

## Oxidation by Persulphate. Part IV.<sup>1</sup> Silver-catalysed Oxidation of Primary Aliphatic Amines

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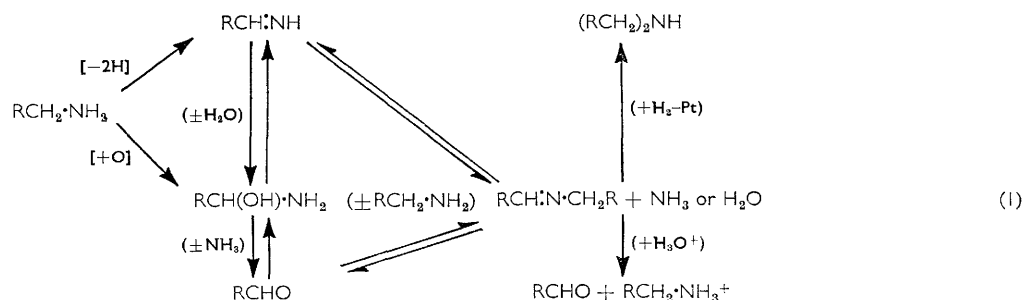
Oxidation of a primary aliphatic amine,  $\text{RCH}_2\cdot\text{NH}_2$ , by aqueous persulphate under alkaline conditions and in the presence of a catalytic amount of silver nitrate, gave the aldimine,  $\text{RCH}:\text{N}\cdot\text{CH}_2\text{R}$ , which was subsequently hydrolysed to the aldehyde,  $\text{RCHO}$ , and the original amine, or was hydrogenated to the corresponding secondary amine,  $(\text{RCH}_2)_2\text{NH}$ . The yield of aldehyde varied from 15 to 95% among  $\text{C}_3$ — $\text{C}_9$  amines, and the conversion was favoured by branching in the alkyl chain or by the presence of an  $\alpha$ -phenyl group. Under similar conditions, a primary amine of the type  $\text{R}^1\text{R}^2\text{CH}\cdot\text{NH}_2$  was converted into the ketone,  $\text{R}^1\text{R}^2\text{CO}$ , without separation of the ketimine. Primary amines of the type  $\text{R}^1\text{R}^2\text{R}^3\text{C}\cdot\text{NH}_2$  were unchanged. Secondary reactions may complicate the oxidations.

OXIDATION of primary and secondary alkyl- or aryl-alkyl-amines by a suspension of silver(II) picolinate in aqueous media yields aldehydes or ketones.<sup>2</sup> Reference has already been made<sup>3</sup> to a related procedure, employing aqueous persulphate with a catalytic amount of silver nitrate. Whereas the picolinate provides complexed  $\text{Ag}^{2+}$  ions, the aqueous  $\text{S}_2\text{O}_8^{2-}\text{-Ag}^+$  reagent is more complicated, since it is a possible source of several species of oxidants, *i.e.*,  $\text{Ag}^{2+}$  or  $\text{Ag}^{3+}$  ions, oxides or oxy-salts of multivalent silver, sulphate radical-ion, and hydroxyl radical.<sup>4</sup> Results of its application to the oxidation of aliphatic amines are reported here and in the following Paper.<sup>5</sup>

The most useful effects were observed with primary amines,  $\text{RCH}_2\cdot\text{NH}_2$  or  $\text{R}^1\text{R}^2\text{CH}\cdot\text{NH}_2$ , in which the amino-function is attached to a primary or secondary

process. Oxidation was therefore preferably performed in the presence of sodium hydroxide. This permitted isolation of the aldimine, which was then hydrolysed to the aldehyde and the original amine, or was hydrogenated to the corresponding secondary amine. Disregarding possible secondary reactions, these transformations are shown in the scheme (1).

