a part of the total volume of the solution corresponding to its own mol. fraction of the dissociating substance present; and if we keep in mind the fact that the total amount of dissociating substance in the solutions in the equilibrium experiments was always 30% or more, it appears improbable that any considerable degree of dissociation could have occurred there.

Bryn Mawr, Pa.

[Contribution from the Chemical Laboratory of the University of Michigan.]

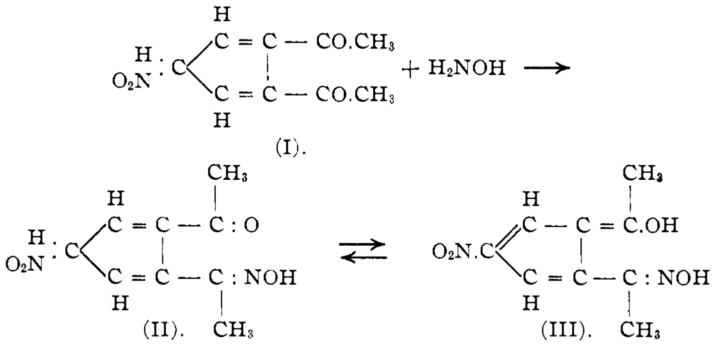
STUDIES IN THE CYCLOPENTADIENE SERIES. IV. THE FORMATION OF CYCLOPENTADIENODIHYDROPYRIDAZINES.

By William J. Hale.

Received September 19, 1916.

In an earlier publication[1] upon 5-nitro-2,3-diacetylcyclopentadiene, attention was called to the fact that only one of the acetyl groups could be involved in the formation of oximes, anils or hydrazones. In a second publication[2] upon 5-nitro-2,3-dibenzoylcyclopentadiene the same general results were experienced. The possibility of steric hindrance interfering with the reaction of hydroxylamine or the hydrazines upon carbonyl groups attached to adjacent carbon atoms presented its usual doubtful significance; its elimination from consideration however followed immediately the study of these monohydrazones.

When, for example, one of the carbonyl groups of diacetylcyclopentadiene (I) enters into reaction there occurs a rearrangement of affinity; a rearrangement from that condition of equilibrium, where either one or the other of these carbonyl groups may exist transitorily in enolic form, to a condition stabilized with reference to one carbonyl group now involved with the basic nitrogen as oxime or hydrazone. The double linking thus established between the nitrogen and the carbon, with the consequent alternate double and single linkings around the ring, leads directly to the enolic form (III) of the second carbonyl group, a form naturally



(I). (II). (III).

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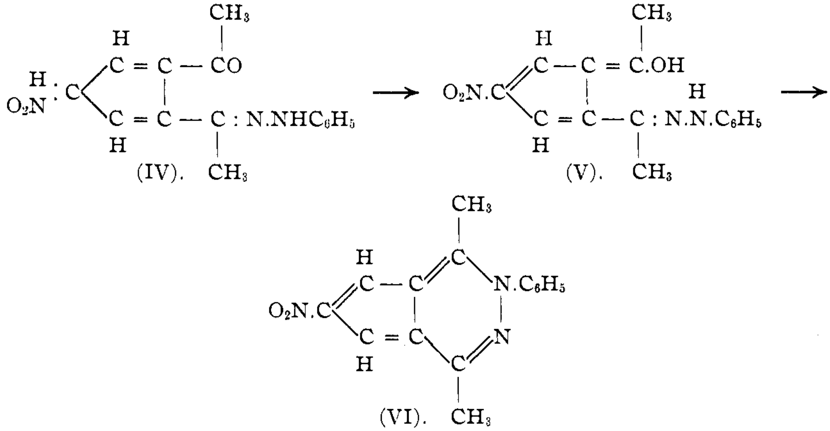
[1] This Journal, 34, 1583 (1912).

