difficulty, provided nitric-sulfuric acid is substituted for the 48° Be. nitric acid of Carter's method for the conversion of tetranitro-diphenylamine into hexanitro-diphenylamine, and a lower temperature of nitration is maintained in that operation.

The very satisfactory results obtained in converting a crude incompletely nitrated tetranitro-diphenylamine product into hexanitro-diphenylamine by the use of nitric-sulfuric acid at a maximum temperature of 32°, suggest the possibility of eliminating altogether the intermediate preparation of tetranitro-diphenylamine and proceeding directly in one operation from dinitro-diphenylamine to hexanitro-diphenylamine. This procedure should result in considerable reduction in time and cost of production.

PITTSBURGH, PA.

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

THE CONDENSATION OF β-AMINO-PROPIOPHENONE WITH NITROMALONIC ALDEHYDE.

BY WILLIAM J. HALE AND EDGAR C. BRITTON.

Received April 8, 1919.

The formation of a pyrrole derivative by the condensation of nitromalonic aldehyde with an ester of aminoacetic acid has been demonstrated in the work of Hale and Hoyt.[1] One aldehydic group of this aldehyde was herein found to react primarily with the amino group of the ester and result directly in the production of an intermediate compound (I) which immediately rearranges itself into the form (II), α-carbethoxy-β-methylamino-α-nitro-acrolein, a point just recently explained by Hale and Honan.[2] The next step in the condensation—that of involving the second aldehydic group in reaction with the methylenic group of the aliphatic ester substituent in (II), was brought about by mild alkali and resulted in the formation of the pyrrole (III). In the work of Hale and Honan[3] this investigation was extended to a study of the condensation of β-alanine ester with nitromalonic aldehyde. In this instance two methylenic groups are situated between the amino group and the carbethoxyl group. It was anticipated accordingly that here, after the formation of the first step in the reaction to an acrolein derivative, we should have present the possibility for a pyridine synthesis through the condensation of the aldehydic group with the second methylenic group or that one adjacent to the carbethoxyl group itself. Negative results, however, dismissed this expectancy, and indicated quite clearly that the carbethoxyl group is

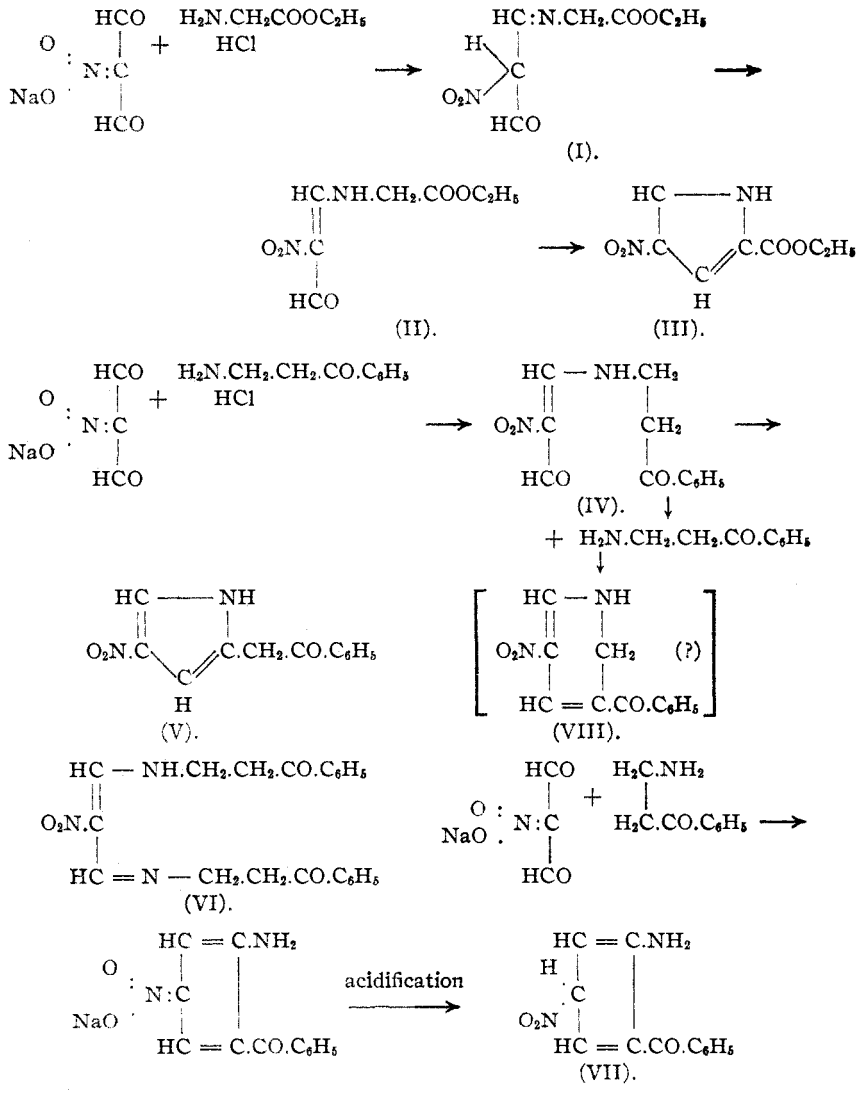
[1] THIS JOURNAL, 37, 2538 (1915).
[2] *Ibid.*, 41, 770 (1919).
[3] *Loc. cit.*

