The *disulfonamide* which was insoluble in dilute alkali was crystallized from ethanol-water. This product melted at 148–149.5°.

Anal. Calcd. for $C_{19}H_{18}N_2O_4S_2$: C, 56.70; H, 4.51; N, 6.96. Found: C, 56.79; H, 4.77; N, 7.36.

4-Ethyl-3-pyridinethiol (X). 3-Amino-4-ethylpyridine (54 g.) was dissolved in a mixture of 90 ml. of concd. hydrochloric acid and 90 g. of ice. The amine was then diazotized with a solution of 20.5 g. of sodium nitrite in 40 ml. of water. The temperature was held below 5° during this process. The solution of the diazonium salt was then added to a solution of 108 g. of potassium ethyl xanthate in 108 ml. of water at 50°. After the addition the mixture was heated to 80°, cooled, and extracted with ether. The ether layer was washed with water, sodium hydroxide, and again with water. Vacuum evaporation of the ether gave 56.2 g. of red oil. This was placed in a solution of 62 g. of potassium hydroxide in 450 ml. of ethanol. A small amount of sodium hydrosulfite was added and the mixture refluxed for 23 hr. The ethanol was then removed by vacuum evaporation and then the solid residue dissolved in water. The aqueous solution was extracted with chloroform to remove unhydrolyzed xanthate and then carefully acidified with acetic acid. The pyridinethiol was then extracted with chloroform. Evaporation of the chloroform gave 15.5 g. of a yellow solid, m.p. 123–128°, which was sublimed under vacuum. Resublimation gave 12 g. m.p. 122–125°.

Anal. Calcd. for C_7H_9NS: C, 60.39; H, 6.52. Found: C, 59.99; H, 6.64.

6-Azathianaphthene (XI). Ten grams of 4-ethyl-3-pyridinethiol was dissolved in 60 ml. of hot pyridine and the solution was passed over 10 ml. of catalyst[2] at 425° during the course of 30 min. Most of the pyridine was removed from the condensate by distillation from an efficient column. The residue was dissolved in ether and washed with dilute sodium hydroxide and the water. After drying the ether solution over magnesium sulfate it was evaporated and the residue vacuum distilled. Yield was 4.5 g. b.p. 106°/5.5 mm. On cooling this material solidified and vacuum sublimation of a sample gave a product of m.p. 55–57°. Recrystallization from ligroin, then alcohol and resublimation gave a product of m.p. 58–59°. The picrate of this material melted at 211–212°.

Herz and Tsai[7] report a melting point of 54–55° and a picrate of m.p. 207.5–208.5°.

Anal. Calcd. for C_7H_5NS: C, 62.18; H, 3.72. Found: C, 62.05; H, 4.02.

CLAREMONT, CALIF.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reaction of Quinoline and Iodine with Quinaldine, and with 2,6-Dimethylquinoline

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When quinaldine reacts with iodine and quinoline, the reaction product is diquino[1,2-*a*,1′,2′-*c*]imidazolium iodide. In a similar manner 2,6-dimethylquinoline reacts with quinoline and iodine to give 10-methyldiquino[1,2-*a*,1′,2′-*c*]imidazolium iodide. This represents a novel one-step synthesis for this type of compound.

In a recent paper from this laboratory[2] it was shown that quinaldine reacts with iodine and pyridine or certain pyridine -like bases to give quaternary salts of type I. Quaternary salts were prepared where N⟨ ⟩R was pyridine, isoquinoline, 3-methylisoquinoline and 3-picoline. When this reaction was carried out using quinaldine, iodine, and quinoline, the expected 1-(2-quinolylmethyl)-quinaldinium salt (IIa) was not obtained. Instead, a different product subsequently shown to be diquino[1,2-*a*,1′,2′-*c*]imidazolium iodide (IIIa), was produced.

The assignment of the structure for IIIa is based on the following lines of evidence.

1. Compound IIIa was synthesized by an independent route, thus 1-(2-quinolylmethyl)quinaldinium bromide (IIb)[3] was prepared from ω-bromoquinaldine[4] and quinoline. Compound IIb on treatment with iodine and pyridine gave compound IIIa in near quantitative yield.

2. Diquino[1,2-*a*,1′,2′-*c*] imidazolium bromide IIIb was synthesized by the method of Brown and Wild[5] and converted to the picrate (IIIc). This picrate was identical with the corresponding substance prepared from IIIa. Furthermore, the ultraviolet[5] and infrared spectra of IIIa and IIIb (Table 1) were similar.

