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GAS–LIQUID CHROMATOGRAPHIC ANALYSES OF CHLORINATION PRODUCTS OF PROPIONYL CHLORIDE

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SUMMARY

Photochlorination of propionyl chloride with chlorine in the liquid phase at room temperature gives all eleven chloropropionyl chlorides from the mono-to the pentachloro isomer. The process was investigated every 2 h by gas–liquid chromatography, and the products were identified and estimated as their methyl esters by comparison with model compounds. The isomer distribution of the products was studied in detail. Because the process favours the 3-position, the main components were 3-chloropropionyl chloride up to 15 h, 3,3-dichloropropionyl chloride between 15 and 29 h, 3,3,3-trichloropropionyl chloride between 29 and 56 h and pentachloropropionyl chloride after 56 h of chlorination.

INTRODUCTION

A large number of investigations have been made of the relative reactivities of carbon–hydrogen bonds in carboxylic acids and their derivatives towards chlorination agents. For example, the chlorination of propionic acid and its derivatives has been studied with respect to the catalyst[1,2], temperature[3,4] and solvent effects[5–8].

In almost all cases the products were monochloro derivatives owing to the minor amounts of chlorination agents and short chlorination times employed. Only the studies described in ref. 2 and 7 have also given dichloro products.

The chlorination of methyl esters of propanoic, butanoic, pentanoic and hexanoic acids has recently been reported[9]. Methyl propionate gives 2- and 3-chloro isomers as well as chloromethyl propionate as a side product. The continuation of this process would produce di- and polychloro derivatives of these compounds. Without model samples the identification of chlorinated chloromethyl isomers is difficult and for this reason they were eliminated by using propionyl chloride as the starting material.

The chlorination of propionic acid would also give the same products, but the accurate determination of isomer distributions by gas–liquid chromatography (GLC) would be impossible because of the incomplete esterification of higher chlorinated propionic acids[2] by the usual esterification methods.

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EXPERIMENTAL

GLC analyses

The GLC analyses of the chlorinated methyl propionates (12–22) were achieved with a Varian Model 2400 gas chromatograph equipped with a flame ionization detector, an automatic integrator connected with a printer, a glass capillary column (90 ft. × 0.012 in. I.D.) containing 5% Carbowax 20M with a carrier gas (nitrogen) flow-rate of 1 ml/min. Temperatures: injector, 200°C; detector, 220°C; column programmed from 50°C to 140°C at 6°C/min. The splitting ratio was 1:20, sensitivity 8×10^{-12} and chart speed 10 mm/min. The elution order, times and weight response correction factors for methyl chloropropionates are in Table I.

TABLE I

WEIGHT RESPONSE CORRECTION FACTORS FOR METHYL CHLOROPROPIONATES

Weight response correction factor. by using a known mixture of esters, it was possible to calculate an area response factor for the separate components on an equal weight basis. By a assigning a factor of 1.00 to 3,3,3-trichloropropionate, a series of relative response factors was calculated. The found area for a given peak is multiplied by the correction factor to obtain the corrected weight percent area. All weight response correction factors are the averages of the results of three independent experiments, agreeing within ±2%. They were determined by GLC; for operating and other details see the Experimental section. RRT = relative retention time.

Methyl chloropropionate	*Parameter*		
	Time (sec)	*RRT*	*Factor*
2-Chloropropionate	195	0.44	0.49
2,2-Dichloropropionate	218	0.49	0.63
3-Chloropropionate	269	0.60	0.51
3,3-Dichloropropionate	348	0.78	0.65
2,3-Dichloropropionate	407	0.91	0.81
3,3,3-Trichloropropionate	448	1.00	1.00
2,2,3-Trichloropropionate	488	1.09	0.94
2,3,3-Trichloropropionate	533	1.19	0.98
2,3,3,3-Tetrachloropropionate	594	1.33	1.13
2,2,3,3-Tetrachloropropionate	648	1.45	1.09
Pentachloropropionate	749	1.67	1.26

