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芳香族 디히드라진에 關한 硏究(第 1 報). 테트라아조늄염을 通한 파라페닐렌디히드라진의 合成 및 디히드라존의 生成

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Studies on Aromatic Dihydrazines (I). Synthesis of *p*-Phenylenedihydrazine via Tetrazonium Salt and Formation of Dihydrazones

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요 약. 芳香族디아민을 강한 광물산의 媒質中에서 디아조化하고, 이때 얻은 테트라아조늄염을 還元함으로서 芳香族 디히드라진類의 合成에 응용할 수 있는 실용적인 方法을 創案하였다.

파라페닐렌디아민을 진한 鹽酸 또는 45 % 過鹽素酸을 媒質로 해서 低溫에서 아질산나트륨으로 디아조化하여 얻은 테트라아조늄鹽을 염화주석(II)으로 還元하여 파라페닐렌디히드라진(PPDH)을 鹽酸鹽의 微細한 針狀結晶으로 分離하였다. PPDH의 遊離鹽基는 空氣中에서 酸化되기 쉽기 때문에 不安定하여 分離할 수 없었다. PPDH·2HCl은 明確한 융점을 보이지 않고 180 °C에서 炭化되면서 分解하였다.

PPDH는 芳香族 모노히드라진과 유사한 性質이 있었으며, 초산염의 緩衝溶液에서 알데히드 및 케톤과 반응시키면 재빨리 反應하여 노랑색 내지 갈색을 띤 縮合化合物인 디히드라존이 生成되었다. 이것은 PPDH가 디카르보닐化合物과 反應하여 高分子의 폴리마나 還狀縮合物을 形成할 것임을 暗示한다.

Abstract. A practical method applicable to the synthesis of aromatic dihydrazines was proposed by reducing tetrazonium salt in strong mineral acid media. By diazotizing *p*-phenylenediamine with sodium nitrite in a medium of concentrated hydrochloric acid or 45 % perchloric acid at −5∼−10 °C and reducing the tetrazonium salt with stannous chloride, *p*-phenylenedihydrazine (PPDH) was separated in the form of hydrochloride as colorless fine needles. Since PPDH was subject to oxidation and unstable, the free base could not be isolated. PPDH·2HCl was decomposed at 180 °C without showing sharp melting point. It behaved largely as aromatic monohydrazines, and reacted immediately with aldehydes and ketones in acetate buffer, giving generally yellow to brownish condensation products, dihydrazones. This suggests that PPDH will react with dicarbonyl compounds producing high molecular polymers or cyclization products.

Introduction

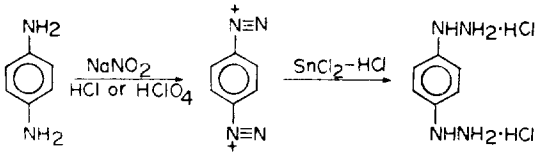
Although the properties and applications of hydrazine and the derivatives have been extensively investigated by many workers, studies on aromatic dihydrazines have rarely been done. In previous communications[1~7], some works on dihydrazines were published. However, synthesis of aromatic dihydrazines in which two hydrazino groups were attached to the same nucleus have been in a trouble situation, though the derivatives were easily prepared.

1, 4-Dihydrazinocyclohexane could not be isolated, though the derivative, 1, 4-bisphenylhydrazinocyclohexane, was obtained by Baeyer and Noyes[1]. Thiele and Barlow[2] also prepared only the derivative of 1, 4-dihydrazinobenzene, N^{β}, $N^{\beta'}$-diguanyl-*p*-phenylenedihydrazine. Stollé and Leffler[3] also failed to prepare *p*-phenylenedihydrazine but got only the derivatives, and wrote in their paper "Über Abkömmlinge des *p*-Phenylendihydrazins" that "……. Ob es möglich ist, das sicher sehr empfindliche *p*-Phenylendihydrazin zu gewinnen, muß weiteren Versuchen vorbehalten bleiben." Franzen[4] succeeded in the synthesis of 2, 3-naphthalenedihydrazine by replacing the hydroxyl groups[5] in 2, 3-dihydroxynaphthalene by hydrazino groups using hydrazine hydrate and hydrazine sulfite. Wieland, Juchum and Maier[6] also obtained *m*-phenylenedihydrazine from resorcinol by means of the Franzen's method. Nevertheless, they failed to get it through diazonium salt and wrote "…. Man bedurfte als Ausgangsmaterial der bisher nicht beschriebenen aromatische Dihydrazine, die auf dem an sich vorgeschriebenen Weg, über die Diazoverbindungen, nicht zugänglich sind."

