Anal. Calcd. for $C_{17}H_{30}O$: C, 81.53; H, 12.08. Found: C, 81.62; H, 12.35.

The infrared spectrum showed the presence of an unconjugated carbonyl (infrared$_{max}$ 5.85 μ) and double bond absorption (infrared$_{max}$ 6.11 μ) with no hydroxyl hydrogen absorption. The ultraviolet absorption spectrum likewise showed no conjugated carbonyl.

Identification of 2,3,4,4,7,7,8,9-Octamethyl-5-hydroxy-6-keto-2,8-octadiene (XII).—The last fraction (5.0 g.) was also fractionated. From this distillation a sample composed of fractions of constant index of refraction was obtained, b.p. 175° (0.2 mm., bath temperature), n^{25}D 1.4825. It had a light yellow color.

Anal. Calcd. for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.30; H, 11.28.

An infrared spectrum of this fraction showed the following maxima: 2.95 μ for hydroxyl hydrogen, 5.86 μ for carbonyl absorption, and double bond absorption at 6.21 μ. Inflections and shoulders in the curve indicated that small amounts of contaminants were present. Thus widening of the carbonyl band at 5.8 μ and oxygen-linked carbon absorption at 9.1 μ can be explained as carboxyl absorption, while a slight inflection at 5.95 μ may be due to dicarbonyl absorption. Quantitatively, these impurities were present in very minor amounts, and could not be isolated.

INDIANAPOLIS, INDIANA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF PURDUE UNIVERSITY AND OF WAYNE UNIVERSITY]

Isomer Distribution in the Sulfuryl Chloride Chlorination of the 1-Chlorobutanes and Related Compounds; the Inductive Effect in Free Radical Substitutions[1]

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The peroxide-catalyzed reaction of 1-chlorobutane with sulfuryl chloride results in the formation of 7% 1,1-, 22% 1,2-, 47% 1,3- and 24% 1,4-dichlorobutane. The similar chlorination of 1,1-dichlorobutane results in 2, 13, 48 and 37% substitution in the 1-, 2-, 3- and 4-positions respectively. The preference for substitution in positions remote from the substituents is accentuated further in 1,1,1-trichlorobutane. In this compound substitution occurs 8, 42 and 50% in the 2-, 3- and 4-positions, respectively. The distribution in *n*-butyryl chloride—3% α-, 49% β- and 48% γ-—suggests that the $-COCl$ and $-CCl_3$ groups are quite similar in their effect in directing further substitution in the aliphatic chain. Sulfuryl chloride chlorination of *n*-propyl acetate results in 25% 1-, 46% 2- and 29% 3-monochloro derivatives. Photochemical chlorination under similar conditions yields 23% 1-, 42% 2- and 35% 3-. It is concluded that the acetoxy group is similar to the $ClCH_2C-$ group in directing chlorination. The following order of influence in directive effects is indicated: $C_6H_5- > CH_3- > H- > ClCH_2- > CH_3CO_2- > Cl_2CH- > Cl_3Si- > HO_2C- > Cl_3C- > ClOC- > Cl_2{=} > Cl_3{\equiv} > F_3C- > F_3{\equiv}$. It is concluded that the inductive effect must play a very important role in directing attack by a chlorine atom at the different available positions along a hydrocarbon chain.

The chlorination of aliphatic hydrocarbons in the vapor phase[4] or in the liquid phase by either chlorine and light[4,5a] or sulfuryl chloride and peroxide[5a,b] indicates that aliphatic carbon–hydrogen bonds have reactivities in the order, primary < secondary < tertiary, the selectivity decreasing with increasing temperature. Further substitution of chlorine in an alkyl chloride by photochlorination or sulfuryl chloride chlorination as well as in thermal chlorination has been observed to occur preferentially at carbon–hydrogen bonds remote from the chlorine substituent.[5b–7]

In order to obtain additional quantitative data on the effect of chlorine substituents in directing further substitution under liquid phase conditions, we have studied the sulfuryl chloride chlorination of 1-chloro-, 1,1-dichloro- and 1,1,1-trichlorobutane. In the course of the investigation it proved desirable to examine also the operation of directive effects in the chlorination of *n*-propyl acetate and *n*-butyryl chloride.

Results

The chlorination of the 1-chlorobutanes was carried out in the liquid phase using sulfuryl chloride with peroxide catalyst as the chlorinating agent.[5] After preliminary studies, experiments were performed on each compound, using 5 or 10 moles of the chlorohydrocarbon to each mole of the chlorinating agent. In this way the formation of higher chlorides usually was maintained below 5% of the total chlorination product. The reactions proceeded readily under reflux. The reaction temperature was maintained in the range 80 ± 10° by control of the heating and addition of carbon tetrachloride as a diluent in cases where that was required.

