alcohol with nitric acid. Fischer and Tafel¹ found that glycerol was oxidized with bromine in alkalin solution to glyceric aldehyde and dihydroxyacetone. It was thought that alkalin bromine solutions might react in the same manner on styrolene alcohol to give benzoylcarbinol and mandelic aldehyde. Two grams of styrolene alcohol, dissolved in water, were added to a solution of 35 grams of potassium carbonate and 15 grams of bromine, the total volume of the reaction mixture being 100 cc. After standing over night, the reaction mixture yielded 0.81 gram of benzoylcarbinol (theory = 1.97 grams, therefore 41.1%), which was identical in every respect with a specimen prepared by the hydrolysis of acetophenone acetate.² In this experiment, benzoic acid and an oil which hardened to a viscous mass were also obtained. This reaction is to be studied further.

Solutions of copper nitrate, sulfate and acetate have no effect on styrolene alcohol, even when the reaction mixtures are kept at 100°.

In conclusion, we wish to thank Mr. C. R. Parkinson of this laboratory for valuable assistance rendered during the progress of this work.

COLUMBUS, OHIO.

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

STUDIES IN THE CYCLOPENTADIENE SERIES. II.

2,3-DIBENZOYL-5-NITROCYCLOPENTADIENE.³

BY WILLIAM J. HALE AND LAMBERT THORP.

Received November 16, 1912.

The condensation of acetylacetone with the 1,3-dialdehyde, nitromalonic aldehyde, has been shown to give a 2,3-diacetyl-5-nitrocyclopentadiene.⁴ The presence of acetone nuclei in this diketone makes possible also the formation of phenol derivatives during the course of the reaction,⁵ but the proportion of the latter (20%) is not large in comparison with the cyclopentadiene produced.

In order to favor only the cyclopentadiene condensation it became necessary, therefore, to employ a diketone of similar structure to acetylacetone but one containing aryl groups in place of the two active methyl groups of the latter. As the simplest example of this 1,4-diketone class we have taken diphenacyl, $C_6H_5.CO.CH_2.CH_2.CO.C_6H_5$. This ketone, however, has the disadvantage of being only slightly soluble in an aqueous-alcoholic solution, the medium of these condensations. Acetylacetone, on the other hand, is very soluble in this medium. Consequently a com-

¹ *Ber.*, 20, 3385.

² *Am. Chem. J.*, 35, 120.

³ The work described in this article formed part of a thesis submitted for the degree of Doctor of Philosophy in the University of Michigan by Lambert Thorp.

⁴ *Ber.*, 45, 1596 (1912); *THIS JOURNAL*, 34, 1580 (1912).

⁵ *Am. Chem. J.*, 39, 680 (1908).

parison of the relative influence of phenyl and methyl groups upon cyclopentadiene ring formation from a 1,4-diketone system is not highly favored. Sodium hydroxide proved to be the best condensing agent and even here a gentle heating, in the neighborhood of 40° , was found necessary to effect a complete reaction in any time short of ten days. From the short time (36-48 hours) required for complete condensation between acetylacetone and this 1,3-dialdehyde even at room temperatures, we may reasonably assume that the influence of the phenyl group retards considerably the activity of the carbonyl group attached to it.

Upon acidification of the reaction mixture, containing unimolecular quantities of sodium nitromalonate aldehyde and diphenacyl, the condensation product appears as a yellow flocculent precipitate. The reaction may be indicated as follows:

The constitution of this product has been established through a study of its reactions of decomposition. With nitric acid, for example, it is oxidized to carbon dioxide, oxalic acid and benzoic acid. The oxidation by potassium permanganate in alkaline solution takes a similar course and gives much more satisfactory results. In the reaction mixture were to be found, as potassium salts, 3 molecules of carbon dioxide, 1 molecule of oxalic acid, 1 molecule of nitric acid and 2 molecules of benzoic acid. The graphical representation of this oxidation may be expressed as follows:

The presence of a nitro group on the 5-carbon atom of a cyclopentadiene would naturally give an acid character to the hydrogen atom attached to this same carbon atom; thus, as with nitromethane, the formation of isonitro salts would be expected. The ease with which this cyclopentadiene dissolves in sodium hydroxide solution to form the soluble sodium salt and yet its failure to form this sodium salt by the action of even a boiling sodium carbonate solution shows at once the weakly acid character of the hydrogen atom. The 5-hydrogen atom of 2,3-diacetyl-5-nitrocyclopentadiene, on the other hand, will readily liberate carbon dioxide from a warm solution of sodium carbonate. It may be concluded, therefore, that the acid character of the 5-hydrogen atom of these 2,3-disubstituted cyclopentadienes is considerably lessened when a benzoyl group replaces

an acetyl substituent. The sodium, barium and silver salts of this dibenzoylcyclopentadiene have been prepared.

