571. *The Sommelet Reaction. Part II. The* ortho-*Effect.*
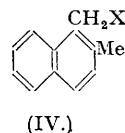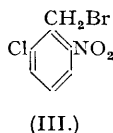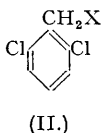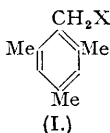
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The Sommelet reaction is shown to be hindered by two substituents in the *ortho*-positions, electron-attracting and -repelling groups acting in the same way. Other methods of oxidising arylmethylamines to aromatic aldehydes were found to be similarly inhibited. One *ortho*-substituent does not prevent the reaction. The preparation, by the Sommelet reaction, of *o*-, *m*-, and *p*-bromo-, and *o*-iodo-benzaldehyde is described.

In Part I (preceding paper) it was shown that the Sommelet reaction of an arylmethyl halide with hexamine proceeds in three steps : (1) a quaternary salt is formed, (2) this is hydrolysed to an equilibrium mixture of amine and methyleneamine, $Ar \cdot CH_2 \cdot NH_2 + CH_2O \rightleftharpoons Ar \cdot CH_2N \colon CH_2 + H_2O$, and (3) the amine is dehydrogenated to an aldimine, $Ar \cdot CH \colon NH$, which is then hydrolysed to an aldehyde, $Ar \cdot CHO$.

Fuson and Denton (*J. Amer. Chem. Soc.*, 1941, **63**, 654) showed that no aldehyde was obtained from 2 : 4 : 6-trimethylbenzyl chloride (I; X = Cl). A quaternary salt was readily formed and heating it in aqueous solution gave a compound, m. p. 154°, to which the authors assigned the structure $(C_6H_2Me_3 \cdot CH_2 \cdot NH)_2CH_2$. In the Experimental section evidence is now adduced to show that this compound is really a polymer of the methyleneamine, $[C_6H_2Me_3 \cdot CH_2 \cdot N \colon CH_2]_n$ ($n = 2$ or 3). The first two steps of the Sommelet reaction therefore proceed as usual, but the third is inhibited. Variations in the conditions of the reaction were tried by us without success, nor was an aldehyde obtained from the amine (I; X = NH_2) and hexamine. However methylation, the usual side-reaction in the Sommelet method, is not hindered : the quaternary salt, formaldehyde, and formic acid readily afforded the tertiary amine (I; X = NMe_2).

$$\text{(I.)} \qquad \text{(II.)} \qquad \text{(III.)} \qquad \text{(IV.)}$$

It was of interest to investigate whether this hindrance is independent of the nature of the *ortho*-group, and the effect of the electron-attracting chlorine atom was studied. 2 : 6-*Dichloro-benzyl bromide* (II; X = Br) also reacted smoothly with hexamine. Absence of steric hindrance in the quaternary salt formation is indicative of an S_N1 mechanism, a conclusion supported by our observation that electron-attracting substituents decrease the rate of this reaction (cf. Part III, to follow). Again, the quaternary salt yielded no aldehyde, but 2 : 6-dichloro-benzylamine (II; X = NH₂) was readily obtained. Replacement of one chlorine by a nitro-group [as in (III)] did not affect these results. The second aromatic ring in naphthalene has the same effect as an *ortho*-substituent, since no aldehyde was obtained from (IV; X = Cl or NH₂), even when the reaction was carried out in a sealed tube at 150°. This is reminiscent of Ziegler and Tiemann's failure (*Ber.*, 1922, **55**, 3406) to oxidise the corresponding alcohol (IV; X = OH) to an aldehyde.

Interesting results were obtained from a comparison with other methods of converting amines into aldehydes. Traube and Engelhardt (*Ber.*, 1911, **44**, 3148) found that benzylamine and isatin gave a 66% yield of benzaldehyde. By this method we obtained 1-naphthaldehyde in 48% yield from 1-aminomethylnaphthalene, but neither (I) nor (II; X = NH₂) gave an aldehyde. Schönberg, Moubasher, and Mostafa (*J.*, 1948, 178) explained this reaction by the assumption of a prototropic rearrangement. We believe, however, that if the reaction proceeded according to such mechanism it would not be sterically hindered.

Analogous results were obtained in chromic acid oxidations. Benzylamine and 1-amino-methylnaphthalene are readily oxidised, giving the corresponding aldehydes and acids in poor yields, but (II; X = NH₂) is not attacked by chromic acid even in boiling 50% sulphuric acid. This passive behaviour is the same as is shown by the nitrogen-free parent substance, 2 : 6-dichlorotoluene, which is very resistant to oxidation (Davies, *J.*, 1921, **119**, 873), being not attacked by chromic acid in 50% sulphuric acid. The additional amino-group therefore does not facilitate oxidation.

From these experiments we conclude that the oxidising agents attack the carbon atom adjacent to the aromatic ring, and not the nitrogen atom. This is in accord with that fact that aliphatic amines are not converted into aldehydes by either isatin or hexamine.

