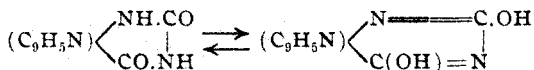with violent ebullition. It was, therefore, necessary to dilute the phenyl-hydrazine with alcohol to secure a smooth reaction.

One gram of the lactam was added to a solution of 1.25 cc. phenyl-hydrazine in 25 cc. alcohol, and the mixture boiled gently for an hour. The lactam slowly dissolved, and a crystallin product soon separated from the solution, causing violent bumping. When the mixture had cooled sufficiently, the crystals were filtered out, washed thoroughly with cold alcohol, dried to constant weight at 110°, and analyzed.

Calculated for $C_{18}H_{14}ON_4$: N, 18.55. Found: N, 18.72.

The compound forms pale brownish needles, melting at 249.5–250.5° (cor.).

2,4 - Diketo - 1,2,3,4 - tetrahydro - 1,3,7 - naphthoisotriazine(2,4 - Dihydroxy-1,3,7-naphthoisotriazine).—

$$(C_9H_5N)\Big\langle \begin{matrix} NH.CO \\ | \\ CO.NH \end{matrix} \rightleftharpoons (C_9H_5N)\Big\langle \begin{matrix} N\!=\!\!=\!\!=\!C.OH \\ | \\ C(OH)\!=\!N \end{matrix}$$

Equal weights of 5-aminoquinoline-6-carboxylic acid and urea were fused together. Water and ammonia were evolved during the fusion and, on cooling, a brown, hard mass was obtained. This was pulverized and extracted with cold, dilute sodium hydroxide solution, which dissolved out the dihydroxytriazine. From this solution the triazine was precipitated by carbon dioxide, or acetic acid, as a yellowish or brownish powder melting above 300°, and difficultly soluble in water or in alcohol.

Calculated for $C_{11}H_7O_2N_3$: N, 19.72. Found: N, 19.54.

With diazotized benzidine, the compound gives a dark red solution; and with diazosulfanilic acid, in alkalin solution, a deep red one.

NEW YORK CITY.

STUDIES IN THE CYCLOPENTADIENE SERIES. [I.]

2,3-DIACETYL-5-NITROCYCLOPENTADIENE.

BY WILLIAM J. HALE.

The discovery of five-membered carbocyclic compounds dates from 1885, when Roscoe[1] first obtained a hydrocarbon of the formula $C_{10}H_{16}$ by the decomposition of crude phenol at a red heat. He succeeded also in separating this same hydrocarbon from the first fractions of coal tar.

The simpler form of the hydrocarbon, C_5H_6, was known to Roscoe and found to polymerize readily into the dimolecular form. It was isolated later from petroleum by Étard and Lambert[2] and called by them "pyro-pentylene;" the dimolecular form received the name "dipyropentylene." Nietzki and Rosemann,[3] arguing from analogy with benzene and its
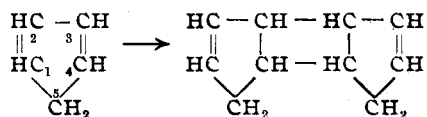
[1] J. Chem. Soc., 47, 669 (1885); Ann., 232, 348 (1886).
[2] Compt. rend., 112, 945 (1891).
[3] Ber., 22, 916 (1889); see also Auerbach, Ibid., 36, 933 (1903).

three double linkings, suggested the name "pentol" for a five-carbon ring compound of this class.

The constitution of this simpler hydrocarbon, C_5H_6, was established by Krämer and Spilker[1] and shown to be a cyclopentadiene. It is a liquid boiling at $41°$ and polymerizes readily into a dicyclopentadiene boiling at $170°$. This latter dissociates again, upon heating, into the monomolecular form:

$$HC\underset{\underset{5}{HC_1\ \ _4CH}}{\overset{\overset{2\ \ \ 3}{-CH}}{\|}}\underset{CH_2}{}\longrightarrow \quad HC\overset{-CH-HC-CH}{}\quad CH_2 \quad CH_2$$

These investigators found that the portion of coal tar distilling between $160–175°$ gave, when redistilled, this monomolecular or lower boiling form; a reaction which takes place no doubt during the so-called "cracking process" in the distillation of heavy petroleum oils.

