solution and stirred with a magnetic stirrer, 15.3 g. (0.117 mole) of XIX was added dropwise. After the addition was completed, the reaction mixture was stirred for 2 hr. and allowed to come to room temperature. The mixture was extracted two times with 200 ml. of ether. The combined ether extracts were washed twice with 200-ml. portions of 5% sodium hydroxide solution and once with water. The ether phase was dried over calcium sulfate. Removal of the ether on a steam bath gave 4.92 g. of crude neutral liquid with a ketonic odor. The infrared spectrum confirmed the presence of a ketone. Gas chromatography of this material showed four peaks. The first two peaks, which were off scale, corresponded to ether and water. The third peak had a retention time of 9.11 min. and the fourth peak had a retention time of 10.64 min.[22] The ratio of the third to fourth peak was 21.7 to 78.3%. An authentic sample of diisopropyl ketone[23] had a retention time of 9.11 min. under the same conditions. This material gave a positive iodoform test. A semicarbazone derivative was prepared, m.p. 111–113°.[24]

The basic extract was acidified and extracted with two 200-ml. portions of ether. The ether was dried over calcium sulfate and then evaporated. The crude residual liquid amounted to 2.5 g. The infrared spectrum of this liquid indicated that a carboxylic acid was present. The amide was prepared from the crude liquid and gave 1.23 g. of 2,4-dimethylpentanoic acid amide, m.p. 88–90° (from petroleum ether); lit.[25] m.p. 90°.

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(22) Flow rate of helium was 45.5 ml. per min., with detector temperature of 128° and column temperature of 105°.

(23) Purchased from Eastman Kodak Co.

(24) Reported for 3,4-dimethyl-2-pentanone semicarbazone, m.p. 112°: J. Colonge and K. Mostafar, *Bull. soc. chim. France*, 335 (1939).

(25) M. W. Burrows and W. H. Bentley, *J. Chem. Soc.*, **65**, 512 (1895).

The Reduction of Acid Adducts of Isoquinoline Reissert Compounds[1]

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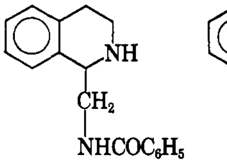
Received June 3, 1963

2-Benzoyl-1,2-dihydroisoquinaldonitrile (isoquinoline Reissert compound) forms adducts with hydrobromic or perchloric acid. Reduction of these adducts either by sodium borohydride or by catalytic hydrogenation affords 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide. The structure of the reduction product is established by an alternative synthesis. A preparation of 2-benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile (dihydroisoquinoline Reissert compound) and the perchlorate salt is described. Whereas isoquinoline Reissert compound yields benzaldehyde on hydrolysis, the dihydro derivative gives only benzoic acid.