[2] *Ibid.*, 35, 70 (1913).

in equilibrium with the ketonic form (II) but one now highly favored through this oxime or hydrazone structure. An illustration is afforded by the diagrams on page 2535.

The instability of the monohydrazones and monophenylhydrazones of these cyclopentadiene derivatives has been noted in the earlier publications.[1] In all cases they were found to undergo readily an intramolecular condensation with the production of colored compounds of double ring structure. The study of these compounds has shown that the double ring formation can have proceeded only from the enolic structure shown in (III). When the monophenylhydrazone of 5-nitro-2,3-diacetylcyclopentadiene (IV) is considered, the inner condensation is found to proceed readily from its enolic form (V), even in solutions in anhydrous solvents, to a structure (VI) of the pyridazine type:



(IV). (V). (VI).

This insoluble product, a beautiful orange-yellow in color, is slowly precipitated also from the alkaline solutions of the monophenylhydrazone, the acid hydroxyl and basic hydrogen thus being lost in the production of a neutral pyridazine. This new type of compound must, however, be classed as a cyclopentadienodihydropyridazine.

This development of a pyridazine ring from the 1,2-diacetyl class of compounds at once recalls the history and discussion of the reactions of hydrazine and phenylhydrazine upon diacetosuccinic ester and especially upon acetonylacetone and diphenacyl—the two compounds which were involved in the syntheses of the cyclopentadienes now under consideration. The work of Alexander Smith[2] and of Gabriel and co-workers[3] has established the mode of formation of pyridazines from 1,4-diketones and their derivatives, but in the study of one member of this latter class—

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[1] *Loc. cit.*

[2] *Ann.*, **289** 310 (1896).

[3] *Ber.*, **32**, 395 (1899); **34**, 3257 (1901); **42**, 654 (1909).

diacetosuccinic ester—Curtius[1] procured also a bismethylpyrazolone and later Bülow[2] isolated from this same reaction an N-aminodimethylpyrrole dicarboxylic ester—a compound formed by the simultaneous condensation of one of the amino groups of hydrazine with both of the 1,4-carbonyl groups. This manner of condensation requires the presence of both carbonyl groups in enolic form; it proceeds best in acetic acid solution and to no large yield. According to the structure of diacetylcyclopentadiene, when one of the carbonyl groups reacts in enolic form the second is forced to assume the ketonic structure. It is therefore impossible for a simple pyrrole type of condensation to proceed directly from the cyclopentadiene derivative. Furthermore, all of the products of the condensations for our consideration have failed to show the presence of the pyrrole ring. It is generally accepted also that 5-membered rings when entering into poly-ring nuclei condense more readily with 6-membered rings; hence the possibility of developing a second 5-membered ring—that of a pyrrole—is here unfavored.

Paal and his co-workers[3] observed that diphenacyl, acetonylacetone and certain γ-keto esters condensed with hydrazines to form dihydropyridazines; these products were sometimes isolated, but more often were oxidized in the air to the corresponding pyridazines. A similar class of compounds therefore may be expected from the action of hydrazines upon diacetylcyclopentadiene, a compound in which the original stem of these γ-diketones, though now without labile hydrogen, is still present. A few examples of condensed nuclei involving a pyridazine ring as one component have been known. The oxidation of such compounds has unfailingly proved their complete structures. Thus Täuber[4] was the first to prove the structure of phenazone by discovering a pyridazine tetracarboxylic acid in the oxidation product which resulted when phenazone was treated with a very large amount (ten times its weight) of potassium permanganate in neutral solution. Through the loss of two molecules of carbon dioxide from the two carboxyl groups on the two carbon atoms adjacent to the nitrogen atoms there remained finally a 4,5-dicarboxylic acid. Gabriel[5] studied the oxidation of phthalazine by use of potassium permanganate and obtained this same pyridazine dicarboxylic acid as is required by theory. In both of these examples the heterocyclic ring appears the more stable. The oxidation of anisyl cinnoline by Stoermer and Gaus[6] yielded a 4-anisylpyridazine-5,6-dicarboxylic acid, a further indication of the stability of the pyridazine ring. In this latter case,

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[1] *J. prakt. Chem.*, [2] **50,** 508 (1894).

