tals in 300 ml. of water plus 38 ml. of concentrated aqueous ammonia was boiled 1 hr., heated on a steam-bath 1 hr., and then was allowed to cool to room temperature. The fine, needle-like, white crystals which separated from the solution were filtered, washed with water, and dried. The solid, 1.88 g., m.p. 117–117.5°, did not dissolve completely in 30 ml. of hot hexane. The mixture was filtered and the collected solid was washed with warm hexane. The dried hexane-insoluble solid, 1.30 g., m.p. 117–117.5°, partly insoluble in water, but completely soluble in sodium carbonate solution, was probably a mixture of *cis*-4-*t*-butylcyclohexanecarboxylic acid and its unstable ammonium salt as indicated by the following observations. The melting point of a mixture of the hexane-insoluble solid with a sample of hexane-soluble *cis* acid (m.p. 118–119°, crystallized from hexane) was 117–118.5°. A strip of moist red litmus paper, when held over a boiling chloroform suspension of the hexane-insoluble solid, instantly became blue. The recovered hexane-insoluble solid amounted to 0.68 g. The combined hexane filtrates yielded 0.45 g. of crystals in the form of colorless plates, m.p. 117–118°. Recrystallization from hexane gave 0.30 g. of similar crystals, m.p. 117–118°.[35]

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.63; H, 11.12.

(B) **Low Pressure Rapid Hydrogenation of *p-t*-Butylbenzoic Acid.**—Four batches of *p-t*-butylbenzoic acid (m.p, 166–167°), each dissolved in 160 ml. of glacial acetic acid, were hydrogenated consecutively at room temperature in the presence of platinum oxide catalyst by the use of a Parr hydrogenation apparatus[37] (initial pressures 33–38 lb./sq. in.). The data are summarized in Table III.

In each run, the acetic acid solution was filtered from the catalyst immediately after the uptake of hydrogen ceased. The bottle and filter were rinsed with 70-100 ml. of glacial acetic acid (in 3-4 portions). Part of the resulting solution (0.6-0.7 ml.) was diluted with 5 ml. of water. The resulting solid was filtered, washed with water, and dried. The infrared spectrum of a 10.0% solution of the solid in carbon tetrachloride was recorded. No absorbance attributable to *p-t*-butylbenzoic acid was detected. The spectra are consistent with a mixture of 70% *cis*- and 30% *trans*-4-*t*-butylcyclohexanecarboxylic acid.

TABLE III

HYDROGENATION OF *p-t*-BUTYLBENZOIC ACID

Run	*p-t*-Butylbenzoic acid, G.	Mole	Platinum oxide, g. added[a]	Time, min.	H_2, % used	II, % in product[b]
2	12.13	0.0681	1.12	120	97	64
3	14.57	.0818	0.68	80	99	74
4	14.55	.0817	.34	90	100	71
5	14.56	.0818	.66	90	99	73

[a] Most of the platinum from run 2 was reused in run 3 with the addition of the amount of platinum oxide indicated. Subsequent runs were similarly conducted. Except for moderate losses during filtration, the amount of catalyst present was cumulative. [b] The tabulated percentages of *cis*-4-*t*-butylcyclohexanecarboxylic acid (II) were calculated by infrared spectroscopic analysis from the absorbancies at 1156 cm.$^{-1}$. The spectrum of run 5 and the spectra of the pure *cis* acid, the pure *trans* acid and *p-t*-butylbenzoic acid which were used in the calculatons have been reproduced in ref. 1. The spectra show that the amount of *p-t*-butylbenzoic acid remaining in the product is negligible, as one would expect from the percentage hydrogen used.

The acetic acid solutions were evaporated to dryness (at about 20 mm.) and the residues were recrystallized once from ethanol–water. The resulting mixture of *cis* and *trans* acids was fractionally recrystallized from hexane. Very slow crystallization from dilute hexane solutions at room temperature produced large colorless crystals of fairly pure *cis* acid. Further recrystallizations from hexane yielded 10.0 g. (17%) of *cis*-4-*t*-butylcyclohexanecarboxylic acid, m.p. 117.5–118.5°, and fractions of lesser purity from which further pure *cis* acid could be obtained by fractional recrystallization.

Acknowledgment.—The author is indebted to Professor David Y. Curtin and Professor Ernest L. Eliel for their invaluable coöperation, encouragement and counsel.

URBANA, ILL.

(35) Other melting points recorded for "4-*t*-butylcyclohexanecarboxylic acid" are: m.p. 89.5-90.5°, ref. 27; and m.p. 111°, ref. 36. The compositions of these samples are not reported.

(36) K. Adler, K. Heimbach and E. Kühle, *Chem. Ber.*, **86**, 1364 (1953).

