4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid, m.p. 227–229°.[3b]

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 75.88; H, 5.57.

A small sample (0.1 g.) of the reference compound, 1,2,-3,4-tetrahydro-1,1′-binaphthyl-3,4-dicarboxylic acid, m.p. 227–229°, was sublimed at 200° (0.3 mm.). The sublimate, m.p. 97–98°, was insoluble in 5% aq. sodium bicarbonate. It was dissolved in 20 ml. of cold 10% aq. potassium hydroxide and reprecipitated with glacial acetic acid. The precipitate was collected with the aid of a centrifuge and was washed with water. The yield was 0.1 g., m.p. 213–215°. When mixed with a sample of the degradation product obtained above, no depression of the melting point was observed.

The 173 mg. of crude residue obtained from the degradation (see above) was decarboxylated and dehydrogenated by the procedure reported previously[3b] to give 18 mg. of a product, m.p. 153–155°. When samples of this material were mixed with an authentic sample of 1,1′-binaphthyl, m.p. 156–158°, there was no melting point depression.

URBANA, ILL.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

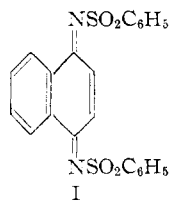
Quinone Imides. XXXII. Reactions of 1,4-Naphthoquinonedibenzenesulfonimide with Pyridine and its Derivatives

BY ROGER ADAMS AND SEYMOUR H. POMERANTZ

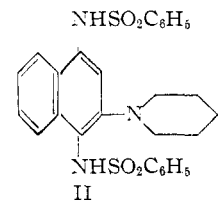
RECEIVED OCTOBER 8, 1953

1,4-Naphthoquinonedibenzenesulfonamide in pyridine reacts with dilute hydrochloric acid to form 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride. This compound is hydrogenated in ethanol with platinum oxide to 2-(N-piperidino)-1,4-naphthalenedibenzenesulfonamide; in aqueous sodium carbonate to a 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole; in ethanolic alkali with Raney nickel to 5-benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole. This last product was also obtained by hydrogenation of the tetrahydro analog in ethanolic alkali with Raney nickel. The structure of the hexahydrobenzimidazole was proved by its identity with the reduction product of the compound formed by interaction of 1,4-naphthoquinonedibenzenesulfonimide with 2-aminopyridine; hydrolysis converts this 5-benzenesulfonamidobenzo[e]pyrido[a]benzimidazole to the known 5-aminobenzo[e]pyrido[a]benzimidazole. Moist silver oxide reacts with the naphthylpyridinium chloride to give 5-benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole. 1,4-Naphthoquinonedibenzenesulfonimide adds the sodium salt of 2-pyridone to form N-(1′,4′-dibenzenesulfonamido-2′-naphthyl)-2-pyridone.

The reaction of 1,4-naphthoquinonedibenzenesulfonimide (I) with pyridine and an excess of aqueous hydrochloric acid resulted in the formation of a colorless product in essentially quantitative yield. It was hygroscopic and readily formed a hydrate containing one mole of water. The compound contained halogen, and its solution in ethanol gave an immediate precipitate with aqueous ethanolic silver nitrate. It was brilliantly fluorescent under ultraviolet light. It dissolved readily in aqueous sodium carbonate with the formation of an orange-red solution from which the original compound could be obtained by acidification.



I



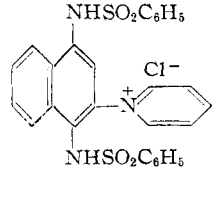
II

Analysis of a dry sample indicated that it was composed of one mole of diimide, one mole of pyridine and one mole of hydrogen chloride. The infrared spectrum in Nujol mull showed the $-SO_2$ band generally associated with sulfonamides at 1171 and 1335 cm.$^{-1}$. There were no bands characteristic of sulfonimides. No normal N–H band appeared in the spectrum of the non-hydrated material, but a broad medium band at about 2720 cm.$^{-1}$ indicated the probability of some sort of bonded N–H in the solid. The limited solubility in a suitable organic solvent prevented a study of the solution spectrum. This same absence of an N–H band also was observed in another sulfonamide described in this communication when the spectrum was determined in Nujol mull, but one appeared in the solution spectrum.

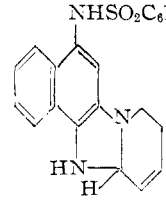
The compound was easily hydrogenated in ethanol solution in the presence of platinum oxide to form 2-(N-piperidino)-1,4-naphthalenedibenzenesulfonamide (II). The latter structure was established by its synthesis from I and piperidine.

