

芳香族 디히드라진에 관한 연구(第2報).  
파라페닐렌디히드라진과 디카르보닐 化合物과의  
縮合反應

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Studies on the Aromatic Dihydrazines(II).  
Condensation Reaction Between  
*p*-Phenylenedihydrazine and Dicarbonyl Compounds

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**요 약.** 파라페닐렌디히드라진(PPDH)과 디카르보닐化合物을 반응시켜서 생기는 縮合生成物들의 構造를 밝혔다.

아세틸아세톤과의 반응에서는 고리화합물인 1,1'-*p*-페닐렌-*bis*-3,5-디메틸피라졸이 생겼고, 아세트산 에틸과의 반응에서는 역시 고리화합물인 1,1'-*p*-페닐렌-*bis*-3-메틸-5-피라졸론이 얻어졌으며, 디아세틸과의 반응에서는 디아세틸 *p*-페닐렌디히드라진이 생성되었다.

그 밖의 디카르보닐化合物에서 얻은 축합생성물은 불안정하여 구조결정이 어려웠다.

**ABSTRACT.** Structures of the products obtained from the condensation reaction between *p*-phenylenedihydrazine(PPDH) and dicarbonyl compounds were determined. From the reaction with PPDH, acetylacetone produced a cyclic compound, 1,1'-*p*-phenylene-*bis*-3,5-dimethylpyrazole; ethyl acetoacetate also formed a cyclic compound, 1,1'-*p*-phenylene-*bis*-3-methyl-5-pyrazolone; diacetyl yielded a simple dihydrazone, diacetyl *p*-phenylenedihydrazone. Condensation products from the other dicarbonyl compounds being generally unstable, the structure determination was quite difficult.

## 1. INTRODUCTION

Recent studies on the tetrazotization of aromatic diamines have shown that the *p*-phenyl-

enediamine could be tetrazotized in strong acid media such as hydrochloric or perchloric acid into tetrazonium salt.<sup>1</sup> Thus, the author also succeeded in the synthesis of *p*-phenylenedi-

hydrazine(PPDH) in the form of dihydrochloride<sup>2</sup> by reducing the tetrazonium salt. In that research, many dihydrazones were prepared by condensing PPDH with various monocarbonyl compounds, e.g. benzaldehyde, cyclohexanone, furfural, salicylaldehyde, cinnamaldehyde and so on.

This is interpreted to mean that the reactions between the dihydrazine and carbonyl compounds proceed in normal way as is encountered in aromatic monohydrazines.

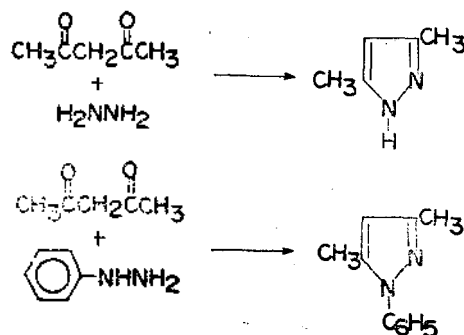
This paper is the second of a series in which the synthesis and properties of aromatic dihydrazines will be investigated. Now it is interesting to synthesize new derivatives of PPDH by condensing it with dicarbonyl compounds such as diacetyl, acetylacetone, ethyl acetoacetate, acetylacetone and glyoxal etc. It will be expected, according to the sort of the dicarbonyl compounds, to obtain not only dihydrazones, but also new heterocyclic compounds and useful polyhydrazones.<sup>3</sup>

## 2. RESULT AND DISCUSSION

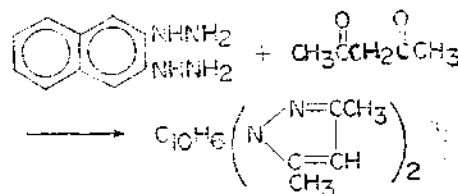
In previous paper<sup>2</sup>, the author found that the *p*-phenylenedihydrazine (PPDH) condensed with monocarbonyl compounds in a ordinary way of hydrazone formation, as being expected in phenylhydrazine, to yield dihydrazones.

However, as is described later, it was found that the dicarbonyl compounds reacted with PPDH in several ways according to the structures. The point that has been investigated is the structure determination of the products.

