range (250° up) on heating no analyses were made. The coronene recovered from this picrate by chromatographic adsorption on alumina was lighter in color than the original coronene but unchanged in melting point. The *sym*-trinitrobenzene derivative of coronene separated in bright orange needles from benzene but melted with decomposition over a wide range (280° up).

Summary

A new synthesis for coronene, VII, is described. The condensation of 3,4,3′,4′-tetrahydro-7,7′-dimethyl-1,1′-binaphthyl, II, with maleic anhydride yields a mixture of two isomers of 1,2,2a,3,4,4a,5,6-octahydro-9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, III, both of which are dehydrogenated by treatment with lead tetraacetate to 1,2,5,6-tetrahydro-9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, IV. On heating with palladium charcoal, IV is further dehydrogenated to a mixture of 9,12-dimethyldibenzo(c,g)phenanthrene-3,4-dicarboxylic anhydride, V, and 3-carboxy-9,12-dimethyldibenzo(c,g)phenanthrene, VI. The fusion of V and VI with potassium hydroxide at high temperatures yields coronene, VII.

A new method for the pinacolic reduction of 7-methyl-1-tetralone, I, is described.

Compounds V and VI are discussed with regard to the spatial location of their methyl groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Quantitative Hydrogenation of Substituted Azo Compounds with Raney Nickel at Normal Temperature and Pressure

BY W. F. WHITMORE AND A. J. REVUKAS[1]

Part I. Hydrogenation and Reductive Fission

The catalytic hydrogenation of azo compounds at normal temperature and pressure over Raney nickel[1a] is not only of scientific interest, but also of considerable practical value. Such a method of reduction is almost an ideal one to the dyestuff analyst, since his scission products are not contaminated with other reagents. In a previous paper[2] it was demonstrated that both the degree of purity and the structure of a number of typical azo food dyes could be simultaneously ascertained.

The quantitative hydrogenation of an additional number of azo compounds, with potentially reducible functional groups in the aromatic nucleus, has been investigated. In the earlier work[2] it was shown that the nuclear substituents $-CH_3$, $-NH_2$, $-OH$, $-COOH$, and $-SO_3Na$ remained unaffected under the conditions employed. In the present paper it will be demonstrated that of the substituents $-NO_2$, $-CHO$, $-COCH_3$, $-OCH_3$, and $-Cl$ in the azo compound, only the $-NO_2$ group is directly affected under the conditions of the hydrogenation. All of the azo compounds hereinafter mentioned were synthesized in the laboratory, since the commercially available products were often found to be of unreliable composition or purity. This publication describes a general procedure for their catalytic reduction, and the isolation and characterization of the scission products.

Experimental Work

Materials.—All of the starting materials were of the purest grade available, and were purchased from the Eastman Kodak Company. Good yields of relatively pure azo products were procured by employing the customary procedures of diazotization and coupling. All of the azo compounds so prepared were recrystallized at least three times from the proper solvent, and finally dried in a vacuum desiccator, to ensure complete purity, after which they were employed in the work to be described.

Hydrogenation Procedure.—The accurately weighed azo compound was carefully washed into the reductor bottle with 125 ml. of solvent (95% ethanol or peroxide free dioxane). Raney nickel was then added so that the ratio of catalyst to hydrogen acceptor (azo compound) was 3 g. for each 0.01 mole. The hydrogenations were carried out at room temperature and atmospheric pressure. The apparatus utilized in the reductions was the same as that reported previously.[3] In general, the scission products were isolated as amine hydrochlorides by first separating the catalyst on a Büchner funnel (solution neutral) in which there was a piece of dry-ice to retard atmospheric oxidation, and then passing dry hydrogen chloride into the filtrate, purifying, and characterizing the products obtained as later described.

(1) An abstract of a thesis submitted to the faculty of the Polytechnic Institute of Brooklyn by Mr. A. J. Revukas in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(1a) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(2) W. F. Whitmore and A. J. Revukas, *ibid.*, **59**, 1500 (1937).

(3) Whitmore and Revukas, *ibid.*, **59**, 1501 (1937).

