XLIV.—*On the Action of Organo Zinc Compounds upon Nitriles and their Analogues.*

By E. FRANKLAND, F.R.S.

IN the year 1857 (*Proc. Roy. Soc.*, **8**, 502), I communicated to the Royal Society the results of an investigation into the action of zinc ethyl upon ammonia and its analogues, showing that an atom of hydrogen (in direct combination with nitrogen) was removed from each molecule of the nitrogenous body, and became replaced by a zinc bond. Thus from ammonia and zinc ethyl, zinc amine was found $\text{Zn}(\text{NH}_2)_2$.

The reaction was followed out with aniline, diethylamine, oxamide, and acetamide, and its general nature is expressed by the following equation:—

In this equation X and Y may be either hydrogen or monad positive radicals. It will be observed that in all the substances operated upon there was at least one atom of hydrogen directly combined with nitrogen, and that this hydrogen was the point of attack for the zinc ethyl. I promised, however, to extend the reaction to nitrile bases, and I propose now in conjunction with some of my pupils to redeem this promise by investigating the action of zinc ethyl and its analogues upon such nitrogenous bodies as do not contain hydrogen in this form of combination. The following examples are a first instalment of the work:—

1. *Action of Zinc Ethyl on Azobenzene.*

By E. FRANKLAND, F.R.S., and D. A. LOUIS, Esq.

When azobenzene is added to an ethereal solution of zinc ethyl, and the mixture is warmed to the boiling point of the ether, a reaction commences, accompanied by evolution of a large volume of gas. If an ethereal solution of the proper concentration has been employed, the action continues without further heating. As soon as it ceases, a fresh quantity of azobenzene must be added, heating as before, in order to start the reaction. This process is repeated until the reaction becomes sluggish, care being taken to employ an excess of zinc ethyl. A too sudden addition of azobenzene, or a too great concentration of the solution of zinc ethyl is to be avoided, since under these circumstances the reaction is apt to take place with explosive violence. Finally, the product is heated on the water-bath, until all the ether has been driven off, and no further gas is evolved.

In our experiments, the resulting substance was an amber-coloured jelly, which, when cold, was almost solid. It was decomposed by the addition of water, a large volume of gas being evolved. At the same time, a reddish-brown oil separated out among the zincic hydrate. On treating a portion with excess of hydrochloric acid, the oil went into solution along with the zincic hydrate. On the other hand, it was found that an excess of caustic soda dissolved the zincic hydrate, leaving the oil floating on the surface. The entire quantity was therefore treated in this way, and the oil was separated from the aqueous solution, which was further shaken with ether, to extract an additional quantity of the oily body. The oil was a base, and formed crystallisable salts. The addition of dilute sulphuric acid to an alcoholic solution of an excess of the oil produced a white crystalline precipitate, which dissolved in hot alcohol, and crystallised, to all appearance pure, in white shining leaflets. Two sulphuric acid determinations yielded the following results:—

I. 0.1284 gram gave 0.1043 gram baric sulphate.

II. 0.2718 gram gave 0.2230 gram baric sulphate.

	Calculated for aniline sulphate, $\text{SO}_2(\text{NPhH}_3\text{O})_2$. In 100 parts.	Found.	
		I.	II.
S	11.26	11.15	11.26

As these numbers seemed to point to aniline, the base was distilled. The entire liquid, with the exception of a small portion boiling above the range of the thermometer, came over between 180° and 190° . After fractioning two or three times, the greater portion distilled between 183.5° and 184.5° , the boiling point of aniline. This portion was almost absolutely colourless, and gave on analysis the following results:—

0.4733 gram gave 1.3423 gram carbonic anhydride, and 0.3321 gram water.

These numbers lead to the formula NPhH_2 :—

	Calculated.		Found.
C_6	72	77.40	77.35
H_7	7	7.54	7.79
N	14	15.06	(14.86)
	93	100.00	100.00

The platinum salt was also prepared and analysed: 0.233 gram of the double salt contained 0.0756 gram platinum.

	Calculated for $\text{PtCl}_4 \cdot 2\text{NPhH}_2\text{Cl}$. In 100 parts.		Found.
Pt	3.29		3.24

The aniline was further identified by the purple coloration with chloride of lime, and by the isonitrile test.

