FIG. II. *Zygadenine crystallized from alcohol.* Magnified about 100 times.

An acid solution of the alkaloid yields a voluminous precipitate with Meyer's reagent, and a beautiful chloroaurate is formed, when to the hydrochloric acid solution of the base, an acid solution of chloroauric acid is added. This salt is soluble in hot water and crystallizes, upon cooling, in elongated, dense prisms. With concentrated sulfuric acid a yellowish orange coloration is obtained, which passes over into a brilliant cherry-red. These color changes greatly resemble those of cevadine.

Specific Rotation.—The alkaloid is levorotatory. 0.7028 gram dissolved in 25 cc. chloroform was found to rotate 2.7° to the left in a 2 dcm. tube. The specific rotation is therefore —48.2°.

Dr. Philip Mitchell reports upon its physiological action as follows: "Toxicologically this preparation is quite different from that of the mixed alkaloids. It shows none of the characteristic effects given by that mixture. Its behavior is, in general, very much like that of veratrine. It kills guinea pigs slowly and only in comparatively large doses, with an effect apparently due to failure of respiration, and clearly involving complete loss of muscular control. No tetanic spasms and no noteworthy effect on the heart could be observed in the guinea pigs. With frog muscle, treatment with the alkaloid dissolved in alcohol, neutralized and diluted with Ringer's solution, gave an effect like that of veratrine. A typical 'veratrine curve' was obtained."

LARAMIE, WYO.

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

STUDIES IN THE CYCLOPENTADIENE SERIES. III. CERTAIN DERIVATIVES OF *2,3-DIBENZOYL-5-NITROCYCLOPENTADIENE.*

BY WILLIAM J. HALE AND LAMBERT THORP.[1]

Received January 18, 1913.

The formation of a cyclopentadiene ring by condensation of a 1,3-

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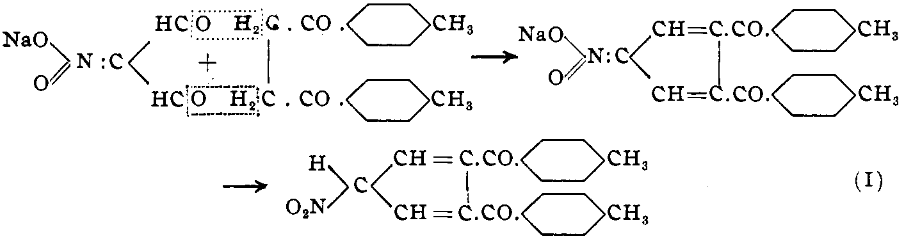
[1] The work described in this article formed part of a thesis submitted for the degree of Doctor of Philosophy in the University of Michigan by Lambert Thorp.

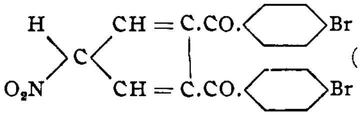
dialdehyde with diphenacyl[1] has been shown to proceed more slowly than with acetonylacetone, the simplest ketone of this class. In order to study further the influence which the end groups of these diketones may exert upon this form of condensation, such derivatives as 4,4′-dimethyl- and 4,4′-dibromo- as well as 4-bromo-diphenylacyl were selected for investigation in this connection. For strict comparison only those compounds with substituents in the para position were employed.

As with diphenacyl itself no second possibility for condensation could be presented when one of these derivatives was allowed to react with nitromalonic aldehyde. The course of the reaction leads directly to the dibenzoylcyclopentadiene ring with the corresponding substituents. In the case of the 4,4′-dimethyldiphenacyl the reaction may be outlined as follows:

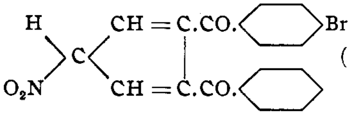


(I)

In the same manner the 4,4′-dibromo- and the 4-bromo-diphenacyl lead to the following derivatives, respectively:



(II)



(III)

The preparation of these diphenacyl derivatives presented no little difficulty. Only one, the 4.4′-dimethyldiphenacyl, has previously been described. In several cases the operations were attended with such poor yields that the preparation of any considerable quantity of condensation product was not attempted. The reactions of decomposition, as by oxidation with potassium permanganate, were here omitted. The constitution of each product naturally accords with the constitution already determined for 2,3-dibenzoyl-5-nitrocyclopentadiene.

