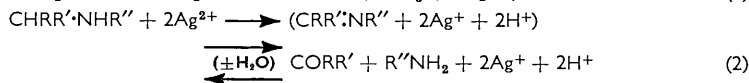
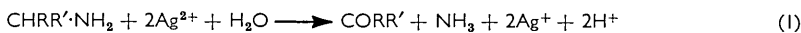
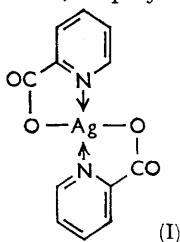


**913. Metal Ions and Complexes in Organic Reactions. Part V.<sup>1</sup>**  
*Oxidations of Primary and Secondary Amines with Argentic Picolinate*

By R. G. R. BACON and W. J. W. HANNA

Results are reported for oxidations of twenty-one primary or secondary alkyl- or arylalkyl-amines, at 0—70°, by a suspension of argentic picolinate in water or a polar organic solvent. Yields of aldehydes or ketones from most primary amines were 10—50%; in one case a cyanide was obtained. Yields of aldehydes or ketones from most secondary amines were 30—90%; in two cases the corresponding imines were obtained. By oxidation of unsymmetrical secondary amines of the type  $\text{ArCH}_2\text{NH}\cdot\text{CR}_3$ , prepared from arylalkyl halides, the latter were efficiently converted into aldehydes,  $\text{ArCHO}$ . Argentic picolinate was superior to mercuric acetate or argentic oxide in cases examined, and some other transition-metal oxidants were ineffective. Mechanistic aspects of the oxidations are discussed.

We previously reported<sup>2</sup> that various types of organic compound are oxidised by bivalent silver, employed in the form of argentic picolinate, and that some amines are particularly vulnerable to this reagent. We now describe preparations of aldehydes or ketones by this method from compounds which contain a primary or secondary amino-substituent on a saturated carbon atom; the presence of an  $\alpha$ -hydrogen atom is necessary. Imines are sometimes thus obtainable from secondary amines, and in other cases they are likely to be intermediates in the oxidations. Overall reactions may be formulated as in (1) and (2), for primary and secondary amines, respectively ( $\text{R}, \text{R}' = \text{H}$ , alkyl, or aryl;  $\text{R}'' = \text{alkyl}$  or arylalkyl):



The reagent, prepared<sup>3,4</sup> by oxidation of an argentous salt with aqueous persulphate in the presence of picolinic acid, is known from X-ray crystallography<sup>4</sup> to be a square-planar complex with the structure (I). It is insoluble in water and in all organic solvents examined. It decomposes to the argentous salt, moderately readily in water at temperatures above about 90°, and very rapidly in cold aqueous ammonia. At 20° it is slowly decomposed, with oxygen evolution, by 6N-sulphuric acid, while at 60° it is rapidly decomposed by the 12N-acid, with appearance of a transient red colour in the solution. Cold aqueous sodium hydroxide converts it into argentic oxide, which is reducible by oxalic acid, and the picolinate can thus be analysed, as in the case of other silver(II) complexes.<sup>5</sup>

Most of the amines examined were liquids or low-melting solids, and they were oxidised in water at 0—70°, with the oxidant present as a stirred suspension. The progress of the reaction is seen by the change in colour of the suspended solid from red to white, as reduction to the sparingly soluble argentous salt occurs. If the substance to be oxidised is a solid at the reaction temperature, or is insoluble in water, a polar organic solvent may be used as the medium; some examples are given in footnotes to Table 2. We have not extensively examined this variation in procedure, but it is evident that the choice of solvent influences the yield of product, and that in some cases, *e.g.*, with ethanol or dioxan, slow

<sup>1</sup> Part IV, R. G. R. Bacon and O. J. Stewart, preceding Paper.

<sup>2</sup> R. G. R. Bacon and W. J. W. Hanna, *Proc. Chem. Soc.*, 1959, 305.

<sup>3</sup> G. A. Barbieri, *Atti Accad. Lincei*, 1933, 17, 1078.

<sup>4</sup> E. G. Cox, W. Wardlaw, and K. C. Webster, *J.*, 1936, 775.