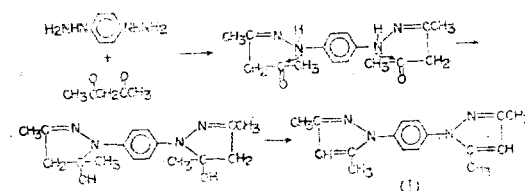
**2.1. Condensation Product from PPDH and Acetylacetone.** It is well-known fact that hydrazines react with 1,3-dicarbonyl compound to form a pyrazole ring: Hydrazine condenses with acetylacetone into 3,5-dimethylpyrazole<sup>4</sup>, and phenylhydrazine converted into 3,5-dimethyl-1-phenylpyrazole<sup>5</sup> by condensing with acetylacetone.



It was also reported by Franzen<sup>6</sup> that 2,3-naphthalenedihydrazine condensed with acetylacetone producing 2,3-naphthalene-3,5-dimethylpyrazole.



As is shown in the experimental part, PPDH reacted quickly with acetylacetone in a acetate buffer as in the case of monohydrazine mentioned above. It might guess that the reaction may be proceeded through the formation of dihydrazone, followed by cyclization into a stable *bis*-pyrazole, 1,1'-*p*-phenylene-*bis*-3,5-dimethylpyrazole (I).



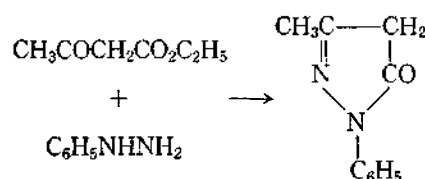
The percentage composition of C, H, N found from elementary analysis of the product showed the exact agreement with the theoretical value calculated from the structure (I).

In the *ir* spectrum, the presence of aromatic-type structure is recognized by the =C—H stretching vibration near 3030  $\text{cm}^{-1}$ (*w*) and C=C vibrations in the region of 1600~1500  $\text{cm}^{-1}$ (*s*).

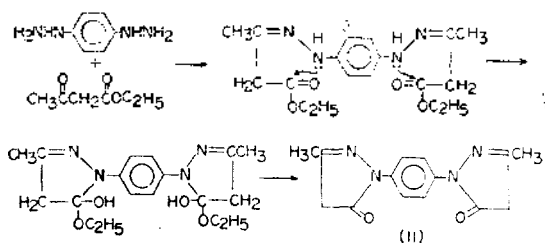
A strong absorption near  $840\text{cm}^{-1}$  may be brought from the two adjacent hydrogen atoms in the *p*-disubstituted aromatic ring. The presence of methyl group would be verified by two absorption bands at  $1450\text{cm}^{-1}(m)$  and  $1380\text{cm}^{-1}(s)$ .

From the well-known reaction between hydrazines and 1,3-diketones, group frequencies in *ir* spectrum, and the data of elementary analysis, the product may undoubtedly be justified as 1,1'-*p*-phenylene-*bis*-3,5-dimethylpyrazole shown in structure (I).

**2.2. Condensation Product From PPDH and Ethyl Acetoacetate.** It is a known reaction that 5-pyrazolones are formed by the condensation between hydrazine and  $\beta$ -keto ester, e. g. 1-phenyl-3-methyl-5-pyrazolone<sup>7</sup> from phenylhydrazine and ethyl acetoacetate.



Therefore it is expected that a *bis*-pyrazolone will be got from the reaction between dihydrazine and  $\beta$ -keto ester. It was found from the experiment that PPDH reacted easily with ethyl acetoacetate precipitating yellowish crystals. The reaction may be proceeded through the formation of dihydrazone. By donating the lone electron pair on nitrogen to the electron-deficient carbonyl carbon, the dihydrazone might be cyclized to a five-membered ring, followed by removing the  $\text{C}_2\text{H}_5\text{OH}$  molecule. Then, the product may be confirmed as 1,1'-*p*-phenylene-*bis*-3-



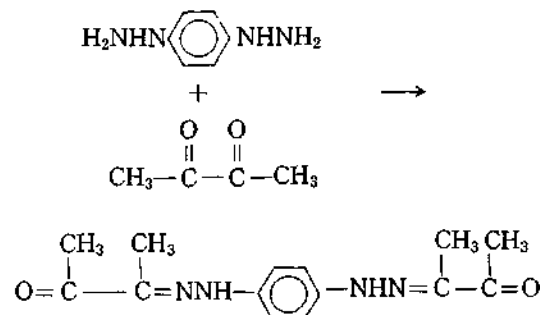
methyl-5-pyrazolone drawn in (II).