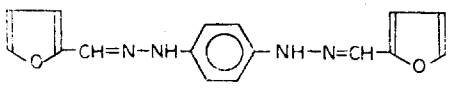
This paper is the first of a series in which the syntheses and properties of aromatic dihydrazines will be investigated. An attempt is made in this paper to prepare PPDH through the reduction of *p*-phenylene-(*bis*)-diazonium salt. In previous paper, the author *et al.*[7] described the synthesis of 1, 4-dihydrazinobenzene through tetrazonium salt in phosphoric acid media. However, since the method gave not only low yield, but also was lacking in reproducibility, it was not suitable for practical application.

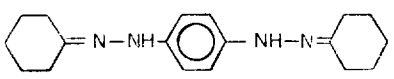
In recent paper, the author *et al.*[8] devised the new methods of tetrazotization of *p*-phenylenediamine in strong mineral acid media, which had been in a difficult situation. It is interesting to reduce the tetrazonium salt to a dihydrazine.

The author, after numerous trials, succeeded in the synthesis of PPDH *via* tetrazonium salt in the media of strong mineral acids: Tetrazotizing *p*-phenylenediamine in hydrochloric acid or perchloric acid and reducing the tetrazonium salt with stannous chloride, PPDH was separated as a colorless needle of dihydrochloride.



PPDH behaved largely as a monohydrazine but was more easily oxidized and decomposed. It reacted immediately with monocarbonyl compounds giving yellow to brown condensation products, dihydrazones. Furfural and cyclohexanone gave dihydrazones of following structures.





Cinnamaldehyde, benzaldehyde, salicylaldehyde,

acetophenone and the other monocarbonyl compounds also gave yellow to brown dihydrazones of similar structures, though some of them were too unstable to recrystallize.

Now, it is very interesting to condense PPDH with dicarbonyl compounds. It may give polyhydrazones or cyclization products. The investigations are being continued.

Experimental

A. Synthesis of *p*-Phenylenedihydrazine *via* Tetrazonium Salt.

1) In 45 % Perchloric Acid Media. In a three-necked round-bottom flask equipped with a mechanical stirrer, 5.4 gr. (0.05 mole) of finely powdered *p*-phenylenediamine was dissolved in 100 *ml* of distilled water by adding 4 *ml* of 60 % perchloric acid. To this solution, 190 *ml* of 60 % perchloric acid was slowly added, with stirring, cooling the solution below 0 °C. Then white suspension was formed. The suspension was cooled to −10 °C by immersion in an ice-salt mixture. An aqueous solution of 8 gr of sodium nitrite in 20 *ml* of distilled water was run in the suspension drop by drop from a separatory funnel, the stem of which reached to the bottom of the flask. Addition was continued for 30 minutes and temperature was maintained at −5∼−10 °C during the addition. Stirring was continued for 3 hours at the temperature. The tetrazonium salt was formed as a bright yellow suspension. To remove excess nitrite, an aqueous solution of 2 gr of urea was introduced and stirred for half an hour. The reaction mixture was cooled below −15 °C and hydrochloric acid solution of 60 gr of stannous chloride was carefully poured into the tetrazonium salt with vigorous stirring. During the addition of reducing agent, temperature was maintained below −5 °C. The reaction being somewhat exothermic, it was advisable to adjust the temperature by direct addition of crushed dry ice into the reaction mixture. Reduction was continued by stirring the reaction mixture for more than 3 hours. At the end, 200 *ml* of concentrated hydrochloric acid was added and kept overnight, then colorless crystals were separated. The crude product was filtered off by suction and washed three times with dilute hydrochloric acid and several times with ethanol and ether respectively. The crude crystals were dissolved in a small quantity of cold distilled water into which a few pieces of crushed ice were added. The aqueous solution, colored yellow, was filtered by suction and a few drops of stannous chloride solution was introduced to the filtrate with stirring, then the solution was reduced promptly to colorless separating colorless crystals. By adding 30∼40 *ml* of hydrochloric acid, the hydrochloride of PPDH was completely precipitated as colorless fine needles. The crystals were filtered off by suction and washed three times with ethanol and ether respectively. The yield was 45∼50 %. It didn't show sharp melting point but charred and decomposed at 180 °C. When it was dissolved in water, the solution quickly colored yellow and darkened slowly to brown by warming. The free base of PPDH could not be obtained as it was unstable in the air: When the aqueous solution of PPDH ·2HCl was neutralized with alkali, it changed quickly to brown. By extracting it with ether and by evaporating the solvent, dark brown residue was left. This showed the free dihydrazine was subject to oxidation. PPDH·2HCl was fairly stable but gradually changed to brownish by long exposure to the sunlight and explosively decomposed by the heat, so that it had to be kept in a brown colored bottle at a cold dark place.

