XLVI.—*On the Action of Aldehydes and Ammonia on Benzil*
(continued).

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Introduction.

THE reactions of benzil with aldehydes and ammonia have as yet been studied only in the case of aldehydes of the benzene series, and the same holds good with regard to the other diketones which have been substituted for benzil in these reactions—phenanthraquinone and chrysoquinone. The reactions of another dicarbonyl-compound (glyoxal) with aldehydes and ammonia have, however, been studied in the case of fatty aldehydes by Radziszewski, who thus effected a new synthesis of homologues of glyoxaline.

In the present communication, we describe the reactions of benzil with fatty aldehydes and ammonia. We have also in one case employed a benzene-fatty aldehyde, cinnamaldehyde.

With fatty aldehydes, the reaction took place according to Equa-

tion II (Trans., 1884, 672) of the general reactions of this class, and substituted glyoxalines were obtained. Thus with acetaldehyde:—

A similar reaction occurred with isovaleraldehyde. Cinnamaldehyde, on the other hand, did not react with benzil and ammonia under the conditions of our experiment.

With cinnamaldehyde, two distinct reactions occur. A part of the substance reacts according to Equation III of the general reactions (*loc. cit.*, p. 673), thus:—

This compound is analogous to that obtained from benzil, salicylaldehyde, and ammonia (*loc. cit.*), but unlike the salicylaldehyde compound, could not be converted into the non-benzoylated derivative. When heated with a solution of caustic potash in methyl alcohol, it parts with 1 mol. of benzoic acid, and is converted into an anhydro-base:—

This base, so far as we know, is the only compound yet prepared which contains the hydrogenated glyoxaline-complex—

A different hydrogenated glyoxaline-complex of the formula—

is, however, assumed to exist in amarine.

Another portion of the cinnamaldehyde above referred to reacts with benzil and ammonia in molecular proportions different from any hitherto observed in this class of reactions:—

This, therefore, constitutes the *fourth* of the distinct reactions (cf. *loc. cit.*) in which aldehydes and dicarbonyl compounds jointly form condensation-products with ammonia. We shall show in a further communication (see following paper) that a similar reaction occurs when ammonia acts on benzil alone to form imabenzil,—nascent benzaldehyde, formed by the breaking up of a portion of the benzil, taking the part of the cinnamaldehyde in the foregoing equation. The reaction is probably, therefore, of more general application. The foregoing analogy has led us to name the compound $\text{C}_{37}\text{H}_{30}\text{N}_2\text{O}_3$ *cinnimabenzil*.

By treatment in the cold with a solution of potash in methyl alcohol, cinnimabenzil is decomposed, according to the equation—

When boiled with dilute sulphuric acid, it is decomposed as follows :—

I. *Acetaldehyde and Ammonia with Benzil.*

20 grams of benzil and 8·5 grams of aldehyde were dissolved in a quantity of alcohol sufficient to keep the benzil in solution at 40°, and the warm liquid was then saturated with gaseous ammonia, after which the whole was allowed to remain for 24 hours. As nothing had separated at the end of that time, the solution was poured into water. A white flocculent substance was precipitated, which was thoroughly washed with water and then boiled with hot *dilute* hydrochloric acid, in which everything dissolved with the exception of a small quantity of resin. If the acid is too concentrated, the hydrochloride of the new base melts to an oil under the liquid, instead of dissolving. The base was precipitated by ammonia, and recrystallised from boiling benzene, which deposited it in tufts of minute colourless needles, with a constant melting point of 235°. It is practically insoluble in water, but dissolves readily in alcohol and in ether. From the solution in hot alcohol, it is deposited on cooling in well-formed crystals of the orthorhombic system (*vide infra*). These had a very faint yellowish tinge.

Analysis of a sample crystallised from benzene gave numbers agreeing with the formula $C_{16}H_{14}N_2$:—

	Substance.	CO ₂ .	H ₂ O.
I.....	0.1138	0.3408	0.0628
II.....	0.1177	0.3528	0.0640

III. 0.1076 gram, burnt with copper oxide in a vacuum, gave 21.91 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18°, and under 391.5 mm. pressure. After absorption of the nitric oxide there remained 21.91 c.c. of dry nitrogen at 17.8°, and under 365 mm. pressure.

