

Chlorination of Butyryl Chloride in the Liquid Phase

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The photochlorination of butyryl chloride in the liquid phase at room temperature has been studied. The progress of the chlorination was followed, the mono- and dichloro products being identified and estimated by GLC as their methyl esters. The isomer distribution has been studied in detail at different stages of chlorination. The main compounds identified in the reaction mixture were substrate until 0.5 h, 3-chlorobutyryl chloride between 0.5 and 2.5 h, 3,4-dichlorobutyryl chloride between 2.5 and 7.5 h, 3,3-dichlorobutyryl chloride between 7.5 and 10.0 h and 4,4-dichlorobutyryl chloride after chlorination for 10.0 h. Polychloro compounds were, however, the main products towards the end of the process.

Earlier studies reported the chlorination of short-chain methyl esters¹ under different conditions and of propionyl chloride² with chlorine in the liquid phase. This paper deals with the chlorination of butyryl chloride in the liquid phase at room temperature giving mono-, di- and polychloro compounds.

Numerous papers have been published on the chlorination of butyryl chloride with various methods.^{3–13} Due to a deficit of chlorinating agent the main products were mostly monochlorobutyryl chlorides. Some papers,^{7,10,12} however, also report the formation of dichlorobutyryl chlorides without a detailed account of the structures that are now reported, probably for the first time.

RESULTS AND DISCUSSION

The chlorination of butyryl chloride was carried out at room temperature by passing dry chlorine through a sample of the neat compound. To follow the progress, a small sample was taken from the reaction mixture every 0.5 h. For gas

chromatographic analysis it was necessary to convert the formed chlorobutyryl chlorides into their methyl esters. The identification of these esters was based on a gas chromatographic analysis. The corresponding reference esters were prepared separately and their structures confirmed by ¹H NMR and ¹³C NMR spectroscopy.

The identified reaction products were 2-chloro- (2), 3-chloro- (3), 4-chloro- (4), 2,2-dichloro- (22), *erythro*-2,3-dichloro- (23*e*), *threo*-2,3-dichloro- (23*t*), 2,4-dichloro- (24), 3,3-dichloro- (33), 3,4-dichloro- (34) and 4,4-dichlorobutyryl chloride (44).

Quantitative analyses of reaction products were performed gas chromatographically using the weight response factors given in Table 1. The factors were determined with an accuracy of $\pm 2\%$ from three independent experiments using an equal weight mixture prepared from reference esters.

Table 1. Weight response factors for methyl butyrate and certain of its chlorinated derivatives.

Compound	Time, s	Response factor ^a
Methyl butyrate	141	0.58
Methyl 2-chlorobutyrate	223	0.72
Methyl 3-chlorobutyrate	248	0.71
Methyl 2,2-dichlorobutyrate	282	1.00
Methyl 4-chlorobutyrate	340	0.72
Methyl 3,3-dichlorobutyrate	340	0.91
Methyl <i>erythro</i> -2,3-dichlorobutyrate	374	1.08
Methyl <i>threo</i> -2,3-dichlorobutyrate	484	1.26
Methyl 4,4-dichlorobutyrate	513	1.11
Methyl 2,4-dichlorobutyrate	561	1.01
Methyl 3,4-dichlorobutyrate	595	1.21

^aRelative to methyl 2,2-dichlorobutyrate.

