

The product was purified by dissolving 0.91 g. in 40 cc. of hot absolute ethanol and allowing to stand at 0° for thirty hours. Cream colored crystals were thus obtained.

The melting point of the brucine salt showed unusual irregularity, some samples partially melting around 70°, others at 80 or 90°. The decomposition points ranged from 108–125°.

The brucine salt had practically a zero rotation and no mutarotation was observed over a period of several hours. In spite of this, active acid was obtained from the salt by hydrolysis. Although the salt was well crystallized, the analyses did not indicate absolute purity.

#### *l*-2-Methoxy-6-nitro-2'-carboxybiphenyl

**A. Hydrolysis with Acid.**—The brucine salt was hydrolyzed with dilute hydrochloric acid (1:1) as described previously for 2-methoxy-6-carboxy-2'-nitrobiphenyl. An exceedingly low yield of active acid resulted.

**B. Hydrolysis with Dilute Sodium Hydroxide.**—At 0° 0.1 g. of brucine salt was shaken with 15 cc. of aqueous 10% sodium hydroxide for one hour. Extraction with chloroform served to remove the brucine. After filtering the alkaline solution, it was acidified with dilute hydro-

chloric acid (1:1) at 0°. The *l*-acid separated but, as it was too fine for filtrations, it was extracted with ether. The solvent was evaporated at a low temperature and the residue dried in a vacuum desiccator at room temperature; weight, 0.022 g., m. p. 195–199°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>O<sub>3</sub>N: N, 5.16. Found: N, 5.10.

### Summary

The following compounds have been prepared: 2-methoxy-6-carboxy-2'-nitrobiphenyl, 2-nitro-6-carboxy-2'-methoxybiphenyl, and 2-methoxy-6-nitro-2'-carboxybiphenyl. The 2-nitro-6-carboxy-2'-methoxybiphenyl proved to be unstable and the least stable of the three. The other two were relatively stable compounds. A more exact comparison of the stability of the latter two was impossible due to the fact that the purity of one of them appeared to be questionable.

URBANA, ILLINOIS

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## Synthesis in the 1,2,3,4-Tetrahydroquinoline Series

BY WILLIAM S. EMERSON AND J. W. DAVIS

The N-alkyl-1,2,3,4-tetrahydroquinolines represent an interesting and but little studied group of compounds. Very few containing alkyl groups in the benzene ring have ever been prepared, much less, thoroughly examined.

These compounds can be prepared readily from the corresponding quinolines either by reduction of the quinoline methiodides<sup>1</sup> or by first reducing the quinolines and then treating the tetrahydro compounds with methyl iodide.<sup>1,2</sup> In examining the second method we were surprised to find that 1,2,3,4-tetrahydroquinolines vary markedly in their stability and reactivity. This paper reports the great differences in these respects between 2,6- and 2,8-dimethyl-1,2,3,4-tetrahydroquinoline.

While the 2,8-compound is relatively stable, forming a well defined picrate and zinc chloride-hydrochloric acid double salt, the corresponding derivatives of the 2,6-compound are unstable, decomposing when attempts are made to crystallize them. In the case of the picrate, 2,6-dimethylquinoline picrate subsequently was isolated from the filtrate. The 2,6-compound also reacted much more violently with methyl iodide

than the 2,8-compound. On the other hand, the N-methyl derivative of 2,6-dimethyl-1,2,3,4-tetrahydroquinoline was found to be stable and normal in its reactions.

Reduction studies of alkyl and aryl quinolines<sup>3</sup> showed that 2,6-dimethylquinoline was reduced readily with nickel and hydrogen at 105°. At the same pressure three monomethylquinolines were reduced at 120°, while a temperature of at least 150° was required in all other cases. 2-Methylquinoline could be reduced at temperatures as low as 110°, but the reaction proceeded more smoothly at 150°. Since this type of hydrogenation is reversible, it is interesting that the tetrahydroquinoline which we have found to be unstable was prepared at the lowest temperature in these reduction studies.

### Experimental

**2,8-Dimethylquinoline** was prepared by the method of Doebner and v. Miller; b. p. 245–255°; *n*<sub>D</sub><sup>20</sup> 1.5955; *d*<sub>4</sub><sup>20</sup> 1.036; *M*<sub>D</sub> calcd. 51.73; *M*<sub>D</sub> found 51.60. Its identity was checked by means of the picrate, m. p. 177–179° (180°).<sup>4</sup>

(3) Von Braun, Petzold and Seemann, *ibid.*, **55**, 3779 (1922); v. Braun, Gmelin and Schultheiss, *ibid.*, **56**, 1338 (1923); v. Braun, Petzold and Schultheiss, *ibid.*, **56**, 1347 (1923); v. Braun, Gmelin and Petzold, *ibid.*, **57**, 382 (1924).