3. On basic hydrolysis IIIa gave a compound which had the same properties as the *N*-(2-quinolylmethyl)carbostyril (IV)[6] prepared by Brown and White[7] from diquino[1,2-*a*,1′,2′-*c*]imidazolium bromide (IIIb).

In view of these observations we believe that the reaction of quinoline with iodine and quinaldine gives a cation identical with the diquino[1,2-*a*,1′,2′-*c*]imidazolium cation described by Brown and White.[7] The reaction described herein

(1) From the Ph.D. Thesis of S. V. Abramo (1956). Present address, E. I. du Pont de Nemours & Co., Wilmington, Del.

(2) L. C. King and S. V. Abramo, *J. Org. Chem.*, **23**, 1609 (1958).

(3) D. L. Hammick, C. N. Lammiman, E. D. Morgan, and A. M. Roe, *J. Chem. Soc.*, 2440 (1955).

(4) D. L. Hammick, *J. Chem. Soc.*, 2882 (1923).

(5) B. R. Brown and E. H. Wild, *J. Chem. Soc.*, 1158 (1956).

(6) Brown and White, ref. 7, were unable to prepare this compound from ω-bromoquinaldine and carbostyril. We confirm this observation.

(7) B. R. Brown and D. White, *J. Chem. Soc.*, 1589 (1957).

TABLE I

INFRARED ABSORPTION PEAKS OF IIIa, IIIb, AND VI[a]

IIIa λin microns	IIIb λin microns	VI λin microns
3.30 m	3.25 m	3.30 m
6.04 s	6.03 s	6.04 s
6.15 m	6.13 m	6.16 m
6.20 w[b]	6.17 w[b]	6.20 w[b]
6.35 s	6.35 s	6.35 m[b]
6.41 m[b]	6.40 m	6.41 s
6.50 w	6.50 w	6.52 w
6.75 m	6.72 m	6.75 m
6.88 s	6.87 s	6.85 w
7.05 w	7.01 w	6.96 s
7.15 m	7.15 m	7.18 w
7.30 w	7.29 w	7.30 w
7.50 w	7.55 w	7.50 w
7.55 w	—	7.55 w
7.70 w	7.70 w	7.71 w
8.01 w[b]	8.01 w	8.03 w
8.18 s	8.17 s	7.18 s
8.30 w	8.29 m	8.35 w
8.70 w	8.70 m	8.70 w
12.39 s	12.39 s	12.29 s
—	—	12.52 s
13.10 s	13.10 s	13.05 s
13.38 m	13.37 m	13.38 m

[a] Concentration, 1–2 mg. of compound in 70–100 mg. of potassium bromide

[b] Indicates a shoulder.

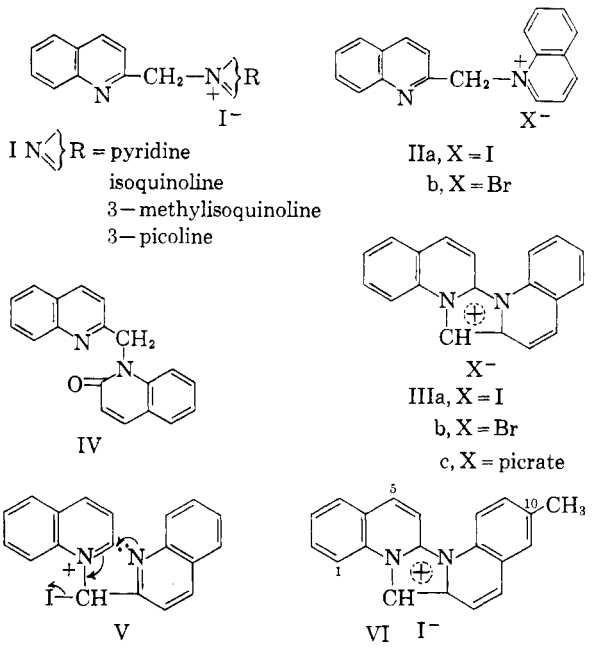
is thus a novel one step synthesis for this type of compound.

When 2,6-dimethylquinoline reacts with iodine and quinoline, the product is 10-methyldiquino-[1,2-*a*,1′,2′-*c*]imidazolium iodide (VI). In this case the assignment of structure is based on the method of preparation, on analysis and on certain other properties which are very similar to those displayed by IIIa. Thus compound VI like IIIa gave no picryl chloride test.[2,8] This was taken as evidence for the absence of an active methylene group. Dilute solutions of VI in polar solvents like those of IIIa and IIIb displayed blue fluoroscence. The ultraviolet and infrared spectra (Table I) of VI and IIIa were similar.

