gave crude 2-benzeneazonaphthalene, m.p. 77–80°. Crystallization from 70% ethanol gave a 19% yield of product with m.p. 82–83° (lit.,[17] m.p. 84°). The phenylhydroxylamine was prepared from nitrobenzene.[18]

1-Phenyl-2-β-naphthylhydrazine was prepared by the reduction of 2-benzeneazonaphthalene in alcohol solution with aqueous ammonium chloride and zinc. The hydrazo compound was isolated as described earlier for 2,2′-hydrazonaphthalene.[8] The slightly yellow product had m.p. 104°. This method of reducing 2-benzeneazonaphthalene did not produce the hydrazo compound initially as an oil[11]; instead, a flocculent white solid was formed which became slightly yellow on filtration and washing.

Rearrangement of the hydrazo compound in aqueous ethanol solution with hydrochloric acid gave an authentic specimen of 1-(2-aminophenyl)-2-naphthylamine, m.p. 152–153° after recrystallization from aqueous ethanol (lit.,[11] m.p. 154–155°).

An authentic specimen of 7-benzo[*c*]carbazole was prepared by heating a sample of the above diamine with concd. hydrochloric acid in a sealed tube at 145–150° for 5 hr. The solids in the tube were then washed well with dilute hydrochloric acid and recrystallized from ethanol after treatment with charcoal. The product had m.p. 133–134° (lit.,[11] m.p. 135°).

Thermal rearrangement of 1-phenyl-2-β-naphthylhydrazine. The following procedure and results are representative of five separate experiments. A flask containing 0.677 g. of the hydrazo compound and 50 ml. of 95% ethanol under nitrogen was degassed on a diffusion pump line by two cycles of the customary freezing-thawing technique. The flask was sealed while under vacuum and placed in an oil bath at 90° for 7 days. It was then cooled and opened. The solution was transferred to a volumetric flask and made up to 100 ml. with ethanol. Analysis by the titanium trichloride–Bindschedler's Green method showed that 0.264 g. of hydrazo compound remained. The alcohol solution was made alkaline with solid sodium hydroxide, cooled in ice, and a gentle stream of oxygen was passed through it for 2 hr. The solution was concentrated by distillation and poured into a large volume of water. The precipitated solid was filtered, dried, and dissolved in benzene. Extraction of the benzene solution with dilute hydrochloric acid and neutralization of the acid solution gave 0.314 g. of product, m.p. 148–150°. Three crops from crystallization of this product gave a total of 0.274 g. of 1-(2-aminophenyl)-2-naphthylamine, m.p. 152–153°. No 2,2′-diamino-1,1′-binaphthyl, m.p. 190–191°, was found. The filtrate remaining from crystallizations of the crude diamine had an ultraviolet spectrum similar to that of a mixture of 1-(2-aminophenyl)-2-naphthylamine and 7-benzo[*c*]carbazole. Spectroscopic analysis on this basis gave 5 mg. of diamine and 0.7 mg. of carbazole in the filtrate. Thus, approximately 34 mg. was lost in crystallizations. There was no evidence in the ultraviolet spectrum in the region of 283 mμ to suggest the presence of benzidine, m.p. 127°. In this region benzidine has a broad pronounced absorption, and the spectrum recorded had the characteristic shape of that of 1-(2-aminophenyl)-2-naphthylamine. It is to be noted that the ultraviolet spectrum of 2,2′-diamino-1,1′-binaphthyl is almost identical with that of 1-(2-aminophenyl)-2-naphthylamine. The absence of the former in the rearrangement products is concluded on the basis of not finding the higher melting less soluble diamine by crystallization.

The benzene solution remaining after acid extraction of diamine was washed, dried and distilled to small volume. Evaporation to dryness under a stream of nitrogen gave 0.272 g. of solid. Successive crystallizations from 95% ethanol gave five crops of 2-benzeneazonaphthalene, each with m.p. within the range 80–82°, weighing a total of 0.211 g. The residual alcohol solution appeared, from its ultraviolet spectrum, to contain a mixture of 2-benzeneazonaphthalene and 7-benzo[*c*]carbazole. Spectroscopic analysis on this basis gave 28.2 mg. of 2-benzeneazonaphthalene and 8.2 mg. of 7-benzo[*c*]carbazole in the residual ethanol solution. Thus, approximately 25 mg. was lost in crystallizations.

In summary, the acid-soluble and acid-insoluble solids accounted for 87% of the original 1-phenyl-2-β-naphthylhydrazine, and appeared to be composed solely of the products of intramolecular rearrangement. The yields of quantitatively identified products, based on the amount of hydrazo compound which rearranged, were 1-(2-aminophenyl)-2-naphthylamine 77.2% and 7-benzo[*c*]carbazole 2.5%.