From these data the most likely structure of the compound was deduced as the pyridine–hydrogen chloride adduct, 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride (III). The facile hydrogenation of III to II is in agreement with earlier work[1] on the catalytic hydrogenation of a number of pyridinium salts.

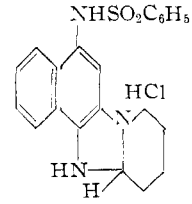
Hydrogenation of III in aqueous sodium carbonate over platinum oxide at ordinary pressure resulted in a compound formulated as IV. The position of the double bond in the pyridine residue was not determined.



III



IV



V

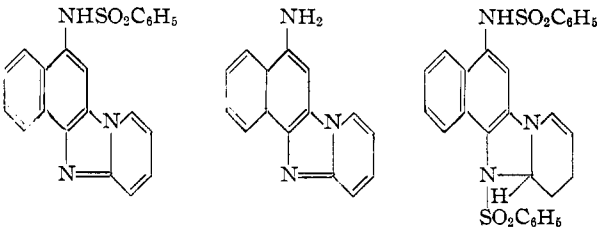
The infrared spectrum of IV in Nujol mull showed no N–H band. In chloroform solution, however, an N–H band at 3360 cm.$^{-1}$ was present and in pyridine solution a very broad N–H band occurred at about 3400 cm.$^{-1}$. A medium band at 1632 cm.$^{-1}$ occurred in both mull and solution spectra. The spectra also showed characteristic $-SO_2$ bands.

(1) T. S. Hamilton and R. Adams, THIS JOURNAL, **50**, 2260 (1928).

The hydrogenation with platinum catalyst in basic solution was unexpected. The reaction stopped after two moles of hydrogen were absorbed. The termination of the hydrogenation before three moles reacted may be explained by the precipitation of the resulting product at that stage and by the poisoning of the catalyst. Attempted hydrogenation of this initial hydrogenation product IV in ethanol solution over platinum oxide failed. However, when a small amount of concentrated hydrochloric acid was added to the ethanolic solution, an additional mole of hydrogen reacted and the product was formulated as 5-benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole hydrochloride (V). The base of compound V was also obtained directly by Raney nickel hydrogenation of III when dissolved in alkaline ethanol solution.

The presence of imino groups in compounds IV and V was established chemically by benzenesulfonation.

Demonstration of the structures IV and V was accomplished in the following way. When 2-aminopyridine was allowed to react with I in chloroform solution a precipitate of benzenesulfonamide appeared after several days and from the filtrate was isolated a product to which was assigned structure VI, 5-benzenesulfonamidobenzo[e]pyrido-[a]benzimidazole. 2-Amino-4-methylpyridine reacted in a similar way. The reaction is not unlike that reported between *p*-benzoquinone and 2-aminopyridine.[2] When VI was hydrolyzed with hydrobromic acid–phenol,[3] the known 5-aminobenzo[e]pyrido[a]benzimidazole (VII) resulted, identical with an authentic sample.[4]



VI VII VIII

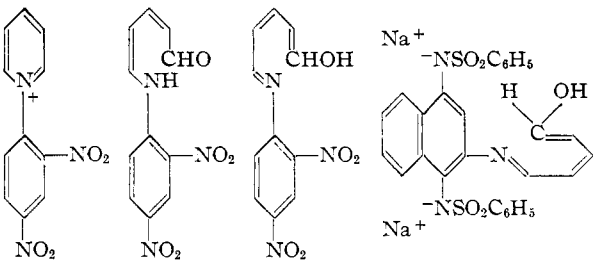
Hydrogenation of VI over platinum oxide in ethanol solution containing a small amount of hydrochloric acid resulted in the formation of V, thus confirming the structures of IV and V. This reaction also demonstrated that hydrogenation of III in basic solution resulted in the cleavage of a benzenesulfonyl group, the partial hydrogenation of the pyridine residue and, finally, the formation of a five-membered ring.

When an aqueous sodium carbonate solution of III was evaporated to dryness in a stream of air and the residue repeatedly extracted with cold absolute ethanol, a red solid was obtained. Attempts at recrystallization of this compound for analysis failed because heating the compound with any solvent caused the formation of a very light orange, halogen-free solid with an analysis corresponding to the formula $C_{27}H_{21}N_3O_4S_2$; this compound was obviously formed from III by loss of the elements of hydrogen chloride. It was formulated as VIII. Compound VIII also was obtained by treating an ethanolic solution of III with moist silver oxide or, in better yield, by exactly neutralizing an aqueous alkaline solution of III with glacial acetic acid.