Throughout these condensations the conditions were made as nearly as possible identical with those under which the condensation with diphenacyl had been studied.[2] The reaction mixture consisted of three parts of 95% alcohol and one part of water. The total volume in each case was held proportional to the weight of nitromalonic aldehyde re-

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[1] This Journal, **35**, 68 (1913).

[2] *Ibid.*, **35**, 71 (1913).

quired, and the concentration of the sodium hydroxide in solution kept a constant. The temperature was maintained throughout at 40°. The results are here tabulated:

	Diphenacyl.	Mono-bromdi-phenacyl.	Di-bromdi-phenacyl.	Di-methyldi-phenacyl.
Alcohol (cc.)	75	45	36	45
Water (cc.)	25	15	12	15
NaOH (2 mols.) (grams)	0.8	0.5	0.4	0.5
Diketone (grams)	2.4	2.0	2.0	1.6
Nitromalonic aldehyde (grams)	1.6	1.0	0.8	1.0
Approx. sol. (grams per 1000 cc.)	0.8	0.7	0.1	0.5
Time (days)	10	5	14	14
Conversion	100%	100%	40%	75%

The solubility of diphenacyl and the monobromodiphenacyl in the reaction mixture are of about the same order (line 6 above), and yet the time required for complete condensation in the case of the latter (5 days) is only one-half that for the former (10 days). With the dimethyldiphenacyl, in solubility only slightly less than that of the monobromodiphenacyl, a much longer time (14 days) was required to effect even a 75% condensation. We may reasonably infer therefore that the presence of a negative substituent in the phenyl group of diphenacyl increases somewhat the activity of the methylenic groups in this ketone toward condensation reactions. With the dibromodiphenacyl, however, a satisfactory comparison is not readily drawn from the data, owing to the very slight solubility of this ketone in the reaction mixture. Since only one-seventh as soluble as the monobromodiphenacyl (condensing in 5 days) the corresponding length of time for its complete condensation might be calculated as 35 days, or 14 days for a 40% condensation—the value indicated by experiment. In other words, we may place the two bromo derivatives of diphenacyl in the same class as regards the influence of negative substituents in the phenyl ring. Upon this method of calculation the length of time that would be required for a 75% condensation with the dimethyldiphenacyl (only five-eighths as soluble as diphenacyl itself) should be 12 days, or a longer time than that required for a corresponding 75% condensation with diphenacyl. From the experimental data a somewhat longer period (14 days) was actually noted. This is indeed twice the length of time required for a 75% condensation with the free diphenacyl.

We conclude, therefore, that the effect of methyl groups, as para substituents in the phenyl rings of diphenacyl, is inhibitive in character and retards the activity of the methylenic groups of this 1,4-diketone to about the same extent as the influence of the corresponding bromine substituents succeeds in promoting reactions of condensation.

Experimental

4,4'-DIMETHYLDIPHENACYL AND NITROMALONIC ALDEHYDE.

4,4'-Dimethyldiphenacyl, $CH_3.C_6H_4.CO.CH_2.CH_2.CO.C_6H_4.CH_3$.—For the preparation of this diketone a modified form of Limpricht's method[1] was employed. In a flask provided with reflux condenser, a mixture of 150 grams of toluene and 25 grams of succinyl chloride was gradually treated with 25 grams of aluminium chloride. The mixture was warmed to 50° on the water bath for one hour and then let stand over night at room temperature. The contents of the flask were then treated with cold water and the excess of toluene removed by distillation with steam. According to Limpricht the dark colored tarry residue was purified by fractional crystallization. It served our purpose better to warm this tarry mass with a slight excess of a 2% sodium hydroxide solution, whereby the lactone present and also the foreign matter were readily removed. The part unacted upon, *i. e.*, the diketone, was then dissolved in hot alcohol, the solution digested with bone-black, filtered, and allowed to crystallize. The yield (2 to 3 grams) is very poor, owing to the fact that the greater part of the acid chloride reacts in the unsymmetrical form.

