weighed 6.3 g. (85% yield). Crystallization from benzenem.p. 72-73.5

Anal. Calcd. for C₁₂H₁₃N₃O₂: C, 62.32; H, 5.67; N, 18.17; neut. equiv., 231. Found: C, 62.43; H, 5.84; N, 18.31; neut. equiv., 234.

Methyl γ -2-phenyl-1,2,3,2H-triazol-4-ylbutyrate (XV). Six tenths of a gram (0.002 mole) of the acid (XIV) was dissolved in 25 ml. of absolute methyl alcohol which had been saturated with dry hydrogen chloride in the cold and the solution was refluxed overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ether and washed thoroughly with 5% sodium carbonate solution, followed by water. The ether solution was dried over anhydrous sodium sulfate and the ether was evaporated on the steam bath, leaving an analytical sample of XV as an almost colorless oil. The sample weighed 0.4 g. (80% yield), too small an amount for the determination of the boiling point. Anal. Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.65; H, 6.16; N, 17.13.

Found: C, 63.98; H, 6.52; N, 17.32.

γ-2-Phenyl-1,2,3,2H-triazol-4-ylbutyramide (XVI). Into a test tube was placed 0.1 g. (0.0004 mole) of XV and 5 ml. of concd. ammonium hydroxide. The contents of the test tube were shaken periodically for several days, after which time crystals formed. The crystals were filtered with suction, washed with water, and air-dried, yielding 0.075 g. (83% yield) of XVI. Crystallization from benzene afforded fine colorless needles, m.p. $105-106^{\circ}$

Anal. Calcd. for C₁₂H₁₄N₄O: C, 62.59; H, 6.13; N, 24.33. Found: C, 62.21; H, 5.89; N, 23.79.

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Hydrogenation of the Imidazole Ring. Formation of Diacetylimidazolidine and of Diacetylbenzimidazoline¹

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The remarkable resistance of the imidazole ring to catalytic hydrogenation is well established.² The only exception that has been described is the hydrogenation of lophine and of amarine which was catalyzed by a suspension of platinum black in glacial acetic acid.³ In the work reported hereit was found that hydrogenation of the imidazole ring proceeded smoothly at room temperature and at atmospheric pressure when acetic anhydride was used as the solvent and platinum oxide as the catalyst. In this way, two hitherto unknown compounds were prepared: diacetylimidazolidine was formed by the hydrogenation of imidazole; diacetylbenzimidazoline was formed by the hydrogenation of benzimidazole, leaving the benzene ring unchanged.

EXPERIMENTAL

Acetic anhydride (150 ml., 1.47 moles) was shaken with hydrogen and 1.0 g. of platinum oxide at room temperature and ordinary pressure until the uptake of hydrogen stopped. About 400-470 ml. of hydrogen (corr.) were absorbed.4 To this pretreated suspension of platinum black in acetic anhydride, 2.04 g. (0.03 mole) of imidazole were added and the shaking continued until no further hydrogen was absorbed. The calculated amount of hydrogen (0.06 mole of hydrogen) was consumed in about 7 hr. The acetic anhydride solution was decomposed with ice water and evaporated to dryness in vacuo (20 mm.). The remaining oil was mixed with a small amount of absolute ethanol and ether. Upon storage in the cold room beautiful crystals of diacetylimidazolidine were formed; the yield was 3.77 g. (80%), m.p. 95°

Anal. Caled. for C₇H₁₂N₂O₂: C, 53.83; H, 7.75; N, 17.94. Found: C, 53.85; H, 7.50; N, 17.88.

Diacetylimidazolidine is very soluble in water and in ethanol, soluble in acetone and in hot benzene, and sparingly soluble in ether. It can be recrystallized from ethanolether. Determination of the acetyl groups: Calcd. as CH₃-COOH: 76.89. Found: 76.97.

Boiling with 2N hydrochloric acid for 45 min. split the imidazolidine ring with the formation of formaldehyde (detected by the fuchsin-sulfurous acid reaction) and ethylenediamine (detected with ninhydrin spray after chromatography in n-propyl alcohol, 75, 28% NH,OH, 1.5, water, 23.5). At room temperature, at the other hand, only a trace of formaldehyde was detected after 18 hr. in 2Nhydrochloric acid.