<sup>5</sup> W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, 1954.

oxidation of the solvent occurs. When petroleum or benzene was solvent, there was no oxidation of the amine in cases which we examined.

The vigorous reaction between argentic picolinate and cold aqueous ammonia produces nitrogen, theoretically according to the equation:



It was found, however, that a large excess of ammonia was required to obtain 1 mole of evolved gas per 6 equivalents of silver(II) and that 2.3 moles of ammonia were required to discharge the colour of 1 mole of the oxidant. Silver(I) generated in the oxidation will co-ordinate strongly with ammonia to give  $\text{Ag}(\text{NH}_3)_2^+$  ions, and the experimental results are explicable if the ammonia is thereby stabilised against reaction with argentic picolinate. Thus, only about 14% of the ammonia may be oxidised, and the reaction may be better represented by the equation:

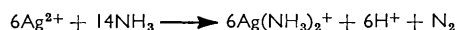


TABLE 1

Oxidation of primary amines in water (0.07M) with argentic picolinate (2 mol.)

Amine	Temp.	Time (hr.)	Product	Yield (%)
$\text{CHMe}_2 \cdot \text{NH}_2$	70°	3	$\text{COMe}_2$	16
$\text{Bu}^n \text{NH}_2$	"	1	$\text{Pr}^n \text{CHO}$	14
$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	"	1	$\text{CHMe}_2 \cdot \text{CHO}$	9
$\text{CHMeEt} \cdot \text{NH}_2$	20	12	$\text{COMeEt}$	26
"	70	2.5	"	27
$\text{CHEtBu}^n \cdot \text{CH}_2 \cdot \text{NH}_2$	"	1	$\text{CHEtBu}^n \cdot \text{CHO}$	1
$\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	"	2	$\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CN}^*$	10
Cyclohexylamine	75	2	Cyclohexanone	41
$\text{PhCH}_2 \cdot \text{NH}_2$	70	1	$\text{PhCHO}$	51

\* No aldehyde found; trace of aldehyde in reaction at 20°.

TABLE 2

Oxidation of secondary amines in water (0.07M) with argentic picolinate (2 mol.)

Amine	Temp.	Time (hr.)	Product	Yield (%)
$(\text{CHMe}_2)_2 \text{NH}$	70°	0.25	$\text{COMe}_2$	31
$\text{Bu}^n_2 \text{NH}$	"	0.25	$\text{Pr}^n \text{CHO}$	67
$(\text{CHMe}_2 \cdot \text{CH}_2)_2 \text{NH}$	"	0.25	$\text{CHMe}_2 \cdot \text{CHO}$	73
$(\text{CHMeEt})_2 \text{NH}$	"	0	$\text{COMeEt}$	45
"	20	2	"	52
"	70	0.1	"	62
$(\text{CHEtBu}^n \cdot \text{CH}_2)_2 \text{NH}$	"	0.25	$\text{CHEtBu}^n \cdot \text{CHO}$	9
$(\text{CMe}_3 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2)_2 \text{NH}$	"	0.1	Corresponding imine	78
Dicyclohexylamine	"	0.25	Cyclohexanone	61
$(\text{PhCH}_2)_2 \text{NH}$	20	2	$\text{PhCHO}$	71
"	70	0.25	"	76
2,5-Dimethylpyrrolidine	60	2.5	2,5-Dimethyl- $\Delta^1$ -pyrroline	28
$\text{PhCH}_2 \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \text{Bu}^t$	20	2	$\text{PhCHO}^*$	89
$\text{PhCH}_2 \cdot \text{NH} \cdot \text{CMe}_3$	"	3	"	64
$\text{PhCH}_2 \cdot \text{NH} \cdot \text{CPh}_3$	70	24	" †	15
$p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CMe}_3$	65	0.25	$p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$	81
$2\text{-(1-Br-C}_{10}\text{H}_8) \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \text{Bu}^t$	"	1	$1,2\text{-Br-C}_{10}\text{H}_8 \cdot \text{CHO}$	95

\* 93% in EtOH (20°, 3 hr.); 93% in Bu<sup>t</sup>OH (65°, 3 hr.); 80% in AcOH (20°, 24 hr.); 72% in dioxan (65°, 3 hr.). † 36% in EtOH (20°, 24 hr.).

