Summary

On the basis of its infrared absorption spectrum the reaction product of α-benzamidoisobutyric acid with phosphorus tribromide has been assigned the structure, 2-phenyl-4,4-dimethyl-5(4)-oxazolone hydrobromide rather than α-benzamidoisobutyryl bromide. This is the first reported instance of an infrared absorption spectrum of a compound of this type.

Since the infrared absorption observed in the reaction of β-methyl benzylpenicilloate with phosphorus tribromide is at distinct variance with that of the above oxazolone hydrobromide, it would appear that this later reaction does not involve an oxazolone hydrobromide.

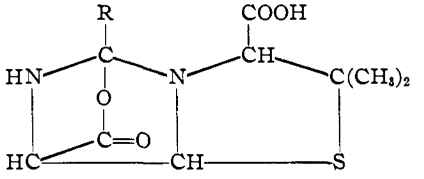
EMERYVILLE, CALIFORNIA RECEIVED AUGUST 23, 1948

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Assignment of Amide Structures to the Supposed 2,3-Dihydro-2-benzimidazolols and their Acylation Products[1]

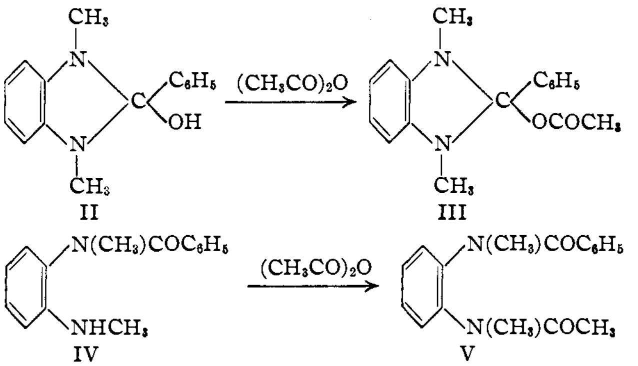
BY CURTIS W. SMITH, ROBERT S. RASMUSSEN AND SEAVER A. BALLARD

One of the structures proposed for penicillin which had received much consideration before acceptance of the fused thiazolidine-β-lactam formula is shown as formula I.



I

As a part of the general program of examining the infrared absorption spectra of model compounds as nearly like the most plausible structures for penicillin as possible, the infrared absorption was obtained of a compound previously presumed from chemical evidence to be 1,3-dimethyl-2-phenyl-2,3-dihydro-2-benzimidazolol acetate[2] (III). However, when the infrared absorption spectrum of this compound was obtained in these laboratories, it was indicated that instead of the ester grouping shown in formula III there existed amide linkages which would be more consistent with the isomeric formula V, namely, N-acetyl-N'-benzoyl-N,N'-dimethyl-o-phenylenediamine. The compound previously thought to have structure III and now indicated as having structure V had been first prepared in the laboratories of Eli Lilly and Company,[2] by acetylation of a compound thought to be 1,3-dimethyl-2-phenyl-2,3-dihydro-2-benzimidazolol (II). The infrared absorption of this parent compound II or IV gave strong indication of the presence of an amide group and was thus in agreement with structure IV and contrary to structure II.



The first example of a compound thought to be of type II was prepared by Niementowski[3] in 1887. Subsequently Fischer and Romer[4] gave a serious and lengthy consideration to the structures of these compounds. The literature now contains a large number of compounds assigned the benzimidazolol structure.

The following discussion is divided into four sections. First is a critique of the literature designed to show the fallacy of some of the steps which led the earlier workers to favor the benzimidazolol formula (II) instead of the amide formula (IV). Second is the presentation of evidence definitely establishing for the first time the diamide structure of a compound N-acetyl-N'-propionyl-N,N'-dimethyl-o-phenylenediamine (XV), similar to V. Thus the benzimidazolol ester formula (III) has been eliminated as a possibility for this type of compound. Third is the presentation of new evidence strongly favoring the amide structure (IV) rather than the benzimidazolol structure (II) for a compound, N-acetyl-N,N'-dimethyl-4-methyl-1,2-phenylenediamine (XIII). Fourth is a short section on the stability of benzimidazolium hydroxides.

