CCII. *On the Action of Nitric Acid on Cymol. First Part.*
By H. M. NOAD, Esq.

Formation of Toluyllic and Nitrotoluyllic Acids.

WE possess in benzoic acid and its derivatives a well-defined group of substances connected in a variety of ways with a large number of organic families. These interesting bodies have been made subjects of investigation by several chemists. The study has been a fascinating one, and has resulted in a thorough development of their history, and of the products of their decomposition.

This group may be considered the prototype, as it were, of several parallel groups, presenting a very close relation with the composition of the benzoyl family. The careful study of the former has gradually made these known to us, in the same manner as the study of alcohol and its derivatives made us acquainted with several corresponding classes of bodies.

The methyl compounds, with which we have become familiar through the experiments of Dumas and Peligot* on pyroxylic spirit, and the amyl series, the origin of which we owe to the investigations of Cahours† on fusel oil, form two groups, the analogy of which with the alcohol series can be traced in every direction; they differ in composition from the former only by a multiple of $C_2 H_2$, thus—

$HO, C_2 H_3 O$ =hydrated oxide of methyl.
 $HO, C_4 H_5 O$ =hydrated oxide of ethyl.
 $HO, C_{10} H_{11} O$ =hydrated oxide of amyl.

* Liebig's *Annalen*, xv. 1.

† Ibid. xxx. 288.

422 Mr. Noad on the Action of Nitric Acid on Cymol.

The same relation is likewise observed in the acids resulting from the oxidation of these bodies, and these acids are perhaps even better adapted to point out this interesting regularity, as the gaps existing between the different alcohols are filled up in the series of the acids, which may be formed in a great variety of ways. A glance at the following table will render the regularity above alluded to at once obvious:—

Alcohols.	Acids.
HO, C ₂ H ₃ O, pyroxylic spirit.	HO, C ₂ HO ₃ , formic acid.
HO, C ₄ H ₅ O, alcohol.	HO, C ₄ H ₃ O ₃ , acetic acid.
	HO, C ₆ H ₅ O ₃ , metacetic acid.
	HO, C ₈ H ₇ O ₃ , butyric acid.
	HO, C ₁₀ H ₉ O ₃ , valerianic acid.
HO, C ₁₀ H ₁₁ O, fusel oil.	HO, C ₁₂ H ₁₁ O ₃ , caproic acid.
	HO, C ₁₄ H ₁₃ O ₃ , cenanthylic acid.
	HO, C ₁₆ H ₁₅ O ₃ , caprylic acid.
	HO, C ₁₈ H ₁₇ O ₃ , pelargonic acid.
	HO, C ₂₀ H ₁₉ O ₃ , capric acid.
&c.	&c.

Now it seems that benzoic acid is a member of a similar series of acids, distinguished from each other by the same amounts of carbon and hydrogen, and that we may expect to find a representative of every single term of the benzoyl series in these other families. An examination of cumen oil by MM. Gerhardt and Cahours* has brought to light a new acid,—cuminic acid, HO, C₂₀ H₁₁ O₃, which exhibits a perfect analogy with benzoic acid, not only in its physical properties, but also in the metamorphoses which it undergoes when acted on by chemical agents. This acid is distinguished from benzoic, HO, C₁₄ H₅ O₃, by containing 3(C₂ H₂) more; it stands to benzoic acid as valerianic acid stands to acetic acid, and when distilled with lime it is converted into cumol, C₁₈ H₁₂, which represents benzol, C₁₂ H₆, in the benzoyl series. The same investigation of cumen oil has made us acquainted with another carbo-hydrogen cymol, C₂₀ H₁₄, which is also a representative of benzol in another series; but up to the present time the acid from which this carbo-hydrogen derives, and which would contain 4(C₂ H₂) more than benzoic acid, has not been discovered.

By the investigations of Pelletier and Walter† on the products of the distillation of resinous substances, of Deville‡ on the distillation of tolu balsam, and of Boudault and Gledard§ on the dry distillation of the dragon's blood, an addi-

* Liebig's *Annalen*, xxxviii. 67.

† Ibid, xxviii. 295.

‡ *Ann. de Chim. et Phys.* 3 sér. t. iii. p. 168.

§ *Journ. de Pharm. et de Chim.* 3 sér. t. vi. p. 250.

tion has been made to the number of carbo-hydrogens, and we have obtained knowledge of a new body, which was described by the first chemists under the name of retinaphtha, by the second under that of benzoène, and by the last under that of dracyl; for all three Berzelius* has proposed the more appropriate name of toluol† ($C_{14}H_8$); this body, which differs from benzol in containing C_2H_2 more, also represents that carbo-hydrogen in a new family, a number of members of which has already become known. Thus Deville has shown that on treating his toluol with sulphuric and nitric acids, the corresponding terms of hypo-sulphobenzolic acid, nitrobenzol, and dinitrobenzol are obtained. Investigations of the action of nitric acid on oil of anise by Cahours‡, and on Oleum dracunculi by Laurent§, have led to the discovery of anisylic, nitransylic acids, and anisol (draconic, nitrodraconic acids and dracol), corresponding respectively to salicylic, nitrosalicylic acid and phenol; more recently Cahours|| has found in hydride of anisyl even the term corresponding to hydride of salicyl, and Drs. Muspratt and Hofmann¶ have produced the organic base corresponding to aniline; in the paper in which this new and remarkable substance is described, these gentlemen have given a table, in which the analogy between the anisyl and salicyl groups has been pointed out.