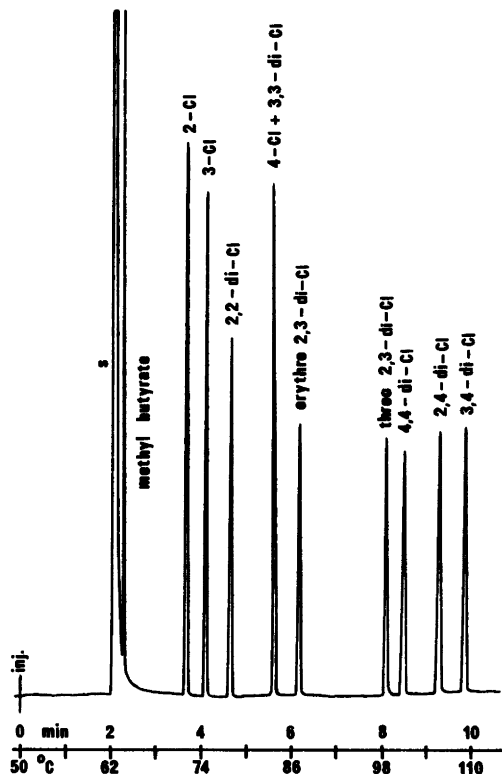


Fig. 1. Gas chromatogram of a standard mixture of methyl butyrate and its mono- and dichloro esters. For operating and other details see the experimental section.

Fig. 1 shows a gas chromatogram of a mixture of methyl butyrate and its mono- and dichloro esters. It can be seen that methyl 4-chlorobutyrate (4-Me) and methyl 3,3-dichlorobutyrate (33-Me) are not separated at all. To get the response factors of these compounds two separate mixtures were made, one excluding 4-Me and the other one 33-Me.

The results from a quantitative analysis of the isomer distribution of mono- and dichlorobutyryl chlorides are presented in Fig. 2. Because of the overlapping of 4-Me and 33-Me the amount of 4, as well as 33, was estimated assuming the amount of 4 to be all the time smaller than that of 3, as in the beginning of the process when the quantity of 33 is minimal.

Butyryl chloride, the starting material, is the main component during the first 0.5 h but disappears in the course of 2.5 h. Monochloro compounds 2, 3 and 4 are the main components between 0.5 and 2.0 h.

After chlorination for 7 h they have almost disappeared.

The distribution of 2:3:4 is approximately 3:50:47. In the chlorination of methyl butyrate¹ the corresponding ratio was 8:50:43. This shows that COCl has a stronger deactivating effect at the 2-position than COOMe. The influence on 3- and 4-positions is insignificant.

The greater reactivities of 3 and 4 compared to 2 quickly increase the amount of a vicinally substituted compound 34. This is the main dichloro compound between 2.5 and 7.5 h, the maximum percentage being as high as 46% after 5.5 h. The reactions leading to geminal dichlorobutyryl chlorides 33 and 44 from 3 and 4 are slower. However, after 7.5 h the amounts of both 33 and 44 exceed that of 34 which easily reacts further to unidentified trichlorobutyryl chlorides. Between 6.0 and 10.0 h the amounts of 33 and 44 are within a few per cent the same but after that the proportion of 33 begins to decrease and the most stable 44 remains.

Due to the sluggish formation of 2, the formation of isomeric dichlorobutyryl chlorides 22, 23 and 24 from 2 is rather insignificant. To form 23 and 24 from 3 and 4 chlorination at the deactivated 2-position is required and therefore the amounts of 23 and 24 only reach levels of 2.4 and 3.1%, respectively.

2,3-Dichlorobutyryl chloride exists as two diastereomers, the *erythro* (23*e*) and *threo* form (23*t*). Both isomers occur among the reaction products. Their mode of formation cannot be stated with certainty because, e.g., *erythro*-2,3-dichlorobutyric acid is isomerized to *threo*-2,3-dichlorobutyric acid by heating with hydrogen chloride. The small total amount of 23*e* and 23*t* points to the formation from 2 rather than from 3.

The amount of tri- and polychloro compounds increases uniformly during the reaction but the identification by GLC is difficult without model compounds. After 8.0 h the total peak area of mono- and dichloro compounds is 32% of the total peak area and after 15.0 h only 1.5%. Bearing in mind that the response factors increase with increasing degree of chlorination, the proportions are, in fact, lower.

The investigations will be continued with the chlorination of monochlorobutyryl chlorides.

