

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE
COLLEGE OF NEW YORK UNIVERSITY]

STUDIES IN THE DIARYL ACYL HYDRAZINE SERIES. II. SALT FORMATION IN THE BENZIDINE AND SEMIDINE REARRANGEMENTS


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In a previous paper¹ the authors described several unsymmetrical diaryl acetyl hydrazines, with a method for determining their structures based upon reduction with phenylhydrazine. The present communication treats of additional new members of this series, the determination of their structures by oxidation with potassium dichromate in glacial acetic acid solution, and the bearing of this work upon the problem of salt formation in the benzidine and semidine rearrangements.

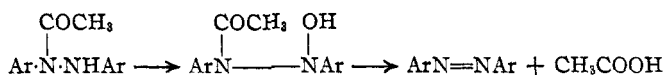
The oxidation of diaryl acetyl hydrazines has been investigated by Goldschmidt and Euler,² who reported the formation of tetrazanes by the oxidation of mono-acetylhydrazobenzene and mono-acetylhydrazo-*p*-toluene in benzene solution with lead dioxide. We have carried out the oxidation of the latter hydrazo compounds and also those described in our previous paper¹ with potassium dichromate in glacial acetic acid at ordinary temperature, and have found that tetrazanes are not formed under these conditions in any case. Two kinds of behavior on oxidation were shown by the acetylhydrazo compounds examined by us. All of the mono-acetylhydrazines previously identified by phenylhydrazine reduction¹ were oxidized with dichromate and were found to divide themselves with reference to behavior on oxidation into two series. The N-acetyl³ derivatives were oxidized in all cases to the corresponding azo compounds, while the N'-derivatives gave brilliant, intensely colored red or violet solutions from which highly colored crystalline products were isolated.

The production of the colored oxidation products appears to depend upon the presence of the group NH—, since the oxidation of mono-acetylhydrazo-*p*-toluene was found to yield, like the N-acetyl derivatives of the unsymmetrical members studied, the corresponding azo compound. The colored oxidation product derived from mono-acetylhydrazobenzene is under investigation in this Laboratory, and its structure has been established with some certainty. The oxidation of the N-derivatives probably takes place through the steps

¹ John J. Ritter and Frank O. Ritter, *THIS JOURNAL*, 52, 2815 (1930).

² Goldschmidt and Euler, *Ber.*, 55, 616 (1922).

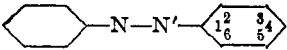
³ N designates the nitrogen atom attached directly to the unsubstituted benzene nucleus, N', the nitrogen atom in direct union with the nucleus carrying a substituent group.



Having discovered this relationship between structure and behavior on oxidation in those cases where the structures were already determined by phenylhydrazine reduction, we were able to extend it to the determination of the structures of the compounds described in this paper, since each member studied had a *p*-substituent in one nucleus. We have in this way determined the structures of the two isomeric mono-acetyl-*p*-iodohydrazobenzenes, of the single acetyl derivative of *p*-acetoxyhydrazobenzene, which is the N-derivative, of the single mono-acetyl-*p*-carboxyhydrazobenzene, which is also the N-derivative, and of the single mono-acetyl-benzenehydrazo-*p*-phenetole, which proved to be the N'-derivative.

The subjoined table summarizes the mono-acetyl hydrazines studied in this and in our previous paper, with the findings as to structure.

TABLE I

				
Substituent group	Position	CH ₃ CO-attachment	Method of structure-determination	M. p. (corr.), °C.
CH ₃	2	N	Red.	78
CH ₃	4	N'	Ox. + red.	140-141
CH ₃	4	N	Ox. + red.	124
Cl	4	N'	Ox. + red.	111-112
Cl	4	N	Ox. + red.	123-124
Br	4	N'	Ox. + red.	83
Br	4	N	Ox. + red.	117-118
I	4	N'	Ox.	156-157
I	4	N	Ox.	135-136
COOH	4	N	Ox.	207-208
OCOCH ₃	4	N	Ox.	105-106
OC ₂ H ₅	4	N'	Ox.	108

The symbol "Ox." signifies dichromate oxidation, and "Red.," phenylhydrazine reduction.

The formation of highly colored products on oxidation of the mono-acetylhydrazo compounds appeared, superficially, to bear a relationship to the behavior of certain hydrazo compounds on treatment with mineral acids. Jacobson and Kunz⁴ reported the significant fact that *p*-acetamidohydrazobenzene in acid solution became deep blue in color. We have noticed that other hydrazo compounds behave in this manner. Hydrazobenzene, hydrazo-*p*-phenetole, *p*-methyl-, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzene suspended in 10% hydrochloric acid at room temperature, and then exposed to the air for several days, yield blue or violet solutions.