Acidification with hydrochloric acid of an aqueous sodium carbonate solution of VIII resulted in the formation of III. However, acidification of such a basic solution with acetic acid caused the regeneration of VIII. Compound VIII could also be converted directly to III by triturating VIII with concentrated hydrochloric acid followed by addition of water to the resultant gummy mass.

Hydrogenation of VIII suspended in ethanol using platinum oxide catalyst proceeded slowly with the formation of II. Hydrogenation of VIII dissolved in aqueous sodium carbonate over platinum oxide resulted in the isolation of IV.

The behavior of III in basic solution is similar in certain respects to other pyridinium compounds such as 2,4-dinitrophenylpyridinium chloride (IX).[5]



IX X XI XII

Both compounds dissolve in cold base with the formation of red solutions. In the case of IX the red compound isolated from solutions is unstable. It has been postulated that its structure is X or its tautomer XI.[5b] By analogy the unstable red compound isolated from III might have structure XII (or its tautomer). On acidification of X (or XI) hydrolysis occurs with the formation of 2,4-dinitroaniline and glutaconic dialdehyde. Acidification of a basic solution of III with dilute hydrochloric acid, however, regenerated III which is stable to boiling aqueous hydrochloric acid. The basic solution of compound III probably contains compound XII which is reconverted through VIII to III by the action of hydrochloric acid but merely converted to VIII when the alkali is neutralized with acetic acid. The ease of hydrolysis of pyridinium compounds is ascribed[6] to the presence of a strongly electron-attracting group on the nitrogen atom. The dibenzenesulfonamidonaphthyl group is much less electronegative than the 2,4-dinitrophenyl group and thus hydrolysis with ring opening in the case of XII is not induced.

The hydrogenations of III carried out in basic solution probably involve ions such as XII through XV. Ring closures probably occur by way of nucleophilic attack by nitrogen on the nearby α-

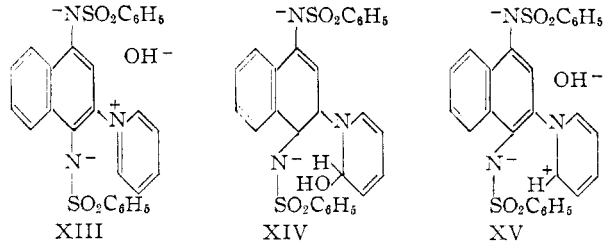
(2) L. Schmid and H. Czerny, *Monatsh.*, **83**, 31 (1952).

(3) H. R. Snyder and H. C. Geller, THIS JOURNAL, **74**, 4864 (1952).

(4) G. Morgan and J. Stewart, *J. Chem. Soc.*, 1057 (1939).

(5) (a) T. Zincke, *Ann.*, **330**, 361 (1904); (b) T. Zincke, G. Heuser and W. Möller, *ibid.*, **333**, 296 (1904); (c) T. Zincke and W. Würker, *ibid.*, **338**, 107 (1905).

(6) H. S. Mosher in R. C. Elderfield, "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 427.



XIII XIV XV

carbon of the pyridine moiety accompanied by a loss of hydroxyl ion.

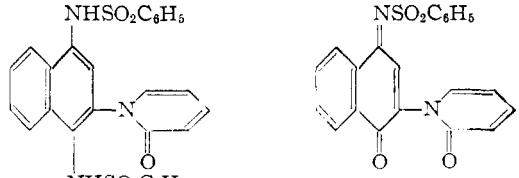
A reaction between I and pyridine was demonstrated. When the red pyridine solution of I was air evaporated a dark gum resulted which could not be purified; trituration of this gum with dilute hydrochloric acid gave III.

A compound analogous to III was made from I, pyridine and hydrobromic acid. It is interesting to note that the infrared spectra of the pyridinium chloride and the bromide are nearly identical. The use of dilute acetic acid or dilute sulfuric acid in place of hydrobromic or hydrochloric acid resulted only in the isolation of starting material.

The substitution of β-picoline for pyridine gave only a low yield of impure product; α-picoline, 2,4- and 2,6-lutidines failed to give adducts under the same conditions as pyridine.

p-Quinonedibenzenesulfonimide did not react similarly to the 1,4-naphthoquinonedibenzenesulfonimide; only reduction occurred.