The elementary analysis of the product suggested a formula  $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2$ , the composition of the structure (II).

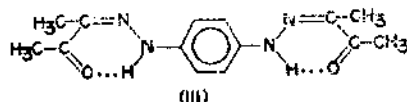
From the *ir* spectrum, the arenic structure was shown by the  $=\text{C}-\text{H}$  stretching absorption at  $3030\text{cm}^{-1}(m)$  and  $\text{C}=\text{C}$  in-plane vibrations in the  $1600\sim 1500\text{cm}^{-1}(s)$  region. The bending vibration of the two adjacent hydrogens in the *p*-disubstituted benzene ring was shown by a strong absorption at  $830\text{cm}^{-1}(s)$ . A absorption at  $1375\text{cm}^{-1}(m)$  may stem from methyl group. The carbonyl frequency was indicated by a strong absorption at  $1735\text{cm}^{-1}$ .

In the light of the elementary analysis, vibrational frequencies, and the general reaction between hydrazine and  $\beta$ -keto ester, it is very likely that the structure of the compound obtained from condensation of PPDH and ethyl acetoacetate is a *bis*-pyrazole as is shown in (II).

**2.3. Condensation Product from PPDH and Diacetyl.** As was described in the experimental part, it was found that PPDH reacted promptly with diacetyl (2,3-butandione) even in the absence of sodium acetate and produced a yellow crystalline solid. In contrast to the 1,3-diketone, diacetyl didn't form a cyclized compound when it was condensed with PPDH. From the analytical and spectral data, it is likely that the formation of hydrazone takes place only at one of the carbonyl groups leaving another carbonyl function to be free.



The reason why one of the carbonyl function was remained unreacted would be interpreted by the hydrogen bridge between C=O and N—H groups which, thus, constitute a stable six-membered ring and by the conjugation in the ring.



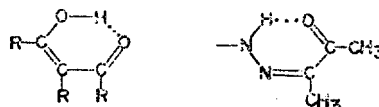
The elementary analysis resulted a good agreement of C, H, N composition with calculated value obtained from the formula  $C_{14}H_{18}N_4O_2$  (mol. wt. 274) that is derived from the structure (III).

In the mass spectrum, the molecular ion of the  $C_{14}H_{18}N_4O_2$  is suggested by a strong peak at  $m/e$  value 274. The methyl and acetyl fragments are recognized by  $m/e$  values of 15( $m$ ) and 43( $s$ ) respectively. Two peaks at the mass number of 84( $m$ ) and 190( $s$ ) are found indicating the two fragments caused by a N—N cleavage of the compound (III).

In the *ir* spectrum, hydrogen bonded N—H stretching vibration is suggested by a absorption at  $3250\text{ cm}^{-1}$ . The arenic structure is recognized by the presence of =C—H stretching vibration near  $3030\text{ cm}^{-1}$  and C=C vibrations in the  $1600\sim 1500\text{ cm}^{-1}$  region. A strong peak near  $830\text{ cm}^{-1}$  may suggest two adjacent hydrogen atoms in the *p*-disubstituted aromatic ring, and three weak bands in  $1670\sim 2000\text{ cm}^{-1}$  region suggest the overtone or combination bands of *p*-disubstituted benzenoid compound. The methyl group is recognized by C—H stretching vibrations at  $2960\text{ cm}^{-1}$ ( $w$ ) and bending frequencies at  $1440\text{ cm}^{-1}$ ( $m$ ) and  $1365\text{ cm}^{-1}$ ( $s$ ).

A strong absorption at  $1640\text{ cm}^{-1}$  indicates the C=O frequency. Such a shift has been frequently observed in  $\beta$ -diketones<sup>9</sup> which have a enolic structure followed by conjugate chelation through hydrogen bond. From the resemblance of structures between  $\beta$ -diketone and compound

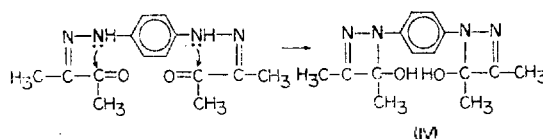
(III), considerable shift from the ordinary carbonyl frequency is very likely expectative.