(37) R. Adams and V. Voorhees, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 66, Fig. 6.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XLVI. The Thermal Decomposition of the Butenyl Chloroformates[1]

BY K. L. OLIVIER[2] AND W. G. YOUNG

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Kinetics and products of the thermal decomposition of α-methylallyl and crotyl chloroformate in a series of solvents have been scrutinized. The experimental findings are discussed in terms of alkyl–oxygen heterolysis and ion pairs. An interpretation of the decomposition of other chloroformates in the light of the present findings is presented.

Introduction

Considerable attention has been given to the reaction of various allylic alcohols with thionyl chloride.[3] However, these investigations have been almost exclusively confined to a study of product composition as a function of such variables as solvent, order of addition of reagents and presence or absence of tertiary amines and their hydrochlorides. Detailed kinetic study of the reaction is virtually precluded by the extreme lability of the intermediate chlorosulfinate ester. Indeed, only one allylic chlorosulfinate, the parent allyl chlorosulfinate, has been reported,[3a] and this substance was found to be highly sensitive to traces of moisture.[3b] Recently the α- and γ-trifluoromethylallyl chlorosulfinates have been isolated in this Laboratory by James Pegolotti, but no kinetic studies have yet been published.

Formally analogous to the decomposition of chlorosulfinate esters is the decomposition of chloroformate esters. It was anticipated that allylic chloroformates would be capable of being isolated, purified and separately decomposed under

(1) This work was supported in part by a grant to W. G. Young from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1956–1957.

(3) (a) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956); (b) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak and W. G. Young, THIS JOURNAL, **80**, 5965 (1958).

carefully controlled conditions, and that their decomposition would hence be more amenable to mechanistic scrutiny than is the decomposition of their sulfur analogs. Accordingly, α-methylallyl and crotyl chloroformate were synthesized and their decomposition was studied.

Three avenues of approach were open. The first approach consisted in a study of the rates of thermal decomposition of these chloroformates in a series of solvents which vary in their ability to solvate ions. The principle in mind was: to the extent that the decomposition reaction shows an increased rate upon going to a solvent of higher ionizing power, then to that extent the reaction can be said to be proceeding by an ionization process. This type of approach is exemplified in the work of Grob and Winstein[4] on the mutarotation of 5α,6β-dibromocholestane.

The second mode of attack on the problem entailed a comparison of the rates of decomposition under a nearly constant set of conditions of several chloroformates of varied structure. In this regard some pertinent ancillary data is available in the literature. If the rate of decomposition of a chloroformate ROCOCl is directly proportional to the stability of the corresponding carbonium ion $R^{\oplus}$, then an interpretation of the process in terms of alkyl–oxygen ionization is warranted.

Finally, further details of mechanism were sought by a study of reaction products as a function of the solvent employed and of the structure of the chloroformate decomposed.

Results

The rates of thermal decomposition of α-methylallyl and crotyl chloroformates were measured titrimetrically by following the rate of disappearance of titrable chloride. Titrable chloride includes the chloroformate and hydrogen chloride, but excludes the butenyl chlorides. The fact that hydrogen chloride is one of the products of the decomposition reaction does not greatly complicate the calculations. In fact, it can be shown that the simultaneous operation of two first-order reactions, one of which produces titrable chloride, leads to over-all first-order kinetics.

First-order rate constants were calculated from the integrated form of the usual first-order rate expression given in equation 1. In equation 1, k is the first-order rate constant for the disappearance of chloroformate

$$k = \frac{2.303 \log (a/(a - x))}{t} \qquad (1)$$

a is taken as the titer at time t minus the infinity titer, and $a - x$ is taken as the initial titer minus the infinity titer. A typical rate run is given in Table I, and the rate contants obtained as described above are listed in Table II. The rate constants given are generally averages of eight to ten values obtained between 15 and 90% reaction. There was no detectable drift in the value of the rate constant in any of the runs. Also included in Table II are the thermodynamic function of activation calculated from transition state theory.[5]

(4) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

TABLE I

THE DECOMPOSITION OF α-METHYLALLYL CHLOROFORMATE IN DIOXANE AT 75.0°[a]

Time, sec.	Silver nitrate titer, ml.[b]	Thiocyanate titer, ml.[c]	$k \times 10^4$, sec.$^{-1}$	Reaction, %
0	4.500	1.467	..	..
630	3.500	0.853	2.97	17.1
1380	2.500	.249	3.03	34.1
1830	2.200	.160	2.99	43.7
2430	2.000	.186	3.12	53.2
3210	2.000	.410	3.04	62.3
4170	1.750	.315	2.81	69.0
5670	1.500	.362	3.00	81.7
8040	1.500	.546	2.73	88.9
21900[d]	1.000	.326	..	..
21900[d]	1.050	.342	..	..

Average k, 2.96 ± 0.10

[a] Initial concentration 0.0694 *M*. [b] 0.107 *M*. [c] 0.105 *M*. [d] Infinity titer.

