

Summary

1. The two compounds which separate in the interaction of auric chloride and benzyl sulfide are addition compounds of gold monochloride and gold dichloride, respectively, with benzyl sulfide. They are conjugate compounds, probably constituted as shown in the formulas, $[\text{ClAu}\dots\text{S}(\text{Bz})_2]$ and $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Au}\dots\text{S}(\text{Bz})_2 \\ \diagup \\ \text{Cl} \end{array} \right]$.

2. Unlike the platinous chloride addition products, $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Pt} \cdot \text{SR}_2 \\ \diagup \\ \text{Cl} \end{array} \right]$ which add additional molecules of the organic sulfides to form interpolation compounds, as $[\text{Pt}.4\text{SR}_2]\text{Cl}_2$, the conjugate compounds of benzyl sulfide with gold monochloride and gold dichloride appear to be incapable of yielding interpolation compounds by the further addition of benzyl sulfide.

3. Dichloro-gold-benzyl sulfide probably exists in chloroform solution as a solvate of the formula $\text{Cl}_2\text{Au}\cdot\text{S}(\text{Bz})_2\cdot\text{CHCl}_3$.

4. The following new compounds have been prepared and described: $[\text{Br}_2\text{Au}\cdot\text{S}(\text{Bz})_2]$, $[\text{BrAu}\cdot\text{S}(\text{Bz})_2]$, $[\text{I}_2\text{Au}\cdot\text{S}(\text{Bz})_2]$ and $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{I} \cdot \text{Au}\cdot\text{S}(\text{Bz})_2 \\ \diagup \\ \text{I} \end{array} \right]$.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY,
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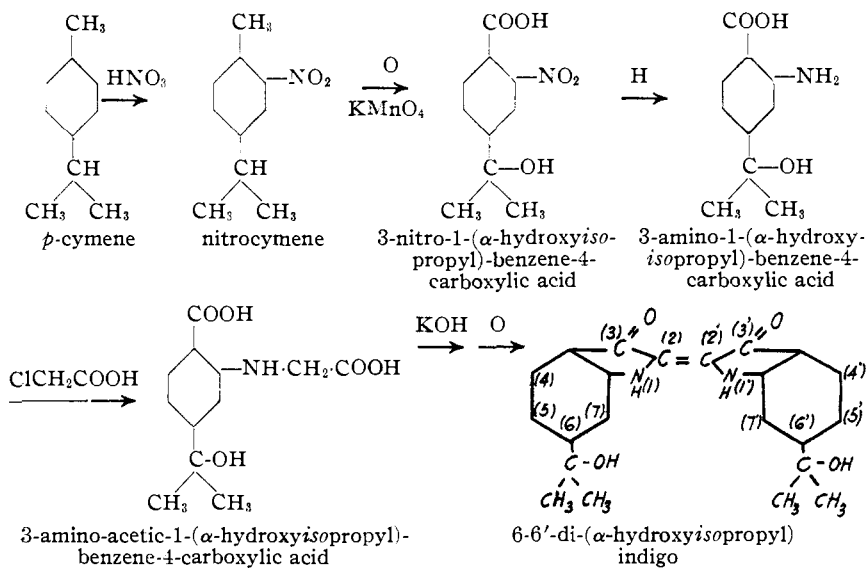
THE PREPARATION OF 6,6'-DI(ALPHA-HYDROXYISOPROPYL) INDIGO FROM PARA-CYMENE

By MAX PHILLIPS

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Since the elucidation of the constitutional formula of indigo by Adolf Baeyer, a number of investigators have been engaged in the preparation of alkyl and other derivatives¹ of this substance. The method usually followed consists in making use of one of the several syntheses of indigo and substituting for the usual indigo-yielding intermediate, one that already contains the particular group or groups that it is desired to introduce in the indigo molecule. From a study of the literature, it became apparent that no indigo derivative containing the *isopropyl* group had hitherto been prepared, and inasmuch as this laboratory has for some time been engaged in carrying on some investigations on *p*-cymene, the chief constituent of so-called spruce turpentine, the possibility of preparing an indigoid dye from this hydrocarbon suggested itself. The method followed in the synthesis of this dye may be represented as follows.