One substituent in the *ortho*-position does not prevent the Sommelet reaction, but a slight retarding effect is noticeable. Graymore and Davies (*J.*, 1945, 293) obtained lower yields of *o*- than of *m*- or *p*-chlorobenzaldehyde. In the present work yields of the three bromobenz-aldehydes under identical conditions were : in 66% alcohol, *o*- 50, *m*- 60, and *p*- 62% ; in 50% acetic acid, 47, 69, and 73%, respectively. This effect is, however, not sufficient to prevent good yields even with bulkier substituents, since under suitably chosen conditions a 76% yield of *o*-iodobenzaldehyde is obtained.

<center>EXPERIMENTAL.</center>

<center>M. p.s are corrected.</center>

Fuson and Denton's Compound, m. p. 154°.—Fuson and Denton's analysis (*loc. cit.*; C, 81·64; H, 9·66; N, 8·83%) does not distinguish clearly between their proposed structure (Calc. for C₂₁H₃₀N₂ : C, 81·2; H, 9·75; N, 9·0%) and the methyleneamine structure (Calc. for C₂₂H₃₀N₂ : C, 81·9; H, 9·4; N, 8·7%). The compound (0·1244 g.) was boiled under reflux with 3N-hydrochloric acid (30 c.c.) for 1 hour and then steam-distilled until 250 c.c. were collected. 0·0210 G. of formaldehyde was found in this distillate by Schulek's method (*Ber.*, 1925, **58**, 732), *i.e.*, 16·9%. A compound of the structure suggested by Fuson and Denton could give no more than 9·7% of formaldehyde on hydrolysis, whereas the methyleneamine can yield 18·6%. The molecular weight (350) indicates a dimer (Calc. : 322) or a trimer partly depolymerised in the boiling chloroform used for this determination. Graymore (*J.*, 1947, 1117) found double molecular weights for several related methyleneamines.

NN-Dimethyl-2 : 4 : 6-trimethylbenzylamine (I; X = NMe₂).—The quaternary salt (16 g.) from 2 : 4 : 6-trimethylbenzyl chloride (Fuson and Denton, *loc. cit.*) was heated under reflux for 2 hours with hexamine, formic acid (16 c.c.), and water (16 c.c.) (cf. Sommelet and Guiot, *Compt. rend.*, 1922, **174**, 687). Excess of hydrochloric acid was added and the mixture boiled under reflux for 15 minutes; on cooling, the *hydrochloride* (7 g.) separated. It was recrystallised from water, m. p. 233—234° (Found : N, 6·5. C₁₂H₁₉N,HCl requires N, 6·6%). The picrate formed yellow needles, m. p. 144—145°, from alcohol.

2-Methyl-1-chloromethylnaphthalene.—2-Methylnaphthalene (50 g.), paraformaldehyde (20 g.), glacial acetic acid (52 c.c.), 85% phosphoric acid (33 c.c.), and concentrated hydrochloric acid (100 c.c.) were stirred at 80—85° for 6 hours. On cooling, a purple solid separated which was washed with water, dissolved in ether (350 c.c.), washed with aqueous sodium carbonate, dried (K₂CO₃), and distilled; the product had b. p. 154°/8—10 mm. and m. p. 53° (47 g., 70%). Recrystallisation from alcohol raised the m. p. to 58°. Darzens and Lévy (*Compt. rend.*, 1936, **202**, 73), who prepared this compound under different conditions, gave no yield.

Sommelet Reaction with 2-Methyl-1-chloromethylnaphthalene.—The above compound (13 g.) and hexamine (11 g.) were boiled under reflux in chloroform (30 c.c.) for 4 hours. The quaternary salt which separated, m. p. 203° (decomp.) (15 g., 62%), is somewhat soluble in chloroform, and an additional amount can be precipitated by the addition of acetone.

(a) This salt (4·7 g.) was heated under reflux with water (25 c.c.) for 1 hour. Concentrated hydrochloric acid (10 c.c.) was added, refluxing continued for 10 minutes, and the mixture steam-distilled. No aldehyde was found in the distillate by extraction with ether and treatment with sodium hydrogen sulphite solution. When the residue from the steam-distillation was evaporated to small volume, 2-*methyl*-1-*aminomethylnaphthalene hydrochloride* (1·9 g.) separated on cooling. It crystallised from water in fine colourless needles, m. p. 290° (Found : N, 6·4. $C_{12}H_{13}N,HCl$ requires N, 6·7%).

(b) The quaternary salt (4·0 g.) was heated in a sealed tube with water (20 c.c.) at 150° for 1·5 hours. No aldehyde was obtained. The primary amine was isolated in 77% yield, and from the mother-liquors, by conversion into a nitrosoamine, the presence of a small amount of a secondary amine was proved.

2 : 6-*Dichlorobenzyl Bromide.*—Bromine (39 g.) was added, through a tube reaching below the surface, to gently boiling 2 : 6-dichlorotoluene (38·3 g.) during 45 minutes. When hydrogen bromide was no longer evolved the mixture was distilled *in vacuo*, giving a forerun, b. p. 60—100/2 mm. (12 g.; mainly unchanged dichlorotoluene), and 2 : 6-*dichlorobenzyl bromide*, b. p. 118°/2 mm., m. p. 45—46° (30 g., 52%) (Found : C, 34·8 ; H, 2·2. $C_7H_5Cl_2Br$ requires C, 35·0 ; H, 2·1%). It is a strong lachrymator.