(4) Eibner, *ibid.*, **34**, 2450 (1901).

(1) Möller, *Ann.*, **243**, 313 (1887).

(2) Doebner and v. Miller, *Ber.*, **16**, 2464 (1883).

The zinc chloride-hydrochloric acid double salt was prepared by mixing one part of the base with two parts of a solution of 13.6 g. of zinc chloride in 20 cc. of concentrated hydrochloric acid and 10 cc. of glacial acetic acid. After filtration from the reaction mixture the white needles were recrystallized from glacial acetic acid. They were filtered and washed free of acid with ether, m. p. 270° dec. This is a modification of Craig's procedure<sup>5</sup> for preparing the zinc-hydrochloride of methyl-diphenylamine.

*Anal.* Calcd. for 2 C<sub>21</sub>H<sub>11</sub>N·2HCl·ZnCl<sub>2</sub>: Cl, 27.2. Found: Cl, 26.9.

**2,8-Dimethyl-1,2,3,4-tetrahydroquinoline** was prepared by dissolving 39 g. of 2,8-dimethylquinoline in 100 cc. of water and 200 cc. of concentrated hydrochloric acid and refluxing the resulting solution for fifteen hours with an excess of tin.<sup>3</sup> The product was isolated by making the mixture alkaline with sodium hydroxide and distilling with steam. After the distillate was extracted with ether, the ether solution dried over sodium hydroxide and the ether distilled, the base distilled at 250–255°: yield 27.9 g. or 69%; *n*<sub>D</sub><sup>20</sup> 1.5610; *d*<sub>4</sub><sup>20</sup> 1.000; *M*<sub>D</sub> calcd. 51.90; *M*<sub>D</sub> found 52.24. The picrate crystallized from alcohol in yellow needles, m. p. 159.5–161.0°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>O<sub>7</sub>N<sub>4</sub>: C, 52.3; H, 4.62. Found: C, 52.3; H, 4.62.

The zinc chloride-hydrochloric acid double salt melted at 270° with decomposition. A mixed melting point determination with the zinc chloride-hydrochloric acid double salt of 2,8-dimethylquinoline showed a depression of fifteen degrees.

*Anal.* Calcd. for 2C<sub>11</sub>H<sub>13</sub>N·2HCl·ZnCl<sub>2</sub>: Cl, 26.7. Found: Cl, 26.5.

The benzoyl derivative, prepared by the Schotten-Baumann method, crystallized from aqueous alcohol in white plates, m. p. 118.5–120°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>19</sub>ON: N, 5.28. Found: N, 5.42.

**1,2,8-Trimethyl-1,2,3,4-tetrahydroquinoline hydriodide** was prepared by allowing a mixture of 20 g. of 2,8-dimethyl-1,2,3,4-tetrahydroquinoline and 17.6 g. of methyl iodide to stand for sixteen hours. The white crystals were recrystallized from absolute alcohol; yield 26.5 g. or 70%, m. p. 154.5–155.5°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>13</sub>NI: I, 41.9. Found: I, 42.0.

**1,2,8-Trimethyl-1,2,3,4-tetrahydroquinoline** was prepared by dissolving 20 g. of 1,2,8-trimethyl-1,2,3,4-tetrahydroquinoline hydriodide in 20 cc. of water and adding 30 cc. of 10% sodium hydroxide. The oil so formed was extracted with ether and the ether solution dried over potassium hydroxide. After the ether had been distilled, the product was distilled at 21 mm., b. p. 130°: yield 10.2 g. or 88%; *n*<sub>D</sub><sup>20</sup> 1.5450; *d*<sub>4</sub><sup>20</sup> 0.9826; *M*<sub>D</sub> calcd. 57.30; *M*<sub>D</sub> found 56.43.

The picrate was crystallized from alcohol, m. p. 177–178°. A mixed melting point determination with the picrate of 2,8-dimethylquinoline (m. p. 177–179°) showed a depression of twenty-seven degrees.

*Anal.* Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>7</sub>N<sub>4</sub>: N, 13.88. Found: N, 14.04.

