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1,2-DI-(2-QUINOLYL)ETHANE AND CERTAIN RELATED COMPOUNDS[1]

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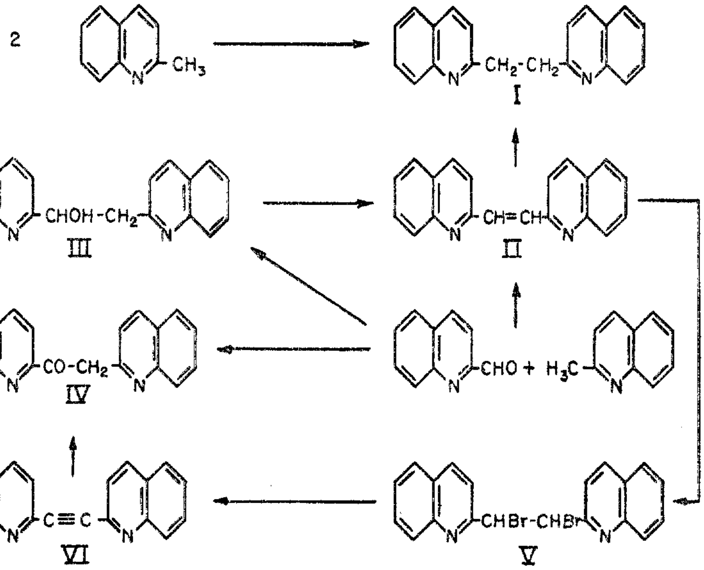
Miller (1) in 1888 reported the isolation of a "diquinaldyl" from the reaction of quinaldine with sulfur, but he gave no evidence as to its structure. We have established its structure as 1,2-di-(2-quinolyl)ethane (I) by relating it to 1,2-di-(2-quinolyl)ethylene (II). The latter was made by the condensation of quinaldaldehyde with quinaldine and also by the dehydration of 1,2-di-(2-quinolyl) ethanol (III). A co-product in the preparation of the ethanol (III) was the ketone (IV), which was shown to be identical with the hydration product of 1,2-di-(2-quinolyl)acetylene (VI), prepared from ethylene II *via* dibromide V.



It should be noted that the yellow diquinolylethylene (II) obtained by us (m.p. 192–194°) was quite different from the diquinolylethylene (white crystalline solid, mp. 326°) reported by Kaplan and Lindwall (2).

The formation of ethane I by the action of sulfur on quinaldine might be postulated to proceed through the coupling of 2-quinolylmethyl radicals as proposed by Horton (3) for certain dehydropolymerization reactions of sulfur with alkylaromatic compounds.

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EXPERIMENTAL[3]

REACTION OF QUINALDINE WITH SULFUR

A. In the absence of sodium hydroxide. Quinaldine (71.5 g.) was heated with 16 g. of sulfur for nine hours at 150–200°, and the reaction mixture was poured into 200 ml. of 6 *N* sulfuric acid and filtered from the unreacted sulfur. Aqueous sodium hydroxide (10%) was slowly added, and precipitates were separated at *p*H's 1.5, 2.0, and 4.5; finally the solution was made strongly alkaline, whereupon an oil separated. The small amounts of solid obtained at *p*H's 1.5 and 2.0 could not be purified; the oil (32.9 g.) was mainly quinaldine. The solid isolated at *p*H 4.5 was 1,2-di-(2-quinolyl)ethane (I); glistening white plates from benzene, m.p. 164–165.5° (1), 17% yield based on non-recovered quinaldine.

Anal. Calc'd for $C_{20}H_{16}N_2$: C, 84.47; H, 5.67; N, 9.85; Mol. wt., 284.
Found: C, 84.67; H, 5.78; N, 9.64; Mol. wt., 284 [benzene, ebulliometric (4)].

The *dihydrochloride* of I was prepared by passing hydrogen chloride into an ethanol solution of the diquinolylethane. It was crystallized from ethanol containing a small amount of hydrogen chloride; brownish-red solid, m.p. 279–281°.

Anal. Calc'd for $C_{20}H_{16}N_2 \cdot 2HCl$: Cl, 19.85. Found: Cl, 19.54 (Volhard).