[2] *Ber.*, **35,** 4311 (1902).

[3] *Ibid.*, **36,** 491, 497, 2538 (1903); **37,** 4382 (1904); **40,** 4598 (1907).

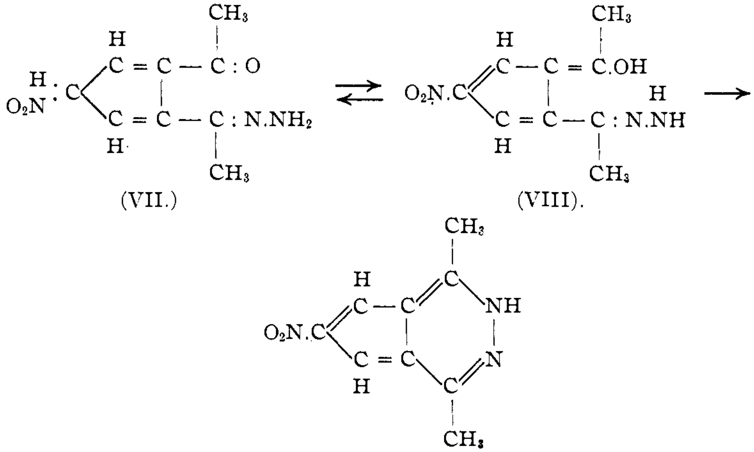
[4] *Ibid.*, **28,** 451 (1895).

[5] *Ibid.*, **36,** 3373 (1903).

[6] *Ibid.*, **45,** 3104 (1911).

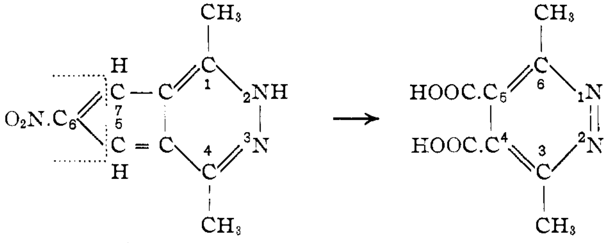
as well as in the others, the action of a neutral solution of potassium permanganate at the temperature of the water bath seems most effective for the oxidation of these condensed nuclei to their simple pyridazine derivatives.

Just as with the monophenylhydrazone of nitrodiacetylcyclopentadiene so also with the monohydrazone (VII) this inner condensation proceeding from its enolic form (VIII) led directly to a cyclopentadienodihydropyridazine (IX) as indicated below:


(VII.) (VIII). (IX).

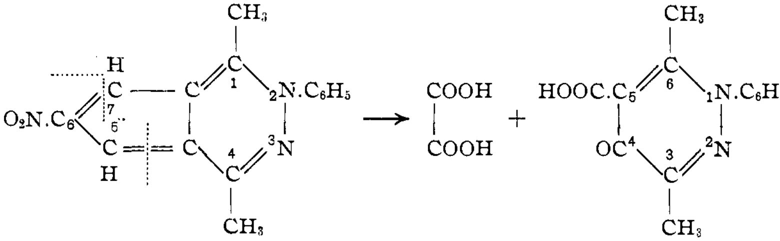
The monohydrazone is very unstable and scarcely can be isolated owing to the great ease with which it undergoes this intramolecular condensation. The absence of any labile hydrogen on a carbon atom adjacent to the second carbonyl group would argue indeed against the appearance of an enolic form in readiness for the further condensation with the hydrazine or phenylhydrazine stem. We may assume, therefore, that the shift in linkings within the cyclopentadiene ring itself, transforming the possible isonitro group to a simple nitro group, is the direct source of this available hydrogen for the second carbonyl group. The replacement of the ketonic oxygen of the first carbonyl group by the basic hydrazine stem acts, of course, as the cause of this directed shift.

