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芳香族 디히드라진에 關한 硏究 (第4報). 테트라아조늄염을 통한 메타페닐렌디히드라진의 새 合成法

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Studies on Aromatic Dihydrazines (IV). A New Synthesis of *m*-Phenylenedihydrazine *via* Tetrazonium Salt

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요 약. Tetrazonium 염을 거쳐서 *m*-phenylenedihydrazine (MPDH)을 합성할 수 있었다. 즉, *m*-phenylenediamine을 진한 염산의 매질 속에서 −10~−5°C로 유지하고 아질산나트륨으로 테트라아조화한 다음, 이때 생긴 tetrazonium 염을 염화주석(II)으로 환원시켜 MPDH를 염산염의 꼴로 얻어 알코올에서 재결정 할 수 있었다. MPDH의 유리염기는 불안정하기 때문에 공기 중에서는 안정한 상태로 얻기 어려우며, 그 염산염은 명확한 녹는 점을 가지지 않고 185 °C에서 분해하였다.

MPDH도 방향족 monohydrazine의 경우 처럼 mono 또는 dicarbonyl 화합물과 쉽게 축합반응을 일으켜서 dihydrazone 또는 고리모양 화합물을 생성하였다. MPDH와 carbonyl 화합물과의 반응에서 얻은 여러가지 화합물의 구조를 결정하였다.

ABSTRACT. *m*-Phenylenedihydrazine(MPDH) was prepared via tetrazonium salt: *m*-Phenylenediamine was tetrazotized with sodium nitrite at −10~−5°C in concentrated hydrochloric acid medium, resueted tetrazonium salt was reduced with stannous chloride and MPDH was separated as dihydrochloride which was recrystallized from alcohol. The free base of MPDH being unstable it could hardly be obtained in the air. MPDH · 2HCl did not show sharp melting point but decomposed at 185 °C.

MPDH, like aromatic monohydrazines, condensed with mono- and dicarbonyl compounds giving dihydrazones or cyclic compounds. The structures of condensation products obtained from the reaction of MPDH with carbonyl compounds are determined.

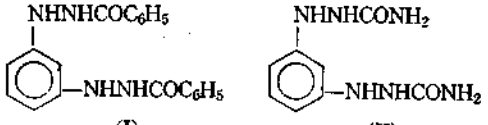
1. INTRODUCTION

In previous paper[1] it was reported that *p*-phenylenedihydrazine(PPDH) could be prepared in the form of dihydrochloride, by tetrazotizing *p*-phenylenediamine with sodium nitrite and reducing the resulting tetrazonium salt with stannous chloride. It was also found that PPDH condenses with mono- and dicarbonyl compounds giving various derivatives.[1,2]

In this paper the author is reporting a new synthetic method of *m*-phenylenedihydrazine (MPDH) via tetrazonium salt, using the similar procedure for PPDH.

Syntheses of the derivatives of MPDH have been investigated by many workers. Franzen and Eichler[3] prepared N, N-dibenzylidene-*m*-phenylenedihydrazine and N, N-*bis*(α-carboxyethylidene)-*m*-phenylenedihydrazine by heating resorcinol at 120 °C with hydrazine sulfite and 50% hydrazine hydrate and treating the resulting product with benzaldehyde and pyruvic acid respectively. 4, 6-Dinitro-1, 3-dihydrazinobenzene[4] was prepared by heating resorcinol at 120°C with hydrazine sulfite and 50% hydrazine hydrate and treating the resulting product with benzaldehyde and pyruvic acid respectively. 4, 6-Dinitro-1, 3-dihydrazinobenzene[4] was prepared by treating 4, 6-dichloro-1, 3-dinitrobenzene or 5-chloro-2, 4-dinitrophenylhydrazine with excess hydrazine.

m-Phenylenedihydrazine was first synthesized by Wieland and his coworkers[5]. They heated resorcinol at 115~120°C with hydrazine hydrate and hydrazine pyrosulfite under nitrogen atmosphere for 8 hours and obtained MPDH as free base after cooling the reaction mixture. They also prepared several derivaties of MPDH, *i. e.*, N, N-dibenzylidene-*m*-phenylenedihydrazine, N, N′-dibenzoyl-*m*-phenylenedihydrazine (I) and *m*-phenylene-4, 4′-disemicarbazide (II).



