Sponagle prepared various methylphenyl ethers, using copper as a catalytic agent. (36) This Journal, 28, 608.—Cook studied aluminium phenolate with reference to the preparation of phenyl ether. (37) *Ber.*, 38, 2490.—Kipper prepared several derivatives of phenyl ether by means of Friedel and Crafts' reaction. (38) *Am. Chem. J.*, 36, 543.—Cook prepared metatolyl ether and several of its derivatives.

State University, Vermilion, S. Dak.

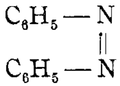
THE STEREOMERIC AZOBENZENES.

By Catherine V. Gortner and Ross Aiken Gortner.

Received June 10, 1910.

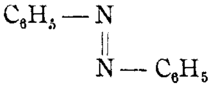
Introduction.

It is apparent from the structural formula of azobenzene that two stereomeric modifications should exist, one in which both aromatic nuclei are on the same side of the nitrogen bridge or *syn*-azobenzene (I), and the other where the nuclei are opposite each other or *anti*-azobenzene (II):



$$\begin{array}{r} C_6H_5-N \\ \| \\ C_6H_5-N \end{array}$$

(I)



$$\begin{array}{l} C_6H_5-N \\ \qquad\ \ \| \\ \qquad\ \ N-C_6H_5 \end{array}$$

(II)

Although many such examples of syn and anti forms are known in the diazo compounds,[1] the authors are not aware of any such isomerism having been observed in the azo group.

Some years ago one of us had occasion to prepare azobenzene during a course in "organic preparations," but could not by any means obtain a compound melting at 68°, the melting point of azobenzene as described in the literature. Crystals were, however, obtained which melted at "about 23°," as the notes were then recorded. It afterward seemed probable that this was the unknown stereomeric form and we have recently taken up the subject again, obtaining results which lead us to believe that such was the case.

Experimental.

The azobenzene was produced by the dry distillation of azoxybenzene and clean iron filings from a small non-tubulated retort. The azoxybenzene was prepared according to the method of Lachman.[2]

Thirty grams of nitrobenzene were added to 250 cc. of methyl alcohol containing 40 grams of sodium hydroxide and the mixture heated during three hours on an actively boiling water bath. The methyl alcohol was then distilled off and the residue poured into ice-water. The azoxybenzene separated as an oil which soon became solid. This solid was well washed, melted with dilute hydrochloric acid to remove traces of aniline, washed free of acid, and recrystallized from 90 per cent. alco-

---

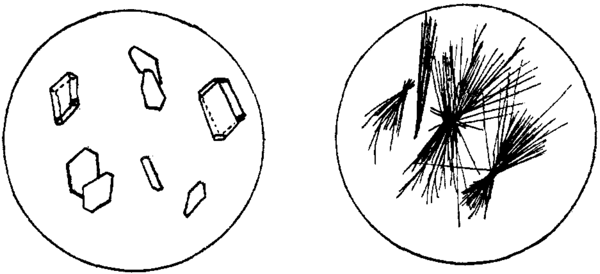
[1] Holleman, "Lehrb. d. Organ. Chem.," Leipzig, 1908, p. 362.

[2] This Journal, 24, 1178 (1902).

hol. Prepared in this manner, azoxybenzene forms small straw-colored needles, which melt at 36° (cor.); yield, 15–18 grams.

The azoxybenzene was dried on a porous plate and lastly at 110° for four hours. It was then finely pulverized and mixed with twice its weight of clean, dry iron filings and the mixture distilled. The distillate, in every case, was a red liquid containing a crystalline substance. The red portion was easily soluble in ligroin, leaving a mass of light gray needles, insoluble in ligroin, soluble to a considerable extent in alcohol and ether; containing nitrogen and melting at 237° (cor.); yield, about 1 per cent. of the azoxybenzene taken. This substance was not further investigated.

The deep red ligroin solution was thoroughly washed with cold dilute hydrochloric acid and then with water, filtered, and allowed to evaporate. In a number of instances preparations of azoxybenzene were obtained which yielded only ordinary azobenzene (m. p. 68°) crystallizing in prisms (see fig.). In several cases, however, only a deep red liquid was obtained, which, for a long time, we despaired of obtaining pure, as with the small amount available, distillations always resulted in considerable decomposition. This same red liquid was, also, often found in the mother liquors from which the 68° compound had crystallized.[1] At last, however, crystals were noticed in one preparation, from which other preparations were easily seeded. The crystals so obtained were pressed out on a porous plate, dissolved in ether, and the ether allowed



m.P. 68° m.P. 25°

Crystals of Azobenzene

---

[1] Gattermann ("Practical Methods of Organic Chemistry," New York, 1903, p. 200) states that "if on heating, a sudden but harmless explosion should occur, it is due to the fact that the substances were not dry; the experiment should be repeated." The authors have found that if the distillation is continued *after the explosion* a small yield of the "red liquid" usually results which can be easily separated from the "tar" by solution in ligroin. In several instances we have obtained fair yields of 25° azobenzene in this manner, but in no instance have we obtained the 68° modifications from the explosion residue.

to evaporate, the crystals again pressed out on a porous plate and the process repeated until the melting point remained constant. For analysis the product was dried *in vacuo* over concentrated sulphuric acid:

0.1171 gram gave 15.2 cc. nitrogen at 16.5° and 772 mm. Calculated for $C_{12}H_{10}N_2$: N, 15.38 per cent.; Found: N, 15.35 per cent.

This variety of azobenzene forms orange-red, stellate groups of needles (see fig.), is easily soluble in ether, ligroin, alcohol, acetone, methyl alcohol, etc., and melts at 25° (cor.) to a deep red liquid. It will not crystallize when "seeded" with the 68° substance, but in two instances we have succeeded in quantitatively transforming the 25° substance into the 68° substance, once by boiling with dilute hydrochloric acid, and in the other instance the cause of conversion is unknown to us. We can give no method which will always insure conversion, nor have we been able to transform the 68° substance into the 25° modification. According to Holleman,[1] the *syn* modifications are the least stable, so it seems probable that the new compound is *syn*-azobenzene. When a mixture of the two compounds occurs, the 68° isomer easily crystallizes out, leaving the 25° azobenzene practically free of the higher melting substance.

Reduction of the 25° Azobenzene.—1.75 grams of azobenzene melting at 25° were dissolved in 60 cc. of 50 per cent. alcohol and an excess of sodium amalgam was added. The reaction was allowed to proceed in the cold until all color had been discharged. The hydrazobenzene was precipitated from this solution by dilution, filtered off, and washed with dilute alcohol and then with water, dried at 100°, and recrystallized from ligroin, yield 1.50 grams, or 83 per cent. of the theoretical yield, m. p. 126° (cor.). When this hydrazobenzene was allowed to oxidize in the air, in the presence of alkali, and the oxidation mixture extracted with ether, only the 68° azobenzene was found to be present.

Summary.

1. A second stereomeric azobenzene has been isolated.

2. The new modification differs from the 68° isomer by melting at 25° (cor.) and crystallizing in stellate groups of needles.

3. From a mixture of the two isomers the 68° compound may be easily separated by crystallization, leaving the 25° isomer in the mother liquor.

4. The 25° azobenzene (probably *syn*-azobenzene) has been converted into the 68° isomer, but the reverse change has not been accomplished.

COLD SPRING HARBOR, LONG ISLAND, N. Y.

---

[1] Holleman, *Loc. cit.*