A study of the oxidation products of these cyclopentadienodihydropyridazines has led to the following considerations: The orange-red product (IX) obtained from the hydrazone we may term 1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine. The diagram on page 2539 will indicate the course of its oxidation by potassium permanganate in neutral aqueous solution. The first break occurs between carbon atoms 6 and 7; the intermediate product—a simple dihydropyridazine derivative—is at once oxidized to the corresponding pyridazine and the second break then occurs between carbon atoms 5 and 6, thus making possible the production of two carboxyl groups attached to adjacent carbon atoms in the pyridazine ring. The final product is 3,6-dimethylpyridazine-4,5-dicarboxylic acid (X) a colorless dibasic acid closely resembling the pyridazine dicarboxylic acid already known.



(IX). (X).

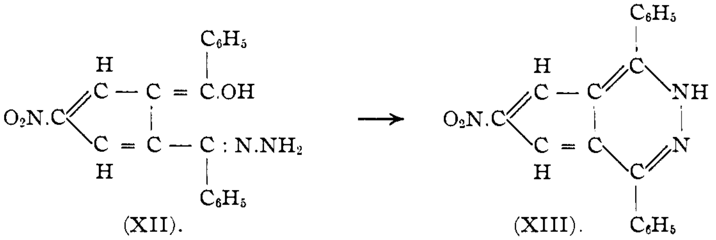
The orange-yellow compound (VI) produced in the intramolecular condensation of the phenylhydrazone of diacetylcyclopentadiene is to be classed as a 2-phenyl-1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine. Its oxidation to a dihydropyridazine was best accomplished by the use of potassium permanganate in acetone solution. Its slight solubility in water and alkalies, together with the tendency for an aqueous potassium permanganate solution to carry the oxidation as far as possible toward a pyridazine, required the presence of some solvent which would permit the oxidation to proceed at lower temperatures. In this way the phenyl group upon the nitrogen atom remained in position and the yield of product was not below the ordinary. According to the diagram below the course of the oxidation may be described as a break first occurring between carbon atoms 6 and 7 with the carbon atom 7 passing into carboxyl; the maintenance of the dihydropyridazine structure then forcing the second break between carbon atom 5 and the pyridazine ring. The keto derivative thus formed is a 1-phenyl-3,6-dimethyl-4-ketodihydropyridazine-5-carboxylic acid (XI). This latter is a colorless insoluble monobasic acid. In the mother liquors the presence of nitric and oxalic acids was detected; the latter naturally arises from the elimination of the pair of carbon atoms 5 and 6 in the cyclopentadiene ring. As a check, trial oxidations, where the permanganate had been employed in aqueous



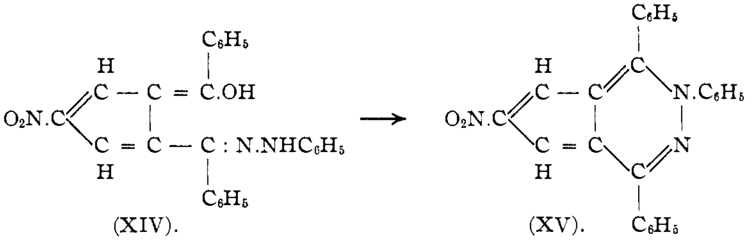
(VI). (XI).

and not in acetone solution, were found to give confirmatory tests for the presence of oxalic acid.

In applying this study to the nitrodibenzoylcyclopentadienes it is found that the monohydrazone (XII) passes most readily into the corresponding 1,4-diphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine (XIII), and that the monophenylhydrazone (XIV) passes almost as quickly into the 1,2,4-triphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine (XV).



(XII). (XIII).



(XIV). (XV).