The presence of the two carbonyl groups can not be proved through simple condensations with hydroxylamine, phenylhydrazine or aniline, since only a monoxime, monophenylhydrazone or monanil could be prepared. Exactly analogous results were obtained in the case of the diacetylnitrocyclopentadiene.¹ The monophenylhydrazone itself is not at all stable, but readily undergoes an intramolecular condensation with the production of a two-ring compound now under investigation. The proof for the structure of the diacetyl derivative as given in the preceding paper may be taken also as substantiating the structure of this dibenzoyl compound. The assumption that each phenyl group occupies the same position as a methyl group of the diacetylcyclopentadiene is verified in the production of the corresponding molecular quantities of benzoic acid in place of acetic acid in the oxidation already mentioned.

The presence of two double bonds in the compound can not be shown through addition reactions with halogens or halide acids. The resistance of dibenzoylnitrocyclopentadiene to this class of compounds is, no doubt, due to the strongly negative substituents already in the ring. The same result was noted in the case of the diacetylnitrocyclopentadiene and also to some extent with triphenylcyclopentadiene of Newmann.² In this connection the work of Wieland and Stenzl³ upon butadienes may be cited. The introduction of two phenyl groups into butadiene was found, by these authors, to alter the character of the double bonds in such manner as to make the compound approach most closely the aromatic type of substances.

The structures assigned to the dibenzoyl and diacetyl derivatives must accord with each other. In fact, the production of the dibenzoyl derivative from a 1,4-diketone of identical structure as that 1,4-diketone from which the diacetyl derivative was prepared, and yet one in which the end methyl groups of this latter diketone are now replaced by phenyl groups that do not in any way enter into the reaction, proves conclusively the course of the condensation between the 1,3-dialdehyde and the 1,4-diketone. There remains, therefore, just one possibility for ring formation, namely, the condensation of the two aldehyde groups severally with the adjacent methylenic groups of the diketone, and the consequent production of a cyclopentadiene. The further assumption that there occurs no shift in the double bonds resulting from this particular condensation rests upon the acidity of the hydrogen atom in conjunction with the nitro group. This same tendency to form isonitro or aci-nitro salts, as

¹ THIS JOURNAL, 34, 1583 (1912).

² *Ann.*, 302, 236 (1898).

³ *Ibid.*, 360, 306 (1908).

was originally present in nitromalonic aldehyde itself, still persists and leaves no room for doubt as to the similarity of the two classes of compounds, and at the same time substantiates the structure already assigned to these cyclopentadienes.

Experimental.

Diphenacyl may be prepared according to the method of Knorr¹ by the action of iodine upon the sodium salt of benzoylacetic ester, and the final saponification of the dibenzoylsuccinic ester thus produced. A somewhat better yield, however, is obtained when the method of Fritz² is followed. According to this latter method, 20 grams of phenacyl bromide were dissolved in 100 grams of absolute alcohol. To this solution, cooled by means of a freezing mixture, a cold solution of 1.2 grams of sodium in 24 grams of absolute alcohol was gradually added. After an hour's cooling the reaction mixture was poured into a large volume of water and the 8-bromodiphenacyl filtered off. This monobrom derivative (12 grams in weight) was now dissolved in 600 grams of warm 95% alcohol and 30 grams of magnesium powder added. This mixture was boiled for 3 hours under a reflux condenser and then filtered. From the filtrate, concentrated over a steam bath to one-third of its original volume, the diphenacyl separated upon cooling. After crystallization from alcohol the yield amounted to 6 grams or 50% of the theoretical.