The reaction products were isolated by fractional distillation and carefully analyzed from boiling point and refractive index data, supplemented by other means where necessary. With the exception of 1-chloro-, 1,4-dichloro- and 1,1,1,3-tetrachlorobutane, which were obtained from other sources, all of the chlorobutanes referred to in this work either were synthesized independently or isolated from the reaction products in pure form.

Chlorination of 1-Chlorobutane.—Of the four possible monochlorination products, 1,1-dichlorobutane was prepared in 39% yield by the reaction of phosphorus pentachloride with butyraldehyde,[8] 1,2- and 1,3-dichlorobutane were isolated in pure form by fractional distillation of the proper center fractions from the chlorination of 1-chlorobutane,

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[1] Directive Effects in Aliphatic Substitutions. II.

[2] This paper is abstracted from a thesis submitted by Arthur B. Ash to Wayne University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] General Motors Corporation Fellow at Wayne University, 1945–1947.

[4] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

[5] (a) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031 (1955); (b) M. S. Kharasch and H. C. Brown, *ibid.*, **61**, 2142 (1939).

[6] D. V. Tishchenko and A. Churbakov, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 658, 897 (1937); *C. A.*, **131**, 5755 (1937); D. Tishchenko and N. Zhokhovets, *ibid.*, **18**, 43 (1948); *C. A.*, **43**, 2925 (1949).

[7] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **5**, 449 (1940); F. F. Rust and W. E. Vaughan, *ibid.*, **6**, 479 (1941).

[8] A. L. Henne and J. B. Hinkamp, THIS JOURNAL, **68**, 1197 (1946).

and 1,4-dichlorobutane was commercially available. Refractive index and boiling point data were obtained on these compounds for analytical purposes inasmuch as the reported values exhibited considerable variation.

Four preliminary experiments were performed, each using five moles of sulfuryl chloride and mole fractions of 1-chlorobutane to sulfuryl chloride of 1:1, 1.5:1 (two experiments), and 2:1. The reaction products were rectified in a 22-plate all-glass column and analyzed by utilizing the boiling point and refractive index values of the individual fractions. The average values of percentage substitution for the four experiments were 7, 23, 46 and 24% for the 1-, 2-, 3- and 4-positions, respectively, of the 1-chlorobutane molecule, with an average mean deviation of about 1% (maximum deviation 1.4%).

A large scale experiment was then performed in which a total of 50 moles of 1-chlorobutane reacted with 10 moles of sulfuryl chloride. The results were nearly identical with those obtained in the small-scale experiments, *viz.*, 7, 22, 47 and 24% expressed as percentage for the 1-, 2-, 3- and 4-positions of the 1-chlorobutane molecule. These results are in substantial agreement with the earlier data reported by Tischenko and Churbakov[6] and Kharasch and Brown.[5b]

Chlorination of 1,1-Dichlorobutane.—To obtain accurate physical data, three of the four monochlorination products of 1,1-dichlorobutane were synthesized. As one of these, 1,1,1-trichlorobutane, was desired also for subsequent chlorination studies, its synthesis was studied in some detail. It was prepared by two routes, both by way of the intermediate 1,1,2-trichlorobutane. The less attractive procedure involved the dehydrochlorination of 1,1-dichlorobutane with solid sodium hydroxide to form 1-chloro-1-butene, followed by addition of chlorine to form 1,1,2-trichlorobutane.[5]

An improved procedure for the preparation of the intermediate 1,1,2-trichlorobutane involved the formation of the hitherto unreported α-chlorobutyraldehyde in 79% yield by the addition of sulfuryl chloride to butyraldehyde in methylene chloride solution at 15–25°. α-Chlorobutyraldehyde is moderately stable. It could be isolated by distillation of the reaction product at atmospheric pressure. The α-chlorobutyraldehyde was converted readily to 1,1,2-trichlorobutane in 58% yield by reaction with phosphorus pentachloride.

1,1,2-Trichlorobutane was dehydrochlorinated by refluxing with 20% aqueous sodium hydroxide to form 1,1-dichloro-1-butene in 75–80% yield. This olefin was converted in 85–90% yield to 1,1,1-trichlorobutane by the aluminum chloride-catalyzed addition of hydrogen chloride in methylene chloride solution at −30°. The reaction temperature of 5 to 10°, recommended for the addition of hydrogen chloride to 1,1-dichloro-1-propene,[9] was unsuitable since 1,1,1-trichlorobutane proved to be unstable to aluminum chloride at this temperature and decomposed to tars and hydrogen chloride. 1,1,1-Trichlorobutane also may be prepared by the addition of chloroform to propylene in the presence of peroxide catalysts.[10] A sample of the compound prepared by this procedure, supplied by Dr. Frank R. Mayo, proved to be identical in all respects with the material prepared by the addition of hydrogen chloride to 1,1-dichloro-1-butene.