(I) (II)

Though they could prepare MPDH by replacing two hydroxy groups of resorcinol with hydrazino groups, they failed to obtain it through diazonium salt, and wrote "Man bedürfte als Ausgangsmaterial der bisher nicht beschriebenden aromatischen Dihydrazines, die auf dem an sich vorgeschriebenden Weg, über die Diazoverbindung, nicht zugänglich sind."

This paper is the fourth of a series in which the syntheses and the properties of aromatic dihydrazines will be investigated. In this paper an attempt is made to prepare *m*-phenylenedihydrazine (MPDH) through the reduction of *m*-phenylene-(bis)-diazonium salt.

2. EXPERIMENTAL

2.1 Synthesis of *m*-Phenylenedihydrazine via Tetrazonium Salt. In a three-necked round-bottom flask equipped with a mechanical stirrer, a thermometer and a separatory funnel 5.43 g(0.03 mole) of fine crystals of *m*-phenylenediamine dihydrochloride was suspended in 300 m*l* of concentrated hydrochloric acid. The suspension was cooled to −10 °C by immersing in ice-salt freezing mixture, and an aqueous solution of 5.0 g (0.07 mole) of sodium nitrite in 15 m*l* of distilled water was added drop by drop through the separatory funnel, the stem of which was immersed into the suspension while the mixture was stirred well. The reaction temperature was adjusted to −10~−50°C. The addition of sodium nitrite took 20 minutes. The reaction mixture colored yellow, yielding the *m*-phenylenetetrazonium salt*. Stirring was continued for two hours and 2 g of urea was added in order to remove excess nitrous acid.

The reaction mixture was stirred for half an hour. To this tetrazonium salt solution was added quickly with vigorous stirring a solution of 40 g of stannous chloride in 50 m*l* of concentrated hydrochloric acid, previously cooled to −10 °C. The mixture colored purple and changed soon to pale violet as the reduction was going on. *m*-Phenylenedihydrazine dihydrochloride was separated as pale violet solid.

The mixture was stirred for an hour and the crude product was filtered off by suction and washed with 6 *N* hydrochloric acid, ethanol and ether succesively. Recrystallization of MPDH·2HCl could not be carried out from aqueous solution by the same method[1] as PPDH · 2HCl owing to the greater solubility of MPDH · 2HCl in water. It was possible to recrystallize MPDH from alcohol. The crude product was dissolved in hot ethanol or methanol and a few drops of stannous chloride solution and a few m*l* of concentrated hydrochloric acid were added to the alcoholic solution. By cooling the solution MPDH · 2HCl was separated as colorless crystals. The yield was 25 ~ 30 %. MPDH · 2 HCl did not show sharp melting point but decomposed at 185 °C.

2.2 Identification of *m*-Phenylenedihydrazine Dihydrochloride

From the elemental analysis, IR spectrum (***Fig.*** 1) and NMR spectrum (***Fig.*** 2), it could be concluded that the compound prepared above is *m*-phenylenedihydrazine dihydrochloride of the structure III. Structure determination is discussed in Sec. 3. IR (KBr): 2,955, 2,650 ($-\overset{+}{N}H_3$), 3,340, 3,200 (N-H), 1,600, 1,570, 1,480 (arom. C=C), and 760, 700 cm^{-1} (*m*-disubstd. aryl hydrogens, bending). NMR (D_2O): 6.7~7.1 (4H, Ar-H), 7.4~7.7 (2H, N-H) and 4.8 ppm (H_2O impurity, averaged with NH_3 by exchange).

*Anal.*** Calcd. for $C_6H_{12}N_4Cl_2$ (211): C, 34.1; H, 5.70; N, 26.5%. Found: C, 33.1; H, 5.65; N, 26.5%.

