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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	9
page range	239-244
year	1957
URL	http://hdl.handle.net/10097/26827

Syntheses of 2,2'-Diamino-Biphenyl and Carbazole from Phenanthrene

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(Received April 11, 1957)

Synopsis

Preparations of 2,2'-diamino-biphenyl and carbazole from phenanthrene were described. Diphenic acid, obtained by the oxidation of phenanthrene, was converted to 2,2'-diamino-biphenyl through diphenic acid diamide in good yield. This diamine undergoes deaminocyclization to carbazole. Some attempted rearrangements in non-aqueous solutions were tried ineffectively.

I. Introduction

As is well known, the fraction of 300~380°C (i. e. anthracene oil) obtained by the distillation of coal tar, when cooled to room temperature and the crystals that separate out are centrifuged, affords a mixture of green crystals. This is the so called anthracene cake. The removal of phenanthrene from this cake, and isolation and purification of anthracene and carbazole from the sparingly soluble portion in the solvent have been the practice in tar industry for a long period. In spite of the fact that over 20 per cent (maximum 48 per cent)⁽¹⁾ of phenanthrene is present in the anthracene cake, phenanthrene had been discarded or used as fuel because of its little use.

The present writers succeeded in deriving phenanthrene (I) to 2,2'-diamino-biphenyl (VII) through diphenic acid diamide (VI). Carbazole (VIII) can easily be formed from this (VII) by the known method. (Fig. 1.)

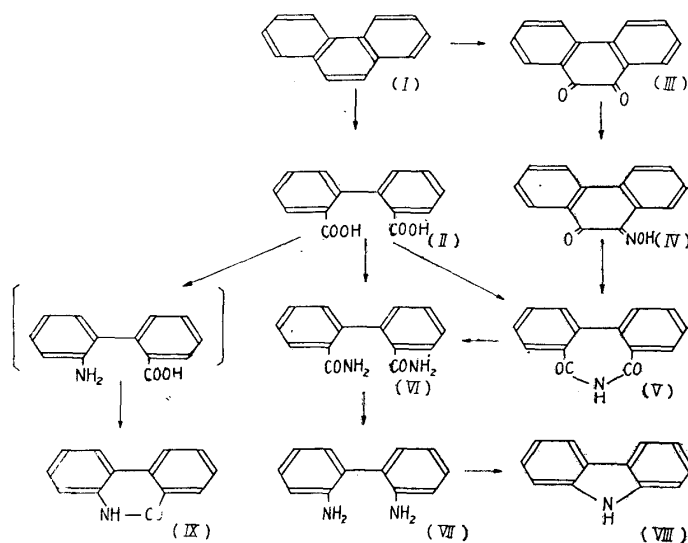


Fig. 1

(1) S. Coffey and J. Van Alphen, *Chemistry of Carbon Compounds*, Elsevier Press, Inc, III B. (1956), P. 1354.

It has become possible in recent years to obtain diphenic acid (II) in comparatively simpler manner, by the action of hydrogen peroxide⁽²⁾ or ozone⁽³⁾ from phenanthrene (I). Therefore, the syntheses of 2,2'-diamino-biphenyl and carbazole by the routes indicated above would be appropriate as a method for utilizing phenanthrene.

The formation of diphenic acid (II) from phenanthrene (I) by hydrogen peroxide-glacial acetic acid solution was in a yield of 64.4 per cent from purified (I), approximately the same as in the literatures.⁽²⁾

The authors, nextly, attempted to obtain diphenic acid imide (V) from (I) through phenanthrenequinone monoxime (IV), submitting the latter to the Beckmann rearrangement in liquid sulfur dioxide. (V) can easily be led to (VI). The formation of (V) by the hitherto operated Beckmann rearrangement of (IV) gave an extremely poor yield and we supposed this was due to the too high a reaction temperature, which made it liable to form fluorenone derivative from (IV).⁽⁴⁾ When liquid sulfur dioxide is used as a solvent for the Beckmann rearrangement,⁽⁵⁾ a lower temperature can be employed that the formation of (V) in a good yield was anticipated. However, the use of various reagents in liquid sulfur dioxide was futile. When thionyl chloride in liq. SO₂ was applied on phenanthrenequinonemonoxime, a crystal m.p. 270°C which sublimates at 170~180°C (5 mm) was obtained.

