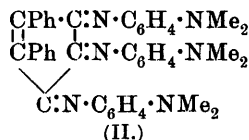
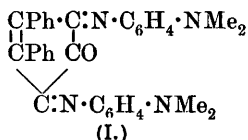


IV.—*Diphenylcyclopentenone.*

By SIEGFRIED RUHEMANN and WILLIAM JOHNSON SMITH NAUNTON.

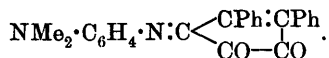
THE study of the cyclic ketonic compounds, in which one of us has been engaged for some time, led to the knowledge of triketohydrindene, the first member of the cyclic triketones containing three adjacent ketonic groups in an *isocyclic* system. This compound appears to be of especial interest on account of its close resemblance to alloxan and of its characteristic colour reactions with proteins and their hydrolytic products.

With the view of preparing similar substances and examining their behaviour, we have subjected 3:4-diphenylcyclopentenone, $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{CPh} \\ | \\ \text{CH}_2 \cdot \text{CPh} \end{smallmatrix}$, which Japp and Burton (Trans., 1887, **51**, 420) obtained by the action of hydriodic acid on anhydroacetonebenzil, to the same treatment as the mono- and di-ketones of hydrindene. On applying Sachs and Barschall's method of transforming methylene groups into ketonic groups (*Ber.*, 1901, **34**, 3047), it was found that *p*-nitrosodimethylaniline reacts with the cyclopentenone mainly to form 2:5-bis-dimethylaminoanilo-3:4-diphenylcyclopentenone (I), but at the same time a compound is produced, the



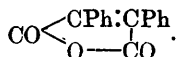
analytical results of which point to a compound of the formula (II).

Its formation is to be explained by the assumption of the partial reduction of the former compound, and its subsequent condensation with another molecule of *p*-nitrosodimethylaniline. This constitution is supported by its behaviour towards mineral acids, since both substances yield 5-dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione :



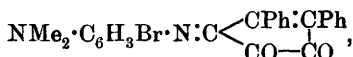
The fact that, under the influence of acids, the groups $\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ are removed with the exception of one of them, is most remarkable in view of the observations of Sachs and his collaborators, and of the fact that bis-dimethylaminoanilo- α -hydrindone on treatment with acids readily yields triketohydrindene hydrate (Trans., 1910, **97**, 1438). The stability of 5-dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione is, in fact, so great that

the removal of the group $\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ could not be accomplished without effecting at the same time a deep-seated change to diphenylmaleic anhydride:



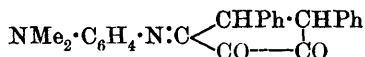
This transformation takes place very slowly and incompletely on boiling the compound with potassium hydroxide or hydrochloric acid under the ordinary pressure, but more readily on heating with concentrated hydrochloric acid at $130\text{--}140^\circ$ for several hours. The change of 5-dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione into 4:5-diphenylcyclopentene-1:2:3-trione, $\text{CO} \begin{array}{c} \diagup \text{CO} \cdot \text{CPh} \\ \diagdown \text{CO} \cdot \text{CPh} \end{array}$, cannot be effected by means of either nitric acid or bromine. These reagents mainly yield substitution products.

With fuming nitric acid it forms a deep red *dinitro*-derivative, $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2(\text{NO}_2)_2$, whereas bromine reacts with the compound to form a yellow *monobromo*-derivative, $\text{C}_{25}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}$, when the reagents are used in molecular proportions. From the fact that this bromo-substitution product, on heating with concentrated hydrochloric acid, yields diphenylmaleic anhydride, it follows that substitution has taken place in the benzene nucleus of the dimethylaminoanilo-group, and that therefore its constitution is to be represented thus:



in which only the orientation of the bromine atom is doubtful. On using, however, two molecules of the halogen to one molecule of the substance, a yellow, crystalline compound is obtained, which loses halogen even on drying in the air. This substance is undoubtedly the perbromide of a bromo-substitution product of the azomethine. On boiling with alcohol, this perbromide decomposes, and yields besides the former yellow monobromo-substitution product, a deep red *dibromo*-derivative of the azomethine.

The red solution of the compound, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$, in glacial acetic acid is readily decolorised by zinc dust to yield colourless base, $\text{C}_{25}\text{H}_{22}\text{O}_2\text{N}_2$, which is to be regarded as 5-dimethylaminoanilo-3:4-diphenylcyclopentane-1:2-dione:



This constitution follows from the fact that the substance on heating with concentrated hydrochloric acid decomposes to form *s*-diphenylsuccinic acid.