In the course of the spectroscopic work the following maxima were recorded. For 1-(2-aminophenyl)-2-naphthylamine: λ 239.5 mμ (log ε 4.82), 283.2 (3.98), and 342.5 (3.52). For 7-benzo[*c*]carbazole: λ 263.5 mμ (log ε 4.76), 284.5 (4.08), 325 (4.19), and 344.5 (3.75). For 2-benzeneazonaphthalene: λ 265 mμ (log ε 4.06), 276.5 (4.12), 287.5 (4.12), and 328 (4.32). The diamine had a pronounced shoulder at 294 mμ, while the carbazole had very weak shoulders at 272 and 312 mμ.

Acknowledgment. This work was generously supported by the Robert A. Welch Foundation, Houston, Tex.

LUBBOCK, TEX.

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[18] A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 2nd ed., Longmans, Green and Co., New York, N. Y., 1954, p. 602.

[CONTRIBUTION FROM THE RESEARCH DIVISION, ABBOTT LABORATORIES]

The Preparation of 1-Halobenzoyl-2-isopropylhydrazines. Selective Hydrogenation of N=CH Function in the Presence of Aromatic Halogen

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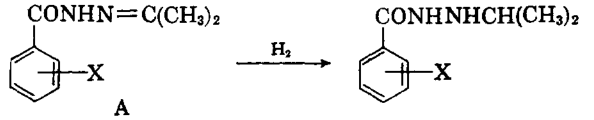
Selective reduction of N=C function in the presence of aromatically bound halogen was carried out with platinum on carbon catalyst. Successful reductions of ten compounds are reported, several of which contain the more labile halogens bromine and iodine.

There are many descriptions in the literature of hydrogenation of reducible groups in the presence of aromatically bound halogen. In most of the reported work little emphasis is placed on selectivity. In many instances the halogen present is chlorine and the catalyst and reaction conditions do not favor dehalogenation.

The effect of strong bases in catalytic dehalogenation is well known.[1] However, except for a few reports, hydrogenation of groups leading to basic constituents of varying degrees of base strengths, in the presence of aryl halides, has not been studied very extensively.

Baltzly and Phillips[2] in an investigation of the hydrogenolysis of halogen compounds with palladized charcoal and Adams catalyst found that amino substitution in the aromatic ring labilizes the bound halogen. The work of Winans[3] indicates that dehalogenation will occur in the reduction of certain halonitrobenzenes even with Raney nickel, which is generally ineffective for removing halogen.

The preparation in this laboratory of a series of 1-halobenzoyl-2-isopropylidenehydrazines (A) gave us the opportunity to investigate the labilizing effect of the NH—CH group on the aromatic halogen of these compounds.



A

Our primary purpose was to find conditions which would enable us to reduce the N═C function without causing dehalogenation. Hydrogenation of both 1-*o*-chloro- and 1-*p*-chlorobenzoyl-2-isopropylidenehydrazines with palladium on charcoal catalyst gave evidence that hydrogenolysis occurred. An examination of these reductions showed that the uptake of the first equivalent of hydrogen was more rapid than that of the second equivalent. The lack of any sharp break in the curve emphasized the danger of overhydrogenation even though the reaction was interrupted at one equivalent of hydrogen.

In a study of the preparation and properties of platinized charcoal catalyst Baltzly[4] points out that it is quite inactive in dehalogenations. The labilizing effect of the basic constituent on halogens led us to use this less active catalyst in our study.

When X is fluorine or chlorine no detectable dehalogenation occurred in the course of reduction when a 10% ratio of catalyst to substrate was used even when the reaction was allowed to continue for many hours after uptake of hydrogen appeared complete. This purported ineffective dehalogenation catalyst caused considerable hydrogenolysis when the halogen was either *o*- or *p*-bromo. In the reduction of the iodo compound loss of iodine was concurrent with reduction of —N═C function. By reducing the catalyst ratio to 2.5% we found that in the reduction of the *o*-bromo derivative we could obtain compound XVIII in good yield while keeping debromination at a very low level. However, when this low catalyst to substrate ratio was used for the reduction of a more labile iodo compound dehalogenation still occurred.