In order to render this parallelism complete one principal term of the new series has hitherto been wanting, viz. the acid corresponding to benzoic acid. In the following paper will be pointed out the formation and properties of this substance, and the corresponding nitrogenous acid, both arising amongst the products of the oxidation of cymol.

* *Jahresbericht*, xxii. p. 354.

† On comparing the properties which Pelletier and Walter ascribe to retinaphtha with those of benzoène given by Deville, it is nearly certain that both substances are identical, though Deville seems to be inclined to establish a difference. A comparative study is however still wanting. Regarding dracyl, I may mention here that when engaged in the investigation of toluidin with Dr. Muspratt, we prepared a portion of this body according to the directions of Glenard and Boudault. The dracyl obtained possessed all the properties of toluol; we converted the body thus prepared into nitrodracyl (nitrotoluol), from which, by treatment with reducing agents, beautiful crystals of toluidin were obtained. In our paper on this organic base an analysis of the sulphate is given, and on referring I find that we forgot to mention that the salt analysed was prepared with the very toluidin obtained from the carbo-hydrogen arising with the distillation products of dragon's blood. This experiment removes any doubt that might have remained as to the identity of toluol and dracyl.—*Dr. A.W. Hofmann*.

‡ Liebig's *Annalen*, xli. 56.

§ Ibid. xlii. 313.

|| Ibid. lvi. 307.

¶ Mem. of Chem. Soc. vol. ii. p. 367.

Preparation of Cymol.

The experiments of Gerhardt and Cahours have shown that cumín oil (*oleum cumini*) is a mixture of two distinct oils,—cuminol ($C_{20}H_{12}O_2$), a body corresponding closely to oil of bitter almonds, and cymol ($C_{20}H_{14}$); by treatment with potash, the oxygen oil is converted into cumínic acid, while the carbo-hydrogen distils over unaltered. As, for the experiments about to be detailed, it was the latter of these two oils that was required, the mode of separation which I found it most convenient to adopt was the following:—The oil was first submitted to distillation alone, and about two-thirds of it drawn over; this portion was then repeatedly distilled with sticks of caustic potash, until the alkali remained unaltered; fresh potash was introduced after every third or fourth distillation, and the oil was regarded as pure when it ceased to lose anything after two or three distillations; latterly I found it advantageous to employ a retort of copper in this operation, the heated alkali proving exceedingly destructive to vessels of glass. The quantity of cymol obtained averaged about 7 oz. for every pound of cumín oil; and here I must be allowed to express my thanks to my friend Mr. Warrington for having kindly undertaken to furnish me with a supply of oil obtained directly from the seeds by distillation: without his assistance I should scarcely have been able to have followed out my investigation, on account of the high price and varying quality of the oil obtained in commerce; from three-quarters of a hundred weight of seed Mr. Warrington obtained at four distillations 2 lbs. 12 oz. of oil, which yielded me 18 oz. of beautiful and pure cymol.

To render cymol perfectly anhydrous, it was left for some time in contact with pieces of fused chloride of calcium and again distilled; in this state it is a limpid, colourless, highly refracting oil, of a very agreeable odour; its specific gravity I found to be 0.8576 at 16°, and its boiling-point, as a mean of two determinations with two specimens of the oil obtained at different periods, and which agreed closely with each other, 171°.5 C.

Cymol has been identified with camphogene, a substance previously obtained by Dumas*, by the action of anhydrous phosphoric acid on camphor, and lately studied by Delalande†. At the commencement of my experiments I thought that this might probably be a useful practical method of procuring the carbo-hydrogen; from the difficulty however of obtaining anhydrous phosphoric acid in sufficient quantities,

* Liebig's *Annalen*, vi. 249.

† Ibid. xxxviii. 343.

and from the small amount of camphogene obtained, I found it otherwise, and I merely prepared a sufficient supply to enable me to obtain an additional proof of the identity of the two oils, which I did in a manner hereafter to be described. I may remark that even after repeated distillations with renewed quantities of anhydrous phosphoric acid I was unable to procure camphogene quite free from the peculiar smell of camphor, nor was there to be discovered in it the slightest approach to that fragrant odour by which cymol is characterized.

Action of Nitric Acid on Cymol.

The action of nitric acid on cymol or camphogene has never hitherto been the subject of minute examination. Gerhardt and Cahours in their paper only mention that nitric acid of moderate concentration does not attack cymol when cold; that on heating nitrous acid is disengaged, and the carbon-hydrogen gradually passes into a peculiar acid, which on cooling is precipitated as a curdy mass; that this acid is rather soluble in water, alcohol and æther, crystallizing only with difficulty, and decomposed by heat, partially subliming in fine light needles or woolly flakes; and that fuming nitric acid decomposes cymol with the formation of the same acid and a yellow resin; none of these substances were however submitted by these chemists to elementary analysis. Delalande states that on treating camphogene with boiling fuming nitric acid it is converted into a white solid matter, becoming crystalline in the acid, and containing nitrogen. From these statements it seemed evident that the action of nitric acid on cymol gives rise to a variety of bodies, a supposition which experiments have completely verified; indeed, by a careful examination of this reaction, I have ascertained that not less than five or six different substances are produced; these bodies, some of which are acid, and some of a neutral character, are separated with considerable difficulty. In the present memoir I propose to confine myself to the acids only, reserving the regular substitution products of cymol, with the basic bodies arising therefrom, the substances representing nitrobenzol, aniline, &c., in the cymol series for a future paper.