TABLE I

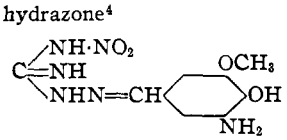
HYDROGENATION AND ANALYTICAL DATA

Hydrogen acceptor	Moles of sample	Moles of H_2	Time hr. min.	Products	Yield, %
(1) *p*-Nitrobenzeneazoresorcinol[a]	0.02	0.10	3:22	*p*-Phenylenediamine dihydrochloride[g]	97
				1,3,4-Tribenzoylaminoresorcinol	15
(2) *m*-Nitrobenzeneazosalicylic acid[b]	.02	.10	1:48	*p*-Aminosalicylic acid hydrochloride[h]	98
				m-Phenylenediamine dihydrochloride	55
(3) *p*-Nitrobenzeneazosalicylic acid[b]	.02	.10	1:48	*p*-Aminosalicylic acid hydrochloride[i]	98
				p-Phenylenediamine dihydrochloride	44
(4) *p*-Nitrobenzeneazo-*o*-nitrophenol[c]	.02	.16	2:48	*p*-Phenylenediamine dihydrochloride[j]	39
				2,4-Diaminophenol dihydrochloride	72
(5) *o*-Nitrobenzeneazo-β-naphthol[d]	.02	.10	3:25	2-Naphthol-1-amine hydrochloride[k]	74
				o-Phenylenediamine dihydrochloride	72
(6) *m*-Nitrobenzeneazo-β-naphthol[d]	.02	.10	2:12	2-Naphthol-1-amine hydrochloride[l]	77
				m-Phenylenediamine dihydrochloride	78
(7) *p*-Nitrobenzeneazo-β-naphthol[d]	.02	.10	2:04	2-Naphthol-1-amine hydrochloride[m]	69
				p-Phenylenediamine dihydrochloride	61
(8) 4-Methyl-2-nitrobenzeneazo-β-naphthol[b]	.05	.25	1:40	2,3-Diphenyl-6-methylquinoxaline[n]	61
				2-Naphthol-1-amine hydrochloride	51
(9) *o*-Chlorobenzeneazo-β-naphthol[d]	.03	.06	0:25	2-Naphthol-1-amine hydrochloride[o]	85
				o-Chloraniline hydrochloride	76
(10) *m*-Chlorobenzeneazo-β-naphthol[d]	.03	.06	0:18	2-Naphthol-1-amine hydrochloride[p]	85
				m-Chloraniline hydrochloride	61
(11) *p*-Chlorobenzeneazo-β-naphthol[d]	.03	.06	0:31	2-Naphthol-1-amine hydrochloride[q]	90
				p-Chloraniline hydrochloride	81
(12) β-Naphtholazobenzene-3-methyl-4-chloro-6-sodium sulfonate[e]	.03	.06	3:47	2-Naphthol-1-amine hydrochloride[r]	65
				2-Chloro-5-aminotoluene-4-sulfonic acid	90
(13) 2-Nitro-4-chlorobenzeneazo-β-naphthol[b]	.03	.15	2:41	2-Naphthol-1-amine hydrochloride[s]	51
				4-Chloro-*o*-phenylenediamine	77
(14) 3-Nitro-4-chlorobenzeneazo-β-naphthol[d]	.03	.15	2:46	2-Naphthol-1-amine hydrochloride[t]	56
				4-Chloro-*m*-phenylenediamine	84
(15) 4-Nitro-2-chlorobenzeneazo-β-naphthol[b]	.03	.15	9:36	2-Naphthol-1-amine hydrochloride[u]	72
				2-Chloro-*p*-phenylenediamine	66
(16) *p*-Acetophenoneazo-β-naphthol[b]	.02	.04	0:26	2-Naphthol-1-amine hydrochloride[v]	70
				p-Aminoacetophenone	74
(17) Benzeneazosalicylaldehyde[b]	.05	.10	3:21	Aniline hydrochloride[w]	32.5
				Brown resin	(3 g.)
(18) Benzeneazovanillin[b,f]	.03	.06	0:12	Nitroguanyl-5-aminovanillin hydrazone[x]	50
				Aniline hydrochloride	65
				Dark red resin	(1 g.)

