[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE REDUCTION OF 2-NITROFLUORENE

BY F. E. CISLAK, I. M. EASTMAN AND J. K. SENIOR

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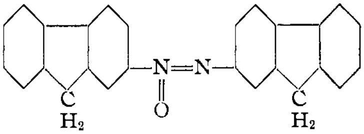
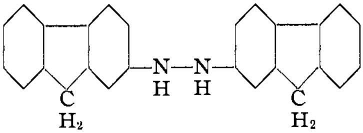
The reduction of 2-nitrofluorene to 2-aminofluorene has been described by both Strasburger[1] and Diels.[2] Strasburger carried out the reduction in acid solution by the use of tin and hydrochloric acid; Diels obtained almost quantitative results with zinc and calcium chloride under very nearly neutral conditions. In a recent paper by Korczynski, Karlowska and Kierzek[3] appears the statement that 2-nitrofluorene may be easily reduced in alkaline medium to azoxyfluorene (hereafter referred to as 2,2′-azoxy*bis*fluorene), which on account of its great insolubility separates from the solution and thus escapes the further action of the reducing agent. We have been able to find no other reference to this compound in the literature. Since we have prepared it, as well as some of its derivatives, we judge it best to report on the results so far obtained, although the work in this field is not yet complete.

2,2′-Azoxy*bis*fluorene (I) may be prepared by the reduction of 2-nitrofluorene with zinc and calcium chloride. The amount of zinc used, however, is only one-tenth of that used by Diels in his preparation of the amine.



I



II

The azoxy compound is a bright orange substance, almost insoluble in alcohol and ether, and only slightly soluble in the higher-boiling organic solvents. It is best recrystallized from boiling xylene in which it is soluble to the extent of about three per cent. When thus treated, it separates in rectangular platelets which melt at 279° (corr.).

After the empirical formula and molecular weight of the compound had been determined, its structure was demonstrated by reducing it further to 2-aminofluorene. Because of the insoluble nature of the substance, it was necessary to carry out the reduction under special conditions. When the compound was suspended in alcohol, even prolonged treatment with a large excess of zinc and calcium chloride failed to produce more than a slight change. Zinc and acetic acid were also without effect. Success was finally obtained by taking advantage of the solubility of the azoxy compound in phenol. Zinc dust was added to a warm phenol solution of the substance. Then hydrochloric acid was added, and the

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[1] Strasburger, *Ber.*, **17**, 108 (1884).

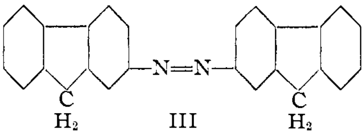
[2] Diels, *Ber.*, **34**, 1759 (1901).

[3] Korczynski, Karlowska and Kierzek, *Bull. soc. chim.* (4), **41**, 68 (1927).

mixture warmed until all the zinc had dissolved. The deep blue-green color, which appeared as soon as the hydrochloric acid was added to the phenol solution, was bleached during the reduction, and from the reaction mixture 2-aminofluorene was isolated in an amount corresponding to 82% of the azoxy compound used. This result, together with the analysis and molecular weight, is considered to demonstrate the structure of the substance in question.

Attempts were made to oxidize 2,2′-azoxy*bis*fluorene to the corresponding *bis*fluorenone by treating it with hot chromacetic acid, but even prolonged boiling with this reagent failed to alter the compound—an unusual result in view of the ease with which most fluorene derivatives are converted to fluorenones under these conditions.

During the reduction of 2,2′-azoxy*bis*fluorene to 2-aminofluorene, there was always formed along with the amine a small amount of a white, difficultly soluble substance which, when recrystallized from xylene, formed hexagonal platelets, melting at 257–258° (corr.). By modifying the method of reduction, this compound could be obtained as the principal reaction product. To prepare it, acetic acid instead of hydrochloric acid was used and the reduction was conducted below 45° with as little acid as possible. The compound was at first supposed to be 2,2′-hydrazo*bis*fluorene (II), a supposition with which its analysis and molecular weight agreed; but the behavior of the substance was incompatible with this assumption. In the first place, it obstinately resisted further reduction with zinc and hydrochloric acid even in phenol solution. Under no conditions could it be converted to 2-aminofluorene. Secondly, the compound, when oxidized, yielded only deeply-colored amorphous products. It was impossible to isolate any substance identifiable as 2,2′-azo*bis*fluorene (III) which ought easily to be formed if the compound had the supposed structure.