The *dipicrate* was prepared by mixing ethanol solutions of I and picric acid. It was washed with hot benzene and alcohol; m.p. 275–280° (dec.).

Anal. Calc'd for $C_{32}H_{22}N_8O_{14}$: C, 51.74; H, 2.99.
Found: C, 52.05; H, 2.98.

B. In the presence of sodium hydroxide. Sodium hydroxide was found to be catalytic for the reaction of 4-picoline with sulfur (5); in the present case, however, it showed but little effect. From a reaction similar to the one described above, except for the presence of 1 g. of sodium hydroxide, there was obtained a 19% yield of diquinolylethane (I), based on non-recovered quinaldine, and small amounts of two unidentified co-products: (1) 0.8 g. of reddish-brown plates, precipitated at *p*H 2, m.p. 276–277.5°, crystallized from ethanol, and showed qualitative tests for sulfur, nitrogen, and chlorine; (2) 0.3 g. of yellow solid from the diquinolylethane mother liquor, m.p. 195–197°, crystallized from ethanol. Mixture melting point determinations showed that the 195–197° compound was neither ethylene II nor ketone IV.

Anal. Calc'd for $(C_{10}H_7N)_n$: C, 85.08; H, 5.00; N, 9.92; Mol. wt., 423 (in=3) or 564 (n=4).
Found: C, 84.90; H, 4.71; N, 9.97; Mol. wt., 501 ± 25 (Rast).

Its *picrate*, after washing with hot ethanol, melted at 263–264° (dec.).

Anal. Calc'd for $(C_{10}H_7N)_3 \cdot C_6H_2(NO_2)_3OH$: C, 66.86; H, 3.74; N, 12.88.
Found: C, 65.49; H, 3.47; N, 12.20.

PROOF OF STRUCTURE

1,2-Di-(1-quinolyl)ethylene (II). (a) Diquinolylethanol (III, 3.4 g.) was dehydrated by refluxing for 15 minutes with 9 ml. of acetic acid and 17 ml. of acetic anhydride. The reaction product was poured into excess aqueous sodium hydroxide and the mixture extracted with benzene to give a solid (yellowish-orange needles) which melted at 192–194° after crystallization from ethanol; yield 75%.

Anal. Calc'd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92; Mol. wt., 282.
Found: C, 85.08; H, 5.37; N, 9.89; Mol. wt., 286 [benzene, ebulliometric (4)].

(b) A mixture of 0.72 g. of quinaldine, 0.79 g. of quinaldaldehyde (6), 2 ml. of acetic acid, and 4 ml. of acetic anhydride was refluxed for 20 minutes. The reaction product was worked up as in (a); the solid product (m.p. 192–194°; yield 70%) did not depress the melting point of the ethylene obtained in (a).

(c) A mixture of 1.43 g. of quinaldine, 1.57 g. of quinaldaldehyde, 2 ml. of acetic acid, and 0.5 ml. of acetic anhydride was heated at 110° for 16 hours in a sealed tube. When the reaction mixture was decomposed by excess ammonium hydroxide, diquinolylethylene (II)

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[3] All melting points were corrected against known standards.

was not obtained, but there was isolated approximately 0.1 g. of a solid product, m.p. 203–206°. From another experiment in which a mixture of 3.58 g. of quinaldine, 3.93 g. of quinaldaldehyde, and 1.71 g. of acetic anhydride was heated in a sealed tube for 16 hours at 155°, the same product was obtained. The crude material was converted to a phenylhydrazone (m.p. 148–149°) which was shown by mixture melting point to be the phenylhydrazone of 1,2-di-(2-quinolyl) ethanone (IV).

1,2-Di-(2-quinolyl)ethanol (III). This alcohol was prepared according to the directions of Kaplan and Lindwall (2). The yield of crude product was 70%; recrystallization from ethanol gave pale yellow plates, m.p. 166–168°. A small amount of ketone IV (m.p. 212–213.5°) was also isolated; identified by mixture m.p.; phenylhydrazone m.p. 148–149°.

Hydrogenation of 1,2-di-(2-quinolyl)ethylene (II). 1,2-Di-(2-quinolyl)ethylene (II) was hydrogenated in methanol at 26° with a platinum catalyst. The absorbed hydrogen corresponded to 1.27 double bonds; the product melted at 164–165.5° and did not depress the melting point of ethane I obtained by the action of sulfur on quinaldine.