I. Critique of the Literature on the Structure of 2-Benzimidazolols

The arguments for the benzimidazolol, structure

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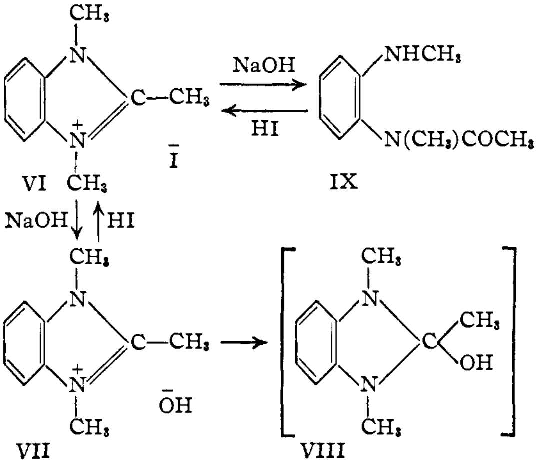
[1] The work discussed in this paper was carried out at Shell Development Company, during a study of the structure of penicillin, under contract with the Office of Scientific Research and Development (O. S. R. D.). *Cf. Science*, **105**, 653 (1947).

[2] O. S. R. D., Penicillin Program, Eli Lilly and Company, L6, 6; **11**, 14 (U. S. Office of Publication Board, PB/L80033 and 80037).

[3] Niementowski, *Ber.*, **20**, 1886 (1887).

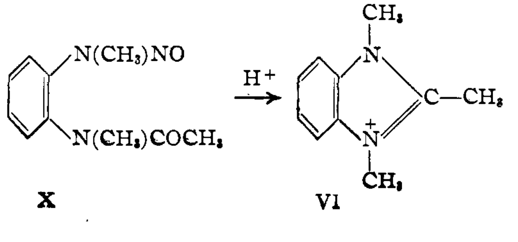
[4] Fischer and Romer, *J. prakt. Chem.*, [2] **73**, 419 (1906).

VIII, seem to have been developed[3,4] in the literature on the following assumptions. The compound had been synthesized from the benzimidazolium iodide by reaction with caustic and could be reverted to the benzimidazolium salt on treatment in the cold with acid. Therefore, it seemed logical to assume that the cyclic structure would be retained. Furthermore, it was thought that inasmuch as the product was not strongly basic and was volatile with steam, it was not the corresponding quaternary hydroxide (VII) but rather had been converted to the benzimidazolol form (VIII).



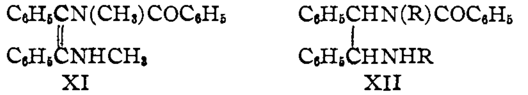
When the open amide form (IX) was eventually considered, it seemed less likely to the original investigators that it would be converted to the quaternary salt (VI) on treatment with acid. And yet in the same paper[4] it was assumed that the amide form (IX) could not be separated in pure condition because it was so readily converted to the benzimidazolol (VIII). It is readily apparent that these two assumptions are irreconcilable, for if both the conversion of the amide (IX) to the benzimidazolol (VIII) and the conversion of the benzimidazolol (VIII) to the quaternary salt (VI) are fast and readily carried out then the over-all reaction (IX to VI) must be rapid and simple.

Several observations reported in the literature furnish corroborative evidence for the conversion of the amide form (IX) to the benzimidazolium salt (VI). Fischer[4] found that treatment of N-acetyl-N,N′-dimethyl-*o*-phenylenediamine (IX), thought to be 1,2,3-trimethyl-2,3-dihydro-2-benzimidazolol (VIII), with cold nitrous acid involving minimal contact with acid gave a nitroso derivative to which he assigned formula (X)



This compound was hydrolyzed readily with acid to give the benzimidazolium salt (VI). If Fischer's structure for the nitroso derivative is correct, as it appears to be, then it is obvious that conversion of the amide structure to the quaternary salt is a simple and feasible reaction.

If we accept the open amide structure postulated for the derivatives of lophin[4] (XI) and amarin[5] (XII) corresponding to structure (IX) then the ready conversion of the amide form (IX) to the corresponding benzimidazolium salt in acid has a ready parallel, for this type of transformation is known to occur with these compounds.