The oxidation of these latter products was not attempted. The compounds were beautifully colored and showed all of the reactions characteristic of the former or dimethylpyridazine class.

All of these compounds showed marked stability; their fusion or decomposition points are high and acids or alkalies are practically without action upon them. Their color from a deep yellow to a red is highly characteristic. This stability of the dihydropyridazine ring is of course to be referred directly to the double ring structure; the formation of the stable pyridazine naturally followed wherever possible in the oxidation products. The inner condensation among members of the monoxime class (III) has not yet been studied. It does not, however, proceed with the ease which we should anticipate were there hydrogen directly tied to the nitrogen atom. The condensation therefore must proceed in the manner of anhydrides and require outside agencies which will be considered at another time.

Experimental Part.

1,4 - Dimethyl - 6 - nitro - 2,3 - cyclopentadieno-1,4-dihydropyridazine $C_7H_3N_2(CH_3)_2(NO_2)$ (IX).—This compound is best prepared by dissolving 1 g. of 5-nitro-2,3-diacetylcyclopentadiene in 20 cc. of water containing 1 g. of sodium carbonate. To the clear yellow solution is then slowly added 1 g. of powdered hydrazine sulfate. The yellow monohydrazone which separates in part again redissolves by the heat of the reaction and the orange-red precipitate of the pyridazine shortly makes its appearance. The mixture (which must still be alkaline) is then heated for a few moments over a free flame to insure the solution of any hydrazone or cyclopentadiene unacted upon. Upon filtering the hot mixture the pyridazine is collected upon the filter fairly pure and in excellent yield. This cyclopentadienopyridazine is readily soluble in acetone or acetic ester; fairly soluble in alcohol, acetic acid or benzene; slightly soluble in chloroform, ether or water and insoluble in ligroin. It crystallizes best from alcohol in small beautiful red prisms decomposing at 240–5°. As noted in the preparation above this pyridazine is not affected by sodium carbonate. It does, however, dissolve in sodium hydroxide solution to give the sodium salt from which the free substance may again be liberated by acids.

0.1288 g. subst. gave 0.2666 g. CO_2, and 0.0570 g. H_2O.

0.1486 g. subst. gave 30.1 cc. N_2 (22.5° and 738.4 mm. over H_2O).

Calc. for $C_9H_9O_2N_3$: C, 56.52; H, 4.75; N, 22.00. Found: C, 56.45; H, 4.95; N, 22.12.

3,6-Dimethyl-4,5-pyridazine Dicarboxylic Acid, $C_4N_2(CH_3)_2(COOH)_2.H_2O$ (X).—One gram of the dimethylcyclopentadienodihydropyridazine just described was brought into solution in 100 cc. of water containing just sufficient potassium hydroxide to convert it into the potassium salt. To this clear red solution 5.6 g. of potassium permanganate dissolved in 140 cc. of water (4%) were slowly added and the reaction mixture heated overnight under a reflux condenser at the temperature of the water bath. In the morning a few cc. of the permanganate solution may still be found necessary to complete the oxidation and after a little further heating the excess of permanganate may be decomposed by alcohol and the mixture filtered. The manganese dioxide remaining upon the filter is boiled up once with water and again filtered. The combined filtrates are then acidified with HCl and evaporated to dryness upon the water bath. The dry residue is now extracted several times with alcohol and the combined alcoholic extracts evaporated to dryness. This final residue is treated with only a few drops of water (to dissolve salt) and the undissolved portion filtered off. This insoluble portion is then dissolved in hot water, boiled with bone black and filtered; the filtrate, upon evaporation to small volume, yields about 0.2 g. of the colorless dimethylpyridazine dicarboxylic acid. This compound is fairly soluble in alcohol or water; slightly soluble in acetic acid and insoluble in ether, ligroin, chloroform, acetone, acetic ester or benzene. It crystallizes best from water in small colorless prisms decomposing at 226–8° and containing one molecule of water of crystallization. In the mother liquors as first obtained in the oxidation described the presence of nitric acid could just be identified, but besides carbonic acid no other acid was found present. The neutral permanganate solution therefore just sufficed for the splitting off of the one carbon atom out of the cyclopentadiene ring and the conversion of the carbon atoms adjacent to the pyridazine ring into corresponding carboxyl groups as explained previously. The dihydropyridazine, formed in the first step, is of course oxidized immediately to the pyridazine but the methyl groups remain in position unattacked. Had the oxidation not progressed to this stage, tests for the presence of imino hydrogen would have shown other than negative.