The azomethine, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$, is orange or red, and has basic

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properties, forming salts with acids, which, with the exception of the platonic salt, are readily dissociated by water. The compound is practically insoluble in cold alcohol, but on boiling it dissolves sparingly, and on cooling small, deep red plates separate from the concentrated solutions, whereas it crystallises from more dilute solutions in absolute alcohol in orange needles. If a little water is added to the hot alcoholic solution of the compound, no crystals separate on cooling, but the whole sets to a transparent jelly, which according to the concentration is yellow or yellowish-red. This gel, when kept at the ordinary temperature, gradually liquefies, and in the course of one to two days completely disappears, with separation from the resulting solution of the azomethine in orange needles. The transformation of the substance into the colloidal state occurs with solvents which are miscible with water, and therefore takes place with acetone, but it is not observed in solvents like chloroform or benzene, which are immiscible with water. It is probable that this phenomenon is accompanied by the formation of a hydrate, which spontaneously loses water and yields the original compound. This exceptional property of the azomethine, which is not to be found with its bromo- or nitro-substitution products, will be subjected to a closer study.

EXPERIMENTAL.

Action of p-Nitrosodimethylaniline on 3:4-Diphenylcyclopentenone.

The cyclopentenone was prepared from anhydroacetonebenzil according to the directions of Japp and Lander (Trans., 1897, 71, 131), with the difference that the product which is obtained on the reduction of anhydroacetonebenzil was twice recrystallised from alcohol with the use of animal charcoal, instead of distilling under diminished pressure, as stated by these authors. The compound was obtained in colourless needles melting at 110°. On treatment with *p*-nitrosodimethylaniline it was found that two condensation products are produced, which contain two and three dimethylamino-anilo-groups respectively, even when the reagents are used in the proportion of one molecule of the pentenone to two molecules of the nitroso-derivative. On account of this fact an excess of the nitroso-compound was used, and the reaction was carried out as follows: The pentenone (5 grams) and *p*-nitrosodimethylaniline (10—12 grams), dissolved in hot alcohol, are mixed, and a little concentrated alcoholic potassium hydroxide is gradually added to the cold solution of the mixture. The green colour of the solution changes to brown, and a dark solid separates, which increases in quantity in the course of three to four days. To remove impurities

it is boiled with alcohol, in which it is only sparingly soluble, and dried in the steam-oven; the product dissolves in hot chloroform to yield a dark red solution, and on cooling partly crystallises in brown needles, whereas the other part does not separate until the solution is considerably concentrated or mixed with alcohol. The substance which is less soluble in chloroform melts at 255° , but on repeated crystallisation from the same solvent it is obtained in chocolate-coloured needles, which melt at 265° after softening a few degrees before:

0.2031 gave 0.5855 CO_2 and 0.1190 H_2O . $\text{C}=78.62$; $\text{H}=6.51$.

0.2012 „ 0.5807 CO_2 „ 0.1175 H_2O . $\text{C}=78.71$; $\text{H}=6.49$.

0.2021 „ 24.5 c.c. N_2 at 21° and 755 mm. $\text{N}=13.67$.

$\text{C}_{41}\text{H}_{40}\text{N}_6$ requires $\text{C}=79.87$; $\text{H}=6.49$; $\text{N}=13.63$ per cent.

The substance appears to be 1:2:3-*tris-dimethylaminoanilo-4:5-diphenylcyclopentene* (II, p. 42).

The deficit in the percentage of carbon is probably due to a small quantity of impurity, although after more frequent recrystallisation results were obtained on analysis which do not materially differ from those given above.

The purification of the main product of the action of *p*-nitrosodimethylaniline on diphenylcyclopentenone, which product is contained in the mother liquor of the former condensation product, can be readily accomplished. It separates on distilling the larger portion of the chloroform and adding alcohol to the hot concentrated solution until crystallisation commences. If the substance is twice recrystallised from a mixture of chloroform and alcohol, it is obtained in bronze needles, which melt at $211-212^{\circ}$:

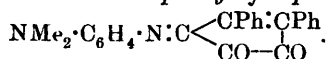
0.1760 gave 0.5125 CO_2 and 0.0965 H_2O . $\text{C}=79.42$; $\text{H}=6.09$.

