XLI.—*On the Action of Acetone on Phenanthraquinone, both Alone and in Presence of Ammonia.*

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THE results obtained by acting with aldehydes upon phenanthraquinone in presence of ammonia (this Journal, 1880, 666; 1881, 225; 1882, 149), led us to examine whether any action occurs when ketones are substituted for aldehydes. Since in the reaction with aldehydes the hydrogen-atom of the COH-group is eliminated, it was evident that any reaction with ketones must possess an essentially different character.

After satisfying ourselves that phenanthraquinone, acetone, and ammonia react very readily at ordinary temperatures, we adopted the following mode of conducting the experiment:—

50 grams of finely-powdered phenanthraquinone were mixed in a thick-walled flask with 60 grams of acetone. (The acetone employed had been purified by conversion into the double compound with hydrogen sodium sulphite; but we have since found that a rectified acetone, boiling between 56° and 58°, answers the purpose equally well.) About 40 c.c. of strong aqueous ammonia were then added, the flask was tightly corked, and the contents were thoroughly mixed by shaking. After standing for a few minutes, the mixture became perceptibly darker in colour, and this change was accompanied by a rise in temperature. A slight pressure was relieved by removing the cork from time to time. The temperature continued to rise, the contents of the flask again became lighter in colour, and the quinone appeared to be

converted into a white granular crystalline powder, whilst the supernatant liquid remained dark-coloured. The reaction was now complete. It is worthy of note that no two of the three substances taking part in this reaction—phenanthraquinone, acetone, and aqueous ammonia—react in the cold without the third. As soon as the temperature had sufficiently fallen, ether was added, and the crystalline substance was filtered off and washed with ether. In this way the substance was obtained almost colourless, but examination with a lens showed the presence of small particles of unaltered quinone.

In attempting to purify the substance by recrystallisation, it was found that it readily underwent decomposition. It dissolved in hot alcohol; but the solution smelt of ammonia, became dark-coloured, and on cooling deposited a brown substance which had the appearance of impure phenanthraquinone. An alcoholic solution, saturated in the cold, yielded by spontaneous evaporation colourless rhomboïdal plates, but these were mixed with a quantity of gummy matter. At last, by taking advantage of the fact that the decomposition of a substance occurs less readily in presence of an excess of its products of decomposition, we succeeded in obtaining the new compound in a state of purity. The crude product was dissolved in boiling acetone (b. p. 56–58°), to which a small quantity of aqueous ammonia had been added. The filtered solution deposited on cooling a small quantity of the new substance in colourless rhomboïdal laminae. By spontaneous evaporation over sulphuric acid, the quantity of crystalline substance increased. The crystals were filtered off, washed with ether, and dried over sulphuric acid. Care must be taken not to leave them too long in contact with the acetone solution, otherwise they redissolve, and only a gummy mass is obtained by further evaporation. The yield of pure substance is small. The fusing point could not be determined with accuracy, since when heated in a capillary tube, the compound begins to change colour about 120°, gradually becoming darker, till at about 130° it fuses, turning black and evolving gas.

Analysis yielded the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1004	0.2824	0.0538
II.	0.1185	0.3341	0.0624

III. 0.1047 gram burnt with copper oxide in a vacuum gave 4.75 c.c. moist nitrogen at 16.5° and 757 mm. pressure, corresponding to 0.0055 gram nitrogen.

IV. 0.1283 gram gave 5.80 c.c. moist nitrogen at 16.5° and 766 mm. pressure, corresponding to 0.0068 gram nitrogen.

These numbers lead to the formula C₁₇H₁₃NO₂.

	Calculated for $C_{17}H_{15}NO_2$.		Found.				Mean.
			I.	II.	III.	IV.	
C_{17}	204	76.98	76.71	76.89	—	—	76.80
H_{15}	15	5.66	5.94	5.85	—	—	5.89
N	14	5.28	—	—	5.25	5.30	5.27
O_2	32	12.08	—	—	—	—	(12.04)
	265	100.00	—	—	—	—	100.00

Another preparation of the substance was analysed with the same result.

The formation of a compound of the above formula would be expressed by the equation—

For the sake of comparison the equation for the reaction with a non-hydroxylated aldehyde may also be given:—

(this Journal, 1880, 669).

The relative molecular quantities of the three generating substances are thus the same in both reactions, but in the case of the aldehyde twice as much water is formed as in the case of the ketone. This is explained by the fact, already alluded to, that in the aldehyde reaction the hydrogen-atom of the COH-group is eliminated.

As we suspected that the compound $C_{17}H_{15}NO_2$ contained an NH-group, we examined the action of acetic anhydride upon it, but found that this reagent decomposed it, even in the cold, with regeneration of phenanthraquinone.