Similar considerations are likely to be applicable when amines are oxidised. Practical results for primary and secondary amines are shown in Tables 1 and 2, respectively; 2 molar proportions of oxidant were used in the experiments, in accordance with equations (1) and (2). Yields of carbonyl compounds were poor from the lower-molecular-weight primary amines, negligible from the higher members, and moderate for cyclohexylamine and benzylamine. Corresponding secondary amines were more reactive, and yields were consistently much higher; within the series there was some correspondence to the pattern

shown by the primary amines. Two factors which may influence an oxidation are the ability of a particular amine to displace picolinic acid as a ligand from the square-planar silver(II) complex,<sup>6</sup> and the extent to which the amine is immobilised by complex-formation with  $\text{Ag}^+$  ions resulting from the oxidation. It may be significant, in the latter connection, that reported stability constants<sup>7</sup> of  $\text{Ag}^+$  complexes are lower for secondary aliphatic amines than for primary aliphatic amines ( $\log \beta_2 = 7-7.5$  for ammonia and primary aliphatic amines,  $5.5-6.5$  for secondary aliphatic amines,  $3-4.5$  for tertiary aliphatic and heterocyclic amines). Since, however, the reagent is usually wholly reduced, even when amines give low yields of carbonyl compounds, it is evident that it may be consumed in reactions (*e.g.*, oxidation of aldehydes) other than those shown in (1) and (2).

An abnormal result shown in Table I is the production of a small amount of the alkyl cyanide, together with polymer, in the oxidation of 3,5,5-trimethylhexylamine; this corresponds to the loss of four hydrogen atoms,  $\text{RCH}_2\cdot\text{NH}_2 \longrightarrow \text{RCN}$ . Such dehydrogenation is known to occur under conditions of heterogeneous catalysis in the gaseous phase.<sup>8</sup> Cyanides have also been reported,<sup>9</sup> in low yield, from oxidations of benzylamine and ethylamine with peroxomonosulphuric acid; they are occasionally formed<sup>10</sup> by hypobromite oxidation of amines in the Hofmann rearrangement; and they are obtainable,<sup>11</sup> sometimes in good yield, by oxidation of amines with iodine pentafluoride. Closer to our own conditions is the recently reported<sup>12</sup> copper(II)-catalysed radical reaction between aldehydes, ammonia, and oxygen, giving cyanides in good yield. In the case of 3,5,5-trimethylhexylamine, there are presumably favourable features in the derived imine,  $\text{RCH}:\text{NH}$ , or in the equivalent  $\text{RCHO}\cdot\text{NH}_2$  system, which lead to the further oxidation by silver(II).

One molecule of secondary amine should give rise to one molecule of the aldehyde or ketone and one of the primary amine [equation (2)], unless, as in two cases shown in Table 2, the intermediate imine is stable. In the case of the preparation of 2,5-dimethyl- $\Delta^1$ -pyrroline from the corresponding pyrrolidine, stability is due to the cyclic structure. Dehydrogenation of cyclic tertiary amines to imines with mercuric acetate is well known,<sup>13</sup> and this method has been applied to cyclic secondary amines.<sup>14</sup> The yield of the pyrroline by silver(II) oxidation was the same as that reported<sup>14</sup> for the mercuric oxidation. The other example of imine formation shown in Table 2 involves the same branched  $\text{C}_9$ -alkyl chain as the abnormal case in Table 1. The imine, which was isolated from the oxidation in high yield, was identical with the product obtained by condensation of the corresponding primary amine and aldehyde. It is known<sup>15</sup> that the stability of aldimines is greatly influenced by the nature of the attached alkyl groups and that chain-branching is a favourable factor. Open-chain imines are rare, however, as end-products of amine oxidation. Here they have been obtained<sup>16</sup> (including the imine referred to in Table 2) from oxidations of primary amines by the aqueous alkaline  $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$  reagent, and have been reported<sup>17</sup> in oxidations by *t*-butyl hydroperoxide.

