

570. The Sommelet Reaction. Part I. The Course of the Reaction.

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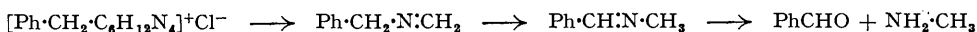
Sommelet showed that when the quaternary salt formed from benzyl chloride and hexamine is heated with water benzaldehyde is obtained in good yield. The first product of the hydrolysis is methylenebenzylamine. Sommelet assumed that migration of a double bond then takes place: $\text{Ph}\cdot\text{CH}_2\cdot\text{N}^+\cdot\text{CH}_2 \longrightarrow \text{Ph}\cdot\text{CH}:\text{N}\cdot\text{CH}_2$. It is now shown that the reaction follows a different course; it is a dehydrogenation, $\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2 \longrightarrow \text{Ph}\cdot\text{CH}:\text{NH}$, and the hydrogen is taken up by $\text{CH}_2\cdot\text{NH}$ (from hexamine) to give methylamine.

Secondary amines, *e.g.*, *N*-methylbenzylamine, give an aldehyde in much poorer yield; tertiary amines do not react at all.

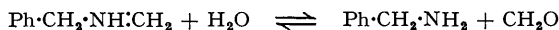
BENZYL halides and substituted benzyl halides combine readily with hexamine to form quaternary salts, *e.g.*, $[\text{Ph}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_{12}\text{N}_4]^+ \text{X}^-$, which can be isolated if an anhydrous solvent *e.g.*, chloroform, is used (Délépine, *Bull. Soc. chim.*, 1895, [iii], **13**, 358). These salts are hydrolysed, by an excess of a strong acid, to a primary amine, ammonia, and formaldehyde (Délépine, *loc. cit.*); this is an excellent method for the preparation of primary amines (Galat and Elion, *J. Amer. Chem. Soc.*, 1939, **61**, 3585). In the presence of water the quaternary salts are unstable and, as Sommelet (*Compt. rend.*, 1913, **157**, 852) discovered, decompose on heating to give an aromatic aldehyde, formaldehyde, ammonia and its methylated products.

This reaction is general for the preparation of aromatic aldehydes, the yields varying from 34% (*o*-ethylbenzaldehyde; Mayer and English, *Annalen*, 1918, **417**, 74) to 80% (2-naphthaldehyde; Mayer and Sieglitz, *Ber.*, 1922, **55**, 1859). Isolation of the quaternary salt is not necessary; the arylmethyl halide can be heated with hexamine in water or aqueous alcohol. Sommelet himself published no experimental details but a year later a patent (Fabriques de Produits de Chimie Organique de Laire, D.R.-P. 268,786; Friedländer, **11**, p. 197) described the preparation of many aldehydes. Contrary to the claims of this patent we found that saturated *aliphatic* aldehydes are not obtainable by this process.

Sommelet (*loc. cit.*) tentatively suggested that the reaction proceeds by the following steps: (1) hydrolysis of the quaternary salt to methylenebenzylamine, (2) shifting of the double bond to give benzyldenemethylamine, and (3) hydrolysis to benzaldehyde and methylamine:



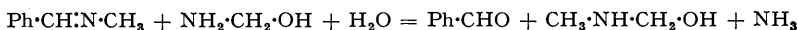
The *first* step of this series is undoubtedly correct, for in those cases where an aldehyde is not obtained because of steric hindrance (cf. following paper) the methyleneamine is the main product of the reaction. It must be added, however, that the methyleneamine is in equilibrium with the amine at the pH of the reaction (3—6):



If methylenebenzylamine is an intermediate, it too should give benzaldehyde under the conditions of the Sommelet reaction, and Graymore and Davies (*J.*, 1945, 293) indeed found that methylenebenzylamine (or a mixture of benzylamine and formaldehyde) can be converted into benzaldehyde in good yield by means of hexamine. Since this process, a smooth conversion of an amine into an aldehyde, is the essential part of the Sommelet method, we propose to refer to it also as the "Sommelet reaction." The necessity for using hexamine in this conversion shows that the rôle of hexamine is not restricted to quaternary salt formation but that it has also another part to play.