Benzimidazole (2.36 g., 0.02 mole) was hydrogenated the same way in acetic anhydride and consumed the calculated amount of hydrogen (0.02 mole) in about 7 hr. After recrystallization from absolute ethanol the yield of diacetylbenzimidazoline was 3.51 g. (86%). The melting point was 168-170°.

Anal. Caled. for C₁₁H₁₂N₂O₂: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.60; H, 6.10; N, 13.60.

Diacetylbenzimidazoline is soluble in ethanol, sparingly in cold water, soluble in hot water, soluble in acetone and in benzene; it is almost insoluble in ether.

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(4) This amount of hydrogen represents approximately 220 ml. (0.01 mole) more than that calculated for the reduction of platinum oxide to platinum black. The mechanism of this partial reduction of the acetic anhydride is unclear. Similar findings have been reported by C. Mannich and A. H. Nadelmann, Ber., 63B, 796 (1930), who found that at room temperature and ordinary pressure, in the presence of palladium black as the catalyst, acetic anhydride consumed a small amount of hydrogen with the formation of aldehyde and a little ethyl acetate.

Preparation of 5(6)-Iodobenzimidazole and 4(7)-Iodobenzimidazole

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During the course of some work concerning a comparative study of the physical properties of

⁽¹⁾ This research was supported by a grant from the National Science Foundation. I am indebted to Dr. Herbert Tabor for valuable suggestions and discussions. The microanalyses were carried out by the Analytical Laboratory of this Institute under the direction of Mr. H. G. McCann.

⁽²⁾ K. Hofmann, Imidazole and Its Derivatives, Interscience Publishers, New York, 1953, p. 16.

⁽³⁾ E. Waser and A. Gratsos, Helv. Chim. Acta, 11, 944 (1928).

NOTES

halogenated benzimidazoles, we have found that 5(6)- and 4(7)-iodobenzimidazoles have not been reported in the literature. As these compounds were needed for another study, we have investigated methods of preparing them.

The most useful method for the preparation of benzimidazoles is Phillips' method which consists in heating the desired diamine with the appropriate acid, in this case formic acid, in the presence of 4N hydrochloric acid for several hours.²

To obtain the 5(6)- and 4(7)-iodobenzimidazole one would have to start from 3- and 4-iodo-1,2diaminobenzenes. Only 4-iododiaminobenzene is reported in the literature. It was obtained by the reduction of 5-iodo-2-nitroaniline but no references are given for the preparation of the nitro compound.³

The nitration of p-iodoacetanilide with concentrated nitric acid in acetic acid at 0° has been reported by Brenans.⁴ Although this nitration is reported to yield 2-nitro-4-iodoacetanilide among other products, we isolated mostly starting material when we followed this procedure.

We decided to use more vigorous conditions and attempted the nitration of p-iodoacetanilide with fuming nitric acid in acetic anhydride at 0°. The product obtained was p-nitroacetanilide, indicating that the iodine atom had been removed during the nitration.

As the preparation of the necessary iodo substituted phenylenediamines did not appear to be a convenient way of obtaining the corresponding benzimidazoles, and since the 5(6)- and 4(7)aminobenzimidazoles are known compounds it was decided to diazotize the amino compounds and treat the resulting diazonium compound with potassium iodide. The yields obtained by this method were very poor even when several modifications of the basic procedure were tried.

As diazonium fluoborates had been previously prepared in this laboratory in very good yields,⁵ it was thought that perhaps they would decompose smoothly when heated with potassium iodide.

Although the decomposition of diazonium chlorides and sulfates with potassium iodide is a standard method of introducing iodine atoms into aromatic compounds, decomposition of diazonium fluoborates has not been reported in the literature.

In this work, we were able to prepare both 5(6)and 4(7)-iodobenzimidazoles by the decomposition of the corresponding diazonium fluoborates with potassium iodide. This suggests that diazonium fluoborates might be more generally used, in place of chlorides or sulfates, for the preparation of other iodinated aromatic compounds.