Chlorination

Photochlorination of propionyl chloride was carried out at room temperature in the liquid phase by bubbling chlorine through the stirred propionyl chloride solution (0.25 mol, 23.0 g). The chlorine gas was dried with concentrated H_2SO_4, the latter solution having been deoxygenated by passage of dry nitrogen. The reaction was accomplished by irradiation with a Philips HPK 125-W mercury lamp. The chlorine flow-rate was about 20–30 ml/min. The progress of the chlorination was monitored by GLC by taking a 100-μl sample from the reaction mixture every 2 h. The acid chlorides were converted into the methyl esters with a small excess of absolute methanol. When the esterification was complete, liberated hydrogen chloride was removed by bubbling dry nitrogen gas through the sample, after which the products were analysed by GLC. Because of the long chlorination time the reaction was stopped several times and for this reason the chlorine flow-rate varied to some extent. The results are plotted in Fig. 3.

Samples

Propionyl chloride was obtained by the reaction of benzoyl chloride with propionic acid[10]. The purity of the substrate was established to be higher than 99% by GLC analysis (a packed column) of its methyl ester.

The methyl esters of chloropropionic acids were obtained as follows: methyl 2-chloropropionate (12) by esterification of 2-chloropropionyl chloride[11] with methanol; methyl 3-chloropropionate (13) from commercial methyl acrylate (Fluka, Buchs, Switzerland) with hydrogen chloride[12]; methyl 2,2-dichloropropionate (14) from the corresponding acid[13]; methyl 2,3-dichloropropionate (15) from commercial methyl acrylate (Fluka) with chlorine[14]; methyl 3,3-dichloropropionate (16) from the corresponding acid[15] by esterification; methyl 2,2,3-trichloropropionate (17) from methyl 2-chloroacrylate[16] with chlorine[14]; methyl 2,3,3-trichloropropionate (18) from methyl 3-chloroacrylate[12] with chlorine[14]; methyl 3,3,3-trichloropropionate (19) by esterification of the corresponding acid[17]; methyl 2,2,3,3-tetrachloropropionate (20) from methyl 2,3-dichloroacrylate[18] with chlorine[14]; methyl 2,3,3,3-tetrachloropropionate (21) according to Laato and Mäkinen[15]; methyl pentachloropropionate (22) from trichloroacrylic acid[19] according to Laato and Hautoniemi[17].

Methyl esters of chloroacrylic acids were obtained as follows: methyl 2-chloroacrylate (23) by dehydrochlorination[16] of methyl 2,3-dichloropropionate[14]; methyl 3-chloroacrylate (*cis* and *trans*) (24) from methyl propiolate (Fluka) and hydrogen chloride[12]; methyl 2,3-dichloroacrylate (*cis* and *trans*) (25) by chlorination[18] of methyl propiolate (Fluka); methyl 3,3-dichloroacrylate (26) from the corresponding acid[20] by esterification; methyl trichloroacrylate (27) from trichloroacrylic acid[19] by esterification.

