were prepared by using the improved Wohl-Aue method.

These four dihydroxyphenzines, i.e. 1,2-, 1,3-, 1,4-, and 2,3-dihydroxyphenazines were oxidized with hydrogen peroxide in the presence of acetic anhydride in benzene, and 1,3-, 1,4-, and 2,3-dihydroxyphenazine di-N-oxides were obtained, respectively. In the case of the 1,2-isomer, its di-N-oxide was not obtained.

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16. **Shun'ichi Yamada, Ichiro Chibata, and Ryoya Tsurui:** Application of Ion Exchangers in Organic Reactions. III[1]. Application to the Rearrangement of Hydrazobenzene Derivatives*.

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In the previous paper[2] on the application of ion exchangers in organic reactions, it was shown that the cation exchangers afford an effective and convenient condensing agent for the Fischer indole synthesis. This result induced the authors to carry out the present experiments of the application of cation exchangers for the rearrangement reaction of hydrazobenzene derivatives, as the Fischer indole synthesis is considered to proceed through the *o*-benzidine type rearrangement.

The rearrangement reaction of the hydrazobenzene derivatives has been investigated in greater detail than any of the others because of its exceptional theoretical interest. Since the publication of the famous general review by Jacobson[3] many reports on the matter have been made.

As catalytic agents for this rearrangement, mineral acids such as sulfuric acid and hydrochloric acid have been employed, especially the latter with stannous chloride have been used as effective agents for the reaction. However, the yields of the reaction are low except in the case of the rearrangement of hydrazobenzene to benzidine. Futhermore, because of the mixed presence of the rearranged product with unreacted material, azo compound and split amine produced during the reaction, the troublesome procedures of separating and purifying the desired products cannot be avoided. It was hoped to simplify the procedure of separation by employing the cation exchangers instead of mineral acids as catalytic agents. Four different type rearrangements of hydrazobenzene derivatives were carried out. When the hydrazobenzenes were heated with the previously activated hydrogen form[2] of the cation exchangers of nuclear sulfonic acid-type resin, such as Amberlite IR-120 and Dowex-50, in water or aqueous alcohol, the unreacted material and azo compound produced during the reaction were recovered from the filtrate of the reaction mixture by concentration and/or by the extraction of the insoluble substances as they were not adsorbed on the resins. The rearranged product was obtained by the elution of the resins with alkaline solution. By this

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[1] S. Yamada, I. Chibata, R. Tsurui: J. Pharm. Soc. Japan, **73**, 123 (1952).

[2] S. Yamada, I. Chibata, R. Tsurui: This Bulletin, **1**, 14 (1953).

[3] Jacobson: Ann., **428**, 76 (1922).

method, benzidine, diphenyline, and *o*-semidine rearrangements were successful, but the *p*-semidine rearrangement, conversion of 4-acetaminohydrazobenzene to 4-acetamino-4′-aminodiphenylamine (V) failed. The hydrazobenzenes employed and the rearranged products are listed.

Judging from the results obtained and the rule given by Dewar4) that the ease of reaction falls in the series benzidine, diphenyline, semidine, the catalytic activity of the cation exchangers is somewhat inferior to that of the mineral acids in this reaction and cannot accomplish the *p*-semidine rearrangement. This inferior activity of resins is considered to be due to the lack of acidity of the resins or the discrepancy between the molecules of the reactants and the physical structure of the resins.

Further, the rearrangement of diazoaminobenzene by using ion exchangers was investigated. Unlike the above-mentioned reaction this rearrangement has been considered to be an intermolecular reaction. Aniline hydrochloride has been the usual catalyst. Unger5) reported lower yields when acetic acid and formic acid were used. By employing strong acid cation exchanger (Amberlite IR-120) or hydrochloride of weak base anion exchanger (Amberlite IR-4B), diazoaminobenzene was converted to aminoazobenzene, the yield, however, was lower than when aniline hydrochloride was used.

The results obtained by employing the ion exchangers for the rearrangement reactions were not always satisfactory, e. g. the inferior activity and the difficulty of elution of rearranged product from resins. The authors hope, however, that this study will contribute to the exploration of a new field in the use of ion exchangers.