¹ *Ber.*, **16**, 817, 2201 (1883); **23**, 59 (1890); **24**, 693 (1891); **25**, Ref. 488 (1892); **45**, 2074 (1912). *Ger. pat.*, 61,171. *Am. Chem. J.*, **27**, 1 (1902).



Experimental Part

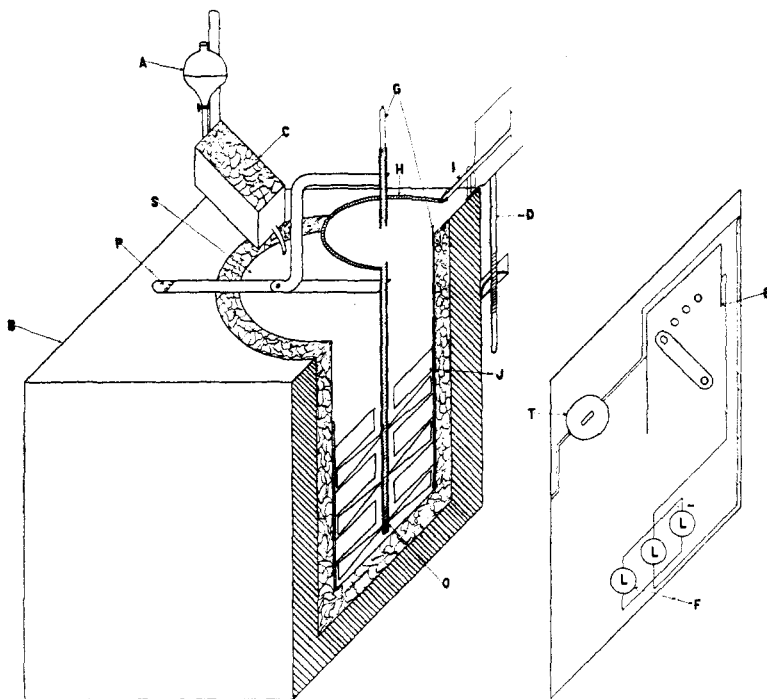
Isolation of *p*-Cymene from Spruce Turpentine.—The “spruce turpentine”² obtained from a pulp mill was first distilled in a current of steam and about 80% of the oil came over in the distillate. At first the distillate was colorless; towards the end of the distillation, however, it had a light yellow color. The oil was washed with dil. sodium hydroxide solution to remove sulfur dioxide, then with water, and it was finally dried over fused calcium chloride. It was subsequently digested over sodium at the boiling temperature and fractionated. By far the largest portion of the oil distilled at 176–178° and this fraction without any further purification³ was used in the preparation of nitrocymene.

² A volatile oil recovered during the manufacture of pulp from spruce and other resinous wood by the sulfite process. It is also sometimes referred to as “sulfite turpentine.” It is at present a waste product; no substantial use for it has, as yet, been developed, although various attempts to find some use for it have been made within the past few years. The amount of this oil that is available, or rather, could be available from the pulp mills of the United States and Canada alone is variously estimated as from 750,000 [Schorger, *J. Ind. Eng. Chem.*, **10**, 258 (1918)] to 2,000,000 gallons per annum [Herty, *ibid.*, **10**, 4 (1918)].

³ Schorger [THIS JOURNAL, **39**, 2672 (1917)] purified cymene from “spruce turpentine” by shaking it repeatedly with fresh quantities of conc. sulfuric acid. He states that pure cymene produces no coloration with this acid. However, the experience in this laboratory has been that, by shaking the oil repeatedly with as many as 30 fresh portions of conc. sulfuric acid it still gives a yellow coloration with sulfuric acid. This method of purification was not used because it was too cumbersome and also because of the fact that the impurity, probably a terpene, did not specially interfere with the nitration of the cymene.