1-Benzamidomethyl-1,2,3,4-tetrahydroisoquinoline (**1**) which was of interest to us in connection with another synthetic problem was prepared earlier by Rupe and Frey by drastic reduction of 2-benzoyl-1,2-dihydroisoquinaldonitrile (**2**, isoquinoline Reissert compound).[2,3] Attempts to hydrogenate **2** under milder conditions than Rupe's method failed to yield any discrete reduction products.[4] The recent isolation of a hydrobromide salt (**3**, $X^- = Br^-$) of isoquinoline Reissert compound suggested that this derivative might be more easily reduced to **1**.[5] In addition to the hydrobromide, a perchlorate salt (**3**, $X^- = ClO_4^-$) of the Reissert compound was prepared. Platinum-catalyzed hydrogenation of **3** ($X^- = ClO_4^-$) at three atmospheres pressure afforded a reduced salt that was converted to the corresponding base, $C_{17}H_{18}N_2O$, formed by the uptake of three moles of hydrogen. The same basic product was obtained unexpectedly on treatment of either salt **3** with sodium borohydride. Although the reduced base was isomeric with Rupe's compound **1**, the failure of our derivative to form an N-nitroso or an acetyl derivative or to yield benzoic acid on hydrolysis excluded **1** and the unrearranged structure **4** from consideration. The first real clue to the structure **5** of the reduction product was obtained when the sulfuric acid-catalyzed hydrolysis mixture was made alkaline; a strong odor of ammonia was observed. A second hydrolysis product ($C_{17}H_{17}NO_2$) proved to be 2-benzyl-1,2,3,4-tetrahydroisoquinaldinic acid (**6**).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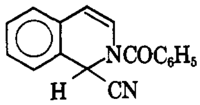
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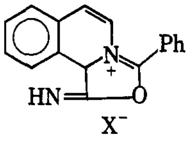
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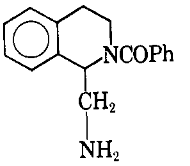
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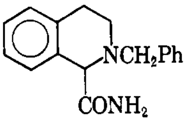
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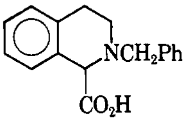
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Confirmation of structure **5** for the reduced base was obtained by an alternative synthesis (Chart I). The Reissert compound **2** was degraded to isoquinaldamide (**7**), and **7** was hydrogenated in acidic solution to form 1,2,3,4-tetrahydroisoquinaldamide (**8**). A reaction between the reduced amide **8** and benzyl chloride at reflux temperature produced the chloride salt **9** that was converted directly to 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide (**5**). The product from this reaction sequence proved identical by infrared spectra and melting point determinations with the reduction product from the salt.

Further support for **5** as the correct structure of the reduced base was adduced from the n.m.r. spectrum.[6] The salient feature in the spectrum was the unsplit band at τ 5.83 due to a single proton. This can be

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(1) (a) We gratefully acknowledge grants in support of this work from the Tennessee Heart Association and the National Institutes of Health (NB-03329); (b) presented in part at the 14th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November 1-3, 1962.

(2) H. Rupe and W. Frey, *Helv. Chim. Acta*, **22**, 673 (1922).

(3) A. Reissert, *Ber.*, **38**, 1603 (1905); W. E. McEwen and R. L. Cobb, *Chem. Rev.*, **55**, 511 (1955).

(4) W. E. McEwen, R. H. Terss, and I. W. Elliott, *J. Am. Chem. Soc.*, **74**, 3605 (1952).

(5) J. W. Davis, *J. Org. Chem.*, **25**, 376 (1960). Davis referred to **3** as a "Reissert imine"; in this paper the same compounds are called Reissert salts or acid adducts.

(6) The n.m.r. measurements were run in deuteriochloroform with tetramethylsilane as internal reference. We thank Dr. Harold Boaz of the Eli Lilly Research Laboratories, Indianapolis, Ind., for this information.

CHART I

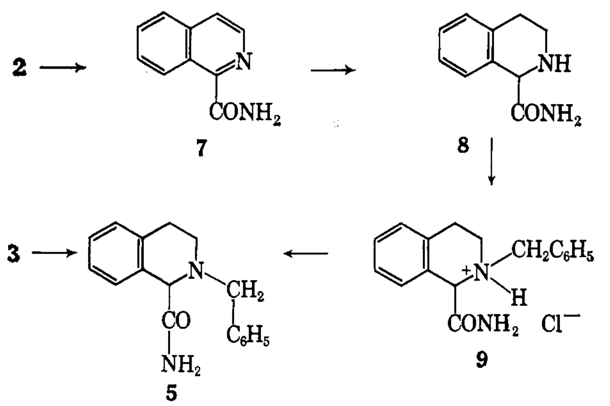
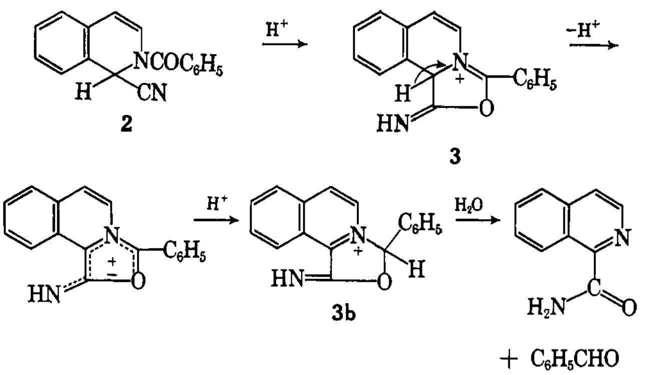
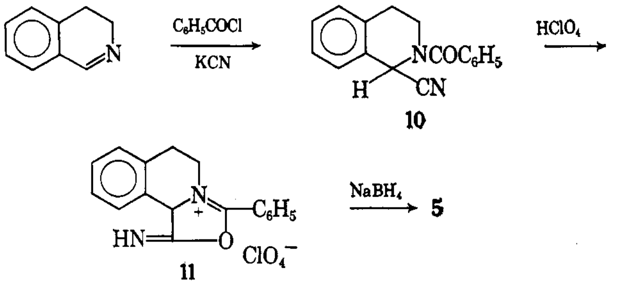