	Calculated for $C_{16}H_{14}N_2$.		Found.		
			I.	II.	III.
C ₁₆ ...	192	82.05	81.67	81.75	—
H ₁₄ ...	14	5.98	6.13	6.04	—
N ₂	28	11.97	—	—	11.95
	234	100.00			

The constitutional formula of this compound, and the equation expressing its formation, have already been given. In accordance with this constitution, it would receive the name *methyldiphenylglyoxaline* :—

Mr. L. Fletcher has had the kindness to measure the crystals deposited from alcohol. He reports as follows :—

“ *Methyldiphenylglyoxaline*.

COLOUR—Faintly yellow.

One crystal, about a millimetre in diameter, was measured.

SYSTEM—Orthorhombic.

ELEMENTS— $a : b : c :: 1.207 : 1 : 1.929$,

or $011.010 = 27^\circ 24' : 101.001 = 57^\circ 58\frac{1}{2}' : 110.100 = 50^\circ 21'$.

FORMS PRESENT— $\{010\}\{001\}\{012\}\{201\}\{111\}\{112\}\{113\}$.

DEVELOPMENT—*Vide* figure.

Angles.	Observed.	Calculated.
001.113	$39^\circ 55' - 40^\circ 23'$	$39^\circ 52'$
113.112	$11^\circ 16', 11^\circ 46'$	11 32
112.111	$16^\circ 11', 16^\circ 19'$	16 50
111.111	$72^\circ 27'$	72 42
111.010	$43^\circ 40' - 44^\circ 16'$	44 21
111.012	$39^\circ 55' - 40^\circ 19'$	40 15
012.113	$26^\circ 18', 26^\circ 25'$	26 29
001.012	$43^\circ 51', 43^\circ 56'$	43 58
001.201	$72^\circ 22' - 73^\circ 32'$	72 38
012.201	$77^\circ 27' - 78^\circ 2'$	77 36
012.112	$29^\circ 54', 29^\circ 56'$	29 55
111.201	$47^\circ 46', 47^\circ 49'$	47 27"

Methyldiphenylglyoxaline is a monacid base. In a solution of the hydrochloride, platinic chloride (freed from excess of acid, which might otherwise cause a separation of hydrochloride) produces a yellow precipitate, consisting of microscopic needles of the formula $(C_{16}H_{14}N_2, HCl)_2PtCl_4 + 2H_2O$.

1.5446 grams of the air-dried salt lost on heating at 120° 0.0583 gram, and the resulting 1.4863 grams of anhydrous salt gave on ignition 0.3279 gram platinum.

	Calculated for $(C_{16}H_{14}N_2, HCl)_2PtCl_4 + 2H_2O$.	Found.
H ₂ O in 100 parts.....	3.94	3.77

	Calculated for $(C_{16}H_{14}N_2, HCl)_2PtCl_4$.	Found.
Pt in 100 parts	22.17	22.06

The hydrochloride itself exhibits a peculiarity in its crystallisation, due probably to the formation of different hydrates. When the hot saturated solution is allowed to cool in an open vessel, the crystallisation starts from the surface of the solution at two or three points and proceeds in tufts of long silky needles, extending through the entire liquid. But if, on the other hand, the hot saturated liquid is corked up in a vessel so as to exclude the air, taking care that none of the needle-shaped crystals are left adhering to the cork or to the sides of the vessel, then the substance is deposited in granular crystals, which

begin growing within the liquid, and sometimes attain a considerable size. Neither long standing nor violent shaking suffices to start the crystallisation of needles in the closed vessel; but on removing the cork, this crystallisation of needles commences from the surface, showing that the liquid was still supersaturated with this form, and wherever the needles touch the transparent granular crystals, these become opaque, and are converted into aggregates of needles.