2,3-Di-paratoluyl-5-nitrocyclopentadiene, $C_5H_3(NO_2)(CO.C_6H_4.CH_3)_2$ (1).—To a solution consisting of 0.5 gram of sodium hydroxide, 1.0 gram of sodium nitromalonic aldehyde, 15 cc. of water and 45 cc. of alcohol, were added 1.6 grams of 4,4'-dimethyldiphenacyl. The mixture was kept at 40° for 14 days, after which the deep red solution was filtered from the unacted-upon ketone; this latter amounted to 25% of the original weight. When diluted with an equal volume of water the clear filtrate was acidified with hydrochloric acid and the precipitated cyclopentadiene filtered off. Calculated upon the weight of diketone actually consumed, the yield was approximately 75% of the theoretical. This 2,3-di-paramethylbenzoyl-5-nitrocyclopentadiene, or di-paratoluyl-nitrocyclopentadiene, crystallizes from acetic ester in beautiful yellow prisms which decompose at 243–4°. It is insoluble in water; very slightly soluble in alcohol or ether; only fairly soluble in glacial acetic acid or acetone; more readily soluble in benzene, chloroform or acetic ester.

0.1642 gram substance gave 0.4372 gram CO_2 and 0.0794 gram H_2O.
0.2264 gram substance gave 8.7 cc. N_2 (21°, 734 mm. over H_2O).

Calculated for $C_{21}H_{17}O_4N$:	C, 72.62; H, 4.90; N, 4.04.
Found:	C, 72.64; H, 5.40; N, 4.20.

Silver Salt, $C_5H_2(:NO.OAg)(CO.C_6H_4.CH_3)_2$.—The condensation product was dissolved in a 10% ammonium hydroxide solution and, after removal of the excess of ammonia by gentle warming, a solution of silver nitrate then added. The silver salt thus precipitated is yellow in color and

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[1] *Ann.*, 312, 115 (1900).

only slightly soluble in water. When heated to about 200° it decomposes with explosive violence.

0.1463 gram salt: 0.0347 gram of metallic silver.
Calculated for $C_{21}H_{16}O_4N.Ag$: Ag, 23.76; found: Ag, 23.72.

2,3-Di-paratoluyl-5-nitrocyclopentadiene Monoxime, $C_5H_3(NO_2)(CO.C_6H_4.CH_3)(C(C_6H_4.CH_3) : NOH)$.—The free ditoluylnitrocyclopentadiene, 1 gram, was dissolved in 60 cc. of 50% alcohol and 0.8 gram of hydroxylamine hydrochloride and 1 gram of sodium hydroxide added. After heating upon the water-bath for four hours, the solution was acidified with dilute hydrochloric acid, upon which the oxime separated as a yellow, flocculent precipitate. Recrystallization from alcohol gave a product which decomposes at 150–1°. It is insoluble in water; slightly soluble in ligroin; fairly soluble in alcohol; readily soluble in ether, benzene or chloroform.

0.1943 gram substance: 13.6 cc. N_2 (23°, 735 mm. over H_2O).
Calculated for $C_{21}H_{18}O_4N_2$: N, 7.73; found: N, 7.58.

4-BROMODIPHENACYL AND NITROMALONIC ALDEHYDE.

Bromobenzene.—Considerable quantities of bromobenzene were required by us in this and other condensations. The ordinary methods described in the literature for its preparation usually record a 60% yield. By the following procedure a yield of 80–85% of pure bromobenzene is easily obtained:

In a 500 cc. distilling flask with outlet tube bent upward at an angle of 45° and attached to reflux condenser, 240 cc. of benzene and 4 grams of iron wire were placed. The flask is provided with a dropping funnel for the delivery of the bromine and a thermometer for observing the temperature of the mixture. It is advantageous also to provide the condenser with an exit tube leading into a vessel of water for absorption of the hydrogen bromide evolved. The bromine, 100 cc., is introduced into the flask very slowly. At first only 5 or 10 cc. were admitted. As the hydrogen bromide is evolved more and more bromine is admitted and at such a rate that the temperature of the mixture does not at any time rise above 40°. The evolution of the hydrogen bromide will thus be found to proceed at a uniform and gentle rate. Upon completing the addition of this quantity of bromine, the flask is maintained at 40° until no further evolution of hydrogen bromide is noted. The product, now washed with water, dilute sodium hydroxide, and again with water and dried, gave, upon fractionation, 240 grams of pure bromobenzene and only two or three grams of *p*-dibromobenzene as residue.

Parabromoacetophenone.—The preparation of this product, first described by Schweitzer[1] and again by Schöpff,[2] was carried out according to the

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[1] *Ber.*, 24, 550 (1891).