2.3 Condensation of MPDH with Monocarbonyl Compounds

2.3.1 Condensation with Benzaldehyde. In a 250 m*l* Erlenmyer flask 1 g of MPDH·2 HCl was dissolved in 20 m*l* of cold distilled water and 1 g of sodium acetate and 50 m*l* of ethanol were added successively. The solution was added dropwise to 2 m*l* of benzaldehyde in 30 m*l* of ethanol while the flask was shaken well. Immediately pale yellow solids were formed. After a few hours the crude product was filtered off by suction and washed with water and ethanol. It was slightly soluble in ordinary organic solvents such as benzene, xylene, ether, ethanol and acetone. Upon recrystallization from a large amount of xylene N,N′-dibenzylidene-*m*-phenylenedihydrazine[5] was obtained as gray-yellow fine needles. Yield 65 %; m. p. 251~253 °C (decomp.). IR (KBr): 3,250 (N-H), 3,030 (arom. C-H), 1,600, 1,580, 1,470(arom. C=C), 1,255, 1,280(arom. C-N), and 750, 680cm^{-1} (*m*-disubstd. aryl hydrogens).

Anal. Calcd. for $C_{20}H_{18}N_4$: C, 76.4; H, 5.80; N, 17.8%. Found: C, 76.0; H, 5.90; N, 16.6 %.

2.3.2 Condensation with Salicylaldehyde. One gram of MPDH · 2HCl was dissolved in 20 m*l* of cold water and one gram of sodium

*The tetrazotization of *m*-phenylenediamine could also be done very effectively in 50% perchloric acid medium. It was found, however, that the *m*-phenylenetetrazonium salt was very sensitive to shock. During the tetrazotization it blew up with a terrific explosion even at low temperature below −5°C. The author have been seriously wounded and we have to take precaution against a laboratory accident.

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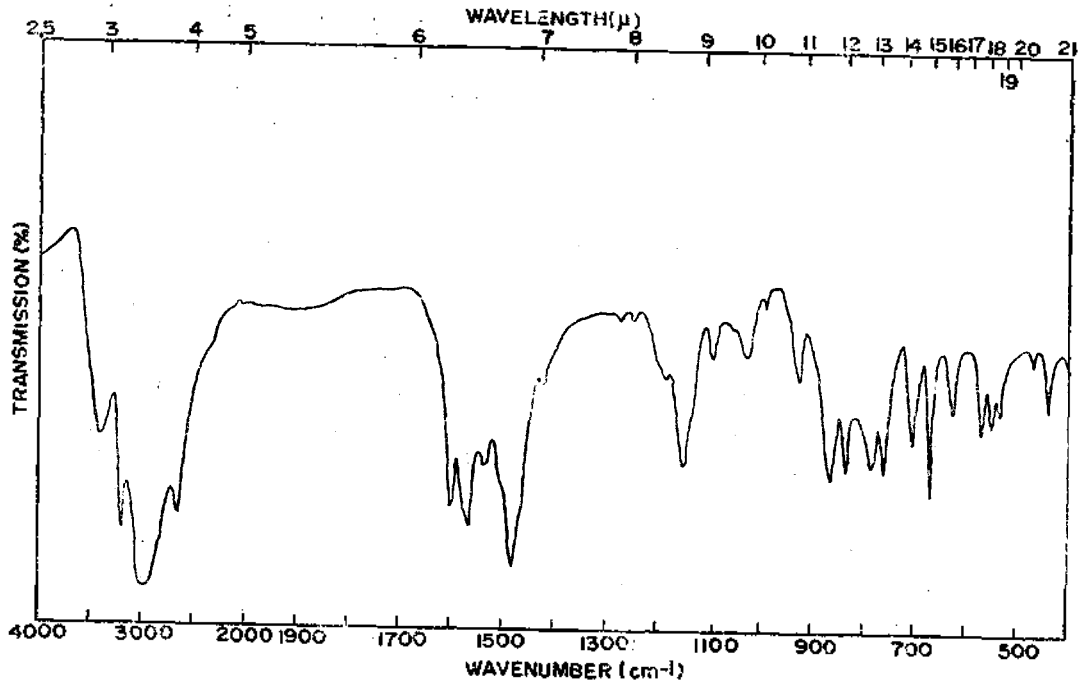


Fig. 1. IR Spectrum of MPDH · 2HCl (KBr pellet).