not sufficiently activating upon the adjacent methylenic group to induce the condensation of the latter with the free aldehydic group of this same acrolein derivative. Further it was noted that the interposition of a second methylenic group between the amino group and the carbethoxyl group, as seen in the formula for β-alanine ester over that of amino-acetic ester, reduces the activating tendency of the carbethoxyl group upon the first methylenic group, or that one situated adjacent to the amino group itself, and to such an extent that a pyrrole synthesis no longer was readily obtainable.

We have undertaken to bring into this investigation a compound containing a keto group in place of the carbethoxyl group of Hale and Honan. The greater activating tendency of the keto group upon neighboring labile hydrogen atoms over that of a carbethoxyl group is of course well known. For this purpose we selected β-amino-propiophenone ($NH_2.CH_2.CH_2.CO.C_6H_5$). The corresponding ketone with an alkyl replacing the phenyl group cannot be employed by reason of the decidedly marked reaction of our 1,3-dialdehyde to condense with it directly to form substituted phenols.[1] The preparation of β-amino-propiophenone offered at first several difficulties but these have been cleared away entirely as reported in our previous communication.[2] When sodium nitromalonic aldehyde and β-amino-propiophenone hydrochloride are simply brought together in aqueous solution and gently warmed to about 50° for $^1/_2$ day there separates slowly an orange-colored precipitate. Upon repeated crystallization from alcohol the product appears in colorless prisms melting at 153°. The structure of this compound as shown in (IV), represents it to be a 2-benzoyl-β-ethylamino-α-nitro-acrolein. Upon repeating this condensation between nitromalonic aldehyde and β-amino-propiophenone in aqueous solution and with the presence now of a little sodium hydroxide we hoped to bring about the intramolecular condensation to a pyrrole (V), analogous, of course, to the transformation of Hale and Hoyt's compound (II) into (III). When, however, a little alkali is added to the aqueous mixture of the aldehyde and the amino ketone in equimolecular quantities a copious white precipitate immediately makes its appearance and when crystallized from alcohol melts at 145°. Upon doubling the quantity of β-amino-propiophenone hydrochloride in the original aqueous mixture we found indeed that we doubled the amount of this compound precipitated. This, of course, is to be inferred from the constitution of the compound which we find accords with the structure (VI), namely, that of 2-benzoyl-α-ethylamino-2-benzoyl-γ-ethylimino-β-nitropropylene. An analysis of its double chloroplatinic salt also checks this formula.

[1] *Am. Chem. J.*, 39, 680 (1908).

[2] THIS JOURNAL, 41, 841 (1919).



It was later found that the pyrrole derivative (V), could be prepared from the acrolein compound (IV), by the use of alcoholic sodium hydroxide. The isolation of the acrolein compound is not at all necessary if considerable sodium hydroxide is added directly to an alcoholic solution of sodium nitromalonic aldehyde and β-amino-propiophenone hydrochloride, in equimolecular quantities, after gently warming for a short time upon a water bath. Upon crystallizing from alcohol α-phenacyl-β′-nitropyrrole (V) appears in light yellow prisms melting at 170°. The analysis of a double chloroplatinic salt further checked the constitution assigned above.

Upon acidification of the strongly alkaline mother liquor left after the separation of the pyrrole we obtained a non-crystalline compound which will be mentioned again shortly.