[a] The solvent was absolute ethanol. [b] The solvent was 95% ethanol. [c] Peroxide free dioxane was the solvent. The hydrogenation time was only one hour when 95% ethanol was employed as solvent, but the isolation and separation of the catalyzates was unusually complicated. [d] The solvent was peroxide-free dioxane. [e] The solvent was distilled water. [f] When dioxane was used the hydrogenation required one hour. However, the tendency to form a Schiff base was minimized. [g] The catalyzates were extraordinarily sensitive to atmospheric oxidation. After separation of the catalyst and introduction of dry hydrogen chloride into the well-cooled filtrate a tan colored precipitate was obtained. It was identified as *p*-phenylenediamine dihydrochloride by treating a water solution of the product with freshly prepared saturated aqueous calcium hypochlorite and recrystallizing from 70% ethanol. The white needles of quinone dichloroimide melted at 127° with decomposition. The hydrogen chloride saturated filtrate was evaporated under reduced pressure on a water-bath to a sirupy consistency. Sufficient aqueous sodium hydroxide to give an alkaline reaction was added to the viscous blue-green liquid and followed by a slight excess of benzoyl chloride. After shaking vigorously, the pasty mass was sucked dry on a Büchner filter. The product was recrystallized several times from benzene–Skellysolve A. The tri-benzoyl derivative of 4-aminoresorcinol melted at 172°. [h] After passing hydrogen chloride into the hydrogenated solution a white crystalline precipitate formed. A half gram of this product was added to 3 ml. of water, made alkaline with sodium hydroxide and then shaken vigorously in the cold with a slight excess of acetic anhydride. The resulting precipitate which was recrystallized from water, melted at 218°. The compound was the N-acetyl derivative of 5-aminosalicylic acid. The hydrogen chloride saturated filtrate was evaporated at reduced pressure on the water-bath to incipient dryness. The black tarry residue was taken up with a little water, made slightly alkaline with sodium carbonate and finally extracted with ether. After drying the ether extract over anhyd. sodium sulfate, decanting, and passing in hydrogen chloride a grayish colored product was obtained. An aqueous alkaline solution of the substance was acetylated