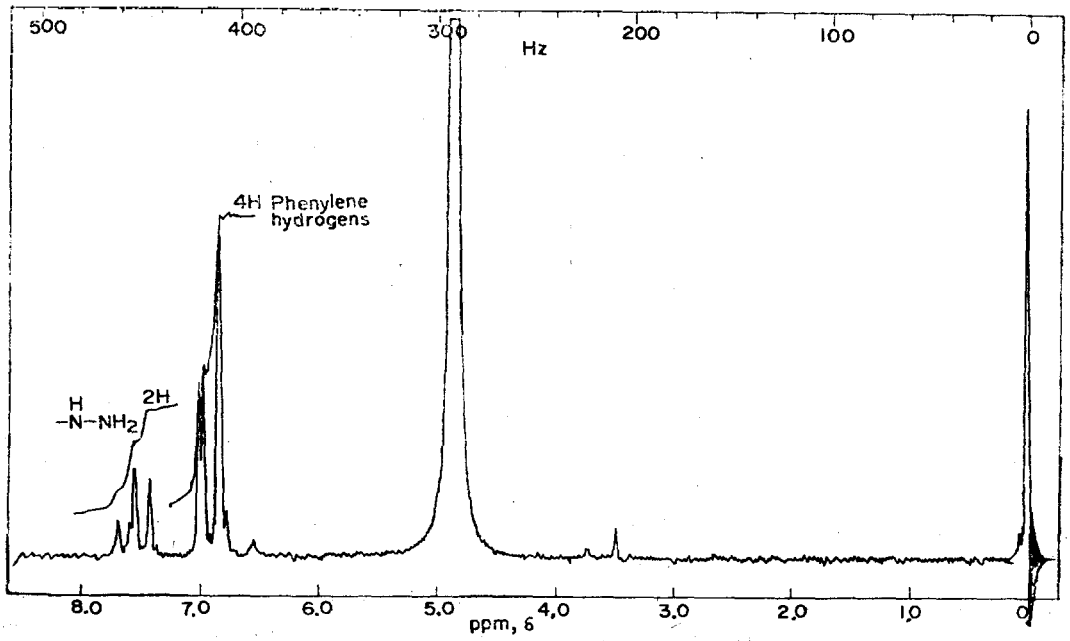


Fig. 2. NMR Spectrum of MPDH · 2HCl (Solv. D_2O).

acetate and 30 m*l* of ethanol were added. To this solution 1 m*l* of salicylaldehyde in 20 m*l* of ethanol was added drop by drop. After a few minutes yellow crystalline solids were formed. The crude product was filtered by suction and washed with water and diluted ethanol. It was soluble in ordinary organic solvents. Upon recrystallization from aqueous ethanol N,N′-di-(*o*-hydroxybenzylidene)-*m*-phenylenedihydrazine of the structure(V) was obtained as pale yellow leaflets. Yield 55 %; m.p 212 °C (decomp.). IR (KBr): 3,300 (N-H), 1,600, 1,580 (arom. C=C), 1,280, 1,260 (arom. C-N), 750 and 680cm^{-1} (m-disubstd. aryl hydrogens). NMR: 8.0 (2H, NH), 7.4 (2H, OH), 6.8 (12H, Ar-H), and 6.3 ppm (2H, N=CH-).

Anal. Calcd. for $C_{20}H_{20}N_4O_2$: C, 69.4; H, 5.21; N, 16.2 %. Found: C, 69.0; H, 5.15; N, 16.2 %.

