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Chlorination of 2-Chloro-, 3-Chloro- and 4-Chlorobutyryl Chloride in the Liquid Phase

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Monochlorobutyryl chlorides were chlorinated with chlorine in the liquid phase at room temperature and the products analyzed every 0.5 h by GLC after conversion to their methyl esters. Nearly identical chlorination rates were observed for 3- and 4-chlorobutyryl chloride, the substrates being fully chlorinated after 2.5 h. Dichloro compounds were the main products in the reaction mixture between 0.5 and 3.5 h amounting to over 90 % maximum percentage after 1.5 h. 3,4-Dichloro compound dominated in the beginning of both cases, whereas after 6 h only 3,3- and 4,4-dichloro compounds were identified, the percentage of polychloro isomers being then about 90 %.

The chlorination of 2-chlorobutyryl chloride was slow and after 15 h the quantity of polychloro products is over 95 % but the reaction mixture still contained all dichloro compounds and a small amount of starting material. The main compounds identified were the substrate until 2 h and dichloro products between 2 and 8.8 h. Maximum proportion of dichloro compounds, almost 80 %, was reached after 5 h, the main product being then 2,4-dichloro isomer.

Recently, the chlorination of butyryl chloride has been reported to produce mono-, di- and polychloro isomers.[1] Because some of the dichloro compounds can be formed by two possible pathways this study, concerning the separate chlorinations of 2-, 3- and 4-chlorobutyryl chlorides, was undertaken.

RESULTS AND DISCUSSION

To compare the chlorination rates all three processes were performed simultaneously with identical chlorine feeds. The following compounds were identified: 2,2-dichloro- (*22*), *erythro*-2,3-dichloro- (*23e*), *threo*-2,3-dichloro- (*23t*), 2,4-dichloro- (*24*), 3,3-dichloro- (*33*), 3,4-dichloro- (*34*) and 4,4-dichlorobutyryl chloride (*44*).

The course of chlorinations is illustrated in Fig. 1 as well as the total percentages of di- and polychloro isomers formed. It can be seen that the chlorination rate of 2-chlorobutyryl chloride (*2*) is much slower than that of 3-chloro- (*3*) and 4-chloro isomer (*4*). The latter were fully chlorinated after 2.5 h, whereas traces of *2* could be identified even after 15 h. In the chlorinations of *3* and *4* dichloro isomers were the main compounds between 0.5 and 3.5 h, amounting to over 90 % maximum after 1.5 h. At the end of the processes the proportion of polychloro products exceeded 90 %. Whereas, in the reaction of *2*, dichloro isomers were the chief products between 2 and 8.8 h, reaching to almost 80 % maximum proportion after 5 h. After 15 h the percentage of polychloro compounds was over 95 %.

Fig. 2 illustrates the product distribution in the chlorination of 2-chlorobutyryl chloride (*2*). The chlorine atoms preferably enter a position on the carbon chain as far as possible from the first chlorine substituent, but the chlorination also at the adjacent 3-position seems to be noticeable. However, the reaction leading to a geminal dichloro isomer (*22*) is difficult due to deactivation of the COCl-group. For that reason only 3.5 % maximum percentage for *22* is observed.

The relative quantities for 2-chlorobutyryl chloride (*2*) and its chlorinated derivatives (*22*, *23e*, *23t* and *24*) are given in Table 1, with respect to the 2,4-dichloro isomer (*24*), which is the main dichloro compound during the first 11.5 h. It can be seen that the values of dichloro compounds vary only slightly in the beginning of the process. The ratio *23/24* changes from 0.6 to 6.7 being quite