If a secondary amine has an unsymmetrical structure, two carbonyl compounds may result from its oxidation, *e.g.*,  $\text{CH}_2\text{R}\cdot\text{NH}\cdot\text{CH}_2\text{R}'$  may give the aldehydes  $\text{RCHO}$  and  $\text{R}'\text{CHO}$ , but this is not the case if one of the alkyl substituents contains no  $\alpha$ -hydrogen,

<sup>6</sup> Cf. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, ch. 4.

<sup>7</sup> "Stability Constants," Parts I and II, The Chemical Society, London, 1957 and 1958.

<sup>8</sup> P. Sabatier and G. Gaudion, *Compt. rend.*, 1917, **165**, 224; A. Mailhe and F. de Godon, *ibid.*, p. 557; 1918, **166**, 215.

<sup>9</sup> E. Bamberger *et al.*, *Ber.*, 1901, **34**, 2262; 1902, **35**, 4293, 4299.

<sup>10</sup> E. S. Wallis and J. F. Lane, *Org. Reactions*, 1946, **3**, 267.

<sup>11</sup> T. E. Stevens, *J. Org. Chem.*, 1961, **26**, 2531.

<sup>12</sup> W. Brackman and P. J. Smit, *Rec. Trav. Chim.*, 1963, **82**, 757.

<sup>13</sup> N. J. Leonard *et al.*, *J. Amer. Chem. Soc.*, 1957, **79**, 5279, and earlier Papers.

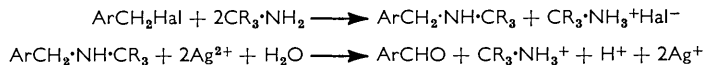
<sup>14</sup> R. Bonnett, V. M. Clark, A. Giddey, and Sir Alexander Todd, *J.*, 1959, 2087.

<sup>15</sup> R. Tiollais, *Bull. Soc. chim. France*, 1947, 708, 716, 959.

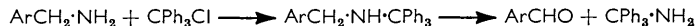
<sup>16</sup> D. Stewart and R. G. R. Bacon, unpublished results; cf. R. G. R. Bacon, *Chem. and Ind.*, 1962, 19.

<sup>17</sup> H. de la Mare, *J. Org. Chem.*, 1960, **25**, 2114.

*e.g.*,  $\text{CH}_2\text{R}\cdot\text{NH}\cdot\text{CR}'_3$  can give only  $\text{RCHO}$ . Secondary amines of the latter type, containing a *t*-alkyl group, can be prepared in high yield from the corresponding *t*-alkyl primary amine.<sup>18</sup> Accordingly, we have carried out preparations of aromatic aldehydes from arylalkyl halides in the following two stages, illustrated by the last group of examples in Table 2:

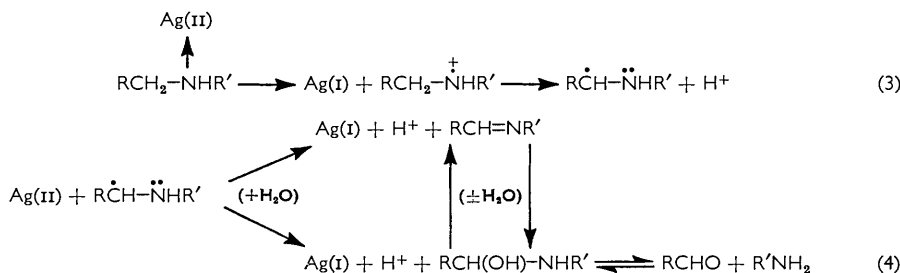


Secondary amines derived from *t*-butylamine or 2-amino-2,4,4-trimethylpentane gave excellent yields of aldehydes in cases examined; this is an alternative to the Sommelet process<sup>19</sup> for converting halides into aldehydes. The following variation, involving a triphenylmethyl derivative, gave inferior results in the example studied:



A few other multivalent-metal oxidants proved to be ineffective, or inferior to argentic picolinate, when used in comparative experiments. Mercuric acetate gave low yields of ketone or aldehyde from di-*s*-butylamine, dibenzylamine, or 2-benzylamino-2,4,4-trimethylpentane. The last-named amine, which reacted almost quantitatively with argentic picolinate (Table 2) gave, under comparable conditions, a 34% yield with argentic oxide,  $\text{Ag}_2\text{O}$ ,<sup>20</sup> and was unaffected by argentous oxide, the complex  $\text{Ag}(\text{NH}_3)_2^+$ , ferric chloride, potassium ferricyanide, cupric acetate, or ceric ammonium sulphate.