Diphenic acid diamide (VI) can be obtained from diphenic acid (II) in two or three steps in good yield.⁽⁶⁾

The derivation of diphenic acid monoamide, via 2-amino-biphenyl-2'-carboxylic acid by the action of bromine and alkali, to phenanthridone⁽⁷⁾ (IX) is being practiced already but there has been no report on the formation of 2,2'-diamino-biphenyl (VII) from diphenic acid diamide in the presence of a halogen and aqueous alkali solution by the Hofmann reaction. Bromine and chlorine were used as the halogen. The yields obtained are listed below :

Table 1.

Formation of 2,2'-Diamino-biphenyl from Diphenic Acid Diamide

Expt. No.	Aq. Alkali soln.	Halogen used.	Yield
1	NaOH	Br ₂	82%
2	KOH	Br ₂	68%
3	NaOH	Cl ₂	58%

- (2) W. F. O'conner and E. J. Moriconi, *J. Am. Chem. Soc.*, **73** (1951), 4044; *Ind. Eng. Chem.*, **45** (1953), 277; R. E. Dean, E. N. White and D. McNeil, *J. Appl. Chem.*, **3** (1953), 469.
- (3) W. J. Schmitt, E. J. Moriconi and W. F. O'conner, *J. Am. Chem. Soc.*, **77** (1955), 5640.
- (4) P. Wergerhoff, *Ber.*, **21** (1898) 2356; W. Borsche and W. Sandar, *Ber.*, **47** (1914), 2825.
- (5) N. Tokura, R. Asami and R. Tada, *Sci. Rep. RITU*, **A8** (1956), 149.
- (6) F. Bishof and J. Adkins, *J. Am. Chem. Soc.*, **45** (1923), 1030; H. W. Underwood and E. L. Kochmann, *ibid.*, **45** (1923), 3071; *ibid.*, **46** (1924), 2067; H. W. Underwood and L. A. Clough, *ibid.*, **51** (1929), 582.
- (7) L. Oyster and H. Adkins, *J. Am. Chem. Soc.*, **43** (1921), 208; J. Moore and E. J. Huntress, *ibid.*, **47** (1927), 1332.

Application of the Schmidt reaction⁽⁸⁾ (action of hydrazoic acid) to diphenic acid has already been made, resulting in a slight quantity of 2,2'-diamino-biphenyl and the majority of phenanthridone (IX).

An attempted decomposition of the diamide (VI) to diamine (VII) via the method of Bergstrom⁽⁹⁾, with potassium amide in liq. ammonia was unsuccessful, only recovering the starting material.

Cyclization-condensation of 2,2'-diamino-biphenyl into carbazole was carried out using phosphoric acid⁽¹⁰⁾. Attempts to effect deamination-condensation in liquid sulfur dioxide, either alone or by the use of various reagents, in the cold or with heating, all ended fruitless.

The crude phenanthrene used in the present work was kindly supplied by the Osaka Gas Co., Ltd., the anthracene cake by the Tokyo Gas Co., Ltd., and liquid sulfur dioxide by the Befu Chemical Industries, Ltd., all of which are hereby gratefully acknowledged. A part of the experiments and microanalyses of nitrogen were carried out by Miss Yoko Endo.

II. Experimental

1. Materials

(i) Phenanthrene

Purified from crude phenanthrene by modifying the known method.⁽¹¹⁾ Crude phenanthrene was treated with approximately two volumes of hot carbon disulfide, filtered, and the filtrate was concentrated. This was cooled and again filtered, the filtrate was evaporated, and the crude crystals thereby obtained was treated with maleic anhydride in xylene, cooled and filtered. The filtrate was washed with dilute alkali, dried and heated to remove xylene.

The residue was submitted to azeotropic distillation with diethyleneglycol to remove fluorene. The crystals obtained on distillation (b. p. 140~145°C (20 mm)) were washed with water and recrystallized from ethanol to crystals of m. p. 96~98°C.

(ii) Liquid sulfur dioxide

The commercial product from a cylinder was used after filtering once through a filter paper.

(iii) Liquid ammonia

The commercial liq. NH₃ was distilled and condensed before use.

2. Experimental result

(i) Diphenic acid⁽²⁾ (II)

To a solution of 17.8 g (0.1 mole) of phenanthrene (I) dissolved in 200 cc of glacial acetic acid, while being stirred at 80~85°C in a water bath, 62 g (0.55 mole) of 30 per cent hydrogen peroxide was added dropwise and the mixture was stirred

(8) G. Caronna, *Gazz. Chim. Ital.*, **71** (1941), 475; *C. A.* 37 (1943), 118.

(9) H. C. White and F. W. Bergstrom, *J. Org. Chem.*, **7** (1942), 497.

(10) H. Leditschke, *Ber.*, **86** (1953), 522.