The reaction of I with the sodium salt of 2-pyridone in dioxane, followed by acidification with dilute hydrochloric acid, resulted in the formation of N-(1′,4′-dibenzenesulfonamido-2′-naphthyl)-2-pyridone (XVI). A similar reaction occurred with the sodium salt of 4-methyl-2-pyridone with formation of the methyl substituted XVI. The infrared spectrum of XVI showed a broad N–H band at



XVI XVII

about 3110 cm.$^{-1}$ and a carbonyl absorption band at 1656 cm.$^{-1}$ assigned to the cyclic amide unit. Oxidation of XVI with lead tetraacetate led to the corresponding diimide.

Compound III was oxidized with lead tetraacetate in glacial acetic acid, benzene and chloroform to give an orange compound formulated as XVII because of its color, analysis and infrared spectrum. The infrared spectrum (Nujol mull) showed an $-SO_2$ band at 1137 cm.$^{-1}$ and several bands in the double bond region at 1696 cm.$^{-1}$, 1620 cm.$^{-1}$ and 1587 cm.$^{-1}$ that are difficult to assign to definite structural units. This reaction is quite similar to that which occurred when 2-methyl-*x*,5-dichloro-*p*-phenylenedibenzenesulfonamide was oxidized with lead tetraacetate.[7] One benzenesulfonamide group was hydrolyzed and the product isolated was 2-methyl-*x*,5-dichloro-*p*-quinone-(1 or 4)-monobenzenesulfonimide. However, in the present case, the isolation of a monoimide from dry solvents such as benzene and chloroform indicate the possibility of an oxidation rather than a hydrolysis in these solvents.

Acknowledgment.—The authors wish to thank Mr. J. Nemeth, Mrs. Lucy Chang and Mrs. Esther Fett for the microanalyses and Miss Helen Miklas for the determination of the infrared absorption spectra.

Experimental[8]

Reactions of 1,4-Naphthoquinonedibenzenesulfonimide with Pyridine and Aqueous Acids. A. Hydrochloric Acid. 1,4-Dibenzenesulfonamido-2-naphthylpyridinium Chloride (III).—To a cold solution of 1.00 g. of 1,4-naphthoquinonedibenzenesulfonimide in 28 ml. of pyridine was added with vigorous shaking 80 ml. of cold 1:1 aqueous hydrochloric acid. A white precipitate appeared. The mixture was further diluted with 200 ml. of water, cooled for 30 min. in ice and filtered. The yield of nearly pure material was 1.27 g. (98%). Several recrystallizations first from ethanol and then from nitromethane gave a pure product, m.p. 242–244° dec. This proved to be hydrated material.

Anal. Calcd. for $C_{27}H_{22}ClN_3S_2 \cdot H_2O$: C, 56.88; H, 4.24; N, 7.37; Cl, 6.22; S, 11.25. Found: C, 57.02; H, 4.18; N, 7.40; Cl, 6.05; S, 11.25.

The compound was dehydrated by heating a sample at 118° for 4 hours in a vacuum over phosphorus pentoxide. Calcd.: % loss in H_2O: 3.16. Found: 2.83, 3.17.

Anal. Calcd. for $C_{27}H_{22}ClN_3O_4S_2$: C, 58.74; H, 4.02; N, 7.61. Found: C, 58.90; H, 4.24; N, 7.61.

The compound dissolved in aqueous sodium carbonate to form an orange-red solution and was reprecipitated by the addition of hydrochloric acid. It gave with aqueous ethanolic silver nitrate an immediate white precipitate which was insoluble in nitric acid.

The pyridinium chloride was also obtained by the evaporation of a solution of pyridine and 1,4-naphthoquinonedibenzenesulfonimide and trituration of the red gummy solid with concd. hydrochloric acid. When a solution of 1,4-naphthoquinonedibenzenesulfonimide in pyridine was added to aqueous 1:1 hydrochloric acid only reduction to the diamide resulted.

B. Hydrobromic Acid. 1,4-Dibenzenesulfonamido-2-naphthylpyridinium Bromide.—In a manner similar to that used in preparation of A, a reaction was carried out with 0.50 g. of diimide, 14 ml. of pyridine and 60 ml. of an aqueous solution containing 20 ml. of 48% hydrobromic acid. The yield was 0.60 g. (88%). The sample was purified by two recrystallizations from water and one from nitromethane; m.p. 231° dec. The compound was dehydrated by drying 1 hour in a vacuum at 100° over phosphorus pentoxide. (Prolonged heating of the sample resulted in high carbon values.)

