

methylaniline in the presence of a mixture of oxalic and acetic acids, we obtained *p*-nitrodimethylaniline (Expt. 30).

We have also prepared several new compounds, notably one from diphenylamine, the nature of which it is hoped to elucidate later.

III. Derivatives of Monobasic Aliphatic Acids.

Formanilide, by direct nitration, gave the *paranitro* derivative (Exp. 46), which was also obtained in the presence of sulphuric acid (Exp. 42).

Acetanilide, by direct nitration, gave a mixture of *ortho*- and *paranitro* derivatives (Expt. 50). In the presence of sulphuric acid, *metanitroacetanilide* was obtained (Expt. 47). The oxalic and trichloroacetic acid nitrations both gave *paranitro* derivatives (Expts. 48, 49).

The nitrations of trichloroacetanilide, propanilide and stearanilide gave products which have not yet been identified.

IV. Derivatives of Monobasic Aromatic Acids.

Benzanilide yields a mixture of *ortho*-, *meta*-, and *paranitro* derivatives by direct nitration (Expt. 72). With sulphuric acid, *paranitro*benzanilide was obtained (Expt. 67). Acetic acid nitration gave *meta*-nitrobenzanilide (Expt. 68). A mixture of oxalic and acetic acids gave the *paranitro* derivative (Expt. 69).

None of the nitration products of *m*-brombenzanilide, benzenesulphanilide, *o*-tolylsulphanilide, phenylacetanilide or picranilide have, as yet, been identified, owing to causes beyond our own control.

The work described in this paper was carried out at the Johns Hopkins University during the session 1906-7.

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August, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

HYDANTOIN TETRAZONES.

BY J. R. BAILEY.

Received May 25, 1908.

Introduction.

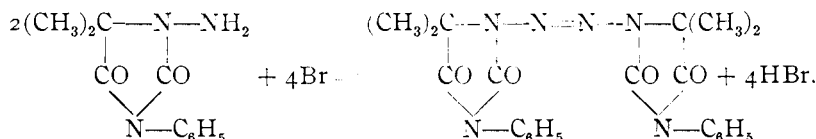
In a paper published in this journal a few years ago, the author described some tetrazones, in which there is the group $N=N$ joined on either side to an hydantoin group.¹ To simplify the nomenclature, these substances were regarded as azohydantoin. Here an attempt is made to further establish the constitution of these compounds by showing the relation of dimethylphenylazohydantoin (I), to dimethylphenylhydantoin (II) and also to aminodimethylphenylhydantoin (III).

The analytical data, published in the first article, did not in all cases closely agree with the tetrazone formulae. At that time, these substances were prepared for analysis by precipitation from a chloroform

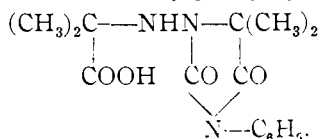
¹ THIS JOURNAL, 26, 1006.

E. Fischer also observed a similar decomposition in his investigation of tetraethyltetrazone,¹ which breaks down into nitrogen, ethylamine, diethylamine, and acetaldehyde, the amounts of each of these substances formed being approximately proportional to its molecular weight. The tetrazones, containing hydantoin complexes, differ in some respects from the simple alkyl tetrazones. The former are solids, which decompose at high temperatures, while the latter are liquids, which decompose below 150°. The hydantoin tetrazones rather resemble the aromatic tetrazones. These two classes of tetrazones are neutral compounds, whereas the alkyl tetrazones are especially characterized by strongly basic properties.

A further proof of the constitution of the hydantoin tetrazones was obtained from the synthesis of dimethylphenylazohydantoin by the action of bromine water on aminodimethylphenylhydantoin:

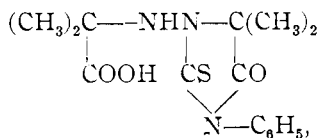


The author, in conjunction with Barney Brooks, found that the amino-hydantoin, employed here, can best be prepared by the action of sulphuric acid on isobutyric-acid-aminodimethylphenylhydantoin,



An attempt to confirm further the constitution of the tetrazones by molecular weight determination of 1-azo-3-methyl-5-dimethylhydantoin in chloroform solution was without avail, owing to the insufficient solubility and high molecular weight of this substance.

The preparation of dimethylphenylhydantoin from the tetrazone, as referred to above, may be regarded as the last step in the proof of the constitution of the reaction products of mustard oils on hydrazo acids.² Like the amino acids, the hydrazo acids react with mustard oils through the hydrogen on the nitrogen in the α -position to the carboxyl group with the formation of thiohydantoin, *e. g.*, hydrazoisobutyric acid gives with phenyl mustard oil 5-dimethyl-3-phenyl-1-isobutyric-acid-amino-2-



¹ *Ann. Chem.*, 199, 321.

² *THIS JOURNAL*, 26, 1006.

thiohydantoin, which, through a series of reactions, referred to above, may yield dimethylphenylhydantoin.