I commenced with fuming nitric acid of the highest degree of concentration, the action of which on cymol is exceedingly violent; to avoid explosions it was necessary to keep the vessel cool by immersion in water; the oil was added gradually, drop by drop, to the acid, which speedily became of a dark red colour; by repeated distillations I obtained a beautiful crystalline acid, the analysis of which, leading to the formula

426 Mr. Noad on the Action of Nitric Acid on Cymol.

$\text{HO}, \text{C}_{16}\text{H}_6\text{NO}_7$, rendered it evident, from the mode of its formation, that it must be considered as a substitution product of a corresponding non-nitrogenous acid, $\text{HO}, \text{C}_{16}\text{H}_7\text{O}_3$, the very acid that is wanting in the toluol series, to the production of which acid my attention was now particularly directed.

Many attempts were made to oxidize the oil without having recourse to nitric acid; long-continued distillations with chromic acid, or with peroxide of manganese and sulphuric acid proved quite ineffectual, but after a great number of tentative operations, I at length succeeded, by the following method, in obtaining the wished-for substance, for which I propose the name of *toluylic acid*:—Ordinary nitric acid was diluted with about six times its bulk of water, and cymol added in the proportion of about 2 oz. of the oil to 1 lb. of the acid; the mixture was then introduced into a capacious retort and the distillation continued for two or three days; with acid of this strength there is no fear of a violent action; the oxidation of the oil proceeds slowly and quietly; it first becomes of a bright blue colour from the absorption of nitric oxide gas, then yellow, and after having been ten or a dozen times poured back into the retort, it begins to change more and more its physical character; it becomes heavier and more tenacious, and finally sinks to the bottom of the vessel; the process is known to be completed by a portion of the newly-formed acid passing over with the vapour of water, and condensing in the receiver, and if the whole operation has been successfully conducted, the contents of the retort become nearly solid on cooling from the crystallization of the acid; the weaker the nitric acid employed, and the longer the time consumed, the whiter and purer is the resulting acid; if a much stronger acid than that above prescribed be employed, violent action takes place when the boiling-point is reached, nearly the whole of the contents of the retort is projected into the receiver, and the new acid is found at the close of the operation to be contaminated with a considerable quantity of the nitrogenous acid, from which it is impossible afterwards entirely to free it; even when the operation has been slowly and carefully conducted with a very weak acid, it still contains a certain quantity of this acid, as numerous analyses proved, from which it is only to be freed by a series of troublesome operations; and it was only after a careful study and comparison of the salts formed by the respective acids that I was enabled to lay down a precise method for their separation. This method is founded on the great solubility of toluylate of baryta in cold water, and the very sparing solubility

of the corresponding salt of the nitrogenous acid in the same menstruum. The crude acid is thrown on a filter, and the adhering nitric acid removed by washing with cold water; it is then boiled with hydrate of lime, and the resulting lime-salt, filtered when quite cold, afterwards decomposed by nitric or hydrochloric acid; if the acid does not precipitate tolerably white, the same operation is repeated, and the well-washed acid is then dissolved in baryta water and carefully evaporated to dryness on the water-bath; it is redissolved in cold water, filtered, reprecipitated by hydrochloric acid, washed, and the process repeated until the dry baryta salt dissolves completely in cold water; it should then be once or twice crystallized, after which it is generally quite pure.

The quantity of pure acid as thus obtained from 2 oz. of cymol is very small, but I have not hitherto been fortunate enough to discover a better or less circuitous method of procuring it; could an oxidizing action be effected on the oil without the use of nitric acid a great saving would undoubtedly be achieved, but, as before stated, all my attempts in this direction proved unavailing; it is not impossible that the object may be obtained by permanganate of potash. I made one experiment with this salt, and there was evidently a reduction of the permanganic acid, but no trace of toluyllic acid could be discovered, from which it seems evident that the oxidation had in this case proceeded too far and the cymol become converted into carbonic acid; this reaction has not however as yet been sufficiently studied.

Composition of Toluyllic Acid.

On submitting toluyllic acid to elementary analysis in the usual manner, by burning it with oxide of copper, I obtained the following results:—

I. Acid obtained by sublimation, not having been previously treated with baryta:—0·2225 grm. gave 0·569 grm. carbonic acid and 0·1190 water.

II. Acid obtained as before from a new preparation:—0·2105 grm. gave 0·540 grm. carbonic acid and 0·1130 water.

III. Acid obtained from the lime salt:—0·160 grm. gave 0·415 grm. carbonic acid and 0·085 water.

IV. Acid obtained from the baryta salt:—0·3120 grm. gave 0·803 grm. carbonic acid and 0·161 water.

V. Acid obtained as before from a new preparation:—0·320 grm. gave 0·825 grm. carbonic acid and 0·1715 water.

These numbers correspond to the following per-centages:—

	I.	II.	III.	IV.	V.
Carbon .	69·74	69·96	70·09	70·19	70·31
Hydrogen	5·94	5·96	5·98	5·98	5·95

428 Mr. Noad on the Action of Nitric Acid on Cymol.

and with consideration of the atomic weight as deduced from the analysis of the silver and baryta salts, lead to the following formula, $\text{HO}, \text{C}_{16} \text{H}_7 \text{O}_3$, as may be seen by the following comparison :—

		Theory.		Mean of the three last experiments.
16 equivs.	Carbon . .	96	70·58	70·20
8 ...	Hydrogen . .	8	5·88	5·97
4 ...	Oxygen . .	32	23·54	
1 ...	Toluylic acid	136	100·00	

This acid thus becomes isomeric with hydride of anisyle and benzoate of oxide of methyl.