2.4 Condensation of MPDH with Dicarbonyl Compounds

2.4.1 Condensation with Pyruvic Acid. One gram of MPDH · 2HCl in 20 m*l* of water was added dropwise to an aqueous solution of 1 g of sodium acetate and 1 m*l* of pyruvic acid in 50m*l* of cold water. By shaking a pale yellow crystalline solid was formed. The crude product was filtered off by suction and washed with water. It was only slightly soluble in ethanol, ether, acetone, methyl acetate and acetic acid. Recrystallization was performed by dissolving the crude product in diluted aqueous ammonia, filtering and neutralizing the filtrate with diluted (1 *M*) sulfuric acid. N,N′-*bis*-(α-Carboxyethylidene)-*m*-phenylenedihydrazine[3] was obtained as pale yellow fine needles: m.p. 190 °C(decomp.). IR (KBr): 3,300(N-H), 1,720 (C=O), 1,600, 1,570 (arom. C=C), 1,470, 1,360 (CH_3), 1,350, 1,290 (arom. C-N), and 770, 680 cm^{-1} (*m*-disubstd. aryl hydrogens).

Anal. Calcd. for $C_{12}H_{14}N_4$: C, 51.8; H, 5.04; N, 20.1 %. Found: C, 51.8; H, 5.14; N, 19.9%.

2.4.2 Condensation with Ethyl Pyruvate. One gram of MPDH · 2HCl dissolved in 20 m*l* of cold water was added dropwise to an aqueous solution of 1 g of sodium acetate and 1 m*l* of ethyl pyruvate in 50 m*l* of cold water. By shaking the mixture reaction was completed in a few minutes and a yellow crystalline solid was precipitated. The crude product was filtered and washed with water. It was soluble in ordinary organic solvents. Upon recrystallization from benzene yellow leaflets of N,N′-*bis*(α-carboethoxyethylidene)-*m*-phenylenedihydrazine of the structure (VI) were obtained. Yield 65 %; m.p. 123 °C (decomp.). IR (KBr): 3,250(N-H), 1,470, 1,380 (CH_3), 1,675 (C=O), 1,600, 1,510, 1,450 (arom. C=C), 1,310, 1,280(C-N), and 1,180, 1,140 cm^{-1} (C-O). NMR: 7.9 (*s*, 2H, -NH-N-), 7.0 (*m*, 4H, Ar-H), 4.3 (*q*, 4H, CH_2), 2.1 (*s*, 6H, CH_3 in -N=C-CH_3), and 1.3 ppm (*t*, 6H, CH_3 in C_2H_5).

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 57.5; H, 6.59; N, 16.8%. Found: C, 57.4; H, 6.72; N, 16.7%.

2.4.3 Condensation with Acetylacetone. One gram of MPDH · 2HCl was dissolved in 20 m*l* of cold water and 1 g of sodium acetate was added. To this solution 1 m*l* of acetylacetone in 50 m*l* of cold water was added drop by drop. After a few minutes white crystalline solids were formed. The crude product was filtered off by suction and washed with water. It was very soluble in organic solvents. Upon recrystallization from aqueous methanol 1,1′-*m*-phenylene-*bis*-3,5-dimethylpyrazole[5] (VII) was obtained as colorless, fine needles. Yield 80 %; m.p. 105 °C. IR (KBr): 3,030(arom. C-H), 1,460, 1,370 (CH_3), 1,600, 1,580(arom. C=C), 1,350, 1,280 (arom. C-N), and 780,

680 cm^{-1} (*m*-disubstd. aryl hydrogens, bending). NMR: 7.5 (*m*, 4H, Ar-H), 6.0 (*s*, 2H, protons in pyrazole ring), 2.33 (*s*, 6H, CH_3), and 2.28 (*s*, 6H, CH_3).

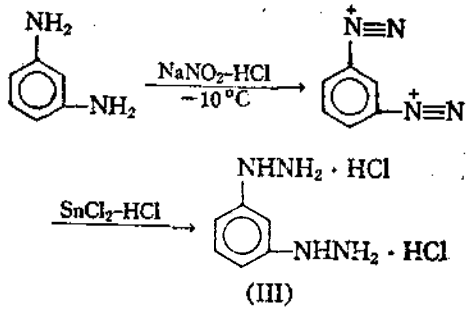
Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.2; H, 6.77; N, 21.1%. Found: C, 72.5; H, 6.59; N, 21.6%.

