XXVII.—*On some Derivatives of Diphenylene Ketone Oxide.*

By A. G. PERKIN.

THE diphenylene ketone oxide employed in the following experiments was prepared by the process recently described by my Father (page 35 of this volume), namely, by distilling a mixture of salicylic acid and acetic anhydride. On concentrating the alcoholic mother-liquors left from the purification of this body, they were found to contain small quantities of a second product. It was afterwards observed that when the mixture of salicylic acid and acetic anhydride was very rapidly distilled, the amount of the new compound produced was larger than when the operation was conducted slowly. At first it was separated from the diphenylene ketone oxide simply by repeated fractional crystallisation, but afterwards the crude diphenylene ketone oxide was macerated with a small quantity of cold alcohol, and, after filtration, the alcohol was removed from the filtrate by boiling with water. Caustic potash was then added to dissolve oily matter present, and the whole was allowed to stand for about an hour, after which the solid matter in suspension was thrown on a filter and well washed. The product thus obtained was crystallised from alcohol, the first crop of crystals separating out being collected apart. By repeated treatment in this way, the new product was obtained in long thin transparent plates, having a beautiful satiny lustre. On analysis, it gave the following numbers:—

I.	0.1391	gram substance	gave	0.3870	of CO_2	and	0.0497	of OH_2 .
II.	0.1319	"	"	0.3646	"	"	0.0478	"
III.	0.1044	"	"	0.2861	"	"	0.0353	"

These numbers give the following percentages agreeing with the formula $\text{C}_{14}\text{H}_8\text{O}_3$:—

		Found.		
	Calculated.	I.	II.	III.
Carbon	75.0	75.16	75.38	74.74
Hydrogen ..	3.57	3.89	4.02	3.75

This substance is only slightly soluble in boiling alcohol, but more so in coal-tar naphtha. It melts at 192° , and distils with partial decomposition. When boiled with alcoholic potash, it is converted into the potassium salt of an acid, and on adding water and boiling off the alcohol, the acid is precipitated by hydrochloric acid as a somewhat gelatinous product if the solution is cold, but as a bulky precipitate on boiling.

This acid may be purified by two or three crystallisations from alcohol, from which it separates in minute needles. Specimens dried at 100° gave on analysis the following numbers:—

I.	0.1265	gram of substance	gave	0.3246	of CO_2	and	0.0431	of OH_2 .
II.	0.097	gram of substance	gave	0.2488	of CO_2	and	0.0328	of OH_2 .
III.	0.1345	„ „		0.3457	„ „		0.0416	„
IV.	0.1496	„ „		0.3838	„ „		0.0452	„

These give percentages agreeing with the formula $\text{C}_{14}\text{H}_8\text{O}_4$ —

		Found.			
	Calculated.	I.	II.	III.	IV.
Carbon	70.0	69.98	69.95	70.1	69.98
Hydrogen.	3.33	3.78	3.76	3.44	3.35

This acid melts at 275° . It sublimes in brilliant needles, and can be distilled apparently with but little decomposition; it is difficultly soluble in alcohol. When gently fused with caustic alkali, it produces salicylic acid, judging from the iron reaction.

Silver Salt.—This was prepared by dissolving the acid in dilute ammonia and boiling the solution until it was free from excess of that substance. Silver nitrate was then added by small quantities at a time, the mixture being well agitated. After some quantity of precipitate had been formed, the solution was filtered and an excess of silver nitrate added, which caused the liquid to coagulate into a gelatinous mass, somewhat like precipitated alumina, but, contracting, and becoming crystalline when heated in a water-bath; it was then collected and well washed with cold water. It gave on analysis the following numbers, the different preparations being examined:—

I.	0.1172	gram of substance	gave	0.0360	gram Ag.
II.	0.1483	gram of substance	gave	0.2642	gram CO_2 and 0.0275 gram OH_2 .
III.	0.1881	gram of substance	gave	0.0582	gram Ag.

These give percentages agreeing with the formula $\text{C}_{14}\text{H}_7\text{AgO}_4$ —

	Calculated.	Found.		
		I.	II.	III.
Carbon.....	48.41	—	48.59	—
Hydrogen ..	2.01	—	2.06	—
Silver	31.1	30.71	—	30.94

This salt is slightly soluble in cold water, more easily in boiling water. From its hot aqueous solution, it is deposited in groups of small transparent needles, which appear very definite under the microscope. It is not coloured by boiling with water.