Anal. Calcd. for $C_{27}H_{22}BrN_3O_4S$: C, 54.36; H, 3.72. Found: C, 54.70; H, 4.01.

Only starting material was recovered when dilute acetic or sulfuric acid was used.

Reactions of 1,4-Naphthoquinonedibenzenesulfonimide with Methylpyridines and Dilute Hydrochloric Acid. β-Picoline. 1,4-Dibenzenesulfonamido-2-naphthyl-β-methylpyridinium Chloride.—To a cold solution of 0.50 g. of 1,4-naphthoquinonedibenzenesulfonimide in 5 ml. of β-picoline was added dropwise 10 ml. of concd. hydrochloric acid. After the solution was allowed to stand in ice for 10 min., 100 ml. of water was added slowly and with thorough shaking. The mixture was filtered and the crude solid triturated with acetone. The yield was 0.20 g. (31%). A sample for analysis was prepared by crystallization from an ethanol–benzene solution; the benzene was distilled as the azeotrope with ethanol and water to ensure a solvated-free product, m.p. 255–256° dec.

Anal. Calcd. for $C_{28}H_{24}ClN_3O_4S_2$: C, 59.41; H, 4.27. Found: C, 59.24; H, 4.26.

(7) R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **4**, 2608 (1952).

(8) All melting points are corrected.

α-Picoline, 2,6-lutidine and 2,4-lutidine did not react in a similar manner. Only starting material or the corresponding diamide was recovered.

Attempted condensation of pyridine and hydrochloric acid with *p*-quinonedibenzenesulfonimide resulted only in formation of *p*-phenylenedibenzenesulfonamide.

Hydrogenations of 1,4-Dibenzenesulfonamido-2-naphthylpyridinium Chloride. A. Hydrogenation in Ethanol with Platinum Oxide Catalyst. 2-(N-Piperidino)-1,4-naphthalenedibenzenesulfonamide (II).—A solution of 0.50 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 100 ml. of ethanol was hydrogenated over 0.05 g. of platinum oxide. The solution was filtered and the ethanol evaporated in a stream of air. The red oil crystallized when treated with 60% ethanol. The yield was 0.32 g. (58%). The compound was purified by recrystallization from dilute ethanol; m.p. 188–190° dec. This melting point was slightly lower than that obtained by the second method of preparation described below.

Anal. Calcd. for $C_{27}H_{27}N_3O_4S_2$: C, 62.16; H, 5.22; N, 8.06. Found: C, 61.88; H, 5.16; N, 8.13.

This same compound was also synthesized in the following way. To a solution of 0.50 g. of 1,4-naphthoquinonedibenzenesulfonimide in 15 ml. of chloroform was added 0.5 ml. of piperidine. The solution which immediately became red was set aside for 12 hours. The solution was evaporated to a red oil in a stream of air, redissolved in chloroform, and carbon tetrachloride added until the solution became cloudy. Cooling and scratching the walls of the flask caused a precipitate to form. The yield was 0.57 g. (97%). Several crystallizations from dilute ethanol gave a pure product, m.p. 191.5–193° dec. The infrared spectra of samples made by the two methods were identical.

Anal. Calcd. for $C_{27}H_{27}N_3O_4S_2$: C, 62.16; H, 5.22; N, 8.06. Found: C, 62.31; H, 5.11; N, 8.20.

B. **Hydrogenation in Aqueous Sodium Carbonate with Platinum Oxide Catalyst. 5-Benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole (IV).**—A solution of 0.97 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 80 ml. of water containing 1.0 g. of sodium carbonate was hydrogenated over 0.05 g. of platinum oxide at 2.5 atm. pressure. A precipitate appeared during the course of the hydrogenation and the red solution became colorless. The material was filtered, dissolved in boiling ethyl acetate, and filtered from catalyst. The filtrate was partially evaporated and cooled. The precipitate which formed weighed 0.27 g. (43%). The compound was recrystallized several times from ethyl acetate; slightly pinkish crystals, m.p. 246–247.5° dec.

Anal. Calcd. for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13. Found: C, 66.75; H, 5.15; N, 11.28.

C. **Hydrogenation in Ethanolic Sodium Hydroxide with Raney Nickel Catalyst. 5-Benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole Hydrochloride (V).**—A solution of 0.91 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 60 ml. of ethanol containing 1.0 g. of sodium hydroxide was hydrogenated over Raney nickel at 1.5 atm. pressure. The red solution which became colorless was heated to boiling and filtered from the catalyst. The filtrate was evaporated to a small volume and filtered from the white precipitate that appeared. This solid was triturated with dilute hydrochloric acid and again filtered; the yield was 0.36 g. (54%). It was crystallized first from ethanol and then from nitromethane; m.p. 305–307° dec.