Because of the lability of allylic systems, it was necessary to establish that neither the starting chloroformate nor the product chlorides undergo rearrangement under the conditions of the decomposition reaction. This was demonstrated by suitable and extensive control experiments.

Products of the decomposition of the butenyl chloroformates were studied in eight solvents. In every case the products obtained were crotyl chloride, α-methylallyl chloride, butadiene, carbon dioxide and hydrogen chloride. The data obtained from the various product runs are summarized in Table III. The yield of butadiene was calculated from the infinity titer, since any residual titrable chloride is undoubtedly hydrogen chloride formed in the reaction yielding butadiene. No hydrogen chloride was formed by hydrolysis of the chloroformate since allylic alcohols were not observed in the chromatographic analysis.

Relative yields of the butenyl chlorides were obtained by the use of vapor phase chromatography. The accuracy of the data obtained by this method is set at ±2% absolute, and the precision is set at ±1.5% absolute. That the relative yields of the chlorides remain constant within a given run was established by control experiments.

Repeated fractional crystallization of the brucine salt of the hydrogen phthalate of α-methylallyl alcohol[6] gave (+)-α-methylallyl alcohol having $[\alpha]^{30}D$ 33.2°. This represents the highest rotation thus far obtained for this alcohol.

(+)-α-Methylallyl chloroformate was reduced with lithium aluminum hydride to give (+)-α-methylallyl alcohol having the same rotation as the alcohol from which the chloroformate was prepared. Thus quantitative retention of configuration is maintained both in the formation of the chloroformate from the alcohol and in the reduction of the chloroformate to the alcohol.

In a control experiment it was shown that optically active α-methylallyl chloride does not undergo racemization upon standing at 50° for three days in acidified methylene chloride. Since methylene chloride is the best ionizing solvent of those employed for decomposition of optically active chloroformate, it is quite probable that α-methylallyl

(6) J. Kenyon and D. Snellgrove, *J. Chem. Soc.*, **127**, 1174 (1925).

TABLE II

SUMMARY OF RATE CONSTANTS

Chloroformate	Solvent	Temp., °C.	k, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
α-Methylallyl	Dioxane	50.0	$(2.15 \pm 0.06) \times 10^{-5}$	22	−11
		75.0	$(2.96 \pm .10) \times 10^{-4}$		
	n-Butyl ether	75.0	$(3.50 \pm .17) \times 10^{-5}$	25	−13
		99.6	$(3.98 \pm .15) \times 10^{-5}$		
	Toluene	75.0	$(3.03 \pm .06) \times 10^{-5}$	22	−15
		99.6	$(2.74 \pm .12) \times 10^{-4}$		
	Tetrahydrofuran	50.0	$(2.70 \pm .09) \times 10^{-5}$	21	−15
		75.0	$(3.19 \pm .08) \times 10^{-4}$		
	Methylene chloride	50.0	$(5.81 \pm .25) \times 10^{-5}$	20	−17
		75.0	$(6.11 \pm .43) \times 10^{-4}$		
	n-Decane	110.6	$(1.58 \pm .09) \times 10^{-5}$	29	− 4
		138.1	$(2.38 \pm .13) \times 10^{-4}$		
	Nitrobenzene	50.0	$(3.11 \pm .55) \times 10^{-4}$		
Crotyl	Methylene chloride	50.0	$(1.59 \pm .03) \times 10^{-5}$		
	n-Decane	138.1	$(1.28 \pm .04) \times 10^{-4}$		
Ethyl	Methylene chloride	75.0	$<10^{-7}$		

TABLE III

DECOMPOSITION PRODUCTS OBTAINED FROM THE BUTENYL CHLOROFORMATES[a]

Solvent	From α-methylallyl chloroformate, % s-Cl[b]	p-Cl[c]	Buta-diene	From crotyl chloroformate, % s-Cl[b]	p-Cl[c]	Buta-diene
n-Butyl ether	58	42	12	60	40	7
Toluene	69	31	9	61	39	6
Tetrahydrofuran	58	42	13	50	50	5
Methylene chloride	71	29	15	51	49	11
Ethyl ether	58	42	..	..	..	..
n-Decane	56	44	..	52	48	..
None	63	37	..	47	53	..
Dioxane	59	41	19	49	51	9
Dioxane + 0.08 M tri-n-butylamine hydrochloride	66	34	..	15	85	..

[a] The data represent averages of two or three runs, in some cases at different temperatures; effect of temperature was very slight and did not show any significant trends. [b] The relative yield of α-methylallyl chloride in the mixture of butenyl chlorides. [c] The relative yield of crotyl chloride.

chloride is also optically stable under the conditions of the decomposition in the other solvents.

