358. *The Sommelet Reaction. Part IV.* The Preparation of Aliphatic Aldehydes.*

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Aliphatic aldehydes are rapidly destroyed under the conditions of the Sommelet reaction, giving complex condensation products. Yet they can be obtained in yields of up to 50% by this reaction if they are removed by steam-distillation as they are formed. Trimethylacetaldehyde, which has no α-hydrogen atoms, is immune from the side reaction and can be made in 80% yield.

N-Alkylhexaminium halides are converted in good yield into dimethylalkylamines by hot formic acid and formaldehyde.

It has been stated (Parts I and II, *J.*, 1949, 2700, 2704) that saturated aliphatic aldehydes are not obtainable by the Sommelet reaction. This is, indeed, true if the reaction is performed in the usual manner, *i.e.*, under reflux for one or more hours. Thus when *N*-hexylhexaminium bromide—or *n*-hexylamine hydrochloride, hexamine, and formaldehyde—was heated in water, 50% ethanol, or 50% acetic acid, no hexanal was obtained. Hexylamine, however, was not recovered; besides some neutral oil, the main product of the reaction, after acid hydrolysis, was a weakly basic oil which did not react with toluene-*p*-sulphonyl chloride and gave no crystalline salts. It boiled over a wide range up to 180°/1 mm.—the approximate molecular weight of the fractions ranging from 230 to 700—and a considerable residue was left. When any fraction was redistilled it again boiled over a wide range and left some residue; obviously condensation or polymerisation occurred during heating. Amongst the fractions the higher-boiling ones had a lower oxygen content, indicating that condensation occurred probably with the loss of water.

The failure to isolate an aldehyde does not prove that none was formed. It seemed unlikely that an aliphatic amine would have given rise to the complex condensation products; rather it appeared probable that an aldehyde was formed and then destroyed by side-reactions. To test this hypothesis, heptanal was submitted to the usual conditions of the Sommelet reaction: after 2 hour's heating only traces of it were recovered. Some polymeric aldehyde was present but the main product was a weakly basic oil, boiling over a wide range, similar to that obtained in the Sommelet reaction of hexylamine. However, it was found that condensation proceeded sufficiently slowly to allow the nearly quantitative recovery of the aldehyde if the reaction mixture was steam-distilled, instead of being heated under reflux.

Accordingly, the Sommelet reaction with hexamine was carried out in a current of steam and hexanal was indeed obtained in small yield; the weakly basic condensation products were again present. It was ascertained that some aldehyde was also produced by the reaction of hexylamine hydrochloride with formaldehyde, in the absence of hexamine (cf. Part I, *loc. cit.*). In this case, however, no polymeric condensation products were formed but hexylamine was recovered together with some methylhexylamine. It follows that ammonia as well as formaldehyde is required for the formation—probably by an initial reaction of the Mannich type—of the high-boiling products. Usually (Part I, *loc. cit.*) it is best to keep the ratio of hexamine to amine in the Sommelet reaction as high as practicable. In the preparation of aliphatic aldehydes, however, though hexamine is

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* Part III, *J.*, 1950, 2141.

necessary, it promotes the side-reaction and therefore it is advisable to keep its proportion to the amine as *low* as possible. *E.g.*, when a solution of hexylamine hydrochloride was added dropwise to a solution of hexamine in 50% acetic acid, through which a current of steam passed, the yield of aldehyde was only 17%; but when a solution of *N*-hexylhexaminium bromide—or of hexylamine hydrochloride and hexamine—was added to 50% acetic acid in the same way the yield of aldehyde was 40—50%. The use of water or dilute ethanol as solvent resulted in somewhat lower yields.

By the same technique heptanal was prepared in 51% yield from *N*-heptylhexaminium iodide but the particularly reactive phenylacetaldehyde was obtained in 12% yield only.

A different technique was used for the isolation of the lower aldehydes. During the reaction, the mixture was distilled through a fractionating column at such a rate that the aldehyde passed over with the minimum amount of water. In this way *iso*valeraldehyde was obtained in 45% yield from *N*-*iso*amylhexaminium iodide; *n*-butaldehyde, however, probably owing to its greater reactivity, was isolated in only 16% yield. Methoxyacetaldehyde could not be obtained from 2-methoxyethylamine.