From the foregoing results, it appears that this acid has the formula $C_{14}H_8O_4$. Its constitution may perhaps be represented thus:—

Its formation from the compound $C_{14}H_8O_3$ is, however, difficult to understand, because if it be an anhydride of the acid, as its properties would indicate, its formula should be $C_{14}H_6O_3$; but this would require 75.6 per cent. carbon and 2.7 of hydrogen. Unfortunately, this matter cannot at present be further investigated, owing to the want of product, which is obtainable from salicylic acid only in small quantities, and then is difficult to purify. I hope, however, to return to this subject.

On the Action of Nitric Acid on Diphenylene Ketone Oxide.

When diphenylene ketone oxide was added to a cold mixture of one part of nitric acid (sp. gr. 1.45) and one part of sulphuric acid, in small quantities at a time, and with constant stirring, it gradually dissolved without evolution of nitrous fumes. As the solution became more and more concentrated, crystals began to separate out, and the operation was continued until the whole had a semi-solid appearance.

The resulting mass was then thrown into a funnel provided with an asbestos plug, and the residue left after the acid had drained off, was washed, first with a little nitric acid (sp. gr. 1.45), then with weaker nitric acid, and finally with water, and dried. The mother-liquor and washings, after standing for some hours, deposited a further crop of these crystals, which were treated in a similar manner.

The product, which consisted of a mass of fine needles having a satiny lustre, was then further purified by crystallisation from alcohol or coal-tar naphtha. On analysis, it gave the following numbers:—

- I. 0.1600 gram of substance gave 0.3200 gram of CO_2 and 0.0301 gram of OH_2 .
 II. 0.1544 gram of substance gave 0.3103 gram of CO_2 and 0.0300 gram of OH_2 .

These numbers agree with those required by the formula $\text{C}_{13}\text{H}_6(\text{NO}_2)_2\text{O}_2$; thus:—

	Theory for $\text{C}_{13}\text{H}_6(\text{NO}_2)_2\text{O}_2$.	I.	II.
Carbon	54.54	54.54	54.80
Hydrogen	2.09	2.09	2.15

Dinitrodiphenylene ketone oxide is very slightly soluble in boiling alcohol, from which it separates on cooling in the form of fine needles, having a beautiful satiny lustre and electrical properties, and which, when viewed under the microscope, affect polarised light. It is more soluble in boiling coal-tar naphtha, and, when heated it sublimes in the form of needles. It melts at 262° .

The acid mother-liquors and washings obtained during the preparation and subsequent purification of dinitrodiphenylene ketone oxide were found to contain a small quantity of a much more soluble compound, which is probably a "mononitro" derivative, but which, up to the present, has not been obtained in a sufficiently pure state to be examined.

Fuming nitric acid (sp. gr. 1.54), well cooled with ice, was found to act on diphenylene ketone oxide in a similar manner to a mixture of nitric and sulphuric acids, but the yield of dinitro-product was not so good, there being produced at the same time a much larger quantity of the more soluble body above referred to.

The Action of Reducing Agents on Dinitrodiphenylene Ketone Oxide.

When dinitrodiphenylene ketone oxide was suspended in alcohol, and digested with tin and hydrochloric acid, it gradually dissolved, and the solution acquired a slightly yellow tint. When the reduction was completed, which was after the lapse of three or four hours, a little water was added and the alcohol boiled off. The solution was then poured into an evaporating dish and set aside to cool. While cooling, it deposited a quantity of semi-crystalline matter, which evidently consisted of the hydrochloride of a new base. This was thrown on a filter, and washed two or three times with dilute hydrochloric acid.

The mother-liquors and washings, when further evaporated, deposited on cooling another crop of crystals, which were treated in a similar manner.

The product was then dissolved in boiling water, filtered, and caustic soda added to the solution. The orange-coloured precipitate thus formed was thrown on a filter, thoroughly washed with water, and dried, after which it was further purified by crystallisation from boiling coal-tar naphtha, from which it separated in the form of orange-coloured needles.