The use of piperidine was of course tried as a condensing agent upon the acrolein compound (IV). When this latter compound was allowed to stand in alcoholic solution with a few drops of piperidine and at a temperature of 40°, the formation of white crystalline precipitate was observed. Upon crystallization from alcohol it gave the melting point of 145° and in all respects proved to be identical with the propylene derivative (VI), obtained by the action of two molecules of β-amino-propiophenone upon one molecule of nitromalonic aldehyde. The presence of free nitromalonic aldehyde was identified in the mother liquor (left after the removal of the propylene derivative) through acidification and the isolation of *sym*-trinitrobenzene.[1] There can be no doubt therefore concerning the influence of the piperidine in effecting here first a hydrolysis of some of the acrolein derivative (IV), and subsequent condensation of free β-amino-propiophenone with unchanged acrolein derivative. When a concentrated alcoholic solution of sodium hydroxide is allowed to act upon the acrolein derivative the same hydrolysis may be effected with precipitation of the propylene derivative; the action, however, is not as complete as when piperidine is employed. The fact however that hydrolysis of the acrolein derivative may take place in strongly alkaline medium gave us a direct clue as to what particular product may be looked for in the mother liquor left after removal of the pyrrole from its strongly alkaline reaction mixture. The free β-amino-propiophenone once liberated from the intermediate stage, that of the acrolein derivative (IV), and even from the propylene derivative (VI), may indeed enter into condensation with free nitromalonic aldehyde directly through the two methylenic groups to the formation of a cyclopentadiene (VII). This type of condensation involving this same nitromalonic aldehyde and acetonyl acetone, was first investigated by Hale.[2] Their product, a diacetyl nitro-cyclopentadiene is acid in character, through the tautomeric isonitro group, and naturally here too we should expect the acid character of 2-amino-3-benzoyl-5-nitrocyclopentadiene to predominate over any basic properties. Such compounds may be expected to be only slightly soluble in the ordinary organic solvents and decomposing at high temperature. The substance precipitated from the alkaline mother liquor of the pyrrole, answers all of these qualifications. It is impossible to purify this brown amorphous substance to any great extent. Analyses, however, would indicate that a benzoyl-amino-nitro-cyclopentadiene was at hand.

A further possibility of the acrolein derivative undergoing a condensation

[1] *Am. Chem. J.*, **22**, 95 (1899).

[2] *Ber.*, **45**, 1596 (1912); THIS JOURNAL, **34**, 1580 (1912).

to a dihydro-pyridine derivative (VIII), seemed at first likely but no actual isolation of any compound possessing such structure could be accomplished. We conclude therefore that in the acrolein derivative (IV), as intermediate step in these condensations, the presence of the keto group separated from the amino group by two intervening methylenic groups is sufficiently able to activate that methylene group adjacent to the amino group to such an extent that its condensation with the free aldehyde group is readily possible. A marked contrast in this respect from that example of β-alanine ester of Hale and Honan where a carbethoxyl group in the same position failed almost entirely to effect this type of condensation. Though the keto group may be expected to render more active the hydrogen atoms on the methylene group adjacent to it, this slight amount of activation would seem outweighed by the greater tendency toward formation of 5-membered rings—that of the pyrrole.

Experimental Part.

2-Benzoyl-β-ethylamino-α-nitro-acrolein, $C_6H_5.CO.(CH_2)_2.NH.CH:C(NO_2).CHO$ (IV).—The preparation of β-amino-propiophenone has been described in our earlier publication.[1] When 5 g. of this ketone in the form of its hydrochloride and 4.2 g. of sodium nitromalonic aldehyde (an equimolecular proportion) were dissolved in 50 cc. of water and the solution allowed to stand at 50° for 10–12 hours the precipitation of this acrolein compound is almost complete. The reaction mixture was then cooled and the orange-colored product filtered off. The yield is about 75% of the theoretical. Upon crystallization from alcohol the product appears in small prisms practically colorless and melting at 153°. This benzoyl-ethylamino-nitro-acrolein is readily soluble in acetone or glacial acetic acid; fairly soluble in alcohol, benzene, chloroform, ethyl acetate, or water; slightly soluble in ether; and insoluble in ligroin.

Calc. for $C_{12}H_{12}O_4N_2$: C, 58.02; H, 4.84; N, 11.34. Found: C, 58.59; H, 5.02; N, 11.35.