0.1676 g. subst. gave 0.2750 g. CO_2, and 0.0755 g. H_2O.

0.1436 g. subst. gave 17.6 cc. N_2 (25° and 738.9 mm. over H_2O).

0.1620 g. subst. lost nothing over H_2SO_4 but lost 0.0138 g. H_2O at 112°.

Calc. for $C_8H_8O_4N_2.H_2O$: C, 44.84; H, 4.71; N, 13.09; 8.42 H_2O. Found: C, 44.75; H, 5.04; N, 13.22; H_2O, 8.52.

From this acid a white insoluble silver salt was prepared in the usual manner. Upon analysis

0.1872 g. silver salt gave 0.1304 g. AgCl.

Calc. for $C_8H_6O_4N_2Ag_2$: Ag, 52.64. Found: Ag, 52.43.

A further check on the presence of two carboxyl groups was made by boiling a solution of this acid with iceland spar contained in a small flask attached to a regular CO_2 absorption train such as used for combustions. The weight of carbon dioxide liberated is a direct measure of the acid hydrogen.

0.1012 g. subst. liberated 0.0206 g. CO_2 from $CaCO_3$.

Calc. for 2H˙ in $C_8H_8O_4N_2.H_2O$: H, 0.96. Found: H, 0.93.

2-Phenyl-1,4-dimethyl-6-nitro-2,3-cyclopentadienodihydropyridazine, $C_7H_2N_2(C_6H_5)(CH_3)_2(NO_2)$ (VI).—This product is readily prepared by adding an excess of phenylhydrazine to an alcoholic solution of nitrodiacetylcyclopentadiene (I) and warming the mixture for an hour or more. Upon cooling the precipitation of the pyridazine is practically completed. The isolation of the intermediate monophenylhydrazone is in no wise necessary and rather to be avoided. The yield is almost quantitative. This phenylcyclopentadienopyridazine is readily soluble in chloroform, acetic ester or acetone; it is fairly soluble in alcohol or benzene; slightly soluble in ether or water and insoluble in ligroin. It crystallizes best from alcohol in the form of small yellow needle clusters melting at 193°. It is unaffected by warming with alkali or with acid. In fact the red alkaline solution of the monophenylhydrazone, just mentioned, slowly precipitates this pyridazine in crystalline form.

0.1202 g. subst. gave 0.2962 g. CO_2 and 0.0552 g. H_2O.

0.1457 g. subst. gave 21.2 cc. N_2 (23.4° and 741.4 mm. over H_2O).

Calc. for $C_{15}H_{13}O_2N_3$: C, 67.39; H, 4.90; N, 15.73. Found: C, 67.22; H, 5.14; N, 15.87.