CHART II



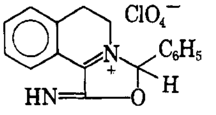
ascribed to the resonance signal from the hydrogen at C-1 in **5**. None of the other models (**1** and **4**) possess this feature. The remainder of the spectrum is in concordance with this assignment.

In connection with these studies it was also of interest to synthesize 2-benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile (**10**, dihydroisoquinoline Reissert compound). Since direct hydrogenation of **2** had failed to yield a simple dihydro product, the preparation of **10** was achieved by treatment of 3,4-dihydroisoquinoline with benzoyl chloride and potassium cyanide. The dihydro Reissert compound **10** afforded a perchlorate salt **11** under the usual conditions.

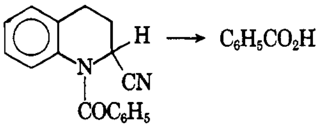


Borohydride reduction of the salt **11** gave the same product, 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide (**5**), obtained from reduction of the acid adduct **3** of the Reissert compound.

More extensive acid hydrolysis of the dihydroisoquinoline Reissert compound **10** or the salt **11** gave only benzoic acid and no benzaldehyde. This result is in accord with the findings of Collins for the analogous dihydroquinoline Reissert compound **13**.[7]



12



13

Structure of the Salts.—The acid adduct **3** of isoquinoline Reissert compound was first proposed as an intermediate in the mechanism of the unique acid-catalyzed hydrolysis whereby the acyl group in the amide state in the Reissert complex is reduced to the corresponding aldehyde (Chart II).[8] Davis' assignment of structure **3** to the hydrobromide salt of isoquinoline Reissert compound is based on the observation that further acid hydrolysis produces benzaldehyde and isoquinaldamide.[5] We concur in the formulation **3** for the salts for the following reasons. First, the results on reduction in which **3** is converted to **5** can most simply be described by a cyclic intermediate (**3** or **3b**) which permits intramolecular transfer of oxygen.[1] Secondly, infrared spectra of **2** and a series of amides related to the Reissert compound show a band at 7.4–7.5 μ that can arise from the N—C=O group frequency vibration. On salt formation this band disappears. Ring closure of the type illustrated in **3** would restrict this group vibration and account for the observed spectral change.

Thirdly, by way of discriminating between **3** and **3b** for the salt we have found that salt formation is reversible. The Reissert compound **2** is rapidly and quantitatively recovered when the salt is treated with base; **3** is a better model for this reaction than **3b** because such a change from **3b** would involve conversion of an isoquinolinium system to a dihydroisoquinoline. Moreover, additional acid appears necessary to complete the hydrolysis of the salt to benzaldehyde and isoquinaldamide; neutral solvents, even boiling water,[5] do not rapidly affect **3**.

Lastly, the formation of an acid adduct **11** from dihydroisoquinoline Reissert compound **10** under the same conditions as for the Reissert compound itself and the properties of the salt **11** have a bearing on this argument. The salt can be represented either by **11** or **12**, but the fact that acid hydrolysis of the salt (or the dihydro Reissert compound) produces only benzoic acid and no benzaldehyde is evidence in favor of **11**. The isomer **12** should be cleaved with water to benzaldehyde, but **11** can be expected to give rise to benzoic acid.

