When only squalene was placed on the paper, it was found that both the commercial and the redistilled commercial materials gave only one spot as detected with iodine vapor and the average R_f value was 0.71. With the regenerated squalenes, however, two zones were noted, one intense at 0.71 and a weak spot at 0.86. It is interesting to note that the appearance of the two zones occurs only with the regenerated samples which also show the terminal methylene group in the infrared spectra. Such a relationship suggests that a separation has been achieved between moieties having different double bond distributions. It is also possible that a separation of *cis–trans* isomers has been performed but in view of the methods of regeneration it would be expected that triply substituted double bonds would be of the *trans* configuration. Thus, one cannot at this time allocate an exact definition to this separation of two zones on "Quilon" paper and more work must be performed along these lines.

Under these same conditions, it has been reported that cholesterol shows a R_f value of 0.56.[17] It has been found that when a mixture of cholesterol and squalene are run together, a separation of these two compounds can be achieved. For analysis, squalene was first detected with iodine vapors and then the cholesterol with silicotungstic acid.[17] The value for squalene remained as reported above but it was noted that the average R_f of cholesterol was somewhat higher than found for cholesterol alone, the value being 0.61 as compared to 0.56. This change in R_f may be due to the solvent action of squalene. Thus, the difference in the R_f values between these two spots suggest that such a method of analysis can be employed to separate squalene and cholesterol and when such a method is coupled with radioautography, a semiquantitative analysis can be performed.

Experimental

The commercial squalene was redistilled, b.p. 213° (1 mm.), n^{20}_{D} 1.4962 (lit.[4] 1.4965) and then converted into its hexahydrochloride as described by Heilbron,[4] m.p. 103–110°. The solid derivative was reconverted to squalene following the published procedure[4] and then redistilled. For regeneration from potassium *t*-butoxide, the hexahydrochloride (4.8 g.) was allowed to react with a solution of 1.4 g. of potassium in 30 ml. of dry *t*-butanol. After heating for three hours at 100°, the reaction mixture was diluted to 200 ml. with water, extracted with ether, washed, dried and distilled, yield 2.15 g. (68%).

All infrared spectra were taken as a film with an I.R. Spectrophotometer manufactured by Baird Associates.

For the chromatography, the papers used were 1.5 × 15 inch strips of Whatman No. 1 filter paper impregnated with "Quilon" (stearato chromic chloride).[16,17] The developing solvent was methanol and in every case about 10 γ of material was placed at the origin. R_f values were measured from the farthest spot of the origin to the foremost point of the moving spot. The squalene was detected by the intense brown spots visible when the strips were suspended in iodine vapor for one minute.[17] Cholesterol was detected with a silicotungstic acid spray.[16,17] In experiments where squalene and cholesterol were run together, the squalene was detected first using the iodine vapor then, after the papers had been kept in a well-ventilated hood overnight to ensure complete evaporation of the iodine, the cholesterol was located with silicotungstic acid. All R_f values reported are an average value of at least twelve separate chromatograms and the standard deviation was ±0.01 R_f unit for squalene run alone and ±0.02 R_f unit for squalene and cholesterol run together.

BERKELEY, CALIFORNIA

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[17] D. Kritchevsky and M. R. Kirk, *Arch. Biochem. Biophys.*, **35**, 346 (1952).

[CONTRIBUTION NO. 242 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

Telomerization of Vinyl Monomers with Hydrogen Chloride[1]

BY T. A. FORD, W. E. HANFORD, J. HARMON AND R. D. LIPSCOMB

RECEIVED MARCH 19, 1952

Ethylene reacts with hydrogen chloride in the presence of free radical initiators and water to yield mixtures of straight-chain primary alkyl chlorides having even numbers of carbon atoms. Other polymerizable unsaturated compounds appear to undergo similar reactions, but the structures of the products have not been established.

The free radical-initiated reaction of halomethanes with olefins yields addition products derived from one or more molecules of olefin per molecule of halomethane.[2-4] For example, ethylene and carbon tetrachloride yield a series of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes.[3] This paper is concerned with a further example of this type of reaction in which hydrogen chloride acts as the telogen.[5]

Reaction of ethylene with hydrogen chloride in the presence of free radical-forming initiators has been found to yield mixtures of straight-chain primary alkyl chlorides having even numbers of carbon atoms and ranging from ethyl chloride *n*-butyl chloride, *n*-hexyl chloride, etc., to greases and waxes having chain lengths of 40 or more carbon atoms.[6] Other polymerizable olefinic compounds, such as styrene and allyl chloride, can also be telomerized with hydrogen chloride.[7]

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[1] Presented in part at the 113th Meeting of the American Chemical Society, Chicago, Ill., April, 1948.