1-Phenyl-3,6-dimethyl-4-keto-1,4-dihydro-5-pyridazine Carboxylic Acid, $C_4N_2O(C_6H_5)(CH_3)_2.COOH$ (XI).—A neutral solution of potassium permanganate acts very slowly upon the insoluble phenyldimethylcyclopentadienopyridazine. A higher temperature however suffices for a somewhat more rapid oxidation, but is likely also to carry the reaction too far. In order that the phenyl group may remain upon its original nitrogen atom, this oxidation must lead to a dihydropyridazine derivative and hence one may look for a ketodihydropyridazine if the oxidation is successful. This desired result was accomplished through the use of potassium permanganate in acetone solution. One gram of the phenyldimethylcyclopentadienodihydropyridazine in 20 cc. of acetone was slowly added to a solution of 30 g. of potassium permanganate in 600 cc. of acetone, to which previously about 50 cc. of water had been added. The contents of the flask, fitted with reflux condenser, were kept at boiling temperature by means of the water bath. After decolorization of the permanganate still more of this powdered reagent was added little by little until almost another 30 g. were consumed. At this point (after 4 hours' boiling) the decolorization proceeded very slowly and the reaction was considered at an end. The clear filtrate from the reaction mixture was next evaporated to dryness, taken up in a little water, acidified with hydrochloric acid and extracted with ethyl acetate. It is well also to digest the large amount of manganese dioxide with water, filter, evaporate to small volume, acidify and extract with ethyl acetate. From these ethyl acetate extracts the colorless oxidation product is obtained by evaporation. This phenyldimethylketodihydropyridazine carboxylic acid is readily soluble in acetone, chloroform, acetic ester, benzene or acetic acid; it is fairly soluble in alcohol or carbon tetrachloride; slightly soluble in ether or water and insoluble in ligroin. It crystallizes best from alcohol in fine, colorless needles melting at 220°.

0.1454 g. subst. gave 0.3414 g. CO_2 and 0.0674 g. H_2O.

0.1359 g. subst. gave 14.6 cc. N_2 (22° and 735.4 mm. over H_2O).

Calc. for $C_{13}H_{12}O_3N_2$: C, 63.90; H, 4.96; N, 11.48. Found: C, 64.04; H, 5.18; N, 11.71.

As this acid does not form an insoluble silver salt or similar product adapted to a simple analysis the presence of the single carboxyl group was determined from the weight of carbon dioxide liberated when the acid, a little water and some alcohol, to aid its solution, were brought in contact with barium carbonate in a small flask as described in a previous experiment.

0.1346 g. subst. liberated 0.0118 g. CO_2 from $BaCO_3$.

Calc. for $1H^{\cdot}$ in $C_{13}H_{12}O_3N_2$: H, 0.41. Found: H, 0.40.

The barium carbonate worked to a better advantage in this case than the iceland spar.

The production of this ketodihydropyridazine carboxylic acid leaves no room for doubt concerning the original structure of the double ring molecule. The oxidation must have proceeded as indicated, (VI) into

(XI), and oxalic acid should be found as a by-product. Both the liquors, from the oxidation at lower temperatures in acetone solution and the trial oxidation carried out in neutral aqueous solution at the temperature of the water bath, gave distinct and positive tests for the presence of oxalic acid. Nitric acid also was present in traces.

1,4-Diphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine, $C_7H_3N_2(C_6H_5)_2(NO_2)$ (XIII).—This product is prepared by dissolving nitrodibenzoylcyclopentadiene[1] in a mixture of benzene and alcohol and adding an excess of hydrazine hydrate in alcoholic solution. The clear red solution is then warmed on a water bath for a few hours when the precipitation of the diphenylcyclopentadienopyridazine will be found complete. This substance is only fairly soluble in acetone, acetic ester, chloroform, benzene, alcohol or acetic acid; it is slightly soluble in ether and insoluble in ligroin or water. It crystallizes best from acetone in small orange-red prisms decomposing at 275–80°. This diphenyl derivative is not affected by acids or dilute alkalies; it is, however, soluble in alcoholic sodium hydroxide and may again be precipitated from this solution by acid. No successful means presented itself for the isolation of the intermediate monohydrazone (XII) owing to its great instability.

0.1376 g. subst. gave 0.3658 g. CO_2 and 0.0562 g. H_2O.

0.1470 g. subst. gave 18.3 cc. N_2 (24.2° and 738.6 mm. over H_2O).