2) In Concentrated Hydrochloric Acid Media. In a three-necked round-bottom flask equipped with a mechanical stirrer, 5.43 gr (0.03 mole) of pure and finely pulverized *p*-phenylenediamine dihydrochloride (or 3.24 gr of the free amine) was suspended in 300 *ml* of concentrated hydrochloric acid. The suspension was cooled to −10 °C by immersion in a freezing mixture, and an aqueous solution of 5 gr of sodium nitrite was added drop by drop from a separatory funnel, the stem of which was immersed in the solution. The addition of nitrite took 30 minutes and the temperature was adjusted to −5∼−10 °C during the addition. Stirring was continued for one and half hours. Two grams of urea was introduced and stirred for 30 minutes. The tetrazonium salt solution colored yellowish orange, in which fine particles of the salt were suspended. Into the suspension, previously cooled below −15 °C, a cold solution of 40 gr of stannous chloride in concentrated hydrochloric acid was quickly poured with vigorous stirring. The reaction was so exothermic that temperature rose above 0 °C where the tetrazonium salt might be unstable. By addition of crushed dry ice, temperature could easily be controlled below −5 °C. The stannous chloride solution should not be added slowly. If it was introduced drop by drop, the reaction mixture was suddenly decomposed evolving nitrogen violently and changed to dark brown. Stirring was continued for 3 hours or more. After being kept overnight, the crystals in the reaction mixture were filtered off and washed three times with dilute hydrochloric acid and several times with ethanol and ether successively. By repeating recrystallization as in *A*—(1), the dihydrochloride of PPDH was obtained as colorless fine needles. The yield was 35∼40 %.

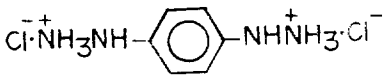
Table 1. Analysis of PPDH·2HCl[a,b]

	C(%)	H(%)	N(%)	Cl(%)
Calcd.	34.1	5.7	26.5	33.6
Found	34.3	5.8	26.3	32∼34

(*a*) Carbon, Hydrogen and nitrogen were determined at the Korean Institute of Science and Technology.

(*b*) Chlorine was determined by Neutron Activation Analysis at the Korean Atomic Energy Research Institute.

3) Identification of PPDH. From the analytical and IR spectral data in *Tables* 1 and 2, it was difficult to avoid the conclusion that the compound prepared above, *A*—(1) and *A*—(2), was the PPDH dihydrochloride of the following structure,



***B*. Condensation of PPDH with Monocarbonyl Compounds.**

1) Dihydrazone of Furfural. Half a gram of freshly recrystallized PPDH dihydrochloride was dissolved in a small amount of cold distilled water containing a few pieces of crushed ice. An aqueous solution of one gram of sodium acetate and 20 *ml* of ethanol were added successively. To this solution 2 *ml* of furfural in 20 *ml* of ethanol was introduced drop by drop, shaking vigorously. The condensation took place almost completely in a few minutes separating yellow crystalline solid. After a few

Table 2. IR absorption spectrum[c] of PPDH·2HCl

Absorption	Functional Groups
3200 cm^{-1}, 800 cm^{-1}	NH_3^+ (solid state)
3000 cm^{-1}	=CH (arom.)
1590 cm^{-1}, 1495 cm^{-1}	C=C (arom.)
1315 cm^{-1}	$C_{arom.}$—N

(*c*) The spectral data was obtained by JASCO IR-G using KBr pellet.

hours, the product was filtered off and washed with distilled water and cold dilute ethanol (1 : 1) respectively. It was soluble in ordinary organic solvents. On recrystallization from 95 % ethanol, *p*-phenylenedihydrazone of furfural was separated as greenish yellow leaflets. Melting point, 198~200°C(decomp.).