0.1633 „ 15.8 c.c. N_2 at 19° and 775 mm. $\text{N}=11.34$.

$\text{C}_{30}\text{H}_{30}\text{ON}_4$ requires $\text{C}=79.51$; $\text{H}=6.02$; $\text{N}=11.24$ per cent.

This compound is 2:5-*bis-dimethylaminoanilo-3:4-diphenylcyclopentenone* (I, p. 42).

5-Dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione,



Both substances which are formed by the condensation of *p*-nitrosodimethylaniline with the cyclopentenone show the same behaviour; they have basic properties, and dissolve in cold hydrochloric or sulphuric acids to yield deep red solutions, which gradually at the ordinary temperature, but rapidly on warming on the water-bath, become turbid; a yellow, tenacious, and elastic product separates, which in the course of a day sets to a hard,

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brittle mass, turning red on washing with water. This substance dissolves in boiling absolute alcohol, and on cooling crystallises in orange needles, melting at $191-192^{\circ}$:

0.1681 gave 0.4865 CO_2 and 0.0790 H_2O . $\text{C}=78.93$; $\text{H}=5.22$.

0.1733 „ 11.4 c.c. N_2 at 23° and 764 mm. $\text{N}=7.45$.

$\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{C}=78.95$; $\text{H}=5.26$; $\text{N}=7.37$ per cent.

5-Dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione is sparingly soluble in ether, almost insoluble in cold alcohol; it dissolves sparingly in boiling alcohol, 1 gram of the substance requiring 110 c.c. of boiling alcohol; from this solution the compound separates in small, deep red plates as compared with the orange needles, in which it crystallises from less concentrated solutions in absolute alcohol. It has been mentioned above (p. 44) that the behaviour of the substance is quite different if water is added even to the dilute solution in absolute alcohol; on cooling in this case no crystals separate, but the whole sets to a transparent jelly, which gradually liquefies, and at the same time deposits orange needles of the original compound. The same phenomenon occurs if acetone is used as a solvent instead of alcohol. The compound, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$, is very soluble in benzene or chloroform, but the red solutions which are formed do not gelatinise on the addition of water.

The azomethine has basic properties, forming salts with acids, which, however, are dissociated by water. On the addition of hydrochloric acid it turns yellow, and yields a gelatinous hydrochloride identical with the salt which is formed in the preparation of the azomethine from the condensation-products of diphenylcyclopentenone with *p*-nitrosodimethylaniline. The hydrochloride gradually solidifies to a brittle mass, which on washing with water loses hydrogen chloride and turns orange. The hydrochloride readily dissolves in alcohol to yield a yellow solution, which on treatment with platinum chloride forms a *platinichloride*, separating in bunches of yellow needles; they soften at 232° , and melt and decompose at 236° :

0.3055 gave 0.0509 Pt. $\text{Pt}=16.66$.

$(\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt}=16.68$ per cent.

The orange substance, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$, also forms a yellow sulphate, which is readily decomposed by water into base and acid.

Formation of Diphenylmaleic Anhydride from 5-Dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione.

The compound, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$, on boiling with concentrated aqueous potassium hydroxide or with hydrochloric acid under the ordinary

pressure is only slightly attacked, but when heated with concentrated acid in a sealed tube to 130—140° for four hours it is transformed into a pale yellow solid. This is collected, washed with water, and digested with dilute potassium hydroxide, when it almost completely dissolves. On adding hydrochloric acid to the alkaline filtrate a flocculent substance is precipitated, which readily dissolves in hot alcohol, and crystallises from dilute alcohol in faintly yellow needles, melting at 156—157°. The melting point and the properties characterise this compound as diphenylmaleic anhydride, $\text{CO} \begin{array}{c} \text{CPh} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{array}$. Its composition has been verified by analysis.

(Found, C=76·85; H=4·01. Calc., C=76·80; H=4·00 per cent.) The action of hydrochloric acid on the azomethine, therefore, not only effects the replacement of the group :N·C₆H₄·NMe₂ by oxygen, but at the same time the removal of the adjacent ketonic group. All attempts to produce 4:5-diphenylcyclopentene-1:2:3-trione (p. 43) or its hydrate from the compound C₂₅H₂₀O₂N₂ have been unsuccessful.

Action of Bromine and Nitric Acid on the Compound C₂₅H₂₀O₂N₂.