in the cold. The white needle-like crystals, which formed after recrystallization from water, melted at 189°. They were the diacetyl derivative of *m*-phenylenediamine. [i] The isolation and identification of scission products was similar to that under (*h*). *p*-Phenylenediamine was identified by preparing dichloroquinoneimide as described under (*g*). [j] The solution of catalyzates was filtered into some hydrogen chloride saturated dioxane. More hydrogen chloride was introduced to ensure complete saturation. The lavender colored precipitate was filtered off and identified as *p*-phenylenediamine dihydrochloride as above. The acid filtrate was evaporated under reduced pressure on a water-bath. One gram of the dark brown residue was acetylated in cold aqueous slightly alkaline solution. The resulting substance was heated with Nuchar in glacial acetic acid, and finally absolute ethanol. The white needles resulting melted at 221–222°. They were N,N-diacetyl-2,4-diaminophenol. [k] After filtering the hydrogenated solution into hydrogen chloride saturated dioxane and then treating further with more hydrogen chloride, a mixture of amine hydrochlorides precipitated. These amine salts were laboriously separated by heating 2-g. portions with 50 ml. of water containing a pinch of sodium sulfite. 2-Naphthol-1-amine hydrochloride came out of solution upon cooling. This compound melted at 255° with decomposition. It was further characterized by acetylating in cold aqueous slightly alkaline solution with acetic anhydride. After recrystallization from 50% methanol the N-acetyl-2-naphthol-1-amine melted at 239°. The aqueous filtrates resulting from the separation of 2-naphthol-1-amine hydrochloride were combined, made alkaline with sodium carbonate, and extracted with ether. The ether extracts were dried over anhydrous sodium sulfate, decanted, and then saturated with hydrogen chloride. The grayish colored precipitate that formed was identified as *o*-phenylenediamine by benzoylating a portion, and then recrystallizing from glacial acetic acid. The 1,2-dibenzoylphenylenediamine melted at 303°. [l,m] The isolation procedure was the same as for (*k*). The cleavage products were characterized by means of derivatives already described. [n] The volume of solvent after hydrogenation was reduced to half by distilling off the alcohol in an atmosphere of hydrogen. A hot concentrated alcoholic solution containing 0.05 mole of benzil was added to the residual solvent plus catalyzates in the distillation flask, and then heated gently in a hydrogen atmosphere on the water-bath for thirty minutes. Water was added, after first cooling, until precipitation set in. The compound was separated on a Büchner filter and recrystallized from ethanol. 2,3-Diphenyl-6-methylquinoxaline melted at 111°. Hydrogen chloride was immediately passed into the first filtrate in order to isolate 2-naphthol-1-amine hydrochloride. The hydrogen chloride saturated solution had to be evaporated under reduced pressure on the water-bath and the residue recrystallized from 10% aqueous hydrogen chloride. [o] After saturation of the reduced solution with hydrogen chloride all of the 1-amino-2-naphthol, and some of the *o*-chloraniline precipitated. The method of separation of the mixed amine salts mentioned under (*k*) was employed. The hydrogen chloride saturated filtrate was subjected to distillation under reduced pressure. Sufficient water to just dissolve the residue was next added. The solution was made alkaline with sodium carbonate and then extracted with ether. After drying the combined ether extracts over anhydrous sodium sulfate, decanting, and passing in dry hydrogen chloride almost colorless crystals were deposited. They were benzoylated and recrystallized from dilute ethanol. The derivative was *o*-chlorobenzoylaniline, m. p. 99°. [p,q] The isolation and characterization procedures were the same as in (*o*). *m*-Chlorobenzoylaniline melted at 119° and *p*-chlorobenzoylaniline melted at 193°. Both derivatives were recrystallized from ethanol–water. [r] The hydrogenated solution was decanted into a separatory funnel, and extracted with ether. The spent catalyst was likewise washed with ether and finally with water. After drying well over anhydrous sodium sulfate the combined ether extracts were saturated with hydrogen chloride in order to form insoluble 2-naphthol-1-amine hydrochloride. The aqueous portion was heated to boiling with Nuchar and a little sodium sulfite. After filtration the colorless solution was acidified with dilute sulfuric acid, and some of the white fluffy product which precipitated was treated with just sufficient sodium carbonate solution to dissolve it. Bromine water was then added until no further decolorization occurred. The resulting compound was recrystallized from Skellysolve A (*n*-pentane). The small white needles melted at 99–100°. This derivative of 2-chloro-5-aminotoluene-4-sulfonic acid was 2,4-dibromo-6-chloro-3-aminotoluene. [s] The solvent was removed by evaporation under reduced pressure on the water-bath. Fifty ml. of water containing 0.04 mole of sodium hydroxide was added to the residue and warmed in an atmosphere of hydrogen. The solution was transferred rapidly to a separatory funnel and extracted with benzene. The dried benzene extract was heated with some Nuchar, filtered, cooled thoroughly, and Skellysolve A was added. The flaky compound that came down melted at 75°, and was 4-chloro-*o*-phenylenediamine. Its 1,2-dibenzoyl derivative melted at 230° after recrystallization from ethanol. The aqueous part of the catalyzate was saturated with hydrogen chloride in order to obtain 2-naphthol-1-amine hydrochloride. [t] The procedure was the same as in (*s*) except that chloroform was used to extract the 4-chloro-*m*-phenylenediamine. The chloroform extracts were dried, decanted, and evaporated to incipient dryness. The residue was recrystallized from Skellysolve A, and melted at 91°. After crystallization from benzene the dibenzoyl compound of 4-chloro-*m*-phenylenediamine melted at 178°. [u] The isolation and separation procedure of scission compounds was the same as in (*s*). The needle-like crystals that were thrown out of the benzene solution by adding Skellysolve A melted at 64°. They were characterized by preparing 1,4-diacetyl-2-chlorophenylenediamine, m. p. 197° after recrystallization from ethanol–toluene. [v] The solvent was removed by distillation at reduced pressure on the water-bath. After addition of 0.04 mole of sodium hydroxide in 50 ml. of water, the solution was extracted with ether. The anhydrous ether solution was evaporated to dryness and the residue was recrystallized from aqueous sodium carbonate. The compound melted at 106°. After acetylization with acetic anhydride the substance melted at 167°. The original product was *p*-aminoacetophenone. Hydrogen chloride was passed into the alkaline aqueous solution to form insoluble 2-naphthol-1-amine-