1,1,3-Trichlorobutane was prepared in 50% yield by the addition of hydrogen chloride to crotonaldehyde to form 3-chlorobutyraldehyde, followed by the immediate reaction of the product with phosphorus pentachloride. 1,1,4-Trichlorobutane was isolated readily as the highest boiling isomer of the monochlorination product of 1,1-dichlorobutane.

A total of 48.2 moles of 1,1-dichlorobutane was treated with 9.64 moles of sulfuryl chloride and the reaction products were rectified carefully at atmospheric pressure through a 22-plate column. The individual fractions were analyzed by boiling point and refractive index data. Refractive index calibration curves were employed for the mixture of 1,1,2- and 1,1,3-trichlorobutane which boil very close to each other and were not separated in the fractionation. The analysis was confirmed by treating the mixture of 1,1,2- and 1,1,3-trichlorobutanes with 20% aqueous sodium hydroxide under reflux. Under these conditions the 1,1,3-isomer was not affected, whereas the 1,1,2-isomer was converted into 1,1-dichloro-1-butene, which could be isolated by fractional distillation.

The results showed that the chlorination of 1,1-dichlorobutane proceeds with 2, 13, 48 and 37% substitution in the 1-, 2-, 3- and 4-positions, respectively.

Chlorination of 1,1,1-Trichlorobutane.—1,1,1,2-Tetrachlorobutane was prepared by the addition of chlorine to 1,1-dichloro-1-butene. 1,1,1,3-Tetrachlorobutane was obtained from the Battelle Memorial Institute where it had been prepared by the addition of carbon tetrachloride to propylene in the presence of a peroxide catalyst.[11] 1,1,1,4-Tetrachlorobutane was isolated as the highest boiling isomer of the monochlorination products of 1,1,1-trichlorobutane.

Two duplicate chlorinations of 1,1,1-trichlorobutane were made. In each experiment, a total of 7.5 moles of 1,1,1-trichlorobutane was treated with 0.75 mole of sulfuryl chloride, using 7.5 moles of carbon tetrachloride as a diluent. After removal of the carbon tetrachloride and excess 1,1,1-trichlorobutane, the tetrachlorobutanes were fractionally distilled at 20 mm. through a 15-plate packed column. Two plateaus were observed, the first comprising a mixture of the close-boiling 1,1,1,2- and 1,1,1,3-tetrachlorobutanes, and the second, 1,1,1,4-tetrachlorobutane. In the two studies, the total tetrachlorides weighed 130.7 and 130.4 g., and the higher chlorination products weighed 5.4 and 5.7 g., respectively.

Boiling point and refractive index data indicated that the combined 1,1,1,2- and 1,1,1,3-tetrachlorobutanes were present to the extent of 65 ± 2 g. or 50 ± 3%. Refractive index measurements indicated that 4% of 1,1,1,2-tetrachlorobutane was formed. Infrared examination of this fraction, using known mixtures of the 1,1,1,2- and 1,1,1,3-

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[9] A. A. Levine and O. W. Cass, U. S. Patent 2,134,103 (May 13, 1938); see also A. L. Henne and M. Whaley, THIS JOURNAL, **64**, 1157 (1942).

[10] F. M. Lewis and F. R. Mayo, *ibid.*, **76**, 457 (1954).

[11] M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

isomers as standards, indicated that 8 to 10% of 1,1,1,2-tetrachlorobutane had been formed in the chlorination. This figure was also indicated by density measurements. From these results the percentage substitution is estimated to be 8, 42 and 50% for the 2-, 3- and 4-positions of the 1,1,1-trichlorobutane molecule with an estimated uncertainty of 3% in the relative values of the 2- and 3-substitution quantities.

Chlorination of *n*-Butyryl Chloride.—It was of interest to compare the effect of the –COCl group with that of the $-CCl_3$ group in directing substitution in the n-C_3H_7 chain. Accordingly, a study of the chlorination of *n*-butyryl chloride was undertaken.

Preliminary experiments on the sulfuryl chloride chlorination of butyryl chloride uncovered a number of difficulties in obtaining precise data in this system. Commercial *n*-butyryl chloride as well as *n*-butyryl chloride prepared by the use of thionyl chloride reacted only very slowly with sulfuryl chloride in the presence of benzoyl peroxide, even after exhaustive fractionation in a 40-plate column. *n*-Butyryl chloride prepared from the reaction of *n*-butyric acid and benzoyl chloride[12] reacted much more readily with the chlorinating agent and this material therefore was utilized for these studies.