On analysis, the following numbers were obtained :—

- I. 0·1129 gram of substance gave 0·2850 gram of CO_2 and 0·0466 gram of OH_2 .
 II. 0·1149 gram of substance gave 0·2912 gram of CO_2 and 0·0471 gram of OH_2 .

These numbers agree with those required by the formula $\text{C}_{13}\text{H}_6(\text{NH}_2)_2\text{O}_2$.

	Theory for $\text{C}_{13}\text{H}_6(\text{NH}_2)_2\text{O}_2$.	I.	II.
Carbon	69·02	68·87	69·11
Hydrogen	4·42	4·58	4·54

It is therefore *diamidodiphenylene ketone oxide*. This substance when crystallised from coal-tar naphtha appears under the microscope as orange-coloured flat needles, which affect polarised light. It is moderately soluble in boiling coal-tar naphtha, very slightly soluble in boiling water: from the latter it separates out on cooling in the form of long needles. Its best crystallising agent is a mixture of equal parts of alcohol and water, which deposits it in ruby-coloured prismatic needles.

This base forms an acid and a neutral hydrochloride, the former being thrown down on the addition of concentrated hydrochloric acid to a solution of the latter salt.

When an aqueous solution of the dihydrochloride mixed with its own bulk of alcohol was treated with a solution of platinic chloride, a crystalline mass was precipitated, which when examined under the microscope was seen to consist of fine transparent needles, having a pale-yellow colour. These were then thrown on a filter, washed with hydrochloric acid, and dried *in vacuo*.

The analysis of this salt did not yield numbers quite so good as could be wished, owing to its containing small quantities of that derived from the monohydrochloride. They, however, clearly showed that it has the formula $[\text{C}_{13}\text{H}_6(\text{NH}_2)_2\text{O}_2 \cdot 2\text{HCl}] \cdot \text{PtCl}_4$.

This salt is decomposed when treated with alcohol or water, becoming opaque and darker in colour, yielding the platinum salt of the monohydrochloride of the base.

This salt can also be obtained by addition of platinum chloride to a solution of the latter body. It forms reddish-brown needles.

On ignition the following amounts of platinum were obtained :—

I.	0.1468	gram of substance	gave	0.0313	gram of platinum.
II.	0.1129	„	„	0.0242	„
III.	0.3876	„	„	0.0835	„

These numbers give percentages agreeing with those required for the formula $2[\text{C}_{13}\text{H}_6(\text{NH}_2)_2\text{O}_2.\text{HCl}].\text{PtCl}_4$.

	Theory.	I.	II.	III.
Platinum....	21.10	21.32	21.43	21.54

Both salts are slightly decomposed at 100°C .

The Action of Sulphuric Acid on Diphenylene Ketone Oxide.

Diphenylene ketone oxide dissolves slowly in cold Nordhausen or ordinary sulphuric acid, forming yellow solutions possessing a bluish fluorescence, but which on treatment with water precipitate the original body unchanged.

With the intention of forming a sulpho-acid, diphenylene ketone oxide was dissolved in a small quantity of Nordhausen sulphuric acid, and the solution gradually heated until it no longer gave a precipitate with water. It was then diluted with water, and the solution neutralised with excess of barium carbonate. More water was then added, and the mixture boiled for some minutes and filtered.

The precipitate on the filter was re-exhausted once or twice with boiling water, and after filtration the combined filtrates were evaporated to dryness on the water-bath. The residue was then dissolved in boiling water and filtered; in the course of a few hours the solution became nearly solid owing to the formation of a mass of minute white crystals; these were pressed in a linen filter, recrystallised, and finally dried at $160\text{--}180^\circ$.

On analysis the following numbers were obtained. It was dried at $160\text{--}170^\circ$.

I.	0.1333	gram of substance	gave	0.1540	gram of CO_2 and	0.0198	gram of OH_2 .
II.	0.1212	gram of substance	gave	0.1401	gram of CO_2 and	0.0165	gram of OH_2 .
III.	0.1786	gram of substance	gave	0.0846	gram of BaSO_4 .		
IV.	0.1333	„	„	0.0635	„		

These numbers give percentages agreeing with those required by the formula $\text{C}_{13}\text{H}_6\text{O}_2\text{Ba}(\text{SO}_3)_2$.