Complete data on the decomposition of the cyclopentadiene ring was furnished by J. Thiele.[2] The addition of bromine first led to a 1,4-dibromocyclopentene and this, by the action of potassium permanganate, gave a dibromodihydroxycyclopentane, which finally could be oxidized by chromic acid into $α,γ$-dibromoglutaric acid. Pure cyclopentadiene, however, is almost impossible to prepare, owing to the great ease with which it polymerizes even at ordinary temperatures. The recent work of Auwers and Eisenlohr[3] upon molecular dispersion points out this fact conclusively.

Recently M. Weger[4] has suggested the possible formation of naphthalene from coal tar products by the passing of cyclopentadienes through red hot tubes. The presence also of cyclopentadiene in illuminating gas has been detected by R. Ross and J. Race.[5]

The first synthesis of the pentamethylene (cyclopentane) ring was accomplished as early as 1887 by W. H. Perkin, Jr.,[6] through the action of trimethylene bromide upon sodium ethyl malonate. Cyclopentadienes, however, were not synthesized till 1894, when Dieckmann[7] condensed oxalic ester with glutaric ester by means of sodium ethylate. The constitution he finally assigned to the product accorded with a 2,3-dihydroxy-1,4-dicarbethoxy-cyclopentadiene:

$$HO.C-C.OH$$
$$C_2H_5OO.C\quad C.COOC_2H_5$$
$$CH$$
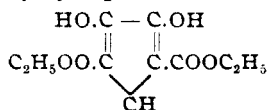
[1] *Ber.*, 29, 552 (1896).

[2] *Ann.*, 314, 296 (1901).

[3] *Ber.*, 43, 806 (1910); see also Eijkman, *Chem. Centr.*, 1907, II, 1205.

[4] *Z. angew. Chem.*, 22, 338 (1909).

[5] *J. Soc. Chem. Ind.*, 29, 604 (1910).

[6] *J. Chem. Soc.*, 51, 240 (1887); *Ibid.*, 65, 590 (1894); *Ber.*, 35, 2118 (1902).

[7] *Ber.*, 27, 965 (1894); *Ibid.*, 32, 1931 (1899); *Ibid.*, 35, 3201 (1902).

WILLIAM J. HALE.

Various derivatives of the cyclopentadiene ring have been prepared from 5-membered ring compounds. Thus Komppa[1] obtained a 5,5-dimethyl-1,4-dicarboxycyclopentadiene from dihydroxyapocamphoric acid; and again a number of aryl derivatives have been prepared from the corresponding hydroxycyclopentanones by the action of alcoholic hydrogen chloride.[2] A study of dicyclopentadienes has recently been published by H. Wieland,[3] in which is described a number of the addition reactions.

Possibly the most interesting synthesis of cyclopentadienes is that of Duden and Freydag.[4] Two molecules of levulinic ester were made to condense by the action of sodium ethylate, and thus gave a 4-methyl-1-carbethoxy-cyclopentadiene-2-propionic ester:

$$HC - C.CH_2.CH_2.COOC_2H_5$$
$$CH_3.C \quad C.COOC_2H_5$$
$$CH_2$$
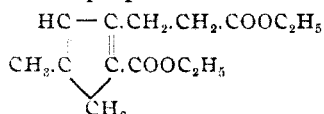
The work of Thiele[5] in this field brought to light that highly colored class of compounds, formed by condensation of aldehydes or ketones with the methylenic group of the cyclopentadienes, and designated by Thiele as "Fulvenes." The formula,

$$\begin{array}{c} HC = C \\ \quad \quad \quad >C = R< \\ HC = C \end{array} ,$$
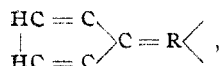
at once suggests a close analogy with the benzoquinone nucleus. It was Thiele, also, who first made mention of a nitro derivative of cyclopentadiene. This he prepared by the action of ethyl nitrate and sodium ethylate upon the free substance. Though the resulting nitrocyclopentadiene readily underwent decomposition, the sodium and silver salts were found very stable.