The *second* step, the double-bond shift, seems less satisfactory. Although Ingold and

Shoppee (*J.*, 1929, 1199) showed that this prototropic rearrangement occurs to some extent in sodium ethoxide solution at high temperature, it seems unlikely under the slightly acid conditions of the Sommelet reaction. Thus, in a recent paper (*Nature*, 1948, **162**, 619), Shoppee called it "in the highest degree unlikely," and von Auwers and Wunderlich (*Ber.*, 1932, **65**, 70) showed that, in general, a shift of the double bond in Schiff's bases does not occur. It is also hard to see what rôle hexamine can play in such a prototropic rearrangement. Graymore and Davies (*loc. cit.*) tried to explain this by incorporating aminomethyl alcohol (from the hydrolysis of hexamine) in the *third* step according to this equation :



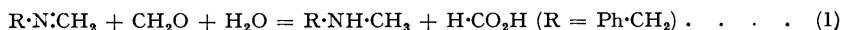
This is not convincing since benzylidenemethylamine is smoothly hydrolysed at the pH of the reaction without the need of any other reagent. The rôle of hexamine in the conversion of benzylamine into benzaldehyde therefore was not clear; and the aim of our work was to discover the mechanism of this reaction and to explore its scope.

After our preliminary publication (*Nature*, 1948, **161**, 173) we discovered that Sommelet had later changed his views, coming to conclusions similar to our own (two papers read to the Société Chimique de France, summarised, without experimental details, in the Proceedings of the Société, *Bull. Soc. chim.*, 1915, [iv], **17**, 82; 1917, [iv], **23**, 96; not recorded in *Chem. Abs.* or *Chem. Zentr.*), but he did not publish these views in any detail; indeed several authors have recently stated that the course of the Sommelet reaction has not been explained (Fieser and Fieser, "Organic Chemistry," 1944, p. 688; Fuson and Denton, *J. Amer. Chem. Soc.*, 1941, **63**, 654; Weygand, "Organic Preparations," 1945, p. 156).

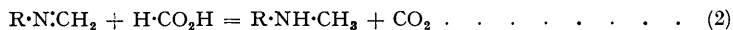
First, the possibility that hexamine acts as a buffer was investigated. Runs with benzylamine and formaldehyde, without hexamine and buffered to different pH's, showed that the reaction is slow below pH 3 and does not proceed at all above pH 7, but that within these limits benzaldehyde was always obtained albeit in poor yield (10—25%). The Sommelet reaction therefore proceeds to some extent even in the absence of hexamine, a conclusion also reached by Graymore (*J.*, 1947, 1117), but hexamine is necessary for good yields.

Since hexamine might act essentially as a mixture of formaldehyde and ammonia, we investigated its replacement by other aldehydes and amines. When acet- or butyr-aldehyde was used in combination with ammonia, no benzaldehyde was formed, and with formaldehyde and methylamine the same low yield was obtained as with formaldehyde alone.

The simple system, benzylamine hydrochloride and formaldehyde in water, was then studied. Attempts to increase the yield of aldehyde by varying the conditions failed, but it was found that the low yield was due to the formation of benzylmethylamine in 50—65% yield. This could be accounted for by the methylating action of formaldehyde (Plöchl, *Ber.*, 1888, **21**, 2117) :



The formic acid formed in this process can itself act as a source of hydrogen in the reduction of a further amount of methyleneamine (Clarke, Gillespie, and Weisshaus, *J. Amer. Chem. Soc.*, 1933, **55**, 4571) :



Analysis showed that formic acid (*ca.* 0.1 mol.) and carbon dioxide (0.06—0.09 mol.) were indeed formed, but in quantity insufficient to account for all the methylation. To explain the formation of 0.5—0.65 mol. of benzylmethylamine the presence of another reducing agent had to be assumed and to find it the reaction mixture was analysed for all known constituents. *No methylamine was found*; Sommelet's double-bond shift therefore does not take place. Instead, an amount of ammonia equivalent to the benzaldehyde was obtained. Since the conversion of benzylamine into benzaldehyde and ammonia is an oxidation, it accounts for the reduction of an equivalent amount of methylenebenzylamine :



Presumably benzylamine is first dehydrogenated to $\text{Ph}\cdot\text{CH}\cdot\text{NH}$, and this is then hydrolysed. (3) is the basic equation of the Sommelet reaction. The yield of aldehyde, in the absence of hexamine, is limited by the conversion of an equivalent amount of benzylamine into benzylmethylamine.