The behaviour of this salt recalls that of a solution of sodium sulphate saturated at the temperature of maximum solubility, and protected from the air.

II. *Isovaleraldehyde and Ammonia with Benzil.*

An alcoholic solution of 20 grams of benzil with 8.2 grams of isovaleraldehyde (boiling point 92—95°) was saturated with gaseous ammonia at 40°, and allowed to stand for 24 hours. The new compound separated in needles, and was filtered off. The mother-liquor on evaporation yielded a further quantity, together with some benzilimide (m. p. 139.5°; verified also by conversion into benzilam, m. p. 114°). It was purified by recrystallisation from benzene, which deposited it in silky needles, melting constantly at 223°; from hot alcohol, it separated on cooling in larger needles.

The analytical results agreed with the formula $C_{19}H_{20}N_2$:—

	Substance.	CO ₂ .	H ₂ O.
I.	0.1123	0.3396	0.0771
II.	0.1058	0.3196	0.0720

III. 0.1130 gram, burnt with copper oxide in a vacuum, gave 21.91 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17.5° and under 352 mm. pressure. After absorption of the nitric oxide there remained 21.91 c.c. of dry nitrogen at 17.5°, and under 323 mm. pressure.

	Calculated for $C_{19}H_{20}N_2$.		Found.		
			I.	II.	III.
C ₁₉ . . .	228	82.61	82.47	82.38	—
H ₂₀ . . .	20	7.25	7.62	7.56	—
N ₂ . . .	28	10.14	—	—	10.16
	<hr/>	<hr/>			
	276	100.00			

The compound is *isobutyldiphenylglyoxaline*:—

The platinichloride, * $(C_{19}H_{20}N_2, HCl)_2PtCl_4$, was prepared by precipitation in the ordinary way, avoiding, however, the presence of free hydrochloric acid. It was thus obtained as an amorphous yellowish-brown precipitate, but small crystals separated from the mother-liquor on standing. The salt was anhydrous.

1.5956 grams dried at 100° gave on ignition 0.3222 gram platinum.

	Calculated for $(C_{19}H_{20}N_2, HCl)_2PtCl_4$.	Found.
Pt in 100 parts	20.23	20.19

III. *Cinnamaldehyde and Ammonia with Benzil.*

100 grams of benzil were dissolved in sufficient alcohol to keep the benzil in solution at 40° , 63 grams of cinnamaldehyde were added, and the whole was saturated with gaseous ammonia at 40° . While the gas was being passed in, a pulverulent white substance separated in considerable quantity, and was filtered off from the warm solution as soon as the saturation was complete. This compound was found to be practically insoluble in alcohol. The ammoniacal filtrate, on standing, deposited a large quantity of a flocculent white compound, which was soluble in alcohol. The filtrate from this compound yielded nothing crystallisable on evaporation.

Examination of the Compound Insoluble in Alcohol.—It was found that this compound dissolved readily in hot phenol, and was precipitated on the addition of three times the volume of alcohol as a crystalline powder, consisting of short microscopic prisms. After repeating this process of solution and precipitation several times, it was obtained with a constant melting point of 264° . The compound was boiled with successive portions of alcohol to remove the last trace of phenol and dried finally at 120° .

Analyses agreed with the formula $C_{32}H_{28}N_2O_2$:—

	Substance.	CO ₂ .	H ₂ O.
I.	0.1342	0.3991	0.0730
II.	0.1250	0.3720	0.0686

III. 0.1120 gram, burnt with copper oxide in a vacuum, gave 13.07 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17° and under 351.5 mm. pressure. After absorption of the nitric oxide, there remained 13.07 c.c. of dry nitrogen at 17° and under 318.5 mm. pressure.

* See footnote, Trans., 1884, p. 676.