The study of this latter class of compounds, the nitrocyclopentadienes, has just recently been made possible through a new synthesis announced by the author.[6] This new condensation involves one molecule of a β-dialdehyde, namely, nitromalonic aldehyde, and one molecule of a γ-diketone. The simplest example of the latter is acetonylacetone. In an earlier publication[7] it was shown that the acetonyl groups of this diketone are very reactive toward this dialdehyde and lead to the formation of a

[1] *Ber.*, **34**, 2472 (1901).

[2] Abell, *Proc. Chem. Soc.*, **19**, 18 (1903); Auerbach, *Ber.*, **36**, 933 (1903); Wislicenus and Carpenter, *Ann.*, **302**, 222 (1898); Wislicenus and Newmann, *Ibid.*, **302**, 236 (1898); see also Noeldechen, *Ber.*, **33**, 3348 (1900).

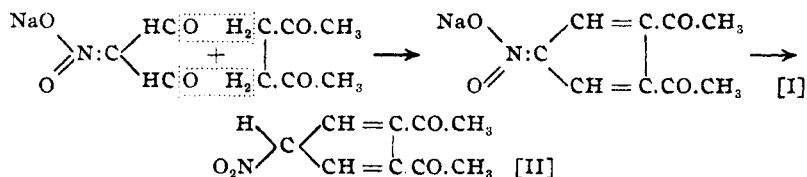[3] *Ber.*, **39**, 1492 (1906); *Ann.*, **360**, 299 (1908).

[4] *Ibid.*, **36**, 944 (1903).

[5] *Ibid.*, **33**, 666 (1900); *Ann.*, **314**, 296 (1901); *Ibid.*, **348**, 1 (1906); see also Albrecht, *Ibid.*, **348**, 31 (1906).

[6] *Ber.*, **45**, 1596 (1912).

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

substituted nitrophenol or dinitrobiphenol depending upon the entrance of either one or both acetonyl groups into condensation. The two methylenic groups, however, are far more reactive toward this aldehyde and, consequently, only a small portion (one-fifth) of the total product is found to consist of phenol derivatives. The main reaction, therefore, may be formulated as follows:

$$\underset{O}{\overset{NaO}{>}}N:C\underset{HC\overset{..}{O}\ \ H_2^{..}C.CO.CH_3}{\overset{HC\overset{..}{O}\ \ H_2C.CO.CH_3}{<}} \longrightarrow \underset{O}{\overset{NaO}{>}}N:C\underset{CH=C.CO.CH_3}{\overset{CH=C.CO.CH_3}{<}} \longrightarrow \quad [I]$$

$$\underset{O_2N}{\overset{H}{>}}C\underset{CH=C.CO.CH_3}{\overset{CH=C.CO.CH_3}{<}} \quad [II]$$

The product, 2,3-diacetyl-5-nitrocyclopentadiene, is procured in the form of a salt, sodium hydroxide or piperidine serving best as the condensing agent, and is readily liberated by addition of acid.[1] A number of derivatives of this compound have just been prepared and the proof of its structure made apparent through these and certain reactions of decomposition.
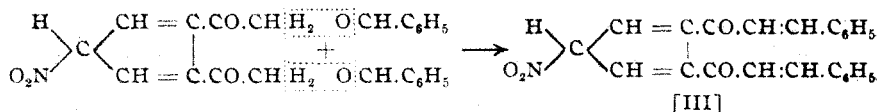
The sodium, potassium and barium salts were made and analyzed, but in no case could an alkyl ether be prepared either from the free substance or by the action of an alkyl halide upon one of these salts. The structure of the salts must undoubtedly fall in the isonitro class of compounds.

Although the monoxime of this nitrocyclopentadiene is easily prepared, many and varied attempts to prepare the dioxime were entirely unsuccessful. In like manner, the preparation of only the monanil, the monohydrazone and the monophenylhydrazone was found possible. In the case of the two latter, any further action with hydrazine or phenylhydrazine was rendered impossible by reason of the ready transformation which these mono-derivatives underwent in the production of a new bicyclic compound. The description and study of this latter class of compounds must be deferred to a later paper. The resistance of this diacetylnitrocyclopentadiene toward these reagents, so easily condensable with ketonic groups, may possibly be due to steric hindrance, but is more likely due to a rearrangement of affinity in which the activity of one carbonyl group is lessened when the other carbonyl group enters into reaction [Stewart's hypothesis].