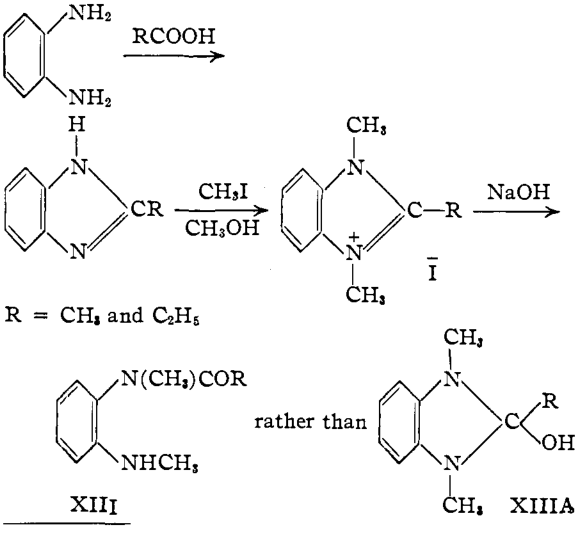
$$\underset{\text{XI}}{\begin{array}{l}C_6H_5CN(CH_3)COC_6H_5\\ \quad\| \\ C_6H_5CNHCH_3\end{array}} \qquad \underset{\text{XII}}{\begin{array}{l}C_6H_5CHN(R)COC_6H_5\\ \quad| \\ C_6H_5CHNHR\end{array}}$$

It is of interest to note that when hydrolysis products of lophonium salts were first obtained, they were assigned the carbinol structure,[6] (related to structure (VIII)), but when diacyl derivatives were prepared both these and the monoacyl derivatives (XI and XII) were assigned the amide structure.

It is also of interest to note that the amide structure has been assigned[7] N-benzoyl-N,N′-diphenyl-*o*-phenylenediamine, and that the diacetyl derivative of N,N′-diphenyl-*o*-phenylenediamine has been assigned[8] the diamide structure. However, no proof of structure was given in either instance.

II. Proof of Structure for N-Acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine

In order to establish the diamide structure of N-acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine (XV) and consequently to eliminate the benzimidazolol ester structure the following series of reactions was carried out.



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[5] Japp and Moir, *J. Chem. Soc.*, **77**, 619 (1900).

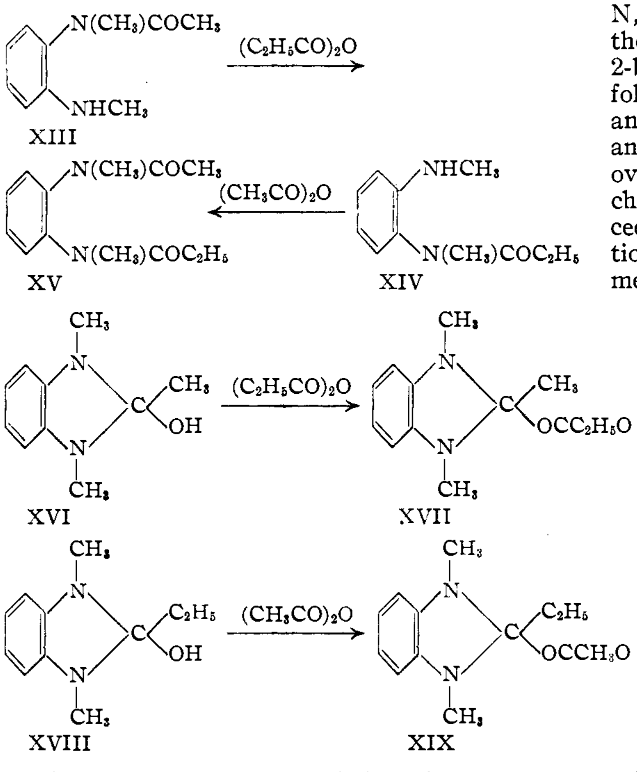
[6] Japp and Davidson, *ibid.*, **67**, 33 (1895).

[7] Chapman and Perott, *ibid.*, 1775 (1932).

[8] Clemo, Perkin and Robinson, *ibid.*, **125**, 1751 (1924).

The reactions follow closely those outlined by workers at Eli Lilly and Company.[2] Starting with *o*-phenylenediamine and acetic acid 2-methylbenzimidazole was readily obtained by the method of Phillips.[9] Treatment of this material with methyl iodide gave the corresponding 1,2,3-trimethylbenzimidazolium iodide which was hydrolyzed with strong sodium hydroxide to give N-acetyl-N,N'-dimethyl-*o*-phenylenediamine (XIII). Starting with *o*-phenylenediamine and propionic acid the same series of reactions was carried out and there was obtained 2-ethylbenzimidazole, 1,3-dimethyl-2-ethylbenzimidazolium iodide and finally N-propionyl-N,N'-dimethyl-*o*-phenylenediamine (XIV)

It can readily be seen that treatment of N-acetyl-N,N'-dimethyl-*o*-phenylenediamine (XIII) with propionic anhydride or of N-propionyl-N,N'-dimethyl-*o*-phenylenediamine (XIV) with acetic anhydride should give the same compound, N-acetyl-N'-propionyl-N,N'-dimethyl-*o*-phenylenediamine (XV). However, if, as it had been previously thought, the products had the benzimidazolol structures, (XVI) and (XVIII), then the products of acylation, compounds (XVII) and (XIX), should be different.



