CXIV.—*A New Series of Hydrazines.*

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SINCE the discovery of the primary and secondary hydrazines, they have become of such importance as synthetic agents, and the results to which their employment has led have been of such magnitude that other substituted derivatives of hydrazine have been but little studied.

Theoretically, hydrazine can yield five series of substituted derivatives, the primary, secondary, symmetrical and unsymmetrical, tertiary, and the quaternary.

Actually only three of these series are known, the primary, the secondary symmetrical, usually known as the hydrazo-compounds, and the secondary unsymmetrical. No simple method of obtaining members of the other series has hitherto been described, and in spite of many efforts, only isolated mixed derivatives have been produced.

The present paper is the introduction to an investigation of the tertiary and quaternary hydrazines which the authors have undertaken, these bodies being of great interest, not only as a new series of well-defined compounds, but also on account of their probable bearing on the theory of the stereo-isomerism of nitrogen. The quaternary hydrazines alone will be dealt with in this paper.

These compounds can be obtained from the secondary amines by a simple general reaction, which renders it possible to prepare any tetra-derivative of hydrazine containing either similar or dissimilar radicles, the constitution of the compound following with certainty from its mode of formation.

The secondary amine is treated with sodium or sodium ethoxide, whereby the hydrogen atom is displaced by sodium.

The equivalent quantity of iodine is then allowed to act on this sodium compound when the sodium atoms are withdrawn, and the two amine residues unite to form the quaternary hydrazine.

The compounds which have so far been carefully examined are those containing simple aromatic residues. They are solid, stable substances, easily obtained in large, measurable crystals, and behaving exactly as would be expected from their constitution. They are not easily oxidised, and scarcely, if at all, basic, but appear to yield double hydrazonium compounds, and bases analogous to those formed from the tertiary amines. The percentage composition of these hydrazines and their molecular weights, determined by Raoult's method, agree well with the theoretical, and the yields are very good, being in some cases nearly quantitative.

Tetraphenylhydrazine, $(C_6H_5)_2N \cdot N(C_6H_5)_2$.

In the preparation of this compound, diphenylamine (melting point 54°) is dissolved in about 10 times its weight of dry ether, and twice the theoretical amount of sodium ethoxide, shaken up with ether or dissolved in the least possible quantity of alcohol, is added; the clear solution of the amine becomes turbid, and a white, bulky precipitate of the sodium compound is thrown down.

To this is added, after a lapse of 12 hours, a quantity of iodine, dissolved in ether, and equivalent to the amount of sodium used; sodium iodide is precipitated, the hydrazine remaining dissolved in the ether.

After having been left for a few hours, the ethereal solution is poured off, washed with water and very dilute sodium carbonate solution, and dried over fused calcium chloride. On distilling off the bulk of the ether, and, if necessary, adding a little hot alcohol, the hydrazine separates as a brownish, crystalline powder. It may be purified by repeated recrystallisation from chloroform and alcohol. As the hydrazine is very easily soluble in chloroform, the operation is best carried out as follows. The compound having been dissolved in a small quantity of warm chloroform, about five times its bulk of hot alcohol is added to the solution, and the whole allowed to cool gradually; the hydrazine then crystallises out in long ortho-

rhombic prisms of a faint brown or flesh colour. The slight coloration is apparently due to some very small admixture of impurity, which cannot be got rid of by recrystallisation, but varies somewhat with the nature of the solvent.

Tetraphenylhydrazine is easily soluble in benzene, chloroform, and acetone, slightly soluble in hot alcohol, and insoluble in water. It melts at 147° , with slight decomposition. It dissolves in hot, glacial acetic acid, giving a violet solution, from which no salt crystallises out, and the compound, on dilution, seems to be reprecipitated in an impure form. It dissolves easily in cold, concentrated, sulphuric acid, giving a deep purple solution, which, on exposure to the air, or on heating, changes to a deep indigo blue. Fehling's solution, boiled with the finely powdered hydrazine, shows no sign of reduction.

The results of the analyses agree well with the formula, as does also the molecular weight found.