This incorporates the alternative possibilities of oxidation occurring by dehydrogenation or hydroxylation, but in either case the aldehyde is one of the resultant species which may be present in equilibrium in the aqueous solution. Participation of unchanged amine in the equilibria yields the aldimine as the predominant species under alkaline conditions, and it appears to be resistant to further oxidation. Effects of acid- and base-catalysis in similar equilibria have been reported<sup>6</sup>



carbon atom. As might be expected, in view of the absence of an  $\alpha$ -hydrogen atom, no oxidation was observed with amines of the type  $\text{R}^1\text{R}^2\text{R}^3\text{C}\cdot\text{NH}_2$ , in which the group is attached to tertiary carbon. Related secondary amines,  $(\text{RCH}_2)_2\text{NH}$  and  $(\text{R}^1\text{R}^2\text{CH})_2\text{NH}$ , gave results inferior to those from primary amines.<sup>5</sup> The reaction mixtures were initially alkaline (pH  $\sim$ 12), and, as long as the pH remained above 7—8, the oxidation products of primary amines of the type  $\text{RCH}_2\cdot\text{NH}_2$  were the corresponding aldimines,  $\text{RCH}_2\cdot\text{N}\cdot\text{CHR}$ , generally appearing as a separate liquid phase. If, however, the solution became acidic, as is normally the case in oxidations by aqueous persulphate, hydrolysis of the aldimine occurred during the

for the related Schiff bases,  $\text{ArCH}:\text{NAr}'$ , which are more amenable to kinetic study than aliphatic aldimines.

Primary amines of the type  $\text{R}^1\text{R}^2\text{CH}\cdot\text{NH}_2$  produced ketones under the alkaline conditions employed, but no intermediate ketimines were isolated in the cases studied. For consistency, however, the ketone-producing amines were treated in the same way as the others, the ketone being isolated, after acidification, from whatever species were present in the aqueous alkaline reaction mixture. The formation of ketimines is said to occur less readily than that of aldimines,<sup>7</sup> but there is not much guidance in the literature concerning possible differences in catalytic effects in the two processes. Aliphatic aldehydes and primary amines react spontaneously, but it is

<sup>1</sup> Part III, R. G. R. Bacon and D. J. Munro, *J. Chem. Soc.*, 1960, 1339.

<sup>2</sup> R. G. R. Bacon and W. J. W. Hanna, *J. Chem. Soc.*, 1965, 4962.

<sup>3</sup> R. G. R. Bacon, *Chem. and Ind.*, 1962, 19; R. G. R. Bacon, W. J. W. Hanna, D. J. Munro, and D. Stewart, *Proc. Chem. Soc.*, 1962, 113.

<sup>4</sup> J. A. McMillan, *Chem. Rev.*, 1962, **62**, 65; D. A. House, *ibid.*, p. 185.

<sup>5</sup> R. G. R. Bacon, W. J. W. Hanna, and D. Stewart, following Paper.

<sup>6</sup> E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, 1962, **84**, 832.

<sup>7</sup> R. W. Layer, *Chem. Rev.*, 1963, **63**, 489.

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considered necessary to add alkali before isolation of the aldimine.<sup>8,9</sup> On the other hand, an acidic catalyst is preferred for the condensation of ketones with amines.<sup>10</sup>

The silver catalyst undergoes an oxidation-reduction cycle, and the overall reaction is theoretically represented

sponse of which to varying reaction conditions is shown in Table 2. Reaction of the amines was generally rapid, was exothermic, and was usually carried out at an initial temperature of  $\sim 0^\circ$ . It was advantageous to increase the proportion of sodium persulphate to 0.75 mole; the reagent was practically all consumed. The

TABLE 1

Oxidation of primary amines with  $\text{Na}_2\text{S}_2\text{O}_8$  (0.75 mol.),  $\text{AgNO}_3$  (0.005 mol.), and  $\text{NaOH}$  (1.0 mol.) in water at  $0-20^\circ$  \*