2,3-Dibenzoyl-5-nitrocyclopentadiene, $C_8H_3(NO_2)(CO.C_6H_5)_2$ (II). To a solution of 1.6 grams (1 mol.) of sodium nitromalonic aldehyde³ and 0.8 gram (2 mol.) of sodium hydroxide in a mixture of 75 cc. of alcohol and 25 cc. of water, 2.4 grams (1 mol.) of diphenacyl were added. The reaction mixture, in which the ketone is only slightly soluble, is kept at a temperature of 40° from eight to ten days or until homogeneous. The dark red solution is then diluted with twice its volume of water, filtered, and acidified with dilute hydrochloric acid. The yellow flocculent precipitate of the cyclopentadiene, filtered off and dried, weighed 2.8 grams, a weight corresponding to 75% of the theoretical value based upon the weight of aldehyde taken. *2,3-Dibenzoyl-5-nitrocyclopentadiene* crystallizes best from acetic ester or acetone in yellow prisms which melt with decomposition at 237–8°. It is insoluble in water; only slightly soluble in alcohol, ether, acetic acid or ligroin; and fairly soluble in benzene, chloroform, acetone or acetic ester.

0.1699 gram substance: 0.4477 gram CO_2 , 0.0584 gram H_2O ; 0.3710 gram substance: 15.2 cc. N_2 (22°, 732 mm. over H_2O).

Calculated for $C_{19}H_{13}O_4N$: C, 71.45; H, 4.11; N, 4.39.

Found: C, 71.86; H, 3.84; N, 4.45.

¹ *Ann.*, **293**, 70 (1896); *Ber.*, **27**, 1168 (1894).

² *Ber.*, **28**, 3033 (1895); *Ibid.*, **29**, 1750 (1896).

³ *Am. Chem. J.*, **22**, 25 (1899).

Sodium Salt, $C_5H_2(NO.ONa)(CO.C_6H_5)_2$ (I).—The cyclopentadiene was treated with one equivalent of sodium dissolved in fifteen parts of alcohol. A little water was then added to complete the solution and the yellow sodium salt precipitated in crystallin condition by the addition of ether. This sodium salt is readily soluble in water, from a concentrated solution in which it may be obtained, by slow crystallization, in the form of thick needles. It holds no water of crystallization.

0.1800 gram salt gave 0.0373 gram Na_2SO_4 .

Calculated for $C_{19}H_{12}O_4N.Na$: Na, 6.76. Found: Na, 6.71.

Barium Salt, $[C_5H_2(COC_6H_5)_2(NO.O)]_2Ba$.—The barium salt was prepared by the addition of barium chloride to a solution of the sodium salt. The precipitated yellow barium salt is only slightly soluble in water and crystallizes from its hot aqueous solution without water of crystallization.

0.2293 gram salt gave 0.0698 gram $BaSO_4$.

Calculated for $(C_{19}H_{12}O_4N)_2Ba$: Ba, 17.77. Found: Ba, 17.92.

Silver Salt, $C_5H_2(NO.OAg)(COC_6H_5)_2$.—The cyclopentadiene was dissolved in dilute ammonium hydroxide solution and the excess of ammonia driven off by evaporation on the water bath. To this diluted solution of the ammonium salt of the cyclopentadiene, silver nitrate was now added. The silver salt is thus precipitated as a yellow crystallin product closely resembling the sodium salt already described. It is slightly soluble in water and decomposes with explosive violence upon heating.

0.1816 gram salt gave 0.0456 gram metallic silver.

Calculated for $C_{19}H_{12}O_4NAg$: Ag, 25.33. Found: Ag, 25.11.

2,3-Dibenzoyl-5-nitrocyclopentadiene Monoxime,

$C_5H_8(NO_2)(COC_6H_5)(C(C_6H_5) : NOH)$.—The free dibenzoylnitrocyclopentadiene (0.5 gram) was dissolved in 30 cc. of a 50% alcoholic solution containing 0.52 gram (excess) of sodium hydroxide. After the addition of 0.44 gram of hydroxylamine hydrochloride, dissolved in a little water, the mixture was kept at the boiling point for 2 hours. Upon acidification with hydrochloric acid the light yellow monoxime was precipitated. Crystallization from alcohol gave the pure product in the form of slender needles and melting with decomposition at $155-6^\circ$. This oxime is readily soluble in benzene or chloroform; fairly soluble in ether, alcohol or carbon disulfide; difficultly soluble in ligroin; and insoluble in water.

