to be avoided. Since these reactions are probably of a relatively high kinetic order,[24] the pH below which their interference would be important must depend on the concentrations of aldehyde and chlorite, and hence on the initial concentrations of amine and chlorine dioxide; the higher the reactant concentrations, the higher this pH. For example, the spectrophotometric kinetic experiments with 10^{-4} *M* chlorine dioxide were carried out successfully even at pH 4.7. By contrast, the attempt to measure the stoichiometry of the reaction titrimetrically at pH 6.2, with initial concentrations of 0.013 *M* chlorine dioxide and 0.0035 *M* triethylamine, gave a final ratio of chlorine dioxide used to triethylamine taken of only about 1.5 instead of 2. High concentrations of reactants were required by the titrimetric procedure, which also required that each sample be titrated immediately. The low pH and temperature were necessary to slow the reaction to a rate at which a sufficient number of samples could be withdrawn and titrated.

The reaction of chlorine dioxide with triethylamine was so rapid that there was no need to go to very high pH levels for the purpose of reaching convenient reaction times. With diethylamine, or more especially with even less reactive amines, the pH levels needed for sufficiently fast reaction (*i.e.*, above 10) might require consideration of the chlorine dioxide disproportionation to form chlorite and chlorate.[7,8]

Acknowledgment.—The authors are indebted to Mr. Raymond C. Roy for technical assistance in measuring acid production and to Mr. Joseph Epstein and Dr. George T. Davis for their stimulating discussion and encouragement of this investigation.

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Reactions of Indole. IV.[1] The Synthesis of Some Aminoindoles

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A procedure for the convenient preparation of 5-aminoindole-3-acetic acid in practical yield is described. This method, employing indoline intermediates, also was used to prepare 5-aminoindole-3-propionic acid as well as 5-amino-, 6-amino-, and 7-aminoindole.

Although investigation of the chemistry of indole is one of the oldest and most intriguing of chemical problems, the preparation of benzene-substituted indole derivatives still remains, by and large, a formidable synthetic effort. Acid-catalyzed substitution reactions on indole derivatives containing only 3-substituents in the pyrrole ring, in general, are prohibited by the acid lability of the indole nucleus, and in those cases where these reactions are possible (*i.e.*, with gramine,[2] 3-carbethoxyindole,[3,4] and indole-3-aldehyde[3-5]), the substituent orientation and the remaining functionality are not always the most desired. Ready access to 3-indoleacetic[6] and propionic acids[1,7] as well as other 3-indolealkanoic acids[8] has provided the impetus to investigate synthetic schemes that might be expected to provide various benzene-substituted derivatives of these acids. Additionally, the carboxyl group would allow for a considerable variety of other transformations. This communication describes general procedures by which 5-, 6-, and 7-aminoindole derivatives may be conveniently prepared.

Indoline and its derivatives may be considered as substituted anilines and, accordingly, aromatic substitution reactions that are applicable to aniline systems should also be useful for the derivatization of indolines. Thus, it is possible to postulate a synthetic sequence whereby: (1) a given indole is hydrogenated to the corresponding indoline; (2) the desired aromatic substitution reaction is performed; and, finally, (3) the indole derivative is recovered by dehydrogenation of the substituted indoline.[9] Chart I illustrates the preparation of 5- and 7-aminoindole derivatives *via* this route and in this manner it was possible to prepare 5-aminoindole-3-acetic acid in *ca.* 50% over-all yield.

A number of aminoindole derivatives have been prepared.[10] The preparations, in general, were made using the classic Fischer indole synthesis on the corresponding nitrophenylhydrazones followed by a reduction to the amine. Low yields invariably were experienced and the desired product was only one of several encountered in the reaction mixture. Of the simple aminoindoles, the preparation of the 6-isomer was reported in 1930,[11] although its identification was not confirmed until 1953 when Brown and Nelson[12] obtained it as a crystalline substance. Both the 4-[13] and 5-[14] isomers were prepared soon after; 7-aminoindole apparently has not been reported. 6-Aminoindole-3-acetic acid is known[15] and derivatives of 5-aminoindole-3-acetic and propionic acids recently have been synthesized.[16]

(1) Part III, H. E. Johnson and D. G. Crosby, *J. Org. Chem.*, **28**, 2030 (1963).

(2) G. Berti and A. Da Settimo, *Gazz. chim. ital.*, **90**, 525 (1960); *Chem. Abstr.*, **55**, 14455*g* (1961).