In order to prove the presence of the two acetyl groups, required by the formula, the well known tendency for these groups to condense with aldehydes was brought into service. Though furfuraldehyde condenses as readily as does benzaldehyde, only the condensation with the latter will be described. Two molecules of benzaldehyde condensed readily
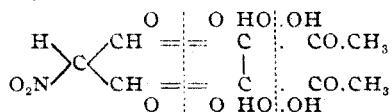
[1] *Ber.*, **45,** 1602 (1912).

with one molecule of the cyclopentadiene under the influence of alkali. The product is, of necessity, a dibenzylidene or, more correctly, a 2,3-dicinnamyl-5-nitro-cyclopentadiene:

$$H_2C \underset{O_2N}{\overset{H}{<}} \overset{CH = C.CO.CH \vert H_2 \quad O \vert CH.C_6H_5}{\underset{CH = C.CO.CH \vert H_2 \quad O \vert CH.C_6H_5}{|}} \quad + \quad \longrightarrow \quad \underset{O_2N}{\overset{H}{>}} C \underset{CH = C.CO.CH:CH.C_6H_6}{\overset{CH = C.CO.CH:CH.C_6H_5}{<}}$$

[III]

In order to obtain the free substance from this product, precipitated in the form of its sodium salt, acidification of its solution in acetone was found necessary.

A second method for confirming the presence of two acetyl groups in this compound rested upon the well known activity of iodine in alkalin solution toward a methyl group directly associated with a carbon atom carrying also oxygen either alone or in hydroxyl form. The methyl group in such cases, and in the presence of mild oxidizing agents, is split off in the form of iodoform. This method, when carried out, gave a weight of iodoform which corresponded to 1.93 molecules calculated to 1 molecule of cyclopentadiene; proving, conclusively the presence of two methyl groups and consequently two acetyl groups.

The most conclusive data upon the relation of the substituent groups in this cyclopentadiene were obtained through its oxidation with potassium permanganate. The use of nitric acid in this connection met with poor results. An alkalin solution of the cyclopentadiene readily decolorized a large amount of potassium permanganate, corresponding to 6 molecules of oxygen for every 1 molecule of cyclopentadiene. In the reaction mixture, after complete oxidation, there were found as potassium salts, 2 molecules of acetic acid, 1 molecule of oxalic acid, and 3 molecules of carbonic acid. The reaction for the decomposition of this cyclopentadiene by oxidation may be illustrated, therefore, as follows:

$$\underset{O_2N}{\overset{H}{>}} C \overset{O \ \vert \ O \ HO \vert .OH}{\underset{O \ \vert \ O \ HO \vert .OH}{\overset{CH == C \ \vert . \ CO.CH_3}{\underset{CH == C \ \vert . \ CO.CH_3}{<}}}}$$

The two acetyl groups are oxidized by 1 molecule of oxygen to 2 molecules of acetic acid, and the two carbon atoms, to which these acetyl groups are attached, are further oxidized by 2 molecules of oxygen to 1 molecule of oxalic acid. The nitromalonic aldehyde, which may be considered as momentarily liberated, is readily oxidized to carbon dioxide (3 molecules) and nitric acid (1 molecule), consuming thereby exactly 3 molecules of oxygen. This totals 6 molecules of oxygen for the complete oxidation, as recorded. This oxidation may, therefore, be considered as affording the best evidence on the structure of this cyclopentadiene. The substituent groups undoubtedly influence strongly the direction which

the oxidation takes, and consequently further study with various oxidizing agents will be necessary before comparing the course of this oxidation with that found by Thiele for dibromocyclopentadienes. The presence of these strongly negative substituents prevents altogether the addition of either halogens or halide acids to the unsaturated linkings.

Experimental.

2,3-Diacetyl-5-nitrocyclopentadiene, $C_5H_3(NO_2)(COCH_3)_2$ (II). — The preparation of this substance has already been described.[1] After the removal of the nitrophenol from the reaction mixture of sodium nitromalonic aldehyde and acetonylacetone, it is possible to obtain this cyclopentadiene as a more crystallin and less colored precipitate, if an equal volume of alcohol is added to the mother liquor just before the final acidification. The weight of product, based upon the weight of aldehyde taken, constituted 75% of the theory. Continued heating at 105° for some hours caused no loss in weight and indicated the absence of water of crystallization. Analyses and molecular weight determinations accorded with the cyclopentadiene type of compound.

