# II. *On the Formation and some of the Properties of Cymidine, the Organic Base of the Cymole Series. By the Rev.* John Barlow, *Chaplain-in-Ordinary to Her Majesty's Household at Kensington Palace, M.A., F.R.S., Vice-President and Secretary of the Royal Institution of Great Britain, &c.*

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By submitting the nitro-compounds of the series of hydrocarbons, of which benzole is the lowest term, to Zinin's well-known process, chemists have successively obtained the organic bases corresponding to these hydrocarbons. Aniline, toluidine, xylidine and cumidine have been prepared in this manner. Aniline was obtained by this process by Zinin[*] himself in 1845; toluidine by Muspratt and Hofmann[†], in 1845; xylidine by Cahours[‡], in 1850; and cumidine by Nicholson, in 1847[§]. Whilst the last-named chemist was engaged in the laboratory of the Royal College of Chemistry with the study of cumidine, the derivative of cumole, Dr. Noad, at the suggestion of Dr. Hofmann, pursued the same direction of research towards cymole, the only remaining hydrocarbon of this group, with a view of completing the series of the alkaloids[||]. In his experiments on the action of concentrated nitric acid on cymole, Dr. Noad found that this hydrocarbon differs somewhat from the other members of the series. Instead of furnishing the nitro-substitute, which is the link of connexion between the hydrocarbon and the alkaloid, cymole was found to undergo a partial oxidation, a portion of the carbon being eliminated in the form of carbonic acid with the simultaneous formation of several acids which belong to a group of bodies standing lower in the scale of organic compounds. The study of these very interesting acids, toluylic and nitrotoluylic, appears to have detached Dr. Noad's attention from the formation of the substitution-product of cymole; and when he again returned to this inquiry he soon quitted it, in order to pursue still further a research in which he had already been successful[¶].

At the suggestion, and under the direction of Dr. Hofmann, the following investigation has been made, in the hope of filling up a gap still existing in the series of

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[*] Journal für practische Chemie, Band xxxvi. S. 98.

[†] Mem. Chem. Soc. vol. ii. p. 367.

[‡] Comptes Rendus, tome xxx. p. 321.

[§] "On Cumidine, a new Organic Base," Reports of Royal College of Chemistry, p. 178.

[||] Mem. Chem. Soc. vol. iii. p. 421.

[¶] "On some of the Products of the Decomposition of Nitrotoluylic Acid," Philosophical Transactions, vol. cxliv.

bases, and the desired alkaloid has been obtained; thus completing the inquiry which was commenced in the Royal College of Chemistry seven years ago.

*Preparation of Nitrocymole.*—It has been already stated that cymole, when heated in the usual way with concentrated nitric acid, produces substances differing greatly from the expected substitution-compound. To prevent this result, cymole and nitric acid, having been severally kept for some minutes in a freezing mixture of ice and salt, were cautiously mixed. The cold cymole was dropped from a pipette into the cold nitric acid. The mixture was at first brown, but, on continued addition of cymole, it gradually changed to green; and when the substitution was complete, it assumed the consistency of cream. It was then projected into cold water, when the oily reddish-brown nitrocymole subsided to the bottom of the vessel. This was washed, first with water, and lastly, with a weak solution of carbonate of soda.

*Properties of Nitrocymole.*—In the purest state in which it has yet been obtained, nitrocymole is a reddish-brown, transparent, oily fluid, of greater specific gravity than water, in which it is insoluble. It does not appear to be readily decomposed by contact of air. When distilled with water it produces a neutral oil, which floats on water, than which it is, consequently, of less specific gravity. It was found impossible to obtain the boiling-point either of nitrocymole or of this oily distillate, or to procure the body in a state fit for analysis. But subsequent examination of substances derived from it removed all doubt that its composition is represented by the formula $C_{20}H_{13}NO_4$.

