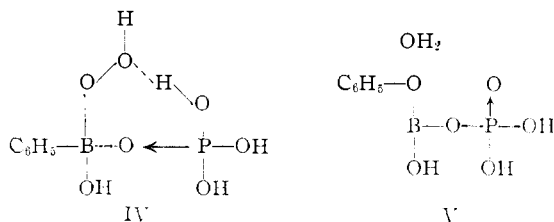tributed to the fact that much un-ionized acid is present in the solutions of the former but not in solutions of the latter. The passage of IV through the transition state to V is an example of bifunc-

tional catalysis.[6b] In the proton transfer to a peroxide oxygen the phosphoric acid is playing the role of electrophilic reagent while in the formation of the covalent boron–oxygen bond it is a nucleophilic reagent. Its ability to function in this dual role accounts for its exceptional catalytic ability.

Thus we have two mechanisms which differ significantly but obey the same kinetic law. Of these, the second is more attractive for at least three reasons. First, there seems to be no reason why one acid should catalyze via assembly I and a second via assembly III. Secondly, the extreme effectiveness of phosphoric acid is easily understood in terms of IV. Finally, the fact that the two acids show different kinds of correlation with acidity becomes reasonable: it is based on a fundamental difference in the nature of solutions of these acids.

Sulfuric Acid.—Table III contains the data obtained in solutions ranging from 2 to 60% sulfuric acid.

It is clear that in the range of acidity covered H_0 does not correlate the data as it does with phosphoric acid. Nor is the product of activities of water and sulfuric acid a linear function of the rate constant as in the case of perchloric acid. Examination of combinations of various exponents (up to two) in the activities of water and acid showed that only the product $(a_{H_2O})^{1/2}(a_{H_2SO_4})^{3/2}$ as indicated in the table correlates the data over

TABLE III

KINETIC DATA IN AQUEOUS SULFURIC ACID

H_2SO_4, mole/ l.	$-H_0{}^a$	10^2 $k_{obs.}{}^d$	10^2 $k_a{}^d$	$-\log k_a$	$\log \dfrac{(a_{A_2O})^{1/2}}{(a_{H_2SO_4})^{3/2}}{}^b - \Delta^c$
0.193	-0.53	0.184	0.107	2.971	-2.08	0.89
0.386	-0.36	0.286	0.209	2.680	-1.79	.89
1.13	+0.20	0.989	0.912	2.040	-1.23	.81
2.26	0.88	3.17	3.09	1.510	-0.63	.88
3.64	1.53	9.19	9.11	1.040	-0.23	.81
6.38	2.85	59.1	59.0	0.229	+0.67	.90
8.99	4.30	360	360	-0.57	+1.41	.84

[a] See footnote b in Table I. [b] S. Shankman and A. R. Gordon, THIS JOURNAL, 61, 2370 (1939). [c] $\Delta = \log k_a - \log[(a_{H_2O})^{1/2}.(a_{H_2SO_4})^{3/2}]$; mean $\Delta = -0.86$. [d] Units, l. mole^{-1} sec.$^{-1}$

the entire range. The correlation is remarkably precise as shown by the fact that a log–log plot of rate constant and activity product has a slope, 1.00 (Fig. 2). However, the actual mechanistic significance of the fractional exponents is not apparent. In view of the effectiveness of phosphoric acid as a catalyst it seems probable that the stronger acid bisulfate plays a significant role in the sulfuric acid solutions. Since it is largely undissociated and is structurally analogous to phosphoric acid it could possibly replace the latter in structure IV.

More information concerning sulfuric acid solutions than is now available would be necessary before the kinetic data could be analyzed reliably.

Experimental

Reagents.—Reagent grade acids were used without further treatment.

Rate Measurements.—The procedure was the same as that previously described[3] with two exceptions. When the stronger acid solutions were used ice was added to the iodide quenching solution to prevent undue heating when the sample was added. The titrations also had to be done more slowly to avoid overtitration. Phosphoric acid diminished the effectiveness of molybdate as a catalyst for the iodide–peroxide reaction to such an extent that when the more concentrated solutions were used the peroxide was determined colorimetrically.[3]

DURHAM, N. H.