XIII

XV

XIV

XVI

XVII

XVIII

XIX

These acylations were carried out by treatment with the respective acid anhydrides in pyridine at room temperature according to the method first used by Eli Lilly and Company.[2]

The two products had the same melting point, gave no depression of melting point in a mixture and gave identical infrared absorption spectra. From these results the structure of this compound has been considered established as N-acetyl-N'-propionyl-N,N'-dimethyl-*o*-phenylenediamine (XV) and not as the benzimidazolol ester (XVII or XIX). With this structure established, it would seem logical that the product prior to acylation should have the amide structure (XIII) and not the benzimidazolol structure (XVI).

However, in consideration of the possibility that the conditions for the acylation of the supposed benzimidazolol might result in the opening of the ring and formation of the diamide, it is to be pointed out that the conditions for the acylation were quite mild, *i. e.*, acid anhydride in pyridine at room temperature followed by recrystallization from benzene–petroleum ether. These conditions were at least as mild as those by which the monoacetylated product is formed, *i. e.*, hot strong alkali on the benzimidazolium salt or acid anhydride on the N,N'-dialkyl-*o*-phenylenediamine.

III. Structural Evidence for N-Acetyl-N,N'-dimethyl-4-methyl-1,2-phenylenediamine

Niementowski[3] who first prepared N-acetyl-N,N'-dimethyl-4-methyl-1,2-phenylenediamine thought it to be 1,2,3,5-tetramethyl-2,3-dihydro-2-benzimidazolol. He purified it by distillation followed by recrystallization from aqueous ethanol and observed that in spite of the fact that the analysis was satisfactory the compound melted over a range, 115–135°. Fischer and Romer[4] checked these results and extending the study succeeded in separating this material into two fractions: One on recrystallization from ligroin melted at 148–150°; the other on recrystallization from aqueous ethanol or slow sublimation melted at 166–167°. However, they believed these to be two crystalline modifications of the benzimidazolol (XX).

If it could be proved that these two isomers isolated by Fischer and Romer[4] were really structural isomers as shown by (XXA) and (XXB) then the amide nature of the product would be established.

To gain additional information concerning these isomers, an attempt was made to repeat the work of Fischer and Romer.[4] The results were in agreement in that the first product gave a satisfactory analysis in spite of the fact that it melted at 115–125° and that a good yield of isomer which melted at 166–167° was obtained upon recrystallization from methanol.

Propionylation of the purified isomer which melted at 166–166.5° gave after evaporation of the excess liquid reagents a highly crystalline residue. One recrystallization from petroleum ether gave an 83% yield of the propionyl derivative which melted at 94.5–95.5°. It would appear that a uniform product had been obtained. Similar

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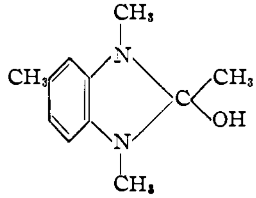
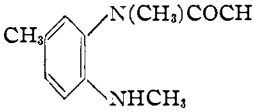
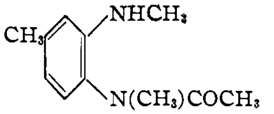
(9) Phillips, *J. Chem. Soc.*, 2393 (1928).



XX



XXA



XXB

propionylation of the mixture of isomers which melted at 115–125° gave after removal of the liquid reagents a sirupy residue which could be converted to soft crystals only with difficulty. Recrystallization of this material gave a 63% yield of a propionyl derivative which melted at 75.3–78.3°. A mixture of this material and that from the preceding experiment (m. p. 94.5–95.5°) melted over a seven-degree range, 76–83°. The difference in the behavior of these two fractions on propionylation is taken as an indication that the fraction melting at 115–125° is a mixture of structural isomers (XXA and XXB) of the amide form.

IV. Stability of Benzimidazolium Hydroxides

During the course of this work it has been found that benzimidazolium hydroxides are quite stable in the absence of excess soluble base. 1,3-Dimethyl-2-ethylbenzimidazolium hydroxide, prepared from the corresponding iodide by treatment with silver oxide, was not destroyed on standing in aqueous solution for a week followed by heating at 90° for two hours. This stability was demonstrated by the fact that the solution remained strongly alkaline, the ultraviolet absorption spectrum remained constant and the hydrolysis product, N,N′-dimethyl-N-propionyl-*o*-phenylenediamine, which is sparingly soluble in water, was not precipitated.