*Formation of Cymidine from Nitrocymole.*—The process of ZININ, although successfully adopted in obtaining the lower bases of this series, was not found equally effectual when applied to this new substitution-product. A better result, though the quantity was still very scanty, was obtained by BÉCHAMP's modification of this method*. Nitrocymole was added to iron-filings brought to the consistency of paste by mixture with acetic acid, whereupon an immediate and considerable elevation of temperature indicated the commencement of chemical action. From the distillation of this mixture at a carefully-regulated heat a complicated product resulted. A considerable proportion of the distillate was found to be insoluble in hydrochloric acid. This was set aside for separate examination, the result of which will be stated at the close of this memoir. To the portion of the distillate which was soluble in hydrochloric acid, soda was added in quantity just sufficient to neutralize the acid. The base (for which the name cymidine is suggested by obvious analogy) was then separated by ether and subsequently distilled. The same instability of composition, and tendency to oxidize, which have been noted as characterizing the hydrocarbon cymole, exist in this base, derived from it. Accordingly, it was found necessary to perform the distillation in an atmosphere of hydrogen, in order to prevent the conversion of the cymidine, at a high temperature, into a resin.

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* Annales de Chimie et de Physique, tome xlii. p. 193.

*Properties of Cymidine.*—The specific gravity of cymidine is less than that of water. Its boiling-point is about 250° Cent.; it has a yellow colour; it is odorous; it does not affect test-paper. It is slightly soluble in water, and completely soluble in alcohol and ether. The quantity of this alkaloid available for experiment was too small to admit of its being entirely purified by distillation. It was therefore necessary to have recourse to the analysis of its platinum-salt for ascertaining its composition.

*Platinum-salt of Cymidine.*—When bichloride of platinum is added to an aqueous solution of the hydrochlorate of cymidine, a characteristic yellow salt is obtained, which, like cymidine itself, is slightly soluble in water, more soluble in alcohol, and most of all in ether.

I. ·4598 grm. of this substance, burnt with chromate of lead and oxide of copper, gave

·5695 grm. of Carbonic acid.
·1935 grm. of Water.
·1270 grm. of Platinum.

This, calculated for 100 parts, gives 33·777 Carbon.
4·675 Hydrogen.
27·620 Platinum.

II. ·4213 grm. of the same substance, ignited, gave ·1178 grm. of platinum, which, calculated for 100 parts, gives 27·699.

These numbers lead to the formula $C_{20} H_{15} N, HCl, PtCl_2$, as may be seen from the following comparison of the theoretical and experimental numbers:—

| | Theory. | | Experiment. |
|---|---|---|---|
| | | Per cent. | Per cent. |
| 20 equivs. Carbon . . | 120 | 33·784 | 33·777 |
| 16 equivs. Hydrogen . | 16 | 4·505 | 4·675 |
| 1 equiv. Nitrogen . . | 14 | 3·941 | |
| 3 equivs. Chlorine . . | 106·5 | 29·983 | |
| 1 equiv. Platinum . . | 98·7 | 27·787 | 27·641 {mean of the two experiments. |
| 1 equiv. Platinum-salt | 355·2 | 100·000 | |

*Hydrochlorate of Cymidine.*—When strong hydrochloric acid is added to cymidine, fumes are evolved, the hydrochlorate of cymidine, in the form of an oily layer, rises to the surface of the fluid, and crystallizes on being agitated and evaporated. Like the salts of aniline, it stains firwood yellow, but, unlike these salts, it produces no reaction with the chloride of lime; it also stains the skin red.

A determination of hydrochloric acid in the hydrochlorate of cymidine was made.

| | |
|---|---|
| Weight of hydrochlorate taken . . . | ·412 grm. |
| Weight of chloride of silver . . . . | ·319 grm. |

From whence the per-centage number 19·679 hydrochloric acid is obtained. This number agrees with the per-centage corresponding to the formula $C_{20}\,H_{15}\,N\,HCl$, as will appear on comparing the theoretical and experimental numbers.

| | Theory. | | Experiment. |
|---|---|---|---|
| | | Per cent. | Per cent. |
| 1 equivalent of Cymidine . . . | 149 | 80·281 | |
| 1 equivalent of Hydrochloric acid . | 36·5 | 19·719 | 19·679 |
| 1 equivalent of Hydrochlorate of Cymidine . . | | 100 | |

*Sulphate of Cymidine.*—A white crystalline salt, soluble in water.

*Oxalate of Cymidine.*—A white crystalline salt, soluble in water.

*Gold Salt.*—A yellow crystalline salt, slightly soluble in water.