It has been stated that a large volume of gas is evolved during this reaction, mixed, of course, with the vapour of ether. In order to procure this gas free from ether vapour, an experiment was performed in which azobenzene was added to pure zinc ethyl. Careful cooling was necessary in order to moderate the violence of the reaction. The gas was collected and submitted to eudiometric analysis, when the following results were obtained:—

	Tension (dry).	Temperature.
Original gas	174.2 mm.	18° C.
After action of SO ₃	45.2 „	„
Vol. of residual gas taken for combustion.....	18.9 „	„
After addition of O	117.0 „	„
After explosion	71.0 „	„
After absorption of CO ₂	32.8 „	„

These numbers show that 18.9 vols. of the gas taken for combustion consumed 65.3 vols. of oxygen, and generated 38.2 vols. of carbonic anhydride, numbers which correspond with the following proportions:—

Vol. of comb. gas.	O consumed.	CO ₂ generated.
1 :	3.46 :	2.02

The gas left after the action of SO₃ is therefore ethylic hydride, and the original gas consists of—

C ₂ H ₄	25.95
C ₂ H ₆	74.05
	<hr/> 100.00

The formation of aniline might be explained in the following manner:—In the first place the zinc ethyl severs the nitrogen-atoms of the azobenzene molecule, forming 2 mols. of dizincmonethyl aniline:—

The dizincmonethyl aniline is then decomposed by water:—

If this explanation is correct, the gas which is evolved during the reaction must consist of equal volumes of ethylic hydride and ethylene, and each molecule of azobenzene must yield 2 mols. of aniline. The gaseous product of the reaction, however, has been shown to consist of 3 vols. of ethylene to 1 vol. of ethylic hydride, and it is therefore

probable that two-thirds of the base is formed by the following consecutive reactions :—

In a quantitative experiment 80 grams of azobenzene yielded 70 grams of aniline. Allowing for unavoidable loss, and taking into account the simultaneous formation of the substance of high boiling point already referred to, this result may be regarded as a satisfactory approximation. It shows clearly that more than half the azobenzene is converted into aniline. In all reactions as yet known in which aniline is formed from azobenzene, only half the azobenzene goes to form aniline. With some substituted azobenzenes the formation of 2 mols. of substituted anilines from each molecule of the substituted azobenzene may be accomplished by means of reducing agents, as, for example, in the case of the azo-colouring matters. The zinc ethyl reaction extends this total reduction to azobenzene itself.

The substance boiling above the range of the thermometer, the yield of which was about one-twentieth of the aniline, was redistilled under reduced pressure. It came over at about 260° under 160 millimeters' pressure of mercury. The distillate formed a clear yellow oil, which when cold was viscid, but did not solidify even in a freezing mixture. It dissolved in hydrochloric acid, but the solution turned rapidly dark-red, and when evaporated did not crystallise. When platinic chloride was added to the hydrochloric acid solution, metallic platinum was precipitated.

The smallness of the quantity at our disposal and the difficulties in the way of purifying this body caused us to abandon its investigation.

2. *On the Action of Zinc Ethyl upon Benzonitrile.*

By E. FRANKLAND, F.R.S., and JOHN CASTELL EVANS, Esq.

About equal parts by volume of zinc ethyl and benzonitrile were heated together in a sealed tube for some hours to 150°. On cooling the contents of the tube had solidified to a brownish mass. This was treated first with alcohol, in order to decompose the excess of zinc ethyl, and afterwards with hydrochloric acid, to remove the zincic hydrate. The substance which remained consisted of white needles, sparingly soluble in alcohol, but dissolving readily in carbonic disulphide. From hot saturated solutions, it was deposited in white ramiform needles fusing at 229°. These characteristics pointed to cya-phenine ($\text{C}_{21}\text{H}_{15}\text{N}_3$)—a substance first obtained by Cloëz (*Annalen*,

115, 27) by heating benzoyle chloride with potassic cyanate. Subsequently Engler (*Annalen*, **133**, 146) obtained the same compound by heating benzonitrile bromide, either alone or with lime. A. W. Hofmann (*Ber.*, **1**, 194) prepared it by the action of sodium on benzonitrile; E. Schmidt (*J. pr. Chem.* [2], **5**, 35), described the formation of traces in the action of carbonic oxydichloride on benzamide; whilst Pinner and Klein (*Ber.*, **11**, 764) discovered a method of obtaining it in large quantities by polymerising benzonitrile with fuming sulphuric acid.