Amine	Imine isolated	Carbonyl compound	% †
$\text{Pr}^n\text{NH}_2$	$\text{Pr}^n\text{N}:\text{CHEt}$	$\text{EtCHO}$	43
$\text{Bu}^n\text{NH}_2$	$\text{Bu}^n\text{N}:\text{CHPr}^n$	$\text{Pr}^n\text{CHO}$	61-75
$\text{Bu}^i\text{NH}_2$	$\text{Bu}^i\text{N}:\text{CHPr}^i$	$\text{Pr}^i\text{CHO}$	61-71
$n\text{-C}_8\text{H}_{17}\text{NH}_2$	$n\text{-C}_8\text{H}_{17}\text{N}:\text{CH}\cdot\text{C}_7\text{H}_{15}\text{-n} \ddagger$	$n\text{-C}_7\text{H}_{15}\text{CHO}$	14-15
$\text{CHEtBu}^n\text{CH}_2\text{NH}_2$	$\text{CHEtBu}^n\text{CH}_2\text{N}:\text{CH}\cdot\text{CHEtBu}^n \ddagger$	$\text{CHEtBu}^n\text{CHO}$	66-70
$\text{CMe}_3\text{CH}_2\text{CHMeCH}_2\text{CH}_2\text{NH}_2$	$\text{CMe}_3\text{CH}_2\text{CHMeCH}_2\text{CH}_2\text{N} \ddagger$	$\text{CMe}_3\text{CH}_2\text{CHMeCH}_2\text{CHO}$	84-89
$\text{CMe}_3\text{CH}_2\text{CHMeCH}_2\text{CH} \geq \text{N} \ddagger$	None	None	
$n\text{-C}_{12}\text{H}_{25}\text{NH}_2$	$\text{PhCH}_2\text{N}:\text{CHPh}$	$\text{PhCHO}$	96
$\text{PhCH}_2\text{NH}_2$	None	$\text{COMe}_2$	55-59
$\text{CHMe}_2\text{NH}_2$	None	$\text{COMeEt}$	50-62
$\text{CHMeEtNH}_2$	"	Cyclohexanone	73-86
Cyclohexylamine	"	None	
$\text{CMe}_3\text{NH}_2$	"	"	
$\text{CMe}_3\text{CH}_2\text{CMe}_2\text{NH}_2$	"	"	

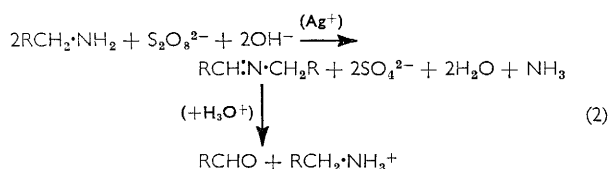
\* Scale: 0.2 mole amine; 200 ml.  $\text{H}_2\text{O}$ . † Results of up to 4 oxidations, with variations in time, method of isolation, etc. (cf. Table 2). All yields are calculated on the basis of equation (2), but those for ketones may be better expressed as two-thirds of the stated figures (*i.e.*, in relation to  $\text{Na}_2\text{S}_2\text{O}_8$ ), since no ketimines were isolated. ‡ New compounds.

TABLE 2

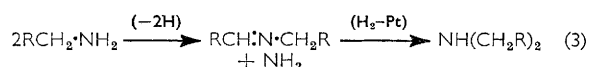
Aqueous isobutylamine (1.0M) with reagents; initial pH 12-13

$\text{Na}_2\text{S}_2\text{O}_8$ (M)	$\text{AgNO}_3$ (M)	Base	(M)	Initial temp.	Time (min.)	Final pH	Aldimine (%)
0.75	0.005	$\text{NaOH}$	1.0	$0^\circ$	70-180	10.2-10.4	61-71
"	"	"	"	"	1140	9.4	63
"	"	"	"	12	75	9.7	53
"	"	"	"	40	25	9.4	52
"	None	"	"	"	140	13.0	None
"	0.05	"	"	"	10	7.5	31
"	0.005	"	0.5	"	15	8.5	33
"	"	"	1.5	"	20	12.3	34
"	"	"	2.0	"	"	13.0	20
"	"	"	1.0	"	15	8.7	43
1.0	"	"	"	"	40	11.1	41
0.5	"	"	"	"	"	8.7	33
"	"	$\text{Na}_2\text{CO}_3$	0.5	"	"	8.0	17
"	"	$\text{NaHCO}_3$	1.0	"	30	8.0	17
"	"	None	"	"	10-15	8-9	20-23
"	"	"	"	"	15-30	$\sim 7.5$	6-12
"	"	"	"	"	>30	<7	None

by equation (2), in which amine, persulphate, and alkali react in a 1 : 0.5 : 1 molar ratio and produce 0.5 mol. of aldehyde after the hydrolysis:



If the aldimine is hydrogenated,<sup>8</sup> the overall result, shown in (3), is the conversion of 2 moles of primary amine into 1 mole of secondary amine:



Preferred conditions for the oxidation were ascertained empirically, principally with isobutylamine, the re-

<sup>8</sup> K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, 1944, **66**, 82.