0.3082 gave 0.9702 CO_2 , and 0.1641 H_2O . $\text{C} = 85.85$; $\text{H} = 5.93$.

0.3680 „ 26.4 c.c. moist nitrogen at 20° , and 768.5 mm. $\text{N} = 8.29$.

$(\text{C}_6\text{H}_5)_4\text{N}_2$ requires $\text{C} = 85.71$; $\text{H} = 5.95$; $\text{N} = 8.33$ per cent.

The molecular weight was determined by Raoult's method, using benzene as a solvent.

0.6718 gram of the substance dissolved in 21.9 grams of benzene, lowered the freezing point by 0.46° .

0.6718 gram of the substance dissolved in 33.9 grams of benzene, lowered the freezing point by 0.3° .

These give the molecular weight as 327 and 324 respectively, whilst the formula $(\text{C}_6\text{H}_5)_4\text{N}_2$ requires 336.

Measurements of Crystals.

Dr. Lapworth, who very kindly undertook the examination of the crystals, has communicated to us the following details.

Crystalline System : Orthorhombic.

$a : b : c = 0.6301 : 1 : 0.9325$.

FIG. 1.

Forms observed :

c	$\{001\}$
k	$\{101\}$
m	$\{011\}$
v	$\{031\}$

The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$mk = 011 : 101$	24	$114^{\circ} 1' - 114^{\circ} 18'$	$114^{\circ} 11'$	—
$mc = 011 : 001$	20	$42 50 - 43 10$	$43 0$	—
$ck = 001 : 101$	14	$55 44 - 56 5$	$55 55$	$55^{\circ} 56'$
$kk = 101 : 10\bar{1}$	14	$67 58 - 68 20$	$68 10$	$68 8$
$mm = 011 : 01\bar{1}$	10	$93 50 - 94 4$	$93 58$	$94 0$
$mp = 011 : 031$	14	$27 14 - 27 25$	$27 20$	$27 20$
$pp = 031 : 03\bar{1}$	6	$39 15 - 39 36$	$39 25$	$39 20$
$kp = 101 : 031$	6	$79 1 - 79 24$	$79 10$	$79 8$
$mm = 011 : 01\bar{1}$	20	$85 46 - 85 15$	$86 0$	$86 0$

Tetraphenylhydrazine crystallises in prisms, the faces of which, as a rule, give excellent images. The predominant forms are $m\{011\}$ and $k\{101\}$, the forms $c\{001\}$ and $p\{031\}$ are usually also present, but less developed.

The acute optic axial bisectrix emerges through $c\{001\}$, the axial plane is $a\{100\}$. The axial angle is very small, so that a hasty examination of the interference figure, with a 1/10 in. immersion objective gives the impression that the crystal is uniaxial. The double refraction is strong and negative, and the dispersion is fairly strong. The crystals show no obvious cleavage.

Tetraparatolyldiazine, $(C_6H_4 \cdot CH_3)_2N \cdot N(C_6H_4 \cdot CH_3)_2$.

In the preparation of this substance, paratolylamine (melting point 79°) is dissolved in 10 times its weight of dry ether, twice the theoretical amount of sodium ethoxide suspended in ether is added, and the mixture left for about 12 hours. A quantity of iodine equivalent to the sodium used is added, and after a few hours the ethereal solution of the hydrazine is treated as in the preparation of the phenyl compound. On distilling off most of the ether, and allowing the residue to cool slowly, the tetraparatolyldiazine crystallises out in nearly theoretical amount; it may be purified by recrystallisation from a mixture of chloroform and alcohol, and finally from acetone; from the latter solvent it separates in very fine, monoclinic tablets. The crystals are soft and brittle, very much like resin in behaviour, and of a pale-yellow colour. It melts at 138° , decomposing slightly, the melting point appearing to vary somewhat with the rapidity of heating. It is very readily soluble in benzene, chloroform and acetone, slightly in hot alcohol, and insoluble in water. Cold, concentrated sulphuric acid readily dissolves the hydrazine, giving a brilliant azure blue solution, which only slowly alters on exposure to air. The addition of a little nitric acid changes this to green, and finally to brown. No reduction takes place when the finely powdered hydrazine is boiled with Fehling's solution.