⁴ Jacobson and Kunz, *Ann.*, 303, 363 (1898).

The formation of these colored products is undoubtedly caused by air oxidation of the original unrearranged products, since hydrazobenzene, even after the development of color when treated in this manner, contains no detectable amount of benzidine. A solution containing the rearranged products of hydrazobenzene developed no color when similarly treated. The colors can be developed in much shorter time by the addition of hydrogen peroxide.

The oxidation of the hydrazo compounds in the presence of hydrochloric acid, furthermore, was found to be quite parallel with the oxidation of their acetyl derivatives by potassium dichromate; the hydrazo compounds which yielded N-acetyl derivatives were found to give brown solutions on air oxidation, presumably representing the formation of the corresponding azo compounds, while those which gave the N'-acetyl derivatives were readily oxidized to deep red or violet colored products. This behavior is most readily explained by assuming that the hydrazo compounds in acid solution form mono salts, which may involve the N- or N'-atom, and oxidize to new colored substances on the one hand, or to the azo compounds, on the other, depending upon the nitrogen atom involved in salt formation, in a manner analogous to the behavior of their acetyl derivatives. The formation of mono salts in the hydrazo series is in harmony with the fact that hydrazine and many of its simple derivatives function chiefly as mono-acid bases. Acylation and salt formation of amines, furthermore, appear in the present work to be quite parallel, as in the previously reported cases of phenylhydrazine⁵ and methylhydrazine.⁶

It may therefore be said with some assurance that some of the unsymmetrical hydrazo compounds studied by us yield only one mono salt when treated with strong acids, while others yield two isomeric mono salts in approximately equal amounts.

Consideration of the products of rearrangement of the seventy-eight hydrazo compounds described by Jacobson⁷ reveals the interesting fact that they show a marked tendency to yield exclusively semidines on the one hand, or diphenyloids on the other. There appear to be only eight outstanding exceptions to this rule, comprising a group in which each member yields both diphenyloids and semidines simultaneously, and in nearly equal amounts; among the eight exceptions occur the members each of which this research has shown to yield two isomeric acetyl derivatives in nearly equal amounts. Thus, benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzenes each yield both diphenyloids and semidines. These facts suggest that the salts of hydrazo compounds are involved in their rearrangement, and, further, that the formation of a

⁵ E. Fischer, *Ann.*, 190, 131 (1878).

⁶ Von Brüning, *ibid.*, 253, 10, 12 (1889).

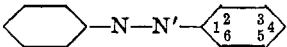
⁷ Jacobson, *ibid.*, 428, 90-97 (1922).

salt of definite structure precedes the formation of a definite type of rearrangement product. Examination of Jacobson's⁷ summary of the rearrangement of the various symmetrical hydrazo compounds (the structures of whose mono salts are known), supplemented by our own observations as to the structures of the salts of various unsymmetrical hydrazo compounds, discloses the following interesting relationship: when salt formation takes place on a nitrogen atom attached to an aryl nucleus in which the *p*-position is open, diphenyloids result, while semidines are formed when the salt in question involves a nitrogen atom attached to a nucleus carrying a *p*-substituent.

Considering the problem from this point of view, it seems that the type of rearranged product is determined by the structure of its mono salt. The tendency to rearrange to one type is so strong that it will often occur even with displacement of para groups already in the ring. However, the character and position of groups (other than para) undoubtedly have an influence, and determine the details within the two main types. It is in the latter sense that Jacobson's⁷ rules apply.

It is planned to study other members of the group to determine whether their behavior on acetylation and on oxidation in acid solution is in harmony with the above generalizations. Table II illustrates the relationship between salt structure and type of rearrangement undergone by those hydrazo compounds the structure of whose mono salts is established by this investigation.

TABLE II

			
Substituent group	Position	Salt formation on	Type of rearrangement
COOH	(4)	N	Diphenyloid
OCOCH ₃	(4)	N	Diphenyloid
CH ₃	(2)	N	Diphenyloid
OC ₂ H ₅	(4)	N'	Semidine
Cl	(4)	N + N'	Diphenyloid + semidine
Br	(4)	N + N'	Diphenyloid + semidine
I	(4)	N + N'	Diphenyloid + semidine
CH ₃	(4)	N + N'	Diphenyloid + semidine

By extending this relationship to benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo and *p*-iodohydrazobenzenes, it may be concluded that diphenyloid rearrangement is preceded by formation of the N-salts, and semidine rearrangement by the formation of N'-salts.