In certain of the initial experiments it was observed that the yield of the α-isomer varied considerably from experiment to experiment, with yields as high as 35% being realized in some experiments. The varying yields suggested that an ionic mechanism leading to the preferred formation of the α-isomer was competing with the free radical–chlorine atom chain mechanism with a preference for substitution in the β- and γ-positions.

To eliminate this ionic reaction, the sulfuryl chloride was distilled in scrupulously clean glass apparatus, carefully protected from exposure to atmospheric moisture. The glass chlorination equipment was carefully cleaned with hot mineral acids, alcoholic potassium hydroxide, washed with distilled water, thoroughly dried and protected from atmospheric moisture until completion of the experiment. Carbon tetrachloride was used as a diluent to facilitate the elimination of hydrogen chloride and sulfur dioxide, as well as maintain the reaction temperature at approximately 90°. With these precautions the yield of the α-isomer dropped to 3%.

One further difficulty was encountered. When the chlorination product was directly distilled, crotonyl chloride was observed, in addition to the three isomeric monochlorobutyryl chlorides. However, when the reaction product was first "flash distilled" at low pressure and the distillate was then fractionated, the formation of crotonyl chloride was avoided. This observation suggests that the crotonyl chloride must arise from a reaction of the residual benzoyl peroxide with either the β- or, less probably, the α-chloro-*n*-butyryl chloride.

Chlorination of 3.75 moles of *n*-butyryl chloride with 0.75 mole of sulfuryl chloride in the presence of 0.75 g. of benzoyl chloride and 0.4 mole of carbon tetrachloride, utilizing the precautions mentioned above, indicated the formation of 3% α-, 49% β- and 48% γ-chloro-*n*-butyryl chloride. The yield of α- and β-isomer was checked by conversion of the acid chlorides to the corresponding ethyl esters, followed by distillation and analysis, utilizing refractive index data for the ethyl esters. The results of both procedures were in complete agreement.

Chlorination of *n*-Propyl Acetate.—It was of interest to examine the isomer distribution in the chlorination of *n*-propyl acetate in order to compare the directive effects of the –Cl and $-OCOCH_3$ groups. Unfortunately, the reaction of sulfuryl chloride with *n*-propyl acetate led to the formation of large amounts (up to 30%) of substances boiling above the monochlorination products. This high-boiling material consisted primarily of sulfonyl chlorides with a small amount of polychlorides. The formation of the sulfonyl chlorides was not significantly reduced by the use of carbon tetrachloride as a diluent to aid in the elimination of sulfur dioxide.

The more volatile constituents were removed from the higher boiling side-products by a "flash distillation" at low pressures. The resulting distillate was then fractionated in a 14-plate column and both the carbon tetrachloride and excess *n*-propyl acetate removed at reduced pressure to avoid decomposition of the labile 1-chloropropyl acetate. The monochloropropyl acetates were separated by distillation at low pressures (10–20 mm.).

The individual fractions were analyzed for the 1-chloro isomer by taking advantage of its rapid solvolysis in aqueous ethanol.

$$CH_3CO_2CHClCH_2CH_3 + H_2O \longrightarrow CH_3CO_2H + HCl + CH_3CH_2CHO$$

The 2- and 3-chloro derivatives were stable to this procedure and sufficiently stable so that they could be subjected to a careful fractionation and analysis based on the usual analytical procedure utilizing refractive index measurements.

The results obtained in the chlorination of 5.0 moles of *n*-propyl acetate with 1.0 mole of sulfuryl chloride led to an isomer distribution of 25% 1-, 46% 2- and 29% 3-chloropropyl acetate. No significant attack of the acetate group was observed.

If the sulfonyl chlorides formed in the side reaction arose more or less statistically from each of the isomeric free radicals formed in the attack of the chlorine atoms on the carbon–hydrogen bonds, the isomer distribution would not be affected seriously. However, if the sulfonyl chloride arose preferentially from one or two of the isomeric free radicals, the observed isomer distribution for the chlorides would not give a true picture of the relative ease of attack on the different positions of the hydrocarbon chain. We therefore had recourse to photochlorination in carbon tetrachloride at 80–85°. There is some evidence that photochlorination and sulfuryl chloride chlorination yield quite similar isomer distribution.[5,13]

The photochlorination of 3.75 moles of *n*-propyl

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[12] H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

[13] Although we realized similar results in the chlorination of *n*-propyl acetate by the two procedures, it should be pointed out that we have recently observed a significant difference in the ratio of tertiary to primary hydrogen attack in the two chlorination procedures (ref. 5a).

acetate in 1.875 moles of carbon tetrachloride at 80–85° resulted in the formation of 145 g. of monochlorides and 20 g. of polychlorides. The analysis of the monochlorides was carried out as previously described for the products from the sulfuryl chloride chlorinations. The results indicated an isomer distribution of 23% 1-, 42% 2- and 35% 3-chloropropyl acetates. A duplicate experiment yielded identical results. The distribution is not significantly different from those obtained in the sulfuryl chloride chlorination and may be considered to agree within the limits of error of the analytical procedure in this case.