Behaviour of the Compound $C_{17}H_{15}NO_2$ towards Acids.—The substance dissolved readily in cold concentrated hydrochloric acid, yielding a pale yellow solution, which speedily became green and turbid. After standing for about a day, the solution deposited a dark indigo-blue substance, the nature of which we have not yet been able to ascertain, as it appears to undergo decomposition when treated with solvents. The filtrate from this blue substance became turbid on adding a small quantity of water, but the addition of a larger quantity caused it to become clear again. On standing, this clear dilute solution again became turbid, and gradually deposited a substance in fine colourless needles. These were dissolved in ether, and the solution allowed to evaporate. The substance was thus obtained in large, thin, colourless

blades, with parallel edges. After two or three crystallisations it fused constantly at $89.5-90^\circ$. Qualitative tests showed that it contained neither nitrogen nor chlorine.

Analysis yielded the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1677	0.4683	0.0802
II.	0.1490	0.4178	0.0712

These numbers lead to the formula $C_{17}H_{14}O_3$.

	Calculated for $C_{17}H_{14}O_3$.		Found.		
			I.	II.	Mean.
C ₁₇	204	76.70	76.47	76.66	76.56
H ₁₄	14	5.26	5.30	5.34	5.32
O ₃	48	18.04	—	—	18.12
	266	100.00	—	—	100.00

In the formation of this compound from the compound $C_{17}H_{15}NO_2$, the elements of water have been added, and the elements of ammonia eliminated:—

In confirmation of this view we found that the hydrochloric acid filtrate from the needle-shaped crystals yielded ammoniac chloride on evaporation. The formation of the insoluble blue compound must therefore be regarded as the result of a totally distinct reaction. In fact we found that by substituting other acids for hydrochloric, the formation of the blue compound was avoided. Thus by dissolving the compound $C_{17}H_{15}NO_2$ in concentrated aqueous oxalic acid, and afterwards diluting, a large yield of the compound $C_{17}H_{14}O_3$, apparently quite free from by-products, was obtained. It is necessary to avoid diluting the oxalic acid solution too much, otherwise no separation of crystals occurs, the oxalate of the compound $C_{17}H_{15}NO_2$ appearing to be capable of existing in dilute solution. Aqueous acetic acid is capable of effecting the same transformation, but a considerable quantity of the substance is converted into phenanthraquinone. It is worthy of remark that formic acid, unlike acetic acid, causes the separation of the pure compound $C_{17}H_{14}O_3$ from the solution of the nitrogenous compound, no regeneration of phenanthraquinone occurring in this case.

The compound $C_{17}H_{14}O_3$ is insoluble in water; on heating with water separation of phenanthraquinone occurs, and this change takes place still more readily on warming with dilute caustic alkalis. Ether, alcohol, and acetone dissolve it freely. In alcoholic solution it is con-

verted by boiling into phenanthraquinone; but by avoiding a temperature above 40° it may be readily recrystallised from alcohol.

Action of Ammonia upon the Compound $C_{17}H_{14}O_3$.—On passing gaseous ammonia into the ethereal solution of the compound $C_{17}H_{14}O_3$, the rhomboïdal laminæ of the compound $C_{17}H_{15}NO_2$ were deposited. These fused with decomposition at 130° , and were further identified by their behaviour towards concentrated hydrochloric acid, in which they dissolved, the solution becoming after a time green and turbid, and ultimately depositing the characteristic dark blue precipitate. This process of formation of the $C_{17}H_{15}NO_2$ is exactly the reverse of that which occurs in the formation of the compound $C_{17}H_{14}O_3$, and would therefore be expressed by the equation—

Action of Heat upon the Compound $C_{17}H_{14}O_3$.—About 0.5 gram of the substance was introduced into a narrow test-tube, which was then drawn out so as to form a retort. The neck of this retort was bent into U-shape. The retort was heated in a bath of sulphuric acid, and the bend was cooled by ice. The temperature was gradually raised to 190° . The substance fused, became darker in colour, and appeared to boil. As soon as this boiling ceased, the operation was interrupted. In the U-tube there had condensed about one drop of a colourless liquid, which had the characteristic odour of acetone, and which on exposure to the air rapidly evaporated, without leaving any residue. The substance in the retort solidified on cooling to a mass of dark orange-coloured needles, having the appearance of impure phenanthraquinone. They dissolved, with the exception of a trace of resinous matter, in hydrogen-sodium sulphite, and were precipitated of a bright orange colour on the addition of dilute sulphuric acid. The fusing point of the substance thus purified agreed exactly with that of phenanthraquinone.