III

The most probable alternative hypothesis is that the hydrazo compound really was formed in the course of the reduction, but that, under the influence of the acetic acid, it underwent one of the molecular rearrangements characteristic of compounds of this class. Acetic acid is not a common reagent for producing such rearrangements, but instances of its use for this purpose are known.[4]

Of the five different forms of rearrangement which have been observed[5]

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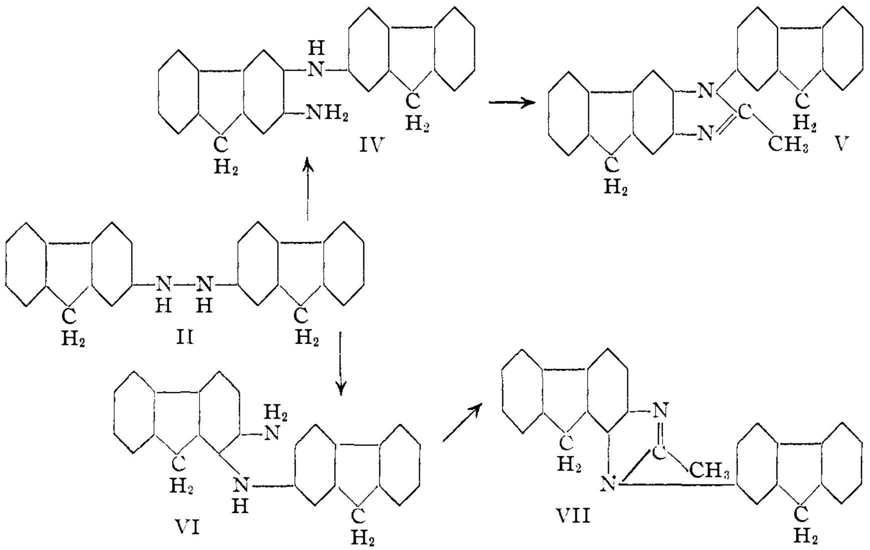
[4] (a) Meisenheimer, *Ber.*, **36**, 4159 (1903). (b) Sachs and Whittaker, *Ber.*, **35**, 1433 (1902). (c) Rassow and Rülke, *J. prakt. Chem.* (2) **65**, 97 (1902).

[5] Jacobson, *Ann.*, **428**, 81 (1922).

among hydrazo compounds, the benzidine, *p*-semidine, and *o*-*p*-diphenyloid forms are inapplicable to the present case, because the positions *para* to the hydrazo group are occupied by the bond between the six-membered rings of the fluorene. The remaining two rearrangements (*o*-*o*-diphenyloid and *o*-semidine) might lead to five different compounds, all isomeric with 2,2′-hydrazo*bis*fluorene.

It was possible to eliminate some of these possibilities by acetylating the compound in question. When treated with acetic anhydride it readily yielded a white derivative which crystallized from xylene in needles melting at 179° (corr.). This compound contained no oxygen and showed by analysis the presence of two more atoms of carbon per molecule than the parent compound. The only simple explanation of these facts is that the acetylated derivative is a C-methyl imidazole. If such is the case, the two nitrogen atoms in the unacetylated compound must occupy two adjacent positions on one phenyl ring, both of them must be amine nitrogens and at least one of them must be primary. Such a configuration is the result of a rearrangement of the *o*-semidine type.

The rearrangement together with the subsequent imidazole formation may be represented by one of the two following schemes.



The two compounds are either 2′-amino-2,3′-difluorylamine (IV) and $\overline{3}$-(2-fluoryl)-2-methyl-2,3-fluorenimidazole (V), respectively, or else they are, respectively, 2-amino-1,2′-difluorylamine (VI) and $\overline{1}$-(2-fluoryl)-2-methyl-2,1-fluorenimidazole (VII). At present, there exist no data which would permit a choice between these two possibilities.

The only property of the unacetylated compound (IV or VI) which is not in harmony with this interpretation is its weak basic nature. If it does contain a primary amine group it ought to form salts. None such could, however, be obtained in aqueous solution. It is probable that the heavy aryl radicals and extreme insolubility of the substance greatly weaken its basic properties.

Other methods of reducing 2-nitrofluorene were also tried. When boiled in aqueous alcoholic solution with ammonium sulfide, it was not altered. This result is rather curious since the reagent used is very effective in reducing the corresponding 2-nitrofluorenone. When 2-nitrofluorene is treated in methyl alcohol solution with sodium methylate, it yields a brown product which has not yet been fully investigated. It is hoped to identify this substance as well as to find methods of preparing the hydrazo and azo compounds (II and III) which have as yet escaped detection.

Experimental Part

Preparation of 2,2′-Azoxy*bis*fluorene.—2-Nitrofluorene (30 g.) was suspended in one liter of boiling aqueous alcohol (sp. gr. 0.87) to which a solution of 10 g. of calcium chloride in 15 cc. of water had been added. Zinc dust (30 g.) was then added and the mixture refluxed for two hours, cooled and filtered. The cloudy filtrate was then evaporated to small volume and again filtered. The combined precipitates were dried in an oven at 100°. The dried material was treated with about 1500 cc. of boiling xylene, and the hot solution filtered to free it from suspended excess zinc. When the xylene solution was cooled, 2,2-azoxy*bis*fluorene separated in orange-yellow, rectangular plates. The first yield was about 15 g. and an additional 5 g. could be obtained by concentrating the mother liquor. After two recrystallizations from xylene, the substance melted with decomposition at 279° (corr.).