Chlorination of *n*-Propylbenzene.—Preliminary experiments also were carried out on the chlorination of *n*-propylbenzene with sulfuryl chloride in carbon tetrachloride solution. The mixture of the monochlorinated product was analyzed for the reactive α-chloro isomer by solvolysis in aqueous ethanol. A yield of 50% of the α-isomer was indicated.

Discussion

A general discussion of some of the more important features of directive effects in aliphatic chlorination, including the "vicinal effect"[7] and radical stabilization has been previously provided.[14] Accordingly, the present discussion will be restricted to a consideration of the role of the inductive factor in directing further chlorination in aliphatic compounds.

In 1-chlorobutane there is observed 47% attack in the 3-position as compared to 22% in the 2-position. That is to say, of the two possible secondary positions, the ratio of substitution in the two positions is 2.14/1 in favor of the more remote position. Similarly, in 1,1-dichlorobutane the ratio is 3.70/1 in favor of the more remote 3-position. Finally, in 1,1,1-trichlorobutane the corresponding ratio is 5.25.

The decreased tendency for attack to occur at the nearer of the two secondary positions is attributed to the inductive effect of the substituent. By decreasing the electron density in the chain, each carbon–hydrogen bond becomes less susceptible to attack by the chlorine atom, the effect decreasing with increasing distance from the substituent. Two chlorine atoms have slightly less than twice the effect of the first, and three chlorine atoms have somewhat less than three times the effect of a single substituent.

From the isomer distribution in *n*-butyryl chloride it can be concluded that the inductive effect of the –COCl group appears to be of the same order of magnitude as that of the $-CCl_3$ group.

The results on *n*-propyl acetate suggest that the inductive effect of the acetoxy group, CH_3CO_2-, is essentially identical with that of the chloromethyl group, $ClCH_2-$, and considerably smaller than that of the chlorine substituent. The three chlorine substituents in *n*-propyl trichloroacetate result in a sharp shift in the isomer distribution from the 1- to the 2- and 3-positions.[15] The distribution caused by the trichloroacetoxy group, Cl_3CCO_2-, resembles closely that observed for the trichloromethyl group, Cl_3C-. This further supports the conclusion that inductive effects play an important role in controlling attack by chlorine atoms along a carbon chain.[16]

The results of the present study along with related data from the literature on the effects of substituents in directing free radical-atom chlorination are summarized in Table I.[17–21]

On the basis of these data the groups may be arranged in the following order of influence on directive effects in aliphatic chlorination: $C_6H_5- > CH_3- > H- > ClCH_2- > CH_3CO_2- > Cl_2CH- > Cl_3Si- > HOOC- > Cl_3C- > ClOC- > Cl_2{=} > Cl_3{\equiv} > F_3C- > F_3{\equiv}$.

While there are doubtless other important factors which play a part in aliphatic substitutions, these results leave little doubt that the inductive effect represents a major factor in the control of directive effects in aliphatic chlorinations.

Experimental Part

Materials.—With the exception of three compounds, 1-chloro-, 1,4-dichloro- and 1,1,1,3-tetrachlorobutane, all of the chloro derivatives referred to in this paper were either synthesized or isolated from the reaction products. All compounds were purified by careful fractionation. The physical properties and analytical data for all intermediates and products are summarized in Table II.

1,1,3-Trichlorobutane was prepared by the addition of hydrogen chloride to crotonaldehyde to form β-chlorobutyraldehyde, followed by reaction with phosphorus pentachloride.[22] In a 500-ml., three-necked flask equipped with a gas disposer, thermometer and solid carbon dioxide condenser were placed 210 g. (3 moles) of freshly distilled crotonaldehyde. The flask was cooled and dry hydrogen chloride admitted, the temperature being maintained between 10° and 25° until a gain in weight of 109.5 g. had been realized (2 hours). The reaction mixture was immediately added through a dropping funnel to 425 g. of phosphorus pentachloride contained in a 1-l. flask. The temperature was raised slowly to 40°, and then the heat of reaction caused a slow temperature rise to around 50°. After addition was complete, the temperature was raised slowly to 100°, and the flask then allowed to cool to room temperature. The reaction mass was then added to 1.5 l. of water in a stirred flask surrounded by an ice-bath. The addition was controlled so that the temperature of the hydrolysis mixture was maintained at 40–50°. When addition was

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[14] A. B. Ash and H. C. Brown, *Record of Chemical Progress*, **9**, 81 (1948).