[2] *Ibid.*, 24, 3766 (1891).

improved methods for the Friedel-Crafts reaction as outlined by Perrier.[1]

In a 500 cc. flask, fitted with condenser, 76.5 grams of aluminium chloride were treated gradually with 50 grams of acetyl chloride. The mixture was warmed upon a water-bath to complete the formation of addition product, and then a solution of 90 grams of bromobenzene in 150 cc. of carbon disulfide gradually admitted to the flask through the condenser. The flask was now heated upon a water-bath for six hours or until all evolution of hydrogen chloride had ceased. The excess of carbon disulfide was then removed by distillation, and the residue poured upon cracked ice and finally submitted to distillation by steam. The ketone distilled over as an oil solidifying altogether in the receiver. This ketone, taken up in alcohol and sufficient water added to maintain a slight turbidity, gave, upon cooling, an oil which gradually solidified (by aid of stirring) into a mass of colorless crystals. The yield amounted to 70% of the theoretical.

Parabromophenacyl Bromide.—The method for preparation differs from that described by Collet[2] in the matter of solvent or diluent. The use of carbon disulfide recommended by Collet is best replaced by glacial acetic acid.

Twenty grams of parabromoacetophenone were dissolved in 80 cc. of glacial acetic acid, and to this solution 16.2 grams of bromine added. The flask with contents was brought to a temperature of 40° and the source of heat then removed. In a few minutes a vigorous reaction set in, which was accompanied by rapid rise in temperature, complete absorption of bromine and a copious evolution of hydrogen bromide. While yet hot the reaction mixture began to deposit crystals of the dibromoketone. The entire contents of flask were finally heated on the water-bath for ten minutes and then poured into 500 cc. of cold water. Recrystallization from 95% alcohol gave 25 grams of product, *i. e.*, 90% of the theoretical value.

Parabromophenacyl benzoylacetic Ethyl Ester, $C_6H_5.CO.CH(CH_2.CO.-C_6H_4Br).COOC_2H_5$.—The reaction here required is exactly analogous to that for the preparation of the simple acyl benzoylacetic esters:

$$C_6H_5.CO.CHNa.COOC_2H_5 + Br.C_6H_4.CO.CH_2Br = C_6H_5.CO.CH(CH_2CO.C_6H_4Br).COOC_2H_5 + NaBr.$$

To a solution of sodium ethylate, obtained by action of 1.8 grams of sodium upon 35 cc. of absolute alcohol, 15 grams of benzoylacetic ester were added. This alcoholic solution of the sodium salt of benzoylacetic ester was now cooled and then one equivalent, 21.7 grams, of parabromophenacyl bromide added in four or five portions; a thorough shaking and cooling of contents of flask preceding each addition. The flask, with

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[1] *Ber.*, **33**, 815 (1900).

[2] *Bull. soc. chim.*, [3] **21**, 68 (1899).

contents, was then placed upon the water-bath and warmed for fifteen minutes to complete the reaction. A separation of sodium bromide is, of course, observed during the operation. After cooling, a separation of the product in crystallin form is usually observed. The entire mixture was finally poured into cold water and the solid mass filtered off. Several crystallizations from alcohol yielded colorless needles melting at 81°. The yield amounted to 75% of the theoretical. Parabromophenacyl benzoylacetic ester is insoluble in water; fairly soluble in alcohol, ether, or ligroin; readily soluble in carbon disulfide, acetic ester, acetone, chloroform or benzene.

0.4537 gram substance: 0.2200 gram AgBr.
Calculated for $C_{19}H_{17}O_4Br$: Br, 20.55; found, 20.63.

Parabromodiphenacyl, $C_6H_5.CO.CH_2.CH_2.CO.C_6H_4Br$.—This substance is readily prepared by the ketonic decomposition of the preceding ester through the action of dilute alkali.

A solution of 6.8 grams (2 mols.) of potassium hydroxide in 150 cc. of water was introduced into a 500 cc. flask provided with reflux condenser. Fifty cc. of alcohol and 20 grams of parabromophenacyl benzoylacetic ester were then added and the mixture boiled for about three hours. At the end of this time the ester had completely dissolved and crystals of the diketone already separated out from the solution. This product filtered off and recrystallized from alcohol amounted to 7 grams, or about 45% of the theoretical value. Parabromodiphenacyl crystallizes in white plates of pearly luster, closely resembling parabromobenzoic acid in appearance. It melts at 116°. It is insoluble in water; slightly soluble in ligroin; fairly soluble in alcohol or ether; readily soluble in benzene, chloroform, acetic acid or acetic ester.