Tinkler[10] observed that an aqueous solution of the supposed 1,3-dimethyl-2,3-dihydro-2-benzimidazolol became strongly basic on standing and that its ultraviolet absorption spectrum changed from that of the "benzimidazolol" to that of benzimidazolium salt. No such change was observed by the present authors with the N-propionyl-N,N′-dimethyl-*o*-phenylenediamine in alcohol or aqueous solution. These solutions remained completely neutral and gave a constant ultraviolet absorption spectrum even after standing for one week. In the light of present knowledge, no explanation of Tinkler's observations presents itself.

Acknowledgment.—The assistance of Mr. Douglas G. Norton and Mr. Lloyd J. Mitchell in carrying out certain preparations is gratefully acknowledged.

Experimental

A. N-Acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine

2-Ethylbenzimidazole.—This material was prepared from *o*-phenylenediamine with propionic acid according to the method of Phillips.[9] The 2-ethylbenzimidazole melted at 172–173° after recrystallization from 50% ethanol.

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74. Found: C, 66.67, 66.88; H, 7.77, 7.80.

1,3-Dimethyl-2-ethylbenzimidazolium Iodide.—A mixture of 40 g. of crude 2-ethylbenzimidazole, 80 g. of methyl iodide and 44 ml. of methanol was heated in sealed tubes at 150° for ten hours. The product was dissolved in 200 ml. of hot methanol and then 200 ml. of ether was added. Cooling the solution caused the separation of 50.2 g. (60% yield) of material which melted at 168–170°. A recrystallization of 40.2 g. of this material from 250 ml. of absolute alcohol involving treatment with charcoal gave 21 g. of crystals which melted at 170.5–172°. Addition of ether to the filtrate caused the separation of 11 g. of product which melted at 172.5–173°. Additional recrystallizations gave 1,3-dimethyl-2-ethylbenzimidazolium iodide which melted at 173–173.5°.

Anal. Calcd. for $C_{11}H_{15}N_2I$: I, 42.00. Found: I, 42.1, 41.7.

N-Propionyl-N,N′-dimethyl-*o*-phenylenediamine.—1,3-Dimethyl-2-ethylbenzimidazolium iodide, 23 g., was hydrolyzed with 46 g. of potassium hydroxide and 230 ml. of water at reflux for ninety minutes. The cooled solution was extracted with three 50-ml. portions of benzene. The extract was dried, concentrated to about 35 ml., and diluted with 60 ml. of petroleum ether. Cooling the solution caused the separation of 7 g. (48% yield) of crystals which melted at 160–162°. Recrystallization from a mixture of 50 ml. of benzene and 50 ml. of petroleum ether involving treatment with charcoal and then from 20 ml. of carbon tetrachloride gave 4.8 g. of N-propionyl-N,N′-dimethyl-*o*-phenylenediamine which melted at 161–162.2°.

Anal. Calcd. for $C_{11}H_{15}N_2O$: C, 69.08; H, 7.91. Found: C, 68.56, 68.61; H, 8.32, 8.34.

N-Acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine (By Acetylation).—A solution of 1.23 g. (0.0066 mole) of crude N-propionyl-N,N′-dimethyl-*o*-phenylenediamine, m. p. 158–160°, in 13.5 g. of pyridine and 5.4 g. (0.053 mole) of acetic anhydride was allowed to stand at room temperature for seventy-two hours. Removal of liquid reagents under reduced pressure left a crystalline mass which melted at 120.5–121.5°. One recrystallization from a mixture of benzene and petroleum ether treated with charcoal gave 0.93 g. (62% yield) of N′-acetyl-N-propionyl-N,N′-dimethyl-*o*-phenylenediamine which melted at 121–121.5°. A mixture of this material with that subsequently obtained upon propionylation of N,N′-dimethyl-N-acetyl-*o*-phenylenediamine melted at 121–121.5°.

N-Acetyl-N,N′-dimethyl-*o*-phenylenediamine.—This material, m. p. 163–164°, was prepared according to the procedure outlined by workers at Eli Lilly and Company,[2] which is very similar to that just described for N,N′-dimethyl-N-propionyl-*o*-phenylenediamine. A mixture with a sample furnished by them melted at 163–164°.