hydrochloride. [w] Some of the catalyzate was in the form of a brown insoluble resin-like solid, and this substance was insoluble in benzene, dioxane, acetone, and ethanol. It dissolved readily, however, in dilute aqueous sodium hydroxide forming a deep brown solution. When acetic acid was added to this solution the brown product reappeared. It melted considerably above 360°. To determine whether this was hydrolyzable one gram of the resin was refluxed for two hours with 10% hydrochloric acid. The insoluble material was removed by filtration. The filtrate was reheated with a little Nuchar and finally evaporated to incipient dryness. A little water was now added, followed by a slight excess of alkali and then some acetic anhydride. This solution was heated under reflux for thirty minutes, cooled, neutralized with sodium bicarbonate, and filtered. The insoluble material was recrystallized from water. It melted at 114° and was acetanilide. No other product was obtained from the hydrolysis of the resin. The initially filtered solution was evaporated on the water-bath and the remaining dark brown oil was taken up in anhydrous ether and saturated with hydrogen chloride. Aniline hydrochloride, m. p. 198°, was precipitated. [z] When the hydrogenation was performed in ethanol a small amount of an insoluble dark red resin was obtained, melting above 360°. There was little evidence of resin formation when the solvent employed was dioxane. A hot (90°) aqueous solution containing 3.6 g. (0.03 *M*) of nitroaminoguanidine and 1 ml. of glacial acetic acid was added to the filtered hydrogenated solution. Upon cooling, a yellow precipitate formed. It was recrystallized from 50% ethanol. The light yellow flaxlike compound melting at 223° with decomposition, was nitroguanyl-5-aminovanillin hydrazone[4]



Anal. Calcd. for $C_9H_{12}O_4N_6$: C, 40.27; H, 4.51. Found: C, 40.12; H, 4.49. The solution from which the nitroguanylhydrazone had been isolated was made alkaline and extracted with ether. After drying over anhydrous sodium sulfate the ether extract was saturated with hydrogen chloride to precipitate aniline hydrochloride, m. p. 198.

Discussion

Hydrogenation, accompanied by hydrogenolysis, of the nitrogen to nitrogen, and nitrogen to oxygen, bonds in nitro substituted azo compounds may be performed quantitatively and with facility at room temperature and 1 atmosphere pressure with the Raney nickel catalyst. The ready reaction of hydrogen with a number of functional groups has been discussed at some length by Adkins.[5] He has summarized the conditions as to catalyst, temperature, pressure of hydrogen, and solvent by which many of the functional groups may be hydrogenated or replaced by hydrogen. In the present investigation it has been demonstrated that only the —N=N— and the —NO_2 groups are directly affected under the conditions of the hydrogenation. With respect to the latter functional group, it was noted that the rate of reduction tended to decrease after the absorption of 2 moles of hydrogen. This quantity corresponds to the amount necessary for a cleavage of the —N=N— linkage. However, if the reaction is stopped at this point, no nitraniline is isolated, but only the ultimate scission products, and unreacted original compound. Apparently hydrogenation of the azo and nitro groups occurs almost simultaneously, or, in other words, the reaction does not proceed progressively. Adkins[6] reports that the reduction of nitro compounds at elevated temperature and pressure is so decidedly an exothermic reaction that considerable care must be exercised to prevent a rapid rise in temperature, and the possibility of decomposition occurring with almost explosive violence. In this investigation the maximum increase in temperature occurring during the reduction of a nitro substituted azo compound at 1 atmosphere amounted to 30°, and it became most apparent after 400 ml. of hydrogen had been consumed. It was also noted that chloro substituted azo compounds hydrogenated at a more rapid rate than those with a —NO_2 group in the nucleus. A glance at the table of hydrogenation data shows that of the three isomeric nitrobenzeneazo-β-naphthols the most readily reducible was the para isomer, 0.02 mole of which required two hours and four minutes for complete reduction. On the other hand, the para chloro-isomer, which was the most slowly reducible of the three isomeric chlorobenzene-azo-β-naphthols, required only thirty-one minutes for 0.03 mole. In other words, as between the chloro substituted, and the nitro substituted varieties the halogen compounds reduce much more readily. It should be noted, however, that this is true only in the absence of other functional groups. Another factor of interest affecting the rate of hydrogenation was the solvent. The ease of hydrogen absorption was invariably at least twice as great in ethanol as in dioxane for all of the compounds studied in this investigation. However, the accelerated rate is not always advan-

(4) W. F. Whitmore, A. J. Revukas and G. B. L. Smith, THIS JOURNAL, **57**, 706 (1935).

(5) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," The University of Wisconsin Press, Madison, Wisconsin, 1937.

(6) *Ibid.*, p. 96.

tageous since the particular solvent may unduly complicate the isolation of the scission products. For the conditions investigated an aldehyde group in an azo compound apparently is unaffected at normal temperature and pressure except for a tendency to form Schiff bases when the hydrogenolysis is carried out in ethanol. However, this difficulty may be largely obviated by employing a solvent like dioxane.