Properties of Toluylic Acid.

From an aqueous solution of any of its salts toluylic acid is precipitated by nitric or hydrochloric acid as a snow-white curdy mass, which under the microscope resolves itself into a great number of small acicular crystals: it is soluble to a considerable extent in boiling water, out of which it crystallizes on cooling in small needles; in alcohol, æther and pyroxylic spirit it is soluble almost to any extent; when heated it fuses and sublimes without decomposition in beautiful needles: in its state of perfect purity it is inodorous and tasteless, but the impure acid has a peculiar and sickening smell, somewhat resembling that of oil of bitter almonds. When boiled for some time with concentrated nitric acid, it loses an atom of hydrogen, in the place of which an atom of hyponitric acid enters, nitrotoluylic acid being formed; and when heated with caustic lime or baryta it is decomposed into carbonic acid and toluol.

In the formation of toluylic acid from cymol four equivalents of carbon and six equivalents of hydrogen are eliminated in the form of oxalic and carbonic acids and water. In several preparations large quantities of oxalic acid were found. There exists a striking similarity in the manner in which nitric acid acts upon cymol and oil of anise, an oil in its composition closely connected with cymol, and which gives rise to anisyllic acid, between which and toluylic acid there is also a marked resemblance. The composition of oil of anise being $\text{C}_{20} \text{H}_{12} \text{O}_2$, we may consider it as cymol which has lost two equivalents of hydrogen and taken two of oxygen. The composition of the acids formed by the action of nitric acid on these two oils is as follows :—

Compounds of Toluyllic Acid.

From the extreme difficulty of obtaining this acid in a state of purity in any quantity, I have not been able to examine as many of its salts as I could have wished; the following will however serve to confirm its composition and establish its atomic weight.

Toluylate of Baryta.—The formation of this salt has been already described; I was unable to obtain it in a well-defined crystalline form. Its analysis yielded the following result:—

0·7955 grm. gave 0·453 sulphate of baryta = 37·37 per cent. baryta, agreeing very closely with the formula

as indicated by the subjoined comparison:—

		Theory.	Experiment.
1 equiv. Anhydrous acid	127		
1 ... Baryta . . .	76	37·44	37·37

Toluylate of Silver.—This salt was formed by dropping nitrate of silver into a perfectly neutral solution of toluylate of ammonia; it fell as a white curdy mass, which was washed on a filter with cold water and purified by two or three crystallizations out of boiling water: it crystallizes in small needles. On analysing this salt the following numbers were obtained:—

I. 0·3785 grm. burned with oxide of copper gave 0·544 grm. of carbonic acid and 0·1045 water.

II. 0·334 grm. ignited gave 0·1485 silver.

III. 0·1725 grm. from another preparation gave 0·0767 silver.

IV. 0·1705 grm. from a third preparation gave 0·0757 silver.

These numbers correspond to the following per-centages:—

	I.	II.	III.	IV.
Carbon . . .	39·198			
Hydrogen . .	3·03			
Silver . . .		44·46	44·46	44·4

and lead to the formula $\text{AgO}, \text{C}_{16} \text{H}_7 \text{O}_3$, as may be seen by the following comparison:—

		Theory.	Experiment.
16 equivs. Carbon . . .	96	39·51	39·198
7 ... Hydrogen . . .	7	2·88	3·03
4 ... Oxygen . . .	32	13·17	
1 ... Silver . . .	108	44·44	44·44
1 ... Toluylate of silver	243	100·00	

430 Mr. Noad on the Action of Nitric Acid on Cymol.

Toluylate of Copper.—This salt was prepared by dropping a solution of sulphate of copper into a perfectly neutral solution of toluylate of potash; it fell as a bright blue precipitate closely resembling the corresponding benzoate. It is very soluble in ammonia, forming a dark blue solution, and soluble to a slight extent in boiling water, separating on cooling as a granular precipitate: its analysis gave the following result.

0·3385 grm. ignited, the residue treated with nitric acid and again ignited gave 0·0822 grm. of oxide of copper = 24·28 per cent., agreeing with the formula CuO , $\text{C}_{16}\text{H}_7\text{O}_3$.

	Theory.		Experiment.
1 equiv. Anhydrous acid	127·0	76·19	
1 ... Oxide of copper	39·7	23·81	24·28
	166·7	100·00	

Toluylate of Oxide of Ethyl.—This compound was formed by transmitting a stream of dry hydrochloric acid gas through a solution of the acid dissolved in strong alcohol, until the latter fumed strongly; it was then distilled, about two-thirds drawn over, and the residue in the retort mixed with water; the new æther precipitated in the form of a dark heavy liquid; it was digested with ammonia to remove any uncombined toluylic acid, well-washed with distilled water, dried, by being allowed to remain for some time in contact with pieces of fused chloride of calcium, and then distilled: it passed into the receiver nearly colourless, but on standing it deposited a small quantity of crystalline matter, which proved to be the æther of the nitrogenous acid, the acid employed not having been obtained from the baryta salt. By a second distillation, collecting only the first portions, the whole of the other æther was removed and a pure substance obtained.

