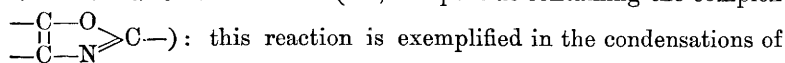


### III.—Action of Aldehydes and Ammonia on $\alpha$ -Diketones.

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THE condensations of  $\alpha$ -diketones with aldehydes and ammonia have hitherto been studied chiefly in the case of phenanthraquinone and benzil. The reaction has been shown to vary both with the diketone and with the aldehyde employed. The most frequently occurring reaction of this class is that in which glyoxalines are formed: as, for example, by the action of fatty aldehydes, and also of certain aldehydes of the benzene series, on benzil. Of less frequent occurrence is the formation of oxazoles (*i.e.*, compounds containing the complex



phenanthraquinone with several of the benzenoid aldehydes. Other reactions, such as those which yield the complex compounds obtained from benzil with salicylaldehyde and cinnamaldehyde respectively, occur only in isolated cases.\*

It appeared of interest to ascertain what the action would be in the case of some typical  $\alpha$ -diketone of the fatty series, such as diacetyl. With the kind consent of Dr. von Pechmann, by whom diacetyl was first described, and by whose method the material employed in this investigation was prepared, I have, therefore, studied its reactions with aldehydes and ammonia.

The aldehydes employed were benzaldehyde, salicylaldehyde, and cinnamaldehyde; but in each case nothing but a glyoxaline was formed, and none of the abnormal reactions which occur in the case of benzil were observed.

I have also studied the action of fatty aldehydes and ammonia on phenanthraquinone, but failed to obtain condensation-compounds. A benzene-fatty aldehyde, however—cinnamaldehyde—gave an oxazole with ammonia.

*Benzaldehyde, Diacetyl, and Ammonia.*—10 grams of diacetyl, with the molecular proportion of benzaldehyde, were dissolved in a small quantity of alcohol, and heated with an excess of alcoholic ammonia for half an hour on the water-bath. The new compound was precipitated by the addition of water, redissolved in dilute hydrochloric acid,

\* Japp and Streatfeild, *Trans.*, 1882, 155; Japp and Hooker, *Trans.*, 1884, 673; Japp and Wynne, *Trans.*, 1886, 464. A fairly complete summary of the results obtained in this field is given in the new *Watts's Dictionary of Chemistry*, vol. i, p. 465.

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the base reprecipitated from the filtered solution by ammonia, and purified by repeated recrystallisation from hot benzene.

Analysis of the substance, dried at  $100^\circ$ , gave figures agreeing with the formula  $C_{11}H_{12}N_2$ :—

	Substance.	CO <sub>2</sub> .	H <sub>2</sub> O.
I.....	0·1525	0·4284	0·0977
II.....	0·1456	0·4089	0·0938

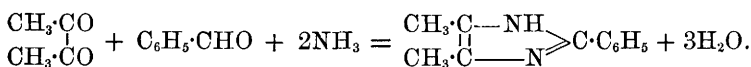
  

	Substance.	<i>v</i>	<i>t</i> .	<i>p</i> .	
III....	0·0832	Dry N + NO	22·32 c.c.	20°	411 mm.
		„ N.....	22·32 „	20	378 „
IV....	0·0827	Dry N + NO	22·32 c.c.	24	416 mm
		„ N.....	22·32 „	24	373 „

	Calculated for C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> .		Found.			
			I.	II.	III.	IV.
C <sub>11</sub> .....	132	76·74	76·60	76·58	—	—
H <sub>12</sub> .....	12	6·97	7·12	7·15	—	—
N <sub>2</sub> .....	28	16·27	—	—	16·30	16·16
	172	99·98				

The compound is formed according to the equation—



and would be *phenyldimethylglyoxaline*.

Phenyldimethylglyoxaline crystallises from benzene in slender needles containing benzene of crystallisation, which is given off on exposure to air. It is readily soluble in alcohol. It melts at  $230$ — $234^\circ$ , and at a higher temperature volatilises, condensing in needles, which showed the same melting point.

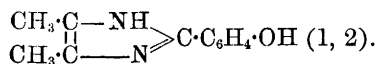
0·6720 gram of the substance, crystallised from benzene and dried by brief exposure to air, lost, on heating at  $100^\circ$ , 0·1294 gram benzene, equal to a loss of 19·26 per cent. The formula  $(C_{11}H_{12}N_2)_2\cdot C_6H_6$  requires a loss of 18·48 per cent.

The platinichloride is precipitated on the addition of platinic chloride to a solution of the base in hydrochloric acid. It forms yellow needles and is anhydrous.

0·1380 gram of the salt, previously dried at  $100^\circ$ , gave on ignition 0·0356 gram of platinum.

	Calculated for (C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> ·HCl) <sub>2</sub> ·PtCl <sub>4</sub> .	Found.
Pt in 100 parts.....	25·82	25·79

*Salicylaldehyde, Diacetyl, and Ammonia.*—The operation was conducted like the foregoing, employing 10 grams of diacetyl and the molecular proportion of salicylaldehyde; and the resulting compound was purified by recrystallisation from dilute alcohol. Analysis gave numbers agreeing with the formula of *orthohydroxyphenyldimethylglyoxaline*.