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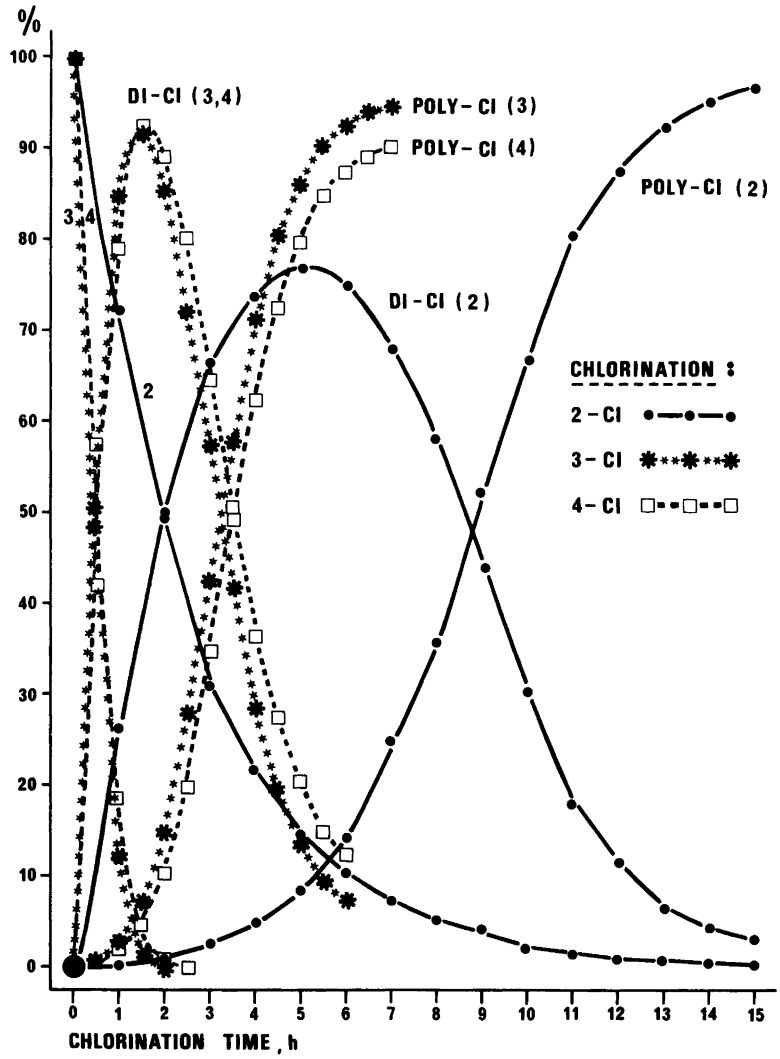

Fig. 1. The chlorination of 2-, 3- and 4-chlorobutyryl chloride. The isomer distribution as a function of reaction time for mono-, di- and polychloro isomers based on GLC analyses after conversion to methyl esters.

constant ~0.7 up till 7 h, after which the amounts of *23* become relatively more abundant due to the easier further chlorination of *24* (Fig. 2).

The quantities of *23e* relative to *23t* vary during the process only slightly, from 4.4 to 5.3, indicating similar behavior towards chlorine. However, the greatest weight response factor[1] of *23t* (1.26) evidences its greater unstability compared to *23e* (1.08) because *e.g.* on a packed column, owing to its longer elution time, *23t* gives a very small peak. Isomerization and dehydrochlorination[2,3] are also possible during the chlorination, the latter forming from *23* as an intermediate 2-chlorocrotonyl chloride, which further reacts with chlorine.

The chlorination processes of 3-chloro- (*3*) and 4-chlorobutyryl chloride (*4*) are illustrated in Fig. 3, *3* being chlorinated slightly faster than *4*. Tables 2 and 3 give the relative quantities for isomers, with