The Acyloin Condensation. II. Free Radical Formation Accompanying the Decarbonylation of An Aliphatic Ester by Sodium
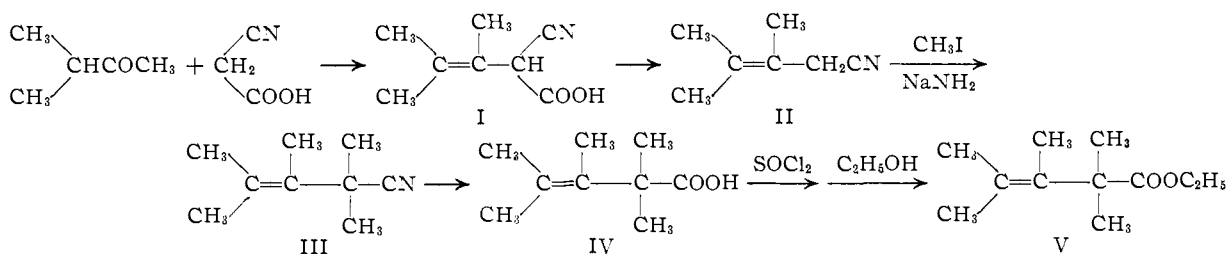
BY EARLE VAN HEYNINGEN

A completely aliphatic ester underwent the acyloin condensation to give products expected from the decomposition or coupling of free radicals.

A recent intensive investigation of the acyloin condensation of certain aralkyl esters has furnished further support for the formulation of the acyloin condensation as a free radical reaction.[1] The purpose of the present study was to determine whether similar evidence could be obtained using a purely aliphatic ester.

Aliphatic esters in the acyloin condensation generally give good yields of the expected acyloins.

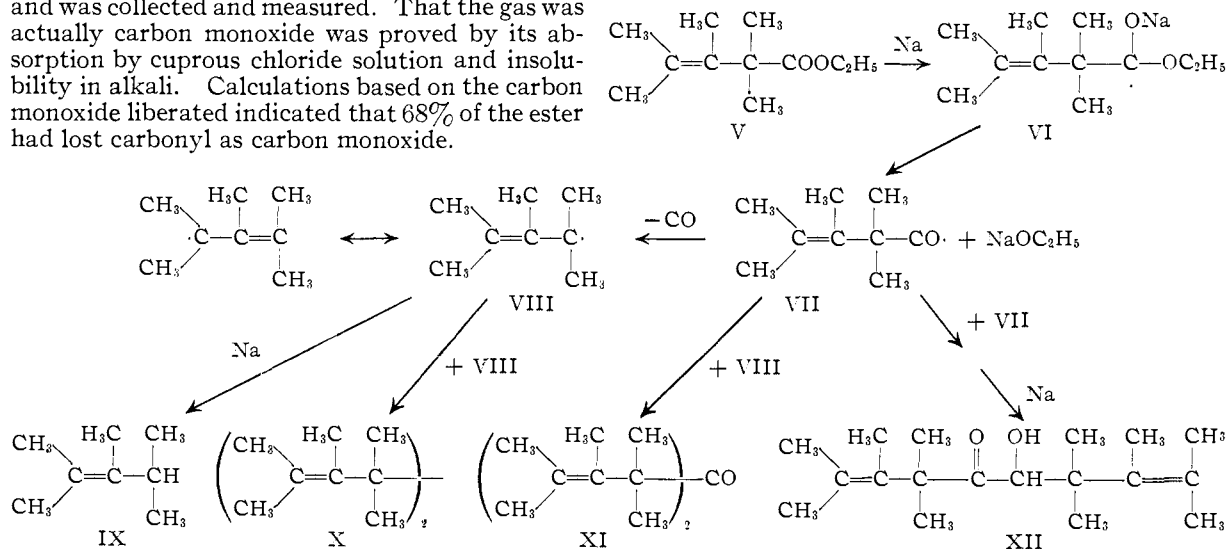(1) E. Van Heyningen, THIS JOURNAL, 74, 4861 (1952).