Since alkyl halides react slowly with hexamine it is necessary to perform this reaction in chloroform and to isolate the hexaminium salts before the actual Sommelet reaction. In order to produce the salts in yields over 80%, alkyl bromides and iodides require about 24 hr.' boiling, and the chlorides somewhat more. An attempt to increase the reaction rate by using a higher-boiling solvent such as chlorobenzene (Long and Troutman, *J. Amer. Chem. Soc.*, 1949, **71**, 2473) failed because of extensive decomposition of the quaternary salt.

The side reaction consuming the aldehyde was thought to involve the hydrogen atoms on the α-carbon atom; therefore an aldehyde with no α-hydrogen atoms, such as trimethylacetaldehyde, should be stable under the conditions of the Sommelet reaction and be obtainable by heating under reflux, as are aromatic aldehydes. This proved to be the case. Because of the well-known unreactivity of *neo*pentyl halides, no attempt was made to prepare a quaternary hexaminium compound but *neo*pentylamine was used as a starting material. The reaction was unusually slow, presumably for steric reasons: after 8 hr.' boiling in 50% acetic acid solution a 59% yield of trimethylacetaldehyde was obtained. There were no high-boiling condensation products: the basic material was nearly pure *neo*pentylamine. When the amount of recovered starting material was taken into account the yield of trimethylacetaldehyde was over 80%.

For identification a sample of dimethylhexylamine was required: but when it was prepared by the reaction of hexylhexaminium bromide with formic acid [a method successful with benzyl- and substituted benzyl-hexaminium salts (Sommelet and Guiot, *Compt. rend.*, 1922, **174**, 687; Part II, *loc. cit.*)] it was obtained in small yield only, accompanied by higher-boiling, weakly basic, condensation products. Yet the reaction of hexylamine, formaldehyde, and formic acid (Clarke, Gillespie, and Weisshaus, *J. Amer. Chem. Soc.*, 1933, **55**, 4571) gave a satisfactory yield. It transpired that the formaldehyde present in combination in the hexaminium salt was insufficient to supply all the methyl groups required for complete methylation of both amine and ammonia: part of the amine therefore escaped methylation and underwent the Sommelet reaction and subsequent condensations. Addition of excess of formaldehyde resulted in a satisfactory yield of dimethylhexylamine.

EXPERIMENTAL

M.p.s are corrected. Microanalyses by Mrs. E. Bielski.

Preparation of Hexaminium Salts.—After a solution of the alkyl halide (0·2 mole) and hexamine (31 g.) in chloroform (200 ml.) had been boiled for 10 hr. the precipitated salt was filtered off, half of the solvent distilled off, and boiling continued for another 14 hr. during which more salt separated. Total yields were: from *n*-hexyl bromide, 78%; from *iso*amyl iodide, 82%; from *n*-heptyl iodide, 90%.

Hexanal.—(i) A solution of *n*-hexylamine hydrochloride (6·8 g.) in water (50 ml.) was added dropwise (15 min.) to a solution of hexamine (8·3 g.) in 50% acetic acid (50 ml.) through which steam was passed. Steam-distillation was continued until the distillate no longer gave a cloudiness with semicarbazide acetate. After the addition of concentrated hydrochloric acid the distillate was extracted with ether which was shaken with sodium carbonate solution, dried, and distilled, giving 0·84 g. (17%) of hexanal, b. p. 128—130° (dinitrophenylhydrazone, m. p. 105·5—106·5°; lit., 107°).

The residue from the steam-distillation was evaporated several times with excess of hydrochloric acid and ethanol until all the formaldehyde was removed, and then made strongly alkaline. The liberated bases (5 g.) were extracted with ether and distilled at 1 mm., fractions being collected at 80—90°, 125—130°, and at 170—180°. Attempts to form solid derivatives were unsuccessful, nor could di- or tri-hexylamine be isolated from them. Fraction (i) (Found: C, 66·6; H, 11·6; N, 14·95%) had an average molecular weight of 230, as determined by " isothermic microdistillation " (Niederl, Kasanof, Kisch, and SubbaRao, *Microchemie*, 1949, **34**, 132); fraction (iii) (Found: C, 67·9; H, 11·5; N, 16·35%) had M = approx. 700.