0.2437 gram substance: 0.1436 gram AgBr.
Calculated for $C_{16}H_{13}O_2Br$: Br, 25.21; found, 25.08.

2-Parabromobenzoyl-3-benzoyl-5-nitrocyclopentadiene, $C_5H_3(NO_2)(CO.C_6H_5)(CO.C_6H_4Br)$. (III).—The condensation of nitromalonic aldehyde with the parabromodiphenacyl is effected with relative ease. Into a solution containing 45 cc. of alcohol, 15 cc. of water, 0.5 gram (2 mols.) of sodium hydroxide and 1.0 gram of sodium nitromalonic aldehyde, 2.0 grams of the diketone were introduced. The temperature of the reaction mixture was maintained at 40° by means of a water-bath. In five days the ketone was completely dissolved and the reaction ended. The mixture was then diluted with an equal volume of water and acidified with hydrochloric acid. The precipitated cyclopentadiene was filtered off and recrystallized from benzene. The yield was about 75% of the theoretical.

2-Parabromobenzoyl-3-benzoyl-5-nitrocyclopentadiene crystallizes in small, yellow prisms which decompose at 240–1°. It is practically insoluble in water, ligroin or acetic acid; only very slightly soluble in alcohol or ether; slightly soluble in acetone, carbon tetrachloride or acetic ester; fairly soluble in chloroform or benzene.

0.1880 gram substance: 0.3974 gram CO_2, 0.0564 gram H_2O.
0.2078 gram substance: 7.4 cc. N_2 (26°, 736 mm. over H_2O).
0.2170 gram substance: 0.04335 gram Br_2.

Calculated for $C_{19}H_{12}O_4NBr$:	C, 57.28; H, 3.04; N, 3.52; Br, 20.08.
Found:	C, 57.64; H, 3.34; N, 3.83; Br, 19.97.

4,4'-DIBROMODIPHENACYL AND NITROMALONIC ALDEHYDE.

Parabromobenzoic Acid.—For the preparation of this acid Beilstein recommends the oxidation of *p*-bromotoluene by means of chromic acid, as described by Jackson and Rolfe.[1] The method, however, is somewhat tedious, and the average yield does not exceed 50% of the theoretical. The following procedure was found to give better results: Into a copper vessel were introduced 1500 cc. of water, 66 grams of *p*-bromotoluene, and 55 grams (a one-third portion) of potassium permanganate. The total weight of potassium permanganate used (165 grams) was 30% in excess of the theoretical quantity. After boiling the mixture for 2–3 hours under a reflux condenser, the permanganate was completely reduced; the second of the one-third portions of permanganate, 55 grams, was then added. Again, after the reduction of this second portion, the remaining 55 grams of permanganate were added. By the time this portion was reduced the oxidation was practically complete. The slight amount of bromotoluene remaining may be removed by distillation with steam, if desired. After settling of the manganese dioxide the clear solution was poured through a filter, and the manganese dioxide boiled up twice with water, 400 cc. at each time, and filtered by aid of suction. These washings were combined with the main filtrate and the entire volume evaporated to a volume of about 500 cc. After cooling, the calculated quantity of concentrated hydrochloric acid was added and the parabromobenzoic acid at once precipitated. When filtered off and dried, the yield amounted to 52 grams, a value calculating to 72% of the theoretical.

Parabromobenzoyl Chloride.—In general, the method of Sudborough was here followed. Thirty-five grams of *p*-bromobenzoic acid were placed in a 500 cc. flask and treated with one equivalent of phosphorus pentachloride. The reaction was brought to completion by gentle warming on the water-bath, and the products then separated by distillation under diminished pressure. Sudborough gives 154–5° as the boiling point of the acid chloride at 50 mm. pressure. At the pressure we employed, 20 mm., all of the acid chloride distilled over at 136–8°, solidifying completely in the receiver. The yield came to 92% of the theory.

Sodium Salt of Parabromobenzoyl Acetoacetic Ester, $CH_3.C(ONa):C$-

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[1] *Am. Chem. J.*, **9**, 84 (1887).
[2] *J. Chem. Soc.*, **67**, 591 (1895).