(11) *Org. Syntheses*, **34** (1954), 31.

at 85°C for 4 hours. After allowing the reaction mixture to stand over night, the majority of acetic acid was removed under a reduced pressure, the residue cooled, and crystals of diphenic acid that separated out were collected by filtration. Evaporation of the filtrate to dryness afforded further crop of crystals, which were combined with the earlier crop and extracted with sodium carbonate solution. Acidification of the extract with hydrochloric acid gave yellowish brown crystals of crude diphenic acid, which were washed with diluted acetic acid to remove tarry substance, again dissolved in sodium carbonate solution, and treated with activated carbon. Acidification of the filtrate afforded diphenic acid as white crystals, m. p. 226~227°C. Yield, 15.6 g (64.4 per cent). Recrystallized from dilute ethanol to m. p. 228~230°C. Reported yield, 65~70 per cent (R. E. Dean and others).⁽²⁾

(ii) Diphenic acid diamide (VI)

(a) Syntheses from diphenic acid (II)

(1) A mixture of diphenic acid, m. p. 228~230°C, and 5 folds weight of acetic anhydride was heated at 120°C for 1 hour, cooled, and the crystals that precipitated out were collected by filtration. This was washed with 2N sodium carbonate solution and water, and dried. The crystals so obtained were refluxed for 1 hour with a mixture of the equal weight of conc. ammonia and water, diluted with water, and acidified by which diphenic acid monoamide separated out. This monoamide was again refluxed with 3 volumes of acetic anhydride for 2 hours and crystals of diphenic acid imide were obtained. The imide was refluxed for 1 hour with 6N ammonia water, the reaction mixture was cooled, and the crystals of the diamide that separated out were recrystallized from hot water, m. p. 211~212°C. Yield, 76 per cent (calcd. from diphenic acid.).

(2) Diphenic acid, m. p. 228~230°C was dissolved in conc. ammonia (slight excess over neutralization amount) and the solution was evaporated to dryness. On heating the salt at 250~260°C for 3 hours, diphenic acid imide is obtained which, per se, was added to an excess of 6N ammonia water and refluxed for 1 hour. The product was recrystallized from hot water, m. p. 211~212°C. Yield, 72.0 per cent (calcd. from diphenic acid.)

(iii) Attempted Beckmann rearrangements of phenanthrenequinone monoxime in liquid sulfur dioxide

Phenanthrenequinone monoxime (IV)

Phenanthrene (I) was oxidized with chromium trioxide in glacial acetic acid to phenanthrenequinone⁽¹²⁾ (III), m. p. 204~205°C, and reacted with hydroxylamine hydrochloride in alcohol, affording phenanthrenequinone monoxime⁽¹³⁾ (IV), m. p. 155~156°C.

(a) Rearrangement with sulfur trioxide in liq. SO₂

To a solution of 1 g of the monoxime (IV) dissolved in 50 cc of liquid sulfur dioxide (brown colored), in a pressurized bottle, a solution of 0.5 g of sulfur

(12) R. Anschütz, Ann. **196** (1879), 37.

(13) R. Pschorr, Ber, **35** (1902), 2734.

trioxide dissolved in 30 cc of sulfur dioxide was added and mixed at room temperature, by which the solution turned purplish black. The mixture was allowed to stand over night, liquid sulfur dioxide was allowed to evaporate, and the black, resinous residue was obtained, which refused further purification.

(b) With thionyl chloride in liq. SO_2

A solution of 1 g of thionyl chloride dissolved in 50 cc of liquid sulfur dioxide was added to the solution of 1 g of the monoxime (IV) dissolved in 50 cc of liquid sulfur dioxide, the two solutions were mixed in a pressurized bottle, and allowed to stand over night. A small amount of white precipitate was observed. After evaporation of liquid sulfur dioxide, the residue was poured into ice water, the precipitate was collected, and washed with water, affording a yellow powder. Recrystallization from ethanol gave long needles, m. p. $272\sim 273^\circ\text{C}$. Yield, 0.7 g. This substance does not contain nitrogen or halogen. Molecular weight, Rast method: 199.4, 194.8, 198.2; mean, 198.0 Sublimes at $170\sim 180^\circ\text{C}$ (5 mmHg) U. V. λ_{max} 252 (max.), 270, and 325 $\text{m}\mu$. This substance is clearly not diphenic acid imide (V). Details on this substance will be reported elsewhere.