The results of the decomposition of (+)-α-methylallyl chloroformate are set forth in Table IV. The optical purity of the α-methylallyl chloride obtained was calculated on the basis of $[\alpha]^{30}D$ 33.2° for optically pure α-methylallyl alcohol and $\alpha^{25}D$ 60° (neat, l 1.0) for optically pure α-methylallyl chloride.[7] The absolute configuration of both alcohol and chloride are known, and it has been established that the alcohol and chloride of like sign have like configuration.[7] Further, the chloroformate is formed without a change in configuration at the asymmetric carbon atom, and has the same sign as the alcohol from which it is prepared. Then any inversion in the decomposition reaction will be accompanied by a change in sign.

(7) W. G. Young and F. F. Caserio, unpublished work. This value was calculated from the rotation of optically pure α-chloropropionic acid[8] and the rotation of the optically active α-chloropropionic acid obtained from ozonolysis of a sample of optically active α-methylallyl chloride.

(8) W. Fickett, H. K. Garner and H. J. Lucas, THIS JOURNAL, **73**, 5063 (1951).

TABLE IV

DECOMPOSITION OF (+)-α-METHYLALLYL CHLOROFORMATE[a]

Solvent	Rotation of α-methylallyl chloride formed[b] $\alpha^{t}D$ (t, °C.) (neat, l 0.5)	Excess retention,[c] %
Dioxane	+1.33 (29)	49
Toluene	+0.40 (27)	15
Methylene chloride	+0.67 (26)	25
n-Butyl ether	+0.78 (27)	28

[a] $\alpha^{28}D$ 0.32° (neat, l 0.5). [b] The precision and accuracy of the rotations is set at ±0.02°. [c] The remainder of the chloride is racemic.

Discussion

Relative rates of decomposition of α-methylallyl chloroformate in the various solvents are presented in Table V. Included in the table are the values

TABLE V

RELATIVE RATES OF DECOMPOSITION OF α-METHYLALLYL CHLOROFORMATE IN VARIOUS SOLVENTS

Solvent	Relative rate at 75°	Dielectric constant at 25°[a]
n-Decane	1.00[b]	2.0[d]
n-Butyl ether	11.3	3.1
Toluene	98.0	2.4
Dioxane	971	2.2
Tetrahydrofuran	1030	7.4
Methylene chloride	1980	9.1[d]
Nitrobenzene	*Ca.* 10000[c]	34.8

[a] The value for tetrahydrofuran is from ref. 21; the other values are from ref. 20. [b] Extrapolated from data at 110.6° and 138.1°. [c] Estimated from data at 50°. [d] 20°.

of the dielectric constant of the solvents. A striking solvent effect is immediately in evidence—the decomposition reaction proceeds faster in nitrobenzene than in n-decane by a factor of 10^4. This very marked increase in rate upon going to solvents of higher ionizing power indicates that, at least for the better ionizing solvents, the rate-determining step of the decomposition reaction is an ionization process.

Correlation of relative rate with the dielectric constant of the solvent is, at best, imperfect. However, this sort of behavior is not unprecedented[4,9]

(9) H. Meerwein and K. von Emster, *Ber.*, **55**, 2500 (1922).

and does not constitute evidence against the operation of an ionization mechanism.

α-Methylallyl chloroformate was found to decompose faster than crotyl chloroformate—in *n*-decane by a factor of 1.9, and in methylene chloride by a factor of 3.6. Since this factor is relatively constant when there is a rate difference of approximately 2000 between decomposition in methylene chloride and decomposition in *n*-decane, it is reasonable to conclude that crotyl chloroformate exhibits a solvent dependence similar to that shown by α-methylallyl chloroformate.

Comparison with the data of Wiberg and Shryne[10] shows that α-methylallyl chloroformate decomposes in dioxane solution at a considerably faster rate than does benzyl chloroformate (factor of 34 at 90°), but at a slower rate than α-phenethyl chloroformate (factor of 12 at 80°). The following series of decreasing reactivity is thus generated: α-phenethyl > α-methylallyl > benzyl ≫ ethyl. This order of reactivity nicely parallels the order of decreasing reactivity of the corresponding chlorides in limiting[11] solvolysis reactions.[12] This close parallel between carbonium-ion stability and decomposition rate constitutes strong evidence in favor of a rate-determining alkyl–oxygen ionization in the decomposition of these chloroformates, with the possible exception of ethyl chloroformate.

Entropies of activation for the decomposition of α-methylallyl chloroformate in the different solvents (Table II) are fairly constant with the exception of the value for the decomposition in *n*-decane. The higher entropy of activation in this solvent is probably ascribable to the very low ion-solvating ability of *n*-decane; relatively few solvent molecules would be expected to be oriented in the transition state. Alternatively, this higher $\Delta S^{\pm}$ for *n*-decane may be an indication that a different mechanism is operating in this solvent. Perhaps there is a contribution of cyclic, concerted processes to the over-all reaction. In general, the order of magnitude of the entropies of activation is not inconsistent with a rate-determining ionization.