(3) R. Majima and M. Kotake, *Ber.*, **63**, 2237 (1930).

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(5) W. E. Noland and R. D. Rieke, *J. Org. Chem.*, **27**, 2250 (1962); G. Berti and A. Da Settimo, *Gazz. chim. ital.*, **91**, 728 (1961); *Chem. Abstr.*, **56**, 1154*i* (1962).

(6) H. E. Johnson and D. G. Crosby, *J. Org. Chem.*, **28**, 1246 (1963).

(7) H. E. Johnson and D. G. Crosby, *ibid.*, **25**, 569 (1960).

(8) H. E. Fritz, *ibid.*, **28**, 1384 (1963).

(9) During the course of this work Terent'ev, *et al.* [see *Zh. Obshch. Khim.*, **30**, 1218 (1960); *Chem. Abstr.*, **55**, 511c (1961), for leading references] reported the first of a series of papers utilizing this sequence for the preparation of various benzene-substituted indoles. T. Kinoshita, H. Inoue, and E. Imoto, *Nippon Kagaku Zasshi*, **78**, 1372 (1957); *Chem. Abstr.*, **54**, 491*i* (1960), also have reported this route.

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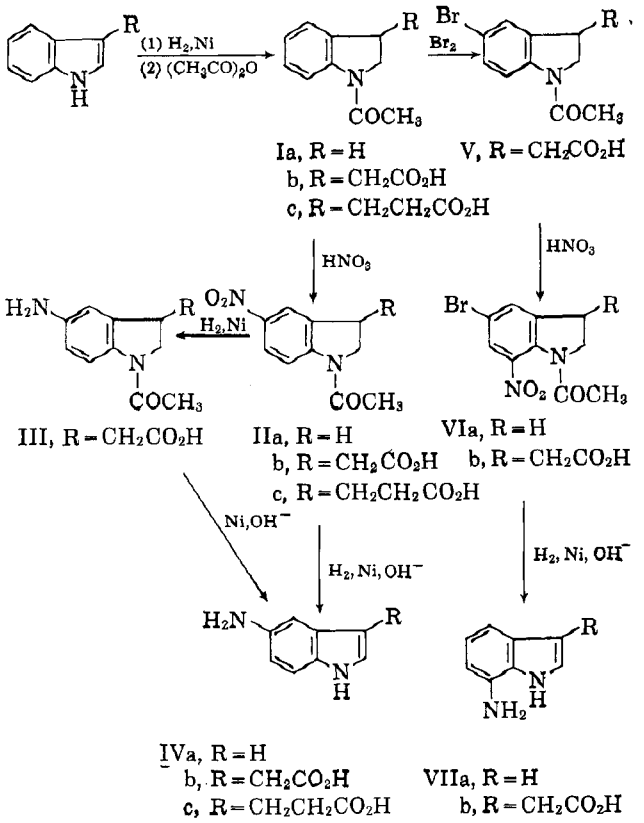
CHART I



In the present investigation potassium indoleacetate was reduced with hydrogen over Raney nickel at about 100° to the corresponding indoline. The reaction was found to be critically temperature dependent over a quite narrow range; higher temperatures resulted in "over-reduction" and slightly lower temperatures were not sufficient to cause a reduction. Treatment of the crude reaction mixture with acetic anhydride resulted in the precipitation of N-acetylindoline-3-acetic acid (Ib) in yields exceeding 70%. Attempts to isolate the free acid (nonacylated) were without success.[17] Nitration of Ib proceeded without incident to provide an 80% yield of 5-nitro derivative IIb. As expected, Ib also could be converted readily to the 5-bromo- (98%) and 5-bromo-7-nitro- (87%) derivatives, and IIb to the amino acid III (~100%). Attempts to prepare the 5-fluoro derivative by the reaction of V with potassium fluoride[18] were not successful.

N-Acetyl-5-aminoindoline-3-acetic acid (III) was converted smoothly to 5-aminoindole-3-acetic acid (IVb) by refluxing an alkaline solution of this material in the presence of Raney nickel catalyst.[19] Later, it was found that the corresponding nitro compound IIb could be converted directly to the amino acid IVb in 93% yield by simultaneous dehydrogenation and reduction.[20] Neither IIb nor V could be converted to the corresponding 5-substituted indoleacetic acids. The nitro derivative IIb was invariably partially reduced, even in the presence of a large excess of nitrobenzene or maleic acid, and the bromine of V was always removed. In fact, it was found possible to terminate this reaction at a time when N-acetylindoline-3-acetic acid (Ia) was the only isolable product. The action of chloranil on IIb and V under a variety of conditions produced none of the desired 5-substituted derivatives.