Böeseken and Cohen[7] have pointed out that aliphatic aromatic ketones yield pinacols by suitable methods of reduction, such as zinc and very dilute acid or the use of an alkaline solution. Delépine and Horeau[8] have reported that the presence of alkali enhances the activity of Raney nickel in the reduction of the carbonyl group. In our work with *p*-acetophenoneazo-β-naphthol, we have found that the —$COCH_3$ group remained unchanged, when the reduction was performed in ethanol, in the presence of 0.01 mole of sodium hydroxide in excess of that required by the phenolic —OH. The rate of reduction was accelerated, however, and required only half as long as without alkali. It is conceivable that the hydrogenation of the carbonyl group in *p*-acetophenoneazo-β-naphthol might succeed at a pressure of 3–4 atmospheres.

Although the chloro group in the azo compounds remained intact during reduction in a neutral solvent, it will be shown subsequently that dehalogenation is possible when the hydrogenation is performed in the presence of alkali.

Part II. Hydrogenation and Dehalogenation of Chloro Substituted Azo Compounds

The catalytic method of dehalogenation of organic compounds was introduced by Sabatier and Mailhe in 1904.[9] By passing a mixture of chlorobenzene vapors and hydrogen over reduced nickel at 160°, cyclohexane, without any chlorocyclohexane, was obtained. At 270°, however, only benzene and a little diphenyl were formed. Furthermore, the presence of substituents in the benzene nucleus facilitated the dehalogenation. Thus chlorotoluene and chlorophenol were reduced more readily than chlorobenzene, and amino derivatives in particular were especially susceptible to this type of reduction. For example, the chloranilines in the vapor phase at 270° yielded aniline hydrochloride, and the chloronitrobenzenes underwent simultaneous reduction and dehalogenation to aniline hydrochloride.

In 1917 Kelber[10] reported the quantitative dehalogenation of organic compounds over a nickel catalyst and at room temperature. He prepared his catalyst by heating basic nickel carbonate in a current of hydrogen at 310–320°. The dehalogenation was performed in aqueous alcohol solution in the presence of sufficient alkali to neutralize the hydrohalide acid formed. After separation of the catalyst by filtration, the halogen was estimated gravimetrically or by titration. Kelber's observations[11] indicated that the ease of halogen removal increased as the atomic weight became greater, and that aromatic compounds dehalogenated more readily than aliphatic types. Furthermore, when there were other substituents in the aromatic nucleus the para halogen was the most readily and the ortho the least readily removed.

Since the Raney nickel catalyst is characterized by its exceptional activity at normal temperature and pressure it is particularly suitable for the reduction of many types of organic compounds. This paper illustrates the application of Raney nickel to the simultaneous hydrogenation and dehalogenation of several chloro and nitrochloro-substituted azo compounds.

Experimental Section

Apparatus, Catalyst and Materials.—The apparatus, catalyst and materials were the same as mentioned previously. The 2-chloro-5-aminotoluene-4-sulfonic acid was a technical product, and was purified by dissolving in sodium carbonate solution, and heating to boiling with Nuchar. After filtering, the clear, colorless solution was acidified to congo red with dilute hydrochloric acid, and the resulting product was reprecipitated twice in the same manner before being finally filtered and washed on a Büchner funnel first with ethanol, and finally with petroleum ether. After drying in a vacuum desiccator, the product was a colorless impalpable powder. The alkali solution employed in the hydrogenations was 5 *M* alcoholic sodium hydroxide.

Hydrogenation and Dehalogenation Procedure.—The reagents were added to the reaction flask in the following sequence: 0.03 mole of hydrogen acceptor (the halogenated azo-compound), 125 ml. of solvent, catalyst (3 g. per 0.01 mole of sample), and then 2 equivalents (0.06 mole) of alkali, one for the —OH group in the azo compound, and the other to neutralize the hydrogen chloride formed by the reduction. In the hydrogenation of the nitrochloro-

(7) W. D. Böeseken and Cohen, *Koninkl. Akad. Wetenschappen Amsterdam*, **16**, 91 (1913).

(8) Delépine and Horeau, *Compt. rend.*, **201**, 1301 (1935); **202**, 995 (1936); *Bull. soc. chim.*, [5] **4**, 31 (1937).

(9) Sabatier and Mailhe, *Compt. rend.*, **138**, 245 (1904).

(10) C. Kelber, *Ber.*, **50**, 305 (1917).

(11) *Ibid.*, **54**, 2255 (1921).