N-Acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine (By Propionylation).—A solution of 1 g. (0.0056 mole) of N-acetyl-N,N′-dimethyl-*o*-phenylenediamine, 14.6 g. of pyridine and 5.85 g. (0.045 mole) of propionic anhydride was allowed to stand at room temperature for seventy-two hours. The solution was concentrated under reduced pressure (3 mm.) to a crystalline mass which melted at 121–121.5°. One recrystallization from a mixture of benzene and petroleum ether gave 1.06 g. of N-acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine which melted at 121–121.5°. Additional recrystallizations did not alter the melting point.

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[10] Tinkler, *J. Chem. Soc.*, **101**, 1245 (1912).

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74. Found: C, 66.67, 66.88; H, 7.77, 7.80.

B. N-Acetyl-N,N′-dimethyl-4-methyl-1,2-phenylenediamine

Hydrolysis of 1,2,3,5-Tetramethylbenzimidazolium Iodide.—This procedure follows that of Fischer.[6] A mixture of 55 g. of 1,2,3,5-tetramethylbenzimidazolium iodide, 70 g. of potassium hydroxide and 210 g. of water was heated on a steam-cone for one hour. The mixture was cooled and the white solid which separated was collected on a filter. After drying in air overnight this material weighed 45 g. and melted from 115–135°. One recrystallization from ethanol and water gave 40 g. of crystalline material which melted at 115–125°. In agreement with the results of Niementowski[3] and Fischer and Romer[4] this material was found to give a satisfactory analysis in spite of the wide range of its melting point. These results have been interpreted as favoring the presence of isomers, *i. e.*, N-acetyl-N,N′-dimethyl-4-methyl-1,2-phenylenediamine and the N′-acetyl isomer, rather than impurity.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39. Found: C, 68.9, 68.9; H, 8.3, 8.4.

In consideration of the possibility that the fraction melting at 115–125° contained some impurity other than a mixture of amide forms, there exist three experimental observations indicating that such is not the case: (1) satisfactory elementary analysis by three independent investigators; (2) infrared absorption spectrum of the fraction melting at 115–125° shows no evidence of impurity; (3) elementary analysis of the propionylation product, reported subsequently, was in close agreement with the theoretical values even though the product melted over a three-degree range.

This material was dissolved in 225 ml. of 95% ethanol and 25 ml. of water was added. Cooling the solution caused the separation of 7.5 g. of crystals which were collected from solution A by filtration and melted at 165–165.6°. After three additional crystallizations from ethanol, the N-acetyl-N,N′-dimethyl-4-methyl-1,2-phenylenediamine melted sharply at 166–166.5°.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57. Found: C, 68.7, 68.6; H, 8.1, 8.3; N, 14.0, 14.2.

Recrystallization of this material from petroleum ether did not change the melting point.

Evaporation of the solvent from solution A to a low volume followed by cooling gave 23 g. of crystalline material which melted at 163.5–167°. The solvent was removed from the residue to leave 9 g. of material which was taken up in petroleum ether. Successive cooling, concentration and cooling gave the following fractions: 1.6 g., m. p. 148–152°; 1.7 g., m. p. 120–125°; 2.0 g., m. p. 124–130°; 3.0 g., m. p. 100–110°. The first fraction was recrystallized from petroleum ether and gave 1.1 g., m. p. 160.0–162.8°. The second and third fractions were crystallized several times from petroleum ether with some elevation of melting point. Finally a sample which melted at 137.5–138° was analyzed.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39. Found: C, 68.7; H, 8.2.

Propionylation of Hydrolysis Products of 1,2,3,5-Tetramethylbenzimidazolium Iodide.—One gram of the isomer, m. p. 166–166.5°, from the above experiment was placed in a glass-stoppered flask with 15 g. of pyridine and 6 g. of propionic anhydride and allowed to stand at room temperature for four days. The liquid materials were removed under reduced pressure. The crystalline residue was taken up in 60 ml. of boiling petroleum ether. After the hot solution had been treated with a little "Norite" it was cooled in ice. The white crystalline material which separated weighed 1 g. (83% yield) and melted at 94.5–95.5°. Another recrystallization from petroleum ether gave 0.75 g. of material, which melted at 95.5–96.3°.

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12. Found: C, 67.9, 67.9; H, 7.9, 8.2.

One gram of the mixture of isomers, m. p. 115–125°, from the previous hydrolysis experiment was placed in a glass-stoppered flask with 15 g. of pyridine and 6 g. of propionic anhydride and allowed to stand at room temperature for four days. Liquids were removed by stripping the product under reduced pressure. The sirupy residue was taken up in 60 ml. of boiling petroleum ether. The hot solution was treated with a little "Norite" and filtered. Cooling the filtrate in ice caused the separation of 0.8 g. (67% yield) of white crystalline material which melted at 75.3–78.3°. Recrystallization from petroleum ether gave 0.5 g. of product which melted at 75.5–78.3°.