<sup>9</sup> R. Tiollais, *Bull. Soc. chim. France*, 1947, 708, 716, 959.

final pH was kept above 9 by addition of 1 mol. of sodium hydroxide, excessive amounts of which were detrimental, since they caused precipitation of silver oxide. No oxidation occurred in the absence of the silver salt, the proportion of which was arbitrarily fixed at 0.005 mol.; large amounts resulted in poorer yields of the aldimine, and, in view of the complexity of the total pattern of reaction (see below), this effect cannot at present be explained.

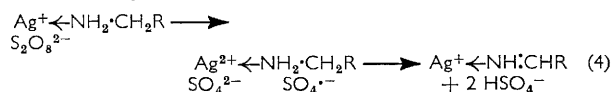
Results for a series of amines, under conditions thus selected, are shown in Table 1. These indicate that the process has preparative value, particularly for  $\text{C}_4$ - $\text{C}_9$  primary amines which are branch-chained or possess an  $\alpha$ -phenyl group. It is probably significant that the same structural factors enhance the stability of imines.<sup>9,11</sup>

Since, under the conditions employed, silver oxide was not precipitated when sodium hydroxide was added to aqueous solutions containing the amine and silver

<sup>10</sup> D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell, and S. A. Ballard, *J. Org. Chem.*, 1954, **19**, 1054.

<sup>11</sup> W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.

nitrate, it can be inferred that  $\text{Ag}^+$  ions were initially complexed with amine molecules. The interaction of persulphate with  $\text{Ag}^+$  ions, producing, *e.g.*, the two oxidant species  $\text{Ag}^{2+}$  and  $\text{SO}_4^{\cdot-}$ , is therefore likely to occur in close proximity to the amine, dehydrogenation of which might then follow as in (4):



Subsequent reactions, represented in (1), are likely to be complicated however by secondary processes, some of which are commented upon below.

(a) Aldimines are susceptible not only to hydrolysis, but also to aldol-type self-condensation, or condensation with an aldehyde, and to additive reactions at the C=N bond.<sup>7,9,12</sup> The observed stability of the isolated aldimines varied considerably during storage or distillation, and their uptake of hydrogen during catalytic hydrogenation was ~85–95% of the theoretical amount.

(b) Ammonia, which has been represented above as a product of the oxidation of primary amines, is readily oxidised by the  $\text{S}_2\text{O}_8^{2-}$ - $\text{Ag}^+$  reagent, or by other sources of multivalent silver,<sup>4,13</sup> giving mainly nitrogen, particularly under alkaline conditions. In the oxidation of a representative amine (isobutylamine) under standard conditions, the extent of gas evolution was extremely small. If an equivalent amount of ammonia was subjected to similar oxidation conditions, it was largely converted into nitrogen (~80%), but this reaction was strongly suppressed by adding the corresponding imine (*N*-isobutylideneisobutylamine), or by first converting the ammonia into its condensation product with isobutyraldehyde. A possible explanation of these facts is that there is competition for silver ions between potential ligands present in the solution, *i.e.*, amine, imine,<sup>14</sup> and ammonia molecules, and hydroxyl ion; preferential complexing with other species may hinder reaction with ammonia.

(c) There is a possibility that any aldehyde present in the reaction system may undergo further oxidation to the carboxylic acid. This is known to occur relatively slowly with benzaldehyde,<sup>15</sup> and it proved even less successful with isobutyraldehyde. Recovery of the latter was nevertheless poor, so other reactions may have occurred. It therefore seems advantageous to conduct oxidations in the way described, the aldehyde being preserved in the form of its aldimine derivative.

#### EXPERIMENTAL

**Oxidation Procedure.**—Water (100 ml.) was stirred, while cooled by an ice-bath, and the amine (0.2 mole) was added, followed by silver nitrate (0.001 mole), and, when the latter

had dissolved, by sodium hydroxide (0.2 mole). Precipitation of silver oxide did not occur. Addition of an ice-cold solution of sodium persulphate (0.15 mole) in water (100 ml.), during about 5 min., led to an exothermic reaction, during which the maximum temperature attained was often about 20°. Stirring was continued until the pH, measured periodically with a glass-electrode system, had fallen from 12–13 to 9–10 (1–3 hr.). No advantage was found in continuing for longer periods.