(.CO.C_6H_4Br).$COOC_2H_5$.—The preparation of this ester in the form of its sodium salt was carried out in the manner described by Claisen[1] for the preparation of benzoylacetoacetic ester, the *p*-bromobenzoyl chloride here taking the place of benzoyl chloride in Claisen's synthesis. According to this method one-half of the sodium acetoacetic ester present is liberated as free ester, consequently further additions of sodium ethylate in half the previous portions must be added to re-form the sodium salt, and this in turn be allowed to react with the acid chloride simultaneously added. The reaction may be indicated as follows:

2 Na-acetoacetic ester + *p*-bromobenzoylchloride = Na-*p*-bromobenzoylacetoacetic ester + acetoacetic ester + NaCl. In Claisen's work the benzoyl chloride was dropped into the flask directly, whereas in this work the *p*-bromobenzoyl chloride was employed in an ether solution. The following proportions were used: 9.15 grams of sodium (2 mols.) dissolved in 150 cc. of absolute alcohol; 25.8 grams of acetoacetic ester (1 mol.); 42.8 grams of *p*-bromobenzoyl chloride (1 mol.) dissolved in 400 cc. of ether.

The entire quantity of acetoacetic ester was mixed with 75 cc. of the sodium ethylate solution. Into this solution, cooled to 5°, 200 cc. of the ethereal solution of *p*-bromobenzoyl chloride were gradually admitted through a buret. The mixture, constantly stirred, was kept under 10° as its upper limit. After standing in the cold for one-half hour, a second portion of the sodium ethylate solution, 37.5 cc., was poured into the beaker containing the reaction mixture, and the corresponding second portion of acid chloride in ether solution, 100 cc., gradually run in. After the lapse of another half-hour the third portions of these solutions, 18.75 cc. of sodium ethylate and 50 cc. of acid chloride, were similarly added. In like manner there were introduced in turn the fourth and fifth portions (each consisting of 9.4 cc. of sodium ethylate solution and 25 cc. of acid chloride solution), thus completing the operation. The entire reaction mixture was now allowed to stand in a cool place for 24 hours, when the separation of the yellow sodium salt of *p*-bromobenzoylacetoacetic ester (already begun after the second addition above) was complete. When filtered off and washed with dry ether the product weighed 58 grams. This salt has the distinctive property of being only very slightly soluble in water.

Parabromobenzoylacetic Ester,[2] BrC_6H_4.CO.CH_2.$COOC_2H_5$.—This ester is readily obtained from the *p*-bromobenzoylacetoacetic ester by gentle warming with aqueous ammonia:

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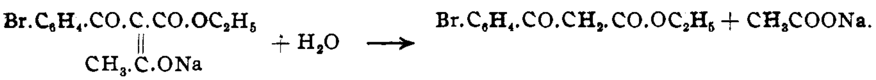
[1] *Ber.*, 20, 651 (1887).

[2] These methods of preparation for this and the preceding ester were embodied in a paper presented by the authors before the Organic Section at the Eighth International Congress of Applied Chemistry, New York, September, 1912.



$$\begin{array}{l} Br.C_6H_4.CO.C.CO.OC_2H_5 \\ \qquad\quad \| \\ \quad CH_3.C.ONa \end{array} + H_2O \longrightarrow Br.C_6H_4.CO.CH_2.CO.OC_2H_5 + CH_3COONa.$$

The entire quantity, 58 grams, of the sodium salt of *p*-bromobenzoylacetoacetic ester just described, was mixed with 600 cc. of water. To this mixture were added 60 cc. of concentrated ammonium hydroxide solution and 30 grams of ammonium chloride, and the entire volume, under constant shaking, warmed to 40–45° for one-half hour. In the course of this time the yellow sodium salt had completely dissolved and a heavy oil had separated out at the bottom of the flask. This oil was removed by extraction with ether and the ether extract dried over calcium chloride. Upon removal of the ether by gentle warming the heavy oil, dried further in a desiccator over sulphuric acid, weighed 28 grams.

Parabromobenzoylacetic ester is a pale yellow, oily liquid, heavier than water and possessing a faint, though not unpleasant, odor. In extremely small quantities, in alcoholic solution, it gives a deep red color with ferric chloride. The test is practically as delicate as the well-known test for ferric iron by ammonium thiocyanate. Attempts to distil this ester even at 5 mm. pressure resulted in its decomposition. These products of decomposition are now under investigation. A determination of bromine was carried out in accordance with Bacon's[1] modification of Stepanow's method.

Calculated for $C_{11}H_{11}O_3Br$: Br, 29.49; found, 29.32.