Calc. for $C_{19}H_{13}O_2N_3$: C, 72.36; H, 4.16; N, 13.34. Found: C, 72.52; H, 4.57; N, 13.48.

1,2,4-Triphenyl-6-nitro-2,3-cyclopentadienodihydropyridazine, $C_7H_2N_2(C_6H_5)_3(NO_2)$ (XV).—This is prepared by digesting a hot benzene solution of nitrodibenzoylcyclopentadiene with an excess of phenylhydrazine for 8 or 9 hours at the temperature of the water bath. The red crystals of the triphenyl derivative are slowly precipitated. The monophenyl hydrazone as described by Thorp and the writer[2] might first have been prepared and its conversion to the pyridazine accomplished simply by boiling its solution in alcohol or benzene; this step, however, is unnecessary and not to be recommended. Triphenylcyclopentadienopyridazine is only fairly soluble in chloroform or benzene; slightly soluble in acetone, acetic ester or acetic acid and insoluble in ether, alcohol, ligroin or water. It crystallizes best from chloroform in small orange-red prisms melting sharply at 287°. It is unaffected by acids and alkalies.

0.1710 g. subst. gave 0.4823 g. CO_2 and 0.0734 g. H_2O.

0.1850 g. subst. gave 19.1 cc. N_2 (25° and 718 mm. over H_2O).

Calc. for $C_{25}H_{17}O_2N_3$: C, 76.70; H, 4.38; N, 10.74. Found: C, 76.93; H, 4.81; N, 10.81.

The formation of this new class of compounds, the condensed 5-carbon ring and pyridazine, is made possible through the presence of a basic hydrogen atom in the hydrazine substituent of the carbocyclic ring in

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[1] *Loc. cit.*

[2] THIS JOURNAL, 35, 73 (1913).

proper position to an hydroxyl in an adjacent substituent. For the aid granted by the trustees of the Wolcott Gibbs Fund in the prosecution of this research and for the assistance rendered on this account by Messrs. G. O. Gutekunst and Edgar C. Britton the writer wishes to express his appreciation and indebtedness.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XIV. BROMINATION OF HYDROCARBONS BY MEANS OF BROMINE AND NITRIC ACID.

BY RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

Received September 19, 1916.

In continuation of the researches of the action of *aqua regia* on organic bodies in general, the study of the action of a mixture of nitric and hydrobromic acids was taken in hand. In analogy with the action of *aqua regia*, it was thought that a mixture of nitric and hydrobromic acids, which is capable of giving bromine in the nascent state, would effect brominations more satisfactorily than bromine, and this has been found to be the case. The bromination of benzene has been effected by this reagent with the formation of monobromobenzene in good yield. As a considerable amount of nitric acid is used up, in the first instance, to liberate bromine from hydrobromic acid, it was found satisfactory to employ bromine and nitric acid only. In fact, the mixture of the acids is less active than bromine and nitric acid on account of the water added as the medium of hydrobromic acid.

As bromination could as well be carried out directly with or without the help of a carrier, the advantages of the method may be pointed out. In the case of ordinary bromination with or without carrier, the reaction is one of substitution, liberating an amount of hydrobromic acid equal to that of bromine which enters the molecule. But in the case of bromination in the presence of nitric acid, all the bromine enters the molecule, the nitric acid helping the oxidation of hydrobromic acid to bromine, as soon as it is formed. This bromine is available for further bromination. Hence it is evident that only half the usual amount of bromine will be required for brominations by this method. Here the nitric acid acts as the oxidizing agent facilitating the introduction of bromine, itself being reduced to nitrous gases. Furthermore, the reagent is very active, effecting brominations very rapidly and energetically, so much so that frequent rupture of substances subjected to its action is the result. Those brominations which require a considerable time for their course even with the help of a carrier, could be effected most speedily and satisfactorily. The method is specially suitable for tolerably light hydrocarbons but with the higher ones the process is not quite satisfactory as the chances of