Sodium Salt, $C_5H_2(:NO.ONa)(COCH_3)_2.3H_2O$ (I).—The free cyclopentadiene, suspended in a small quantity of water, was treated with scarcely enough sodium hydroxide to dissolve it, and the undissolved portion filtered off. The clear red filtrate, somewhat concentrated, yielded large prismatic crystals of the yellow sodium salt upon standing over night. A second crystallization was sufficient for purification. Practically all of the three molecules of water of crystallization were lost in two days by standing over sulfuric acid, after which gentle heating for a few hours at 90–95° sufficed to remove the last traces of water.

0.5583 gram air dried salt lost at 90–95° 0.1108 gram H_2O, and gave 0.1442 gram Na_2SO_4.

Calculated for $C_9H_8O_4NNa.3H_2O$: H_2O, 19.92; Na, 8.48. Found: H_2O, 19.85; Na, 8.37.

Potassium Salt, $C_5H_2(:NO.OK)(COCH_3)_2.1\frac{1}{2}H_2O$.—The potassium salt was made in exactly the same manner as the sodium salt. It is, however, somewhat more soluble than the sodium salt. Owing to the ease with which it becomes completely dehydrated in dry air, considerable care must be taken to dry the red hexagonal prisms of this salt by pressing between filter paper. Practically all of its one and one-half molecules of water of crystallization were lost over sulfuric acid in one day and, consequently, no heating found necessary.

0.4442 gram dry salt lost 0.0466 gram H_2O over H_2SO_4, and gave 0.1477 gram K_2SO_4.

Calculated for $C_9H_8O_4NK.1\frac{1}{2}H_2O$: H_2O, 10.38; K, 14.99. Found: H_2O, 10.49; K, 14.93.

Barium Salt, $[C_5H_2(COCH_3)_2(:NO.O.)]_2Ba.5H_2O$.—The barium salt was also made in the same manner as the sodium salt, care being taken to

[1] *Ber.,* **45,** 1602 (1912).

let the concentrated solution evaporate slowly in a desiccator over soda-lime. As the thin, yellow prisms of the barium salt are partly dehydrated in air, the drying must be accomplished by pressing between filter paper.

0.3869 gram dry salt lost 0.0571 gram H_2O at 105°, and gave 0.1417 gram $BaSO_4$. Calculated for $(C_9H_8O_4N)_2Ba.5H_2O$: H_2O, 14.63; Ba, 22.31. Found: H_2O, 14.76; Ba, 21.55.

2,3-Diacetyl-5-nitrocyclopentadiene Monoxime,

$$C_5H_3(NO_2)(COCH_3)(C(CH_3) : NOH).$$
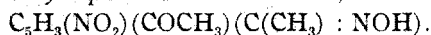
—A solution of the sodium salt of the cyclopentadiene was treated with one molecule of free hydroxylamine prepared by neutralizing one molecule of the hydrochloride in concentrated aqueous solution with sodium carbonate. To this deep red solution an equal volume of alcohol was added, and in the course of a few minutes this was followed by acidification with hydrochloric acid. The presence of the alcohol insures the separation of the oxime in crystallin form; otherwise, a flocculent precipitate, difficult for purification, is thrown down. This monoxime dissolves to a deep red color in sodium hydroxide but no further condensation was noted. All attempts to prepare the dioxime by the action of hydroxylamine in excess either upon the cyclopentadiene or the monoxime itself were unsuccessful.

The monoxime is insoluble in ligroin or carbon disulfide and only sparingly soluble in benzene, chloroform, ether or water, even hot. It is readily soluble in acetone, from which it may be crystallized upon the addition of ligroin. It is fairly soluble in alcohol, acetic ester or acetic acid, crystallizing from each, but best from alcohol, in clusters of glistening, orange yellow leaflets. It melts with decomposition at 155°.

0.2268 gram substance: 0.4257 gram CO_2, 0.1032 gram H_2O; 0.1619 gram substance: 19.5 cc. N_2 (23°, 745.7 mm. over H_2O).