2.4.4 Condensation with Diacetyl. One gram of MPDH · 2 HCl was dissolved in 20 m*l* of cold water and 1 g of sodium acetate was added. To this solution 1 m*l* of diacetyl in 50 m*l* of water was added and the mixture was shaken well. Yellow crystalline solids were immediately formed. The crdude product was filtered by suction and washed with water. It was soluble in ethanol, methanol and acetone, but slightly soluble in ether, chloroform, benzene and *n*-hexane. Upon recrystallization from diluted methanol N,N′-*bis*(*α*-acetylethylidene)-*m*-phenylenedihydrazine, a dihydrazone of the structure (VIII), was obtained as a yellow, fine crystal. Yield 60 %; m.p. 294 °C(decomp.). IR (KBr): 3,230 (N-H), 1,640(C=O, shifted), 1,600, 1,550 (arom. C=C), 1,360, 1,450 (CH_3), 1,320, 1,260 (arom. C-N), and 760, 680 cm^{-1} (*m*-disubstd. aryl hydrogens, bending). Mass spectrum, *m/e*; 274 (M^+), 43 (acetyl), and 84, 190 (fragments from a N-N bond cleavage).

Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C, 61.3; H, 6.57; N, 20.4 %. Found: C, 61.4; H, 6.37; N, 20.6%.

3. RESULT AND DISCUSSION

Although Wieland and his coworkers[5] have failed in synthesizing *m*-phenylenedihydrazine (MPDH) via tetrazonium salt, the author found that *m*-phenylenetetrazonium salt could also be reduced into MPDH. Tetrazotizing *m*-phenylenediamine with sodium nitrite at around −10 °C in strong acid media and reducing the tetrazonium salt with stannous chloride, MPDH was obtained as dihydrochloride.



(III)

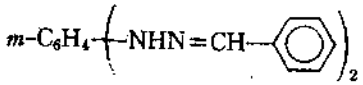
The free base of MPDH could not be obtained. By neutralizing the aqueous solution of MPDH dihydrochloride with alkali and by extracting the alkaline sclution with ether no trace of the dihydrazine could be found. The impossibility might be due to the facts that the free base of MPDH is easily oxidized in the aqueous solution[5] and that aromatic hydrazines are generally oxidized to aromatic hydrocarbons and nitrogen in the presence of sodium hydroxide and oxygen[6]. The MPDH dihydrochloride was gradually oxidized in the air or in an aqueous solution and finally colored deep purple.

The data of elemental analysis are in good agreements with the calculated ones as shown in Section 2.2. The IR Spectrum of MPDH dihydrochloride is shown in *Fig.* 1. The strong bands at 2,955 and 2,650 cm^{-1} indicate the presence of $-NH_3^+$, the hydrochloride of the dihydrazine. The N-H stretching vibration of imino group is assigned at 3,200 and 3,430 cm^{-1}. The aromatic structure is recognized by C=C vibration at 1,570 and 1,600 cm^{-1}. The C-H bending in *m*-disubstituted aromatic ring is shown by the absorption at 700 and 760 cm^{-1}. The NMR spectrum (solvent, D_2O) is shown in *Fig.* 2. The multiplet around 7 ppm indicates the phenylene protons. The imino protons are recognized by the signal around 7.5

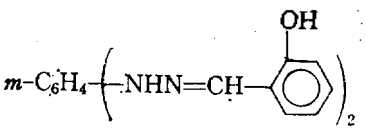
ppm. The $\overset{+}{N}H_3$ protons could be exchanged chemically with H_2O present as impurity in D_2O solvent, the spin orientations are considered to be averaged, and a sharp singlet peak is resulted at around 4.8 ppm.

The structure of MPDH could also be confirmed by the structures of derivatives obtained from the condensation of MPDH with carbonyl compounds, which were just what we expected.

MPDH, like aromatic monohydrazines, condensed in acetate buffer with monocarbonyl compounds such as benzaldehyde and salicylaldehyde to give yellow products. These products were identified as dihydrazones (IV, V) of corresponding carbonyl compounds by elemental analyses and spectroscopic methods.