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

[3] R. M. Joyce, W. E. Hanford and J. Harmon, *ibid.*, **70**, 2529 (1948).

[4] J. Harmon, T. A. Ford, W. E. Hanford and R. M. Joyce, *ibid.*, **72**, 2213 (1950).

[5] These reactions represent a type of polymerization, and the process by which the end groups are formed is sometimes referred to as chain transfer. For reactions of this sort that lead to short chain compounds in which the end groups are chemically significant, rather than to high polymers in which the end groups are relatively insignificant, we have found it convenient to refer to the reaction as telomerization, to the products of the reaction as telomers, and to the molecule which gives rise to the end groups as the telogen (derived from the Greek roots "telos" meaning "end," and "gen" meaning "former").

[6] W. E. Hanford and J. Harmon, U. S. Patent 2,418,832 (April 15, 1947).

[7] W. E. Hanford and J. Harmon, U. S. Patent 2,440, 801 (May 4, 1948).

Table I

Ethylene/Hydrogen Chloride Telomers

A. Ether-soluble chloride, 40 g.		B.p. (at flat), °C.	Mm.	$n^{20}D$	Chlorine, %	Weight % of A
n-Butyl	Found	77–78	760	1.4020		6
	Lit.[a]	78.0	760	1.4022		
n-Hexyl	Found	54	50	1.4204	29.66, 29.58	6
	Lit.	134	760	1.4200	29.40	
n-Octyl	Found	68–70	15	1.4310	23.94, 23.65	9
	Lit.	182–182.5	760	1.4315	23.84	
n-Decyl	Found	105	15	1.4386		9
	Lit.	105	15[b]	1.4382		
n-Dodecyl	Found	140	15	1.4446	17.61	8
	Lit.	135.6–137.5	16	1.4433	17.33	
n-Tetradecyl	Found	153–162	15	1.4481		5
	Lit.	152.4–154	13	1.4485		
n-Hexadecyl	Found	134	1.5	1.4501		6
	Lit.	186.2–187.5	16	1.4504		
n-Octadecyl	Found	157–158	1.5	1.4524	12.57	6
	Lit.	199–202	9	1.4525	12 28	
n-Eicosyl	Found	189	1.5	$(1.4476)^{40°}$		5
	Lit.	193–196	2	$(1.4483)^{40°}$		
Higher alkyl chlorides (residue) (av. compn. $C_{33}H_{67}Cl$)						40
B. Ether-insoluble part, 6 g. (av. compn. $C_{38}H_{77}Cl$)						

[a] The literature values for the boiling points and refractive indices of the *n*-butyl and *n*-hexyl chlorides were selected from Huntress, "Organic Chlorine Compounds," John Wiley and Sons, New York, N. Y., 1948. The remainder were taken from Schrauth, *Chem. Z.*, **58**, 877 (1934). Comparison of the observed boiling points with those of Schrauth by plotting on a vapor pressure chart showed excellent agreement in most cases. [b] Found for an authentic specimen of *n*-decyl chloride.

The conditions for the reaction are in general those that would result in polymerization if the hydrogen chloride were not present. Thus, for the telomerization of ethylene, pressures of several hundred atmospheres are used, while the reaction with styrene can be carried out at atmospheric pressure. The concentration of hydrogen chloride and the nature of the olefinic compound both influence the average chain length of the products. Water is the preferred reaction medium. In the case of ethylene, other media such as isoöctane give lower yields of telomer; with other monomers that tend to add hydrogen chloride readily in the absence of water to yield simple addition products the use of water is particularly important. For example, styrene adds hydrogen chloride under anhydrous conditions to give α-chloroethylbenzene. However, when styrene containing benzoyl peroxide was treated with aqueous hydrochloric acid, the product was a highly viscous liquid having an average chain length of about seven styrene units as calculated from the chlorine content on the basis of one chlorine atom per molecule. Allyl chloride in the presence of a free-radical initiator yielded a product of which 45% was a trichlorohexane and 30% consisted of higher-boiling chlorine compounds. The remaining 25% was 1,2-dichloropropane, showing that the peroxide did not effect the reversal of normal addition of the hydrogen chloride. The structure of the trichlorohexane, which is the 2:1 telomer, has not been determined.