An excess of sodium chloride solution was added to precipitate the silver. Aldimine, generally present as an upper oily layer, was separated, and was augmented by ether-extraction of the aqueous solution. Iodometric analysis<sup>16</sup> of the aqueous solution showed 90–100% consumption of persulphate. The extracted aqueous solution was treated with a 2*N*-hydrochloric acid solution of 2,4-dinitrophenylhydrazine for the determination<sup>17</sup> of any residual aldehyde or aldimine. Immediately after isolation, the aldimine was hydrolysed by refluxing for 10 min. with 2*N*-hydrochloric acid, followed by steam distillation. The yield of aldehyde in the distillate was determined by conversion of aliquots into the 2,4-dinitrophenylhydrazone, which was compared with an authentic sample. Distilled samples of aldimines were compared with those produced<sup>9</sup> by condensation of the requisite aldehyde and amine; they showed infrared absorption peaks, due to the C=N group,<sup>18</sup> at 1650–1675  $\text{cm}^{-1}$ . In some cases the aldimine was not isolated, but the reaction mixture, after treatment with sodium chloride, was acidified, boiled, and the aldehyde removed by steam distillation. The same procedure was used for the ketone-producing amines, from which no ketimines were isolated. Conversion of an aldimine into the corresponding secondary amine was effected by hydrogenation, at ordinary temperature and pressure, in ethanol solution or aqueous suspension, with Adams catalyst (100 mg. per g. of imine).

Table 2 shows the effect of varying reaction conditions for the oxidation of isobutylamine. Table 1 gives a comparison of results, under standard conditions, from oxidation of various amines, further details of which appear below.

***n*-Propylamine.**—The solution remained homogeneous and, when extracted with ether, gave an unstable yellow oil, of indefinite b. p., which did not furnish the pure imine<sup>9,12</sup> and gave only a low yield of aldehyde on hydrolysis. *n*-Propionaldehyde, b. p. 49–50°, was best obtained by steam distillation of the acidified reaction mixture.

***n*-Butylamine.**—*N*-*n*-Butylidene-*n*-butylamine separated as a yellow oil, and was hydrolysed to *n*-butyraldehyde, b. p. 75–76°. The imine deteriorated when kept, and partially polymerised on distillation. Distilled imine, b. p. 146–150°, 38–40°/9 mm., was identical with an authentic sample.<sup>19</sup> Hydrogenation was effected with absorption of 90–94% of the theoretical quantity of hydrogen and gave di-*n*-butylamine, b. p. 159–160°, which was characterised by conversion into NN-*di-n*-butyl-*N'*-1-naphthylurea, m. p. and mixed m. p. 73° (Found: C, 76.5; H, 8.5; N, 9.6.  $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}$  requires C, 76.5; H, 8.8; N, 9.4%).

<sup>12</sup> H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 401, 1197.

<sup>13</sup> W. F. Pickering, *Austral. J. Chem.*, 1963, **16**, 969; 1964, **17**, 731.

<sup>14</sup> D. F. Martin, in "Preparative Inorganic Reactions," vol. 1, ed. W. M. Jolly, Interscience, New York, 1964.

<sup>15</sup> R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.*, 1960, 1332.

<sup>16</sup> I. M. Kolthoff and E. M. Carr, *Analyt. Chem.*, 1953, **25**, 298.

<sup>17</sup> H. I. Iddles and C. E. Jackson, *Ind. Eng. Chem., Analyt.*, 1934, **6**, 454.

<sup>18</sup> J. Fabian and M. Legrand, *Bull. Soc. chim. France*, 1956, 1461.

<sup>19</sup> W. S. Emerson, S. M. Hess, and F. C. Uhle, *J. Amer. Chem. Soc.*, 1941, **63**, 872; C. W. C. Stein and A. R. Day, *ibid.*, 1942, **64**, 2569.