Analysis.—0·223 grm. gave 0·596 carbonic acid and 0·151 water. Centesimally,—

Carbon	72·9
Hydrogen	7·52

agreeing closely with the formula $\text{C}_4\text{H}_5\text{O}$, $\text{C}_{16}\text{H}_7\text{O}_3$, as the following comparison of the theoretical with the experimental numbers shows:—

	Theory.		Experiment.
20 equivs. Carbon . . .	120	73·17	72·90
12 ... Hydrogen . . .	12	7·31	7·52
4 ... Oxygen . . .	32	19·52	
1 ... Toluylic æther .	164	100·00	

When perfectly pure this compound is a colourless, fra-

grant liquid, having an odour closely resembling that of cin-
namic or benzoic æther, and a pungent and slightly bitter
taste. It boils at 228° C., which temperature may perhaps
be one or two degrees too high, the determination having been
made before the last traces of the nitrogenous æther had been
removed; still it exhibits a new confirmation of the obser-
vation of H. Kopp, that the difference in the boiling-points of
two analogous compounds, which differ by two equivalents of
carbon and two of hydrogen, is 19° C. Benzoic æther, the
composition of which is C_4H_5O , $C_{14}H_5O$, boils at 209° .
Unfortunately I had not a sufficient quantity of the liquid
after purification for a second determination.

The following salts I have examined qualitatively only,
considering the composition and atomic weight of the acid
well-enough established by the preceding analyses.

Toluylate of Potash, formed by exactly neutralizing the
acid with caustic potash, is a very soluble salt, crystallizing
with great difficulty in small needles.

Toluylate of Soda is still more soluble than the preceding.
I could not obtain it in the crystalline state.

Toluylate of Ammonia crystallizes in small prisms.

Toluylate of Lime crystallizes out of a concentrated aqueous
solution in long shining needles.

Products of the Decomposition of Toluylic Acid.

Nitrotoluylic Acid.—I have already observed that on treat-
ing cymol with concentrated and fuming nitric acid violent
action ensues, and that by repeated distillations a crystalline
acid containing nitrogen is obtained. I must now describe
this action more in detail. The nitric acid employed should
be concentrated and fuming, otherwise there will be a con-
siderable formation of another crystalline substance, which is
in its chemical character neutral, and which is not easily con-
verted into nitrotoluylic acid. The properties and composi-
tion of this new product will be fully considered hereafter.
The distillation must be continued as long as nitrous fumes
continue to be evolved, and the retort then allowed to cool,
upon which a considerable quantity of crystalline matter is
deposited, and on adding cold water a copious precipitate
takes place. The whole is now thrown on a filter and washed
with cold water till all the nitric acid is removed; the pre-
cipitate is then digested with ammonia, the greater part
dissolves; a portion however collects at the bottom of the
vessel in the form of a red oil, which is to be separated. The
ammoniacal salt is next decomposed by hydrochloric acid, the
acid collected on a filter and well-washed with cold water, in

432 Mr. Noad on the Action of Nitric Acid on Cymol.

which it is very sparingly soluble; it is then dissolved in hot alcohol, boiled for a few minutes with animal charcoal, and filtered; by spontaneous evaporation the new acid crystallizes out in beautiful rhombic prisms of a pale yellow colour.

Composition of Nitrotoluylic Acid.

The powdered crystals by combustion with oxide of copper yielded the following numbers:—

I. 0.330 grm. gave 0.640 carbonic acid and 0.1205 water.

II. 0.382 grm. gave 0.7396 carbonic acid and 0.136 water.

III. 0.4145 grm. gave 0.806 carbonic acid and 0.152 water.

IV. The nitrogen was determined by Dumas' method in an atmosphere of carbonic acid. The particulars of the experiment are as follows:—

0.600 grm. gave 41.5 cubic cent. of moist nitrogen. Barometer 0^m.7973; Thermometer 18°·5 C.

These numerical results correspond with the following per cents.:—

	I.	II.	III.	IV.
Carbon . . .	52.89	52.80	53.03	
Hydrogen . .	4.06	3.95	4.07	
Nitrogen . . .	...	...	...	79.6

and lead to the formula $\text{HO}, \text{C}_{16} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{NO}_4 \end{smallmatrix} \right\} \text{O}_3$, as the following comparison of the calculated numbers with the mean of analysis shows:—

	Theory.		Mean of expt.
16 eqs. Carbon . . .	96	53.03	52.90
7 ... Hydrogen . . .	7	3.86	4.00
1 ... Nitrogen . . .	14	7.74	7.96
8 ... Oxygen . . .	64	35.37	
1 ... Nitrotoluylic acid	181	100.00	

By the following analyses of some of the salts of this acid the above formula is fully confirmed, and the atomic weight of the acid proved.