Experimental

Ethylene/Hydrogen Chloride Telomer.—The reactions were carried out under ethylene pressures of 100–1000 atm. Since aqueous hydrochloric acid was required for best results, reactors lined with corrosion-resistant material were used. "Hastelloy B" and silver both proved to be suitable. No appreciable corrosion of a silver-lined reactor was observed when a little silver oxide was added to each charge to saturate the hydrochloric acid with silver chloride at reaction temperature. A typical experiment was as follows: A 400-ml. high-pressure tube lined with "Hastelloy B" was charged with 100 g. of 18.5% aqueous hydrochloric acid and one-half gram of benzoyl peroxide, closed, and pressured with ethylene to 200 atm. Heating and agitation were begun and, when the temperature reached 100°, additional ethylene was admitted to bring the pressure to 500 atm. The pressure was maintained in the range 400–500 atm. by the intermittent addition of ethylene as required. The reaction was virtually complete at the end of 4.5 hours as indicated by the rate of pressure drop; after a total of 11 hours the reactor was cooled and excess ethylene was bled off along with a small amount of ethyl chloride. The remaining liquid product was washed with sodium carbonate solution and then separated into an ether-insoluble part and an ether-soluble part. Distillation of the ether-soluble product through a 12-inch Vigreux column gave a distillation curve with well-defined flats at the boiling points of the straight-chain alkyl chlorides having even numbers of carbon atoms.

By analysis of selected fractions for chlorine and determination of refractive indices, the fractions corresponding to the observed flats were identified as the normal alkyl chlorides: butyl chloride, hexyl chloride, octyl chloride, etc., up to eicosyl chloride, which is a solid melting at 27.8° (Table I).

The undistilled portion of the ether-soluble product was a soft grease that contained 7.00% chlorine, corresponding to an average composition $C_{33}H_{67}Cl$. The ether-insoluble product, amounting to 6 g., was a soft white wax that contained 6.11% chlorine by analysis, corresponding to an average composition $C_{38}H_{77}Cl$.

The effects of some reaction variables on the average chain length of the products are illustrated in Table II, and in Fig. 1.

In the absence of a free radical-producing agent neither ethyl chloride nor telomers were formed. Suitable initiators were found to include, in addition to benzoyl peroxide, the azodinitriles, oxygen and tetraphenyllead.

Styrene/Hydrogen Chloride Telomer.—One hundred grams of freshly distilled styrene and 100 g. of 12 *N* hydrochloric acid were placed in an all-glass apparatus consisting of a flask fitted with sealed stirrer, thermometer and reflux condenser, and subjected to vigorous mechanical stirring to disperse the styrene in the acid. The mixture was warmed to gentle reflux (103–104°) and 0.5 g. of benzoyl peroxide

TABLE II

TELOMERIZATION OF ETHYLENE WITH HYDROGEN CHLORIDE

Aqueous HCl concn., %	Aqueous HCl g.	Benzoyl peroxide, g.	Ethylene pressure Initial (atm.)	Ethylene pressure At temp. (atm.)	Temp., °C.	Liquid product (above EtCl) Yield, g.	Liquid product (above EtCl) Soluble in ether, %	Liquid product (above EtCl) Insoluble in ether, %
18.5	100	0.5	200	390-500	100	46	87	13 (C_{38})
18.5	140	0.7	400	540-950	100	57.5	42	58 (C_{50})
30	100	1.0	400	350-560	100	30	100	0
37	100	1.0	350	395-600	100	60	87	13

was then added; stirring and heating were continued for 10 hours without visible change. The organic layer was separated and washed with water. The clear liquid product was thoroughly steam distilled in order to remove any monomeric styrene and α-chloroethylbenzene. The remaining product was a sticky, viscous mass which contained 4.75% chlorine, corresponding to an average molecular weight of 747 or an average chain length of 6.7 styrene units.

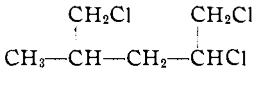
Allyl Chloride/Hydrogen Chloride Telomer.—When allyl chloride was refluxed with hydrochloric acid and benzoyl peroxide at atmospheric pressure no reaction took place. Accordingly, the reaction was carried out in a pressure vessel at 100° under autogenous pressure. Seventy grams of allyl chloride, 100 g. of 12 *N* hydrochloric acid and 1 g. of benzoyl peroxide were placed in a tube, which was then agitated and heated to 100° for 11 hours. At this time the agitation was stopped and the tube was allowed to cool overnight. The product was discharged and the organic layer was separated, washed with water and 5% sodium bicarbonate, and dried over magnesium sulfate. Unreacted allyl chloride was stripped by distillation on a steam-bath through a 16-inch Vigreux column. The dark liquid residue weighed 24.7 g. Upon distillation two principal fractions were obtained. The first, boiling at 94-96.5° (760 mm.), weighed 5 g. This proved to be 1,2-dichloropropane:

	Found for Fraction 1	Reported values for 1,2-Dichloropropane	Reported values for 1,3-Dichloropropane
Boiling point, °C.	94-96.5	96.8	119
Refractive index, n^{20}_D	1.4396	1.4387	1.452
Chlorine, %	62.22	62.74	62.74

The second fraction, boiling at 147° (100 mm.) or 92° (10 mm.), weighed 9 g. A sample was redistilled at 10 mm. and analyzed.