Experimental Part.

Preparation of Dimethylphenylhydantoin from Azodimethylphenylhydantoin.—3.8 grams of 1-azo-5-dimethyl-3-phenylhydantoin in 20 cc. of concentrated sulphuric acid was heated at 60° for three hours. On pouring the solution into water, there was a partial precipitation of the hydantoin and a further amount was obtained by extraction of the solution with chloroform. The total yield of hydantoin was 1.75 grams. This yield indicates that only one of the hydantoin groups in the tetrazone goes to hydantoin. To determine the fate of the other half of the molecule, the sulphuric acid in the filtrate was precipitated with barium hydroxide and the solution was then evaporated. The residue proved very soluble in water and insoluble in organic solvents, with the exception of alcohol, and could not be made to crystallize. For analysis, the hydantoin was crystallized from water with the addition of charcoal and then from benzene.

Calculated for $C_{11}H_{12}O_2N_2$: C, 64.71; H, 5.88; N, 13.72.

Found: C, 65.13; H, 5.94; N, 13.99.

Boiling alcoholic potassium hydroxide also decomposes the tetrazone with the formation of hydantoin. The substance, obtained in this way, before being purified, has a strong terpene odor. The hydantoin, obtained from the tetrazone by the action of sulphuric acid, as described above, crystallizes in long needles, with a characteristic mother-of-pearl luster and, to the naked eye, these are different from the crystals obtained by the action of alcoholic potash on the tetrazone. Under the microscope, the hydantoin, obtained by the acid treatment, consists of long, narrow prisms with very steep dome-shaped end faces, while the hydantoin, obtained by the action of alcoholic potash, appears in the form of thin, broad prisms with dome-shaped end faces not so steep. The hydantoin, obtained by either method, melts undecomposed at 171° (corr.). The substance is readily soluble in alcohol, chloroform, and benzene, more difficultly soluble in water, and only sparingly soluble in ether.

*Preparation of Dimethylphenylhydantoin from Phenylisocyanate and Aminoisobutyronitrile.*¹—Aminoisobutyronitrile, as obtained in ethereal solution, reacts readily with phenylisocyanate with the generation of considerable heat and the hydantoic-acid-nitrile, $C_6H_5NHCONHC(CH_3)_2CN$, separates out. This, without further purification, is saponified by boiling with concentrated hydrochloric acid. From the cold, acid solution the dimethylphenylhydantoin separates out almost pure. The hydantoin,

¹ Ber., 37, 1921.

prepared in this way, is identical with that obtained by the action of alcoholic potash on the tetrazone.

*Determination of the Density of the Inert Gas Evolved in the Reaction between Sulphuric Acid and Dimethylphenyltetrazone.*¹—In the lower of two bulbs, connected through a glass stop-cock, about 2 grams of tetrazone was placed. The top bulb was then sealed off from the air, and, with the stop-cock between the two bulbs open, the whole system, through a connection with the lower bulb, was exhausted by a Toepler pump. The stop-cock, the capillary of which was in this way evacuated, was now closed, the top bulb opened and 20 cc. of sulphuric acid (sp. gr. 1.84) introduced into the top bulb. After the greater part of the acid in the upper bulb had been allowed to flow into the lower bulb, the decomposition of the tetrazone was effected by heating the acid to 75°. In the beginning, the stop-cock on the pump was shut off and the gas through its own pressure forced itself into a container, filled with mercury and inverted in a mercury trough, through a small tube connected with the lower bulb and of sufficient height to allow the mercury to rise in it to the barometric height. After the gas, so collected, had been freed from carbon dioxide and sulphur dioxide by standing over potassium hydroxide solution, it was dried in the usual way, by being passed over phosphorus pentoxide, and its density was then determined by the method described by Travers.²

The following work was carried out conjointly with Barney Brooks.

Preparation of 1-Amino-5-dimethyl-3-phenylhydantoin.

$(\text{CH}_3)_2\text{C}=\text{N}-\text{NH}_2$



—Fifty grams of concentrated sulphuric acid are mixed with 50 grams of water and to this 10 grams of 5-dimethyl-3-phenyl-1-isobutyric-acid-amino-2-thiohydantoin are added. The mixture is then heated, until complete solution is effected, the temperature not being allowed to rise higher than necessary. For the isolation of the hydrazine, the acid solution is allowed to drop slowly into concentrated ammonium hydroxide with constant stirring. The hydrazine separates out and, after being filtered off, is purified by crystallization from benzene, containing a little petroleum ether. The yield is about 65 per cent. of the theoretical. If pure, the substance melts at 154.5° (corr.). It is soluble in the common organic solvents, with the exception of petroleum ether, and is almost insoluble in water. This substance forms a hydrazone with benzaldehyde, it also reacts normally with one molecule of phenyl

¹ ALAN HIRSCH assisted in this experiment.