Calculated for $C_9H_{16}O_4N_2$:   C, 51.40; H, 4.80; N, 13.34.
Found: C, 51.23; H, 5.09; N, 13.25.

2,3-Diacetyl-5-nitrocyclopentadiene Monanil, $C_5H_3(NO_2)(COCH_3)(C(CH_3):-NC_6H_5)$.—A solution of the cyclopentadiene in alcohol was treated with an excess of aniline hydrochloride and gently warmed for a few minutes. Upon cooling, the monanil separated out in yellow clusters of needles. Free aniline may be used in place of the salt, but the separation of the anil is not so satisfactory. An excess of aniline, either upon the cyclopentadiene or the monanil, failed to give a dianil. The monanil is readily soluble in benzene, chloroform, acetone, or acetic ester; it is insoluble in water or ligroin, slightly soluble in ether, and fairly soluble in alcohol, carbon disulfide, or acetic acid, crystallizing from either of these three, but more easily from slightly diluted acetic acid or from alcohol, in yellow clusters of needles, melting at 166.5°.
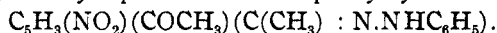
0.1686 gram substance: 0.4131 gram CO_2, 0.0783 gram H_2O; 0.3047 gram substance: 29.2 cc. N_2 (22°, 741.8 mm. over H_2O).

Calculated for $C_{15}H_{14}O_3N_2$:   C, 66.64; H, 5.22; N, 10.37.
Found: C, 66.82; H, 5.19; N, 10.54.

Attempts to prepare an oxime of this monanil by various methods met with negative results.

2,3-Diacetyl-5-nitrocyclopentadiene Monophenylhydrazone,
$$C_5H_3(NO_2)(COCH_3)(C(CH_3) : N.NHC_6H_5).$$

—The light yellow flocculent monophenylhydrazone is precipitated at once from an alkalin solution of the cyclopentadiene by the addition of an excess of a solution of phenylhydrazine hydrochloride. The addition of the hydrochloride should not be too rapid at the beginning, else some of the original cyclopentadiece may be thrown down. The product should be crystallized at once from alcohol, from which it separates in slender, yellow needles melting with decomposition at 175–80°. It is readily soluble in chloroform, acetic ester or acetone; only fairly soluble in acetic acid, alcohol or benzene, and practically insoluble in ether, water or ligroin. In solutions of anhydrous solvents, continued boiling effects a transformation of this phenylhydrazone into a bicyclic compound now under investigation. The same result is accomplished by the action of alkalin solutions, in which the phenylhydrazone is readily soluble to a deep red color.

0.1853 gram substance: 24.9 cc. N_2 (23.5°, 738.4 mm. over H_2O).
Calculated for $C_{15}H_{15}O_3N_3$: N, 14.74.   Found: N, 14.60.

2,3-Diacetyl-5-nitrocyclopentadiene Monohydrazone,
$$C_5H_3(NO_2)(COCH_3)(C(CH_3) : N.NH_2).$$
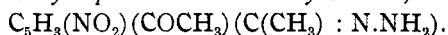
—When an excess of hydrazine sulfate, in warm aqueous solution, is added to a solution of the sodium salt of the cyclopentadiene, containing about one-half molecule of free sodium hydroxide, a yellow precipitate of the monohydrazone soon makes its appearance. Too rapid an addition of the hydrazine salt may precipitate some of the unacted upon cyclopentadiene, a result almost unavoidable when there is not sufficient free alkali present as directed above. The yield of yellow monohydrazone is good. It crystallizes best from alcohol in small nodules, which decompose at 185–90°. It is slightly soluble in benzene, acetic ester, chloroform, acetone, ether or acetic acid; it is insoluble in ligroin, water or carbon disulfide, and fairly soluble in alcohol when first prepared. The presence of any free cyclopentadiene may be removed by digestion in ether, which dissolves scarcely any hydrazone. The crude product when dry is not so readily dissolved by hot alcohol. It is difficult to powder, owing to electrostatic conditions. This hydrazone is soluble in alkali with deep red color, but upon standing over night this red solution deposits crystals of a second substance now under investigation. This latter product also results when the cyclopentadiene remains for any length of time in the presence of free hydrazine.