REDUCTION OF 1-*o*-BROMOBENZOYL-2-ISOPROPYLIDENEHYDRAZINE WITH A 2.5% RATIO OF CATALYST TO SUBSTRATE

% Hydrogen Uptake	% Ionic Bromine
37.5	0
47.6	0
67	0
85.6	0
102	4.7

Baltzly and Phillips[2] noted that excess hydrogen chloride or hydrogen bromide suppressed dehalogenation. We were able to make use of this finding to reduce successfully the *p*-bromo derivative to obtain compound XIX if we kept the catalyst ratio at 4%. The use of more catalyst resulted in debromination.

The use of excess mineral acid in the reduction of the iodo derivative cause heavy precipitation in every solvent used. As a result uptake of hydrogen was extremely slow. We found, however, by carrying out the reduction in alcohol containing at least three equivalents of acetic acid we could obtain compound XX in fair yield.

EXPERIMENTAL

The following experiments are typical of the methods used to prepare compounds I thru XX.

Hydrazide of p-chlorobenzoic acid. Sixty-five grams (0.353 mole) of ethyl *p*-chlorobenzoate was refluxed for 4 hr. with a mixture of 50.0 g. (1.0 mole) of hydrazine monohydrate and 75 cc. of absolute ethanol. The solvent, unchanged hydrazine and water were removed under reduced pressure. The residual white solid was recrystallized from 95% ethanol; weight 57.2 g. (95%), m.p. 164–165° (lit.,[5] m.p. 163°).

1-p-Chlorobenzoyl-2-isopropylidenehydrazine (VI). Twenty-five grams (0.147 mole) of the hydrazide of *p*-chlorobenzoic acid and 200 cc. of acetone were refluxed for 5 hr. The reaction mixture was held at 4° overnight and the resulting crystals removed by filtration; weight 26.9 g. (87%), m.p. 188–189°.

1-p-Chlorobenzoyl-2-isopropylhydrazine (XVI). Twenty grams (0.095 mole) of 1-*p*-chlorobenzoyl-2-isopropylidenehydrazine was dissolved (or suspended) in 250 cc. of 95% ethanol. Thereafter 1.5 g. of 5% platinum on carbon[6] was added and the mixture hydrogenated under 2 atm. pressure. Uptake of hydrogen was complete in one hour or less. No additional absorption was observed after allowing reaction

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[1] M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916) show that dehalogenation occurs quantitatively in reductions with palladium in the presence of potassium hydroxide. In this laboratory we have used sodium acetate as the acid acceptor with equal success.

[2] R. Baltzly and A. P. Phillips, *J. Am. Chem. Soc.*, **68**, 261 (1946).

[3] C. F. Winans, *J. Am. Chem. Soc.*, **61**, 3564 (1939).

[4] R. Baltzly, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

[5] S. Shih, *Sci. Repts. Natl. Tsing Hua Univ.*, **2**, 354 (1934).

[6] Obtained from Baker and Co. Division of Engelhard Industries, Newark (2), N. J.

TABLE I

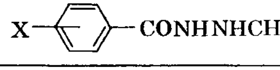
Physical Properties of the 1-Halobenzoyl-2-isopropylindenehydrazines

	X	M.P.[j]	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Halogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	2-F	112–113	47	$C_{10}H_{11}FN_2O$	61.84	62.21	5.71	5.94	14.43	14.54		
II	3-F	144–146	87	$C_{10}H_{11}FN_2O$	61.84	62.04	5.71	5.99	14.43	14.49	9.78	9.80
III	4-F	152–154	65	$C_{10}H_{11}FN_2O$	61.84	62.09	5.71	5.81	14.43	14.57		
IV	2-Cl	120–122[a]	81	$C_{10}H_{11}ClN_2O$[g]	57.01	57.10	5.26	5.17	13.30	13.23	16.83	16.90
V	3-Cl	124–126[b]	63	$C_{10}H_{11}ClN_2O$[h]	57.01	56.80	5.26	5.29	13.30	13.10	16.83	16.99
VI	4-Cl	188–189[c]	86	$C_{10}H_{11}ClN_2O$	57.01	56.96	5.26	5.20	13.30	13.41		
VII	3,4-diCl	148–149	80	$C_{10}H_{10}Cl_2N_2O$	49.00	49.13	4.11	4.18	11.44	11.61		
VIII	2-Br	131–132[d]	57	$C_{10}H_{11}BrN_2O$	47.07	47.27	4.35	4.41	10.98	11.18	31.33	31.30
IX	4-Br	197–198[e]	87	$C_{10}H_{11}BrN_2O$	47.07	47.37	4.35	4.55	10.98	10.85	31.33	31.12
X	4-I	215–216[f]	91	$C_{10}H_{11}IN_2O$	39.75	39.71	3.67	3.94	9.27	9.24	42.05	42.01[g]