Analysis:	Calcd. (%)	Found (%)
C	65.3	66.1
H	4.76	4.87
N	19.1	18.9

2) Dihydrazone of Cinnamaldehyde. Half a gram of pure PPDH dihydrochloride was dissolved in 30 *ml* of ice water, and one gram of sodium acetate in 10 *ml* of distilled water was added into the solution. The solution was run, with stirring, in a solution of 2 *ml* cinnamaldehyde in 40 *ml* of pure ethanol. The reaction took place immediately separating brownish crystalline solids. After two hours, the crystals were filtered off by suction and washed with distilled water, cold ethanol and ether succesively. It was hardly soluble in nonpolar solvents such as benzene, ether and carbon tetrachloride, slightly soluble in methanol and ethanol and fairly soluble in hot acetone. The crude product was recrystallized from acetone: It was dissolved in a large amount of hot acetone, filtered the solution after treating with charcoal if necessary, evaporated the most of the solvent and cooled the solution, then cinnamaldehyde *p*-phenylenedihydrazone was separated as bright yellow leaflets, which was filtered off and washed with cold acetone and ether. Melting point, 246~248°C(decomp. at 250°C).

Analysis:	Calcd. (%)	Found(%)
C	78.7	77.8
H	6.00	5.88
N	15.0	14.9

3) Dihydrazone of Cyclohexanone. One gram of PPDH dihydrochloride was dissolved in 50 *ml* of cold distilled water containing a few pieces of crushed ice. To this solution 2 gr of sodium acetate in 20 *ml* of water and 30 *ml* of pure ethanol were added and shaked well, then a yellow solution was formed. A solution of 3 *ml* of cyclohexanone in 20 *ml* of ethanol was run, with stirring, in the solution prepared above. A yellow product was formed in a few minutes. After stirring 10 minutes, the reaction mixture was kept in an ice bath. After a few hours, the precipitate was filtered off and washed with distilled water and cold dilute acetone(1 : 1). It was easily soluble in ordinary organic solvents. The crude product was recrystallized from hot ethanol. *p*-phenylenedihydrazone of cyclohexanone was obtained as beautiful yellow leaflets. It began to char at 120°C, melted at 135~137°C and decomposed above 150°C. Being unstable, it was gradually darkened to brown in the sunlight and by heat, so that long heating should be avoided in recrystallization. It was necessary to keep it in a colored bottle at a dark place.

Analylis:	Calcd. (%)	Found(%)
C	72.5	73.8
H	8.72	8.30
N	18.8	18.2

4) Dihydrazone of Salicylaldehyde. An aqueous solution of 0.5 gr of PPDH dihydrochloride containing 1 gr of sodium acetate was added, with stirring, into a solution of 2 *ml* of salicylaldehyde in 50 *ml* of ethanol. The condensation took place immediately, precipitating deep yellow crystalline solids. After 30 minutes the crystals were filtered off by suction and washed with water, acetone and ether successively. It was hardly soluble in all ordinary organic solvents, including alcohol, acetone, benzene, toluene, xylene, carbon tetra-

chloride and ether. So that it was very trouble to purify. The recrystallization was carried out from ethanol: Dissolving the crude product in a large quantity of hot ethanol, filtering the solution after treating with charcoal, evaporating the most of solvent and cooling the rest solution, *p*-phenylenedihydrazone of salicylaldehyde was separated as bright yellow fine needles. Melting point, 252~254 °C.

Analysis:	Calcd. (%)	Found (%)
C	69.4	70.0
H	5.21	5.23
N	16.2	16.4

5) Dihydrazone of Benzaldehyde. Half a gram of pure PPDH dihydrochloride was dissolved in 30 *ml* of ice water, and an aqueous solution of 1 gr of sodium acetate and 30 *ml* of pure ethanol were introduced successively. The solution was run slowly, with stirring, in a solution of 2 *ml* of benzaldehyde in 30 *ml* of ethanol. The reaction occurred almost quantitatively and completed in a few miutes, separating a bright yellow crystalline solid. After 30 minutes, the crystals were filtered off by suction and washed with ethanol and acetone. It was only slightly soluble in all ordinary organic solvents. Recrystallization was a hard problem. It was carried out, with difficulty, from a large amount of hot methanol and yellow fine needles were obtained. Melting point, 272~273 °C.

Analysis:	Calcd. (%)	Found (%)
C	76.4	75.9
H	5.77	5.88
N	17.8	18.1

6) Dihydrazones of the Other Carbonyl Compounds. Acetone, acetophenone, crotonaldehyde and methyl ethyl ketone also reacted immediately with PPDH in the acetate buffer, giving yellow to brownish condensation products. But they were always unstable and gradually changed the color or decomposed to brown tar by heating in recrystallization. So that, long heating should be avoided in the recrystallization. It was generally trouble to obtain and keep them in pure state.