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12. Found: C, 67.7, 67.6; H, 8.1, 8.2.

A mixture of this material and that from the preceding experiment which melted at 94.5–95.5°, melted at about 76–83°.

C. 1,3-Dimethyl-2-ethylbenzimidazolium Hydroxide

A solution of 1,3-dimethyl-2-ethylbenzimidazolium iodide, 0.5 g. (0.00167 mole) in 60 ml. of water, was treated with silver oxide. (A solution of 0.425 g. (0.0025 mole) of silver nitrate in 2.1 ml. of water was treated with 0.112 g. (0.0028 mole) of sodium hydroxide in 1 ml. of water. The silver oxide was collected on a filter and washed well with water.) The silver iodide and slight excess of silver oxide were removed by filtration. The filtrate was strongly alkaline and gave a negative test for iodide ion. The ultraviolet absorption spectra of the solution shortly after preparation, and again after standing at room temperature for one week followed by additional heating at 90° for two hours were identical. The solution was still strongly alkaline after this heating had been completed. The fact that no material separated from this solution on cooling indicated that only a very small amount, if any, of N-propionyl-N,N′-dimethyl-*o*-phenylenediamine could have been formed since this material is insoluble in water.

Interpretation of Infrared Spectra

I. **N-Acetyl-N′-propionyl-N,N′-dimethyl-*o*-phenylenediamine.**—The spectrum of this material as a 5% (wt./vol.) solution in chloroform showed one strong band at 6.04 μ (1656 cm.$^{-1}$) attributable to the amide carbonyl and a weaker band at 6.25 μ (1600 cm.$^{-1}$) attributable to the phenyl ring but with increased intensity due to the fact that the phenyl ring is attached to an amine nitrogen atom. If this compound were an ester of a benzimidazolol as this type of compound had been previously thought to be, it would be expected to show a strong band in the double bond region near 5.75 μ (1739 cm.$^{-1}$) and no band near 6.0 μ (1667 cm.$^{-1}$).

II. **N-Acetyl-N′-benzoyl-N,N′-dimethyl-*o*-phenylenediamine.**—The spectrum of this material (10% (wt./vol.) solution in chloroform) was very similar to that of the previous compound, I, but exhibited the additional weak band near 6.30 μ (1587 cm.$^{-1}$) arising from the benzoyl group.

III. **N-Acetyl-N,N′-dimethyl-*o*-phenylenediamine.**—The spectrum of this material (5% (wt./vol.) solution in chloroform) showed a weak band near 3.0 μ (3333 cm.$^{-1}$) attributable to —NH and a strong band at 6.07 μ (1647 cm.$^{-1}$) attributable to amide carbonyl. Weaker bands at 6.22 μ and 6.59 μ (1608 cm.$^{-1}$ and 1517 cm.$^{-1}$) are ascribable to the phenyl ring. This compound had been previously thought to be 1,2,3-trimethyl-2,3-dihydro-2-benzimidazolol. The absorption to be expected from such a compound would be a strong band near 3.0 μ (3333 cm.$^{-1}$) and only weak to moderate absorption in the double-bond region (5.5–6.4 μ) (1818–1562 cm.$^{-1}$) due to the ring system, as indicated by studies on simpler benzimidazole derivatives.

IV. **N-Benzoyl-N,N′-dimethyl-*o*-phenylenediamine.**—The spectrum of a 3% (wt./vol.) solution of this material in carbon tetrachloride was very similar to that of the previous compound III, except that again a 6.32 μ (1582 cm.$^{-1}$) band was present, due to the benzoyl group.

The spectra reported in Table I were obtained with a 0.15 mm. cell width. The wave lengths are in "μ." The intensities (figures in parentheses) are expressed in units of 10% absorption. The letter "S" represents solvent absorption.