[a] Tak-Ho Sun and P. Sah, *Sci. Repts. Natl. Tsing Hau Univ.*, [A] **2**, 359 (1934), report m.p. 110–111°. [b] P. Sah and Chung-Shu Wu, *Sci. Repts. Natl. Tsing Hau Univ.*, [A] **3**, 443–449 (1936), report m.p. 97°. [c] Tak-Ho Sun and P. Sah, *Sci. Repts. Natl. Tsing Hau Univ.*, [A] **2**, 353–357 (1934), report m.p. 169–171°. [d] Chung-Hsi Kao, *Sci. Repts. Natl. Tsing Hau Univ.*, [A] **3**, 555–556 (1936), report m.p. 153–154°. [e] Si-Ming Wang, Chen-Heng Kao, Chung-Hsi Kao, and P. Sah, *Sci. Repts. Natl. Tsing Hua Univ.*, [A] **3**, 279–284 (1935), report m.p. 198–199°. [f] P. Sah and Chang-Lin Hsü, *Rec. trav. chim.*, **59**, 349–356 (1940), report m.p. 214–215°. [g] Calcd.: O, 7.60. Found: O, 7.24. [h] Calcd.: O, 7.60. Found: O, 7.92. [i] The infrared spectra of all the compounds were compatible with the desired structures. [j] All the melting points were obtained by the use of a calibrated Hershberg melting point apparatus.

TABLE II

Physical Properties of the 1-Halobenzoyl-2-isopropylhydrazines



	X	M.P.	Yield,[a] %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Halogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XI	2-F	97–98	89	$C_{10}H_{13}FN_2O$	61.21	61.35	6.67	6.87	14.27	14.35		
XII	3-F	119–120	79	$C_{10}H_{13}FN_2O$	61.21	61.08	6.67	6.87	14.27	13.98	9.68	9.92
XIII	4-F	126	74.3	$C_{10}H_{13}FN_2O$	61.21	61.40	6.67	6.96	14.27	14.31		
XIV	2-Cl	116	75	$C_{10}H_{13}ClN_2O$	56.46	56.22	6.15	6.22	13.17	13.32	16.67	16.69
XV	3-Cl	130–131	73	$C_{10}H_{13}ClN_2O$	56.46	56.72	6.15	6.07	13.17	13.03	16.67	16.69
XVI	4-Cl	135	94.3	$C_{10}H_{13}ClN_2O$	56.46	56.34	6.15	6.29	13.17	12.95	16.67	16.47
XVII	3,4-diCl	116–117	92.5	$C_{10}H_{12}Cl_2N_2O$	48.59	48.64	4.89	4.83	11.33	11.57	28.69	28.61
XVIII	2-Br	134–135	78	$C_{10}H_{13}BrN_2O$	46.70	46.91	5.09	5.27	10.89	10.81	31.08	31.10
XIX	4-Br	141–142	80	$C_{10}H_{13}BrN_2O$	46.70	46.68	5.09	5.12	10.89	10.79	31.08	30.96
XX	4-I	164–165	58	$C_{10}H_{13}IN_2O$	39.48	39.70	4.30	4.44	9.21	9.19	41.73	41.88

[a] Except for XX yields of unrecrystallized products ranged between 90 and 100%.

to continue for a number of hours. The catalyst was filtered, washed with alcohol, and the solution concentrated to the beginning of crystallization. In general the resultant solutions were concentrated to dryness and the solid products recrystallized from dilute alcohol.

Use of low catalyst ratio. 1-o-Bromobenzoyl-2-isopropylhydrazine (XVIII). A solution of 4.2 g. (0.0164 mole) of 1-*o*-bromobenzoyl-2-isopropylidenehydrazine was hydrogenated in the presence of 0.1 g. 5% platinum on carbon. Uptake of hydrogen was completed in 6–7 hr. The slow uptake of the final 10–20% of hydrogen was enough to indicate that with this decreased catalyst ratio the possibility of overhydrogenation would be negligible.

The reaction mixture was filtered and worked up as described in the previous example.

The *p*-bromo derivative XIX was also prepared in the same manner. In one experiment using a 10% catalyst ratio we did get XIX in 62% yield but we were never able to duplicate the results. With a 7% catalyst ratio we obtained a mixture of products. The poor solubility of 1-*p*-iodobenzoyl-2-isopropylidenehydrazine made reduction with a low catalyst ratio not feasible.