0.1473 gram substance: 0.3668 gram CO_2 , 0.0567 gram H_2O ; 0.1174 gram substance: 9.2 cc. N_2 (23° and 737 mm. over H_2O).

Calculated for $C_{19}H_{14}O_4N_2$: C, 68.25; H, 4.22; N, 8.39.

Found: C, 67.94; H, 4.31; N, 8.52.

2,3-Dibenzoyl-5-nitrocyclopentadiene Monanil,

$C_5H_9(NO_2)(COC_6H_5)(C(C_6H_5) : N.C_6H_5)$.—An excess of aniline (5 molecules) was added to a concentrated solution of the cyclopentadiene dissolved in benzene and the solution heated on a water bath for one-half

hour. Upon standing, this solution slowly yields a yellow crystallin precipitate of the monanil; 3-4 days are required for the complete separation. The product was purified by crystallization from a solution in benzene to which ligroin has been added. The monanil appears in slender, yellow needles which melt at $264-5^{\circ}$. It is insoluble in water or ligroin; slightly soluble in alcohol or ether; fairly soluble in benzene, carbon disulfide, acetic acid, chloroform, acetone or acetic ester.

0.1700 gram substance: 11.1 cc. N_2 (22° and 732 mm. over H_2O).

Calculated for $C_{26}H_{18}O_3N_2$: N, 7.11. Found: N, 7.08.

2,3-Dibenzoyl-5-nitrocyclopentadiene Monophenylhydrazone, $C_6H_5(NO_2)(COC_6H_5)(C(C_6H_5) : N.NHC_6H_5)$. — One gram of the free dibenzoylnitrocyclopentadiene was dissolved in water containing three equivalents of sodium hydroxide and in concentration approximately normal. A warm aqueous solution of phenylhydrazine hydrochloride was then added in an amount more than sufficient to react with the sodium salt as well as with all alkali present. The yellow crystallin monophenylhydrazone, which appears in a short time, is filtered off as soon as possible and thoroughly washed with water. Though the product appears here in the form of yellow needles, it is practically impossible to recrystallize owing to its tendency to undergo an intramolecular transformation. This change takes place when its solutions in various solvents are gently warmed. For this reason also no definite melting point can be obtained, a temperature of 90° practically sufficing for the total transformation. The product is insoluble in water; slightly soluble in ligroin or acetic acid; fairly soluble in ether; readily soluble in alcohol, benzene, chloroform or carbon disulfide. For final purification it was found expedient to dissolve the substance in alcohol and precipitate again by the addition of sodium chloride solution. The addition here of water alone throws out the phenylhydrazone in a colloidal condition. This new product, formed so readily from the phenylhydrazone, consists undoubtedly of two rings, but its constitution is not yet determined.

0.1555 gram substance: 15.1 cc. N_2 (24° and 728 mm. over H_2O).

Calculated for $C_{26}H_{19}O_3N_3$: N, 10.27. Found: N, 10.36.

Oxidation of 2,3-Dibenzoyl-5-nitrocyclopentadiene. (a) *With Nitric Acid.* — One gram of the dibenzoylnitrocyclopentadiene, together with 40 cc. of dilute nitric acid (sp. gr. 1.22), were placed in a 100 cc. flask, fitted with glass connections to a reflux condenser, and the mixture boiled until complete solution was brought about. The presence of carbon dioxide was detected in the acid vapors. The contents of the flask were finally diluted, filtered and made alkaline with ammonium hydroxide, after which the solution was acidified with acetic acid and a calcium chloride solution added. The precipitated calcium oxalate corresponded only approximately to one molecule of oxalic acid per molecule of cyclopentadiene. Benzoic

and nitrobenzoic acid were also found to be present in the reaction mixture. The production of oxalic and carbonic acids, through this oxidation, seemed to vary between wide limits, hence no data sufficiently instructive could be relied upon. The oxidation, however, with potassium permanganate yielded much better results.