	Theory for $C_{13}H_6O_2Ba(SO_3)_2$		I	II.	III.	IV.
Carbon	31.77		31.51	31.53	—	—
Hydrogen ..	1.22		1.65	1.51	—	—
Barium	27.90		—	—	27.89	28.00

Barium diphenylene ketone oxide disulphonate is moderately soluble in boiling water, from which it separates out on cooling in the form of small colourless needles which, when viewed under the microscope, do not affect polarised light.

It is a remarkably stable salt, not being decomposed by a temperature of 200° . When crystallised from water, it was found to contain water of crystallisation, which was only expelled by prolonged heating to 160° .

The following determination was made of the water in this salt. A specimen dried in a vacuum when heated to 100° , lost scarcely any weight.

1.3897 dried at 100° , when heated up to 195° , lost $0.0421 OH_2 = 3.29$. Theory for one molecule of water = 3.53 per cent.

The free acid was prepared by adding sufficient sulphuric acid to a solution of the foregoing salt to exactly precipitate all the barium, filtering and concentrating the solution on the water-bath, and afterwards further evaporating over sulphuric acid. In this way it was obtained crystallising in minute needles. It is easily soluble in water, and its solution has a rough bitter acid taste. Its aqueous solution gives with barium chloride a precipitate of the barium salt. Solutions of calcium and strontium chloride are not precipitated with it. When fused with caustic alkali the mixture becomes pale-yellow. The resulting products have not yet been examined.

The Action of Bromine on Diphenylene Ketone Oxide.

Diphenylene ketone oxide was heated in a sealed tube with bromine to 180° , the proportion of each used being those requisite for the formation of a "dibromo" compound. After the expiration of about three hours, the contents of the tube were found to be nearly colourless, and as soon as it was opened quantities of hydrobromic acid escaped.

The contents of the tube were then dissolved in boiling alcohol, and on leaving this solution to cool, it was found that the principal portion separated out quickly in the form of long needles.

These were then filtered off and recrystallised two or three times. F. p. = 212.5 — 213.5° .

On analysis the product gave the following numbers:—

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I. 0.1274 gram of substance gave 0.2051 gram of CO_2 and 0.0233 gram of OH_2 .

II. 0.1919 gram of substance gave 0.3122 gram of CO_2 and 0.0350 gram of OH_2 .

These numbers give percentages agreeing with those required by the formula $\text{C}_{13}\text{H}_6(\text{Br})_2\text{O}_2$.

	Theory for $\text{C}_{13}\text{H}_6(\text{Br})_2\text{O}_2$.	I.	II.
Carbon	44.06	43.93	44.36
Hydrogen.	1.70	2.03	2.02

It is therefore *dibromodiphenylene ketone oxide*.

It was afterwards observed that this body combined with bromine at the ordinary temperature, when exposed to its vapour or otherwise, only a comparatively small quantity of hydrobromic acid being produced. As it appeared that an addition-product was probably formed, weighed quantities were exposed to the action of bromine vapour, then kept over caustic potash, and finally heated to 100° ; as no change appeared to take place at this temperature. The following results were obtained:—

I. 0.4605 gram of substance absorbed 0.4357 gram bromine.

II. 0.6536 " " " 0.5945 "

These quantities are rather more than those required to form an addition-product. A quantity of the product obtained in this way was crystallised three times from benzene and then from alcohol, and on analysis gave the following numbers:—

0.1292 gram of substance gave 0.2094 gram of CO_2 and 0.0204 gram of H_2O .

These give 44.2 per cent. carbon and 1.76 of hydrogen. It was in fact dibromodiphenylene ketone oxide. It does not, however, appear to be the only body produced in the reaction, and it is thought that, as so little hydrobromic acid is liberated in its formation, it may be taken up as it is produced by part of the ketone to form another product. It is curious that bromine dissolved in carbon disulphide does not act or acts but slowly on this body.

Dibromodiphenylene ketone oxide crystallises from alcohol, in which it is difficultly soluble, in the form of long thin transparent needles. It is moderately soluble in boiling glacial acetic acid, and is easily soluble in coal-tar naphtha and low-boiling petroleum. It melts at 210°C ., and when heated a little above this point sublimes as long rod-shaped needles. Cold concentrated sulphuric acid dissolves it, forming a yellow solution which is devoid of fluorescence. It is not decomposed by boiling with alcoholic potash.