Products of the decomposition of the butenyl chloroformates were studied in eight solvents. In every case the products obtained were crotyl chloride, α-methylallyl chloride, butadiene, carbon dioxide and hydrogen chloride. That no appreciable quantity of butenyl chloride is produced by recombination of butadiene and hydrogen chloride can be concluded from the facts that (1) the addition of hydrogen chloride to butadiene gives a mixture of butenyl chlorides rich (75–80%) in α-methylallyl chloride,[13] and (2) in control experiments the relative yields of the two chlorides remained constant throughout the course of the decomposition reaction.

Chart I presents a mechanism consistent with the experimental findings in the decomposition of α-methylallyl chloroformate. This chloroformate (I) undergoes a rate-determining alkyl–oxygen heterolysis to form the very unstable carbonium–chloroformate ion pair II, which ejects a molecule of carbon dioxide to produce the unsymmetrical carbonium–chloride ion pair III. An unsymmetrical intermediate is necessitated by the observation that, although the relative yields of the butenyl chlorides are fairly constant from solvent to solvent, yields of α-methylallyl chloride and butadiene are higher in the decomposition of α-methylallyl chloroformate than in the decomposition of crotyl chloroformate (Table III). The chloride in III is well situated both for a preferential collapse to the secondary position and for an abstraction of a proton from the methyl group.

Collapse of III to covalency leads to the observed products V, VI and VII. Dissociation of III to give the free ions IV is probably unimportant even for the better ionizing solvents, since the relative yields of the butenyl chlorides are almost constant from solvent to solvent.

It is possible that the rate-determining alkyl–oxygen fission is preceded by a rapid ionization equilibrium involving the carbon–chlorine bond. The available data do not allow a decision on this point.

It is postulated that the decomposition of crotyl chloroformate proceeds by way of a set of intermediates completely analogous to those postulated for the decomposition of α-methylallyl chloroformate. Ion pair III would be expected to be more stable than VIII (from crotyl chloroformate) since in VIII the bulk of the positive charge would be localized at the primary position. The greater stability of III may account for the facts that (1) α-methylallyl chloroformate decomposes at a faster rate than does crotyl chloroformate, and (2) α-methylallyl chloride solvolyzes faster than does crotyl chloride.[3a]

The effect of solvent on the course of the decomposition of (+)-α-methylallyl chloroformate (Table IV) is unclear. Specific solvent effects probably play an important role.

Two points of comparison between the behavior of allylic chloroformates and the behavior of their sulfur counterparts, the chlorosulfinates, are noteworthy. The first, and more striking, observation is that the SNi′ reaction is relatively unimportant in the former case. Indeed this reaction cannot be made to predominate even in ether, the solvent so well suited to SNi′ in the chlorosulfinate area.[3] It is quite probable that this phenomenon is due to the greater lability of the first-formed carbonium–chloroformate ion pair as compared to the relative stability of the initially formed carbonium–chlorosulfinate ion pair. Thus the more stable carbonium–chlorosulfinate ion pair is able to attain the structural orientation[14] required for selective collapse to the SNi′ product.

A second difference in behavior is made manifest by a comparison of relative susceptibility of chlorosulfinates *vs.* chloroformates to SN2-type attack. Whereas the former compounds are readily converted by amines or amine hydrochlorides to allylic chlorides with preservation of allylic structure,[3a] addition of large amounts of chloride ion (Table III) in the present work resulted in the formation of a mixture of butenyl chlorides.

(10) K. B. Wiberg and T. M. Shryne, THIS JOURNAL, **77**, 2774 (1955).

(11) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

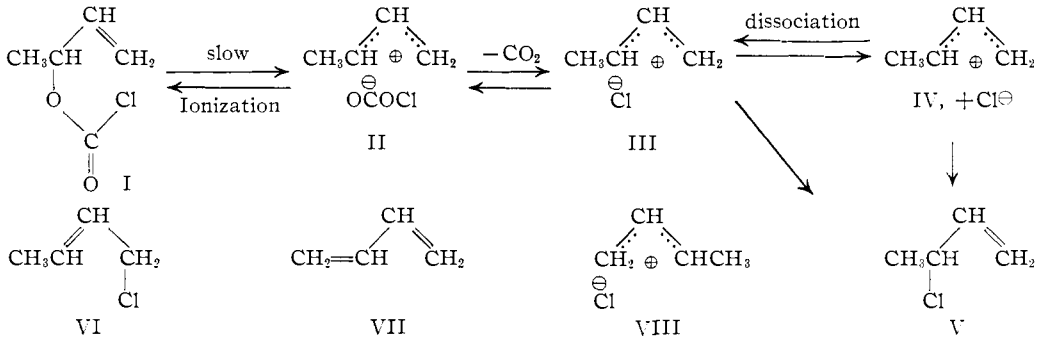
(12) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(13) M. S. Kharasch, J. Kritchevsky and F. R. Mayo, *J. Org. Chem.*, **2**, 489 (1937).