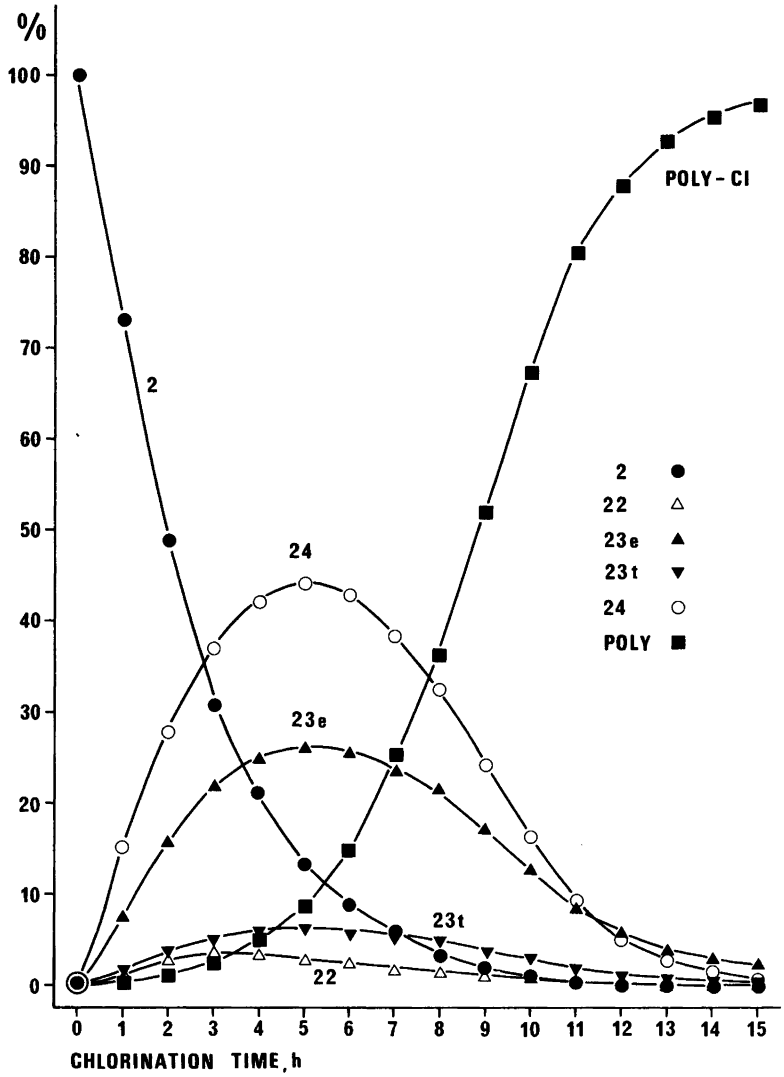

Fig. 2. The isomer distribution for chlorination of 2-chlorobutyryl chloride.

respect to *33* and *44*.

Vicinally substituted compound (*34*) is the main product in chlorinations of *3* and *4* until 1.2 and 1.4 h, respectively, *4* forming *34* slightly easier than *3*. The maximum values 1.4 and 1.6 for ratios *34*/*33* and *34*/*44* are observed. After that the amounts of *33* and *44* become relatively more abundant, the former being the only product identified after 5.5 h and the latter after 6 h.

The maximum percentages about 6.0, 1.0 and 3.5 % for *23e*, *23t* and *24*, respectively, indicate easier chlorination of *3* relative to *4* at the 2-position. As a consequence of that, the %-proportions of *34* are lower in the chlorination of *3*.

From Tables 2 and 3 it can be seen that due to the rapid processes the relative quantities change continuously. Hence, the ratio of formation of dichloro isomers can only be seen in the beginning of

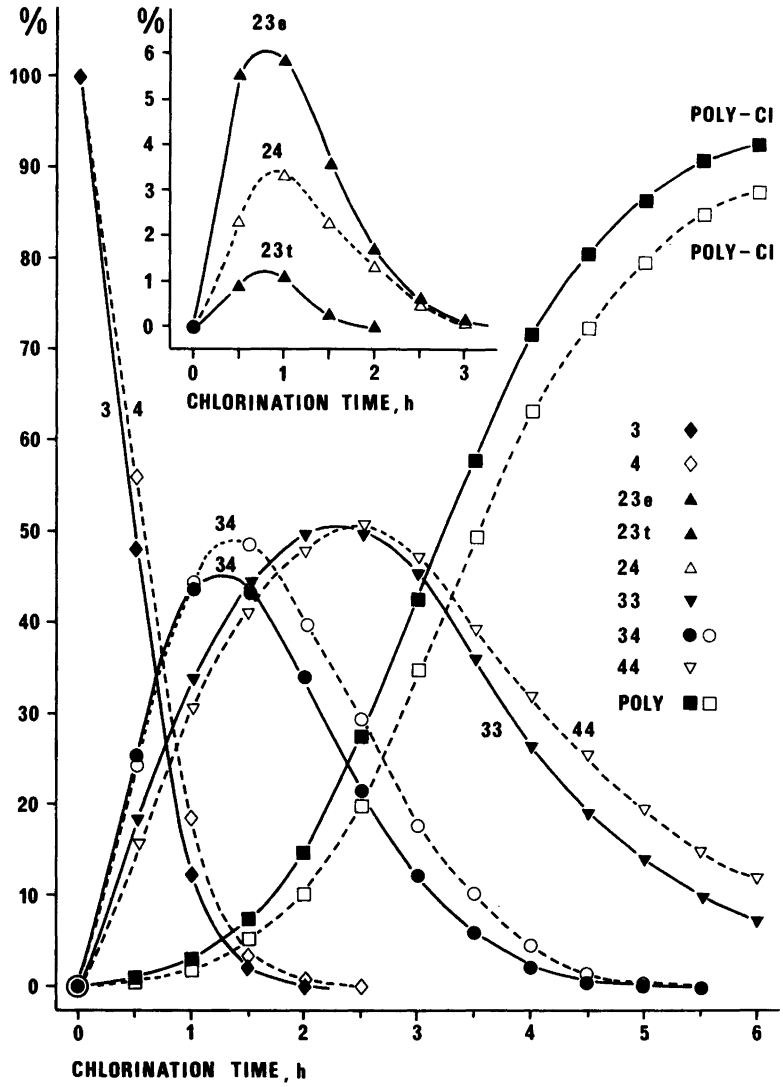

Fig. 3. The isomer distributions for chlorinations of 3-chloro-(——) and 4-chlorobutyryl chloride (– – –).

the chlorinations when the amounts of polychloro products formed are negligible.