This nitro-acrolein derivative gives with silver nitrate the characteristic test for an aldehyde and by means of the Liebermann test a secondary amine group was shown to be present.

2-Benzoyl-α-ethylamino-2-benzoyl-γ-ethylimino-β-nitropropylene, $C_6H_5.CO.(CH_2)_2.NH.CH : C(NO_2).CH : N.(CH_2)_2.CO.C_6H_5$ (VI).—Five g. of β-amino-propiophenone (2 mol.) and 2.1 g. of sodium nitromalonic aldehyde (1 mol.) were dissolved in 100 cc. of water, and 2 cc. of 20% sodium hydroxide solution added. A white precipitate appeared immediately. This precipitate filtered off and crystallized from alcohol, gave fine, colorless needle clusters melting at 145°. The yield is 84% of the theoretical amount. This nitropropylene derivative is readily soluble in

[1] *Loc. cit.*

acetone, chloroform or glacial acetic acid; fairly soluble in alcohol, benzene or ethyl acetate; and insoluble in ether, ligroin or water.

Calc. for $C_{21}H_{21}O_4N_3$: C, 66.47; H, 5.58; N, 11.08. Found: C, 66.59; H, 5.60; N, 11.07.

When a slight excess of chloroplatinic acid is added to an alcoholic solution of this nitropropylene compound an orange-colored precipitate appears at once. This product was filtered off, well washed with dil. hydrochloric acid and dried over sulfuric acid. It melted at 208°. By analysis it served well to check the value required for the molecular weight of the nitropropylene.

Calc. for $(C_{21}H_{21}O_4N_3)_2.H_2PtCl_6$: Pt, 16.71. Found: Pt, 16.60.

By the application of either the Hinsberg or Liebermann tests indication of the presence of a secondary amine was well marked. Upon boiling a portion of this nitropropylene compound with conc. hydrochloric acid and allowing the yellow solution to cool a precipitate of the nitro-acrolein derivative appears and β-amino-propiophenone may be shown to be present in the solution. This decomposition corresponds exactly with the decomposition in acid solution of the so-called nitromalonic di-anil reported by Hill and Torrey.[1] Upon the addition of sodium hydroxide to an aqueous solution of the nitro-acrolein derivative (IV) the immediate precipitation of this colorless nitropropylene compound was observed. In all respects the precipitate here and that produced in the prescribed manner above were identical. In the hydrolysis of the acrolein derivative, which must have ensued, we should expect to find nitromalonic aldehyde left free in the solution in that the liberated β-amino-propiophenone must necessarily have combined with a portion of the unhydrolyzed acrolein derivative. The point was proved by concentration of the mother liquor to small volume and addition of hydrochloric acid. After a short time beautiful crystals of *sym*-trinitrobenzene made their appearance, a condensation distinctly characteristic of nitromalonic aldehyde.[2]

α-Phenacyl-β′-nitropyrrole, $C_6H_5.CO.CH_2.C_4H_3N.NO_2$ (V).—Equimolecular quantities of β-amino-propiophenone hydrochloride (5 g.) and sodium nitromalonic aldehyde (4.2 g.) were dissolved in 25–30 cc. of 50% alcohol, and 15 cc. of 20% sodium hydroxide solution added. The red solution is warmed for a few moments and then allowed to stand a 50°. The red precipitate which slowly forms, is filtered off and washed with dil. alcohol. The yield is only 30% of the theoretical amount. Crystallization from alcohol yielded small, lemon-yellow prisms melting at 170°. α-Phenacyl-β′-nitropyrrole is readily soluble in acetone or glacial acetic acid; fairly soluble in alcohol, chloroform, benzene or ethyl acetate; and insoluble in ether, ligroin or water.

[1] *Am. Chem. J.*, **22**, 100 (1899); see also Hale and Honan, *Loc. cit.*

[2] *Loc. cit.*

This same pyrrole may be prepared by mixing a portion (one g.) of the benzoyl-ethylamino-nitro-acrolein (IV) with 70% alcohol (10 cc.) and adding to this suspension a 20% sodium hydroxide solution (3 cc.). After gently warming for a half hour at 50°, the reaction is complete and the pyrrole derivative may be filtered off and treated as above. The yield in this procedure is however, scarcely better than when carrying out the reaction between the original components.