Oxidations by argentic picolinate presumably occur at the solid-solvent interface by single-electron transfer processes, in consequence of displacement of a picolinic acid ligand by a molecule of a primary or secondary amine. There is evidence<sup>21</sup> that homolytic oxidations of aliphatic amines involve a radical formed by loss of hydrogen from the  $\alpha$ -carbon atom, as suggested in equation (3); the prior production of radical-cations has been postulated by Horner<sup>22</sup> and others. There is recent physical evidence<sup>23</sup> concerning the structure of radical intermediates in oxidations of amines by a peroxide,<sup>17</sup> but the presence of oxygen in these radicals makes the situation somewhat different from that under consideration. The second step in amine oxidations by silver(II) can plausibly be represented [equation (4)] as an oxidation of the radical by another molecule of argentic picolinate, leading to an imine directly or through a hydroxy-aldehyde. It was considered unlikely, in recent discussions<sup>24</sup> of similar effects in oxidations of alkyl or alkoxy-radicals by cupric ions, that a discrete intermediate carbonium ion is formed.



<sup>18</sup> N. Bortnick, L. S. Luskin, M. D. Hurtwitz, W. E. Craig, L. J. Exner, and J. Mirza, *J. Amer. Chem. Soc.*, 1956, **78**, 4039; "Tertiary-alkyl Primary Amines," Rohm and Haas Co., Philadelphia, 1955.

<sup>19</sup> S. J. Angyal, *Org. Reactions*, 1954, **8**, 197.

<sup>20</sup> J. H. de Boer and J. van Ormondt, U.S.P. 2,478,166 (1949); G.-M. Schwab and G. Hartmann, *Z. anorg. Chem.*, 1955, **281**, 183; V. Scatturin, P. L. Bellon, and R. Zannetti, *J. Inorg. Nuclear Chem.*, 1958, **8**, 462.

<sup>21</sup> W. H. Urry and O. O. Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322.

<sup>22</sup> L. Horner and W. Kirmse, *Annalen*, 1955, **597**, 48.

<sup>23</sup> G. M. Coppinger and J. D. Swalen, *J. Amer. Chem. Soc.*, 1961, **83**, 4900.

<sup>24</sup> H. de la Mare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 1963, **85**, 1437; J. K. Kochi, *ibid.*, p. 1958.

Alternatively, the imine results from disproportionation of amine radicals:



### EXPERIMENTAL

*Argentio Picolinate.* Picolinic acid (0.25 mole) was dissolved in water (~2 l.) and treated with a solution of silver nitrate (0.125 mole), and a saturated solution of sodium carbonate was added with stirring until the precipitated argentous picolinate redissolved. Stirring was continued while a solution of sodium or potassium persulphate (0.0625 mole) was added. The argentio picolinate, which soon appeared as a red precipitate, was filtered off, washed, dried at room temperature, and stored in the dark. Yields of ~90% were obtained, and the oxidising capacity of the reagent, determined<sup>5</sup> as follows, was 98% of the theoretical value. Samples (0.5—1.0 g.) were converted into argentio oxide by 2N-sodium hydroxide (20 ml.); the precipitate was filtered off and reduced to argentous oxalate by treatment on the filter paper with 0.1N-oxalic acid (50 ml.) previously warmed to 60°. The filtrate, containing excess of oxalic acid, was combined with 2N-sulphuric acid washings of the argentous oxalate, and the total unchanged oxalic acid was determined by permanganate titration. To determine the silver content of the reagent, or of mixtures of argentous and argentio picolinate, samples were decomposed by excess of 2N-aqueous ammonia, and the resulting solution was acidified with 2N-nitric acid and titrated with thiocyanate solution.

Argentio picolinate was practically unchanged in oxidising power after being stirred for three days in water at 20°, but was largely decomposed after 3 hr. at 90°, and completely in a few minutes at the boiling point. Its colour was discharged in ethanol during three days at 20°, or in 5 min. at the boiling point, but not, during several days, in boiling t-butyl alcohol. No change was observed during several days at 20° in hydrocarbons, chlorinated hydrocarbons, or acetic acid. In boiling acetic acid, rapid decomposition occurred, with formation of a brown precipitate and silver mirror; the reagent behaved similarly in dioxan during two days at 20°.