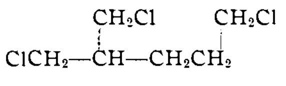
	Chlorine, %	Mol. wt.	Density at 25°	n^{25}_D
Calcd. for $C_6H_{11}Cl_3$	56.11	189.5	....	....
Found	54.35, 54.73	171, 169	1.2084	1.4790

The somewhat low values for chlorine and molecular weight may be ascribed to the presence of the unsaturated compound derived by loss of HCl. The structure has not been determined. The configuration expected by analogy with that of the 1:1 product formed at the same time would be



$$CH_3-\overset{CH_2Cl}{CH}-CH_2-\overset{CH_2Cl}{CHCl}$$

The infrared spectrum of the product was in agreement with the above structure rather than that of the isomer which would be expected if "abnormal" addition occurred,



$$ClCH_2-\overset{CH_2Cl}{CH}-CH_2\overset{CH_2Cl}{CH_2}$$

in that it had an absorption at 7.2 microns which appeared in reference dichloroalkanes containing a methyl group and did not appear in those without a methyl group. Other peaks were noted at 5.8 and 6.0 microns that correspond to the wave lengths usually assigned to carbonyl groups and unsaturation. Washing of a sample with aqueous sodium bisulfite solution followed by redistillation did not eliminate these latter peaks but so diminished them that their presence may be ascribed to a small amount of impurity. In attempts to confirm the 1,2-dichloro configuration by dehalogenation with zinc in ethanol, none of the halogen was removed.

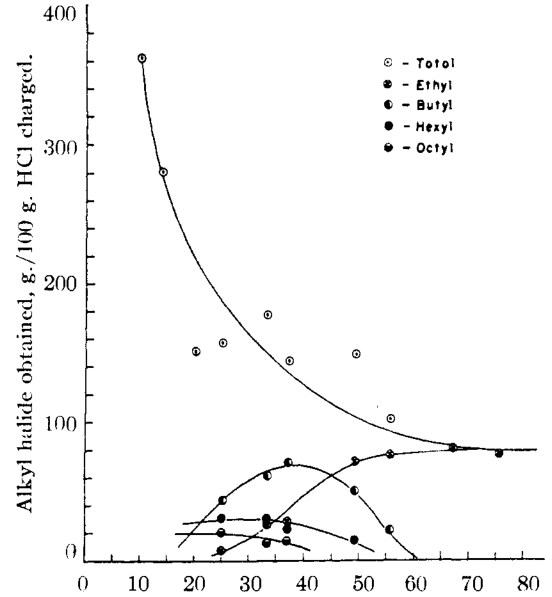


Fig. 1.—Telomerization of ethylene at 500-700 atm. with aqueous hydrogen chloride in the presence of 1,1-azodicyclohexanecarbonitrile.

The residue from the distillation was a dark viscous liquid weighing 5.7 g. This was probably a mixture of higher molecular weight telomers.

Discussion

The following mechanism is suggested for the telomerization of ethylene with hydrochloric acid.

$$\text{Initiator} \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + HCl \longrightarrow RCl + H\cdot \qquad (2)$$

$$H\cdot + C_2H_4 \longrightarrow CH_3CH_2\cdot \qquad (3)$$

$$CH_3CH_2\cdot + n(C_2H_4) \longrightarrow CH_3CH_2(CH_2CH_2)_n\cdot \qquad (4)$$

$$CH_3CH_2(CH_2CH_2)_n\cdot + HCl \longrightarrow CH_3CH_2(CH_2CH_2)_n\,Cl + H\cdot \qquad (5)$$

There appears to be no doubt that this telomerization is a chain reaction involving free radicals since it is induced by free radical-forming initiators, and a large number of molecules of telomer are formed for each molecule of initiator employed. The fact that the products are straight-chain primary chlorides is further evidence that the growth of the chains takes place through a free-radical mechanism, inasmuch as an ionic polymerization mechanism would be expected to give branched-chain secondary chlorides.