A typical example of several analysed runs is given in the table under *A*. It can be seen that the reduction (to benzylmethylamine) is balanced by the total oxidation ($\text{H}\cdot\text{CO}_2\text{H} + 2\text{CO}_2 + \text{Ph}\cdot\text{CHO}$). Reaction (1) accounts for 0.105 mol. of methylation, (2) for 0.192, and (3) for 0.28.

Products formed in the Sommelet reaction (in mols.).

A. Benzylamine hydrochloride (13.5 g., 1 mol.), 40% formaldehyde (10.73 g., 1.38 mols.) in water (100 c.c.), heated under reflux for 3.5 hours.

B. Benzyl chloride (10.6 g., 1 mol.), hexamine (12.0 g., 1.02 mols.) in water (70 c.c.), heated under reflux for 1.5 hours.

	H·CO ₂ H.	CO ₂ .	CH ₂ O.	Ph·CHO.	NH ₃ .	NH ₂ Me.	Ph·CH ₂ ·NH ₂ .	Ph·CH ₂ ·NHMe.
A.	0.105	0.096	0.55	0.28	0.27	<0.02	0.11	0.61
B.	0.68	trace	1.78	0.81	2.76	1.09	trace	0.11

When hexamine is used (*B* in the table), it can be seen that the methylation of benzylamine is repressed; instead, methylamine is formed according to reactions (1) and (3) ($R = H$) (but not by reaction (2), since no CO_2 is produced) from methyleneimine, $CH_2=NH$, a hydrolysis fragment of hexamine.* Ammonia is, apparently, more readily methylated than benzylamine and thereby protects the latter from this side reaction. Hexamine therefore acts as a hydrogen acceptor in the dehydrogenation of benzylamine. Methylamine is further methylated to a small extent to di- and tri-methylamine, but these have not been determined quantitatively.

Such a dehydrogenation mechanism for the Sommelet reaction is unexpected but not unprecedented. A mixture of formaldehyde and amines can react as a dehydrogenating agent, not only in the conversion of formaldehyde into formic acid and of formic acid into carbon dioxide, but also of alcohols into aldehydes and ketones (Hess, *Ber.*, 1913, **46**, 4104; Hess, Merck, and Uibrig, *ibid.*, 1915, **48**, 1886). On the other hand, benzylamine can be converted into benzaldehyde, not only by inorganic oxidising agents such as permanganate and dichromate, but also by isatin and alloxan (Traube and Engelhardt, *Ber.*, 1911, **44**, 3148) and by "thionylaniline," $PhN:SO$ (Michaelis, *ibid.*, 1893, **26**, 2162).

The conclusion that ammonia and benzylamine are competitively methylated indicates the way to better yields of aldehyde. Obviously the ratio of hexamine to benzylamine should be kept high, and this was confirmed by experiments. Under otherwise identical conditions benzyl chloride with 1, 2, or 3 mols. of hexamine gave 70, 77, and 80%, respectively, of benzaldehyde. When benzyl chloride was added dropwise to a boiling solution of hexamine in water yields of over 80% were obtained. Graymore and Davies (*loc. cit.*) already noted that less than one mol. of hexamine gave a considerably smaller yield.

According to reaction (3) any methyleneimine might act as a hydrogen acceptor. Whether it will give a good yield of benzaldehyde will depend on the comparative methylation rates of the amine and benzylamine. When benzylamine hydrochloride was slowly added to a large excess of methylamine and formaldehyde [$R = Me$ in (3)], the yield of benzaldehyde was 41% and dimethylamine was isolated. Methylmethyleneimine can therefore function as a hydrogen acceptor, but it reacts more slowly than does methylenebenzylamine. Hexamine (or ammonia and formaldehyde) can therefore be regarded as the best reagent for the Sommelet reaction.