A criticism of the hypothesis of Frantzen and Furst,⁸ may also be offered. These authors suggest that the benzidine and semidine rearrangements involve the formation of mono salts which then separate into the corresponding amine and halamine

⁸ Frantzen and Furst, *Ann.*, **412**, 19 (1917).



The latter are supposed to react, either as such or with intermediate rearrangement of the halamine to the *o*- or *p*-quinol form, to yield the final rearrangement products. Jacobson⁹ has pointed out that this scheme does not harmonize with the "maintenance of the aryl combination" in the rearranged products, *i. e.*, the fact that the products of rearrangement always contain the original combination of aryl groups. He says that salt formation and breakdown in only one sense must be assumed in order that the aryl combination remain fixed. Our work has shown that this assumption cannot be made in those cases where the formation of two acetyl derivatives shows the ability of the compound in question to form two different salts. In those cases where only one acetyl derivative is formed, and hence only one salt, the hypothesis is on surer ground. Here only one type of amine and halamine is possible and the aryl combination is maintained.

Experimental Part

The preparation of the azo compounds, their reduction and the formation and separation of their acetyl derivatives were carried out as outlined in an earlier communication.¹ The experimental details of these operations will therefore be omitted in the present report.

Azo Compounds.—*p*-Iodoazobenzene, m. p. 105°, in agreement with Noelting and Werner;¹⁰ *p*-carboxyazobenzene, made by condensation of *p*-aminoethylbenzoate with nitrosobenzene followed by saponification of the ester with alcoholic potassium hydroxide, m. p. 237–238° (corr.), in agreement with Jacobson and Steinbrenk;¹¹ *p*-acetoxyazobenzene, m. p. 82–83°. Wallach and Kiepenheuer¹² reported 84–85°; benzeneazo-*p*-phenetole, m. p. 77–78°, in agreement with Jacobson and W. Fischer.¹³

Hydrazo Compounds.—*p*-Iodohydrazobenzene, m. p. 105–106°, in agreement with Noelting and Werner;¹⁰ *p*-carboxyhydrazobenzene, m. p. 192–193° (corr.), in agreement with Jacobson and Steinbrenk;¹¹ *p*-acetoxyhydrazobenzene, pearly plates from 95% alcohol, m. p. 117–118° (corr.).

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2$: N, 11.57. Found: (micro Dumas) N, 11.14.

Acetylhydrazo Compounds.—The more important characteristics of the new acetyl compounds are listed below. N-Acetyl-*p*-iodohydrazobenzene, clusters of needles from 95% alcohol, m. p. 135–136° (corr.).

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OI}$: N, 7.95. Found: (micro Dumas) N, 7.45.

N'-Acetyl-*p*-iodohydrazobenzene, prisms from 95% alcohol, m. p. 156–157° (corr.).

Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OI}$: N, 7.95. Found: (micro Dumas) N, 7.89.

N-Acetyl-*p*-carboxyhydrazobenzene, needles from 95% alcohol, m. p. 207–208° (corr.).

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3$: N, 10.37. Found: (micro Dumas) N, 10.70.

⁹ Jacobson, *Ann.*, **428**, 118 (1922).

¹⁰ Noelting and Werner, *Ber.*, **23**, 3255 (1890).

¹¹ Jacobson and Steinbrenk, *Ann.*, **303**, 384 (1898).

¹² Wallach and Kiepenheuer, *Ber.*, **14**, 2617 (1881).

¹³ Jacobson and W. Fischer, *ibid.*, **25**, 994 (1892).

N'-Acetyl-benzenehydrazo-*p*-phenetole.—This compound was difficult to prepare from the corresponding hydrazo compound because the latter underwent self-oxidation-reduction in the presence of acetic anhydride. The acetyl derivative was obtained in good yield by reduction of benzeneazo-*p*-phenetole with zinc dust and glacial acetic acid in acetic anhydride solution; colorless nodules composed of fine needles, m. p. 108°.

Anal. Calcd. for $C_{16}H_{18}N_2O_2$: N, 10.37. Found: (micro Dumas) N, 10.54.

N-Acetyl-*p*-acetoxylhydrazobenzene, fine colorless needles from alcohol, m. p. 105–106°.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: N, 9.86. Found: (micro Dumas) N, 9.22.