The hypothetical relationship in the hydrolysis mechanism between **3** and **3b**, or **11** and **12** revives the concept that "an important driving force in the reaction is the gain in resonance energy attendant on conversion of the dihydroquinoline to a completely aromatic system." [9]

A plausible series of changes for reductive cleavage of the five-membered ring and intramolecular transfer of oxygen from **3** to produce **5** can be outlined by the following formulas. The reduction by sodium borohydride of the carbon–carbon double bond of the isoquinoline ring in **3** requires little comment. It has been

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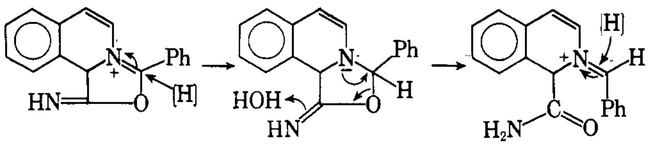
[7] R. F. Collins, *J. Am. Chem. Soc.*, **77**, 4921 (1955).

[8] R. L. Cobb and W. E. McEwen, *ibid.*, **77**, 5042 (1955).

[9] W. E. McEwen and R. N. Hazlett, *ibid.*, **71**, 1949 (1949).



observed by others when aqueous alcohol is the solvent.[10]

Experimental

Hydrobromide Salt of Isoquinoline Reissert Compound (3).—This compound was prepared by the method of Davis,[5] but samples prepared at different times varied considerably in melting points although the infrared spectra were the same. Typical ranges were: 156–158°, 160–161°, and 166–168° (lit.[5] m.p. 158–160°). The analytical sample had m.p. 159–160°.

Anal. Calcd. for $C_{17}H_{13}N_2OBr$: C, 59.84; H, 3.84; N, 8.21. Found: C, 59.47; H, 4.21; N, 8.26.

Acetonitrile was a satisfactory solvent in place of acetic acid for these salt preparations. When acetic anhydride was used, a mild exothermic reaction ensued on addition of the mineral acid, and only isoquinaldamide hydrobromide was isolated.

Perchlorate Salt of Isoquinoline Reissert Compound.—A solution of 5.0 g. of 2-benzoyl-1,2-dihydroisoquinaldonitrile **2** in 50 ml. of glacial acetic acid was treated with 5 ml. of 70% perchloric acid. A heavy yellow precipitate formed after about 5 min., and the product 5.4 g. (78%), m.p. 202–204°, was collected after 20 min. and washed with ethanol. Recrystallization of the salt from ethanol gave yellow prismatic crystals, m.p. 204–205°.

Anal. Calcd. for $C_{17}H_{13}N_2O_5Cl$: C, 56.57; H, 3.64; N, 7.77. Found: C, 56.98; H, 3.81; N, 8.09.

Hydrolysis of the Hydrobromide Salt of Reissert Compound by Base.—The salt (**3**, 0.10 g.) was dissolved in warm water containing 10% methanol, and the solution was treated with excess ammonium hydroxide. A precipitate formed immediately which was collected, washed with water, and dissolved in hot methanol. On cooling there was obtained 0.71 g. (93%) of isoquinoline Reissert compound, as identified by melting point and infrared spectrum.

Reduction of the Perchlorate Salt of Isoquinoline Reissert Compound. A. Catalytic Hydrogenation.—A suspension of 12 g. (0.033 mole) of isoquinoline Reissert perchlorate salt **3** in 200 ml. of ethanol and 0.3 g. of platinic oxide was hydrogenated at 3 atm. until the uptake of hydrogen virtually ceased (*ca.* 6 hr). The reaction mixture was heated on the steam bath and diluted with water to dissolve the salt. The hot mixture was filtered to remove the catalyst, and the filtrate was allowed to cool. A greenish yellow solid (9.2 g.) separated from the fluorescent green liquid. On recrystallization from ethanol the salt was obtained as pale yellow crystals, m.p. 251° dec.