Anal. Calcd. for $C_{26}H_{18}N_2O$: N, 7.49; C, 83.38; H, 4.85. Found: 7.24, 7.45; 83.14, 83.05; 5.10, 5.08.

The molecular weight was determined by the camphor method of Rast.[6]

Mol. Wt. Calcd. for $C_{26}H_{18}N_2O$: 374. Found: 411, 404, 417.

Reduction of 2,2-Azoxy*bis*fluorene to 2-Aminofluorene.—2,2-Azoxy*bis*fluorene (2 g.) was dissolved in 25 cc. of warm phenol to which zinc dust (5 g.) had been added. Strong hydrochloric acid (20 cc.) was added in small amounts while the mixture was warmed on a hot-plate. By the time the zinc had all dissolved, the deep blue-green color formed when the acid was first added had almost entirely vanished. The entire reaction mixture was poured into water, and sodium hydroxide added in large enough excess to dissolve the zinc hydroxide formed. The insoluble precipitate was removed by filtration and dissolved in alcohol. The filtered solution was poured into excess water and the precipitate removed by filtration. When dried, it weighed 1.65 g., and was identified as 2-aminofluorene. It melted at 124°, and the melting point of a mixture of the compound with 2-aminofluorene (m. p. 129°) was 127°.

The Reduction and Subsequent Ortho-semidine Rearrangement of 2,2,-Azoxy*bis*fluorene.—2,2-Azoxy*bis*fluorene (5 g.) was dissolved in 60 cc. of hot phenol. Zinc dust (10 g.) was added and the mixture cooled to 40° while constantly agitated. The azoxy compound separated as a thick paste. Glacial acetic acid (1.75 cc.) was added, a few drops at a time, in the course of about 15 minutes, during which time the mixture

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[6] Rast, *Ber.*, **55**, 1051 (1922).

was kept well stirred. The temperature was held below 45°. As the reduction proceeded, the mass became more fluid, and the end of the reaction was marked by the disappearance of the yellow color. The entire reaction mixture was then poured into 1200 cc. of water. The rather oily precipitate became granular when stirred. It was removed by filtration and suspended in 100 cc. of warm alcohol. It was again collected on a filter and then treated with 200 cc. of boiling xylene. The hot xylene solution was filtered to remove excess zinc. When the filtrate was cooled, it deposited a grayish substance, crystallizing in irregular hexagonal scales. This was the substance IV or VI.

As thus prepared the compound contained colored impurities very difficult to remove by recrystallization. It was best purified by dissolving it once more in phenol and treating it with zinc and hydrochloric acid. From the reaction mixture the compound was isolated in the manner already described. After two recrystallizations from xylene, it was obtained in the form of white crystals which, when moist, tended to darken on exposure to the air. The dried compound turned red at 240–245° and melted with decomposition at 257–258° (corr.). The yield was about 50%. The substance is only very slightly soluble in alcohol and ether. It may be recrystallized by adding alcohol to a warm nitrobenzene solution.

Anal. Calcd. for $C_{26}H_{20}N_2$: N, 7.78; C, 86.62; H, 5.60. Found: 7.69, 7.53, 86.35, 86.75, 5.91, 5.84.

The molecular weight was determined by the camphor method.

Mol. Wt. Calcd. for $C_{26}H_{20}N_2$: 360. Found: 312, 330.

Preparation of Compound V or VII.—Compound IV or VI (3 g.) was boiled for two hours with 15 cc. of acetic anhydride. When the cooled reaction mixture was poured into 40 cc. of alcohol, a paste of needle-shaped crystals formed. When dried these melted at 146°. Two recrystallizations from xylene raised the melting point to 179° (corr.), where it remained constant on further recrystallization. The yield was about 65%. The substance is fairly soluble in alcohol, benzene and acetone.

Anal. Calcd. for $C_{28}H_{20}N_2$: N, 7.29; C, 87.45; H, 5.25. Found: 7.26, 7.30 87.33, 87.83, 5.66.

The molecular weight was determined cryoscopically in benzene.

Mol. Wt. Calcd. for $C_{28}H_{20}N_2$: 384. Found: 437, 438, 438.

Summary

The preparation and properties of 2,2′-azoxy*bis*fluorene are described. This substance may be reduced, but at the same time it undergoes a rearrangement of the *o*-semidine type. The substituted orthodiamine thus formed readily yields an imidazole derivative.

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