The zinc chloride-hydrochloric acid double salt was also prepared as white crystals, m. p. 213–214°.

*Anal.* Calcd. for 2C<sub>12</sub>H<sub>17</sub>N·2HCl·ZnCl<sub>2</sub>: Cl, 25.4. Found: Cl, 25.4.

The hydriodide was prepared by mixing equal volumes of the base and hydriodic acid of sp. gr. 1.50. After crystallization had been induced by adding ethyl acetate, the product was filtered and crystallized from absolute alcohol to give white crystals, m. p. 155–157°. A mixed melting point determination with a sample prepared by treating 2,8-dimethyl-1,2,3,4-tetrahydroquinoline with methyl iodide (m. p. 154.5–155.5°) gave 155–157°.

**2,6-Dimethylquinoline** was prepared by the method of Doebner and v. Miller<sup>2</sup>; b. p. 255–265°; m. p. 60°.

The picrate was crystallized from alcohol in yellow needles, m. p. 186–187°. Doebner<sup>6</sup> gives 178° as the melting point of this compound.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>7</sub>N<sub>4</sub>: N, 14.51. Found: N, 14.45.

The zinc chloride-hydrochloric acid double salt was prepared as white crystals, m. p. 211.5–213°.

*Anal.* Calcd. for 2C<sub>11</sub>H<sub>11</sub>N·2HCl·ZnCl<sub>2</sub>: Cl, 27.1. Found: Cl, 27.1.

**2,6-Dimethylquinoline methiodide** was prepared by warming equimolar quantities of methyl iodide and 2,6-dimethylquinoline. It crystallized from absolute alcohol in yellow crystals, m. p. 239–240° (236–237°,<sup>7</sup> 246–247°<sup>8</sup>).

**2,6-Dimethyl-1,2,3,4-tetrahydroquinoline** was prepared by reducing 52 g. of 2,6-dimethylquinoline with tin and hydrochloric acid using the same procedure as for 2,8-dimethyl-1,2,3,4-tetrahydroquinoline. In this way 37.3 g. (70%) of product was obtained; b. p. 142–149° (25 mm.).

To a solution of 6 g. of this crude product in a mixture of 10 cc. of concentrated hydrochloric acid and 30 cc. of water was added 3 g. of sodium nitrite. After the oil which separated had been extracted with ether, the ether was evaporated in the cold and the residue added with cooling to 15 g. of stannous chloride and 75 cc. of concentrated hydrochloric acid. This mixture was allowed to stand for one-half hour before being heated on the steam-bath for fifteen minutes. It was then diluted with water and made basic with sodium hydroxide. The oil which volatilized on steam distillation was extracted from the distillate with ether. After drying over potassium hydroxide, the ether was distilled and then the product was distilled at 24 mm.; b. p. 147–149°; yield 2.5 g.

The benzoyl derivative prepared by the Schotten-Baumann method and crystallized from aqueous alcohol melted at 104–105° (103–105°).<sup>9</sup>

The zinc chloride-hydrochloric acid double salt melted at 187–195° after one crystallization from acetic acid.

The picrate when first prepared melted at 126–128°. After one crystallization from alcohol it melted at 150–155°. Another raised it to 165–169°. In both cases the solution turned red on heating, and, while the color disappeared on cooling, it reappeared after the filtrate had stood for one hour. (This red color was not encountered

(6) Doebner, *Ber.*, **33**, 677 (1900).

(7) Möller, *Ann.*, **242**, 300 (1887).

(8) Lund and Wise, *Ind. Eng. Chem.*, **11**, 458 (1919).

(9) Pope and Rich, *J. Chem. Soc.*, **75**, 1093 (1899).

(5) Craig, *THIS JOURNAL*, **55**, 3723 (1933).

in recrystallizing the picrate of 2,8-dimethyl-1,2,3,4-tetrahydroquinoline and filtrates from this recrystallization were yellow after standing for thirty days.)

When the deep red filtrate from the recrystallization of the picrate of 2,6-dimethyl-1,2,3,4-tetrahydroquinoline was allowed to stand for thirty days, orange crystals separated. They were recrystallized from alcohol, m. p. 185-186°; mixed m. p. with the picrate of 2,6-dimethylquinoline (m. p. 186-187°) 186-187°. No crystals separated from the orange filtrate from the recrystallization of the picrate of 2,8-dimethyl-1,2,3,4-tetrahydroquinoline.