The fusing point of cyaphenine is given by Cloëz at 224° , and by Pinner and Klein at 231° . Cyaphenine is, according to the above formula, a trimolecular benzonitrile, and is an aromatic analogue of the base cyanethine, first described by one of us in conjunction with Kolbe (*Chem. Soc. J.*, **1**, 60).

An experiment was then made to ascertain whether the reaction would take place under ordinary pressure. 60 grams of benzonitrile with an equal volume of zinc ethyl were heated in a flask fitted with a reversed condenser for some hours to the boiling point of the mixture. At first no change was apparent, but gradually the liquid assumed a reddish-brown colour; and, after the lapse of about four hours, a reaction commenced, accompanied by an evolution of gas. At the same time the contents of the flask became pasty. As soon as the gas ceased to be evolved an ordinary condenser was substituted for the reversed condenser, and the excess of zinc ethyl was distilled off. The product of the reaction was treated with alcohol and hydrochloric acid as above described, and in this way a large yield of cyaphenine was obtained. It was noticed that in decomposing the mass with alcohol a strong ammoniacal odour was evolved.

The cyaphenine was crystallised from hot carbonic disulphide, and the crystals were washed on the filter with cold alcohol, in which they are almost insoluble. In this way the substance was obtained perfectly pure and colourless after two crystallisations. Analysis yielded the following results:—

I. 0.3730 gram gave 1.1117 gram carbonic anhydride, and 0.1645 gram water.

II. 0.2278 gram gave 0.1152 gram ammoniac chloride.

	Calculated for $(C_7H_5N)_3$.		Found.
C.....	84	81.55	81.26
H.....	5	4.85	4.90
N.....	14	13.60	13.23
	103	100.00	99.39

Cyaphenine may, as has been stated by former investigators, be boiled with caustic potash or hydrochloric acid without undergoing

change; but by heating it with concentrated hydrochloric acid in a sealed tube to 250° we have succeeded in converting it entirely into benzoic acid and ammonia.

The liquid obtained by treating the product of the zinc ethyl reaction (after decomposition by alcohol) with hydrochloric acid in order to remove the zincic hydrate, deposited on standing faintly greenish six-sided plates. The colour was removed by a single recrystallisation from very dilute alcohol. This substance proved to be the hydrochlorate of a base. It yielded on analysis the following results:—

I. 0.1869 gram gave 0.4722 gram carbonic anhydride and 0.1192 gram water.

II. 0.1112 gram gave 15.136 c.c. (calibrated volume) of dry nitrogen at 20° under 477 mm. pressure corresponding to 0.01112 gram.

III. 0.3748 gram gave 0.1962 gram argentic chloride.

These results lead to the formula $C_{16}H_{19}N_2Cl$:—

	Calculated.		Found.
C_{16}	192	69.95	69.89
H_{19}	19	6.92	7.30
N_2	28	10.20	10.00
Cl	35.5	12.93	12.95
	274.5	100.00	100.14

Another determination of carbon and nitrogen *in vacuo* gave C 70.02 and N 10.06 per cent.

The hydrochlorate dissolves readily in alcohol, but is very sparingly soluble in water, even at 100° . It fuses at 257° , and when heated much above its fusing point gives off an odour of benzonitrile. It yields with platinic chloride a very badly characterised platinum salt, which was not analysed.

The base separates out as a colourless oil on the addition of caustic alkali to the solution of the hydrochlorate.

We must reserve the further investigation of this compound until we have been able to obtain it in larger quantities.

The gas given off during the action of zinc ethyl on benzonitrile was collected and analysed; two experiments gave the following results:—

	I.	II.
Pressure of original gas 0° (dry) ..	58.3 mm.	44.2 mm.
„ after action of SO_3	28.4 „	22.7 „
„ „ addition of oxygen ..	175.9 „	197.2 „
„ „ explosion	105.3 „	139.9 „
„ „ absorption of CO_2 ...	48.7 „	95.1 „

One volume of the combustible gas left after action of SO :—

	I.	II.	Mean.
Consumed	3.47	3.49	3.48 vols. of O.
Generated	1.99	1.97	1.98 vols. of CO ₂ .

1 vol. of ethylic hydride consumes 3.5 vols. of oxygen, and generates 2 vols. of carbonic anhydride. The gas therefore consists of an olefine (C_nH_{2n}) and ethylic hydride in the following percentage proportions :—

	I.	II.	Mean.
C _n H _{2n}	51.28	48.64	49.96
C ₂ H ₆	48.72	51.36	50.04
	100.00	100.00	100.00

No determination of the molecular composition of C_nH_{2n} was made, but there can be no doubt that its molecular formula is C₂H₄, and that the mixture of equal volumes of ethylene and ethylic hydride is produced by the very usual transformation of ethyl into equal volumes of these gases.