Anal. Calcd. for $C_{17}H_{19}N_2O_5Cl$: C, 55.67; H, 5.22; N, 7.64. Found: C, 55.31; H, 5.37; N, 7.95.

A solution of 5.0 g. of the reduced salt in hot water was treated with charcoal, filtered, and cooled. To the crystallized salt was added aqueous ammonia, and after 0.5 hr. the flocculent white solid, 32 g. (88%), was collected and recrystallized from ethanol as colorless prisms, m.p. 150–151°. The melting point was undepressed on admixture with the base from borohydride reduction of the salt; moreover, the infrared spectra were identical.

B. Borohydride Reduction.—A hot solution of isoquinoline Reissert perchlorate (4 g.) in aqueous alcohol was treated with 1 g. of potassium borohydride. After 0.5 hr. the mixture was heated to boiling, and water was added almost to the point of turbidity. On standing 2.1 g. (71%) of a white solid was collected and after several recrystallizations gave colorless crystals, m.p. 150–151°; infrared spectrum ($CHCl_3$): 2.83 and 2.95 (monomeric NH_2 asymmetric and symmetric stretch, respectively); 2.90, 3.05, 3.15 (dimeric NH_2—OC stretch); 5.95 μ (amide CO).

Anal. Calcd. for $C_{17}H_{18}N_2O$: C, 76.69; H, 6.76; N, 10.52. Found: C, 76.80; H, 6.72; N, 10.81.

The same reduction product (63%) was obtained from a parallel reduction of the hydrobromide salt.

A solution of the base in ethanol was mixed with perchloric acid and after a few minutes in an ice bath almost colorless crystals separated from the magenta solution. The product, m.p. 251° dec., was identical with the yellow perchlorate from the catalytic reduction by mixture melting point and infrared spectra.

Acid Hydrolysis of 2-Benzyl-1,2,3,4-tetrahydroisoquinaldamide.—To 0.5 g. of 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide was added 4 ml. of concentrated sulfuric acid and 5 ml. of water. A clear violet-red solution resulted that changed on heating to a deep yellow. The solution was allowed to reflux 1.5 hr. and to stand 12 hr. The acid solution was diluted with water and extracted with ether, but the ether extracts gave no evidence of benzoic acid. The aqueous layer was made strongly alkaline with 20% sodium hydroxide solution, and a strong odor of ammonia was noticed. The basic reaction mixture was acidified slightly with acetic acid, and a small amount of a gum separated. The mixture was extracted with ether (20 ml.), ether–dichloromethane (20 ml.), and dichloromethane (20 ml.). The extracts were combined and evaporated, and the residue was taken up in warm ethanol, filtered, and allowed to cool. The acid was obtained as clusters of fine colorless needles (0.17 g.), m.p. 174–175°.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.25. Found: C, 76.30; H, 6.68; N, 5.20.

1,2,3,4-Tetrahydroisoquinaldamide.—Hydrogenation of isoquinaldamide hydrobromide[5] (3.0 g.) in 70% aqueous methanol (150 ml.) was catalyzed by platinic oxide (0.1 g.) at 40 p.s.i. After the theoretical uptake of hydrogen (1 hr.) the reaction was stopped and the catalyst was removed by filtration. The filtrate was made basic with ammonium hydroxide, and 1.5 g. of reduced amide, m.p. 181–183°, was collected. A sample, m.p. 182–183°, was recrystallized for analysis.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.15; H, 6.87; N, 15.90. Found: C, 67.89; H, 6.95; N, 15.78.

2-Benzyl-1,2,3,4-tetrahydroisoquinaldamide.—A suspension of 1.5 g. of 1,2,3,4-tetrahydroisoquinaldamide in 15 ml. of benzyl chloride gave a clear yellow solution during 2 hr. refluxing. After standing 20 hr. the semisolid mixture was diluted with 50 ml. of acetone, and 0.9 g. of an insoluble solid, m.p. 218–222°, was collected and washed with 10 ml. of acetone. The crude salt (0.6 g.) was dissolved in warm water and filtered, and the filtrate was treated with cold 20% sodium hydroxide solution. The amine was collected as a gummy white solid that was recrystallized from aqueous methanol as pale yellow crystals (0.3 g.), m.p. 147–149°. This product proved identical with the compound **5** from reduction of the isoquinoline Reissert salts by mixture melting point and infrared spectra.