(14) S. Winstein and G. Robinson, THIS JOURNAL, **80**, 169 (1958).

CHART I

MECHANISM OF DECOMPOSITION OF α-METHYLALLYL CHLOROFORMATE



Expansion of the reactivity series for decomposition of chloroformates (*vide supra*) by including qualitative data from the literature gives the following extended series: triphenylmethyl[15] > benzhydryl[15] > *t*-alkyl[16,17] α-phenethyl[10] > α-methylallyl > crotyl > benzyl[10] >> primary alkyl. Again, a close correspondence between rate of decomposition of ROCOCl and stability of $R^{\oplus}$ (as evidenced by the behavior of RCl in solvolysis reactions) is to be noted throughout. This harmony constitutes strong evidence for a rate-determining alkyl–oxygen heterolysis in the liquid-phase decomposition of the whole gamut of compounds cited, with the possible exceptions of decomposition of primary alkyl chloroformates and of decompositions in highly non-polar solvents. Gas-phase decomposition of chloroformates is best interpreted in terms of cyclic, concerted processes, as has been well substantiated.[18]

Experimental[19]

Preparation and Purification of Materials. Toluene.—Baker C.P. toluene was allowed to reflux overnight over sodium, and was then fractionated through a large packed column. The pure solvent had b.p. 52° (99 mm.) and $n^{25}D$ 1.4933 (lit.[20] $n^{25}D$ 1.4941). Toluene was stored over sodium hydride.

***n*-Butyl Ether.**—The purification of this solvent has been given.[3b]

Tetrahydrofuran.—Eastman Kodak Co. white label grade product was allowed to reflux overnight over potassium hydroxide. The liquid was then flash distilled, dried over sodium hydride, and fractionated through a large packed column. The center cut had b.p. 66.5°, $n^{25}D$ 1.4046 (lit.[21] $n^{25}D$ 1.4045). The pure solvent was stored in the dark over sodium hydride and under nitrogen.

Dioxane.—Eastman Kodak Co. white label dioxane was treated by the method of Fieser.[22] Final distillation was effected through a large packed column. The distillate had b.p. 101° and $n^{25}D$ 1.4199 (lit.[20] $n^{25}D$ 1.4203). Purified dioxane was stored in the dark over sodium hydride and under nitrogen.

Methylene Chloride.—The procedure of Weissberger[20] was used to purify the technical grade material. Fractionation through a large packed column gave a center cut having b.p. 40°, $n^{20}D$ 1.4244 (reported[20] $n^{20}D$ 1.4246).

***n*-Decane.**—Humphrey–Wilkinson *n*-decane was allowed to boil under reflux overnight over sodium, and was then fractionated through a large packed column to give material of b.p. 71° (20 mm.) and $n^{25}D$ 1.4095 (lit.[20] $n^{25}D$ 1.4097). *n*-Decane was stored over sodium hydride.

Nitrobenzene.—Eastman Kodak Co. white label nitrobenzene was crystallized five times from its own melt. The resulting liquid was dried over Drierite and distilled from phosphorus pentoxide through a large packed column (3mm.). The distillate was light green in color and had $n^{25}D$ 1.5495 (lit.[20] $n^{20}D$ 1.5526).

Phosgene.—The phosgene used for most of the runs was obtained from the Matheson Co. The procedure of Erdmann[23] was used to prepare additional quantities; 20% oleum was substituted for the 80% material used by Erdmann; yield 160 g. (80%).

Butenyl Chlorides.—The isomeric butenyl chlorides were prepared by the previously described method.[24] α-Methylallyl chloride had b.p. 38° (300 mm.) and $n^{25}D$ 1.4122 (lit.[24] $n^{25}D$ 1.4120). Crotyl chloride gave b.p. 39° (140 mm.) and $n^{25}D$ 1.4320 (reported[24] $n^{25}D$ 1.4330).

Crotyl Alcohol.—Crotonaldehyde was reduced by the procedure of Nystrom and Brown.[25] Hydrolysis was effected by the method of Leonard.[26] The pure alcohol showed b.p. 122–123° and $n^{25}D$ 1.4260 (lit.[27] $n^{25}D$ 1.4270); yield 62%.

α-Methylallyl Alcohol.—The procedure used to prepare crotyl alcohol was adapted to the reduction of methylvinyl ketone (Pfizer); yield 49%, b.p. 98°, $n^{25}D$ 1.4110 (lit.[27] $n^{25}D$ 1.4125).

α-Methylallyl Chloroformate.—To a solution of 224 g. (2.3 moles) of phosgene in 800 ml. of anhydrous ether was added 79 g. (1.1 moles) of α-methylallyl alcohol. The addition required two hours, during which time the reaction vessel was cooled by a Dry Ice–acetone-bath. Excess phosgene and ether were removed by distillation at reduced pressure to give a light yellow pot residue, which was flash distilled at reduced pressure and finally fractionated through a 40-inch glass-helices-packed column. A colorless lachrymatory liquid (89 g., 60% yield) was collected at 32° (21 mm.). It had $n^{25}D$ 1.4185 and d^{25}_4 1.058 (lit.[28] b.p. 130° and $n^{20}D$ 1.427).