TABLE II

HYDROGENATION AND ANALYTICAL DATA

Hydrogen acceptor	Moles H_2	Time hrs. min.	Products	Yield, %
o-Chlorobenzeneazo-β-naphthol	0.09	1:45	2-Naphthol-1-amine hydrochloride[b]	68
			Aniline hydrochloride[c]	91
m-Chlorobenzeneazo-β-naphthol	.09	1:56	2-Naphthol-1-amine hydrochloride[b]	53
			Aniline hydrochloride[c]	94
p-Chlorobenzeneazo-β-naphthol	.09	1:39	2-Naphthol-1-amine hydrochloride[b]	77
			Aniline hydrochloride[c]	93
β-Naphtholazobenzene-3-methyl-4-chloro-6-sodium sulfonate[a]	.09	2:44	2-Naphthol-1-amine hydrochloride[d]	51
			3-Toluidine-4-sulfonic acid[e]	92
2-Chloro-5-aminotoluene-4-sulfonic acid	.03	1:12	3-Toluidine-4-sulfonic acid[f]	96
2-Nitro-4-chlorobenzeneazo-β-naphthol[a]	.18	4:21	2-Naphthol-1-amine hydrochloride[g]	71
			o-Phenylenediamine dihydrochloride[h]	58
3-Nitro-4-chlorobenzeneazo-β-naphthol	.18	9:00	2-Naphthol-1-amine hydrochloride[g]	69
			m-Phenylenediamine dihydrochloride[h]	70
4-Nitro-2-chlorobenzeneazo-β-naphthol[a]	.18	3:21	2-Naphthol-1-amine hydrochloride[g]	76
			p-Phenylenediamine dihydrochloride[h]	73

[a] The dehalogenating part of the reduction was performed at 3 atmospheres absolute pressure since the hydrogenation occurred too slowly or not all at 1 atmosphere. [b] Since in all instances the reduction products were soluble in the solvent employed, the catalyst was separated rapidly from the solution by filtering through a Büchner funnel which contained some dry-ice to retard atmospheric oxidation of the catalyzates. The solvent was removed by distillation in an atmosphere of hydrogen, and the remaining oily residue was extracted with benzene to dissolve the aniline. A small volume of water was added to the residue, and this was treated with hydrogen chloride until 2-naphthol-1-amine hydrochloride was completely precipitated. [c] Hydrogen chloride was passed into the benzene solution to form aniline hydrochloride, m. p. 198°. [d] The filtered solution was transferred to a separatory funnel, acidified with 3.6 g. (0.06 mole) of glacial acetic acid, and then extracted with ether. After drying over anhydrous sodium sulfate, hydrogen chloride was passed into the ether extract to throw down 2-naphthol-1-amine hydrochloride. [e] The aqueous ether-extracted solution was acidified with sulfuric acid in order to precipitate insoluble 3-toluidine-4-sulfonic acid. The product was recrystallized from water, dried *in vacuo* at 90°, and then analyzed for sulfur content. Calcd. for $C_7H_7O_3NS$: S, 17.07. Found: S, 16.93, 16.91. [f] The filtered solution was acidified with dilute sulfuric acid to obtain white crystals of 3-toluidine-4-sulfonic acid. [g] The solvent was removed by distillation in an atmosphere of hydrogen, and the residue was extracted with ether. A small volume of water was added to the insoluble material which then dissolved; hydrogen chloride was passed in to form insoluble 2-naphthol-1-amine hydrochloride. [h] The ether extract was dried over anhydrous sodium sulfate, and then saturated with hydrogen chloride to precipitate the insoluble phenylenediamine dihydrochloride.

substituted azo compounds, it was found more expedient to add the alkali after the reduction of the —N=N— and —NO_2 groups, since the alkali tended to retard the hydrogenation. The reductions were performed at room temperature and atmospheric pressure unless otherwise specified. Distilled water was the solvent employed for β-naphtholazobenzene-3-methyl-4-chloro-6-sodium sulfonate and 2-chloro-5-aminotoluene-4-sulfonic acid. 95% ethanol was used for the other compounds. The catalyzates (reduction products) were isolated and identified in a manner similar to that previously described.