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Experimental

Benzidine Rearrangement: Benzidine (I)—A mixture of hydrazobenzene (2 g.), Amberlite IR-120 (8 g.), and water (30 cc.) was stirred at 90° for 2 hours whereupon the crystals of hydrazobenzene disappeared. The resins were collected by filtration and eluted with aqueous sodium hydroxide. The separated solid and resins were filtered and washed with water to remove excess sodium hydroxide, and then extracted with hot alcohol. On cooling the extract after adding some water, crystals separated, 1.2 g., m.p. 128~130°. By successive elution of the resins a second crop was obtained, 0.4 g.; total yield, 80%. A mixed melting point determination with authentic sample showed no depression. β-Naphthol salt: Colorless scales, m.p. 177°.

Diphenyline Rearrangement: 5-Chlorodiphenyline (II)—To a stirred-solution of 4-chlorohydrazobenzene (8.7 g.) in alcohol (120 cc.) and water (80 cc.) was added. Dowex-50 (40 cc.), and heated under reflux for 4 hours. The resins were filtered hot, and by cooling the filtrate a small amount of the azo compound produced during the reaction was separated. The resins were eluted with aqueous sodium hydroxide, the eluted material being extracted with hot alcohol. After removing alcohol, the remainder, 6 g. of viscous oil, was dissolved in alcohol (60 cc.). Salicylaldehyde (6.8 g.) was added to the solution and heated on a water bath for 20 minutes. On cooling, yellow crystals separated which were dissolved in benzene and the insoluble materials were removed by filtration. Addition of ligroine to the filtrate yielded 2.2 g. of salicylaldehyde derivative of 5-chlorodiphenyline, the main rearrangement product. Further recrystallization from benzene and ligroine yielded pale yellow needles, m.p. 174.5~175.5°. *Anal.* Calcd. for $C_{26}H_{19}O_2N_2Cl$: C, 73.46; H, 4.72; N, 6.45. Found: C, 73.02; H, 4.47; N, 6.59.

***o*-Semidine Rearrangement:** a) **6-Amino-3,4′-dimethyldiphenylamine** (III)—A mixture of 4,4′-dimethylhydrazobenzene (2.1 g.), Amberlite IR-120 (10 cc.), alcohol (15 cc.), and water (30 cc.) was refluxed while stirring. After refluxing for about 2 hours, separated insoluble substances were filtered with resins, and extracted with hot alcohol to give azotoluene. As described in the case of the benzidine rearrangement, the resins were eluted with aqueous sodium hydroxide and then extracted with hot alcohol, yielding 1.1 g. (52.3%) of (III). Recrystallization from aqueous alcohol gave colorless needles, m.p. 114~116°. *Anal.* Calcd. for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20.