2-Benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile (10).[11]—To 200 ml. of dichloromethane and 70 ml. of water were added 10 g. of 3,4-dihydroisoquinoline[12] and 18 g. of potassium cyanide. The mixture was stirred vigorously and cooled in an ice bath while 24 g. of benzoyl chloride was added dropwise over a period of 2 hr. After 6 hr. stirring the layers were separated, and the dichloromethane solution was extracted successively with water, 5% sodium hydroxide, 5% hydrochloric acid, and water again. The solution was dried over sodium sulfate and evaporated under reduced pressure to leave a viscous orange oil. The oil was diluted with 5 ml. of ethanol, cooled, and scratched. Fine crystals began to form after 15 min., the mixture was kept near 0° for 12 hr., and the first crop of crystals (1.5 g.), m.p. 113–115°, was collected. Recrystallization of this product raised the melting point to 114–115°, but it did not correspond to dihydroisoquinoline Reissert compound **10** and was not studied further.

Anal. Found: C, 79.81; H, 6.47; N, 5.79.

The second and third crops of crystals (7.3 g., m.p. 96–98°), were sticky colorless crystals. Recrystallization from aqueous ethanol and finally ethanol–ether gave the Reissert compound **10** as colorless prisms, m.p. 104–105°.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.94; H, 5.37; N, 10.68. Found: C, 78.05; H, 5.66; N, 10.62.

Perchlorate Salt of Dihydroisoquinoline Reissert Compound.—To 1.0 g. of recrystallized dihydroisoquinoline Reissert compound was added glacial acetic acid (5 ml.) until all of the solid dissolved on shaking. The solution was cooled slightly, and 1.5 ml. of 70% perchloric acid was added. After 10 min., the salt precipitated nearly all at once when the solution was scratched.

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[10] R. Mirza, *J. Chem. Soc.*, 4400 (1957); J. W. Huffman, *J. Am. Chem. Soc.*, **80**, 5193 (1958).

[11] This general method is described by F. D. Popp, W. Blount, and P. Melvin, *J. Org. Chem.*, **26**, 4930 (1960).

[12] W. J. Dale, L. Starr, and C. W. Strobel, *ibid.*, **26**, 2225 (1961).

The mixture was chilled 10 min. in an ice bath and the product (1.1 g., m.p. 205–208°), was collected as a bright yellow solid. An analytical sample, m.p. 213–214°, was recrystallized from ethanol; infrared spectrum (KBr): 3.00–3.08 (doublet), 6.05 μ.

Anal. Calcd. for $C_{17}H_{15}N_2O_6Cl.H_2O$: C, 53.63; H, 4.50; N, 7.30. Found: C, 53.41; H, 4.51; N, 7.34.

Borohydride Reduction of Dihydroisoquinoline Reissert Perchlorate Salt.—A suspension of sodium borohydride (0.5 g. in 30 ml. of ethanol) was treated with 0.95 g. of dihydroisoquinoline Reissert perchlorate. The color at first was orange, but this quickly faded on heating. A white solid that remained undissolved after heating 10 min. was dissolved by addition of water. Further dilution with water brought the boiling solution to the point of turbidity, and a small quantity of alcohol was added to give a clear solution. On chilling in an ice–water bath a colorless granular solid was deposited (0.8 g.), m.p. 146–148°; this was raised to 147–149° by recrystallization. This compound was identified as 2-benzyl-1,2,3,4-tetrahydroisoquinaldamide (5) by mixture melting point and infrared spectrum.

Hydrolysis of Dihydroisoquinoline Reissert Compound.—To 0.5 g. of dihydro Reissert compound 10 was added 11 ml. of concentrated hydrochloric acid, and the mixture was allowed to reflux 8 hr. The cooled mixture deposited a feathery colorless solid (0.18 g., 78%), m.p. 118–120°. This product proved to be benzoic acid.