The compound $C_{17}H_{14}O_3$ appears therefore to be decomposed by the action of heat into phenanthraquinone and acetone, according to the equation—

Synthesis of the Compound $C_{17}H_{14}O_3$ by the Direct Union of Phenanthraquinone and Acetone.—In order to ascertain whether the above process of decomposition could be reversed, and the compound $C_{17}H_{14}O_3$ produced by the direct union of phenanthraquinone and acetone, phenanthraquinone was heated with a large excess of pure acetone in sealed tubes. Nothing was formed up to 150° . After heating for four hours at 200° , the contents of the tubes appeared black and as if decomposed. The liquid portion was poured off from the

solid, and gently heated to drive off the acetone, when a pitchy mass was left. This was digested with a warm (not hot) solution of hydrogen sodium sulphite, in order to remove any unattacked quinone, and the residue, after washing with water, was dissolved in ether. The dark-coloured ethereal solution was shaken with freshly ignited animal charcoal, after which it appeared of a pale yellow colour, and by spontaneous evaporation deposited the characteristic straight blades of the compound $C_{17}H_{14}O_3$. These after recrystallisation fused at $88-89.5^\circ$.

In presence of an excess of acetone the compound $C_{17}H_{14}O_3$ is therefore stable at a temperature above that at which it otherwise undergoes decomposition.

Acetic anhydride is without action upon the compound at ordinary temperatures, whilst at higher temperatures phenanthraquinone is regenerated.

Theoretical Considerations.—For the compound $C_{17}H_{14}O_3$ two formulæ might be suggested, which would account for its formation from phenanthraquinone and acetone, and its decomposition into these two substances—

A formula in which the two carbon-atoms, which in phenanthraquinone are united to quinonic oxygen, are represented as attached to each other by double bonds, appears to be inadmissible. The only such formula is—

and this, in addition to its inherent improbability, would not readily account for the formation of the compound $C_{17}H_{15}NO_2$.

Various formulæ might of course be constructed, in which the phenylene groups or the methyl groups are represented as having undergone modification during the reaction, or in which the C_3 -group of the acetone is directly united to the phenanthrene nucleus; but such formulæ would fail to explain the ready decomposition of the substance into acetone and phenanthraquinone. Rejecting, therefore, these formulæ, the above three alone remain for discussion.

It might, however, be suggested that the compound is a so-called molecular combination of phenanthraquinone with acetone. This is, we think, very improbable. The compound fuses without decomposi-

tion more than 30° above the boiling point of acetone. Its mode of formation by the action of acids on the compound $C_{17}H_{15}NO_2$ also speaks very decidedly against this view. The compound $C_{17}H_{15}NO_2$ would, on this supposition, have to be regarded as a molecular combination of phenanthraquinonimide with acetone. But phenanthraquinonimide does not dissolve in hydrochloric acid, whereas the compound $C_{17}H_{15}NO_2$ is readily soluble.

We have above stated our belief that formula (3) must be rejected. Between formulæ (1) and (2) we are at present unable to decide, but we hope by a further study of the compound to clear up points that are still obscure. We refrain meanwhile from discussing the bearings of this reaction upon the formula of phenanthraquinone, beyond expressing the opinion that the reaction appears to render Graebe's formula somewhat improbable.*

The compound $C_{17}H_{15}NO_2$, which is formed by replacing O in the compound $C_{17}H_{14}O_3$ by NH, would receive the formula—

according as formula (1) or formula (2) is adopted for the compound $C_{17}H_{14}O_3$.

As regards nomenclature, it will, we think, be best to adopt for these compounds, provisionally at all events, names which express their mode of formation rather than their constitution. We propose to name the compound $C_{17}H_{14}O_3$, *acetonquin of phenanthrene*. Since the compound $C_{17}H_{15}NO_2$ is formed from the acetonquin by the substitution of NH for O, it will receive the name *acetonquinimide of phenanthrene*.

We intend to continue the study of these reactions, and if possible to apply them to other quinones and ketones, and to replace ammonia by amines. According to the above interpretation of the reactions, only primary amines ought to be capable of taking part in them.

We are also engaged in studying the action of ethylic aceto-acetate upon phenanthraquinone. The reaction is quite distinct from that which occurs with acetone. Instead of a direct union of the elements of ketone and quinone, combination occurs with elimination of water :—

The reaction is probably analogous to the condensations between

* This is certainly in direct opposition to the view frequently maintained by one of us in former communications.

ethylic aceto-acetate and aldehydes, described by Claisen (*Ber.*, **14**, 345). Ethylic malonate may be expected to react with phenanthraquinone in a similar manner.

We trust that the study of these reactions will throw some light upon the constitution of phenanthraquinone.