Sommelet Reaction with 2 : 6-*Dichlorobenzyl Bromide.*—The above bromide and hexamine gave a quaternary salt in 80% yield. When this salt was boiled with water or 50% acetic acid and then steam-distilled, none of the related aldehyde was obtained. After the removal of all formaldehyde by steam-distillation, addition of sodium hydroxide and extraction with ether gave 2 : 6-dichlorobenzylamine (80%), b. p. 242—244°. The *hydrochloride* crystallised from water in colourless needles, m. p. 237—238° (Found : N, 6·3. $C_7H_7NCl_2,HCl$ requires N, 6·6%). The picrate formed yellow needles, m. p. 207°, from alcohol.

Sommelet Reaction with 2-*Chloro*-6-*nitrobenzyl Bromide.*—The bromide (D.R.-P. 107,501 ; Friedländer, **5**, p. 50) (10 g.) and hexamine (6 g.) in chloroform (25 c.c.) gave 7 g. of the quaternary salt after the solution had been boiled for 1 hour. This salt was heated under reflux with water (30 c.c.) for 1·5 hours, but no aldehyde was formed.

Reaction with Isatin.—(a) 1-Aminomethylnaphthalene (0·9 g.), isatin (1·8 g.), and water (30 c.c.) were heated under reflux for 1 hour. After the addition of concentrated hydrochloric acid (10 c.c.) the solution was extracted with ether, and the extract shaken with saturated sodium hydrogen sulphite solution. From the bisulphite compound 1-naphthaldehyde (0·5 g.) was obtained.

(b) 2 : 6-Dichlorobenzylamine and 2 : 4 : 6-trimethylbenzylamine were treated in the above way. No aldehyde was isolated.

Oxidations with Chromic Acid.—(a) Benzylamine (3 g.), potassium dichromate (5·6 g.), water (14 c.c.), and concentrated sulphuric acid (8 c.c.) were heated under reflux for 45 minutes. The green solution was extracted with ether, and the extract washed with sodium hydrogen carbonate solution. From the ethereal solution benzaldehyde (0·3 g.) was isolated, and from the alkaline washings benzoic acid (0·3 g.). From the green solution benzylamine (1·6 g.) was recovered.

(b) 1-Aminomethylnaphthalene (1·6 g.) was treated as above. The solution became green very quickly. 1-Naphthaldehyde (0·08 g.) and 1-naphthoic acid (0·72 g.) were obtained.

(c) 2 : 6-Dichlorobenzylamine (0·4 g.), potassium dichromate (1·7 g.), water (4 c.c.), and concentrated sulphuric acid (2·5 c.c.) were heated under reflux for 2 hours. Working up as above gave 0·35 g. of the unchanged amine (picrate, m. p. 205—206°) but no aldehyde or acid.

(d) 2 : 6-Dichlorotoluene (3 g.) was oxidised as above. The solution did not become green, and 2·7 g. of the substance were recovered unchanged.

Bromobenzaldehydes.—(a) Each bromobenzyl bromide (Shoesmith and Slater, *J.*, 1926, 214) (8·3 g.) was heated under reflux with hexamine (5·5 g.) in chloroform (50 c.c.) for 1·5 hours. Yields of the quaternary salts were : *o*-, 95 ; *m*-, 94 ; *p*-, 98%. These salts (10 g.) were heated under reflux with 50% acetic acid (30 c.c.) for 2 hours. On dilution with water and cooling the *p*-compound crystallised ; the *o*- and *m*-compounds were extracted with ether, and the extracts washed with aqueous sodium carbonate, dried, and evaporated. Yields, given on p. 2705, can be improved somewhat by longer heating.

(b) Each bromobenzyl bromide (5 g.) was heated under reflux with hexamine (3·4 g.) and 66% alcohol (27 c.c.) for 2 hours. After the addition of hydrochloric acid (15 c.c.) the boiling was continued for 15 minutes, and the mixture worked up as above. Yields are given on p. 2705 ; that of the *p*-compound could be increased to 69% by adding more hexamine (1·7 g.) after 2 hours' refluxing and heating for another 2 hours. Dropwise addition of the bromide to hexamine did not improve the yield.

o-*Iodobenzaldehyde.*—*o*-Iodobenzyl bromide (20 g.) reacted in the cold with hexamine (10·5 g.) in chloroform (100 c.c.). After being kept overnight the quaternary salt was filtered off (28·0 g., 95%) (Jacobs and Heidelberger, *J. Biol. Chem.*, 1915, **21**, 467). This salt was heated under reflux with 50% acetic acid (60 c.c.) for 2 hours and then diluted with 3N-hydrochloric acid (60 c.c.). The heavy oil solidified on cooling with ice and had m. p. 30—31° (11·9 g., 76% calc. on *o*-iodobenzyl bromide). Aqueous alcohol as a solvent gave lower yields.

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