EXPERIMENTAL

Nitration of p-iodoacetanilide. Method I. The procedure of Brenans⁴ was followed but the only product isolated in appreciable yield proved to be p-iodoacetanilide. A mixture of this product with starting material showed no depression in melting point. The infrared spectrum of this product proved to be identical to the infrared spectrum of a known sample of p-iodoacetanilide.

Method II. p-Iodoacetanilide (16.5 g., 0.063 mole) was added slowly to a stirred mixture of 17 ml. (0.364 mole) of fuming nitric acid and 15 ml. of acetic anhydride. The temperature of the solution was maintained at 0° for 1 hr.

After standing overnight at room temperature, the dark red solution was poured into an excess of water. Yellow crystals formed on standing. They were recrystallized from ethanol-water and then from benzene, m.p. $210-212^{\circ}$. The melting point of *p*-nitroacetanilide is $215-216^{\circ}$. No positive test could be obtained for the presence of iodine.

5(6)-Nitrobenzimidazole. This compound was prepared by the procedure described by Fisher and Joullié.⁵ Yield, 84%, m.p. 203-205°.

5(6)-Aminobenzimidazole dihydrochloride. 5(6)-Nitrobenzimidazole (12 g., 0.074 mole) and 0.5 g. of platinum dioxide were suspended in 150 ml. of absolute ethanol and the suspension hydrogenated in a Paar hydrogenation apparatus.

The catalyst was removed by filtration, the solution poured into 100 ml. of anhydrous ether and treated with dry hydrogen chloride. 5(6)-Aminobenzimidazole dihydrochloride precipitated and was removed by filtration; yield, 92%.

5(6)-Benzimidazolediazonium fluoborate. This compound was prepared according to the procedure of Fisher and Joullié⁵; yield, 91%, m.p. 197-200° dec.

5(6)-Iodobenzimidazole. Method I. 5(6)-Aminobenzimidazole dihydrochloride (14 g., 0.068 mole) was dissolved in 56 ml. of water and the resulting solution cooled to 0°. Sodium nitrite (4.8 g., 0.07 mole) in 15 ml. of water was added slowly with stirring while the temperature was maintained at 0°. Any solid material formed was removed by filtration and the solution added with stirring to a solution of 19.4 g. (0.117 mole) of potassium iodide in 60 ml. of water at 0°. The solution was neutralized and the precipitate which formed removed by filtration. This precipitate was dissolved in acid and treated with decolorizing carbon. The carbon was removed by filtration and the solution neutralized with ammonium hydroxide. The precipitate formed was recrystallized twice from benzene-petroleum ether (b.p. 60-110°). Only enough material for an analytical sample was obtained. The melting point was 144-145°.

Anal. Caled. for $C_7H_5N_2I$: C, 34.45; H, 2.07; N, 11.48; I, 52.01. Found: C, 34.52; H, 2.03; N, 11.67; I, 51.88.

Method II. This procedure was similar to method I except that the diazotization was carried out in sulfuric acid and the addition of the potassium iodide solution was followed by the addition of finely divided cast bronze. Evolution of nitrogen and iodine was observed and although a precipitate formed the yield of product was negligible.

Method III. 5(6)-Benzimidazolediazonium fluoborate (5 g., 0.0216 mole) was dissolved in 300 ml. of water and the solution added slowly with stirring to a solution of 3.57 g. (0.0216 mole) of potassium iodide in 10 ml. of water. Gas was evolved and the solution turned dark red. It was heated on a steam bath for 8 hr., cooled and neutralized with concentrated ammonium hydroxide. The yellow-brown precipitate which formed was removed by filtration and extracted with benzene in a Soxhlet apparatus. The benzene extract was treated with Skellysolve H⁶ until the solution

⁽¹⁾ To whom all inquiries should be addressed.

⁽²⁾ M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

⁽³⁾ B. N. Feitelson, P. Mamalis, R. J. Moualim, V. Petrow, O. Stephenson, and B. Sturgeon, J. Chem. Soc., 2398 (1952).