0.1312 gram substance: 24 cc. N_2 (21.4°, 741.6 mm. over H_2O).

Calculated for $C_9H_{11}O_3N_3$: N, 20.10.   Found: N, 20.18.

Sodium   Salt   of   2,3-Dicinnamyl-5-nitrocyclopentadiene,

$C_5H_2(: NO.ONa)(CO.CH : CH.C_6H_5)_2$.
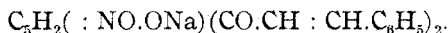
—One molecule of the sodium salt of diacetylnitrocyclopentadiene was dissolved in 10 times its weight of water and the volume doubled by the addition of an equal volume of alcohol.   To this solution 3 to 4 molecules of benzaldehyde and an excess of sodium hydroxide (7 or 8 molecules) were then added.   This large excess of alkali hastens materially the condensation.   In the course of 36 hours the reaction may be considered complete, and the large quantity of yellow crystallin precipitate filtered off.   From 1 gram of the free cyclopentadiene there was obtained, as sodium salt, 1.92 grams of condensation product, a weight equal to 95% of the theoretical sodium dicinnamyl derivative and indicating at once that two molecules of benzaldehyde had entered into condensation with one molecule of cyclopentadiene.

The product is almost insoluble in water and only sparingly soluble in alcohol, but fairly soluble in acetone.   From its solution in acetone it is easily precipitated by ligroin in small, yellow prisms.   When suspended in water and warmed with concentrated hydrochloric acid there is apparently no action: the free substance at first formed undoubtedly precipitates upon the mass of sodium salt and prevents further action by the acid.   If, however, this sodium salt is dissolved in acetone and an acid added, the free substance is at once precipitated.   The sodium salt is anhydrous and accorded with the following analysis:

0.2610 gram substance: 0.0466 gram Na_2SO_4.

Calculated for $C_{23}H_{16}O_4N.Na$: Na, 5.85.   Found: Na, 5.79.

2,3-Dicinnamyl-5-nitrocyclopentadiene, $C_5H_3(NO_2)(CO.CH : CH.C_6H_5)_2$ (III).—As just stated, this compound was obtained by the action of an acid, preferably acetic acid, upon the acetone solution of its sodium salt. The product first precipitated is practically pure.   It is only slightly soluble in alcohol, acetone, acetic ester, acetic acid, carbon tetrachloride, benzene or ether; somewhat more soluble in carbon disulfide, and fairly soluble in chloroform.   It is insoluble in water or ligroin.   From its solution in chloroform, ligroin precipitates the substance in small, orange yellow needles melting with decomposition at 253–5°.

0.1946 gram substance: 0.5286 gram CO_2, 0.0842 gram H_2O; 0.3054 gram substance: 11.1 cc. N_2 (27°, 729.8 mm. over H_2O).

Calculated for $C_{23}H_{17}O_4N$:   C, 74.37;   H, 4.62;   N, 3.78.

Found: C, 74.10;   H, 4.84;   N, 3.83.

Determination of Acetyl Groups in Acetylnitrocyclopentadiene.—The action of iodine upon this cyclopentadiene in alkalin solution readily gave

the corresponding amount of iodoform. The method differs in no respect from that usually employed save that the iodoform itself was determined by weighing. Four-tenths gram of the cyclopentadiene was dissolved in 10 cc. of water by the aid of sufficient alkali to bring all into solution as a potassium salt. To this were now added 25 cc. of a solution containing per liter 250 grams of potassium iodide and 200 grams of potassium hydroxide. Into this strongly alkalin solution was run a solution of sodium hypochlorite until no further precipitation of iodoform occurred. A deep red color is developed by means of the presence of free iodine.

The precipitate of iodoform was filtered off through a Gooch crucible and dried over calcium chloride for 12 hours. The weight of iodoform was 1.56 grams. Calculated upon the basis of 1 molecule of iodoform to 1 molecule of cyclopentadiene, we should have 0.81 gram of iodoform from the 0.4 gram of substance employed. The value 1.56/0.81 or 1.93 represents, therefore, the number of molecules (2) of iodoform produced in the decomposition of 1 molecule of the cyclopentadiene. We conclude, therefore, that this value indicates the presence of 2 acetyl groups as substituents in the original compound.