*Oxidation of Amines.*—The usual procedure (see Tables 1 and 2) consisted in gently stirring the oxidant (0.02 mole) with the amine (0.01 mole) in water (150 ml.), at a constant temperature, until the colour of the suspension changed from red to white. Air was not excluded. The pH of the solution fell during the reaction, *e.g.*, from 7.35 to 4.75 in the case of benzylamine (Table 1). The argentous picolinate was filtered off and washed; a trap containing 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid was interposed before the filter pump to retain vapours of volatile carbonyl compounds. The filtrate was treated with 2N-hydrochloric acid, silver chloride was filtered off, and the solution steam-distilled. Aldehydes or ketones sparingly soluble in water were kept in solution by adding just sufficient methanol. They were estimated in the distillates by adding excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid, cooling to 0° for 2 hr., collecting the precipitate on a sintered-glass crucible, and drying it to constant weight in a vacuum-desiccator. Good reproducibility was observed. The identity of each dinitrophenylhydrazone was checked by analysis and by comparison with an authentic sample. Residual solutions were tested for unchanged amine in some cases; *e.g.*, after the isolation of cyclohexanone 2,4-dinitrophenylhydrazone in 41% yield (Table 1), the acidic residual solution was made alkaline, and again steam-distilled, to give cyclohexylamine, which was isolated from the distillate in 40% yield as its hydrochloride, m. p. 205°.

*3,5,5-Trimethylhexylamine.*—The amine, together with the corresponding aldehyde and acid, was supplied by Imperial Chemical Industries Limited, Heavy Organic Chemicals Division. When the amine was oxidised in water at 70° (Table 1), there remained a gelatinous mass, which was broken up by the addition of an excess of 2N-hydrochloric acid. The mixture was filtered and extracted with ether, yielding a brown oil, which when distilled left some resin and gave 1-cyano-2,4,4-trimethylpentane (10%), b. p. 90°/10 mm. (Found: C, 77.6; H, 12.5; N, 9.8. Calc. for C<sub>9</sub>H<sub>17</sub>N: C, 77.6; H, 12.3; N, 10.1%). Its infrared absorption spectrum showed a peak due to C≡N at 2230 cm.<sup>-1</sup> and was identical with the spectrum of an authentic sample, prepared as follows. 3,5,5-Trimethylhexanoic acid was treated with excess of boiling thionyl chloride, the acid chloride was isolated (90%), b. p. 185° (lit.,<sup>25</sup> 188—190°), and treated at a low temperature in ether with anhydrous ammonia to give the amide (98%), m. p. 94° (lit.,<sup>25</sup> 96°); the latter was heated with phosphorus pentoxide to give the cyanide (86%), b. p. 95—100°/15 mm.

<sup>25</sup> W. M. Bruner, *Ind. Eng. Chem.*, 1949, **41**, 2860.

A sample of the cyanide was isolated unchanged after being stirred in water with argentic picolinate (2 mol.) for 24 hr. at 75°. An authentic sample of 3,5,5-trimethylhexanal was oxidised to the acid (>60%) by stirring in water with argentic picolinate (2 mol.) for 4 hr. at 70°.

*Di-3,5,5-trimethylhexylamine*.—Oxidation of the amine (Imperial Chemical Industries Limited, Heavy Organic Chemicals Division) in water for 5 min. at 70° (Table 2) left a gelatinous mass, which was broken up by treatment with excess of 2*N*-hydrochloric acid, and extracted with ether to yield the imine, 3,5,5-trimethylhexylidene-3',5',5'-trimethylhexylamine (78%) (Found: C, 80.5; H, 13.7; N, 5.0. Calc. for C<sub>18</sub>H<sub>37</sub>N: C, 80.8; H, 13.9; N, 5.2%). If, instead of being extracted, the acidified product was steam-distilled, 3,5,5-trimethylhexanal came over. The infrared absorption spectrum of the imine showed a peak due to C=N at 1160 cm.<sup>-1</sup> and was identical with the spectrum of authentic imine prepared (95%) by heating a mixture of the amine and aldehyde. The imine showed b. p. 95—100/0.7 mm. (lit.,<sup>16</sup> 123°/2.5 mm.), but distillation was sometimes difficult owing to frothing, and it was alternatively purified by chromatography on alumina with ether—light petroleum (b. p. 40—60°) (5:95).