Nitration of Para-Cymene.—This apparatus⁴ was found extremely useful in the nitration of *p*-cymene and although it has no strikingly novel features it is, nevertheless, described here, because it is felt that it may be of sufficient interest to those engaged in this line of work to warrant a brief description.⁵

S is a 10-liter container made of sheet iron 1.6 mm. thick and held in place under support P by a projection not shown in the drawing. B is a wooden box filled with sawdust and containing a metal well, made water tight. The space between B and S is filled with a freezing mixture. The nitrator S is provided with baffles J and stirring device O and is operated through motor shaft I, which is controlled by rheostat E, lamps



F, and switch T. D is an elevating screw to release the driving mechanism from bevel gear H, to permit the nitrator S to be taken out. A is a dropping funnel to let in the nitrating mixture, which is cooled as it passes through the freezing mixture C.

The method used in making nitrocymene was essentially the one worked out in this laboratory by Andrews.⁶ However, one or two modifications were introduced, as will become apparent from the following description.

Twenty four hundred and sixty g. (1340 cc.) of sulfuric acid (sp. gr., 1.84) was put into the nitrator, the stirring device was set in motion, and when the temperature of the

⁴ This was constructed by R. Hellbach of the mechanical staff of this laboratory.

⁵ The drawing was made by M. J. Goss of this laboratory. Some of the work in connection with the nitration of nitrocymene was also performed by Mr. Goss.

⁶ Andrews, *J. Ind. Eng. Chem.*, 10, 453 (1918).

acid was 0°, 2144 g. (2508 cc.) of cymene was added. A nitrating mixture consisting of 1624 g. (1144 cc.) of nitric acid (sp. gr. 1.42) and 3280 g. (1784 cc.) of sulfuric acid (sp. gr. 1.84), previously cooled to 0°, was added drop by drop through the dropping funnel. The temperature throughout the nitration was maintained at 0° to +5°. When all of the nitrating mixture had been added, which required about 16 hours, the stirring was continued for another hour. The product was poured into a large separatory funnel. On standing, two layers separated, the upper one consisting largely of nitrocymene and the lower one of acid mixed with "tarry matter" and practically no nitrocymene. The crude nitrocymene was separated and washed with water until free from acid. Inasmuch as nitrocymene and dil. alkali tend to form an emulsion which is rather difficult to break, a fact also pointed out by Wheeler and Smithey,⁷ the nitrocymene was washed with water only. The washing was conveniently done by placing the crude nitrocymene in a suitable container and immersing in that a spraying device. This was a cylindrical vessel 10 cm. in diameter, and 25 mm. high, made of brass and provided with a water inlet. The top and sides of the cylinder were perforated. The water inlet was attached to the tap and the spray of water that came through thoroughly washed the nitrocymene. In about half an hour the nitrocymene was free from acid. The washed nitrocymene was subsequently distilled in a current of superheated steam and the first portion of the distillate containing an oil lighter than water was discarded. The nitrocymene came over as a yellow oil heavier than water. The yield was usually from 45 to 50% of the calculated amount.

3-Nitro-1-(α -Hydroxyisopropyl)-benzene-4-carboxylic Acid.—For the preparation of this compound a modification of the method of Söderbaum and Widman⁸ was used. To 100 g. of nitrocymene, 500 cc. of 20% sodium hydroxide solution and 6 liters of potassium permanganate solution (40 g. per liter) were added and the mixture was heated on the steam-bath for 12 hours. Ten to 15 cc. of ethyl alcohol was then added to reduce the excess of potassium permanganate and the solution was filtered. The filtrate was neutralized with dil. sulfuric acid, evaporated to dryness on the steam-bath, and the residue extracted successively with four 400cc. portions of 95% alcohol. The alcohol was distilled and the residue made acid with hydrochloric acid, which gave a crystalline mass. For further purification, it was dissolved in hot 40% alcohol, boiled with animal charcoal, filtered, and allowed to crystallize. A colorless crystalline product was obtained; yield, 36 g. (39.4%); m. p., 168° (corr.).