The facile removal of nuclear bromide from V suggested that this reaction might be useful in the preparation of 7-aminoindole-3-acetic acid (VIIb). Nitration of V provided an 87% yield of a presumed mixture of nitro derivatives, assumed to consist predominantly of N-acetyl-5-bromo-7-nitroindoline-3-acetic acid (VIb). Treatment of VIb with Raney nickel and base as described for IIb did not lead to the isolation of 7-aminoindole-3-acetic acid (VIIb). The 7-amino isomer did not conform to the ready isolation experienced for the 5-isomer IVb and, disappointingly, the corresponding benzamide derivative could be isolated in only 25–38% yield *via* benzoylation of the reaction mixture. Attempts to obtain pure VIIb by hydrolysis of the benzamide were not successful as the free amino acid oxidized readily and was always accompanied by insoluble dark oxidation products. The possibility that the benzamide of VIIb is a 4-aminoindole-3-acetic acid derivative is considered unlikely since, in the unsubstituted series Ia, etc., VIIa is obtained which is different from 4-amino indole.[13]

Application of these series of reactions to the preparation of 5-aminoindole-3-propionic acid and of 5-, 6-, and 7-aminoindole produced these materials in about 85, 54, 43, and 49% yield, respectively, based on the corresponding nitro- and nitrobromoindolines. Although the strikingly high yields of the simple aminoindoles were not obtained, as was observed in the preparation of the aminoindole acids, in all cases the aminoindole precipitated in very high purity upon cooling the filtered, strongly basic reaction mixture. The use of Raney nickel alloy for this conversion was found to be more efficacious than Raney nickel catalyst. 5- and 6-Aminoindole were also prepared by heating the corresponding aminoindolines with a catalytic quantity of palladium on carbon.

Experimental

Melting points are corrected and boiling points are uncorrected. Except where noted, purification of intermediate reaction products is optional.

N-Acetylindoline-3-acetic Acid (Ib).—A quantity of 234 g. (2.0 moles) of indole, 240 g. (2.2 moles) of 70% aqueous glycolic acid, and 180 g. (2.7 moles) of 85% potassium hydroxide was charged to a 3-l. stainless steel rocking autoclave and heated at 250° for about 20 hr.[1] The autoclave was cooled and 700 ml. of water and 100 g. of wet Raney nickel catalyst added. Hydrogen pressure was adjusted to 1000 p.s.i. and the mixture rocked at about 100° until the theoretical amount of hydrogen was absorbed (4–24 hr.). After cooling the contents, they were filtered to remove the catalyst and 816 g. (8 moles) of acetic anhydride was added. An oil precipitated that readily solidified and was collected after a reaction time of 3 hr. at about room temperature. A total of 612 g. (70%) of solids was collected, m.p. 169–172°. Additional material could be obtained by acidification of the reaction mixture but was of poorer quality. An analytical sample was obtained as colorless needles, m.p. 170–172°, after several crystallizations from ethanol.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.83; H, 5.88; N, 6.25.

5-Nitro-N-acetylindoline-3-acetic Acid (IIb).—To 22 g. (0.1 mole) of N-acetylindoline-3-acetic acid in 300 ml. of acetic acid was added 150 ml. of fuming nitric acid at about 15°. The

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(20) Best results were obtained by using Raney nickel catalyst in a quantity sufficient to supply the required hydrogen.

mixture was allowed to warm to 25° over a 1-hr. period and was then poured over 700 g. of ice. When all of the ice had melted the product was collected to give 20 g. (77%) of light yellow solids, m.p. 206–208°. An analytical sample, m.p. 208–209, was obtained as light yellow crystals by crystallization from ethyl acetate.

Anal. Calcd. for $C_{12}H_{12}N_2O_5$: C, 54.54; H, 4.58; N, 10.60. Found: C, 54.64; H, 5.00; N, 10.50.

5-Amino-N-acetylindoline-3-acetic Acid (III).—A mixture of 20 g. (0.076 mole) of 5-nitro-N-acetylindoline-3-acetic acid, 75 ml. of water, 75 ml. of ethanol, and 10 g. of Raney nickel catalyst was shaken under 38 p.s.i. of hydrogen for 3 hr. The catalyst was removed by filtration and washed well with hot water. Evaporation of the filtrate gave 18 g. (100%) of light brown solids, m.p. 188–194°. Crystallization from ethanol afforded an analytical sample as colorless crystals, m.p. 192.5–194°.