[15] C. W. Gayler and H. M. Waddle, THIS JOURNAL, **63**, 3358 (1941).

[16] For a recent theoretical treatment of the influence of the inductive effect of substituents on neighboring carbon–hydrogen bonds see H. Eyring and R. P. Smith, *J. Phys. Chem.*, **56**, 972 (1952).

[17] Bruylants and his co-workers recently have reported the results of the chlorination of a number of acids, acid chlorides, nitriles and esters by chlorine and light in the vapor phase. His results on *n*-propyl acetate, 0% 1-, 69% 2- and 31% 3-, are quite different from our results at 80° in the liquid phase. The failure to observe any chlorination in the 1-position may possibly arise from the thermal instability of the 1-chloropropyl acetate, as noted in the present study. Bruylants' results on the isomer distribution in *n*-butyryl chloride agree with ours in the low yield of the α-isomer, but differ somewhat with our conclusions as to the relative amounts of the β- and γ-isomers produced. A. Bruylants, M. Tits and R. Dauby, *Bull. soc. chim. Belg.*, **58**, 310 (1949); A. Bruylants, N. Tits, C. Dieu and R. Gauthier, *ibid.*, **61**, 366 (1952).

[18] L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, THIS JOURNAL, **68**, 488 (1946).

[19] M. S. Kharasch and H. C. Brown, *ibid.*, **62**, 925 (1940).

[20] A. Michael and W. W. Garner, *Ber.*, **34**, 4046 (1901).

[21] A. L. Henne and J. B. Hinkamp, THIS JOURNAL, **67**, 119 (1945).

[22] The preparation by the reaction of ethylidene chloride with vinyl chloride in the presence of aluminum chloride at 20° has been reported, with physical properties in excellent agreement with those reported here: R. Dulou and G. Bulteau, *Bull. soc. chim. France*, 924 (1947).

TABLE I

DIRECTIVE EFFECTS IN ALIPHATIC CHLORINATION

Compound	Reaction	Group	Isomer distribution, % 1-(α-)	2-(β-)	3-(γ-)	4-	Lit. ref.
n-Propylbenzene	SO_2Cl_2, ~80°	C_6H_5–	50				[a]
n-Butane	Cl_2	CH_3–	40	40	20		[b]
1-Chlorobutane	SO_2Cl_2, ~80°	$ClCH_2$–	24	51	25		[a]
n-Propyl acetate	SO_2Cl_2, ~80°	CH_3CO_2–	25	46	29		[a]
	Cl_2, liq. ~80°		23	42	35		[a]
	Cl_2, gas, 101.5°		0	69	31		17
1,1-Dichlorobutane	SO_2Cl_2, ~80°	Cl_2CH–	13	49	38		[a]
n-Propylsilicon trichloride	SO_2Cl_2, ~80°	Cl_3Si–	13	46	41		18
n-Butyric acid	SO_2Cl_2, ~80°	HO_2C–	10	45	45		19
1,1,1-Trichlorobutane	SO_2Cl_2, ~80°	Cl_3C–	8	42	50		[a]
1-Chlorobutane	SO_2Cl_2, ~80°	Cl–	7	22	47	24	[a]
n-Butyryl chloride	SO_2Cl_2, ~80°	ClOC–	3	49	48		[a]
	Cl_2, gas, 101.5°		5	65	30		17
	Cl_2, liq., r.t.		20	60	20		20
n-Propyl trichloroacetate	Cl_2		3	50	47		15
1,1-Dichlorobutane	SO_2Cl_2, ~80°	Cl_2^{-}	2	13	48	37	[a]
1,1,1-Trichlorobutane	SO_2Cl_2, ~80°	Cl_3^{-}	..	8	42	50	[a]
1,1,1-Trifluorobutane	Cl_2, liq., 16°	F_3C–	0	45	55		21
1,1,1-Trifluorobutane	Cl_2, liq., 16°	F_3^{-}	..	0	45	55	21

[a] Present study. [b] Calcd. from the data in ref. 3.