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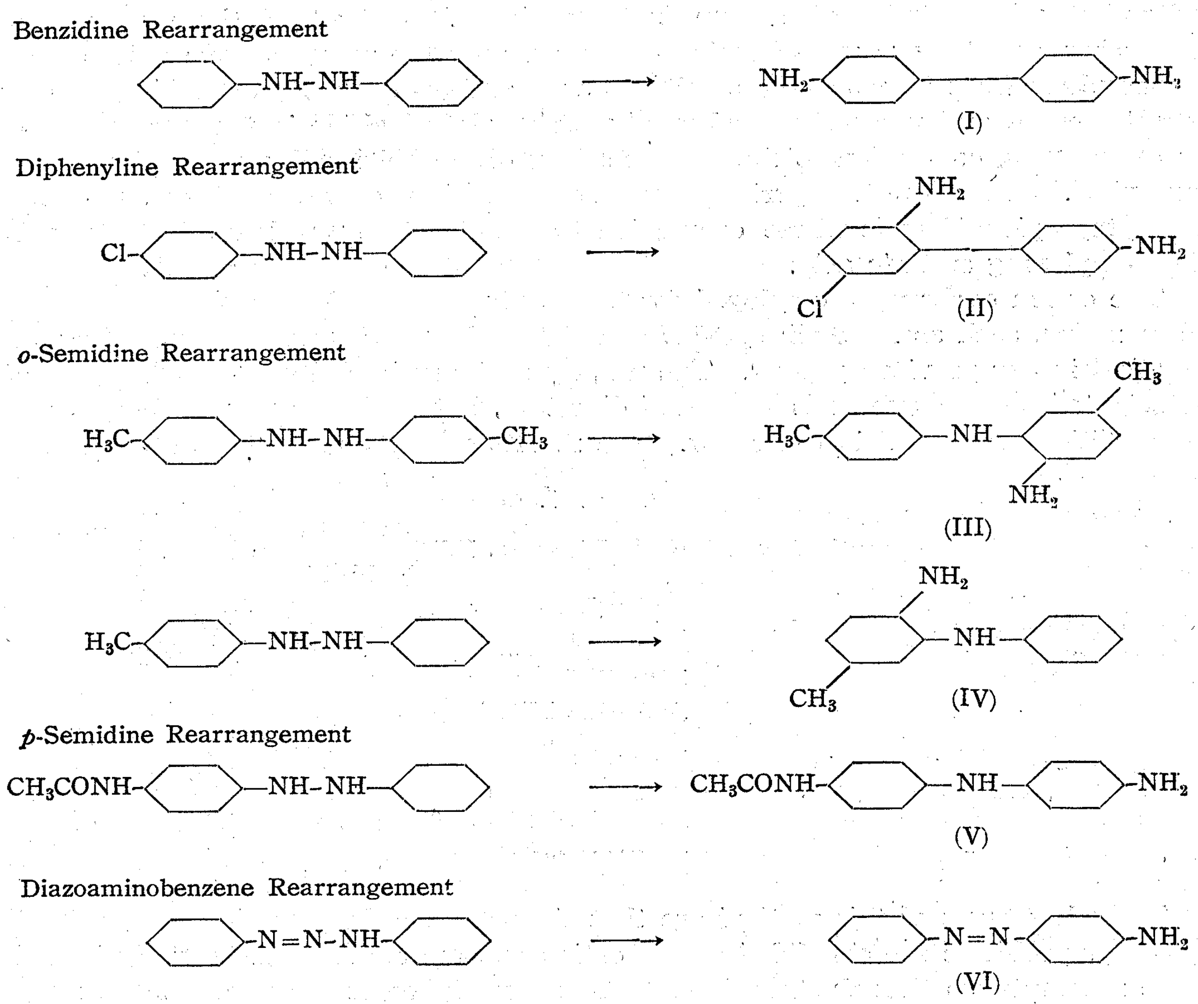
4) Dewar: Nature, **176**, 784 (1945).
5) Unger: Ber., **61**, 392 (1928).

Found: C, 79.18; H, 7.70; N, 12.96.

b) 2-Amino-5-methyldiphenylamine (IV)—To a solution of 4-methylhydrazobenzene (2 g.) in 50% aqueous alcohol (40 cc.) was added Amberlite IR-120 (17 cc.), while stirring, and then heated under reflux for 4 hours. The usual isolation procedure (see above) yielded a small amount of azo compound and 0.5 g. of (IV), which was made to react with acetic anhydride, yielding acetyl derivative, colorless needles, m.p. 149~150°. *Anal.* Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71. Found: C, 75.07; H, 6.80.

Rearrangement of Diazoaminobenzene—A mixture of diazoaminobenzene (2 g.), aniline (5 g.), and hydrochloride of Amberlite IR-4B (1 g.) was heated at 50° for 15 hours and then allowed to stand at room temperature for several days. The resins were removed by filtration and resulting solution was poured into water. The aminoazobenzene separated as reddish yellow crystals, 1.0 g. (50%), m.p. 151~153°. When this substance was mixed with the authentic sample, no melting point depression was observed. In another experiment, Amberlite IR-120 was used under the same condition and aminoazobenzene was obtained in almost the same yield.



Summary

The authors carried out the rearrangement reaction of hydrazobenzene derivatives and diazoaminobenzene by employing ion exchangers as a catalyst. It was found that the ion exchangers are effective for these reactions but have some inferior properties as a catalyst.

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