Jacobson and Schwarz, *Ann.*, **277**, 260 (1893).

[20] Diels, *Ber.*, **54**, 226 (1921).

[21] Bamberger and Schieffelin, *ibid.*, **22**, 1376 (1899).

[22] Fries, Walter and Schilling, *Ann.*, **516**, 271 (1935).