TABLE I

I	II	III	IV
2.90(1)	~2.90(1)	2.93(3)	2.95(2)
3.2–3.4 S	3.2–3.4 S	3.2–3.4 S	3.38(1)
6.04(9)	6.06(10)	6.07(10)	6.08(6)
6.25(3)	6.24(3)	6.21(4)	6.20(3)
6.67(5)	6.31(2)	6.58(8)	6.32(2)
6.85(3)	6.66(8)	7.02(6)	6.56(5)
7.24(7)	~7.0(8)	7.22(8)	6.78(1)
7.38(3)	7.25(9)	7.38(4)	6.90(1)
7.65(1)	7.38(4)	7.57(5)	7.02(2)
7.75(1)	7.63(5)	7.71(6)	7.25(4)
8.0–8.4 S	7.9(2)	8.0–8.4 S	7.37(3)
8.76(4)	8.0–8.4 S	8.54(4)	7.56(3)
9.02(1)	8.45(1)	8.75(8)	7.67(2)
9.27(4)	8.77(3)	9.01(1)	7.98(4)
9.57(2)	8.88(2)	9.26(3)	8.54(3)
9.98(2)	9.08(2)	9.43(2)	8.97(2)
10.20(3)	9.26(4)	9.63(4)	9.12(2)
>11.5 S	9.56(1)	10.23(2)	9.35(1)
	9.74(2)	>11.5 S	9.59(1)
	9.91(2)		9.70(1)
	10.17(3)		9.93(2)
	>11.5 S		10.81(1)
			11.40(1)
			>12 S

Summary

Spectroscopic and chemical data are presented which furnish strong evidence that the hydrolysis product of a 1,3-dialkylbenzimidazolium salt has an amide structure, N-acyl-N,N′-dialkyl-*o*-phenylenediamine instead of a 1,2,3-trialkyl-2,3-dihydro-2-benzimidazolol structure as previously supposed.

The product derived by subsequent acylation has been established as a diamide, N,N′-diacyl-N,N′-dialkyl-*o*-phenylenediamine rather than the previously supposed 1,2,3-trialkyl-2,3-dihydro-2-benzimidazolol ester.

In view of this disagreement, a critique of prior literature has been presented.

Finally it has been shown that the benzimidazolium hydroxides are stable in aqueous or alcohol solution in the absence of excess soluble base.

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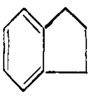
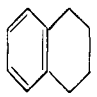
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Tetrahydroacenaphthene and the Mills–Nixon Effect

BY WILLIAM S JOHNSON AND HOWARD J. GLENN[1]

The original postulate of Mills and Nixon[2]—that the double bonds of the hydrindene and tetralin molecules are stabilized in the forms I and II due to steric effects exerted on the benzenoid nucleus by the fused alicyclic rings—although not literally acceptable in view of current concepts, nevertheless leads to the suggestion that molecules containing these ring structures might be expected to exhibit behavior attributable to steric inhibition of resonance in which the forms I and II contribute more than the alternate (Kekulé) canonical forms to the electronic state of the molecule. Since all attempts thus far to detect any marked degree of such resonance inhibition have failed, it occurred to us that such an effect might be more recognizable with a molecule such as tetrahydroacenaphthene (IIIa or b) in which the tetralin molecule is superimposed on the hydrindene structure in such a way that the postulated straining effect of the exocyclic rings is reinforced.[3] Thus if this strain were sufficient to render the structure IIIb enough higher in energy than IIIa, it might be expected that tetrahydroacenaphthene and its derivatives would behave chemically more like IIIa than a hybrid of IIIa and IIIb. With a view to studying this hypothesis, we have prepared tetrahydroacenaphthene and certain derivatives, and have made preliminary observation of some of their properties.


I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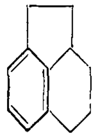
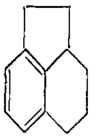

IIIa


IIIb

Tetrahydroacenaphthene was readily secured in 95% yield by hydrogenation of acenaphthene over Raney nickel catalyst. The difficulty in stopping the reduction at the tetrahydro stage, which has been the experience of previous workers,[4] was eliminated by limiting the amount of hydrogen available in the bomb to the calculated quantity. The reduction was thus simply carried out by shaking until all of the hydrogen was absorbed.[5] The in-

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[2] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

[3] This hypothesis involves the assumption—justified only on the basis of examination of crude molecular models—that the mutual fusion of the five-six-membered alicyclic rings of tetrahydroacenaphthene does not in some way counteract the steric influence which these rings independently exert upon the benzenoid nucleus.

[4] (a) v. Braun and Kirschbaum, *Ber.*, **55**, 1680 (1922); (b) Goswami, *Compt. rend.*, **179**, 1269 (1924); (c) Orlow and Belopolski, *Ber.*, **62**, 1226 (1929); (d) Ipatiev, *Ber.*, **42**, 2092 (1909).

[5] We are indebted to Dr. Homer Adkins for suggesting this procedure.