Discussion

The simultaneous hydrogenation and dehalogenation of chloro substituted azo compounds is conveniently accomplished at room temperature, and at pressures varying from 1–3 atmospheres. The procedure consists in dissolving the compound in alcohol or water, adding the catalyst, and sufficient alkali to combine with the halogen hydride formed during the reduction, and finally supplying hydrogen until the required amount has been consumed. When alkali is absent, the hydrogen acts only on the azo bond to produce the normal fission, and the halogen on the aromatic nucleus remains unaffected. It may be that in the absence of alkali, during the hydrogenation of a chlorosubstituted azo compound, the energy of activation is either too small for dehalogenation to occur, or perhaps immediately after the complete reduction of the azo group the first few molecules of hydrogen halide produced may react with the catalyst to form sufficient Ni^{++} ions to poison the catalyst, thus terminating the reduction. Reductive dehalogenation is exothermic because of the heat of neutralization. Although the chlorosubstituted azo compounds reduce easily at one atmosphere, the presence of other substituents in the same nucleus retards the rate of hydrogenation appreciably. For example, the presence of a nitro group may increase the time required five-fold or even longer, at one atmosphere, making reductions at this pressure

impractical. β-Naphtholazobenzene-3-methyl-4-chloro-6-sodium sulfonate undergoes only a hydrogenolysis, and does not give up its chlorine at one atmosphere pressure. Since steric hindrance does not seem to be involved, and since 2-chloro-5-aminotoluene-4-sulfonic acid, the diazonium component, dehalogenates quite readily at one atmosphere, the behavior of this particular azo compound is rather peculiar. However, if the removal of halogen from the same compound is attempted in the presence of a chemically equivalent amount of α-amino-β-naphthol, a higher hydrogen pressure must be employed to obtain dehalogenation.

Another point of interest is the fact that no dehalogenation occurs when dioxane is the solvent. This is generally true, and it is believed that failure to obtain dehalogenation when employing dioxane is due to the insolubility of the alkali which forms an emulsion with this solvent, and then coats the Raney nickel and renders it inactive. If sodium ethylate, which is soluble in dioxane, is employed as a substitute for the alkali, only a hydrogenolysis of the azo group occurs, and no dehalogenation. It would appear, therefore, as though hydroxyl ion is indispensable for a successful dehalogenation by this method.

The Raney nickel catalyst should prove useful in the quantitative dehalogenation of organic compounds both in synthetic and analytical work. The reductive procedure employing this catalyst eliminates many of the undesirable features of the well-known Carius method for halogen determination. For example, the long heating period, the possibility of contaminating the reaction products with fragments of glass, and the many hazards are entirely avoided. In addition, the catalytic method yields results that are within the usual limits of error, and provides two different criteria for quantitative evaluation. The volume of hydrogen consumed serves as one, and an estimation of the alkali halide formed serves as the second.

Summary

The catalytic hydrogenation and dehalogenation of substituted azo compounds with Raney nickel, at room temperature and from 1 to 3 atmospheres absolute pressure, has been demonstrated. These reactions occur quantitatively, the hydrogen adding to and cleaving the compounds with greater ease in ethanol than in dioxane. For dehalogenation to occur, the presence of a stoichiometrical equivalent of alkali is indispensable in order to neutralize the hydrogen halide formed. In the presence of other substituents in the same benzene nucleus, the removal of halogen proceeds best at 3 atmospheres absolute pressure. Dioxane is not a satisfactory solvent for catalytic dehalogenation. This general method of reduction, employing the Raney nickel catalyst, should prove to be a useful tool in the analysis and estimation of the azo dyestuffs.

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On the Nature of the Enzyme Tyrosinase. II

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One of the reasons why the phenolic oxidase, tyrosinase, has attracted attention is that it is supposed to catalyze two essentially different reactions: first, the oxidation of certain monohydric phenols by inserting a hydroxyl group ortho to the one already present, and, second, the oxidation of certain *o*-dihydric phenols to their corresponding *o*-quinones. *p*-Cresol and catechol have been used quite generally as substrates in the study of these two enzymic activities, which will therefore be referred to as cresolase and catecholase activities.

One of the convenient sources for tyrosinase is the common mushroom, *Psalliota campestris*. When a water extract of the ground mushroom is permitted to stand exposed to air, it darkens and gradually loses enzymic activity. This loss in activity also occurs when the enzyme in the water extract is purified by the usual methods, such as precipitation by cold acetone, ammonium sulfate, dialysis, etc. On comparing the losses of the two activities, it is found that the loss of cresolase activity is greater than that of the catecholase activity. In fact, often the major portion of the cresolase activity is lost. This loss in the latter activity, as the purification pro-