(ii) When a solution of *n*-hexylamine hydrochloride (6·8 g.), hexamine (8·3 g.), and formaldehyde (3·7 ml. of 40%) in water (50 ml.) was added dropwise to 50% acetic acid (50 ml.) as above, 2·1 g. (42%) of aldehyde were obtained. When *N*-hexylhexaminium bromide was used, the yield was 49%.

(iii) *Without hexamine.* A mixture of *n*-hexylamine (6 g.), formaldehyde (4·5 ml. of 40%), and water (60 ml.) was boiled, after being adjusted to pH 5 with hydrochloric acid, under reflux for 1 hr. Excess of hydrochloric acid was added and the aldehyde separated in 6% yield by steam-distillation and ether-extraction. From the residue the basic material was isolated in the usual way; it boiled between 128° and 138° and was shown, by treatment with toluene-*p*-sulphonyl chloride, to consist mainly of *n*-hexylamine, with a small amount of a secondary amine.

Heptanal.—A suspension of *N*-heptylhexaminium iodide (40·7 g.) in water (150 ml.) was added in portions to 50% acetic acid (120 ml.) through which steam was passed. Worked up as above, 6·5 g. (51%) of heptanal, b. p. 152—154°, were obtained.

iso*Valeraldehyde.*—50% Acetic acid (300 ml.) was placed into a two-necked flask fitted with a fractionating column (Dufton) and a dropping funnel. After the solution was brought to the boil a suspension of *iso*amylhexaminium iodide (100 g.) in water was added during 30 min. The temperature at the column head was 90—95°; distillation was continued till it rose to 100°. The distillate (50 ml.), worked up as above, gave 11·5 g. (45%) of *iso*valeraldehyde, b. p. 91—93° (dinitrophenylhydrazone, m. p. 122°; lit., 123°).

Direct steam-distillation of the hexaminium salt dissolved in 50% acetic acid gave a 35% yield of the aldehyde.

Trimethylacetaldehyde.—*neo*Pentylamine was prepared by the sequence of reactions proposed by Hughes and Ingold (*J.*, 1933, 67). Treatment of pivalic acid with thionyl chloride, followed by concentrated ammonia solution, gave the amide in 73% yield. Distillation of the latter with phosphoric anhydride gave a 91% yield of the nitrile which was hydrogenated according to Walter and McElvain (*J. Amer. Chem. Soc.*, 1934, **56**, 1614). *neo*Pentylamine boils at 80—82°, its *toluene*-p-*sulphonyl* derivative is insoluble in dilute alkali solution and melts at 117° (Found: N, 6·0. $C_{12}H_{19}O_2SN$ requires N, 5·8%).

The amine (12·0 g.) was treated with concentrated hydrochloric acid to pH 5, then hexamine (21·6 g.), formaldehyde (10·4 ml. of 40%), acetic acid (14 ml.), and water (30 ml.) were added and the mixture boiled under reflux for 4 hr. After the addition of more hexamine (6 g.) and acetic acid (6 ml.) boiling was continued for 4 hr. Concentrated hydrochloric acid (30 ml.) was added and the mixture extracted with ether (3 × 25 ml.). The ethereal extract was washed with sodium carbonate solution, dried, and distilled through a short column: 7·0 g. (59%) of trimethylacetaldehyde, b. p. 77—78°, were obtained. The unchanged amine was recovered from the acidic reaction mixture by evaporation with concentrated hydrochloric acid and ethanol, and extraction of the residue with anhydrous ethanol. The hydrochloride thus obtained (5·5 g.) melted, after one crystallisation from ethanol–ether, at 273° (Hughes and Ingold, *loc. cit.*, m. p. 274°), the toluene-*p*-sulphonamide at 116°.

NN-*Dimethylhexylamine.*—(i) *N*-Hexylhexaminium bromide (21·6 g.) was heated on the water-bath with formic acid (25 ml.) and water (25 ml.) for 3 hr. The mixture was made alkaline and extracted with ether; distillation of the extract gave hexyldimethylamine, b. p. 146—150° (1·2 g., 13%), and a fraction boiling at about 275—280° (4·5 g.).

(ii) *N*-Hexylhexaminium bromide (20 g.), formic acid (51 ml.), and formaldehyde (50 ml. of 40%) were heated for 3 hr. on the water-bath. Five grams (60%) of hexyldimethylamine, b. p. 146—150°, were obtained.

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