Oxidation of the Acetyl Derivatives.—The acetyl derivatives (one mole) were dissolved in glacial acetic acid to form a 10–15% solution, and then shaken for twenty-four hours on a mechanical bottle-shaker with finely ground potassium dichromate (0.66 mole). The N-derivatives yielded deep violet solutions immediately under these conditions, although the completed reaction required ten or more hours. The N-derivatives yielded brown solutions. The solutions were filtered after oxidation to remove any unused potassium dichromate, and then diluted with about five volumes of cold water. After standing overnight, the oxidation products appeared as precipitates which were separated by filtration. The brown solutions yielded in each case the corresponding azo compounds, which were identified by their melting points, and by comparison with authentic samples. The violet solutions yielded dark red crystalline solids. The product so obtained from acetylhydrazobenzene has been recrystallized from petroleum ether and then from alcohol in large plates of dark red color melting at 163° (corr.).

Oxidation of the Hydrazo Compounds.—Small quantities (0.1–0.2 g.) of the hydrazo compounds were suspended in 10% hydrochloric acid at room temperature, and allowed to stand exposed to the air for several days. Those which were found to yield N'-acetyl derivatives were found also to impart a deep violet color to the acid solutions, while those yielding N-acetyl derivatives became brown in color. Benzenehydrazo-*p*-toluene, *p*-chloro-, *p*-bromo- and *p*-iodohydrazobenzenes gave violet solutions in which the brown oxidation products were presumably formed also, although their presence could not be detected visually because of the intense violet color of the solutions. *p*-Acetoxy- and *p*-carboxylhydrazobenzenes, under the same conditions, gave orange-colored solutions. To make certain that the colored products resulted from the oxidation of the hydrazo compounds and not their products of rearrangement, the following experiment was performed: 0.1–0.2 g. of hydrazobenzene was boiled for five minutes with 5 cc. of concentrated hydrochloric acid. A clear solution was obtained, which was diluted with water until the acid concentration was approximately 10%. The solution was exposed to the air for several days, and remained colorless. Further work upon the isolation and identification of these colored air-oxidation products is in progress.

Summary

1. Several new diaryl acyl hydrazines have been prepared.
2. A method for their identification by means of oxidation has been described.
3. The formation of highly colored products from hydrazo compounds in contact with acids has been shown to be caused by air oxidation.
4. A relationship between the salt-forming properties of the nitrogen atoms in hydrazo compounds and their rearrangement in acid solution has been established.
5. The oxidation of hydrazo compounds in acid solution has also been

investigated and correlated with the oxidation of their acetyl derivatives. The phenomena observed have been found to have intimate bearing upon the benzidine and semidine rearrangements.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE REDUCTION OF TRIPHENYLMETHANE DYES AND RELATED SUBSTANCES WITH THE FORMATION OF FREE RADICALS

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The work of Clark and collaborators¹ has shown that the reduction of many different dyes by soluble reducing agents is a process analogous to the reduction of quinones in that the leuco compound and the dyestuff form a mobile oxidation-reduction system. The reduction and reoxidation occur rapidly at room temperature even in dilute solution and characteristic and significant oxidation potentials may be measured. The indigoids, many anthraquinone dyes, indophenols, indamines and methylene blue are all of this type. The reduction of azo dyes and triphenylmethane dyes is of a different sort; here, the reduction product (or products) are not rapidly reoxidized and no significant oxidation-reduction potentials can be measured by the usual methods. An examination of the behavior of the azo dyes has already been made in this Laboratory;² the present paper deals with the unraveling of the chemical reactions involved in the action of soluble reducing agents on triphenyl methane dyes; a quantitative study of certain of these reactions will be included in a later paper.

The color bases of the triphenylmethane dyes are substituted triphenylcarbinols; the dyes themselves are salts which are related to the halochromic salts of triphenylcarbinol. The exact method of formulating the structure of the colored positive ion of the triphenylmethane dyes and that of the halochromic salts has been the subject of much discussion. We shall not attempt to take sides in this controversy; the distinction between triphenylmethyl sulfate and malachite green appears to be one of degree rather than of kind as far as our work is concerned. It was shown some years ago,³ that the halochromic salts of triphenylcarbinol and related substances are reduced by powerful reducing agents in appropriate solutions with the formation of the corresponding free radical (*e. g.*, triphenylmethyl). The free radical and halochromic salt form a mobile oxidation-

¹ W. M. Clark and co-workers, "Studies in Oxidation-Reduction," Reprints I-X Hygienic Laboratory Bulletin No. 151.

² Conant and Pratt, *THIS JOURNAL*, **48**, 2468 (1926).

³ Conant, Small and Taylor, *ibid.*, **47**, 1959 (1925).