By the action of these reagents the removal of the group :N·C₆H₄·NMe₂ does not take place, but substitution products are formed instead. If bromine (1 gram) is gradually added to the solution of the azomethine (2·3 grams) in chloroform, the halogen rapidly disappears, the colour of the solution becomes yellow, and no precipitate is formed if the reagents are used in exact equimolecular proportions. On mixing the chloroform solution with light petroleum a yellow solid is precipitated, which dissolves in much boiling alcohol, and on cooling slowly crystallises in long, yellow prisms, which soften at about 152°, and melt at 154° to a red liquid:

0·2017 gave 0·4828 CO₂ and 0·0770 H₂O. C=65·28; H=4·24.

0·2545 „ 0·1038 AgBr. Br=17·35.

C₂₅H₁₉O₂N₂Br requires C=65·36; H=4·14; Br=17·43 per cent.

The bromo-derivative is sparingly soluble in ether or cold alcohol. With mineral acids it forms salts, which are readily dissociated by water. The hydrochloride dissolves in warm alcohol, and the cold yellow solution on the addition of platinic chloride yields a *platinichloride*, which gradually separates in yellow needles, softening at 189° and melting at 195°:

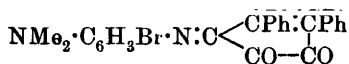
0·2730 gave 0·0395 Pt. Pt=14·47.

(C₂₅H₁₉O₂N₂Br)₂·H₂PtCl₆ requires Pt=14·67 per cent.

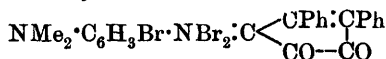
The bromo-derivative, which does not show the phenomenon of

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being transformed into the colloidal state, on heating with concentrated hydrochloric acid in a closed tube at 135—140° for about five hours, suffers a similar decomposition to the azomethine, $C_{25}H_{20}O_2N_2$. An almost colourless solid is formed, which dissolves in hot dilute potassium hydroxide, and is precipitated from the alkaline solution on the addition of hydrochloric acid. The substance crystallises from dilute alcohol in pale yellow prisms, which are free from halogen and melt at 156—157°. These properties characterise it as diphenylmaleic anhydride. Its formation leads to the conclusion that the bromine has entered into the benzene nucleus of the dimethylaminoanilo-group of the azomethine, and that, therefore, the bromo-derivative has the formula:



Quite different, however, is the action of bromine on the azomethine, $C_{25}H_{20}O_2N_2$, if two molecules of halogen are slowly added to a solution of one molecule of the compound in chloroform; in this case a precipitate consisting of bunches of yellow needles is produced. This product, which is very sparingly soluble in chloroform, is very unstable, since it constantly loses bromine in a vacuum desiccator or even on drying in the air. This behaviour, which points to the view that the substance is a perbromide, prevented us from fixing its composition by analysis, but the decomposition which it suffers on boiling with alcohol, in which it yields a mixture of the mono- and dibromo-derivatives of the azomethine, indicates that it is the perbromide of the yellow monobromo-compound, $C_{25}H_{19}O_2N_2Br$, and that, therefore, it is probably represented by the formula:



The perbromide dissolves in much boiling alcohol to yield a yellow solution, from which, on cooling, red needles separate; these, however, do not represent a pure substance, but a mixture of the yellow bromo-compound, $C_{25}H_{19}O_2N_2Br$, and a red dibromo-derivative of the azomethine. Owing to the fact that the dibromo-compound is less soluble than the monobromo-derivative, the isolation of the former can be effected by recrystallisation from boiling alcohol. After repeating the process of purification three times, the *dibromo*-derivative is obtained in long, scarlet needles, which soften at 212°, and melt at 214°:

0.2076 gave 0.4262 CO_2 and 0.0625 H_2O . $C = 55.99$; $H = 3.34$.

0.2090 „ 0.1450 $AgBr$. $Br = 29.53$.

$C_{25}H_{19}O_2N_2Br_2$ requires $C = 55.76$; $H = 3.34$; $Br = 29.73$ per cent.

The alcoholic liquor from this compound, on concentration, yielded yellow prisms, which were identified as the monobromo-compound, $C_{25}H_{19}O_2N_2Br$, by the melting point.