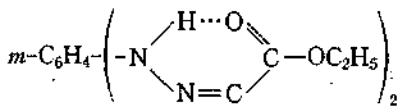
(IV)



(V)

Acetone, furfural, cyclohexanone and acetophenone also reacted with MPDH, but the products were unstable and gradually changed their color into dark brown ones during the recrystallization. So that it was difficult to obtain them in pure forms.

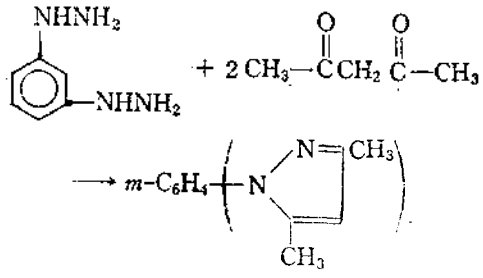
Dicarbonyl compounds also condensed with MPDH. Dihydrazone of ethyl pyruvate must have a chelate ring structure by intramolecular hydrogen bond. In the IR spectrum the stretching vibration of C=O bond is shown at 1,675 cm^{-1}. The shift of C=O frequency must be due to the possibility of intramolecular hydrogen bond between hydrogen of N-H and oxygen of C=O as shown in structure VI. The frequeucy of C=N vitration is considered to be concealed by conjugation with carbonyl function[7].



(VI)

As Wieland and his coworkers reported previously, MPDH condensed with acetylacetone to give 1, 1'-*m*-phenylene-*bis*-3, 5-dimethylpyrazole (VII). In IR spectrum the methyl groups are recognized by the absorption at 1,460 and 1,370 cm^{-1}. The aromatic C=C stretching is assigned at 1,600 and 1,580 cm^{-1}. The absorptions at 680 and 780 cm^{-1} indicate the *m*-disubstituted benzene ring. In NMR spectrum two signals at 2.3 ppm show the presence of two kinds of methyl groups. The other protons in pyrazole rings are shown by a singlet signal at 6.0 ppm. Phenylenic protons are recognized by multiplet signal around 7.5 ppm.

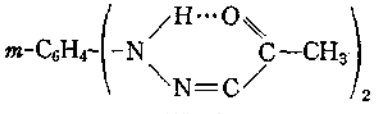
The formation of *bis*-pyrazole would proceed through dihydrazone, followed by cyclization to form stable pyrazole ring (VII).



(VII)

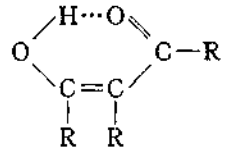
The reaction product of MPDH with diacetyl must be a simple dihydrazone, VIII, in the light of elemental analysis, IR and Mass spectral data. The condensation took place at only one carbonyl group of diacetyl, the other carbonyl group remaining free, even if MPDH existed in excess during the reaction. The reason why one of the two carbonyl groups re-

mained unreacted could be interpreted by the hydrogen bond between oxygen in C=O and nitrogen in N-H, which constitutes a stable six-membered ring shown in structure VIII.



(VIII)

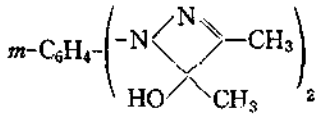
The presence of this kind of hydrogen bond is ascertained by the strong absorption at 1,640 cm^{-1} in IR spectrum. Such a shift of carbonyl frequency to lower value has been frequently encountered in β-diketones which has enolic structure followed by chelation to form a stable six-membered ring (IX).



an enolic form of β-diketone

(IX)

A less stable four-membered ring of the structure (X) might also be considered to be formed. However, it could be neglected by data of elemental analysis and mass spectrum. In mass spectrum the molecular ion peak of $C_{14}H_{18}N_4O_2$ (M. W 274.3) is shown by a strong peak at m/e value 274. Acetyl group is recognized by a peak of *m/e* 43. Therefore, a cyclic compound X could not be expected. This is also ascertained by the absence of O-H absorption in IR spectrum.



(X)

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