Parabromophenacyl-p-bromobenzoylacetic Ethyl Ester, $BrC_6H_4.CO.CH(.CH_2.CO.C_6H_4Br).COOC_2H_5$.—To a solution of 1.7 grams (1 mol.) of sodium in 35 cc. of absolute alcohol 20 grams of *p*-bromobenzoylacetic ester were added. This alcoholic solution of the sodium salt of *p*-bromobenzoylacetic ester was then cooled and treated gradually with 20.6 grams (1 mol.) of *p*-bromophenacyl bromide.[2] In the reaction, heat was developed and the mixture separated into two liquid phases. When further heated upon a water-bath the reaction is completed in a short time. The entire mixture was now poured into cold water and the heavy oil separating out was taken up in ether. This ether extract, dried over calcium chloride, yielded a dark viscous oil upon evaporation. Even after several days standing in a vacuum desiccator this oil showed no tendency to solidify, but by addition of a few drops of alcohol and constant stirring the entire volume solidified to a yellow, crystallin mass, calculating to a 60% yield. The product was purified by dissolving in hot alcohol, treating with bone-black, and evaporating the clear alcoholic solution to small volume. The oil which at first separates is gradually transformed to a crystallin product. Further crystallization from a

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[1] THIS JOURNAL, **31**, 49 (1909).

[2] *Loc. cit.*

dilute alcoholic solution gave a pure product in small colorless prisms melting at 75°.

Parabromophenacyl-*p*-bromobenzoylacetic ethyl ester is insoluble in water; slightly soluble in ligroin; fairly soluble in acetic acid or alcohol; readily soluble in ether, chloroform, acetone, benzene, carbon tetrachloride or acetic ester.

Calculated for $C_{19}H_{16}O_4Br_2$: Br, 34.16; found: Br, 34.36.

4,4'-Dibromodiphenacyl, $BrC_6H_4.CO.CH_2.CH_2.CO.C_6H_4Br$.—Eight grams of *p*-bromophenacyl-*p*-bromobenzoylacetic ester were added to a solution of 2.2 grams (2 mols.) of potassium hydroxide in a mixture of 40 cc. of water and 20 cc. of alcohol and the solution boiled under reflux condenser. The ester gradually went into solution and the plate-like crystals of the diketone soon began to separate out. One-half hour's boiling sufficed for the completion of the reaction, after which the crystallin product was filtered off and recrystallized from benzene. The weight, 2 grams, calculates to a 30% yield.

4,4'-Dibromodiphenacyl crystallizes from benzene or glacial acetic acid in colorless, glistening plates which melt at 182°. It is insoluble in water; almost insoluble in ligroin; slightly soluble in alcohol or ether; fairly soluble in benzene, acetic acid, acetone or acetic ester; readily soluble in chloroform.

Calculated for $C_{16}H_{12}O_2Br_2$: Br, 40.37; found: 40.46.

2,3-Diparabromobenzoyl-5-nitrocyclopentadiene, $C_5H_3(NO_2)(CO.C_6H_4Br)_2$ (II).—In a mixture of 36 cc. of alcohol and 12 cc. of water, 0.4 gram (2 mols.) of sodium hydroxide and 0.8 gram of sodium nitromalonic aldehyde were dissolved. Two grams of 4,4'-dibromodiphenacyl were then added, and the mixture maintained at 40° for 14 days. At the end of this time 60% of the diketone remained unacted upon and was removed by filtration. The clear filtrate, of deep red color, was acidified with dilute hydrochloric acid and the yellow precipitate of cyclopentadiene filtered off and crystallized from a mixture of benzene and ligroin. The pure product decomposes at 230–2°.

2,3-Di-parabromobenzoyl-5-nitrocyclopentadiene is insoluble in water; slightly soluble in ether, alcohol or ligroin; more readily soluble in benzene, chloroform or acetic ester. It forms soluble alkali salts and an insoluble silver salt as in the case of the other cyclopentadienes already described.

0.1899 gram substance: 0.3340 gram CO_2, 0.0426 gram H_2O; 0.2877 gram substance: 8.4 cc. N_2 (24°, 738 mm. over H_2O): 0.1943 gram substance titrated for 0.06543 gram Br_2.

Calculated for $C_{19}H_{11}O_4NBr_2$: C, 47.80; H, 2.33; N, 2.94; Br, 33.51.
Found: C, 47.97; H, 2.51; N, 3.17; Br, 33.68.

ANN ARBOR, MICH.