	Calculated for $C_{32}H_{28}N_2O_2$.		Found.		
	I.	II.	I.	II.	III.
$C_{32} \dots$	384	81.35	81.11	81.16	—
$H_{28} \dots$	28	5.93	6.04	6.09	—
$N_2 \dots$	28	5.93	—	—	6.08
$O_2 \dots$	32	6.79	—	—	—
	472	100.00			

The yield of pure substance was 11 grams from 100 grams of benzil, but was greatly increased in a subsequent experiment by employing 2 molecular proportions of cinnamaldehyde to 1 of benzil.

The reaction in which this substance, *dibenzoyldicinnylenediamine*, is formed, and its constitutional formula, are given on p. 463. The action of various reagents on this compound was tried, but only with potash was a definite result obtained.

Action of Potash on Dibenzoyldicinnylenediamine.—When the compound was heated with a 10 per cent. solution of caustic potash in methyl alcohol in a sealed tube for three hours at 150° , it went into solution, and, on cooling, the liquid was filled with lustrous laminæ, probably potassium benzoate. On opening the tube, a smell of ammonia was perceptible. The contents of the tube were evaporated to a semi-solid state on a water-bath, mixed with water and filtered hot. The filtrate, on acidifying, gave benzoic acid. The brownish residue on the filter was dissolved in hot benzene, from which it was obtained, after two crystallisations, in small faintly yellow crystals with a constant melting point of 207° .

The results of analysis agreed with the formula $C_{25}H_{22}N_2$:—

	Substance.	CO_2 .	H_2O .
I.	0.1246	0.3898	0.0763
II.	0.1317	0.4116	0.0806

III. 0.1085 gram, burnt with copper oxide in a vacuum, gave 13.79 c.c. of dry nitrogen at 23° and under 413.5 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{25}H_{22}N_2$.		Found.		
	I.	II.	I.	II.	III.
$C_{25} \dots$	300	85.71	85.32	85.24	—
$H_{22} \dots$	22	6.29	6.80	6.80	—
$N_2 \dots$	28	8.00	—	—	8.02
	350	100.00			

The compound, which we have named *benzenyldicinnylenediamine* (see p. 463), is formed from the dibenzoyl-compound by the abstraction
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tion of 1 mol. of benzoic acid. It may be regarded as an anhydro-base derived from the hypothetical monobenzoyldicinnylenediamine—

by the abstraction of the elements of water.

When this base is boiled with hydrochloric acid, it is converted into a hydrochloride, but dissolves only very slightly. The hydrochloride is, however, soluble in alcohol. On the addition of aqueous platinum chloride to the alcoholic solution, the platinum chloride separates in yellow silky needles of the formula $(\text{C}_{25}\text{H}_{22}\text{N}_2, \text{HCl})_2\text{PtCl}_4 + 2\text{H}_2\text{O}$. The salt thus prepared was washed with alcohol, air-dried, and analysed.

0.9084 gram of the air-dried salt lost, on heating at 120° , 0.0282 gram, and the resulting 0.8802 gram of anhydrous salt gave, on ignition, 0.1540 gram of platinum.

	Calculated for $(\text{C}_{25}\text{H}_{22}\text{N}_2, \text{HCl})_2\text{PtCl}_4 + 2\text{H}_2\text{O}$.	Found.
H_2O in 100 parts.	3.14	3.10

	Calculated for $(\text{C}_{25}\text{H}_{22}\text{N}_2, \text{HCl})_2\text{PtCl}_4$.	Found.
Pt in 100 parts.	17.53	17.50

Examination of the Compound soluble in Alcohol.—The flocculent white compound (p. 468) from the benzil-cinnamaldehyde-ammonia reaction was dissolved in boiling alcohol. The solution deposited two sorts of crystals—slender needles and minute short prisms—which, however, proved to be merely different crystalline forms of the same substance, and could be converted one into the other by slightly varying the conditions of crystallisation. Both melted at the same temperature, 188° , and gave the same figures on analysis. Neither contained alcohol of crystallisation. The compound is also soluble in boiling benzene. The yield, using the proportions given on p. 468, is about one-tenth of the weight of benzil taken.