1094 CHATTAWAY AND INGLE: NEW SERIES OF HYDRAZINES.

The numbers obtained for its composition and molecular weight agree closely with the theoretical ones, whilst the constitution is established by its mode of formation.

0.2155 gave 0.6651 CO₂ and 0.1344 H₂O. C = 85.76; H = 7.07.

0.3317 „ 21.6 c.c. moist nitrogen at 20° and 750.6 mm. N = 7.34.

(C₆H₄·CH₃)₄N₂ requires C = 85.71; H = 7.14; N = 7.14 per cent.

The molecular weight was determined by Raoult's method, using benzene as a solvent.

0.5212 gram of the hydrazine dissolved in 23.96 grams of benzene, lowered the freezing point by 0.265°.

This gives 402 as the molecular weight, whilst the formula (C₆H₄·CH₃)₄N₂ requires 392.

Measurements of Crystals.

Dr. Lapworth has furnished us with the following description of the crystals.

Crystalline system: Monoclinic.

$$a : b : c = 2.3217 : 1 : 2.6330.$$

$$\beta = 59^\circ 45'.$$

Forms observed:

<i>a</i>	{100}
<i>c</i>	{001}
<i>m</i>	{101}
<i>q</i>	{102}
<i>p</i>	{111}
<i>n</i>	{011}

FIG. 2.

Angle.	No. of observations.	Limits.		Mean.	Calculated.
<i>cn</i> = 001 : 011	16	66°	5'—66° 55'	66° 16'	—
<i>an</i> = 100 : 011	16	78	11—78 31	78 18	—
<i>cm</i> = 001 : 101	8	66	14—66 36	66 22	—
<i>nn</i> = 011 : 011	8	47	13—47 40	47 28	47° 28'
<i>ac</i> = 100 : 001	6	59	41—59 46	59 43	59 45
<i>am</i> = 100 : 101	6	53	22—53 57	53 40	53 53
<i>mq</i> = 101 : 102	3	31	50—32 5	31 59	31 56
<i>cq</i> = 001 : 102	3	34	15—34 31	34 20	34 26
<i>np</i> = 011 : 111	2	40	25—40 34	40 29	40 32
<i>np</i> = 011 : 111	6	26	8—26 24	26 13	26 13
<i>ap</i> = 100 : 111	6	74	58—75 39	75 24	75 29
<i>nq</i> = 011 : 102	4	69	3—71 3	70 22	70 37
<i>mn</i> = 101 : 011	2	80	31—80 39	80 35	80 42

Angle.	No. of observations.	Limits.			Mean.	Calculated.
$pq = 100 : 102$	3	68	50—69	13	69 3	68 51
$mn = 101 : 01\bar{1}$	6	99	12—99	35	99 25	99 18
$cp = 001 : \bar{1}11$	4	99	30—99	59	99 44	99 49
$pm = 111 : 101$	4	64	40—64	51	64 44	64 49
$pp = 111 : \bar{1}1\bar{1}$	2	50	12—50	24	50 18	50 21

Tetraparatolyldrazine crystallises in monoclinic prisms or plates of considerable size; they are of a faint yellow colour, and appear readily to undergo a process of re-solution, as the faces are invariably somewhat convex; in spite of this, however, they give very definite images, so that concordant measurements can be obtained.

The crystals are usually prismatic, having the appearance shown in Fig. 2, but some are plate-like, the form $a\{100\}$ being enormously developed.

The forms $n\{011\}$ and $g\{102\}$ are usually absent from the plates, the forms $a\{100\}$, $a\{001\}$, and $p\{111\}$ predominating, both in the prisms and the plates.

The optic axial plane is the plane of symmetry, the acute bisectrix emerging through $a\{100\}$. The axial angle is large; the double refraction is negative and strong; the dispersion is weak. The crystals show an imperfect cleavage parallel to a .

The authors are continuing this investigation, and later hope to communicate the results to the Society.

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