As benzylmethylamine is a by-product in the Sommelet reaction it was of interest to determine whether it too was capable of giving benzaldehyde. Experiments in acetic acid (a solvent in which the Sommelet reaction is faster than in water; cf. Hewett, *J.*, 1940, 297) showed that benzaldehyde was formed, but in very low yields—2—3% without, and 8% with, hexamine; dimethylbenzylamine was isolated as a by-product. Dibenzylamine, however, is much more reactive and yields of 14 and 38% of benzaldehyde were obtained without and with hexamine, respectively. In this case dibenzylmethylamine was isolated. Dibenzylamine is converted into benzylamine and benzaldehyde, and the former undergoes the reaction again, giving a total of 2 mols. of benzaldehyde; the yields have been calculated on this basis. The formation of benzaldehyde from dibenzylamine, formaldehyde, and formic acid has been observed by Clarke, Gillespie, and Weisshaus (*loc. cit.*) but they explained it by the assumption of a double-bond shift. Benzyl dimethylamine and tribenzylamine gave, as expected, no benzaldehyde under the conditions of the Sommelet reaction.

* The $CH_2=NH$ molecule is given in the above discussion only as one of the possible reactants. The hexamine equilibrium, $C_6H_{12}N_4 + 6H_2O \rightleftharpoons 6CH_2O + 4NH_3$, involves many intermediates and several of these might be the actual hydrogen acceptors, e.g., $NH_2\cdot CH_2\cdot OH$ or (what we consider most likely) the mesomeric ion $NH_2^+\cdot CH_2 \leftrightarrow NH_2\cdot CH_2^+$. The pH limits to the Sommelet reaction are explained by the fact that above pH 7 and below pH 3 the equilibrium is almost completely on one side or the other and the labile intermediates are not present in appreciable amounts. Similarly, it is not certain that it is benzylamine which is dehydrogenated; it might be the benzylammonium ion or even methylenebenzylamine. Our general knowledge of the mechanism of oxidations and reductions in solution is not yet sufficiently advanced to enable us to draw up the full mechanism of this reaction.

EXPERIMENTAL.

M. p.s are corrected.

Sommelet Reaction without Hexamine.—To benzylamine (10 g.) in water (80 c.c.), neutralised with hydrochloric acid to pH 7, formaldehyde (10 c.c. of 40%), also adjusted to pH 7, was added; the mixture then had a pH of 4.0 (owing to the formation of some Schiff's base). After 1 hour's boiling under reflux the pH had changed to 2.1 (mainly because of the formation of formic acid). On addition of excess of hydrochloric acid and steam-distillation, benzaldehyde (1.5 g.) was obtained. The residue from the steam-distillation was twice evaporated to dryness with alcohol and concentrated hydrochloric acid to remove all formaldehyde. The bases were isolated by sodium hydroxide and ether, and treated with *p*-toluenesulphonyl chloride in dilute alkali. The derivative, m. p. 114° (4.7 g., 19%), of the primary amine was identified by mixed m. p. with *p*-toluenesulphonbenzylamide, and that, m. p. 94° (14.7 g., 57%), of the secondary base with *N*-benzyl-*N*-methyl-*p*-toluenesulphonamide.

Sommelet Reaction at Controlled pHs.—Benzylamine (20 g.), formaldehyde (20 c.c. of 40%), phosphate buffer of pH 7.0 (100 c.c.), and alcohol (160 c.c.) were heated under reflux for 3 hours (pH unchanged). On acidification and steam-distillation no benzaldehyde was obtained. Similar runs with buffers of pH 3—6 gave 15—20% yields of the aldehyde; at pH 2.5, however, none was formed.

Sommelet Reaction with Other Aldehydes.—When a mixture of benzylamine (10 g.) and aqueous acetaldehyde (22 c.c. of 20%), neutralised to pH 4.5 with hydrochloric acid, was heated under reflux for 40 minutes, acidified, and steam-distilled, no benzaldehyde was obtained. When *n*-butyraldehyde (7.2 g.) replaced acetaldehyde the result was the same.