*2,5-Dimethylpyrrolidine*.—2,5-Dimethylpyrrole<sup>26</sup> was reduced<sup>27</sup> with zinc and hydrochloric acid to a mixture of 2,5-dimethyl-Δ<sup>1</sup>- and -Δ<sup>3</sup>-pyrrolidine, which was isolated (41%) from its hydrochloride by treatment with 40% aqueous sodium hydroxide, ether extraction, and distillation at 106—115°. Hydrogenation in methyl acetate at 5 atm. with Adams catalyst gave 2,5-dimethylpyrrolidine, b. p. 110—115°, which showed no infrared absorption peaks due to C=N or C=C and gave the known hydrochloride, m. p. 190°. After oxidation of the pyrrolidine (Table 2), the reaction mixture was filtered, treated with 2*N*-hydrochloric acid, silver chloride was removed, and the solution made alkaline and steam-distilled. The distillate was neutralised with hydrochloric acid, evaporated, the residue treated with 40% sodium hydroxide, the free base extracted into ether, and an ethereal solution of picric acid added to give 2,5-dimethyl-Δ<sup>1</sup>-pyrrolidine picrate (28% yield from the pyrrolidine), m. p. 135° (lit.,<sup>14</sup> 135°) (Found: C, 43.9; H, 4.6; N, 17.6. Calc. for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>7</sub>: C, 44.1; H, 4.3; N, 17.3%).

*2-Benzylamino-2,4,4-trimethylpentane*.—2-Amino-2,4,4-trimethylpentane (0.4 mole) was heated under reflux, while benzyl chloride (0.2 mole) was added, and then for 1 hr. more; the b. p. rose to 210°. The semicrystalline product left on cooling was treated with 4*N*-sodium hydroxide, and the organic layer was distilled to give 2-amino-2,4,4-trimethylpentane, b. p. 35—40°/0.05 mm., and 2-benzylamino-2,4,4-trimethylpentane (98%), b. p. 110—120°/0.01 mm. The benzylamino-compound gave a hydrochloride, m. p. 237° (from propan-2-ol) (lit.,<sup>18</sup> 225—227°) (Found: C, 70.8; H, 10.1; N, 5.3. Calc. for C<sub>15</sub>H<sub>26</sub>ClN: C, 70.5; H, 10.2; N, 5.5%). It was oxidised to benzaldehyde in various solvents (Table 2).

*N-Benzyl-t-butylamine*.—The preparation was carried out as in the preceding case; the b. p. rose to 76°. *N*-Benzyl-*t*-butylamine, b. p. 50—56°/0.05 mm., was obtained (80%) and characterised as the hydrochloride, m. p. 246° (lit.,<sup>28</sup> 228°) (from propan-2-ol) (Found: C, 66.1; H, 9.1; N, 7.2. Calc. for C<sub>11</sub>H<sub>18</sub>ClN: C, 66.2; H, 9.0; N, 7.0%). Oxidation gave benzaldehyde (Table 2).

*N-Benzyltriphenylmethylamine*.—Chlorotriphenylmethane (0.02 mole) was treated with benzylamine (0.04 mole) in boiling dry dioxan (50 ml.) for 2 hr. Benzylamine hydrochloride was filtered off from the cooled mixture, and the evaporated filtrate was extracted with light petroleum (b. p. 40—60°) to yield *N*-benzyltriphenylmethylamine<sup>29</sup> (98%), m. p. 91° (from light petroleum) (Found: C, 89.3; H, 6.3; N, 4.1. Calc. for C<sub>26</sub>H<sub>23</sub>N: C, 89.4; H, 6.6; N, 4.0%). Oxidation gave benzaldehyde (Table 2), and when this was done in ethanol the 2,4-dinitrophenylhydrazone appeared to be contaminated with the acetaldehyde derivative.