*Isobutylamine*.—*N*-Isobutylideneisobutylamine<sup>20</sup> separated as a yellow oil, distilling at 129–130°, with partial polymerisation (Found: C, 75.3; H, 13.2; N, 11.3. Calc. for C<sub>8</sub>H<sub>17</sub>N: C, 75.5; H, 13.5; N, 11.0%). The polymeric residue gave dimeric and higher-boiling fractions when distilled in a high vacuum. Hydrolysis of the crude imine gave isobutyraldehyde, b. p. 64–66°. Hydrogenation resulted in absorption of 86% of the theoretical quantity of hydrogen and yielded di-isobutylamine, b. p. 139–140°, characterised as *NN*-di-isobutyl-*N'*-1-naphthylurea, m. p. 124° (from light petroleum) (lit.,<sup>21</sup> 118–119°).

When oxidation of isobutylamine was conducted under standard conditions (Table 1), but with 1,1,3,3-tetramethylbutylamine ("t-octylamine") (0.1 mole) also present, the resulting imine layer was mainly *N*-isobutylideneisobutylamine. Authentic *N*-isobutylidene-"t-octylamine," b. p. 34°/0.7 mm., was prepared (80%) from isobutyraldehyde and "t-octylamine" in refluxing benzene, with azeotropic removal of water (Found: C, 78.6; H, 13.5; N, 7.6. C<sub>12</sub>H<sub>25</sub>N requires C, 78.7; H, 13.7; N, 7.6%). This was hydrogenated to *N*-isobutyl-"t-octylamine," characterised as *N*-isobutyl-*N'*-1-naphthylurea, m. p. 110° (Found: C, 78.2; H, 9.4; N, 8.1. C<sub>23</sub>H<sub>34</sub>N<sub>2</sub>O requires C, 78.0; H, 9.6; N, 7.9%).

*n*-Octylamine.—The reaction mixture was an emulsion, and on extraction with ether it yielded a yellow oil, which when distilled left a polymeric residue and gave *N*-*n*-octylidene-*n*-octylamine, b. p. 104–105°/0.2 mm., also prepared (70%) from condensation<sup>9</sup> of *n*-octanal and *n*-octylamine (Found: C, 80.1; H, 13.4; N, 5.8. C<sub>16</sub>H<sub>33</sub>N requires C, 80.3; H, 13.9; N, 5.9%). *n*-Octanal, b. p. 163–165°, was obtained by acidic hydrolysis of the crude imine from the oxidation, or by steam distillation of the acidified reaction mixture. An alternative preparation of *n*-octanal from *n*-heptylmagnesium bromide and ethyl orthoformate gave a poor yield, whilst application of Stephen's method<sup>22</sup> to caprylonitrile gave some caprylamide.

3-Aminomethylheptane (2-Ethylhexylamine).—The layer of amine initially present was replaced during oxidation by a layer of *N*-2-ethylhexylidene-2-ethylhexylamine, b. p. 88°/0.05 mm. (Found: C, 80.7; H, 13.6; N, 5.9. C<sub>16</sub>H<sub>33</sub>N requires C, 80.3; H, 13.9; N, 5.9%). This was more stable than the isomeric *n*-octylamine derivative described above. On hydrolysis, it yielded 2-ethylhexanal,<sup>23</sup> b. p. 62–63°/19 mm., characterised as the 2,4-dinitrophenylhydrazone,<sup>23</sup> m. p. 121–122°. Hydrogenation of the imine resulted in absorption of 95% of the theoretical quantity of hydrogen, giving di-2-ethylhexylamine, b. p. 124°/0.01 mm. (Found: C, 79.3; H, 14.4; N, 5.8. Calc. for C<sub>16</sub>H<sub>35</sub>N: C, 79.6; H, 14.6; N, 5.8%).