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.62; H, 6.44; N, 11.74.

5-Aminoindole-3-acetic Acid (IVb).—To a solution of 93 g. (0.353 mole) of 5-nitro-N-acetylindoline-3-acetic acid in 1160 ml. of water containing 75 g. of sodium hydroxide was added, in portions, 350 g. of wet Raney nickel catalyst keeping the temperature at about 20°. The mixture was heated slowly to boiling and refluxed for a total of 16 hr. After removal of the catalyst, 117 ml. of acetic acid was added (pH 5.5) and the precipitated product collected. The filter cake was washed well with water, ethanol, and ether and dried to give 69 g. (93% as the monohydrate) of light gray flakes, m.p. 242–244° dec. A sample was purified by dissolving it in sodium hydroxide solution, filtering to remove any insoluble impurities, and reprecipitating with acetic acid to yield light gray microcrystals, m.p. 242–243° dec.

Anal. Calcd. for $C_{10}H_{10}N_2O_2 \cdot H_2O$: C, 57.68; H, 5.61; N, 13.46. Found: C, 57.82; H, 5.67; N, 13.22.

An anhydrous sample was obtained by dissolution in hot dimethylformamide followed by precipitation with ethanol. A light brown solid was obtained, m.p. 240–242° dec.

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.75; H, 5.59; N, 14.72.

The benzamide of IVb was prepared in the usual way using benzoyl chloride and was obtained as light tan needles, m.p. 186–188°, after several crystallizations from aqueous ethanol.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 69.37; H, 4.80; N, 9.52. Found: C, 69.59; H, 4.91; N, 9.36.

The ethyl carbamate of IVb was prepared by the action of ethyl chloroformate and was obtained as long light tan needles, m.p. 145–147°, after several crystallizations from water.

Anal. Calcd. for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.50; H, 5.24; N, 10.80.

5-Bromo-N-acetylindoline-3-acetic Acid (V).—To a slurry of 105 g. (0.45 mole) of N-acetylindoline-3-acetic acid in 500 ml. of acetic acid was added a solution of 80 g. (0.5 mole) of bromine in 250 ml. of acetic acid over a period of 20 min. at 25°. After stirring the mixture an additional 30 min. at 25° it was added to 3 l. of water. The precipitated solids were collected and dried to give 142 g. (98%) of product, m.p. 191–195°. Several crystallizations from isopropyl alcohol gave an analytical sample as fine, nearly colorless needles, m.p. 199–200°.

Anal. Calcd. for $C_{12}H_{12}BrNO_3$: Br, 26.82. Found: Br, 26.78.

5-Bromo-7-nitro-N-acetylindoline-3-acetic Acid (VIb).—Thirteen grams (0.044 mole) of the bromoindoline V in 100 ml. of acetic acid was treated with 50 ml. of fuming nitric acid over a 10-min. period at 15°. The mixture was stirred at 15° for an additional 1 hr. and then poured over 600 g. of ice. The precipitate was collected by filtration and dried to give 13 g. (87%) of product as a bright yellow solid, m.p. 175–177°. Repeated crystallizations from ethanol (slow) raised the melting point to 190–192°. Using a slight stoichiometric excess of nitric acid did not change the quality of the crude reaction product.

Anal. Calcd. for $C_{12}H_{11}BrN_2O_5$: C, 42.02; H, 3.23; N, 8.17. Found: C, 42.00; H, 3.33; N, 8.13.

7-Benzamidoindole-3-acetic Acid.—A mixture of 3.43 g. (0.01 mole) of the bromonitroindoline VIb (m.p. 190–192°) and 30 g. of Raney nickel catalyst in 100 ml. of water containing 16 g. (0.4 mole) of sodium hydroxide was heated under reflux for 1 hr. After cooling the mixture the catalyst was removed by filtration and 14 g. (0.1 mole) of benzoyl chloride added at 0–5°. When all of benzoyl chloride had reacted, the mixture was acidified and the solids collected. The solids were washed several times with hot water and dried to give 6.0 g. of gray solids, m.p. 118–162°. Crystallization from xylene removed the benzoic acid present and resulted in 0.72 g. (38%) of light gray needles, m.p. 217–220°. Further crystallization from the same solvent changed the melting point to 219–220°. Scaled-up preparations resulted in greatly decreased yields of the benzamide.