Analyses. Subs., 0.2637, 0.2716: (Kjeldahl), 11.9 cc., 11.7 cc. of 0.1 *N* acid. Calc. for $C_{10}H_{11}O_6N$: N, 6.22. Found: 6.32, 6.04.

3-Amino-1-(α -Hydroxyisopropyl)-benzene-4-carboxylic Acid.—This can be prepared from the nitro acid by the reduction with tin and hydrochloric acid, or with ferrous sulfate and ammonia. Much better results were obtained, however, by the use of barium hydroxide and ferrous sulfate. This method has the added advantage that the amino acid is obtained free from inorganic salts. Twenty g. of the nitro acid was added to 100 cc. of boiling water and the solution, after neutralization with barium hydroxide solution, was added to a hot ferrous sulfate solution, consisting of 170 g. of ferrous sulfate heptahydrate (7 moles to one of nitro acid) dissolved in 400 cc. of water. This solution was stirred by means of a mechanical stirrer and heated to boiling. A 20% barium hydroxide solution was added until the mixture was distinctly alkaline in reaction. The stirring and heating were continued for another 30 minutes, the barium sulfate and iron hydroxides were removed by filtration, and a current of carbon dioxide

⁷ Wheeler and Smithey, *THIS JOURNAL*, **43**, 2613 (1921).

⁸ Söderbaum and Widman, *Ber.*, **21**, 2127 (1888).

was passed into the filtrate until all the barium was precipitated as barium carbonate. This was filtered off, and the filtrate was concentrated on the steam-bath to a volume of about 100 cc., cooled to room temperature, and made acid with acetic acid. On standing, the amino acid crystallized in the form of light brown plates. When recrystallized from benzene, a colorless product was obtained, yield, 14 g. (80.0%); m. p. 158° (corr.).

Analyses. Subs., 0.2495, 0.2525: (Kjeldahl), 12.75 cc., 12.80 cc. of 0.1 *N* acid. Calc. for $C_{10}H_{13}O_3N$: N, 7.16. Found: 7.15, 7.11.

3-Amino-acetic-1-(α -Hydroxyisopropyl)-benzene-4-carboxylic Acid.—This compound has not hitherto been described in the literature. It was prepared by the condensation of the above described amino acid with mono-chloroacetic acid; 19.7 g. ($1/10$ mole) of the amino acid and 9.4 g. ($1/10$ mole) of monochloro-acetic acid were added to 100 cc. of a 10% sodium carbonate solution. The reaction mixture was heated on the steam-bath for 2 hours, allowed to cool, and acidified with hydrochloric acid. The free acid separated as a yellow crystalline precipitate. It was recrystallized from water and yellow needles were obtained; yield, 13.2 g. (52.3%).

OPTICAL PROPERTIES.⁹—In ordinary light: habit: short rods, plates, and irregular grains, probably triclinic. Color, faintly yellow; with one Nicol, γ -direction pale, yellow, β -direction slightly paler yellow, α -direction practically colorless.

Refractive indices: (*D*) α , 1.430; β , 1.625; γ , 1.670; γ - α , 0.240; all \pm 0.005. Mean values of the indices are usually shown, but α and γ are not infrequently shown by sharply extinguishing grains, while β is often shown by grains exhibiting the dispersion phenomena noted below.

In parallel polarized light, Nicols crossed: double refraction extreme, the colors being of high orders. Extinction and elongation determinate, but obviously variable. Many grains show instead of extinction a brilliant and striking play of colors from intense blue on one side of the extinction position to orange just on the other side. This effect is apparently due to the presence of strong dispersion of the optic axes.

In convergent polarized light, Nicols crossed: because of the extreme dispersion, no normal interference figures are shown. The optic axis figure on the grains with the color play shows intense blue on one side and orange on the other. Optic sign negative.

This compound is soluble in alcohol, ether, methyl alcohol, and acetone, the solution in each case showing a blue fluorescence. It is sparingly soluble in cold, but quite soluble in hot water, and insoluble in both hot and cold chloroform and benzene. It melts at 232.6° (corr.).