EXPERIMENTAL

Materials and methods. Monochlorobutyryl chlorides used as starting materials were prepared in our laboratory and purities checked by GLC after conversion to their methyl esters. The preparations of model samples were carried out as described earlier.[1]

Quantitative analyses were performed gas chromatographically using the running conditions and weight response factors for mono- and dichloro compounds given in Ref. 1. Because the preparation of model samples would have been laborious, an approximate value of 1.5 was used for polychloro isomers.

Table 1. The relative[a] quantities for 2-chlorobutyryl chloride and its chlorinated derivatives.

Chlorination time, h	Compound					
	2	*22*	*23e*	*23t*	*24*	Poly-Cl
1	4.84	0.09	0.54	0.11	1.00	0.03
2	1.74	0.10	0.57	0.13	1.00	0.06
3	0.82	0.09	0.59	0.13	1.00	0.07
4	0.52	0.08	0.58	0.13	1.00	0.12
5	0.30	0.06	0.59	0.13	1.00	0.20
6	0.21	0.06	0.60	0.13	1.00	0.34
7	0.15	0.05	0.61	0.14	1.00	0.66
8	0.10	0.05	0.67	0.15	1.00	1.11
9	0.08	0.04	0.71	0.15	1.00	2.15
10	0.05	0.04	0.79	0.17	1.00	4.17
11	0.05	0.04	0.95	0.21	1.00	9.38
12	0.04	0.04	1.13	0.22	1.00	16.8
13	0.03	0.03	1.48	0.30	1.00	34.2
14	0.02	0.02	2.23	0.54	1.00	73.1
15	0.01	0.01	6.67	2.00	1.00	324

[a] Relative to the 2,4-dichlorobutyryl chloride (*24*).

The chlorinations of monochlorobutyryl chlorides were carried out at room temperature on a water bath as described earlier[1] using equal amounts of starting materials (0.05 mol). The processes were performed parallel to identical chlorine feed rates (7 l/h) by dividing the chlorine stream into three identical portions. Hence, chlorine concentrations in the three reaction vessels are supposed to be the same.

Table 2. The relative[a] quantities for 3-chlorobutyryl chloride and its chlorinated derivatives.

Chlorination time, h	Compound					
	3	*23e*	*23t*	*33*	*34*	Poly-Cl
0.5	2.58	0.30	0.05	1.00	1.37	0.05
1.0	0.36	0.17	0.03	1.00	1.29	0.09
1.5	0.03	0.08	0.01	1.00	0.99	0.16
2.0	0.01	0.03		1.00	0.69	0.29
2.5		0.02		1.00	0.43	0.62
3.0		0.01		1.00	0.26	0.94
3.5				1.00	0.16	1.60
4.0				1.00	0.08	2.68
4.5				1.00	0.03	4.24
5.0				1.00	0.01	6.19
5.5				1.00		9.53
6.0				1.00		12.5

[a] Relative to the 3,3-dichlorobutyryl chloride (*33*).

Table 3. The relative[a] quantities for 4-chlorobutyryl chloride and its chlorinated derivatives.

Chlorination time, h	Compound				
	4	*24*	*34*	*44*	Poly-Cl
0.5	2.03	0.10	1.61	1.00	0.02
1.0	0.59	0.10	1.38	1.00	0.06
1.5	0.08	0.06	1.19	1.00	0.12
2.0	0.02	0.03	0.83	1.00	0.21
2.5		0.01	0.58	1.00	0.40
3.0			0.37	1.00	0.74
3.5			0.29	1.00	1.26
4.0			0.13	1.00	1.96
4.5			0.06	1.00	2.80
5.0			0.03	1.00	3.98
5.5				1.00	5.67
6.0				1.00	7.00

[a] Relative to the 4,4-dichlorobutyryl chloride (*44*).

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