(iv) 2,2'-Diamino-biphenyl (VII)

(a) Decomposition with sodium hypobromite

To a solution of 50 cc of 10 per cent sodium hydroxide containing 12.8 g (2.4/30 mole) of bromine, 8 g (1/30 mole) of diphenic diamide (VI) was added and allowed to stand at below 5°C in an ice bath with occasional agitation. The amide dissolved in about 10 minutes. This solution was allowed to stand for 30 minutes at room temperature, by which the solution changed from pale yellow to red color, and further heated for 30 minutes on a water bath. The oily substance that separated out was taken up in ether and the ether residue was dissolved in dilute hydrochloric acid. The acid solution was treated with activated carbon, the filtrate was rendered alkaline with sodium hydroxide, and 2,2'-diamino-biphenyl separated out as white crystals, m. p. $77.5\sim 78.5^\circ\text{C}$ 5.0 g, 82 per cent. Recrystallization from ethanol afforded crystals melting at $80\sim 81^\circ\text{C}$ (reported m. p. 81°C).

Anal. found: N, 15.4 per cent. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2$: N, 15.21 per cent.

(b) Decompositions with potassium hypobromite and sodium hypochlorite were carried out similarly as in (a), using potassium hydroxide solution and bromine or sodium hydroxide solution and chlorine in the similar mole ratios but the respective yield was 68 and 58 per cent, being far less than that from (a).

(c) An attempted Bergstrom's method with potassium amide in liq. ammonia

Potassium amide was prepared in 50 cc liq. ammonia from 0.5 g of metallic potassium and a trace of ferric catalyst. To this solution in a pressurized bottle, 1.0 g of diphenic diamide (VI) and 0.5 g of potassium nitrate in 50 cc of liq. ammonia were added, and the solution was allowed to stand for four days. After the reaction, the ammonia was evaporated, the residue was treated with ethanol and the filtrate was condensed. The crystals obtained was subjected to repeated recrystallizations m. p. $210\sim 211^\circ\text{C}$. 0.8 g, No depression of melting point with an

authentic diphenic diamide (VI).

(v) Formation of carbazole

(a) Cyclodeamination with phosphoric acid

The method of Tauber as modified by Leditschke⁽¹⁰⁾ was used. A mixture of 2 g of the diamino-biphenyl (VII) and 10 g of 88 per cent phosphoric acid was heated at 200~210°C in an oil bath for 5 hours. After 30 minutes, the carbazole formed was seen to sublime in the reaction tube. After 5 hours, the whole mixture solidified was dissolved out with acetone, the solvent was evaporated, and the residue was washed with dilute hydrochloric acid to remove unreacted material and inorganic substances. The crude carbazole (VIII), m. p. 241~243°C was sublimed and then recrystallized from benzene to m. p. and mixed m. p. 242~243°C. Yield, 1.4 g (78 per cent).

Anal. Found: N, 8.82 per cent. Calcd. for $C_{12}H_9N$: N, 8.38 per cent. Picrate: m. p. and mixed m. p. 183~181.5°C. Anal. Found: N, 14.57 per cent. Calcd. for $C_{12}H_9N \cdot C_6H_3O_7N_3$: N, 14.14 per cent.

(b) Attempted deamination-condensations in liquid SO_2 with or without sulfur trioxide, sulfuric acid, or phosphorus pentoxide

A solution of 1 g of the diamino-biphenyl (VII) dissolved in 50 cc of liquid sulfur dioxide and a solution of 1 g of each reagent dissolved in 50 cc of liquid sulfur dioxide were combined and the mixtures were allowed to stand in a pressurized bottle over night. In any of the cases, liquid sulfur dioxide as allowed to evaporate, the residue was taken up in acetone, and the residue obtained on evaporation of the solvent was washed with dil. hydrochloric acid, with which the substances totally disappeared. The diamino-biphenyl was recovered from this dilute acid solution with sodium hydroxide.

The diamino-biphenyl (VII) was dissolved in 53 cc of liquid sulfur dioxide and allowed to stand in the cold in a pressurized bottle over night or warmed on a water bath for five hours. After-treatment as above failed to indicate the formation of carbazole and diamino-biphenyl was recovered.

(c) An attempted reaction in sulfurous acid solution

In accordance with an example on the formation of naphthocarbazole,⁽¹⁴⁾ the diamino-biphenyl (VII) was suspended in water and sulfur dioxide gas was passed through this solution over a long period but no formation of carbazole was detected.

Summary

(1) Preparations of 2,2'-diamino-biphenyl and carbazole from phenanthrene were experimented.

(2) Diphenic acid, obtained by the oxidation of phenanthrene, was derived to diphenic acid diamide and 2,2'-diamino-biphenyl was obtained from it in a maximum yield of 82 per cent. The diamino-biphenyl undergoes cyclization to carbazole.

(14) W. Facho and F. Nizsel, Ber., **60** (1927), 209.