The analyses agreed with the formula $\text{C}_{37}\text{H}_{30}\text{N}_2\text{O}_3$:—

	Substance.	CO_2 .	H_2O .
I.	0.1252	0.3701	0.0645
II.	0.1326	0.3918	0.0675

III. 0.1074 gram, burnt with copper oxide in a vacuum, gave 13.07 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17°C . and under 284.5 mm. pressure. After absorption of the nitric

oxide, there remained 13.07 c.c. of dry nitrogen at 17°, and under 269.5 mm. pressure.

IV. 0.1193 gram gave 13.07 c.c. dry nitrogen and nitric oxide at 17.4° and under 325 mm. pressure, and after absorption of the nitric oxide, 13.07 c.c. dry nitrogen at 17.2° and under 297.5 mm. pressure.

	Calculated for $C_{37}H_{30}N_2O_3$.		Found.			
	I.	II.	III.	IV.		
C_{37}	444	80.73	80.62	80.58	—	—
H_{30} ...	30	5.45	5.72	5.65	—	—
N_2	28	5.09	—	—	5.24	5.30
O_3	48	8.73	—	—	—	—
	550	100.00				

Analyses I and III were made with the prismatic crystals, II and IV with the needles.

The equation for the formation of the compound $C_{37}H_{30}N_2O_3$ —which for reasons already stated we propose to name *cinnimabenzil*—is given on p. 464.

Action of Potash on Cinnimabenzil.—The finely-powdered compound was mixed with a 10 per cent. solution of caustic potash in methyl alcohol, and allowed to stand in a corked flask over night. The mixture became semi-solid, and on opening the flask a smell of ammonia was perceptible. Water was added, and the insoluble matter was filtered off. On acidifying the filtrate, it yielded only benzoic acid (identified by its melting point); but a faint cinnamon-like smell was perceptible during evaporation. The substance separated by filtration was shaken with ether; this removed a small quantity of a yellow gum, leaving the insoluble portion quite white. The substance thus obtained was practically insoluble in the ordinary organic solvents, but dissolved in hot phenol, and was precipitated from this solution as a crystalline powder on the addition of alcohol. By repeating this treatment three times, it was obtained with the constant melting point of 283°.

Analyses agreed with the formula $C_{30}H_{26}N_2O_3$:—

	Substance.	CO_2 .	H_2O .
I.....	0.1596	0.4691	0.0848
II.....	0.1547	0.4547	0.0824

III. 0.1140 gram, burnt with copper oxide in a vacuum, gave 13.79 c.c. of dry nitrogen at 23.5° and under 339 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{30}H_{26}N_2O_2$.		Found.		
			I.	II.	III.
C ₃₀	360	80.72	80.16	80.16	—
H ₂₆ ...	26	5.83	5.90	5.92	—
N ₂	28	6.28	—	—	6.24
O ₂	32	7.17	—	—	—
	446	100.00			

The substance contained a small quantity of ash which was weighed and deducted. The mode of formation of this compound has already been discussed (p. 464). In order to indicate its derivation from cinnimabenzil, we have named it *cinnidimabenzil*.

Action of Sulphuric Acid on Cinnimabenzil.—By boiling cinnimabenzil for a short time with dilute sulphuric acid (2 vols. of acid with 3 vols. of water), it is decomposed, yielding benzilimide, cinnamaldehyde, benzoic acid, and ammonia. Benzoic acid and benzilimide were identified by the melting point, the latter also by conversion into benzilam; the cinnamaldehyde was distilled with steam, and obtained as an oil with the characteristic odour. The reaction appears to take place according to the equation—

The action of *concentrated* sulphuric acid on imabenzil (see following paper) corresponds with this, except that benzaldehyde is eliminated instead of cinnamaldehyde, and the benzilimide is converted by the concentrated acid into benzilam ($C_{21}H_{15}NO$). Both the mode of formation and the decomposition of cinnimabenzil, therefore, countenance the view that this compound is an imabenzil in which a benzaldehyde residue has been replaced by a cinnamaldehyde residue.

Various other reactions were tried with cinnimabenzil, but none of them yielded definite results.

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