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.63; H, 5.24; Cl, 26.35. Found: C, 44.64; H, 5.41; Cl, 25.88.

Crotyl Chloroformate.—The procedure is analogous to that given above for the preparation of α-methylallyl chloroformate; yield 76%. This chloroformate is a colorless lachrymatory liquid, b.p. 33° (10 mm.) and $n^{25}D$ 1.4327.

Anal. Calcd. for $C_5H_7O_2Cl$: C, 44.63; H, 5.24; Cl, 26.35. Found: C, 44.63; H, 5.26; Cl, 26.77.

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α-Methylallyl α-Naphthylurethan. (A) From α-Methylallyl Alcohol and α-Naphthyl Isocyanate.—A mixture of 2 g. of α-methylallyl alcohol and 1 ml. of α-naphthyl isocyanate was warmed on a steam-bath for 15 minutes. The pink solid which separated upon cooling was recrystallized three times from Skellysolve B to give white needles, m.p. 93.0–93.5°.

(B) **From α-Methylallyl Chloroformate and α-Naphthylamine.**—To a solution of 2 g. of α-naphthylamine in 30 ml. of benzene was added 2 ml. of α-methylallyl chloroformate. The solution was warmed on a steam-bath for 20 minutes. The precipitate was collected on a filter and the filtrate was extracted with successive 5-ml. portions of water, 5% aqueous hydrochloric acid, 5% aqueous sodium hydroxide and water. Evaporation to dryness on a steam-bath gave a reddish solid, which was converted by three recrystallizations from Skellysolve B to white needles, m.p. 94.5–95.0°.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.68; H, 6.27. Found: C, 74.54; H, 6.50.

A finely powdered mixture of the urethans prepared by procedures A and B gave m.p. 93–94°.

Crotyl α-Naphthylurethan. (A) From Crotyl Alcohol and α-Naphthyl Isocyanate.—The procedure is completely analogous to procedure A above; thread-like crystals, m.p. 97.5–98.0°, were obtained.

(B) **From Crotyl Chloroformate and α-Naphthylamine.**—The procedure is completely analogous to method B above. The product (thread-like crystals) had m.p. 96.0–96.5° (reported[29] m.p. 89°).

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.68; H, 6.27. Found: C, 74.86; H, 6.43.

A finely powdered mixture of the urethans prepared by methods A and B gave m.p. 95.5–96.5°. A finely powdered mixture of α-methylallyl α-naphthylurethan and crotyl α-naphthylurethan had m.p. 62–89°.

(+)-α-Methylallyl Alcohol.—Resolution of the racemic alcohol was effected by the method of Kenyon and Snellgrove.[6] Five recrystallizations of the brucine salt led to (+)-α-methylallyl alcohol (7% yield) having b.p. 97.5°, $n^{25}D$ 1.4118, $\alpha^{30}D$ 13.8° (neat, *l* 0.5), $[\alpha]^{30}D$ 33.2° [lit.[6] b.p. 97°, $n^{20}D$ 1.4120, $[\alpha]^{30}D$ 31.7° (linear interpolation of data at five temperatures)].

For subsequent experiments 10 g. of pure (+)-α-methylallyl alcohol was diluted by the addition of 90 g. of racemic alcohol. The resulting alcohol had $\alpha^{29}D$ 1.24° (neat, *l* 0.5).

(+)-α-Methylallyl Chloroformate.—By the procedure given above for the racemic alcohol, (+)-α-methylallyl alcohol,, $\alpha^{29}D$ 1.24° (neat, *l* 0.5), was converted into (+)-α-methylallyl chloroformate, $n^{25}D$ 1.4178, $\alpha^{25}D$ 0.32° (neat, *l* 0.5), $[\alpha]^{28}D$ 0.60°, in a yield of 58%.

Lithium Aluminum Hydride Reduction of (+)-α-Methylallyl Chloroformate.—To a slurry of 3.0 g. (0.08 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added a solution of 10.6 g. (0.08 mole) of (+)-α-methylallyl chloroformate, $\alpha^{28}D$ 0.32° (neat, *l* 0.5), in 50 ml. of dry ether. The reaction vessel was cooled by means of an ice–salt-bath during the 30-minute addition period.

Hydrolysis was effected by the addition of 6 ml. of water and 4.8 ml. of 10% sodium hydroxide solution.[26] The precipitate was removed and washed with ether. The combined ethereal solutions were dried over Drierite and fractionated through a micro-Vigreux column; yield 4.3 g. (75%) of (+)-α-methylallyl alcohol, b.p. 98°, $n^{25}D$ 1.4110 and $\alpha^{27}D$ 1.28 (neat, *l* 0.5).