Results and Discussion

In spite of many attemps which have been failed to devise a method practically applicable in the synthesis of PPDH, it was possible to reduce *p*-phenylenetetrazonium salt to corresponding dihydrazine by means of Meyer and Lecco's method[9] in which stannous chloride was used as a reducing agent. However, it was not possible to reduce the tetrazonium salt by any other usual reducing agents such as sodium sulfite, sodium bisulfite, sodium hydrosulfite, metallic zinc and tin. A synthetic method of phenylhydrazine[10], in which benzenediazonium salt was reduced by heating with sodium sulfite, was not applicable because tetrazonium salt and PPDH were unstable and decomposed by heating.

The author succeeded, as shown in the experiments, in reducing *p*-phenylenetetrazonium salt with stannous chloride to PPDH, with a fairly good yield, in the media of concentrated hydrochloric and 45 % perchloric acid.

From the experiments, however, following observations were particularly noteworhty:

1) Near or above 60 % of the perchloric acid media, the tetrazonium salt being explosive and dangerous, acidity of the media had to be well-adjusted to 40~45 %. Nevertheless, in the media of perchloric acid below 50 %, the tetrazonium salt was fairly stable and it was free from danger. But, near or below 35 % of the media, tetrazonium salt was hydrolysed before reduction.

2) In concentrated hydrochloric acid media, it was advisable to reduce the tetrazonium salt

by quickly pouring the stannous chloride solution with vigorous stirring at a temperature below −5 °C. Otherwise, the reaction mixture was immediately and completely decomposed, even below −20 °C, by addition of even a few drops of stannous chloride solution, with violent evolution of nitrogen. Reaction might take place through different mechanism.

Free base of PPDH being unstable, it was isolated only in the form of hydrochloride. The dihydrochloride, however, was also subject to oxidation in an aqueous solution and gradually changed to brown on warming.

On recrystallization of PPDH·2HCl, it was necessary to introduce a few drops of stannous chloride solution into the yellow aqueous solution of the salt previously filtered, by which the solution promtply reduced to colorless, separating colorless fine needles. Recrystallization without addition of stannous chloride gave a yellow crystalline solid, which was not PPDH dihydrochloride.

The analytical data, in *Table* 1, shows exact agreement with the theoretical one of PPDH dihydrochloride. The group frequencies are shown in the IR spectrum of PPDH·2HCl, in *Fig.* 1. The presence of aromatic-type structure is recognized by the =C—H streching vibration near 3030 cm^{-1} and C=C vibration

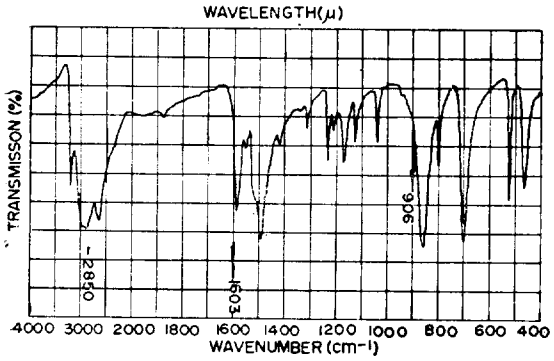


Fig. 1. IR absorption spectra of PPDH·2HCl (JASCO IR-G, KBr Pellt)

in the 1600∼1500 cm^{-1} region. The absorption in the 1350∼1250 cm^{-1} region shows $C_{arom.}$—N streching vibration[11]. The absorption in the 3350∼3150 cm^{-1} region may indicate the presence of NH_3^- group in solid state[12]. The NH_3^+ rocking frequency appeared at 800 cm^{-1}.

PPDH behaved like aromatic monohydrazines, and reacted immediately with monocarbonyl compounds, such as acetone, acetophenone, benzaldehyde, furfural, cinnamaldehyde, cyclohexanone, salicylaldehyde and so on, giving yellow to brownish dihydrazones, though some of them were unstable.

In view of the results described above, it may be suggested that the other aromatic dihydrazines will be prepared through tetrazonium salt, and that dihydrazines will condense with dicarbonyl compounds to form characteristic polyhydrazones and cyclization products. Further investigations on those points are being done.

Acknowledgement

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