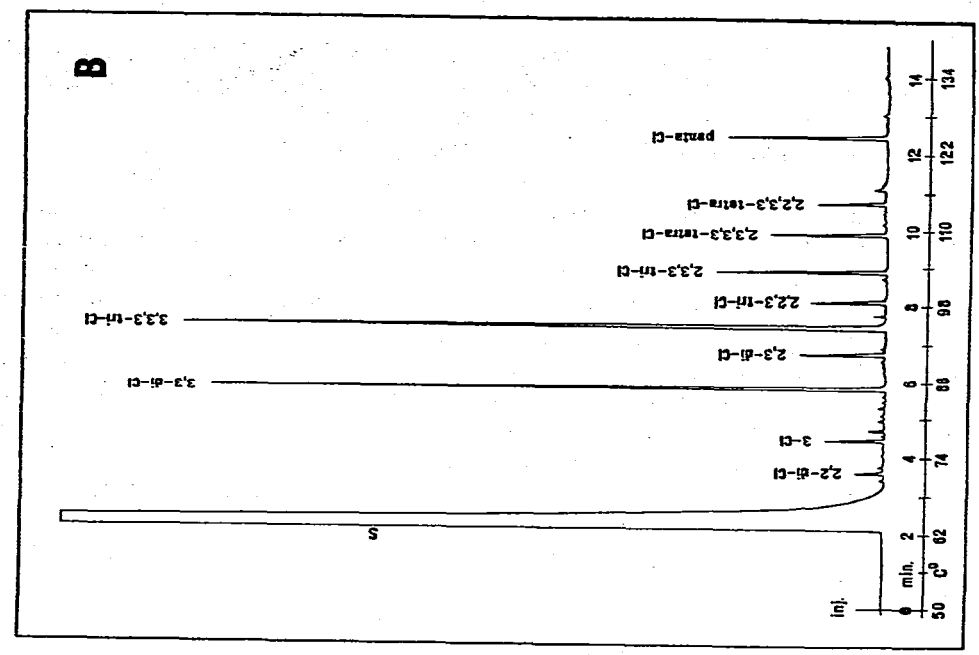
Before ^{1}H NMR analyses, all products were analysed by GLC and when required they were purified by preparative GLC on a column (10 ft. × 3/8 in. O.D.) packed with 10% Carbowax 20M on Chromosorb W (60–80 mesh) using a Perkin-Elmer F 21 instrument with a carrier gas (nitrogen) flow-rate of 100 ml/min.

RESULTS AND DISCUSSION

The photochlorination of propionyl chloride was carried out at room temperature without diluent because of the long time required, 180 h. All eleven possible chloropropionyl chlorides were obtained: 2-chloro- (1); 3-chloro- (2); 2,2-dichloro- (3); 2,3-dichloro- (4); 3,3-dichloro- (5); 2,2,3-trichloro- (6); 2,3,3-trichloro- (7); 3,3,3-trichloro- (8); 2,2,3,3-tetrachloro- (9); 2,3,3,3-tetrachloro- (10) and pentachloropropionyl chloride (11). Negligible amounts of chloroacryloyl chlorides, as a result of dehydrochlorination of compounds 3–10, as well as unidentified products were formed particularly towards the end of the process.

The products (1–11) as well as chloroacryloyl chlorides were analysed by GLC as their methyl esters (12–27). The esterification of the acid chlorides was assumed to be complete in the presence of an excess of methanol. GLC analyses were achieved with a glass capillary column using a temperature programme that leads to short analysis times and narrow peaks. Gas chromatograms of a standard mixture and of chlorination products are illustrated in Fig. 1.