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.37; H, 4.80; N, 9.52. Found: C, 69.38; H, 4.99; N, 9.80.

5-Nitro-N-acetylindoline-3-propionic Acid (IIc).—To a mixture of 23.3 g. (0.1 mole) of N-acetylindoline-3-propionic acid[19] in 200 ml. of acetic acid was added 50 ml. of fuming nitric acid at about 15°. After stirring the mixture an additional 30 min. it was poured over 700 g. of ice, and the product collected to give 25 g. (90%) of light yellow solids, m.p. 165–167°. Several crystallizations from ethyl acetate produced an analytical sample as light yellow needles, m.p. 167–168°.

Anal. Calcd. for $C_{12}H_{14}N_2O_5$: C, 56.11; H, 5.07; N, 10.07. Found: C, 56.24; H, 4.98; N, 9.56.

5-Aminoindole-3-propionic Acid (IVc).—To a solution of 52 g. of N-acetyl-5-nitroindoline-3-propionic acid in 500 ml. of water containing 40 g. of sodium hydroxide was added 150 g. of wet Raney nickel catalyst in portions, keeping the temperature at about 20°. The mixture was then refluxed for a total of 19 hr., cooled, filtered, and adjusted to neutral pH with 64 ml. of acetic acid. The precipitated product was collected to give 33 g. (85%) of light gray solids, m.p. 204–212°. An analytical sample, m.p. 207–209°, was prepared by reprecipitation from an alkaline solution and was obtained as the hemihydrate.

Anal. Calcd. for $C_{11}H_{12}N_2O_2 \cdot 0.5H_2O$: C, 61.96; H, 6.15; N, 13.14. Found: C, 62.16; H, 6.21; N, 13.41.

The benzamide of IVc was prepared in the usual way with benzoyl chloride and was obtained as light tan clusters of needles, m.p. 189–190°, after several crystallizations from aqueous alcohol.

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09. Found: C, 70.09; H, 5.31; N, 9.01.

The ethyl carbamate of IVc was prepared from ethyl chloroformate and was obtained as light tan needles, m.p. 158–160°, after several crystallizations from water.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.91; H, 5.88; N, 10.08.

5-Aminoindole (IVa). A. From IIa.—A mixture of 5 g. of 5-nitro-N-acetylindoline (IIa),[21] 50 ml. of water containing 5 g. of sodium hydroxide, and 20 g. of wet Raney nickel catalyst was refluxed a total of 4 hr. and then filtered while still hot. Upon cooling the filtrate, 1.7 g. (53%) of nearly colorless short needles precipitated, m.p. 129–130°. A sample was crystallized from water and was obtained as short tan needles, m.p. 130–131.5° (lit. m.p. 129–130°,[4] 127–129°[22]).

B. From 5-Aminoindoline.—A mixture of 99 g. of 5-aminoindoline[22] and 0.70 g. of 10% palladium on carbon was heated over a period of 2 hr. to 190° at which point hydrogen evolution had nearly ceased. Vacuum was applied to the system and the mixture was distilled. A total of 54 g. (56%) of product was obtained, b.p. 173–182° (5.0 mm.), m.p. 126–131°.

6-Aminoindole. A. From 6-Nitroindoline.—A mixture of 5.0 g. (0.031 mole) of 6-nitroindoline,[22] 75 ml. of water, and 20 g. of Raney nickel alloy was heated under reflux and a solution of 30 g. of sodium hydroxide in 100 ml. of water slowly added. After stirring the mixture an additional 30 min. it was filtered while hot to remove the nickel. Upon cooling the filtrate, 1.7 g. (43%) of product precipitated and was obtained as colorless needles, m.p. 64–67° (lit.[12] m.p. 66–67°).

B. From 6-Aminoindoline.—A 26.4-g. quantity of 6-aminoindoline[22] was converted to 19 g. (73%) of 6-aminoindole, b.p. 161–166° (2.25 mm.), m.p. 52–57°, by the procedure described for the dehydrogenation of 5-aminoindoline.

7-Aminoindole (VIIa).—A mixture of 8 g. (0.028 mole) of 5-bromo-7-nitro-N-acetylindoline (VIa),[21] 75 ml. of water, and 20 g. of Raney nickel alloy was treated with a solution of 40 g. of sodium hydroxide in 100 ml. of water as described in part A for the synthesis of 6-aminoindole. A 1.8-g. (49%) quantity of nearly colorless crystalline product was obtained, m.p. 95–97°

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(22) A. P. Terent'ev, M. N. Preobrazhenskaya, A. S. Bobkov, and G. M. Sorokina, *J. Gen. Chem. USSR*, **29**, 2504 (1959).