When Brown and co-workers[5,7] treated ω,ω-dibromoquinaldine with pyridine or iosquinoline, they were able to prepare salts similar to IIIb which they described as pyridino[1′:2′–1:2]quinolino-[1″:2″–3:4]glyoxalinium bromide and quinolino-[1″:2″–3:4]isoquinolino[1″:2″–2:1]glyoxalinium bromide. In contrast the reaction of iodine and pyridine or of iodine and isoquinoline with quinaldine gave only quaternary salts of type I.[2] Thus it appears that the reaction of iodine and quinoline with quinaldine takes a different course.

The appearance of IIIa when quinaldine reacts with iodine and quinoline is explained as follows:

It is assumed (1) that quinaldine, iodine, and quinoline react to form 1-(2-quinolylmethyl)quinolinium iodide (IIa); (2) that IIa is iodinated as rapidly as formed to give V; and (3) that V readily undergoes cyclization under the reaction conditions to give IIIa, with elimination of the elements of hydriodic acid. Since the above sequence of events could be postulated equally well for the reaction of quinaldine and iodine with pyridine or with isoquinoline it seems probable that IIa is much more easily iodinated than salts of type I, wherein N⟨ ⟩R is a base other than quinoline.



EXPERIMENTAL[9]

Diquino[1,2-a,1′,2′-c]imidazolium iodide (IIIa). a. To a mixture of 15.3 g. of quinaldine and 27 g. of quinoline, 25.4 g. of iodine was added. This mixture was heated for 12 hr. on a steam bath. The heavy oil was extracted successively with ether, acetone, and water, and then crystallized several times from 50% ethanol. Yield 13.6 g. (33% based on quinaldine, or 66% based on iodine); m.p. 311–312°. This compound gave a negative picryl chloride test.[8] A dilute aqueous solution displayed blue fluorescence.

Anal. Calcd. for $C_{19}H_{13}N_2I$: C, 57.60; H, 3.31. Found: C, 57.33; H, 3.51.

Ultraviolet light absorption at a concentration of 1.22 × $10^{-5}M$ in methanol: Max. at 390, 370, 350, 330, 285, and 252 mμ (log ε 4.45, 4.53, 4.35, 4.09, 4.54, 4.74); min. at 380, 360, 320, 275, and 240 mμ (log ε 4.11, 4.09, 3.65, 4.10, and 4.40).

b. To 0.1 g. of 1-(2-quinolylmethyl)quinolinium bromide (IIb)[3] in 15 cc. of pyridine, 0.07 g. of iodine was added. The mixture was heated for 1 hr. at 100°. The reaction mixture was extracted with ether and the precipitate which formed was washed with acetone. Yield 0.103 g. (93%) of IIIa;

(8) F. Krohnke and H. Schmeiss, *Ber.*, **70**, 1728 (1937), demonstrated that compounds containing a reactive methylene group react in basic solution with picryl chloride or chloranil to give an intense color. This test is used to identify a reactive methylene group (ref. 2) and is used herein to distinguish between compounds of type II and type III.

(9) Analyses by H. Beck. All melting points were observed on a calibrated Fisher-Johns Block.

m.p. 307–308°, after crystallization from aqueous ethanol. The dilute aqueous solution gave a blue fluorescence and the ultraviolet and infrared spectrum of this substance were identical with those from preparation *a* above.

Diquino[1,2-a,1',2'-c]imidazolium bromide (IIIb). This substance was prepared from ω,ω-dibromoquinaldine and quinoline using the method of Brown and Wild;[5] m.p. 306°. It was converted to the picrate; m.p. 267–270°.

Diquino[1,2-a,1',2'-c]imidazolium picrate (IIIc). This compound separated from an alcoholic solution of IIIa, prepared by method *a* or *b*, or from IIIb when alcoholic solutions of these preparations were treated with picric acid. It was recrystallized from ethanol; m.p. 267–270°[10]; mixed melting points using the three preparations were not depressed.

N(2-quinolylmethyl)carbostyril (IV). Two grams of IIIa was added to a solution of 15% potassium hydroxide in 50% water-ethanol. The solution was boiled for 20 min. After cooling, the dark oil which separated was extracted with chloroform. After removal of the chloroform, the residue was leached with 500 cc. of boiling pentane. Concentration of the pentane solution gave 200 mg. (21%) of colorless needles; m.p. 125–126° (after melting and resolidifying at 105–107°).