TABLE II

PHYSICAL PROPERTIES OF INTERMEDIATES AND PRODUCTS

Compound	B.p., °C., corr.	Press., mm.	Density d^{25}	Refractive index, $n^{25}D$	Chlorine, %[a] Found	Calcd.
1-Chlorobutane	77.5–78.5	745		1.3995		
1,1-Dichlorobutane	114.8–115.1	752	1.0797	1.4305		
1,2-Dichlorobutane	122.9–123.3	743	1.1118	1.4425		
1,3-Dichlorobutane	133.0–133.2	744	1.1083	1.4414		
1,4-Dichlorobutane	154.1–154.2	749	1.1324	1.4522		
1,1,1-Trichlorobutane	133.1–133.3	750	1.2242	1.4483	65.76	65.88
1,1,2-Trichlorobutane	156.3–156.8	746	1.2787	1.4667	65.95	65.88
1,1,3-Trichlorobutane	153.2–153.8	750	1.2514	1.4593	65.92	65.88
1,1,4-Trichlorobutane	183.6–183.8	754	1.2967	1.4753	65.92	65.88
1,1,1,2-Tetrachlorobutane	69.1–69.4	20.0	1.3952	1.4812	72.63	72.39
1,1,1,3-Tetrachlorobutane	69.5–69.8	20.0	1.3747	1.4772	72.18	72.39
1,1,1,4-Tetrachlorobutane	86.8–87.1	20.0	1.4001	1.4858	72.81	72.39
1,1-Dichloro-1-butene	103.3–103.5	747		1.4465	56.21[b]	56.74
α-Chlorobutyraldehyde	106–108[c]	740		1.441	35.38[d]	33.28
n-Butyryl chloride	101–101.5[c]	745		1.4098		
α-Chlorobutyryl chloride	51.5–51.7	40.0		1.4410		
β-Chlorobutyryl chloride	53.0–53.3	20.0		1.4477		
γ-Chlorobutyryl chloride	71.0–71.2	20.0		1.4597		
Ethyl α-chlorobutyrate	64.2–64.4[c]	20.0		1.4202		
Ethyl β-chlorobutyrate	69.9–70.1[c]	20.0		1.4222		
n-Propyl acetate	101–102	745		1.3823		
1-Chloropropyl acetate	48.6–48.8	20.0		1.4143		
2-Chloropropyl acetate	57.1–57.6	20.0		1.4205		
3-Chloropropyl acetate	58.4–58.8	10.0		1.4275		
n-Propyl chloroacetate	52.6–52.8	10.0		1.4233		

[a] Chlorine analysis by reaction with sodium diphenyl in dimethyl Cellosolve [L. M. Liggett, *Anal. Chem.*, 26, 748 (1954)]. [b] Av. of three analyses (56.17, 56.22 and 56.25%). [c] Uncorrected. [d] See footnote 23.

complete, the condenser was fixed for downward distillation and the chlorinated hydrocarbon and water were azeotropically distilled out. The oil was washed with several portions of water to remove crotonaldehyde and dried over calcium chloride. The fraction boiling at 151–153° was collected. A total of 231 g. (47.7%) was obtained.

α-Chlorobutyraldehyde was synthesized by the treatment of *n*-butyraldehyde with sulfuryl chloride. Since large quantities of the compound were required for subsequent conversion to 1,1,2- and 1,1,1-trichlorobutane, considerable time was devoted to the development of a satisfactory procedure. The use of methylene chloride as a diluent proved highly desirable. Moreover, the quantity of methylene chloride appeared critical. Either too much or too little appeared to result in vigorous foaming. Investigation also indicated that the reaction temperature should be kept above 10°. Otherwise unreacted sulfuryl chloride can build up in the reaction mixture and result in a rapid and violent reaction.

To 360 g. (5.0 moles) of *n*-butyraldehyde mixed with 150 ml. of methylene chloride were added 675 g. (5.0 moles) of sulfuryl chloride in 50 ml. of methylene chloride over a 2-hour period. Agitation was employed and the temperature was maintained between 15 and 25°. The reaction mixture was maintained at 25° for 30 min., and was then heated to reflux for 5 min. The mixture was cooled and separated from a small lower layer of aqueous acid. (Failure to remove this material resulted in difficulties with foaming in the subsequent distillation.) Approximately 50 ml. of ethylene chloride was added to remove the last traces of moisture during the distillation process. Finally, the addition of 50 ml. of *sym*-tetrachloroethane to the reaction mixture greatly reduced the formation of decomposition products during the last stages of the distillation. This mixture was distilled through a short column. After removal of the water–ethylene chloride azeotrope, the balance of the ethylene chloride and a small intermediate fraction, α-chlorobutyraldehyde distilled at 104 to 108°. The yield was 420 g., 79%.