Nitrotoluylate of Baryta.—This salt was formed by adding chloride of barium to a neutral solution of nitrotoluylate of ammonia. A white curdy precipitate was determined, soluble to a considerable extent in boiling water, out of which it crystallized on cooling in beautiful stellated tufts, having a shining appearance when dry: after two or three recrystallizations it was submitted to analysis, and yielded the following results:—

0.738 grm. gave by ignition 0.290 grm. of carbonate of

baryta = 30·54 per cent. baryta, corresponding with the formula $\text{BaO}, \text{C}_{16}\left\{\begin{smallmatrix} \text{H}_6 \\ \text{NO}_4 \end{smallmatrix}\right\}\text{O}_3$, as may be seen by the following comparison :—

	Theory.		Experiment.
1 equiv. Anhydrous acid	171·50	69·24	
1 ... Baryta . . .	76·66	30·76	30·54
	248·16	100·00	

Nitrotoluylate of Silver.—This salt was formed by dropping nitrate of silver into a neutral solution of nitrotoluylate of ammonia; it fell as a white curdy mass resembling chloride of silver. It is soluble to a considerable extent in hot water, and by long boiling becomes partially decomposed; it crystallizes from a hot aqueous solution in beautiful feathery tufts; it is only sparingly soluble in alcohol.

By combustion with oxide of copper the following results were obtained :—

I. 0·3505 grm. gave 0·424 grm. carbonic acid and 0·070 water when ignited alone.

II. 0·3385 grm. gave 0·127 grm. of silver.

III. 0·230 grm. gave 0·086 grm. silver. Centesimally :—

	I.	II.	III.
Carbon . .	33·0		
Hydrogen .	2·12		
Silver . . .		37·52	37·38

corresponding with the formula $\text{AgO}, \text{C}_{16}\left\{\begin{smallmatrix} \text{H}_6 \\ \text{NO}_4 \end{smallmatrix}\right\}\text{O}_3$.

	Theory.		Experiment.
16 equivs. Carbon . .	96	33·33	33·00
6 ... Hydrogen . .	6	20·8	2·12
1 ... Nitrogen . .	14	4·86	
8 ... Oxygen . .	64	22·22	
1 ... Silver . . .	108	37·51	37·45
1 ... Nitrotoluylate } of silver .	288	100·00	

I have already mentioned that I prepared a small quantity of camphogene by the action of anhydrous phosphoric acid on camphor; in order to obtain an additional experimental proof of the identity of this substance with cymol, I have studied the action of concentrated nitric acid on it. I found it most convenient to prepare a silver salt of the acid thus obtained, the analysis of which yielded me the following numbers :—

434 Mr. Noad on the Action of Nitric Acid on Cymol.

I. 0.396 grm. gave 0.486 carbonic acid and 0.85 water.

II. 0.372 grm. gave 0.139 silver.

III. 0.2935 grm. gave 0.110 silver.

These numbers correspond in per cents. to—

	I.	II.	III.
Carbon . . .	33.46		
Hydrogen . .	2.38		
Silver . . .	...	37.36	37.47

And by comparing them with the preceding they will be found sufficiently near to warrant the conclusion that the two carbo-hydrogens are identical. On treating the acid formed by the action of fuming nitric acid on camphogene with ammonia, the same heavy oil which was observed in the case of cymol separated, and after a while crystallized; but from the small quantity of camphogene at my command, I was unable to procure sufficient of this substance for a comparative experiment, or to bring forward any additional proof of the identity of the two oils.

Nitrotoluylate of Lime.—This salt was prepared by decomposing nitrotoluylate of ammonia by chloride of calcium. It fell as a granular crystalline mass, much more soluble in water than the corresponding baryta salt, and crystallizing out of its aqueous solution in small clustering groups of oblique rhombic prisms; it was obtained perfectly pure by two or three recrystallizations.

Analysis.—0.6965 grm. gave by ignition, treatment with carbonate of ammonia, and a second gentle ignition, 0.1775 grm. carbonate of lime = 14.27 per cent. of lime, agreeing exactly with the formula $\text{Ca}, \text{OC}_{16} \left\{ \begin{smallmatrix} \text{H}_6 \\ \text{NO}_4 \end{smallmatrix} \right\} \text{O}_3$.

	Theory.		Experiment.
1 equiv. Anhydrous acid	171.50		
1 ... Lime . . .	28.5	14.25	14.27
	200.00		

Nitrotoluylate of Oxide of Ethyl.—A solution of the pure acid in strong alcohol was submitted to a current of dry hydrochloric acid gas till copious fumes were evolved; it was then distilled; the first portions that passed into the receiver consisted of a mixture of alcohol and hydrochloric æther; the distillation was continued until a few drops collected on a watch-glass gave a milky whiteness when mixed with water; it was then stopped, and the retort allowed to cool; a considerable quantity of the yellow heavy oil collected at the bottom of the vessel, which was poured off into a beaker; in a few

minutes it solidified into a yellow crystalline mass. This impure æther was next treated with carbonate of potash, by which all adhering undecomposed acid was removed; it was then thrown on a filter, well-washed with cold water, and dried by pressure between folds of bibulous paper; it was now of a pale amber colour, and possessed a very agreeable odour; it was redissolved in hot alcohol and filtered, the alcoholic solution on cooling solidified into a light lemon-coloured crystalline mass; this was dried between folds of blotting-paper, transferred to a watch-glass, and, placed in the water-bath, it immediately liquefied: after remaining about an hour it was removed, and on cooling it gradually crystallized into a mass of needles radiating from a common centre and having a very beautiful appearance.