*N-p-Nitrobenzyl-t-butylamine*.—*p*-Nitrobenzyl bromide (0.1 mole) was treated with *t*-butylamine (0.2 mole) in refluxing dioxan (200 ml.) for 3 hr. *N-p-nitrobenzyl-t-butylamine* separated as the hydrobromide, which was filtered off, treated with 40% aqueous sodium hydroxide, and extracted with ether to give the free base, which solidified, and when sublimed gave colourless crystals (54%), m. p. 28° (Found: C, 63.4; H, 7.5; N, 13.4. C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires C, 63.4; H, 7.7; N, 13.5%). After oxidation (Table 2), *p*-nitrobenzaldehyde was extracted from the precipitated silver salts with benzene. The 2,4-dinitrophenylhydrazone showed m. p.

<sup>26</sup> *Org. Synth.*, Coll. Vol. II, 219.

<sup>27</sup> L. H. Andrews and S. M. McElvain, *J. Amer. Chem. Soc.*, 1929, **51**, 887.

<sup>28</sup> A. Einhorn and H. Pfeiffer, *Annalen*, 1899, **310**, 225.

<sup>29</sup> K. Elbs, *Ber.*, 1884, 701.

328° (lit.,<sup>30</sup> 320°) (from dioxan) (Found: C, 47.3; H, 3.0; N, 20.9. Calc. for C<sub>13</sub>H<sub>9</sub>N<sub>5</sub>O<sub>6</sub>: C, 47.1; H, 2.7; N, 21.1%).

N-(1-Bromo-2-naphthylmethyl)-2-amino-2,4,4-trimethylpentane.—1-Bromo-2-bromomethyl-naphthalene (0.05 mole) was treated with 2-amino-2,4,4-trimethylpentane (0.1 mole) in refluxing dioxan for 24 hr., and, after partial evaporation of the solvent, 2-amino-2,4,4-trimethylpentane hydrobromide was filtered off, the filtrate evaporated, and the residue extracted with light petroleum to give N-(1-bromo-2-naphthylmethyl)-2-amino-2,4,4-trimethylpentane (69%), m. p. 46° (from light petroleum) (Found: C, 65.3; H, 7.5; N, 4.0. C<sub>19</sub>H<sub>26</sub>BrN requires C, 65.5; H, 7.5; N, 4.0%). After oxidation (Table 2), extraction of precipitated silver salts with ether gave 1-bromo-2-naphthaldehyde (95%), m. p. and mixed m. p. 117° (lit.,<sup>31</sup> 119—120°).

*Oxidants Other than Argentic Picolinate.*—(a) The amine (0.02 mole) was treated with mercuric acetate (0.08 mole) in 5% aqueous acetic acid (100 ml.). After reaction, the mixture was acidified to ~pH 2 with acetic acid, steam-distilled, and the carbonyl compound estimated. Di-*n*-butylamine gave 9% butanone in 24 hr. at 100°, dibenzylamine gave 47% benzaldehyde in 4 hr. at 95°, and 2-benzylamino-2,4,4-trimethylamine gave 6% benzaldehyde in 24 hr. at 95°.

(b) Argentic oxide (44 g.) was obtained as a black precipitate by treating sodium persulphate (100 g.) in water (1 l.) with aqueous silver nitrate (60 g.) at room temperature. When used as an oxidant in the same manner as argentic picolinate, it gave benzaldehyde in 34% yield from 2-benzylamino-2,4,4-trimethylpentane after 3 hr. at 65°.

(c) The same amine (0.01 mole) gave ~2% benzaldehyde by air oxidation when stirred in water (150 ml.) at 65—70° for 24 hr. The same yield of benzaldehyde (1—2%) was also obtained, under these conditions, when the following oxidants (0.02 mole) were present: precipitated argentous oxide, ammonia-complexed silver(I) (obtained by adding aqueous ammonia to aqueous silver nitrate until the precipitate just dissolved), ferric chloride, potassium ferricyanide, cupric acetate, ceric ammonium sulphate.

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<sup>30</sup> O. L. Brady, *J.*, 1931, 756.

<sup>31</sup> D. M. Hall and E. E. Turner, *J.*, 1955, 1242.