In view of the analytical and spectral data, the author was difficult to avoid the conclusion that the product obtained from the reaction between PPDH and diacetyl must have the structure shown in(III).

The structure would be stabilized not only by the fully conjugated system, but also by the chelation through hydrogen bond. Thus, one of the two carbonyl function may be leaved unreacted even in the excess amount of the dihydrazine.

Also, a cyclization through the donation of the lone electron pair on the nitrogen atom to the carbonyl carbon atom would be considered. In this case, however, the reaction must proceed through an intermediate of unfavourable four-membered ring system shown in (IV). Although (III) and (IV) have same molecular weight, there were no evidence for the presence of hydroxyl group in the *ir*, *nmr* and mass spectral data. Thus the production of cyclization compound could not be expected.



### 3. EXPERIMENTAL

**3.1. Condensation of PPDH with Acetylacetone.** In a 100 ml Erlenmeyer flask, 1 gr of *p*-phenylenedihydrazine dihydrochloride was dissolved in a small amount of distilled water adding some pieces of crushed ice. Then a yellow solution was formed. To this solution were added an aqueous solution of 1 g sodium acetate

and subsequently 1 ml of acetylacetone (2,4-pentandione) in 10 ml of dilute ethanol (1:1). The mixture was shaken vigorously. After a few minutes, white crystalline solid was precipitated.

The raw product was filtered off by suction and washed twice with water, and recrystallized from dilute methanol treating with Norit. A colorless fine crystal, 1,1'-*p*-phenylene-*bis*-3,5-dimethylpyrazole, was obtained. Yield 74 %, m. p 124~125 °C.

The compound was very easily soluble in ordinary organic solvents such as methanol, ethanol, acetone and ether etc. It was also soluble in dilute hydrochloric acid and dilute sulfuric acid.

*Analysis* (at KIST\*)

	C (%)	H (%)	N (%)
Calcd.	72.2	6.77	21.1
Found	72.2	6.83	21.7

*IR spectrum* (JASCO IR-G, KBr pellet)

Group frequency (cm <sup>-1</sup> )	Group
3030( <i>w</i> )	C-H(arom.)
2960( <i>m</i> )	C-H
1550( <i>s</i> ), 1520( <i>s</i> )	C=C(arom.)
1450( <i>m</i> ), 1380( <i>s</i> )	C-CH <sub>3</sub>
~1300( <i>w</i> )	C <sub>arom.</sub> -N
840	Two adjacent arom. H

**3.2. Condensation of PPDH with Ethyl Acetoacetate.** In an Erlenmeyer flask, 1g of PPDH dihydrochloride was dissolved in a small amount of cold distilled water. To this solution, about 10g of crushed ice and 1ml of pure ethyl acetoacetate in 10ml of ethanol was added and mixed by shaking. An aqueous solution of 0.5g of sodium acetate was added drop by drop with shaking. At the beginning, white crystalline solids were formed, which gradually dissolved and then disappeared after a few minutes.

\*Korean Institute of Science and Technology

On standing the reaction mixture in an ice-bath at a dark place for an hour, an orange-yellow crystal was settled down. The material was filtered off by suction and washed several times with water and once with cold dilute ethanol. Yield 75 %.

The product was easily soluble in ordinary organic solvents, *e.g.* methanol, ethanol, acetone, ether etc., and was also soluble in dilute hydrochloric acid.

The crude product was recrystallized from dilute ethanol: The crystals were dissolved and saturated in warm (not hot) ethanol (3:1), treated with Norit, filtered, and the filtrate was cooled in an ice-bath, shutting out the sunlight.

The yellow-orange crystals formed were filtered off and washed once with cold ethanol. The pale yellow (slightly orange) crystal was dried in a vacuum desiccator at a dark place. m. p 133~134 °C.

The compound, being unstable, was gradually darkened to orange, brown, and finally dark red-brown even at a dark place. So that, it has to be analyzed as soon as possible.

This substance could be diagnosed as *p*-phenylene-1,1'-*bis*-3-methyl-5-pyrazolone, the structure (II).