Iodine has no perceptible reaction on cymidine.

Bromine produces a very feeble reaction on this base.

When chloride of cyanogen was added to cymidine, a slight action took place, and the resulting substance, after having been boiled with water, and filtered, gave a precipitate on the addition of caustic soda; thus affording evidence of the presence of a salt of a new solid base, probably analogous to melaniline.

On adding chloride of benzoyle to cymidine, a slight action ensued, and a few minute crystals appeared, probably of benzo-cymidide.

Nitric acid acts violently on cymidine; a semi-solid substance separating on addition of soda.

These are, however, merely qualitative experiments, and require further elaboration.

### *Examination of substance, insoluble in hydrochloric acid, produced during the formation of Cymidine.*

Having been purified by repeated distillation, this substance was burnt with oxide of copper, when the following result was obtained:—

·2623 grm. gave ·8615 carbonic acid and ·2530 water.

The formula of cymole is $C_{20}\,H_{14}$. On comparing the per-centage numbers derived from this formula with those obtained from the substance by experiment, we find

| | Theory. | | Experiment. |
|---|---|---|---|
| | | Per cent. | Per cent. |
| 10 equivalents of Carbon . . | 120 | 89·552 | 89·213 |
| 14 equivalents of Hydrogen . | 14 | 10·448 | 10·672 |
| | 134 | 100·000 | 99·885 |

The chemical identity of this substance with cymole is thus established.

The boiling-point 175° C. also coincides with that of camphogene, which is recognized as the isomer of cymole. There is however an important physical distinction between cymole and this isomeric substance. It has already been stated, that when cymole is submitted to the action of fuming nitric acid at $-17\frac{7}{9}^{\circ}$ C. a reddish-brown nitrocymole is produced, which is specifically heavier than water. But when this cymole-isomer (α-cymole) is similarly treated, there results a dark oily liquid, which, on being projected into water, first blackens, then becomes pale yellow, and finally floats on the surface, indicating a specific gravity less than that of water.

From this *nitro-α-cymole*, an α-cymidine was also obtained by BÉCHAMP's process, and from this a platinum-salt was formed. The platinum determination of this salt gave the following result:—

| | |
|---|---|
| Weight of platinum-salt taken . . . . . | ·1840 grm. |
| Weight of platinum obtained . . . . . | ·0509 grm. |

This gave a per-centage weight of 27·662 platinum, differing only by ·125 from the theoretical per-centage 27·787, calculated from the formula $C_{20}H_{15}N$, HCl, $PlCl_2$. Further researches are however necessary to establish the relation of this substance to cymidine.

An unsuccessful attempt to obtain the boiling-point of nitrocymole has been already noticed. The distillate from this operation was lighter than water, and had the colour and general appearance of α-cymole; when treated with fuming nitric acid in a freezing mixture, the resulting substance presented a close resemblance to nitro-α-cymole.

Nitrocymole and cymidine, the formation of which is described in the preceding memoir, complete the series of nitro-substitutions and bases corresponding to the hydrocarbons, of which benzole is the lowest homologue, as will appear from the following synoptical table:—

| Hydrocarbons. | | Nitro-substitutions. | | Bases. | |
|---|---|---|---|---|---|
| Benzole | $C_{12}H_6$ | Nitrobenzole | $C_{12}H_5NO_4$ | Aniline | $C_{12}H_7N$. |
| Toluole | $C_{14}H_8$ | Nitrotoluole | $C_{14}H_7NO_4$ | Toluidine | $C_{14}H_9N$. |
| Xylole | $C_{16}H_{10}$ | Nitroxylole | $C_{16}H_9NO_4$ | Xylidine | $C_{16}H_{11}N$. |
| Cumole | $C_{18}H_{12}$ | Nitrocumole | $C_{18}H_{11}NO_4$ | Cumidine | $C_{18}H_{13}N$. |
| Cymole | $C_{20}H_{14}$ | *Nitrocymole* | $C_{20}H_{13}NO_4$ | *Cymidine* | $C_{20}H_{15}N$. |

The author of this memoir desires, in conclusion, to record his sense of the valuable assistance he received from Mr. ALFRED NOBLE, Student in the College of Chemistry.