1,2-Di-(2-quinolyl)ethylene dibromide (V). The bromination and dehydrobromination procedures were patterned after those described for similar compounds (7). Bromine (1.82 g.) was added to a carbon tetrachloride solution (200 ml.) of 1,2-di-(2-quinolyl)ethylene (II, 2.82 g.). Upon concentration of the reaction mixture to half-volume, 4.0 g. of a yellow-orange solid was deposited, m.p. *ca.* 167° (dec.); yield 90%. Recrystallization from chloroform-methanol gave light yellow crystals; m.p. 173° (dec.). The melt in the capillary tube was opaque, but the original bromide did not appear to contain ionic bromide (negative silver nitrate test), nor did it appear to be a perbromide (non-liberation of iodine from sulfuric acid-potassium iodide-acetic acid solution).

Anal. Calc'd for $C_{20}H_{14}Br_2N_2$: C, 54.32; H, 3.19; Br, 36.15.
Found: C, 54.16; H, 2.54; Br, 36.30.

1,2-Di-(2-quinolyl)acetylene (VI). Dehydrobromination was accomplished by refluxing a mixture of 1.65 g. of 1,2-di-(2-quinolyl)ethylene dibromide (V), 80 ml. of ethanol, and 0.8 g. of potassium hydroxide for one hour. The product was allowed to evaporate to dryness at room temperature; water was then added and the mixture was extracted with chloroform. Evaporation of the chloroform gave a solid which was crystallized from methanol; yellow-orange plates, 0.77 g., m.p. 171–178°, yield, 74%. Recrystallization gave material melting at 179–180°.

Anal. Calc'd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.32; N, 9.99.
Found: C, 85.73; H, 4.38; N, 10.00.

1,2-Di-(2-quinolyl)ethanone (IV). Hydration (7) of acetylene VI was accomplished by dissolving 0.28 g. of the acetylene in 10 ml. of 65% sulfuric acid at 125°, refluxing the solution for one hour, allowing it to stand overnight, diluting with ice-water, and rendering alkaline with concentrated aqueous amonia. A bright yellow solid precipitated (0.25 g., m.p. 190–200°, 83% yield) which was obtained as yellow-orange electrostatic needles after three recrystallizations from ethanol; m.p. 213.5–215° (IV).

Anal. Calc'd for $C_{20}H_{14}N_2O$: C, 80.51; H, 4.73; N, 9.39.
Found: C, 80.57; H, 4.64; N, 9.59.

The *phenylhydrazone* prepared from this ketone melted at 149–150.5°.

Anal. Calc'd for $C_{26}H_{20}N_4$: C, 80.38; H, 5.19; N, 14.43.
Found: C, 80.23; H, 4.97; N, 14.67.

SUMMARY

The action of sulfur on quinaldine gave a 17–19% yield of 1,2-di-(2-quinolyl)-ethane (I), and trace amounts of several unidentified co-products.

Three new compounds were prepared in the course of proof of structure: 1,2-di-(2-quinolyl)ethylene (II), 1,2-di-(2-quinolyl)acetylene (VI), and 1,2-di-(2-quinolyl)ethanone (IV), together with several derivatives.

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REFERENCES

(1) Miller, *Ber.*, **21**, 1827 (1888).
(2) Kaplan and Lindwall, *J. Am. Chem. Soc.*, **65**, 927 (1943).
(3) Horton, *J. Org. Chem.*, **14**, 761 (1949).
(4) Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).
(5) Thayer and Corson, *J. Am. Chem. Soc.*, **70**, 2330 (1948).
(6) Monti, *Atti. accad nazl. Lincei*, **18**, 505 (1933); Henze, *Ber.*, **67**, 750 (1934); Kaplan, *J. Am. Chem. Soc.*, **63**, 2654 (1941); Ramsey, doctoral dissertation, University of Pittsburgh, 1946.
(7) Scheuing and Winterhalder, German Patent 594,849 [*Chem. Abstr.*, **28**, 4541^9 (1934)]; Smith, Stewart, Roth, and Northey, *J. Am. Chem. Soc.*, **70**, 3997 (1948).