*Analysis* (at KIST)

	C (%)	H (%)	N (%)
Calcd.	62.2	5.19	21.0
Found	62.0	5.08	20.7

*IR spectrum* (JASCO IR-G, KBr pellet)

Group frequency (cm <sup>-1</sup> )	Group
~3030( <i>w</i> )	C-H(arom.)
1735( <i>s</i> )	C=O
1620( <i>s</i> ), 1530( <i>s</i> )	C=C(arom.)
1375( <i>m</i> )	C-CH <sub>3</sub>
830	Two adjacent arom. H

**3.3. Condensation of PPDH with Diacetyl.** 1g of PPDH dihydrochloride was dissolved

in a small amount of cold water in which some pieces of crushed ice were added. To this solution, colored yellow, about 1 ml of diacetyl (2,3-butandione) in 10 ml of ethanol was poured, and shaken for minutes. Then, promptly a yellowish brown suspension was formed. The reaction was completed by adding 2~3 ml of sodium acetate slution and heating it in a water bath for 10 minutes,

The crude product was filtered off on a filter paper using a usual funnel: The product was so fine that the particles passed through filter, and so it could not be collected by suction. It was washed with hot water, cold ethanol and ether successively. The yielded 85 %.

The product was hardly soluble in most organic solvents, inorganic acids and bases. Thus the purification was a troubled problem.

It could just be recrystallized by dissolving it in a large amount of hot methanol, filtering the solution after treated with Norit, and evaporating the most part of the solvent. A deep yellow crystal was obtained. It didn't melt even by raising the temperature above 300 °C, but began to char from near 250 °C. When is attached to a flame, it sublimed or decomposed yielding a yellow varpor.

There are ample evidence to show that the product is a simple dihydrazone, diacetyl *p*-phenylenedihydrazone, as is shown in the structure (III), in spite of the carbonyl functions that are remained partly in the compound.

Analysis (at Beilstein Inst., Frankfurt/Ger.)

	C(%)	H(%)	N(%)
Calcd.	61.3	6.57	20.4
Found	61.2	6.59	19.8

Mass spectrum (RMU-7M)

<i>m/e</i>	Fragment
274( <i>s</i> )	Molecular ion
15( <i>m</i> )	CH <sub>3</sub>
43( <i>s</i> )	CH <sub>3</sub> CO

84(*m*), 190(*s*) Two fragments from a N-N cleavage

IR spectrum (JASCO IR-G, KBr pellet)

Group frequency(cm <sup>-1</sup> )	Group
3250( <i>s</i> )	N-H(bonded)
3030( <i>m</i> )	C-H (arom.)
2960( <i>w</i> )	C-H
1640( <i>s</i> )	C=O(Conjugate chelation)
1565( <i>s</i> ), 1515( <i>s</i> )	C=C (arom.)
1440( <i>m</i> ), 1365( <i>s</i> )	C-CH <sub>3</sub>
1300	C <sub>arom</sub> -N
1900~1650 (3 weak bands)	<i>p</i> -disubst. arom. H

NMR spectrum

3.1 ppm, 3.6 ppm (1 : 1)	Two CH <sub>3</sub> groups
7.4 ppm	phenyl protons

**3.4. Condensation of PPDH with Acetylacetone.** To an aqueous solution of 1 g PPDH dihydrochloride, some pieces of ice and a ethanol solution of 1 ml acetylacetone (2,5-hexandione) was added. By shaking the reaction mixture, immediately appeared a pale yellow crystalline solid. After 30 minutes, being kept in an ice-bath, the crystal was filtered off and washed with cold water. During the drying, it, being unstable, gradually darkened and finally to a dark brown mass even in a dark place.

When the pale yellow crystals were dissolved in an organic solvent, *e.g.* ethanol, acetone or ether, it converted on warming into a tacky material, which gradually hardened to a brittle mass. It was too unstable to purify by recrystallization. As a corollary, the structure of the compound could not be determined.

**3.5. Polyhydrazones.** The other dicarbonyl compounds such as diformyl, *p*-benzoquinone, and terephthalaldehyde also condensed with PPDH forming brown to black products, which were quite insoluble in all ordinary solvents.

In view of the structures of the dicarbonyl compounds, the condensation products might be expected as polyhydrazones. Purification being

troublesome, they are not yet completely examined. The investigation on polyhydrazones is a interesting problem and is now being done.

#### ACKNOWLEDGEMENT

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