An analytical sample, m.p. 99–101°, was obtained as light gray prisms after several crystallizations from isopropyl ether.

Anal. Calcd. for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.65; H, 6.38; N, 21.26.

The benzamide of 7-aminoindole was prepared from benzoyl chloride and was obtained as flat off-white needles, m.p. 217–218°, after three crystallizations from ethanol.

Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.43; H, 5.30; N, 11.73.

Acknowledgment.—The authors are grateful to C. R. McClure for capable assistance and to Q. Quick and his associates for microanalyses and spectral data.

The Reduction of 2-Indanone Oxime to 2-Aminoindane. Methods and Mechanisms

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Several methods are described for the reduction, in high yield, of 2-indanone oxime (I) to 2-aminoindane (III), a conversion previously considered to be difficult. A study of the variables has been made of the nickel hydrogenation and the palladium hydrogenation. The data from various reductions, including the isolation of several by-products, have permitted speculation on the mechanism of reduction. A novel isomerization of 2-indanone oxime (I) to 2-amino-1-indanone (V) has been observed.

The conversion of 2-indanone oxime (I) to 2-aminoindane (III) has been considered to be a difficult reduction. Attempted reduction with sodium amalgam in acetic acid gave[1] only a small amount of III, and hydrogenation with palladium on charcoal in ethanolic hydrogen chloride reportedly failed completely.[2,3] Catalytic hydrogenation of I with platinum oxide in alcohol has been reported[4] to give diindanylamine (II), although no yield was specified. Until now, the only satisfactory method for conversion of I to III has required the use of specially prepared palladium catalysts.[2] Unfortunately, "these catalysts are extremely active, sensitive, and pyrophoric and care must be used in working with them."[2] In our studies of the preparation of 2-aminoindane hydrochloride, a nonnarcotic analgesic,[5] we investigated the reduction of the oxime (I) of 2-indanone[6] in detail in order to find a safer, more convenient, and less expensive method. Several such satisfactory reduction procedures are reported, together with a study of the variables in the palladium and in the nickel reductions. The results of the reduction studies permit speculation on the mechanisms involved in the reductions.

Attempts at chemical reduction, using methods which had been applied successfully to reductions of other oximes or of nitro compounds to their corresponding amines, were largely unsuccessful. Ferrous sulfate in aqueous ethanolic sodium hydroxide[7] (25°, 2 days) left I completely unchanged, whereas iron powder in aqueous ethanolic acetic acid[8] (reflux, 6 hours) gave a small amount of III. Zinc and acetic acid[9] (40–45°, 20 hours) gave 90–95% recovered oxime plus a trace of III. Clemmenson reduction conditions (zinc amalgam, concentrated hydrochloric acid, reflux, 22 hours) gave 2% III and 68% crude indane. Sodium borohydride in aqueous methanol, either with or without added 10% palladium on charcoal,[10] gave back starting I. Reduction of I with a two molar quantity of lithium aluminum hydride[11] in ethyl ether (reflux, 2 hours) gave a 45% yield of crude III hydrochloride. Stannous chloride and hydrochloric acid[12] (reflux, 6 hours) gave recovered I plus *ca.* 9% 2-amino-1-indanone (V), isolated as the hydrochloride salt. The conversion of I to V, which caused skin, wood, and fabric to turn "shocking pink," is discussed in connection with palladium–methanolic hydrogen chloride reduction. Addition of a solution of I in aqueous potassium hydroxide to a suspension of nickel–aluminum alloy in aqueous methanol[13] gave a 75% yield of III, when isolated as the hydrochloride salt.

Oximes are known to react with hydrogen in the presence of nickel catalysts, but the proportions of primary and secondary amine products can vary widely.[14] The general usefulness of Raney nickel for *low pressure* hydrogenation of aliphatic oximes has been reported,[15] but the method has not been applied widely. Experiments using active nickel catalyst for low pressure hydrogenation of I are listed in Table I. Yields from the reduction of I in neutral or acidic solution were poor even at elevated temperatures and pressures. When the residue from the mother liquor of III hydrochloride from reduction of I with nickel in acetic acid was slurried with a small amount of methylene chloride, some diindanylamine (II) hydrochloride was isolated directly as an insoluble white solid, m.p. 299–302°.

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