The weight response correction factors for compounds 12–22 (Table I) were determined from an equal weight mixture using methyl 3,3,3-trichloropropionate (19) as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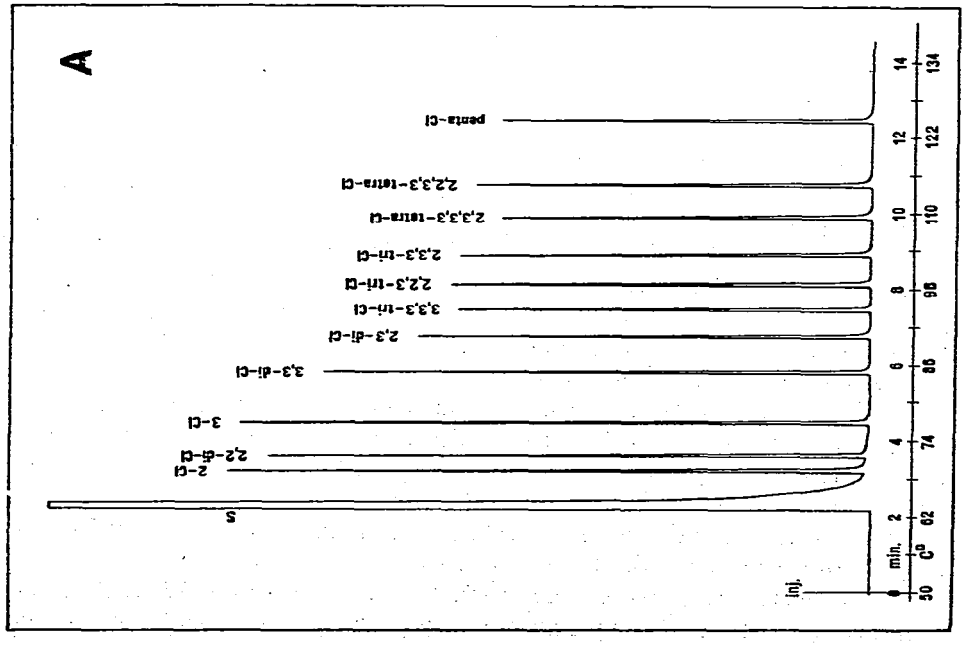
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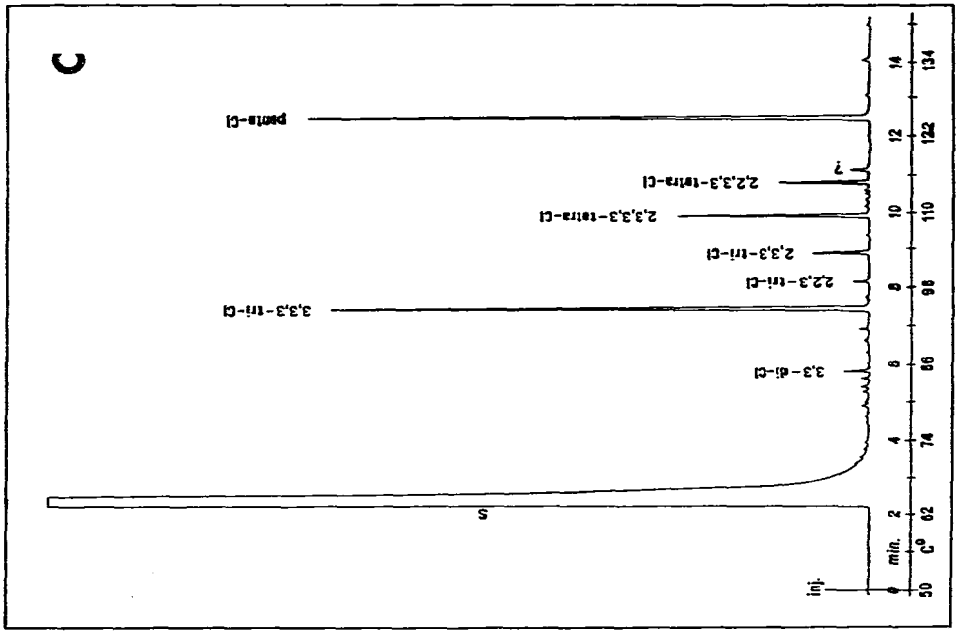

Fig. 1. Gas chromatograms of a standard mixture of methyl chloropropionates (A) and of the chlorination products of propionyl chloride (converted into the methyl esters) after 32 (B) and 64 h (C). S = Solvent. For operating and other details see the *Experimental* section.

a standard compound because of its medium retention time. As expected, monochloro compounds have the smallest factors and the pentachloro compound the largest. The relatively high value for methyl 2,3-dichloropropionate (15) compared with 14 and 16 may arise from its instability. The ready cleavage of hydrogen chloride from 15, particularly in a packed column, results in formation of methyl 2-chloroacrylate (23).

Fig. 2 illustrates the chlorination process of propionyl chloride and in Fig. 3 the isomeric distribution of the products is presented. In this case it was impossible to determine by GLC the quantities of unreacted substrate because in a glass capillary column the solvent and methyl propionate overlap each other and in a packed column methyl propionate and excess of methanol are not resolvable. However, from Fig. 3 it seems that no starting material is left in the reaction mixture after 20 h, when the amounts of monochloro compounds formed are quite small.