Quantitative Determination of the Products of the Sommelet Reaction (Runs A and B, see table).—(a) *Carbon dioxide.* The reagents, in the amounts given in the table, were heated under reflux with a slow stream of nitrogen bubbling through the mixture. The effluent gases were led from the top of the reflux condenser through 3 potash bulbs containing saturated barium hydroxide solution. At the end of the refluxing period concentrated hydrochloric acid was added to the reaction mixture (20 c.c. to *A*, 50 c.c. to *B*; it was found that these amounts sufficed to prevent further methylation or Sommelet reaction during steam-distillation). After the stream of nitrogen had been continued for further 2.5 hours, the precipitated barium carbonate was collected, washed with water, and titrated with *N*-acid.

(b) *Benzaldehyde.* The reaction mixture was steam-distilled until 1 l. had been collected. In an aliquot of the distillate, benzaldehyde was determined by oxidation with hydrogen peroxide (Methods of Analysis, Ass. Off. Agric. Chem., 1940, p. 328). The benzoic acid obtained melted at 120—121°. In run *B*, where there was more benzaldehyde than 1 l. of water could dissolve, the distillate was extracted with ether, and benzaldehyde determined in both phases.

(c) *Formic acid.* The total acidity of the distillate was determined by titration, and the amount of hydrochloric acid as silver chloride. The difference between total acidity and hydrochloric acid was taken as formic acid. In control experiments the direct (but more time-consuming) determination of formic acid (*loc. cit.*, p. 466) gave the same results.

(d) *Formaldehyde* was determined in the distillate by Schulek's iodometric method (*Ber.*, 1925, 58, 734). Control experiments showed that the presence of benzaldehyde does not interfere in this method.

(e) *Ammonia.* The residue from the steam-distillation was evaporated to dryness. In aliquots of the run *A* hydrochlorides ammonia was determined by Erdmann's method (*J. Biol. Chem.*, 1910, 8, 42), freshly precipitated mercuric oxide being used. After filtration the mercuric oxide-ammonia complex was distilled with sodium hydroxide and sodium sulphide, and the ammonia collected in *N*/10-acid. Control experiments with pure ammonium sulphate showed that ammonia was quantitatively recovered by this method. It was identified by conversion into benzamide [m. p. (crude) 128°]. In run *B*, where the amount of ammonia was larger, the dry hydrochlorides were extracted with absolute alcohol (150 c.c.), pure ammonium chloride (10.62 g.) remaining undissolved. In the alcohol-soluble fraction ammonia was determined as above.

(f) *Methylamine.* Run *A*. An aliquot of the hydrochlorides and an excess of 50% potassium hydroxide solution were warmed to 80°, and the volatile bases removed in a current of air and absorbed in dilute hydrochloric acid. Treatment with *p*-toluenesulphonyl chloride and alkali gave only a very small amount of a sulphonamide, m. p. 108—110° (benzylamine). A control experiment to which 0.02 equivalent of methylamine was added showed that this amount was readily isolated as its *p*-toluenesulphonamide. Run *B*. An aliquot of the alcohol-soluble hydrochlorides was converted into *p*-toluenesulphonamides; the alkali-soluble derivative (m. p. 68—70°) was nearly pure *p*-toluenesulphonmethylamide.

(g) *Benzylamine* and *methylbenzylamine* were isolated as *p*-toluenesulphonamides. In run *B* the more volatile bases were first removed as described above. In some cases the alkali-insoluble *p*-toluenesulphonamide was a mixture which could be separated by extraction with hot alcohol into the more soluble *N*-benzyl-*N*-methyl-*p*-toluenesulphonamide and a sparingly soluble compound, m. p. 156°. The latter was *di-p*-toluenesulphonylbenzylamine which crystallised from a large amount of alcohol in colourless needles, m. p. 161° (Found: C, 60.5; H, 5.2. C₂₁H₂₁O₄NS₂ requires C, 60.7; H, 5.1%). Its structure was proved by synthesis from *p*-toluenesulphonbenzylamide and *p*-toluenesulphonyl chloride in alkaline solution, and by hydrolysis to *p*-toluenesulphonbenzylamide by alcoholic sodium ethoxide. To eliminate the error in the separation of benzylamine and benzylmethylamine, caused by the formation of the disulphonyl derivative, the alkali-insoluble sulphonamide fraction was treated with alcoholic sodium ethoxide whenever its m. p. was not sharp.