Anal. Calcd. for $C_{21}H_{21}N_3O_2S \cdot HCl$: C, 60.64; H, 5.33; N, 10.10. Found: C, 60.75; H, 5.00; N, 10.12.

The filtrate from the above product was made slightly acid and the red precipitate filtered; yield 0.16 g. (38%). This was recrystallized once from ethyl acetate; m.p. 246.5–248.5° dec. It was identified as 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole.

Hydrogenation of 5-Benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole.—A solution of 0.26 g. of 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole in 80 ml. of ethanol containing 0.7 ml. of concentrated hydrochloric acid was hydrogenated over platinum oxide catalyst. The hydrogenation was complete in about 2 minutes. The solution was boiled, filtered, evaporated to a small volume, cooled and filtered. The yield was 0.27 g. (93%); m.p. 300–306° dec. The compound was identified as 5-benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole hydrochloride.

Attempted hydrogenation of 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole in ethanol without addition of acid resulted in no uptake of hydrogen. Only starting material was isolated.

5-Benzenesulfonamidobenzo[e]pyrido[a]benzimidazole (VI).—To a boiling solution of 0.50 g. of 1,4-naphthoquinonedibenzenesulfonimide in 20 ml. of reagent chloroform was added 0.20 g. of 2-aminopyridine. The solution, which turned from yellow to red in color, was boiled for one minute and then set aside for 4 days. It was then cooled and filtered. The precipitate (A), m.p. 148–151°, was identified as benzenesulfonamide. The filtrate (B) from this precipitate was evaporated to dryness and triturated with ethanol. The precipitate (C) weighed 0.35 g. (81%). From the filtrate an additional amount of benzenesulfonamide was isolated.

(C) was purified for analysis by several recrystallizations from ethanol; m.p. 235–237° dec. The sample had to be heated at 200° under vacuum for 4 minutes in order to drive off water of hydration.

Anal. Calcd. for $C_{21}H_{15}N_3O_2S$: C, 67.54; H, 4.05; N, 11.25. Found: C, 67.42; H, 4.16; N, 11.04.

Attempts to prepare this compound by the use of glacial acetic acid instead of chloroform solvent resulted in the formation of 2-acetoxy-1,4-naphthalenedibenzenesulfonamide.[9]

This product was reduced in ethanol solution in presence of hydrochloric acid with platinum oxide catalyst to 5-benzenesulfonamido-8,9;10,11;11a,12-hexahydrobenzo[e]-pyrido[a]benzimidazole hydrochloride identical with the product prepared by hydrogenation of the pyridinium chloride.

5-Aminobenzo[e]pyrido[a]benzimidazole (VII).—This was prepared by hydrolysis of the corresponding benzenesulfonamide, using the general method of Snyder and Geller.[3] A mixture of 0.77 g. of 5-benzenesulfonamidobenzo[e]pyrido[a]benzimidazole, 1 g. of phenol and 7 ml. of 48% hydrobromic acid was heated under reflux for 30 min. The red mixture was quickly cooled and extracted several times with ether. The aqueous layer was carefully neutralized with 10% aqueous sodium hydroxide and then filtered; yield 0.34 g. (71%). The compound was recrystallized several times from benzene (Darco); yellow needles, m.p. 238–240° (lit.[4] m.p. 238–239°).

Anal. Calcd. for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.02. Found: C, 77.27; H, 4.64; N, 17.89.

This product was identical with an authentic sample prepared according to the method of Morgan and Stewart[4] from 1-chloro-2,4-dinitronaphthalene[10] and 2-aminopyridine. The infrared spectrum of the compound (nujol mull) showed N–H bands at about 3400, 3305 and 3195 cm.$^{-1}$ and a broad band at about 1640 cm.$^{-1}$ which might be assigned to the $-NH_2$ deformation vibration.

5-Benzenesulfonamido-10-methylbenzo[e]pyrido[a]benzimidazole.—To a boiling solution of 0.50 g. of 1,4-naphthoquinonedibenzenesulfonimide in 15 ml. of chloroform was added 0.20 g. of 2-amino-4-methylpyridine. The deep red solution was boiled for a moment and then set aside for 3 days. The solution was filtered from a very small amount of high melting precipitate (not further investigated) and the filtrate was evaporated to a red gum. This was triturated with ethanol and the crystals filtered. The yield was 0.39 g. (88%). Several recrystallizations from ethanol (Darco) gave an analytical sample, m.p. 266° dec.