(b) *With Potassium Permanganate.*—One gram of the cyclopentadiene was dissolved in 100 cc. of water containing four equivalents of potassium hydroxide, and the solution heated on the water bath under a reflux condenser provided with a soda-lime tube. A tenth-normal potassium permanganate solution was now added in portions of 10 cc. and at the same time the reaction mixture was kept distinctly alkaline by further additions of potassium hydroxide. In all, about 500 cc. of the permanganate solution were required. With the oxidation completed, the addition of a little alcohol destroyed the excess of permanganate. The manganese dioxide was now filtered off and washed thoroughly with water. The washings and original filtrate were then treated with an excess of ammonium chloride, in order to decompose the potassium hydroxide, and finally with a solution of calcium chloride. The dried precipitate, consisting of calcium oxalate and carbonate, weighed 1.5634 grams. When this precipitate was dissolved in dilute sulfuric acid and the solution titrated with 0.05 *N* KMnO_4 , 114 cc. of this permanganate were required. This, therefore, is equivalent to 0.3648 gram CaC_2O_4 . Subtracting this weight from the weight of total precipitate just mentioned (1.5634) we have 1.1986 grams as the weight of CaCO_3 present.

The filtrate from the mixed precipitate of oxalate and carbonate was made strongly alkaline with potassium hydroxide and evaporated to a small volume. After acidification with hydrochloric acid the solution was extracted repeatedly with ether. The ether extract was evaporated and the residual benzoic acid purified by sublimation. The weight obtained, 0.737 gram, corresponds well with the theoretical value for two molecules of benzoic acid. Calculated upon one molecule of cyclopentadiene as giving two molecules of benzoic acid, one of oxalic acid and three of carbon dioxide, we have the following tabulation representing the respective weights of products from 1 gram of cyclopentadiene:

	Calculated.	Found.
CaC_2O_4 from 1 mol. oxalic acid.....	0.400	0.365
CaCO_3 from 3 mol. CO_2	0.940	1.198
$\text{C}_6\text{H}_5\text{COOH}$ from 2 mol.	0.764	0.737

The nitric acid present in the reaction mixture was indicated by the diphenylamine test.

So far, attempts to reduce this cyclopentadiene either in acid or alkaline solutions have met with no success. It was found, also, that neither with halogens, halogen acids, nor with benzoquinone, could this cyclopentadiene

be involved in reactions analogous to those which characterize the parent substance of the group.

ANN ARBOR, MICHIGAN.

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

**MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. XI.
DERIVATIVES OF ISOCAMPHORIC ACID; ISOAMINO-
CAMPHONANIC ACID AND ITS DECOM-
POSITION PRODUCTS.¹**

BY WILLIAM A. NOYES AND LEONIDAS R. LITTLETON.

Received November 20, 1912.

There are four acids derived from camphor that have the general formula C_8H_{14} $\begin{matrix} \text{COOH} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{NH}_2 \end{matrix}$. Two of these, aminocamphonan acid² and aminodihydrocampholytic acid,³ are derived from *d*-camphoric acid, and the other two, isoaminocamphonan acid⁴ and isoaminodihydrocampholytic acid,⁵ are derivatives of isocamphoric acid. The first two have the carboxyl groups in the tertiary position while the other two are secondary acids. These four amino acids have the following structures:

Aminocamphonan acid.

Aminodihydrocampholytic acid.

Isoaminocamphonan acid.

Isoaminodihydrocampholytic acid.

On treatment with nitrous acid aminocamphonan acid⁶ is decomposed into lauronic acid, $C_8H_{13}\text{COOH}$, hydroxylauronic acid, laurolene, C_8H_{14} ,

¹ Abstract of a thesis presented by Leonidas R. Littleton in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.

² For the nomenclature used in this paper see THIS JOURNAL, 34, 1067 (1912); *Am. Chem. J.*, 16, 506 (1894); *Ber.*, 33, 2963 (1900).

³ *Am. Chem. J.*, 16, 310, 503 (1894); *Ibid.*, 24, 290 (1900).

⁴ This paper.

⁵ THIS JOURNAL, 32, 1672 (1900).

⁶ *Am. Chem. J.*, 16, 508 (1894); THIS JOURNAL, 31, 279 (1909); *Ber.*, 33, 294 (1900).