Fuming nitric acid readily reacts with the azomethine, $C_{25}H_{20}O_2N_2$. On adding an excess of the acid to the cold solution of the compound in glacial acetic acid, a dinitro-derivative, $C_{25}H_{18}O_2N_2(NO_2)_2$, gradually separates. It is sparingly soluble in boiling alcohol, readily so in hot glacial acetic acid, and crystallises in well-defined scarlet prisms, which soften at 220° and melt and decompose at 224° :

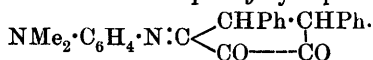
0.2027 gave 0.4766 CO_2 and 0.0733 H_2O . $C=64.12$; $H=4.01$.

0.2254 „ 24 c.c. N_2 at 20° and 759 mm. $N=12.16$.

$C_{25}H_{18}O_6N_4$ requires $C=63.83$; $H=3.83$; $N=11.91$ per cent.

The positions of the nitro-groups in this compound have not been ascertained, but judging from the action of bromine on the azomethine, $C_{25}H_{20}O_2N_2$, there can hardly be any doubt that at least one of them is contained in the benzene nucleus of the dimethylaminoanilo-group. Simultaneously with the formation of the dinitro-derivative, there is produced a small amount of diphenylmaleic anhydride, which is contained in the mother liquor of the product of the reaction, and is precipitated on the addition of water. It was purified by dissolving it in warm alkali, and reprecipitating it with acid. After recrystallisation from dilute alcohol, it melted at $156-157^\circ$.

5-Dimethylaminoanilo-3:4-diphenylcyclopentane-1:2-dione,



As yet only the action of zinc dust on the solution of the azomethine in glacial acetic acid has been examined, with the result that a colourless compound, with the composition $C_{25}H_{22}O_2N_2$, is produced. The red solution of the azomethine (5 grams) in acetic acid is readily decolorised by zinc dust, and on adding water to the filtrate a colourless solid (3.5 grams) is precipitated, which dissolves in much boiling alcohol, and, on cooling, crystallises in colourless needles, melting at $210-211^\circ$:

0.2168 gave 0.6255 CO_2 and 0.1155 H_2O . $C=78.68$; $H=5.92$.

0.1997 „ 13.3 c.c. N_2 at 18° and 742 mm. $N=7.50$.

$C_{25}H_{22}O_2N_2$ requires $C=78.53$; $H=5.75$; $N=7.33$ per cent.

The substance has basic properties, forming a hydrochloride which, with platinic chloride, yields a *platinichloride*:

0.2470 gave 0.0393 Pt. $Pt=15.91$.

$(C_{25}H_{22}O_2N_2)_2 \cdot H_2PtCl_6$ requires $Pt=15.72$ per cent.

The base, $C_{25}H_{22}O_2N_2$, on heating with concentrated hydrochloric acid at $130-140^\circ$ for three hours, decomposes in a manner similar to 5-dimethylaminoanilo-3:4-diphenylcyclopentene-1:2-dione to yield *s*-diphenylsuccinic acid. The colourless solid which is produced in this reaction is collected, washed with water, and dissolved in hot dilute alcohol or acetic acid; from these solutions the acid separates in colourless needles or prisms, which melt at 252° . (Found, $C=71.18$; $H=5.30$. Calc., $C=71.11$; $H=5.19$ per cent.)

This acid is β -diphenylsuccinic acid. The statements as to its melting point differ widely. Reimer (*Ber.*, 1881, **14**, 1803), as well as Chalaney and Knoevenagel (*Ber.*, 1892, **25**, 296), give 229° ; Anschütz and Bendix (*Annalen*, 1890, **259**, 61), 245° ; whereas Roser (*Annalen*, 1888, **247**, 152) found 252° , which latter statement agrees with our observation. An explanation for these great differences cannot as yet be given. The acid mother liquor from β -*s*-diphenylsuccinic acid, which is formed by the decomposition of dimethylaminoanilodiphenylcyclopentanedione, also contains, in addition to dimethyl-*p*-phenylenediamine, α -*s*-diphenylsuccinic acid. This was extracted with ether, and after evaporation of the ether was recrystallised from water, in which it is rather soluble. It fuses at 183° , then solidifies, and finally melts at $220-221^\circ$; this observation agrees with Reimer's statement (*loc. cit.*).

The behaviour of diphenylcyclopentenone recorded in this paper is of sufficient interest to merit a closer study. This work is in progress as well as the investigation of other cyclic ketonic compounds on the same lines as those employed in the case of the ketones of the hydrindene series.

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