² Study of gases by Travers, page 121.

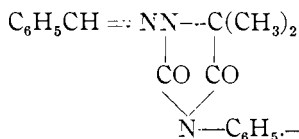
mustard oil, and, on treatment with bromine water, passes into the corresponding tetrazone. Similarly to all aminohydantoin, thus far investigated, it does not form salts with acids.¹

Calculated for $C_{11}H_{13}O_2N_3$: C, 60.27; H, 5.93; N, 19.18.

Found: C, 60.28; H, 5.93; N, 19.17.

Action of Bromine Water on Aminodimethylphenylhydantoin.—To the hydrazine dissolved in a little alcohol, bromine water was rapidly added, until no further reduction of the bromine took place. There was an immediate separation of the difficultly soluble tetrazone in almost quantitative yield. To insure a completion of the reaction, the solution was allowed to stand some minutes and the excess of bromine then removed with sulphur dioxide. Purified by crystallization from acetacetic ester, the substance showed the correct decomposition point of the tetrazone and, on treatment with alcoholic potassium hydroxide yielded dimethylphenylhydantoin. This reaction goes so smoothly that the tetrazone formation can no doubt be used as a test for 5-dimethylaminohydantoin. Unlike the secondary hydrazines investigated by Fischer and by Renouf,² this aminohydantoin is not oxidized by mercuric oxide.

1-Benzalamino-5-dimethyl-3-phenylhydantoin,



The above hydrazone was prepared by the action of benzaldehyde on aminodimethylphenylhydantoin and also by the action of phenylisocyanate on the benzalhydrazone of hydrazinoisobutyric acid. The substance was prepared by the first method in that the aminohydantoin was heated in a sealed tube with a slight excess of benzaldehyde up to 200°. The reaction product solidifies and can be extracted with benzene. The second method of preparation consists in heating the hydrazone of hydrazinoisobutyric acid in benzene solution to boiling for a few minutes with a slight excess of phenylisocyanate. On the addition of petroleum ether to the benzene solution, diphenylurea first precipitates and the hydantoin hydrazone is obtained by evaporating the filtrate from the diphenylurea. The hydrazone is separated from the last traces of diphenylurea by extraction with small amounts of ether and benzene and, finally, by crystallization from 96 per cent. alcohol and acetic ester. The hydrazone crystallizes from alcohol in which it is difficultly soluble in the cold, in long, slender needles of a very light yellow color. It melts, apparently undecomposed, at 154° (corr.). It is readily soluble in the common organic solvents, with

¹ Compare *Ber.*, 31, 162; *Ibid.*, 34, 322; *THIS JOURNAL*, 26, 1009.

² *Loc. cit.*

the exception of petroleum ether, and very difficultly soluble in water. On heating with acids, benzaldehyde is split off.

Calculated for $C_{18}H_{17}O_2N_3$: C, 70.36; H, 5.54; N, 13.68.

Found: C, 70.04; H, 5.52; N, 13.69.

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[CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON.]

SOME CHARACTERISTIC COLOR REACTIONS PRODUCED BY SODIUM HYPOBROMITE.

BY WILLIAM M. DEHN AND SILAS F. SCOTT.

Received July 10, 1908.

Since hippuric acid gave with sodium hypobromite a very characteristic color reaction,¹ it was thought that other substances also would be affected characteristically by this reagent. This has proved to be the case and to such an extent that sodium hypobromite alone or combined with the use of ammonia can now be considered one of the most valuable reagents for detecting and distinguishing many phenolic and nitrogenous aromatic compounds.

For the purpose of uniformity and of determining the limits of tests and comparing their respective delicacies, solutions of the various substances were prepared in the following concentrations: I, 1 gram in 100 cc. of water; II, in 1,000; III, in 10,000; IV, in 100,000; V, in 1,000,000.

Alcohol was added when necessary to produce complete solution; with bases, hydrochloric acid was used for the same purpose. With various concentrations of solutions quite different color effects may often be obtained and thus one sometimes obtains results quite different from the results described in the literature. For this reason the concentrations of solution should always be indicated, also the quantity used, method of applying the reagent, quantity of reagent and the temperature. In the following experiments the reagent was applied, a drop at a time, to about 5 cc. of the solutions tested. When a series of colors are given they indicate the progressive effect either on standing or on adding more of the hypobromite solution. The following abbreviations are used to indicate the conditions and manner of applying tests.

A. Treated with sodium hypobromite at ordinary temperature.

A'. Treated with ammonia, then with sodium hypobromite at ordinary temperature.

B. First heated to boiling, then treated with sodium hypobromite.

B'. Treated with ammonia, then heated and finally treated with sodium hypobromite.

Of course solutions should not be acid in reaction for then bromine is liberated from the hypobromite. Excess of ammonia should be avoided

¹ THIS JOURNAL, this Number, Note 1.