3. Action of Zinc Ethyl on Phenylacetonitrile.*

By E. FRANKLAND, F.R.S., and HARRY K. TOMPKINS, Esq.

The phenylacetonitrile employed in the following experiments was prepared by digesting benzylic chloride with a solution of crude potassic cyanide in dilute alcohol. The benzylic chloride was obtained by fractional distillation from a commercial product, and came over between 172—180°. The preparation of phenylacetonitrile has been frequently described in detail (Cannizzaro, *Annalen*, **96**, 246; Radziszewski, *Ber.*, **3**, 198); we may, however, record an observation which seems not to have been made before. In one experiment on a large scale, in which 2,000 grams of benzylic chloride with an equal weight of potassic cyanide were employed, and the digestion was continued for about a week, we obtained, in addition to some unattacked benzylic chloride and a large yield of phenylacetonitrile boiling between 200—230°, a considerable quantity of a substance distilling with decomposition above 300°. The distillation was therefore interrupted, and the retort allowed to cool, when the contents partially solidified to a mass

* In studying the action of zinc ethyl upon nitriles and cyanides, the following typical examples of these two classes of compounds have been selected :—Nitriles—acetonitrile (fatty), benzonitrile (aromatic), phenylacetonitrile (fatty aromatic). Cyanide—phenylic cyanide. Cyanide with acid radical—benzoyle cyanide. The results obtained with benzonitrile have already been communicated to the Society; in the case of acetonitrile the work was unavoidably interrupted, but I have again taken it up in conjunction with Mr. Tompkins. With benzoyle cyanide Mr. D. A. Louis has obtained interesting results which are almost ready for publication.—E. F.

of lamellar crystals. These, after pressing from the adhering oily matters, were purified by crystallisation from hot alcohol. The substance was thus obtained in large colourless tabular crystals, sometimes more than an inch square, fusing at 92° . From *dilute* alcoholic solutions, the substance was deposited in needles. Analysis yielded results agreeing with the formula of tribenzylamine, to which substance the characteristics above described also pointed (see Limpricht, *Annalen*, **144**, 307). The formation of tribenzylamine by the action of an excess of benzylic chloride on the ammonia produced by the saponification of the potassic cyanide, needs no further comment.

We were unable to obtain phenylacetoneitrile in a state of perfect purity. The fraction boiling between $200\text{--}230^{\circ}$ was distilled ten times and collected in fractions of from five to five degrees, but the thermometer showed no tendency to remain stationary at any point. The phenylacetoneitrile was contaminated with some substance containing oxygen, as was shown by its giving off water every time it was distilled, however carefully it might have been dried.

An attempt was made to prepare pure phenylacetoneitrile by distilling ammoniac phenylacetate with phosphoric anhydride, but nothing was obtained except an oil boiling above the range of the thermometer. The boiling point of phenylacetoneitrile is given by Radziszewski at 229° .

We therefore employed in the following experiments the product boiling between $200\text{--}230^{\circ}$; but by saponifying a portion of it and obtaining a large yield of phenylacetic acid, we first satisfied ourselves that it consisted for the most part of the product sought.

Thirty grams of phenylacetoneitrile with an equal weight of zinc ethyl, were introduced into a flask fitted with a wide tube intended to act as an inverted condenser. The reaction began spontaneously: the temperature of the mixture rose and gas was evolved. When the reaction became too violent, it was checked by immersing the flask in cold water. Care must be taken not to use too large quantities of the substances, otherwise the reaction is apt to become unmanageable. Towards the close, the mixture is heated in an oil-bath, the temperature of which is not allowed to exceed 130° . The operation must be carefully watched, as the mixture becomes viscid and is apt to froth. When gas ceases to be evolved, the flask is allowed to cool, and the product is decomposed with alcohol, in which process gas is evolved in great quantity. When the decomposition is complete, the contents of the flask are boiled with excess of alcohol and filtered hot. The residue is extracted a second time with hot alcohol, after which nothing but white oxide of zinc is left on the filter. The united filtrates deposit, on standing, a small quantity of a crystalline substance, the separation of which requires some days for its completion.