Anal. Calcd. for $C_{22}H_{17}N_3O_2S$: C, 68.20; H, 4.42; N, 10.85. Found: C, 68.14; H, 4.35; N, 10.97.

The alcohol filtrate from the above product was evaporated and the gummy solid crystallized from chloroform and filtered; yield 0.09 g., m.p. 150–153°. This was identified as benzenesulfonamide.

5-Benzenesulfonamido-12-benzenesulfonyltetrahydrobenzo[e]pyrido[a]benzimidazole.—A solution of 0.25 g. of 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole and 1 ml. of benzenesulfonyl chloride in 10 ml. of pyridine was refluxed for 1.5 hours. The solution was poured into a solution of 20 ml. of hydrochloric acid and 100 ml. of water. After standing in ice for a time, the gummy

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solid was removed and made to crystallize by the addition of ethanol. The white solid weighed 0.18 g. (49%). After digestion with aqueous ammonia to remove hydrogen chloride, the product was recrystallized from ethanol; m.p. 247.5–248° dec.

Anal. Calcd. for $C_{27}H_{23}N_3O_4S_2$: C, 62.65; H, 4.48; N, 8.12. Found: C, 62.65; H, 4.59; N, 7.98.

5-Benzenesulfonamido-12-benzenesulfonamido-8,9;10-11;11a,12-hexahydrobenzo[e]pyrido[a]benzimidazole.—The benzenesulfonation was carried out as just described. The yield was 62%. The resultant hydrochloride was digested with dilute aqueous ammonia and the base was recrystallized from ethanol; m.p. 248° dec.

Anal. Calcd. for $C_{27}H_{25}N_3O_4S$: C, 62.41; H, 4.85; N, 8.09. Found: C, 62.56; H, 4.52; N, 8.36.

5-Benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole (VIII). A.—To a solution of 0.50 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 150 ml. of ethanol was added moist silver oxide. The mixture was stirred for a time and then filtered. The filtrate was evaporated to a small volume and the compound was filtered; yield 0.34 g. (75%). The compound was recrystallized twice from a comparatively large volume of ethanol to form light orange crystals, m.p. 220–221° dec. A better yield results in the second procedure for the preparation as described below.

Anal. Calcd. for $C_{27}H_{21}N_3O_4S_2$: C, 62.89; H, 4.11; N, 8.15. Found: C, 62.59; H, 4.34; N, 7.97, 8.08.

B.—A solution of 0.50 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 10% aqueous sodium hydroxide was exactly neutralized with glacial acetic acid. The precipitated orange compound was filtered and then triturated with ethanol; yield 0.41 g. (91%), m.p. 218–220°. It was identical with the product formed in A.

C.—A solution of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in aqueous sodium carbonate was evaporated to dryness in a stream of air and the residue was repeatedly extracted with cold absolute ethanol. The red solution was filtered from inorganic salt and partially evaporated in a stream of air to leave a red solid. Attempts to recrystallize the product always led to the formation of an orange solid identified as 5-benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole.

The compound dissolved in aqueous sodium carbonate. Addition of hydrochloric acid to the alkaline solution or trituration of the solid with hydrochloric acid caused the formation of the pyridinium chloride, whereas addition of acetic acid to the alkaline solution resulted in the regeneration of the starting material.

Hydrogenations of 5-Benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole. A. 2-(N-Piperidino)-1,4-naphthalenedibenzenesulfonamide.—A suspension of 0.50 g. of 5-benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido[a]benzimidazole in 100 ml. of ethanol was hydrogenated over 0.05 g. of platinum oxide catalyst. During the course of the hydrogenation the material dissolved, forming a colorless solution. The solution was filtered from catalyst and evaporated. The residue was crystallized from aqueous ethanol; 0.25 g. (50%), m.p. 188–193° dec. It was 2-(N-piperidino)-1,4-naphthalenedibenzenesulfonamide.

B. **5-Benzenesulfonamidotetrahydrobenzo[e]pyrido[a]-benzimidazole.**—A solution of 0.40 g. of 5-benzenesulfonamido-12-benzenesulfonyl-11a,12-dihydrobenzo[e]pyrido-[a]benzimidazole in 50 ml. of aqueous solution containing 0.5 g. of sodium carbonate was hydrogenated over 0.05 g. of platinum oxide catalyst. The solution was filtered and the product extracted from the catalyst with boiling ethyl acetate; yield 0.21 g. (72%). The material was recrystallized once from ethyl acetate, m.p. 246–247.5° dec. It proved to be 5-benzenesulfonamidotetrahydrobenzo[e]pyrido[a]benzimidazole.