This is no doubt due to the high reactivity (instability as free radicals) of the initial sodium ketyls which immediately couple with each other. An aliphatic ester, which in the course of the acyloin condensation could give a resonance stabilized free radical, might form products that would be more indicative of the free radical nature of the reaction. Such an ester is ethyl 2,2,3,4-tetramethyl-3-pentenoate (V). In view of the earlier work with aralkyl esters, it would be expected to form the free radical

Reaction scheme (I–V):

$$CH_3CHCOCH_3 + CH_2(CN)(COOH) \rightarrow \text{(I)} \rightarrow \text{(II)} \xrightarrow[NaNH_2]{CH_3I}$$

$$\text{(III)} \rightarrow \text{(IV)} \xrightarrow{SOCl_2} \xrightarrow{C_2H_5OH} \text{(V)}$$

VIII which is resonance stabilized and possesses equivalent resonance forms, important in limiting the number of possible products.

For the preparation of the ester V, isopropyl methyl ketone was condensed with cyanoacetic acid and then the resulting acid decarboxylated to give the pentene nitrile II. Although there was probably some α,β-unsaturated nitrile also formed, it was not separated, for it was assumed that the latter would be rearranged to the β,γ-unsaturated compound by reaction with the sodamide used in the subsequent alkylation. The product of the dimethylation III is undoubtedly the desired α,α-dimethylnitrile. An infrared absorption spectrum of the nitrile gave a band at 4.4 μ. Kitson and Griffith[2] have shown that this is typical of β,γ-unsaturated nitriles; α,β-unsaturated nitriles have an absorption band at 4.48 μ. Further confirmation of the β,γ-position for the double bond was obtained from the ultraviolet absorption spectrum of the ester V resulting from the saponification and esterification of the nitrile. No conjugated double bond absorption was present.

The acyloin condensation was run in refluxing toluene. The products obtained were those expected from a free radical decomposition of the sodium ketyl VI. Carbon monoxide was evolved and was collected and measured. That the gas was actually carbon monoxide was proved by its absorption by cuprous chloride solution and insolubility in alkali. Calculations based on the carbon monoxide liberated indicated that 68% of the ester had lost carbonyl as carbon monoxide.

tion. IX might be expected to react in this manner because of the probable easy replacement of an allylic tertiary hydrogen. The product had an analysis that indicated one bromine was present in a compound of the approximate size of IX.

The liquid crude product from the reaction was distilled and separated into three main fractions. The coupling of VIII with itself would give the hydrocarbon X; it was isolated from the lowest boiling fraction by further fractionation. The infrared spectrum was consistent with this structure, although a small trace of the ketone XI was indicated to be present. The middle fraction was mainly this ketone XI which would be formed by the condensation of the free radicals VII and VIII. It was obtained both analytically and spectrophotometrically pure. The highest boiling fraction was likewise fractionated and the acyloin XII isolated in small amount. It was yellow and so may have had some diketone contaminant in it. Although the analytical values and the main absorption bands of the infrared spectrum indicated that the compound XII was obtained, trace amounts of an ester impurity were detected from absorption bands in the infrared. In addition to the above compounds which were isolated, there are probably other com-

Reaction scheme (V → VI, VII, VIII, IX, X, XI, XII):

$$\text{(V)} \xrightarrow{Na} \text{(VI)}$$
$$\text{(VII)} + NaOC_2H_5 \xleftarrow{-CO} \text{(VI)}$$

Compound IX, the hydrocarbon which would be formed by the reduction of the free radical VIII, was not unequivocally characterized, because the bromo derivative made from the fractions in which it should have been found could not be readily purified. This bromo derivative was a substitution product rather than an addition product since hydrogen bromide was evolved during the bromina-

(2) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

pounds which were not separated because of the small amounts present.

Experimental[3]

3,4-Dimethyl-3-pentene Nitrile (II).—The method of

(3) All melting points and boiling points are uncorrected. The microanalyses were performed by G. M. Maciak, W. J. Schenck, H. L. Hunter and W. L. Brown. The infrared and ultraviolet absorption spectra were obtained by H. E. Boaz, D. Wolff and J. W. Forbes.

Whyte and Cope[4] was used. In a 2-l. flask a mixture of 255 g. (3.0 moles) of cyanoacetic acid, 258 g. (3.0 moles) of isopropyl methyl ketone, 90 g. (1.5 moles) of glacial acetic acid, 46.3 g. (0.6 mole) of ammonium acetate and 150 ml. of benzene was heated under a Dean-Stark trap until no more water separated (36 hr.). The reaction product was then distilled at 40 mm. The distillate was washed with water and then dried and finally distilled, b.p. 166–173° (atm.), n^{25}D 1.4321–1.4370, yield 154.1 g. (1.41 moles, 47%). It is assumed that the range in boiling point and index of refraction is due to a small amount of α,β-unsaturated compound being present.