The crystals obtained from a number of such operations were united and recrystallised from hot alcohol. In this way two distinct substances were isolated from the crystalline product: the first crystallising in tufts of silky needles fusing at 170—171°; the second, which was obtained on further evaporation of the mother-liquor from the needles, separating in well-formed crystals, apparently rhombohedra, fusing at 150°. The rhombohedra were sometimes mixed with hexagonal plates which had the same fusing point, and, in all probability, belonged to the same crystalline system.

The needles yielded the following results on analysis:—

I. 0.1755 gram gave 0.5287 gram carbonic anhydride and 0.0974 gram water.

II. 0.0701 gram gave 6.263 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.007836 gram nitrogen.

III. 0.1342 gram gave 12.1 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.01514 gram nitrogen.

	Calculated.		Found.			
			I.	II.	III.	Mean.
C ₈	96	82.05	82.16	—	—	82.16
H ₇	7	5.98	6.16	—	—	6.16
N	14	11.97	—	11.17	11.27	11.22
	117	100.00	—	—	—	99.54

The substance employed in II and III had a yellowish tinge, and was not so pure as that used in I. The smallness of the quantity at our disposal precluded the possibility of a further purification.

The substance has thus the same empirical formula as phenylacetone nitrile, from which, however, it differs in all its physical properties. The formula must probably be tripled in accordance with the analogy of the trimolecular nitriles, cyanmethine and cyanethine. The molecular formula of cyaphenine rests entirely on a similar analogy. The present compound would be the fourth known member of this class, and the name to be assigned to it would be *cyanbenzine*.

It would probably be possible to determine the molecular weight of cyanbenzine on surer grounds than those of analogy, inasmuch as it appears to form salts. When treated with warm dilute hydrochloric acid, it forms a gummy mass—probably a hydrochlorate. The small quantity of substance at our disposal, the yield not being more than one per cent. of the phenylacetone nitrile employed, rendered it impossible for us to extend our investigations in the direction of the salts of cyanbenzine.

Cyanbenzine is sparingly soluble in hot, almost insoluble in cold alcohol. Glacial acetic acid, benzene, and carbonic disulphide dissolve it readily.

This polymerising action of zinc ethyl was also observed in the case of benzonitrile, and has been described in a former communication.

The following results were obtained in the analysis of the rhombohedral crystals :—

I. 0.2816 gram gave 0.8397 gram carbonic anhydride and 0.1473 gram water.

II. 0.2206 gram gave 0.6590 gram carbonic anhydride and 0.1166 gram water.

III. 0.1073 gram gave 7.635 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.009551 gram nitrogen.

IV. 0.0783 gram gave 5.598 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.007004 gram nitrogen.

These data agree with the formula $C_{32}H_{27}N_3O$, as is seen from the following comparison :—

Calculated.				Found.				
				I.	II.	III.	IV.	Mean.
C_{32}		384	81.88	81.32	81.47	—	—	81.39
H_{27}		27	5.75	5.81	5.87	—	—	5.84
N_3		42	8.96	—	—	8.90	8.94	8.92
O		16	3.41	—	—	—	—	(3.85)
469				100.00	—	—	—	100.00

The formation of the substance, $C_{32}H_{27}N_3O$, for which we propose the name *benzacin*, may be explained by the equation—

Benzacin is a neutral body. We are not in a position to offer any suggestions as to its constitution, and till some method has been discovered by which it can be obtained in greater quantity, a study of its reactions must remain a practical impossibility.

The filtrate from the first crop of mixed crystals, containing all the other soluble matters from the zinc ethyl reaction, was next examined. On distilling off the alcohol, a large quantity of a neutral oil of high boiling point was left, which when cold was viscid, but did not show any tendency to solidify, even after standing for some days in an ice safe. On attempting to distil this oil, it first gave off a small quantity of unchanged phenylacetoneitrile; after which the temperature rose suddenly, and the residue distilled with decomposition above the range of the thermometer. An attempt to rectify this liquid *in vacuo* failed, owing to the constant evolution of salts of ammonia, which choked the condenser and rendered the operation dangerous.

As the oil contained nitrogen, we thought it possible that we might be dealing with a nitrile, and boiled it with alcoholic potash, in the hope of obtaining the corresponding acid; but the oil was recovered from the operation apparently unchanged. Not being able to find any method of purifying this substance, or of preparing any well characterised derivative from it, we abandoned its investigation.