	Substance.	CO <sub>2</sub> .	H <sub>2</sub> O.
I.....	0.2100	0.5395	0.1213
II.....	0.1475	0.3790	0.0864

Substance.		v.	t.	p.	
III ....	0.0856	{ Dry N + NO	22.32 c.c.	29°	396 mm.
		{ „ N.....	22.32 „	29	375 „

	Calculated for C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O.		Found.		
			I.	II.	III.
C <sub>11</sub> .....	132	70.21	70.06	70.07	—
H <sub>12</sub> .....	12	6.38	6.41	6.50	—
N <sub>2</sub> .....	28	14.89	—	—	15.02
O.....	16	8.51	—	—	—
	<hr/>	<hr/>			
	188	99.99			

The compound crystallises from dilute alcohol in colourless, satiny needles melting at 218°, and from benzene in star-shaped forms. The alcoholic solution shows a blue fluorescence.

The hydrochloride is very sparingly soluble in cold water. From its solution the platinichloride is precipitated in yellow needles of the formula (C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O, HCl)<sub>2</sub>PtCl<sub>4</sub>·2H<sub>2</sub>O on the addition of platinic chloride, but owing to the sparing solubility of the hydrochloride, is apt to be contaminated with the latter salt, for which reason the percentage of platinum was found too low.

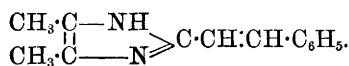
0.3358 gram of the air-dried platinum salt lost on heating at 100° 0.0150 gram, and the remaining 0.3208 gram gave on ignition 0.0772 gram platinum.

	Calculated for (C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O, HCl) <sub>2</sub> PtCl <sub>4</sub> ·2H <sub>2</sub> O.	Found.
H <sub>2</sub> O in 100 parts.....	4.38	4.46

	Calculated for (C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O, HCl) <sub>2</sub> PtCl <sub>4</sub> .	Found.
Pt in 100 parts.....	24.74	24.06

*Cinnamaldehyde, Diacetyl, and Ammonia.*—10 grams of diacetyl with the molecular proportion of cinnamaldehyde were heated with alcoholic ammonia in a sealed tube at 100° for about an hour. The contents of the tube, after expelling the alcohol by evaporation, were acidified with strong hydrochloric acid and diluted with 3 to 4 times their bulk of water; this precipitated most of the resin, which is formed in large quantity in this reaction. The resin was filtered off as quickly as possible, after which the hydrochloride of the new base began to separate from the filtrate in the form of yellowish needles, the separation being facilitated by the addition of a large excess of fuming hydrochloric acid to the solution. This salt was freed from adhering resin by washing with ether, then dissolving in a small quantity of alcohol and reprecipitating with ether, by which means it was obtained colourless. From a hot aqueous solution of the hydrochloride, ammonia precipitated the base, which was then purified by recrystallisation from benzene. It formed colourless, warty crystals melting at 201–202°, very soluble in alcohol and in ether, sparingly soluble in petroleum, very slightly soluble in boiling water.

A nitrogen determination showed that in this case also a glyoxaline *cinnamenyldimethylglyoxaline*—



had been formed.

Substance.		<i>v.</i>	<i>t.</i>	<i>p.</i>
0·0878 ..	{ Dry N + NO ..	13·5 c.c.	19°	597 mm.
	{ „ N .....	13·5 „	19	582 „

	Calculated for $\text{C}_{13}\text{H}_{14}\text{N}_2$ .	Found.
N in 100 parts .....	14·00	14·14

On the addition of platinic chloride to a solution of the hydrochloride, the platinichloride is precipitated in the form of microscopic yellow needles, which are anhydrous.

0·1624 gram of the salt, which did not lose weight at 120°, gave on ignition 0·0394 gram platinum.

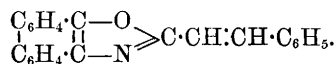
	Calculated for $(\text{C}_{13}\text{H}_{14}\text{N}_2, \text{HCl})_2\text{PtCl}_4$ .	Found.
Pt in 100 parts .....	24·22	24·15

*Cinnamaldehyde, Phenanthraquinone, and Ammonia.*—10 grams of phenanthraquinone with the molecular proportion of cinnamaldehyde were heated with an excess of alcoholic ammonia in a sealed tube at

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100°. On cooling, a substance was deposited in a solid state; this was separated by filtration and dissolved in hot glacial acetic acid, from which it crystallised in slender, yellow needles: these, after recrystallising twice from the same solvent, melted constantly at 171—172°. The compound is also readily soluble in benzene and in carbon bisulphide. It does not form salts with acids.

The results of analysis pointed to the formula  $C_{23}H_{15}NO$ , which is that of a *cinnamenediphenyleneoxazole*.



		Substance.	CO <sub>2</sub> .	H <sub>2</sub> O.	
I	.....	0.1220	0.3844	0.0532	
		Substance.	v.	t.	p.
II	.....	0.1259	9.02 c.c.	20°	408 mm.
		{ N + NO..	9.02 „	20	405 „
		{ N .....	9.02 „		
		Calculated for		Found.	
		C <sub>23</sub> H <sub>15</sub> NO.		I.	II.
C <sub>23</sub>	.....	276	85.98	85.92	—
H <sub>15</sub>	.....	15	4.67	4.84	—
N	.....	14	4.36	—	4.48
O	.....	16	4.98	—	—
		—	—		
		321	99.99		

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