Anal. Calcd. for $C_7H_{11}N$: C, 77.01; H, 10.16. Found: C, 76.66; H, 10.38.

2,2,3,4-Tetramethyl-3-pentene Nitrile (III).—Sodamide was prepared from 64.5 g. (2.8 atoms) of sodium in 2 l. of liquid ammonia using an iron catalyst. Then 150.1 g. (1.37 moles) of 3,4-dimethyl-3-pentene nitrile was added, followed by 400 g. (2.82 moles) of methyl iodide at as rapid a rate as possible with the reaction still under control (5 minutes). The ammonia was allowed to evaporate and the product then isolated by solution of the salt in water and extraction of the product with ether. The ether extract was washed with water, dried, and evaporated. The residue was distilled to give two fractions. The first proved to be the desired nitrile, b.p. 37–38° (7 mm.), n^{25}D 1.4275; yield 82.1 g. (0.6 mole, 43.7%).

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.10. Found: C, 78.69; H, 11.07; N, 10.10.

The second fraction (b.p. 50° (8 mm.), n^{25}D 1.4486, 26.8 g.) was not further investigated since the analysis did not correspond to any readily conceivable product.

Anal. Found: C, 76.71; H, 10.60; N, 10.18.

2,2,3,4-Tetramethyl-3-pentenoic Acid (IV).—A 500-ml. pressure bomb was charged with 68.5 g. (0.5 mole) of 2,2,3,4-tetramethyl-3-pentene nitrile and 100 g. (1.5 moles) of 85% potassium hydroxide in 100 ml. of methanol and 10 ml. of water. The mixture was heated at 140° for 56 hours. Then the resulting potassium salt was removed and the entrained methanol removed by heating in an evaporating dish on a steam-bath. The solid residue was dissolved in water and the solution acidified with hydrochloric acid and ice. The acid was extracted with ether. The ether extract was dried and evaporated to give a solid acid; yield 77 g. (0.495 mole, 99%). Recrystallized from petroleum-ether it melted at 46–47°.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.38. Found: C, 69.38; H, 10.33.

Ethyl 2,2,3,4-Tetramethyl-3-pentenoate (V).—An attempt to prepare the ester by distilling off water in a toluene-ethanol-water ternary mixture with an acid catalyst gave the ester in only 34% yield. Consequently, two other methods were used.

A.—A solution of 20 g. (0.128 mole) of the acid in 150 ml. of water containing 5.2 g. (0.13 mole) of sodium hydroxide was heated on the steam-bath with stirring while 21 g. (0.135 mole) of ethyl iodide was added dropwise. After complete addition, the reaction was heated for 12 hours. The ester was then extracted with benzene. Acidification of the water solution gave a 10% recovery of acid. The benzene solution of the ester was evaporated. Distillation yielded the ester, b.p. 64° (10 mm.), n^{25}D 1.4300; 12.6 g. (0.075 mole, 58%).

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.50; H, 11.01.

An ultraviolet absorption spectrum of this compound showed no conjugated carbonyl absorption.

B.—The acid (41.4 g., 0.265 mole) was added to 53.5 g. (0.45 mole) of thionyl chloride. After the initial vigorous reaction subsided, the mixture was heated on the steam-bath for 2 hours. The excess thionyl chloride was removed with water-pump vacuum, and the product was distilled, b.p. 41° (0.4 mm.), n^{25}D 1.4513; yield 40.5 g. (0.232 mole, 87.5%).

Anal. Calcd. for $C_9H_{15}OCl$: C, 61.88; H, 8.66. Found: C, 61.62; H, 8.53.

This acid chloride was added carefully to 100 ml. of dry ethanol and refluxed two hours. The ethanol and hydrogen

chloride were evaporated *in vacuo* and the residue distilled, b.p. 43° (1.05 mm.), n^{25}D 1.4301; yield 34.5 g. (0.187 mole, 80.5%).

The Acyloin Condensation of Ethyl 2,2,3,4-Tetramethyl-3-pentenoate.—In a 500-ml., 3-necked flask protected from moisture and equipped with a stirrer, reflux condenser and a tube so arranged as to enable collection of escaping gases over water, 7.3 g. (0.318 atom) of sodium was dispersed in 200 ml. of refluxing, dry toluene. Then 29.3 g. (0.159 mole) of the ester was added dropwise over a period of 40 minutes. To render the reaction more fluid, 100 ml. of toluene was added and refluxing and stirring continued for one hour.