A similar result was obtained when the perchlorate salt 11 was heated with aqueous hydrochloric acid (1:1 by volume) and 2,4-dinitrophenylhydrazine. No benzaldehyde derivative was obtained, but benzoic acid was recovered from the reaction mixture.

Deoxymercuration in the Presence of Both Acid and Iodide Ion[1]

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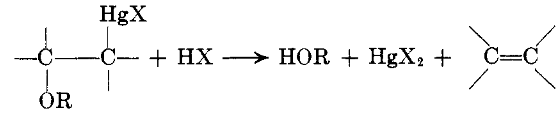
Received May 13, 1963

The deoxymercuration rate of 2-methoxyethylmercuric iodide in solutions containing both hydronium ion and iodide ion contains contributions from terms of the first and second order in iodide as well as a term of the zeroth order in iodide. The rate is of the first order in hydronium ion throughout. A previous report that 2-isopropoxyethylmercuric chloride is inert to perchloric acid (ref. 3) is in error. Substantial differences are found between deoxymercuration rates of 2-methoxyethylmercuric iodide and the corresponding hydroxy compound at all iodide concentrations. This precludes a fast reversible formation of the olefin–mercuric iodide complex and it is suggested that the formation of this complex, in fact, is rate determining.

The hydrohalic acid-induced deoxymercuration reaction, shown in equation 1, has been reported to be first order in hydrochloric acid[2] and also second order in hydrochloric acid.[3] Both of these reports pertain to alcohol rich alcohol–water mixtures in which kinetic salt effects may be quite large,[4] and in which incomplete ion-pair dissociation may be a factor.[5] In neither study was the halide ion concentration varied independently of the acid concentration. The present paper reports a study of the deoxymercuration reaction induced by combinations of acid and sodium iodide in water as a solvent (containing 2% methanol). The principal substrate was 2-methoxyethylmercuric iodide, but certain points were established by using 2-hydroxyethylmercuric iodide and 2-isopropoxyethylmercuric chloride.



$$-\underset{\text{OR}}{\underset{|}{\overset{|}{\text{C}}}}-\overset{\text{HgX}}{\overset{|}{\underset{|}{\text{C}}}}- + \text{HX} \longrightarrow \text{HOR} + \text{HgX}_2 + \text{>C=C<} \quad (1)$$

Results

Rates were measured spectrophotometrically using previously described techniques.[6a] The build-up of absorption at 3200 Å. due to mercuric iodide and its iodide ion complexes was followed. This absorption is primarily due to HgI_4^{-2} and HgI_3^-, which are in equilibrium with HgI_2 in the presence of excess iodide ion. Since the I^- concentration did not change appreciably in the course of any one experiment, the fraction of HgI_2 converted to each absorbing species was fixed and the change in optical density was proportional to the fraction of the reaction which had taken place. Thus the usual form of the integrated first-order rate law (equation 2) could be used.[6b] Plots of $\log\{(D_\infty - D_0)/(D_\infty - D_t)\}$ *vs.* t were precisely linear. (The optical density is D with the subscript indicating the time, t, at which it was measured. The pseudo first-order rate constant is k_1.) The slopes of such plots, obtained graphically, were used to get values of k_1. Substrate concentrations were in the range 10^{-4}–10^{-6} M.

$$k_1 = \frac{2.303}{(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \qquad (2)$$

All reactions were pseudo first order. The iodide concentration exceeded the substrate concentration by at least a factor of 12 in all experiments and in most by far more than that. The acid concentration was either in excess over the substrate by at least a factor of 100 or else it was held constant by buffering.

All measurements were made at least in duplicate and generally did not differ by more than 5%. In case of discrepancies of 10% or more, the measurement was repeated until the difficulty could be eliminated. This suggests a reliability of about ±5% for cited values of k_1.

All of the rate constants reported in this paper were measured at 25.0 ± 0.1°. All measurements were made in water containing 2% by volume of methanol because the substrates were handled as stock solutions in that solvent.

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