In equations (2) and (5) the free radicals are represented as combining with the chlorine of the hydrogen chloride, leaving the hydrogen atom as the chain-propagating radical. This is in agreement with the fact that the direction of addition of hydrogen chloride to olefinic double bonds is not usually reversed by peroxides and in fact was not reversed in the case of allyl chloride under conditions leading to the simultaneous formation of telomers. The generally accepted mechanism for the peroxide-reversed addition of hydrogen bromide to unsymmetrical olefins[8] involves reaction of a free radical with the hydrogen of the hydrogen bromide, leaving the bromine atom to propagate the chain. The bromine atom then attacks the olefin double bond at the point of highest electron density. If hydrogen chloride reacts in the opposite way so that the chlorine is combined with the free radical, leaving the hydrogen atom to propagate the chain, the hydrogen atom should attack the point of highest electron density, and the same isomer should be formed by the free-radical chain reaction as by the ionic addition.

Reversal of the direction of hydrogen chloride addition to double bonds by free radicals has seldom been noted. Raley, Rust and Vaughan,[9] have reported that infrared analyses indicated the presence of small amounts of both *n*-propyl chloride and isopropyl chloride in the products of vapor-phase reactions of propylene with hydrogen chloride in the presence of di-(*t*-butyl) peroxide. From the reaction of 3,3-dimethyl-1-butene with hydrogen chloride in the presence of benzoyl peroxide, Ecke, *et al.*,[10] found some of the "abnormal" primary alkyl chloride along with the secondary alkyl chloride corresponding to "normal" addition. In both instances anhydrous systems were used. In the latter case it should be noted also that the experimental data show formation of some "abnormal" product even in the absence of added peroxide, and addition of a free-radical-forming initiator caused a large increase in the quantity of the "normal" adduct formed.

In order to reach a firm conclusion as to the manner in which hydrogen chloride is attacked by free radicals, it would be necessary to establish the structure of one of the 2 : 1 or higher telomers that are formed only in the presence of a free-radical initiator.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. H. S. Young and the staff of the Pressure Research Laboratory, who designed and operated the pressure equipment.

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[8] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[9] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 2767 (1948).

[10] G. G. Ecke, N. C. Cook and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Chromones in the Mannich Reaction

BY PAUL F. WILEY

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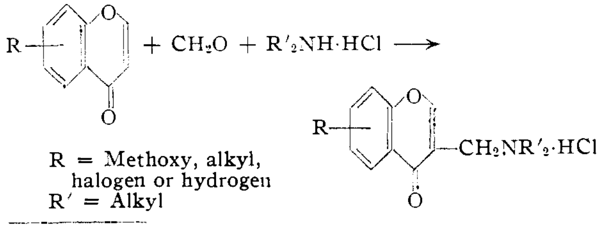
The reaction of chromones with formaldehyde and secondary amine hydrochlorides has been studied. Chromones unsubstituted in the 2- and 3-positions react to form 3-dialkylaminomethylchromone hydrochlorides. This reaction does not occur with 2-methylchromones.

The replacement of an α-hydrogen atom in a saturated ketone by an alkyl- or dialkylaminomethyl group in the Mannich reaction is well known. However, 2-hydroxy-1,4-naphthoquinone is the only α,β-unsaturated ketone that has been reported[1,2] to undergo a similar reaction, and it is unlikely that this compound participates as an α,β-unsaturated ketone, but either as 1,2,4-triketotetralin or as a phenol. In the research reported here it has been found that a special type of α,β-unsaturated ketone does undergo α-substitution in the Mannich reaction. These ketones are chromones which are not substituted in the 2- or 3-positions. The reaction is as follows



The chromones found to react were chromone and its 6-methoxy-, 7-methoxy-, 6-chloro- and 6-methyl- derivatives. The amine hydrochlorides used were those of dimethylamine, diethylamine, piperidine and morpholine. Yields varied from 7.5 to 60%.

The structure of the Mannich bases from chromones is shown by several lines of evidence. Analytical data agree completely with the chromone structure. Absorption spectra, both ultraviolet and infrared, indicate that the chromone nucleus is still present. The reaction must thus have occurred by attack at the 2- or 3-position in the pyrone ring (or by opening of this ring and subsequent closure giving the same net effect) or by substitution at a vacant position in the benzene ring, which can be eliminated since such substitution in non-activated benzene rings is unknown. Substitution in the 3-position is proved by the fact that the product of the reaction of 7-methoxychromone with formaldehyde and dimethylamine hydrochloride has been reduced to the known 3-dimethylaminomethyl-7-methoxychromanone hydrochloride. This proof is somewhat weakened by the 1.5% yield obtained in the reduction but is strengthened by the finding that 2-dimethylamino-

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[1] M. T. Leffler and R. J. Hathaway, THIS JOURNAL, **70**, 3222 (1948).

[2] C. E. Dalgleish, *ibid.*, **71**, 1697 (1949).