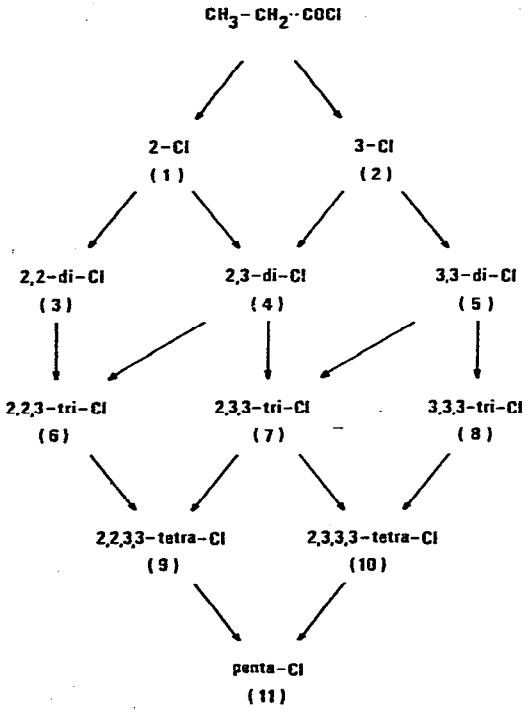

Fig. 2. The chlorination process of propionyl chloride.

It is well known that chlorine atoms attack hydrogen atoms more readily in the order: tertiary > secondary > primary hydrogen. Owing to the deactivation by the COCl group in propionyl chloride, the primary hydrogen is more readily substituted than the secondary one because of the lower electron density at the 2-position[7]. The chlorination of propionyl chloride is assumed to be a radical process in which the ease of hydrogen abstraction determines the relative amounts of the monochlorosubstitution products[8]. During the first 15 h the monochloro compounds 1 and 2 were the main products the ratio of 3-Cl : 2-Cl varying between 3.4 and 4.3, being smallest at the beginning of the process. In the case of methyl propionate[9], this ratio was 2.0,