It was analysed by combustion with oxide of copper, and furnished the following results:—

0.362 grm. gave 0.760 grm. carbonic acid and 0.175 grm. water. Centesimally—

Carbon	57.26
Hydrogen	5.37

agreeing with the formula $C_4H_5O, C_{16}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}O_3$, as shown by the following comparison:—

	Theory.		Experiment.
20 eqs. Carbon	120	57.42	57.26
11 ... Hydrogen	11	5.26	5.37
1 ... Nitrogen	14	6.69	
8 ... Oxygen	64	30.63	
1 ... Nitrotoluylic æther .	209	100.00	

The remainder of the æther was dissolved in a strong alcoholic solution of ammonia and set aside with the view of procuring nitrotoluylicamide: this substance, however, which it would have been interesting to have compared with the corresponding term of the benzoyl series lately obtained by Mr. Field*, I have not yet been able to obtain.

Nitrotoluylic Oxide of Methyl.—To prepare this substance, nitrotoluylic acid was dissolved in pure pyroxylic spirit, and the solution subjected to a long-continued stream of dry hydrochloric acid gas, as in the corresponding ethyl compound. On distilling the fuming acid liquid, a considerable quantity of a dense, black oily substance collected at the bottom of the vessel: this was evidently the methyl compound contaminated with results of the decomposition of the

* Memoirs of the Chemical Society, vol. iii. p. 104.

436 Mr. Noad on the Action of Nitric Acid on Cymol.

pyroxylic spirit by the hydrochloric acid gas. On cooling the acid liquid was poured off and the oil repeatedly washed with water; in a few hours it solidified into a confused crystalline mass, still however black and having a peculiar vinous smell: an attempt was made to purify it by distillation with water; in consequence, however, of its high boiling-point, very little passed over into the receiver after two or three hours' distillation. It was then heated with strong nitric acid, and after boiling for a few minutes, water added; the æther now readily separated in clear, light yellow oily drops: ammonia was then added to remove any nitrotoluylic acid that might have been present, and the oil collected on a watch-glass; in a few minutes it solidified into a crystalline mass, which was dissolved in æther, filtered and recrystallized, and then exposed for some time to the heat of the water-bath; on cooling it solidified as before, and was then considered sufficiently pure for analysis.

0.376 grm. gave by combustion with oxide of copper 0.756 grm. of carbonic acid and 0.164 grm. of water, corresponding in per cents. to

Carbon	54.84
Hydrogen	4.83

and agreeing with the formula $C_2H_3O, C_{16}\left\{\begin{smallmatrix} H_6 \\ NO_4 \end{smallmatrix}\right\}O_3$.

	Theory.		Experiment.
18 eqs. Carbon	108	55.38	54.84
9 ... Hydrogen	9	4.61	4.83
1 ... Nitrogen	14	7.18	
8 ... Oxygen	64	32.83	
1 ... Nitrotoluylate of } oxide of methyl . . }	195	100.00	

After standing two or three days, beautiful colourless stellar crystals were deposited on the sides of the vessel containing an aqueous solution of this æther; it is probable, therefore, that this as well as the last-described compound is, when perfectly pure, colourless. The two æthers closely resemble each other in their physical characters, the smell of the latter is, however, less agreeable than that of the former; both are decomposed by potash into nitrotoluylic acid and alcohol or pyroxylic spirit.

The following salts of this acid I merely examined qualitatively.

Nitrotoluylate of Potash is a very soluble salt crystallizing with great difficulty in small needles.

Nitrotoluylate of Soda, like the corresponding salt of toluyllic acid, I could not obtain in any definite crystalline form.

Nitrotoluylate of Ammonia crystallizes out of its aqueous solution in long needles; it is very easily decomposed, losing the whole of its ammonia when boiled with animal charcoal. I intend to return to the study of this salt, and hope to obtain from it the body which I failed to procure from nitrotoluylic ether, viz. nitrotoluylamide.

Nitrotoluylate of Strontia.—This salt, which in appearance is not to be distinguished from the corresponding baryta salt, was formed by dropping chloride of strontium into neutral nitrotoluylate of ammonia: it is rather more soluble in boiling water than the baryta compound, and the crystals deposited on cooling are rather larger.

Nitrotoluylate of Copper.—On adding solution of sulphate of copper to perfectly neutral nitrotoluylate of ammonia a basic salt is formed. I have not yet obtained a definite copper salt of this acid.

Action of a mixture of Sulphuric and Nitric Acids on Nitrotoluylic Acid.

When nitrobenzol is boiled repeatedly with the strongest nitric acid it loses an atom of hydrogen, in the place of which another atom of hyponitric acid enters. The transformation proceeds very slowly. The new substance (dinitrobenzol) is however obtained very speedily, as Drs. Muspratt and Hofmann* have shown, by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid and concentrated sulphuric acid as long as the liquid remains homogeneous. This method has lately been employed with great success by M. Cahours, who, amongst many other interesting products, has obtained trinitranisic acid, $C_{16}\left\{ \begin{smallmatrix} H_5 \\ 3(NO_4) \end{smallmatrix} \right\} O_6$; dinitrocuminic acid, $C_{20}\left\{ \begin{smallmatrix} H_{10} \\ 2(NO_4) \end{smallmatrix} \right\} O_4$; and dinitrobenzoic acid, $C_{14}\left\{ \begin{smallmatrix} H_4 \\ 2NO_4 \end{smallmatrix} \right\} O_4$. It appeared interesting to submit nitrotoluylic acid to a similar treatment, but after digesting the acid with the mixture for several days the anticipated transformation had not taken place, the numbers obtained by analysis being those given under III., "composition of nitrotoluylic acid." I intend however to repeat this experiment.