Oxidation of 2,3-Diacetyl-5-nitrocyclopentadiene.—The oxidation is best accomplished by adding potassium permanganate to an aqueous solution of the potassium salt, containing an excess of potassium hydroxide. One-half gram free cyclopentadiene was dissolved in 300 cc. of water containing 4 grams of potassium hydroxide, and to this solution, heated upon a water bath, 4 grams of powdered potassium permanganate slowly added. About 20 hours were required for the completion of the oxidation at this temperature. The slight excess of potassium permanganate was removed by action of sulfur dioxide and the large mass of manganese dioxide filtered off. The clear, yellow filtrate from the oxidation mixture was acidified with phosphoric acid and distilled till only a small volume, 5 to 10 cc., remained. The distillate was titrated with a barium hydroxide solution (0.03132 N) of which 127 cc. were required. This amount of barium hydroxide corresponds to 0.238 gram of acetic acid, a value approaching that weight of acetic acid, 0.307 gram, calculated in the production of 2 molecules of acid from 1 molecule (*i. e.*, 0.5 gram) of the cyclopentadiene.

The residue in the distilling flask held the phosphoric and oxalic acids. The estimation of oxalic acid was carried out by making the solution slightly alkalin with ammonia and then adding an excess of acetic acid, upon which the oxalic acid was precipitated by calcium chloride as calcium oxalate. This oxalate, filtered off and dried at 100°, weighed 0.318 gram, a value agreeing well with the weight, 0.328 gram, as calculated for 1 molecule of calcium oxalate per molecule (0.5 gram) of cyclopentadiene.

When a second sample of 0.5 gram cyclopentadiene was oxidized in an exactly similar manner to that just described, and the clear, yellow filtrate from the manganese dioxide treated at once with ammonium chloride and calcium chloride, the precipitate obtained consisted of carbonate and oxalate of calcium. This collected precipitate weighed 1.03 grams. This precipitate was then dissolved in dilute sulfuric acid and the solution titrated with 0.05 N potassium permanganate. The weight of oxalic acid thus determined was found to accord with 1 molecule as in the previous determination; hence, this same weight of calcium oxalate determined here and in the previous case, 0.318 gram, may be subtracted from the total weight of precipitated oxalate and carbonate (1.03 grams). The remainder, or calcium carbonate, was thus found to weigh 0.712 gram. When calculated for 3 molecules of CO_2 the oxidation of 1 molecule of cyclopentadiene (i. e., 0.5 gram in this example) should give 0.769 gram of calcium carbonate, a value in fair agreement with the determinations.

This complete oxidation by means of potassium permanganate requires 6 molecules of oxygen per 1 molecule of cyclopentadiene. The weight of permanganate necessary to furnish this amount of oxygen is 1263 grams, or 8 molecules, about 3.2 grams of $KMnO_4$ for 0.5 gram of substance, a weight corresponding fairly well with the weight of permaganate consumed in the reaction. There result, therefore, from this oxidation, 1 molecule of oxalic acid, 2 molecules of acetic acid, 3 molecules of carbon dioxide and 1 molecule of nitric acid. This latter was indicated only qualitatively by the diphenylamine-sulfuric acid test.

Nitric acid also sufficed to break up the cyclopentadiene molecule, but difficulty was experienced in securing uniform results. The acid employed was required to be of such concentration that the oxalic acid itself was attacked. The yellow oxidation mixture, however, always gave the requisit amount of acetic acid upon distillation with steam.

Action of Halogens and Halide Acids upon 2,3-Diacetyl-5-nitrocyclopentadiene.—Samples of the cyclopentadiene were exposed in closed vessels to the vapors of bromine for many weeks, and in no case was any absorption of bromine detected. In a similar manner, there was found no tendency for this substance to take up hydrogen bromide or iodide. So, also, when dissolved in chloroform and other anhydrous solvents, the halides and halide acids, as well as sulfuryl chloride and nitrosyl chloride, were without action.

For the kind assistance of Mr. G. B. Britton and Dr. Lambert Thorp upon much of the analytical data in this paper, the author desires to express his indebtedness.