Calc. for $C_{12}H_{10}O_3N_2$: C, 62.59; H, 4.35; N, 12.17. Found: C, 63.36; H, 4.26; N, 12.70.

In order to check the molecular weight of the pyrrole molecule the chloroplatinic salt of the compound was prepared in the usual manner. The orange-colored precipitate was thoroughly washed with dil. hydrochloric acid, then with water and finally with acetone, after which it was dried *in vacuo* over sulfuric acid. The compound decomposes above 300° without melting.

Calc. for $(C_{12}H_{10}N_2O_3)_2.H_2PtCl_6$: Pt, 22.43. Found: Pt, 21.97.

It was hoped that by means of an oxidizing agent we could reduce the side chain to a carboxyl itself and thus be able to check the constitution of the pyrrole through identification with the well-known β'-nitro-α-carbopyrrolic acid, previously established by Hale and Hoyt.[1] But all attempts at oxidation have failed. Alkali fusion mixtures were of course, disastrous, owing to the presence of the nitro group. The identification of a secondary amine in the pyrrole was easily accomplished through the agency of either the Hinsberg reaction or the Liebermann nitroso-amine reaction. The familiar pyrrole red color upon a pine stick moistened with hydrochloric acid was most marked. There can be little or no doubt concerning the structure we have assigned. The previous investigations of Hale and Hoyt have thoroughly established the course of the reaction.

The red alkaline mother liquor left after separating the pyrrole yielded no further quantity of pyrrole either upon long standing or upon slow evaporation to small bulk (temperature of 50°). When, however, the liquor was acidified there appeared a considerable quantity of a red amorphous precipitate. This precipitate no longer gives the characteristic tests for a pyrrole and shows a much less degree of solubility in the ordinary solvents than does the pyrrole itself. Its purification was brought about by solution in acetone and precipitation therefrom by addition of ligroin. The precipitate was then dissolved in hot alcohol and upon cooling the light brown or yellow amorphous product separates out. The product thus purified decomposes between 127° and 132° and analyzes well for 2-amino-3-benzoyl-5-nitro-cyclopentadiene (VII). This cyclopentadiene is readily soluble in chloroform, acetone, ethyl acetate or glacial acetic

[1] *Loc. cit.*

acid; fairly soluble in alcohol; slightly soluble in benzene; and insoluble in ether, ligroin or water.

Calc. for $C_{12}H_{10}O_3N_2$: C, 62.59; H, 4.35; N, 12.17. Found: C, 62.00; H, 4.50; N, 12.50.

The hydrolysis of the acrolein derivative in the presence of alkali, as stated in an earlier part, undoubtedly makes possible the condensation between nitromalonic aldehyde and the two methylene groups of the liberated amino ketone. Of course too great a concentration of alkali is likely to decompose this amino ketone so soon as liberated but this does not occur with the concentration of alkali employed by us. The cyclopentadiene thus made possible of formation contains an isonitro group and readily forms salts. The free substance cannot be precipitated from its alkali salts by the addition of carbon dioxide and thus is analogous to the nitro-cyclopentadiene described by Hale.[1]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

NEW ADDITION COMPOUNDS OF QUINOLINE WITH CERTAIN INORGANIC SALTS.

BY JAMES H. WALTON AND CHUAN LING LIANG.

Received April 12, 1919.

The fact that quinoline is an unusually good solvent for a large number of the common substances has not been generally recognized. Not only does it dissolve organic compounds, but a large number of inorganic salts, in particular the acetates, iodides and chlorides of most of the metals, are readily soluble in this substance. Hydrogen peroxide is very soluble in quinoline[2] and the solution undergoes catalytic decomposition quite similar to aqueous solutions of this substance.[3] Quinoline shows a great tendency, moreover, to form addition products with many inorganic substances. This paper describes the preparation of addition compounds of quinoline with certain thiocyanates and acetates.

Experimental.

Reagents.—Synthetic quinoline was used. It was dried over caustic potash and distilled, the portion coming over between 230° and 237° being used in the experiments.

The salts used were the purest obtainable, and were recrystallized whenever possible. Those insoluble in water were prepared from pure materials according to standard methods.

Method of Procedure.—The quinoline was saturated with the particular

[1] *Loc. cit.*

[2] Walton and Lewis, THIS JOURNAL, 38, 633 (1916).

[3] Walton and Jones, *Ibid.*, 38, 1956 (1916).