**1,2,6-Trimethyl-1,2,3,4-tetrahydroquinoline hydriodide** was prepared by mixing 17.6 g. of methyl iodide and 20.6 g. of the crude tetrahydroquinoline. So vigorous a reaction immediately took place that the mixture boiled violently. The resulting sticky red product was crystallized from alcohol giving 24 g. of a mixture of yellow and white crystals. Two crystallizations from water dissolved the yellow crystals to leave the white crystals, m. p. 187-188.5°. A mixed melting point of these with the hydriodide of 1,2,6-trimethyl-1,2,3,4-tetrahydroquinoline prepared below (m. p. 187.5-188.5°) was 187-188°.

**1,2,6-Trimethyl-1,2,3,4-tetrahydroquinoline** was prepared by refluxing 22 g. of 1,2,6-trimethylquinoline hy-

driodide with excess tin and hydrochloric acid for seven hours. The product obtained as in preceding preparations weighed 8.3 g. (64%); b. p. 145° (20 mm.);  $n_D^{20}$  1.5611;  $d_4^{20}$  0.9906;  $M_D$  calcd. 57.29;  $M_D$  found 57.31.

The hydriodide prepared by mixing equal volumes of the base and hydriodic acid of sp. gr. 1.50 crystallized from water in white crystals, m. p. 187.5-188.5°.

*Anal.* Calcd. for  $C_{12}H_{13}NI$ : I, 41.8. Found: I, 41.8.

The picrate after four crystallizations from alcohol appeared as yellow crystals, m. p. 141-142°.

*Anal.* Calcd. for  $C_{12}H_{13}O_7N_3$ : N, 13.88. Found: N, 13.76.

### Summary

2,6-Dimethyl-1,2,3,4-tetrahydroquinoline has been found to be very much more unstable and reactive than 2,8-dimethyl-1,2,3,4-tetrahydroquinoline. Its N-methyl derivative, however, is stable. Eleven new compounds in the 2,6- and 2,8-dimethylquinoline series have been prepared and characterized.

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## Osage Orange Pigments. II. Isolation of a New Pigment, Pomiferin<sup>1</sup>

BY M. L. WOLFROM, F. L. BENTON, A. S. GREGORY, W. W. HESS, J. E. MAHAN AND P. W. MORGAN

The isolation of a new yellow pigment from the fruit of the osage orange (*Maclura pomifera* Raf.) has been reported previously<sup>2</sup> from this Laboratory. The name osajin was assigned to the substance and the data reported were shown to be in harmony with a provisional formula of  $C_{26}H_{22}O_8(OH)_2$ .

Osajin melts at 189°<sup>3</sup>. In the preparation of further material from the natural source it was found that material of this same melting point could be prepared which, however, depressed the melting point of highly purified samples of osajin that melted at the same point. Further investigation showed that two yellow pigments were present, the original osajin of melting point 189° and a second of melting point 200.5°. The name pomiferin is suggested for this second product. The data so far obtained for pomiferin and its derivatives indicate a probable formula of  $C_{25}H_{21}O_8(OH)_3$ , thus differing from osajin by the presence of one additional oxygen atom combined as an

hydroxyl group. We now find that the substance described by us<sup>2</sup> as osajic acid di-*p*-toluenesulfonate was actually pomiferin di-*p*-toluenesulfonate (m. p. 148°) of high purity. The correct *p*-toluenesulfonate derivative of osajin has been prepared and has been found to be a mono-*p*-toluenesulfonate (m. p. 152°) crystallizing in beautiful, lustrous plates of a golden yellow color. We have also established the melting point of osajin diacetate as 164°. Other than this, the properties of osajin (m. p. 189°), osajin monoacetate (m. p. 159°), and of osajin diacetate (m. p. 164°) have been found correct as previously reported.

We also postulated the probable presence of a lactone group in osajin. We now believe that no lactone group is present but that the consumption of one equivalent of alkali by osajin is due to the presence of an acidic phenolic group, such as is present in gossypol and in other naturally occurring phenolic structures.

Pomiferin has been characterized by a number of derivatives. It forms a diacetate and a triacetate, a dimethyl ether and a trimethyl ether, and also a dimethyl ether monoacetate.

Both osajin and pomiferin are isomerized to

(1) Presented before the Division of Organic Chemistry at the 97th Meeting of the American Chemical Society, Baltimore, Maryland.

(2) E. D. Walter, M. L. Wolfrom and W. W. Hess, *THIS JOURNAL*, **60**, 574 (1938).

(3) All melting points herein reported are uncorrected.