N-(1′,4′-Dibenzenesulfonamido-2′-naphthyl)-2-pyridone (XVI).—A mixture of 1 g. of 1,4-naphthoquinonedibenzenesulfonimide in 25 ml. of purified dioxane and 0.27 g. of sodium 2-pyridone was stirred for 11 hours. The red mixture was acidified with hydrochloric acid and diluted with water. A red gummy material separated which crystallized in the course of stirring for an hour. The yield of fairly pure material was 1.10 g. (90%). Two crystallizations from glacial acetic acid gave a pure product, m.p. 244–244.5° dec.

Anal. Calcd. for $C_{27}H_{21}N_3O_5S_2$: C, 61.00; H, 3.98; N, 7.91. Found: C, 60.87; H, 4.05; N, 7.96.

The infrared spectrum of the sample showed a broad N–H band at 3120 cm.$^{-1}$, a band at 1655 cm.$^{-1}$ attributed to the cyclic amide unit, and bands at 1332 cm.$^{-1}$ and 1167 cm.$^{-1}$ assigned to the $-SO_2$ structural unit.

This reaction is very sensitive to the purity of the dioxane used. Commercial dioxane results in a very low yield of impure product.

N-(1′,4′-Dibenzenesulfonamido-2′-naphthyl)-4-methyl-2-pyridone.—The experiment above was repeated using the sodium salt of 4-methyl-2-pyridone. A yield of 69% of pure material was obtained. An analytical sample was prepared by twice recrystallizing from glacial acetic acid; m.p. 241.5–244.5° dec.

Anal. Calcd. for $C_{28}H_{23}N_3O_5S_2$: C, 61.63; H, 4.25; N, 7.70. Found: C, 61.75; H, 4.29; N, 7.47.

2-(2′-Pyridono)-1,4-naphthoquinonedibenzenesulfonimide (XVII).—To a suspension of 0.53 g. of N-(1′,4′-dibenzenesulfonamido-2′-naphthyl)-2-pyridone in 25 ml. of dry benzene was added 1.0 g. of dry lead tetraacetate and the mixture was stirred for 12 hours. The excess lead tetraacetate was decomposed by the addition of a few drops of ethylene glycol. The two liquid layers were separated and the red benzene layer was evaporated leaving 0.35 g. (66%) of product. The compound was purified by two recrystallizations from glacial acetic acid; orange-yellow needles, m.p. 192–193° dec.

Anal. Calcd. for $C_{27}H_{19}N_3O_5S_2$: C, 61.23; H, 3.62. Found: C, 60.92; H, 3.91.

The infrared spectrum of the compound showed a carbonyl absorption at 1678 cm.$^{-1}$, a broad C=N absorption band at 1575 cm.$^{-1}$ and two bands associated with sulfonimides at 1155 cm.$^{-1}$ and 1308 cm.$^{-1}$.

2-(2′-Pyridono)-1,4-naphthoquinone-4-benzenesulfonimide.—To a suspension of 0.50 g. of 1,4-dibenzenesulfonamido-2-naphthylpyridinium chloride in 25 ml. of dry benzene was added 1.0 g. of dry lead tetraacetate. The mixture was stirred for 2 hours and the excess lead tetraacetate was destroyed with ethylene glycol. The mixture was filtered and the red gummy solid was extracted with boiling chloroform. The chloroform solution was partially evaporated and cooled; yield 0.26 g. (76%). Several recrystallizations from chloroform gave a pure product, orange needles, m.p. 262–263° dec.

Anal. Calcd. for $C_{21}H_{14}N_2O_4S$: C, 64.60; H, 3.61; N, 7.18. Found: C, 64.51, 64.65, 64.60; H, 3.55, 3.53, 3.85; N, 7.17, 7.01.

The infrared spectrum showed a band characteristic of sulfonimides at 1137 cm.$^{-1}$ and several bands in the double bond region at 1696 cm.$^{-1}$, 1620 cm.$^{-1}$ and 1587 cm.$^{-1}$.

Similar results were obtained by oxidation with lead tetraacetate in glacial acetic acid or in reagent chloroform.

Attempts to prepare this product by addition of sodium pyridone to 1,4-naphthoquinonemonobenzenesulfonimide failed.

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