EXPERIMENTAL

Materials and methods. Butyryl chloride was obtained by the reaction of benzoyl chloride with

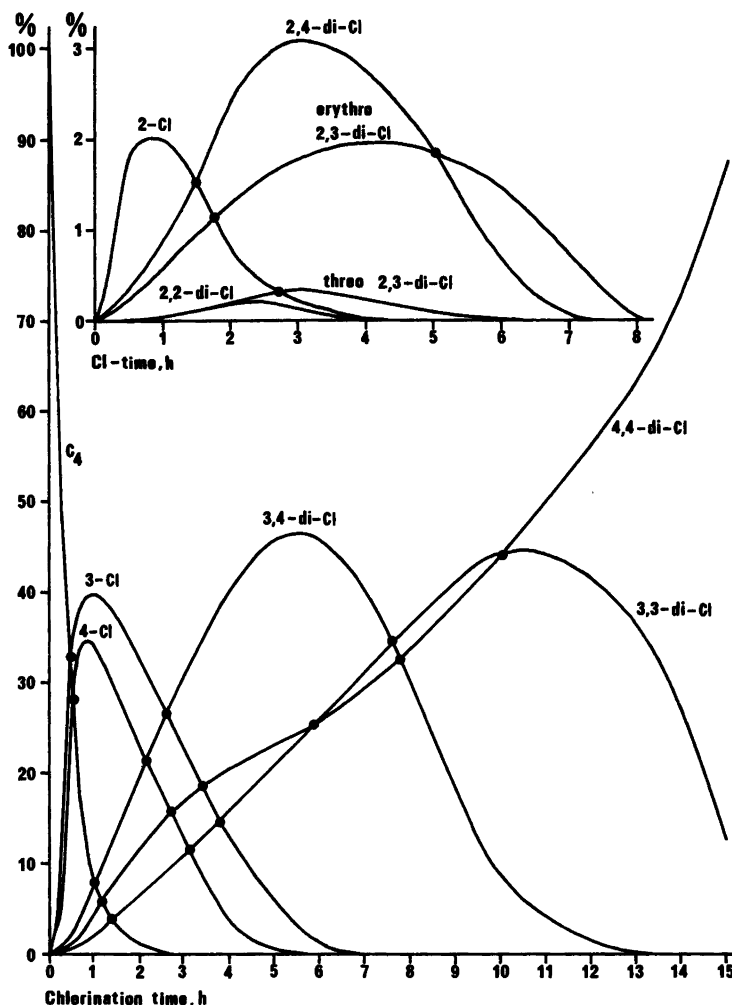


Fig. 2. The isomer distribution for mono- and dichlorobutyryl chlorides during the chlorination of butyryl chloride based on GLC analyses.

butyric acid.¹⁴ Authentic methyl mono- and dichlorobutyrate were prepared as described earlier.^{15,16}

The purities of all compounds were checked by GLC and when required the samples were purified by preparative GLC. The structures of compounds were confirmed by NMR spectroscopy.

Chlorination of butyryl chloride was carried out as described earlier² with the exception that the irradiation was performed with a normal 150 W lamp. On the basis of previous work¹ this lamp and a 125 W UV lamp give identical results. The amount of butyryl chloride was 10.6 g (0.1 mol). Chlorine was

passed through the solution at a rate of about 7 l/h. A 100 μ l sample was taken every 0.5 h and the products esterified with excess methanol before GLC analysis.

GLC analyses were performed on a Varian Model 2400 GC equipped with a flame ionization detector. A 50 m \times 0.3 mm (I.D.) 3% Carbowax 20 M glass capillary column was used with a split ratio of 1:20. The flow rate of N₂ carrier gas was 1.4 ml/min and the chart speed 10 mm/min. The column temperature was programmed from 50 to 110 $^{\circ}$ C at 6 $^{\circ}$ C/min and the recorder was connected to a Perkin-Elmer Model M-2 Calculating Integrator.

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