Use of excess hydrogen chloride. 1-p-Bromobenzoyl-2-isopropylhydrazine (XIX). A mixture of 2.55 g. (0.01 mole) 1-*p*-bromobenzoyl-2-isopropylidenehydrazine, 55 cc. of absolute alcohol containing 0.03 mole dry hydrogen chloride and 0.1 g. (4% ratio) of 5% platinum on carbon was hydrogenated under 2 atm. pressure. After reduction was complete the suspension was treated with water to dissolve the hydrochloride salt. The mixture was then filtered from the catalyst and the solvent evaporated to dryness. The residue was treated with hot water and filtered from any insoluble material. It was then neutralized with aqueous ammonia or sodium bicarbonate, cooled, filtered, and washed with cold water. There was no difference in melting point between the product before and after recrystallization.

When a 5% catalyst ratio was used, 4.7% ionic bromine was found by analysis. When a 6% ratio was employed it was noted that more over-hydrogenation was occurring. The crude product isolated from this experiment melted at 136–140° and was raised to 141–142° after recrystallization. The yield of unrecrystallized product was much lower than usual. See footnote (a) Table II.

1-p-Iodobenzoyl-2-isopropylhydrazine (XX). A suspension of 1.51 g. (0.005 mole) of 1-*p*-iodobenzoyl-2-isopropylidenehydrazine in 100 cc. 95% ethanol containing (0.15 mole) acetic acid and 0.075 g. 5% platinum on carbon was hydrogenated under 2 atm. pressure. When uptake was complete the material appeared to be in solution. The solution was filtered from the catalyst and concentrated to dryness. The residue was treated with 100 cc. of water and 2–3 cc. of concd. hydrochloric acid, stirred for a few minutes, and filtered. The filtrate was neutralized with sodium bicarbonate, cooled, and filtered. After washing with water and drying the product melted at 162–164°.

Acknowledgment. The authors wish to thank Mr. E. F. Shelberg and Mr. Orville Kolsto for the microanalyses, and Mr. W. Washburn for infrared examination of the compounds in Table I.

NORTH CHICAGO, ILL.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Preparation of *N*-(Aryl)amino Acids from Nitroaryl Compounds and Alcohols

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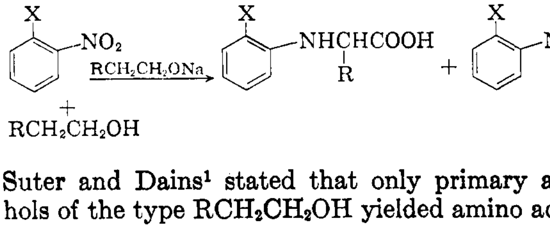
The redoxidative condensation of primary and secondary alcohols with aromatic nitro compounds by means of sodium alkoxides is described. The reaction offers a synthesis of *N*-(aryl)amino acids.

Suter and Dains[1] in 1928 reported that reduction of *m*- and *p*-halonitrobenzenes with alcohol-alkoxide mixtures gave substituted azoxybenzenes, but that *N*-(*o*-haloaryl)amino acids were formed as the primary products from the *o*-halonitrobenzenes; the reaction was also accompanied by the formation of the substituted anilines:



(1)

Suter and Dains[1] stated that only primary alcohols of the type RCH_2CH_2OH yielded amino acids, *i.e.*, isobutyl and cinnamyl alcohols failed to undergo this condensation.

In our hands, the synthesis of *N*-(aryl)amino acids by this method gave yields of only 10–32%, whereas 40–60% were reported. The condensation was therefore reinvestigated, and the effect of the structure of the alcohol and of the nitro compound on the course of the reaction was determined.

The products derived from a representative redoxidative condensation of *o*-chloronitrobenzene and 1-propanol included *N*-(*o*-chlorophenyl)alanine (31.9%), *o*-chloroaniline (51.3%), and 2,2′-dichloroazobenzene (16.7%). In several experiments the aromatic amine and the amino acid were formed in approximately equimolar amounts. The isolation of azo rather than azoxybenzenes among the products of the reaction is at variance with previous results,[1] however. The identification of 2,2′-dichloroazobenzene (m.p. 134–136°)[2,3] and 2,2′,5,5′-tetrachloroazobenzene (m.p. 182.5–184°)[4] was based on the correspondence of the melting points with literature values. The reported melting points of the related azoxy com-

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(1) C. M. Suter and F. B. Dains, *J. Am. Chem. Soc.*, **50**, 2733 (1928).

(2) K. Brand, *J. prakt. Chem.*, [2], **67**, 148 (1902).

(3) D. Vorländer and F. Meyer, *Ann.*, **320**, 129 (1902).