Analyses. Subs., 0.2126, 0.2103: CO_2 , 0.4406, 0.4381; H_2O , 0.1178, 0.1195. Subs., 0.2305, 0.3501: 9.75 cc., 13.55 cc. 0.1 *N* acid. Calc. for $C_{12}H_{15}O_5N$: C, 56.89; H, 5.97; N, 5.53. Found: C, 56.51, 56.80; H, 6.20, 6.35; N, 5.45, 5.42.

6,6-Di-(α -Hydroxyisopropyl) Indigo.—A mixture of 1 part of 3-amino-acetic-1-(α -hydroxyisopropyl)-benzene-4-carboxylic acid (10.1 g., $=1/25$ mole) and 5 parts of potassium hydroxide (50.5 g.) was fused in a nickel crucible, out of contact with air. During the fusion the mass was well stirred. The fusion was at first conducted at 180° to 200° but was completed at 220° to 230°. The time of fusion was 15 minutes. The reddish-yellow mass was allowed to cool and was then dissolved in water. A current of air was led through the solution until a test portion no longer produced a bluish precipitate when air was drawn through. The oxidation product then formed was filtered off, washed successively with water,

⁹ Optical properties determined by Edgar T. Wherry of this Bureau.

then with very dil. hydrochloric acid, and finally dried; yield, 2.32 g. (31.0%).

Subs., 0.1332, 0.1256: CO₂, 0.3415, 0.3224; H₂O, 0.0761, 0.0683. Subs., 0.2334, 0.1886: 12.45 cc., 10.00 cc. of 0.1 N acid. Calc. for C₂₂H₂₂O₄N₂: C, 69.80; H, 5.86; N, 7.40. Found: C, 69.91, 69.99; H, 6.39, 6.08; N, 7.47, 7.43.

In powdered form this dye has the appearance of indigo. It dyes cotton from a hydrosulfite bath greenish-blue and compares rather favorably with indigo as regards fastness to light, acid, washing and rubbing. It differs from indigo notably in its solubility in most organic solvents as shown in Table I.

TABLE I
COMPARATIVE SOLUBILITIES OF INDIGO AND 6,6'-DI-(α -HYDROXYISOPROPYL)INDIGO IN VARIOUS ORGANIC SOLVENTS

| Solvent | Indigo | | 6,6'-Di-(α -hydroxyisopropyl)indigo | |
|---------------------------|------------------------------|----------|---|----------------|
| | Solubility | Color | Solubility | Color |
| Alcohol | insol. | | sol. cold | deep blue |
| Ether | insol. | | sol. cold | deep blue |
| Chloroform | sl. sol. | blue | readily sol. | deep blue |
| Methyl alcohol | insol. | | sol. | deep blue |
| Benzene | sl. sol. | amethyst | sol. cold | violet |
| Acetone | sl. sol. | blue | sol. cold | reddish-violet |
| Carbon tetra- chloride | insol. cold, sl. sol. hot | violet | sol. cold | violet |
| Carbon disulfide | insol. | | sol. cold | violet |
| Nitrobenzene | insol. cold, sol. hot | violet | sol. cold | violet |
| Aniline | sl. sol. | blue | sl. sol. | bluish-green |
| Acetic acid | insol. cold, sl. sol. hot | blue | sol. cold | deep blue |

Summary

A new indigoid dye has been prepared from *p*-cymene. The method followed consists in first preparing nitrocymene, then oxidizing with alkaline potassium permanganate solution to 3-nitro-1-(α -hydroxyisopropyl)-benzene-4-carboxylic acid; reducing this to the corresponding amino compound; condensing the amino compound with monochloro-acetic acid, and obtaining 3-amino-acetic-1-(α -hydroxyisopropyl)-benzene-4-carboxylic acid. The last compound upon fusion with potassium hydroxide and subsequent air oxidation gives the new dye.

WASHINGTON, D. C.