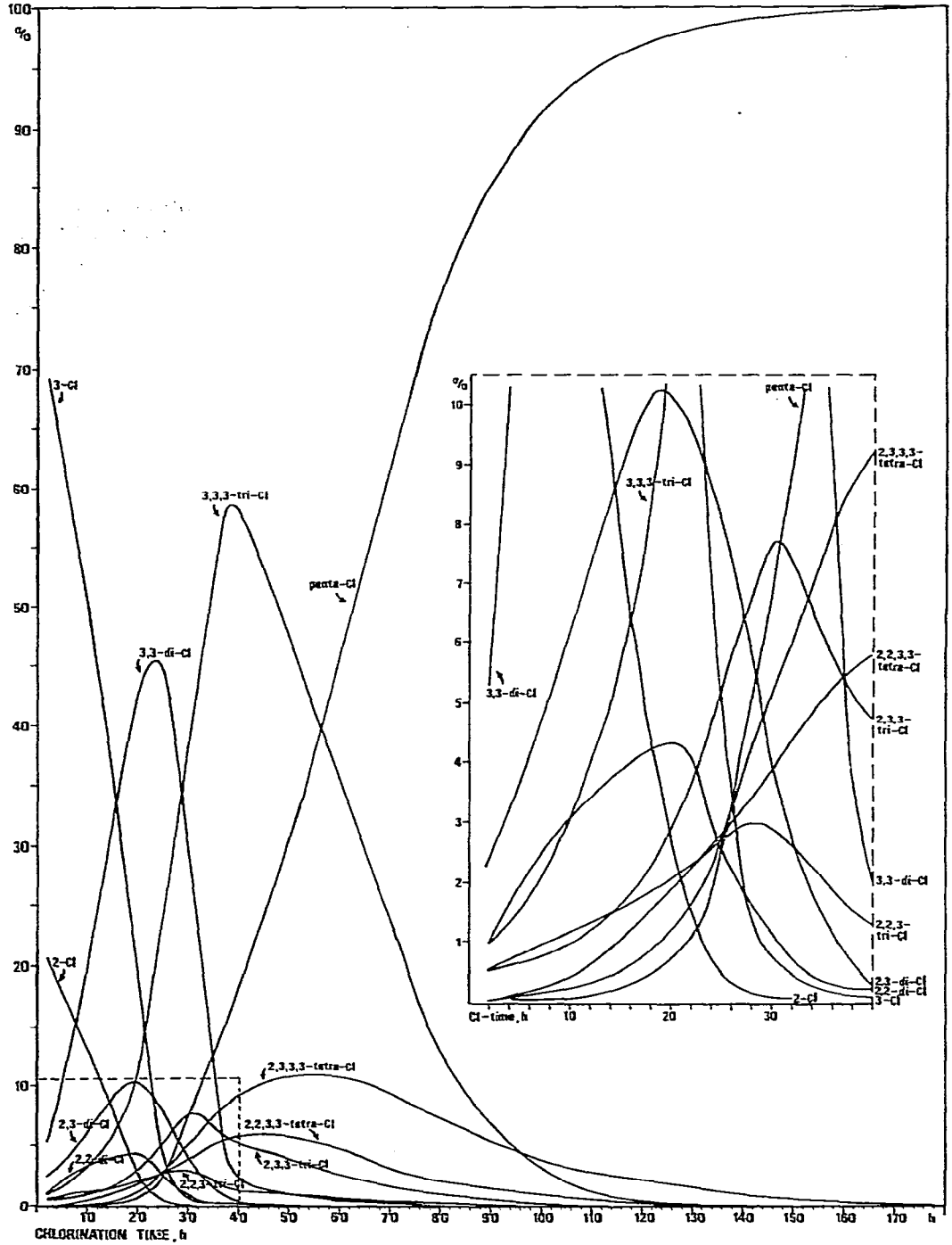

Fig. 3. Isomer distribution of the chlorination products of propionyl chloride at different stages of chlorination. Analysed by GLC.

indicating that the methoxy group has a smaller deactivating effect on the 2-position than the COCl group.

Continued chlorination gives di- and polychloro compounds but the substitution of successive chlorine atoms becomes more difficult, slowing the chlorination process. Of the dichloropropionyl chlorides (3–5), only the 2,3-dichloro compound (4) can be formed by two pathways (Fig. 2). Because the chlorination favours the 3-position, 1 gives 4 rather than 3. Further, because the ratio of compound 4 to 3 varies at the beginning of the chlorination between 1.9 and 2.4, being a maximum when the quantities of 3 and 4 are greatest (Fig. 3), the greater portion of 4 formed must arise from 1 rather than from 2. However, if the relatively small amount of 4 is a consequence of its instability, the more abundant 3-chloro isomer (2) might also produce a greater portion of 4. This instability would explain why the chlorinations of propionic acid[2,7] did not give the 2,3-dichloro compound.

In general, the formation of a geminal dichloro compound is difficult and a second chlorine atom tends to enter a position on the carbon chain as far removed from the first chlorine substituent as possible[1]. However, the 3,3-dichloro isomer (5) is the main component in the process after between 15 and 29 h, amounting to a maximum of 46% after 24 h. This can be explained only by the strong deactivating effect of the COCl group.

From Fig. 3 it is seen that 3,3,3-trichloropropionyl chloride (8) is the main product after between 29 and 56 h, reaching its maximum near 60% after 38 h. The quantities of the two other trichloro compounds (6 and 7) are small, that of 2,2,3-trichloropropionyl chloride (6) being smallest owing to the low contents of its parent compounds (3 and 4). Further chlorination of tri- and tetrachloropropionyl chlorides is very slow, particularly in the cases of 8 and 10, and a reaction time of 64 h is needed to reach a 50% level for pentachloropropionyl chloride (11), which amounts to over 90% after 100 h.

Because some products have two parent compounds and some parents produce two products, which in turn are chlorinated, a more thorough evaluation of the chlorination process would demand a separate chlorination of each intermediate followed by a product analysis.

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