Distillation of Toluylic Acid with Baryta—Toluol.

Although the preceding analyses of toluylic and nitroto-

* Mem. Chem. Soc. vol. iii. p. 111.

438 Mr. Noad on the Action of Nitric Acid on Cymol.

luylic acids have established the composition of these two compounds in a perfectly satisfactory manner, there still remained one experiment to be made in order to prove that toluylic acid occupies in the toluyl series the same place which benzoic acid has in the benzoyl series; in order to prove that the acids analysed are really the true toluylic and nitro-toluylic acids, and not merely bodies having the same composition, being isomeric with them: this experiment was to attempt the transformation of toluylic acid into toluol under the same circumstances by which benzoic acid becomes converted into benzol. I devoted the acid from four ounces of cymol to this experiment, and by distillation with caustic baryta, which I found to answer much better than lime, I obtained some grammes of a beautiful limpid colourless liquid, having the precise smell of the carbo-hydrogen sought for. By distillation from a fresh portion of baryta the oil was rendered perfectly anhydrous; in this state its boiling-point was taken. It began to boil at 109° , the thermometer gradually rose to $110^{\circ}5$, barometer $0^m.763$ (30.1 inches).

It was burned in the ordinary manner with oxide of copper and yielded the following results:—

0.2410 grm. gave 0.809 grm. of carbonic acid and 0.196 grm. of water, corresponding in per cents. to

Carbon	91.50
Hydrogen	9.03

and agreeing exactly with the formula of toluol, $C_{14}H_8$, as the following comparison shows:—

	Theory.		Experiment.
14 eqs. Carbon . . .	84	91.3	91.50
8 ... Hydrogen . . .	8	8.7	9.03
	22	100.0	100.53

The formation of toluol from toluylic acid is perfectly analogous to the production of benzol from benzoic acid.

The remainder of the carbo-hydrogen was converted into nitrotoluol by the action of fuming nitric acid: the well-washed oily fluid was then dissolved in alcohol, saturated with ammoniacal gas and treated repeatedly with sulphuretted hydrogen, the whole being distilled after each saturation with hydrosulphuric acid, to facilitate the deposition of the sulphur; the dark red solution was evaporated to expel the alcohol, water added, and then submitted to distillation with

potash, in addition to ammonia and aqueous vapour, a yellow oil passed into the receiver, which did not however solidify on cooling, probably in consequence of the presence of ammonia; it was therefore saturated with oxalic acid, evaporated to dryness in the water-bath, redissolved in boiling alcohol and filtered; on cooling, oxalate of toluidine separated in fine white needles, these were washed, dissolved in boiling water, and decomposed by potash; the toluidine, which separated in colourless oily drops, was taken up by æther, on the evaporation of which it remained in the form of a crystalline mass. Although the nature of this substance was sufficiently obvious, nevertheless, to remove all doubt respecting it, I converted it into the double platinum salt by mixing it with hydrochloric acid and bichloride of platinum. The beautiful orange-yellow spangular mass was washed with æther and dried on the water-bath. Its analysis gave the following result:—

0·930 grm. gave by ignition 0·292 grm. of platinum = 31·398 per cent.

This determination agrees with the formula for chloride of platinum and toluidine— $C_{14}H_9N, HCl, PtCl_2$.

		Theory.	Experiment.
14 eqs. Carbon	. . .	84·00	
9 ... Hydrogen	. . .	9·00	
1 ... Nitrogen	. . .	14·00	
3 ... Chlorine	. . .	106·50	
1 ... Platinum	. . .	98·68	31·6
		312·18	31·398

By the production of toluylic and nitrotoluylic acids there is not only filled up a gap which has hitherto existed in the toluylic series, but an important step has been made in the series of acids to which I have alluded at the commencement of this paper, of which indeed at the present time a few scattered members only are known. The following table presents a general view of some of the most important members of the different groups, and exhibits the gaps which remain to be filled up by future experiments.

* This beautiful base has lately been prepared by Mr. Nicholson in the laboratory of the Royal College of Chemistry.

* This beautiful base has lately been prepared by Mr. Nicholson in the laboratory of the Royal College of Chemistry.

On the Oxidation of Cumol by Nitric Acid. 441

The preceding table shows that there are indeed a great number of substances still to be discovered. In the first series it will be seen that as yet we have only one member, seminaphthalidine*, the base corresponding to aniline and toluidine, and obtained by Zinin in a very curious reaction of sulphide of ammonium on dinitronaphthalol. The second series is best known; it is closely connected with the indigo series by salicylic acid, nitrosalicylic acid and aniline. As however the term of indigo is as yet not represented in any of the other families I have omitted to connect them. The third is the toluyll series, which has become enriched by the present investigation with two of the principal terms: of the following no term whatever is known. The next contains a series of interesting compounds arising from oil of cumin, and of the last group we have at present only cymol. In a future paper I hope to introduce some of the substances deriving from this carbo-hydrogen.

This investigation was conducted in the laboratory of the Royal College of Chemistry, and I cannot bring it to a conclusion without acknowledging the great obligation I am under to Professor Hofmann for the constant advice and assistance which he afforded me during its prosecution, and expressing my warmest thanks to him for his valuable instructions in the method of conducting organic investigations generally.