The product apparently contained a small amount of a higher chlorinated material not separable by distillation. Thus on refractionation of this material, the major portion distilled at 106–107° at 740 mm., but the distillate showed a variation of 0.0010 unit in the refractive index. Chlorine analyses were high, *viz.* 35.38% Cl *vs.* 33.28% calcd. Since the impurity did not interfere with the subsequent utilization of the product, no effort was made to effect further purification.[23]

1,1,2-Trichlorobutane was prepared by the reaction of α-chlorobutyraldehyde with phosphorus pentachloride. By following the usual procedure for the reaction of phosphorus pentachloride with aldehydes, as previously described for the synthesis of 1,1,3-trichlorobutane, the yield was only 35–45%. The yield was raised to 64% by two variations in the procedure. First, a slurry of phosphorus pentachloride in methylene chloride was utilized. The diluent was apparently beneficial in bringing the butyraldehyde into rapid contact with the halide while avoiding local overheating with resulting loss of the aldehyde through side reactions. Second, the reaction mass was hydrolyzed without heating it, as recommended in the usual procedures. Such heating is unnecessary and can result in losses of the product. Indeed, it was observed that if this final heating was avoided the yields were remarkedly constant and were essentially independent of changes in the reaction temperature from −30 to 40°.

To a slurry of 625 g. (3.0 moles) of phosphorus pentachloride in 250 ml. of methylene chloride there was added over a 2-hour period 319.5 g. (3.0 moles) of α-chlorobutyraldehyde diluted with 60 ml. of methylene chloride. The temperature was maintained between 10 and 20°. After an additional hour, it was hydrolyzed in 2.5 kg. of an ice-water mixture. The mixture was steam distilled and the recovered oil was fractionated through a short column. A total of 280 g. of 1,1,2-trichlorobutane, 58% yield, was obtained, b.p. 154–158°. On redistillation through an efficient column, the pure product can be isolated (Table II).

1,1-Dichloro-1-butene was prepared in 79% yield by the reaction of 646 g. of 1,1,2-trichlorobutane with 1 kg. of 20% aqueous sodium hydroxide.

After considerable experimentation, the following procedure was developed for the addition of hydrogen chloride to 1,1-dichloro-1-butene to form 1,1,1-trichlorobutane. Anhydrous aluminum chloride, 3–5 g., was added to a mixture of 125 g. (1.0 mole) of 1,1-dichloro-1-butene in 125 g. of methylene chloride at −35°. The mixture was stirred vigorously and dry hydrogen chloride was introduced rapidly, maintaining the temperature at −35 to −20°. When absorption was complete (approximately 30 min.), the reaction mixture, still at −20° or lower, was poured rapidly into a flask of cold water. The product is separated, washed, dried and distilled. An 82% yield, 132 g., of 1,1,1-trichlorobutane was obtained, b.p. 133–134.5° at 740 mm. In other preparations, yields as high as 94% were realized.

1,1,1,2-Tetrachlorobutane was prepared by the reaction of 1,1-dichloro-1-butene with chlorine in the dark at 0°. A 55% yield was realized. The boiling point and refractive index value (Table II) differ markedly with the constants reported by Gilman and Abbott for this compound.[24]

1-Chloropropyl acetate was synthesized in 56% yield by the reaction of 173 g. of acetyl chloride with 116 g. of propionaldehyde.[25]

Chlorination Procedure.—The following general procedure was used throughout. The compound to be chlorinated, sulfuryl chloride, carbon tetrachloride diluent (if used), and benzoyl peroxide were mixed in the proper proportions in a weighed round-bottom flask possessing a ground glass joint and an all-glass thermometer well. A few boiling chips were added. The reaction was initiated by heating under gentle reflux. The sulfur dioxide and hydrogen chloride passed through the reflux condenser, a safety trap, and a bubbler, and finally to a suitable absorption system. The course of the reaction was followed readily by observation of the rate of gas evolution and by measurement of the loss in weight of the flask and its contents.

When the chlorination was complete, the reaction flask was attached to the distillation column and fractionated without further treatment. In the experiments with *n*-butyryl chloride and *n*-propyl acetate, the reaction mixture was "flash distilled" before the fractionation.

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(23) Professor Calvin Stevens of Wayne University has observed recently that *sym*-tetrachloroethane distills azeotropically with the α-chlorobutyraldehyde (private communication). The high chlorine analyses doubtless are due to the presence of a small amount of the tetrachloroethane in the product.

(24) H. Gilman and R. K. Abbott, Jr., *J. Org. Chem.*, **8**, 224 (1943).

(25) A. Kirrmann, *Bull. soc. chim.*, [5] **4**, 502 (1937).