⁽⁴⁾ M. P. Brenans, Bull. Soc. Chim. France [4] 15, 90 (1914).

⁽⁵⁾ E. C. Fisher and M. M. Joullié, J. Org. Chem., 23, 1944 (1958).

became cloudy. The precipitate obtained was removed by filtration and recrystallized from benzene-Skellysolve H; yield, 21%, m.p. $144-145^{\circ}$.

4(7)-Iodobenzimidazole. Several attempts were made to prepare this compound by methods similar to those used for the preparation of 5(6)-iodobenzimidazole. The only method which yielded the desired product started from the 4(7)-benzimidazolediazonium fluoborate prepared by the procedure described by Fisher and Joullié.⁵

4(7)-Benzimidazolediazonium fluoborate (5 g., 0.0216 mole) was dissolved in 300 ml. of water and the resulting solution was added slowly with stirring to a solution of 3.57 g. (0.0216 mole) of potassium iodide in 10 ml. of water. Gas was evolved and the solution turned dark red. It was heated on a steam bath for 6 hr., cooled and neutralized with ammonium hydroxide. The precipitate formed was extracted with benzene in a Soxhlet apparatus. It was recrystallized from benzene-Skellysolve H; yield, 10%, m.p. $188-189^{\circ}$.

Anal. Caled. for $C_7H_5N_2I$: C, 34.45; H, 2.07; N, 11.48; I, 52.01. Found: C, 34.33; H, 2.18; N, 11.38; I, 51.83.

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(6) A petroleum hydrocarbon fraction (b.p. range 70-74°). Sold by Skelly Oil Company, Kansas City, Mo.

Transformation of 2-Amino-5-phenyl-1,3,4oxadiazole to 3-Phenyl-1,2,4-triazolin-5-one

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A survey of the literature pertaining to 3substituted 1,2,4-triazolin-5-ones reveals a state of disorder caused by the contradictory claims of various workers.

The 3-phenyl member, which may be considered typical of the series, can be described in part by the tautomeric structures I to IV. Argument as to which best represents the properties of the compound has created much confusion.



3-Phenyl-1,2,4-triazolin-5-one was first prepared by Young and Witham¹ by the oxidation of benzaldehyde semicarbazone (V) with ferric chloride. They pictured the product as either I or II. Nearly thirty years later Bougault and Popovici² assigned structure III to the product of the action of iodine and sodium hydroxide at room temperature on the semicarbazone of phenyl glyoxylic acid (VI) and Girard^{3,4} in 1941 reported that this material was changed to I-II by hot alkali. More recently Gehlen⁵ proposed a cyanohydrazide structure, C₆H₅-CONHNHCN, instead of structure III for the Bougault-Popovici compound, on the basis of its independent synthesis from cyanogen bromide and 1-benzovlhydrazine (VII). He also reported the synthesis of a compound considered to be I-II from 1-benzoylsemicarbazide (VIII) and alkali. Gehlen's proposal was criticized by Mautner and Kumber⁶ who showed that the cyanohydrazide structure was inconsistent with the physical and chemical properties of the Bougault-Popovici product, which Mautner and Kumber regarded as III. They considered Young and Witham's product to be best represented by the tautomer IV, a view with which we agree. We thought, however, that the physical and chemical dissimilarities of the two isomers might well be the result of skeletal, rather than tautomeric differences.

For example, we considered it unlikely that tautomers III and IV would be so slowly interconverted that their individual K_a 's and K_b 's could be determined; however, the Bougault-Popovici product was found to be a weak base and IV a weak acid.⁶ As an alternative for III we were considering 2-amino-5-phenyl-1,3,4-oxadiazole^{7,8} (IX) as the structure for the Bougault-Popovici product when we discovered that Gehlen's cyanogen bromide reaction had been recently patented by Swain⁹ as a method of synthesis for IX. We have now compared Swain's product with an authentic sample



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⁽²⁾ J. Bougault and L. Popovici, Compt. rend., 189, 188 (1929).