Gradual Addition of Benzyl Chloride.—Benzyl chloride (50 g.) was added dropwise during 1 hour to a boiling solution of hexamine (60 g.) in water (100 c.c.). Refluxing was continued for 20 minutes and, after the addition of concentrated hydrochloric acid (100 c.c.), for another 15 minutes. The benzaldehyde layer was separated after cooling, and the remainder steam-distilled; an ether extract of the distillate was combined with the aldehyde and distilled. Benzaldehyde (34.5 g.; 82.3%) was collected at 80—81°/25 mm.

Sommelet Reaction with Excess of Hexamine.—When benzyl chloride (50 g.) and hexamine (112 g.) in

water (180 c.c.) were boiled under reflux for 1.5 hours, 32.4 g. of benzaldehyde were obtained. The use of 168 g. of hexamine increased the yield to 33.1 g.

Sommelet Reaction with Methylamine.—Benzylamine hydrochloride (13.5 g.) in the minimum amount of water was added during 30 minutes to a boiling mixture of formaldehyde (20 c.c. of 40%) and aqueous methylamine (40 c.c. of 30%) adjusted to pH 4.0 with hydrochloric acid. The pH changed to 3.0, and after readjustment of it to 4.0 with sodium hydroxide, refluxing was continued for 1.5 hours. Ether-extraction and peroxide-oxidation indicated a 41% yield of benzaldehyde. After evaporation the hydrochlorides were treated with potassium hydroxide (as above), and the volatile bases converted into *p*-toluenesulphonamides. The secondary derivative, after crystallisation from alcohol, melted alone and mixed with *p*-toluenesulphondimethylamide at 78—79°.

Sommelet Reaction of Benzylmethylamine.—Benzylmethylamine (3.8 g.), formaldehyde (3 c.c. of 40%), and glacial acetic acid (10 c.c.) were heated under reflux for 4 hours. After the addition of hydrochloric acid (20 c.c.), steam-distillation, and oxidation with hydrogen peroxide, 0.10 g. of benzoic acid was obtained (2.6% yield of benzaldehyde). After evaporation, the amines were converted into *p*-toluenesulphonamides and the unchanged amines treated with picric acid. *N*-Benzyl-*N*-methyl-*p*-toluenesulphonamide, m. p. 94°, and benzyldimethylamine picrate, m. p. 93° (King and McMillan, *J. Amer. Chem. Soc.*, 1946, **68**, 1469), were obtained.

Interaction of benzylmethylamine hydrochloride (4.3 g.), formaldehyde (3 c.c. of 40%), and hexamine (4.0 g.) in boiling glacial acetic acid (30 c.c.) during 4 hours gave an 8% yield of benzaldehyde. Benzyl-dimethylamine was again isolated as its picrate.

Sommelet Reaction of Dibenzylamine.—When dibenzylamine (5.1 g.), formaldehyde (3 c.c. of 40%), and glacial acetic acid (10 c.c.) were heated under reflux for 6 hours, 0.69 g. of benzaldehyde was obtained. After treatment with *p*-toluenesulphonyl chloride etc., the tertiary amine, expected to be dibenzylmethylamine, was converted into its picrate, m. p. 129° (from alcohol). Since this m. p. is different from the value (107°) given for methyl-dibenzylamine picrate (Hughes and Ingold, *J.*, 1933, 75), our picrate was converted for identification into the hydrochloride, m. p. 198—200°, and the hydrobromide, m. p. 155—156°, of dibenzylmethylamine (*lit.*, 200—201° and 157°, respectively). These salts were reconverted into the picrate which then melted at 129.5°. Hughes and Ingold's m. p. therefore seems to be incorrect.

Interaction of dibenzylamine (5.4 g.), formaldehyde (3 c.c. of 40%), and hexamine (3.0 g.) in glacial acetic acid (20 c.c.) during 4 hours gave 2.2 g. of benzaldehyde.

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