

REACTIONS OF TERTIARY BUTYL HYPOCHLORITE*

II. RATE OF REACTION WITH SOME 4-NITROANILINES

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It has been shown in Part I of this series (Pausacker and Scroggie 1959) that tertiary butyl hypochlorite (TBH) reacts with 4-nitroaniline, and its *N*-methyl derivatives, to form nuclear-chlorinated compounds in excellent yield.

It has now been found that there is a complete lack of reproducibility of the concentration-time curves when these reactions are followed quantitatively, but, as further work has been discontinued, it is desired to record the results obtained.

Significant induction periods (50–125 min) were observed during the reaction of TBH with 4-nitroaniline in daylight and even longer induction periods (400–1500 min) were noted when the reaction was carried out in complete darkness. The induction period for the dark reaction was reduced considerably (100–250 min) when the solutions were degassed. In one experiment, which had lost 1 per cent. of its oxidizing power in 600 min, only *c.* 60 per cent. of the TBH could be recovered by distillation under reduced pressure. Independent experiments showed that at least 90 per cent. TBH should distil under these conditions. Similar results were obtained from experiments involving *N*-methyl-4-nitroaniline. This would indicate that some oxidant, other than TBH, is present in the reaction mixture and it is proposed that *N*-chloro compounds have been formed. Aliphatic amines can be converted into the corresponding *N*-chloro derivatives with TBH (Bachmann, Cava, and Dreiding 1954; Zimmer and Audrieth 1954) and acetanilide forms *N*-chloroacetanilide with TBH in the presence of sodium hydroxide (Zimmer and Audrieth 1954). However, as TBH is rapidly hydrolysed in dilute alkaline solution to form sodium hypochlorite (Anbar and Dostrovsky 1954), it would appear that sodium hypochlorite could be the chlorinating agent in the latter example.

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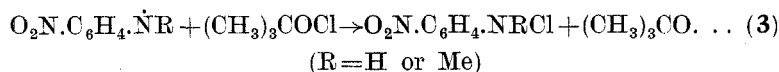
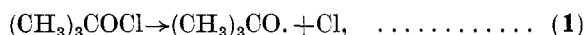
‡ Deceased July 20, 1959.

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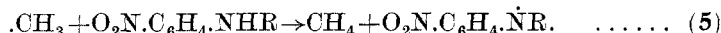
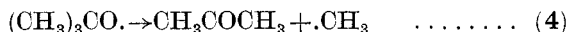
The reactions of *N*-methyl-4-nitroaniline and *NN*-dimethyl-4-nitroaniline with TBH also failed to furnish reproducible results and, once again, light-catalysis was noted.

It would appear that these reactions involve free radical intermediates because of (i) light-catalysis, (ii) oxygen-inhibition, and (iii) non-reproducibility of the concentration-time plots. Walling (1957) has shown that other reactions of TBH can display these features. In addition, the simultaneous formation of 4,4'-dinitroazobenzene from 4-nitroaniline, and demethylation products from *N*-methyl-4-nitroaniline and *NN*-dimethyl-4-nitroaniline (see Part I), also suggest free radical intermediates (Pausacker and Scroggie 1954; Mitchell and Pausacker 1957).

It is therefore proposed that the chlorination of 4-nitroaniline and *N*-methyl-4-nitroaniline proceeds, at least in part, by the following mechanism:

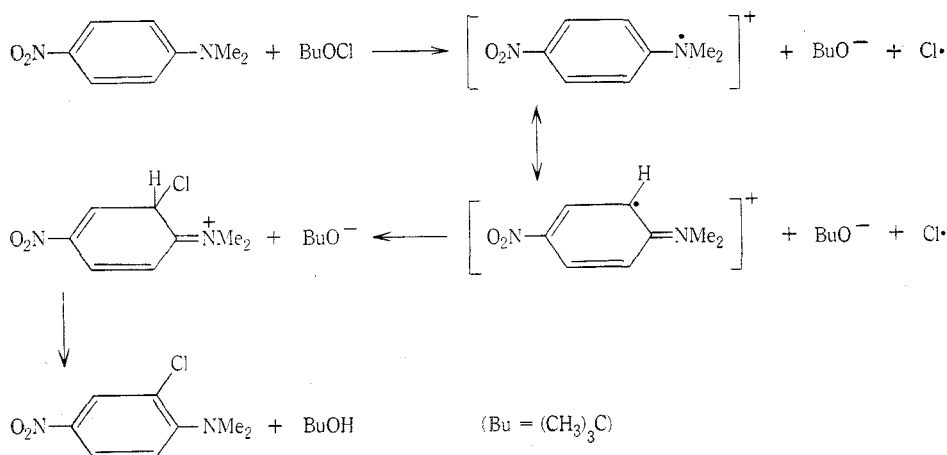


This is similar to the radical chain process proposed for chlorination with TBH by Walling (1957), who has also pointed out that reactions (4) and (5) may be alternative to reaction (2).



It is then assumed that the *N*-chloro compound formed rearranges by a mechanism similar to that proposed by Ayad *et al.* (1957).

It is also possible to explain the formation of nuclear chlorination products from *NN*-dimethyl-4-nitroaniline as follows:



This mechanism may also be invoked for any direct nuclear chlorination of 4-nitroaniline and *N*-methyl-4-nitroaniline without the intermediate formation of an *N*-chloroamine.

It was thought originally that the reaction may be autocatalytic with respect to the *tert*.-butanol formed. In some cases, notably the reactions of 4-nitroaniline in daylight, the induction period was indeed eliminated when *tert*.-butanol was added. However, it is now considered that this more polar solvent may actually facilitate electrophilic chlorination, at least in part. Ginsburg (1951) has found that 4-methoxybenzaldehyde and TBH yield 3-chloro-4-methoxybenzaldehyde in 90 per cent. acetic acid, but anisoyl chloride is formed in carbon tetrachloride. The first reaction probably proceeds by electrophilic substitution, whereas the second reaction involves a radical mechanism.

Experimental

(i) *Reagents*.—All reagents were prepared and purified as described in Part I.

(ii) *Apparatus and Method of Estimation*.—The amine ($0.859-4.45 \times 10^{-3}$ mol) was accurately weighed into the reaction flask (100 ml) and benzene (c. 90–95 ml) was added. The flask and contents were placed in a constant temperature bath at either 20.10 or 30.10 °C and, when temperature equilibrium was obtained, a preheated solution of the appropriate amount of TBH ($0.805-5.25 \times 10^{-3}$ mol) in benzene (5 or 10 ml) was added. The flask was then made up to the mark with preheated benzene and the contents were thoroughly mixed. Aliquot portions (5 or 10 ml) were withdrawn at definite times and added to acidified potassium iodide solution. The liberated iodine was titrated with standardized sodium thiosulphate solution (c. 0.035*N*).

When the rate of reaction was too high, the above procedure was adapted to use with a "Dreischenkelrohr" (Criegee 1932).

The original stock-solution of TBH was maintained under the same conditions as the reacting solutions and was found to be quite stable.

The reactions were initially performed under normal laboratory conditions but, as it is known that TBH is photosensitive (Chattaway and Backeberg 1923), later reactions were carried out in the dark. For this purpose, *all* operations involving TBH were performed in a specially darkened room, the only illumination being provided when necessary by a Wratten Series I photographic safe-light; the reacting solutions were not exposed directly even to this illumination.

The products formed in these rate experiments were occasionally checked qualitatively by evaporation of any residual reaction solution, followed by m.p. and mixed m.p. determinations. In every case, the product identified in this way corresponded with the major product obtained in the appropriate reaction described in Part I.

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