Anal. Calcd. for $C_{19}H_{14}N_2O$: N, 9.79. Found: N, 9.76.

The remainder of the above residue was dissolved in ethanol and converted to the picrate. Yield 1.5 g. (70%); m.p. 195–197°.[11] The overall conversion of IIIa to IV was 91%.

10-Methyldiquino[1,2-a,1',2'-c]imidazolium iodide (VI). Iodine, 12.7 g. was added to 8.0 g. of 2.6-dimethylquinoline and 30 cc. of quinoline. After heating for 12 hr. the mixture was extracted successively with ether, acetone, and water. The residue was crystallized from ethanol-water. Yield 8.0 g. (78% based on iodine); m.p. 319°.

Anal. Calcd. for $C_{20}H_{15}N_2I$: C, 58.54; H, 3.69. Found: C, 58.32; H, 3.88.

This compound gave no picryl chloride test.[2,8] Dilute solutions in polar solvents showed blue fluorescence. The infrared spectra and the ultraviolet spectra (Table 1) were similar to those of compound IIIa. Light absorption at a concentration of $1.34 \times 10^{-5}M$ in methanol: Max. at 390, 375, 350, 335, 310, 300, 295, 286, 260, 255, and 225 mμ (log ε 4.30, 4.36, 4.17, 3.87, 4.02, 4.43, 4.45, 4.31, 4.59, 4.50, 4.57); min. at 385, 360, 325, 275, and 240 mμ (log ε 4.13, 4.11, 3.65, 4.20, 4.42).

Acknowledgment. We wish to thank the American Cyanamid Company for a research fellowship.

EVANSTON, ILL

(10) Brown and Wild, ref. 5, reported the m.p. as 261–262°.

(11) Brown and White, ref. 7, reported m.p. 125° for the base and 189° for the picrate.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reactions of Terpenes with Acid and Thiourea III.[1] Preparation and Nitrosation of Some 1(*S*),8(*N*)-*p*-Menthyleneisothioureas

L. CARROLL KING AND ERIC W. STERN[2]

When limonene reacts with *p*-toluenesulfonic acid and methylthiourea or with phenylthiourea, the products are 3-methylamino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene and 3-anilino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene respectively. On methylation of 1(*S*),8(*N*)-*p*-menthyleneisothiourea, 3-imino-1,4,5,5-tetramethyl-2-thia-4-azabicyclo[4.2.2]-decane was produced. Each of the above compounds was nitrosated. The structure of these compounds and their nitroso derivatives is discussed herein.

In paper II of this series the preparation, properties, and structure of 1(*S*),8(*N*)-*p*-menthyleneisothiourea (I) were discussed.[1] This derived name was adopted because of its simplicity and suggestion of the terpene origin of I. However, in discussing the derivatives described herein the need for a more systematic nomenclature became evident. After consultation with L. T. Capell,[3] we chose the bicyclic system so that I becomes 3-amino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2.]dec-3-ene (II).

When II was treated in strong acid solution with aqueous sodium nitrite, no reaction occurred. Only the salt of II corresponding to the strong acid used was isolated. However when II was dissolved in glacial acetic acid and treated with aqueous sodium nitrite, a golden yellow solid, 3-nitrosoimino-1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]decane (III), precipitated after a few minutes.

Compound III gave a positive Liebermann's nitrosoamine test. When warmed with concentrated hydrochloric acid, it evolved nitrous acid and gave II as the hydrochloride. When III was treated with dilute aqueous sodium hydroxide it was converted to sodium 1,5,5-trimethyl-2-thia-4-azabicyclo[4.2.2]dec-3-ene-3-diazoate (IV), a white compound. Compound IV regenerated III on acidification with glacial acetic acid. Combustion of the white compound IV gave the expected amount of ash.

Compound III was formulated as a primary rather than as a secondary nitrosoamine because of the intense color and because the reversible change III ⇆ IV would be difficult to explain in terms of the secondary nitrosoamine structure. Thus if the yellow compound had the structure V, the nitroso group would not be in conjugation with the CN group and the color would be expected to be like that of most secondary nitrosoamines. Furthermore, if the yellow compound had the structure V the addition of a base would predict disruption of a bond V → VI → VII, an irreversible procedure,

(1) Paper No. II of this series, L. C. King, L. A. Subluskey, and E. W. Stern, *J. Org. Chem.*, 21, 1232 (1956).

(2) From the Ph.D. thesis of Eric W. Stern (1954).

(3) Private communication.