3,5,5-Trimethylhexylamine.—The layer of amine<sup>2</sup> initially present was replaced during oxidation by a layer of the imine,<sup>2</sup> *N*-(3,5,5-trimethylhexylidene)-3,5,5-trimethylhexylamine, a yellow oil, which distilled at 123°/2.5 mm. with little polymerisation (Found: C, 80.7; H, 13.8; N, 5.2. C<sub>18</sub>H<sub>37</sub>N requires C, 80.8; H, 13.9; N, 5.2%). Hydrolysis yielded 3,5,5-trimethylhexanal,<sup>24</sup> b. p. 170–171°, characterised as the 2,4-dinitrophenylhydrazone, m. p. 94–95° (lit.,<sup>25</sup> 92–93°). When oxidation of the amine was effected by adding aqueous persulphate to the other re-

agents dissolved in 1:4 (by vol.) acetone-water, the reaction was less vigorous and gave less aldehyde (52%). Hydrogenation of the imine resulted in absorption of 96% of the theoretical amount of hydrogen and yielded di-3,5,5-trimethylhexylamine,<sup>2</sup> b. p. 124°/2 mm. (Found: C, 80.2; H, 14.2; N, 5.2. Calc. for C<sub>18</sub>H<sub>39</sub>N: C, 80.2; H, 14.6; N, 5.2%), which was converted into *NN*-di-3,5,5-trimethylhexyl-*N'*-1'-naphthylurea, m. p. 110–112° (Found: C, 79.5; H, 10.2; N, 6.5. C<sub>29</sub>H<sub>46</sub>N<sub>2</sub>O requires C, 79.4; H, 10.6; N, 6.4%).

*n*-Dodecylamine.—The amine, m. p. 29–31°, was unchanged under standard oxidation conditions; silver oxide was present as a precipitate. No improvement resulted when an organic solvent was used to dissolve the amine.

*Benzylamine*.—Oxidations were carried out under nitrogen. The layer of amine was replaced during oxidation by one of *N*-benzylidenebenzylamine,<sup>26</sup> b. p. 130°/0.2 mm., identical with a sample prepared from the aldehyde and amine. Hydrolysis of the imine gave benzaldehyde. An oxidation carried out in the absence of sodium hydroxide resulted in a lower yield of aldehyde (60 instead of 96%).

*Isopropylamine, s*-Butylamine, and Cyclohexylamine.—All three amines reacted readily under the standard oxidation conditions, producing no layer of ketimine, but yielding acetone, methyl ethyl ketone, and cyclohexanone, respectively, when the reaction mixtures were acidified and steam-distilled. After an oxidation of cyclohexylamine, ether extraction of the acidified mixture furnished a large amount of brown oil, which polymerised when distillation was attempted.

*Oxidation of Aldehydes*.—When isobutyraldehyde was subjected (3 hr.) to the conditions used for oxidation of the amines (Table 1), a precipitate of silver oxide was present; the treatment was also carried out in the absence of alkali. These reactions furnished some isobutyric acid (<10%), identified as its *S*-benzylthiuronium salt, and some unchanged isobutyraldehyde, but much of the aldehyde was not accounted for; about half of the persulphate was consumed. Benzaldehyde, oxidised in the absence of alkali, gave benzoic acid (17%); 40% of the persulphate was consumed.

*Reactions Involving Ammonia*.—When isobutylamine (0.2 mole) was oxidised under the standard conditions (Table 1), the evolved gas, collected in a burette, amounted to only 3% of the calculated volume of nitrogen (theoretically 0.05 mole, from 0.1 mole of NH<sub>3</sub>). Oxidation of ammonia (0.1 mole), under identical conditions, gave 78% of the theoretical quantity of nitrogen. Oxidation of ammonia (0.1 mole) in the presence of *N*-isobutylideneisobutylamine (0.1 mole) gave 13% of the theoretical quantity. Aqueous ammonia reacted exothermically with isobutyraldehyde, giving liquid condensation products, b. p. mainly 98–104°/18 mm., which, when oxidised under standard conditions, gave a volume of gas corresponding to about 30% of the combined ammonia.

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<sup>23</sup> C. Weizmann, E. Bergmann, and L. Haskelberg, *Chem. and Ind.*, 1937, 15, 587.

<sup>24</sup> W. M. Bruner, *Ind. Eng. Chem.*, 1949, 41, 2860.

<sup>25</sup> S. V. Lieberman, *J. Amer. Chem. Soc.*, 1955, 77, 1114.

<sup>26</sup> R. Juday and H. Adkins, *J. Amer. Chem. Soc.*, 1955, 77, 4559; L. M. Soffer and M. Katz, *ibid.*, 1956, 78, 1705.

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