Gas was evolved at the very start of the reaction and a total volume of 2420 ml. at standard conditions was collected. This corresponded to 0.108 mole of carbon monoxide[5]; consequently, 68% of the ester had lost its carbonyl group as carbon monoxide. Solubility of the gas in cuprous chloride and insolubility in alkali indicated that the gas was carbon monoxide.

The reaction mixture was worked up by the addition of 200 ml. of water. The toluene layer was separated and the water solution extracted with more toluene. The combined organic layers were dried with magnesium sulfate. The toluene was removed by distillation through a Widmer column at atmospheric pressure, and a yellow liquid residue was left in the distillation flask.

Identification of 2,3,4-Trimethyl-2-pentene (IX).—The entire toluene solution was treated with a 15% bromine in chloroform solution. Only 2.36 g. of bromine was adsorbed and hydrogen bromide was liberated. The solvents were removed *in vacuo* at room temperature. About 6 ml. of a black liquid residue was obtained which was distilled at 0.16 mm. from a micro-distillation apparatus,[6] bath temperature 59–66°. The product was not homogeneous, n^{25}D 1.5100–1.5125. It darkened on standing.

Anal. Found: C, 48.73; H, 6.89; Br, 43.50.

The expected product from the acyloin condensation is 2,3,4-trimethyl-2-pentene. The monobromo derivative would form by substitution of the tertiary hydrogen in the allyl position.

Anal. Calcd. for $C_8H_{15}Br$: C, 50.27; H, 7.91; Br, 41.81.

This is not in very good agreement with the values found. If a tribromoöctane contaminant were present, formed by the addition of bromine to the monosubstitution product, it would cause the analytical values to approximate those found. Because of the small amount of material ultimately obtained, it could not be further purified.

The residue from the removal of the toluene was distilled through a 7 inch, helices packed column at reduced pressure. In this way three main fractions (total weight, 14.5 g.) were obtained, the subfractions being combined on the basis of similarity of refractive index. The fractions were then purified by fractionation in a microdistillation apparatus.[6]

Identification of 2,3,4,4,5,5,6,7-Octamethyl-2,6-octadiene (X).—The first fraction (6.1 g.) was fractionated, but the samples obtained seemed to be composed of a hydrocarbon consistently contaminated with 10% or less of a ketone. This was indicated by analyses and infrared spectra. When a small piece of sodium was added to the distillation a red, tarry material was formed during the distillation and an analytically pure sample of hydrocarbon was obtained, b.p. 111° (0.32 mm., bath temperature), n^{25}D 1.4718.

Anal. Calcd. for $C_{16}H_{30}$: C, 86.40; H, 13.60. Found: C, 86.23; H, 13.68.

This analysis corresponds to that of X. The infrared spectrum was also consistent with this structure although traces of ketone were indicated as still present.

Identification of Di-(1,1,2,3-tetramethyl-2-butenyl) Ketone (XI).—The identity of the main constituent of the middle fraction was established through analysis and infrared. It distilled at 144° (bath temperature) at 0.32 mm., n^{25}D 1.4714.

(4) D. E. Whyte and A. C. Cope, THIS JOURNAL, **65**, 1999 (1943).

(5) The author is indebted to Prof. N. J. Leonard, of the Univ. of Illinois, for pointing out that carbon monoxide is formed in this type of reaction.

(6) S. A. Shrader and J. E. Ritzer, *Ind. Eng. Chem.*, **11**, 54 (1939).

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

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

By Herbert C. Brown and Arthur B. Ash[2,3]

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$_2$C– group in directing chlorination. The following order of influence in directive effects is indicated: C_6H_5– > CH$_3$– > H– > ClCH$_2$– > CH$_3$CO$_2$– > Cl$_2$CH– > Cl$_3$Si– > HO$_2$C– > Cl$_2$C– > ClOC– > Cl$_2$= > Cl$_3$≡ > F$_3$C– > F$_3$≡. 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.

(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).

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,

(8) A. L. Henne and J. B. Hinkamp, This Journal, **68**, 1197 (1946).