Isolation and Identification of 1,3-Butadiene as the *meso*-1,2,3,4-Tetrabromobutane Derivative.—α-Methylallyl chloroformate (10.6 g., 0.79 mole) was pipetted into 100 ml. of dry tetrahydrofuran in a 200-ml. pressure bottle. The bottle was tightly sealed and placed in a 50° thermostated bath for a period of 82 hours.

At the end of this time the bottle and its contents were cooled to −78° by means of a Dry Ice–acetone-bath. The cold solution was quickly transferred to a 200-ml. three-necked flask fitted with a gas dispersion tube extending to the bottom of the flask and a condenser. The outlet of the condenser was connected to a glass tube extending into a solution of bromine in carbon tetrachloride in a large test-tube.

Nitrogen was passed slowly through the system for about two hours, during which time the flask was gradually heated to 60°. The carbon tetrachloride solution was transferred to a flask and the bulk of the solvent and bromine was removed on a steam-bath. The crystals which separated upon cooling were recrystallized from ethanol to give white needles, m.p. 113–114° (lit.[30] m.p. 117°). A mixture of this material and authentic *meso*-1,2,3,4-tetrabromobutane[30] had m.p. 114.5–115.5°.

Kinetic Method.—A solution (approx. 0.1 *M*) of the chloroformate in the given solvent was prepared in a 100-ml. volumetric flask. The solution was then pipetted into ampules, approximately 5.5 ml. per ampule. The ampules were then sealed and thermostated at the given temperature. Tubes were removed at regular intervals and immersed in ice-water to quench the reaction. The cooled tubes were brought to 25° by means of a water-bath and were opened. A 5-ml. aliquot was allowed to run into 5 ml. of a 10% solution of piperidine in a suitable solvent (*vide infra*). The resulting solution was swirled for two minutes, at the end of which time were added in succession: 20 ml. of water, 7 ml. of indicator solution composed of three parts by volume of ferric alum indicator[31] and four parts of 6 *N* nitric acid, 5 ml. of nitrobenzene and an aliquot of standard silver nitrate solution. Excess silver nitrate was then back-titrated with standard thiocyanate.

In the runs involving the solvents dioxane, tetrahydrofuran, methylene chloride or nitrobenzene, piperidine was employed as a 10% solution in nitrobenzene. In runs involving the solvents toluene, *n*-butyl ether or *n*-decane, piperidine was employed as a 10% solution in the respective solvent.

Prior to the use of each solvent, control experiments were carried out in order to determine the validity of the analytical technique for that solvent. A given solvent was considered to be suitable for use in a rate run if (1) analysis of a 0.1 *M* solution of ethyl chloroformate in the solvent gave a titer corresponding to essentially 100% titration of the chloroformate, and (2) analysis of a 0.1 *M* solution of crotyl chloride in the solvent gave a titer corresponding to essentially 0% titration of the allylic chloride. In this manner nitromethane, dimethyl sulfoxide and acetonitrile were found to be unsatisfactory.

Determination of Product Composition.—A solution (0.1–0.2 *M*) of the chloroformate in the given solvent was prepared in a 25-ml. volumetric flask. Four 5-ml. aliquots were pipetted into ampules, which were then sealed and thermostated. The temperature at which the ampules were thermostated and the length of time were generally taken to correspond to ten half-lives in the decomposition of α-methylallyl chloroformate in the given solvent. The contents of two tubes were analyzed by the titration technique described above to obtain the total yield of allylic chlorides (and by difference the yield of butadiene). The contents of the other two tubes were analyzed by vapor phase chromatography to determine the relative yields of the butenyl chlorides.

Analyses by vapor phase chromatography were carried out on a Perkin–Elmer model 154B vapor fractometer. Optimum conditions for most of the analyses were: column A, 70°, flow 6.5 (20 p.s.i.g.). Area under the different peaks was calculated as the product of the peak height and the half-band width. Analysis of known mixtures revealed that none of the allylic chlorides or chloroformates isomerizes under the conditions of the analysis.

Decomposition of (+)-α-Methylallyl Chloroformate.—The procedure is illustrated for dioxane solution: (+)-α-Methylallyl chloroformate (10 ml., 10.6 g., 0.079 mole) having $\alpha^{28}D$ 0.32° (neat, *l* 0.5) was pipetted into 150 ml. of purified dioxane in a pressure bottle. The bottle was sealed and thermostated at 75° for 6.7 days (10 half-lives). At the end of this time the bottle was cooled to 0° and was opened. The contents of the bottle were transferred to a 300-ml. flask for fractionation through a 30-cm. center-rod column. The best cuts had rotations corresponding to $\alpha^{29}D$ 1.29°, 1.33° (neat, *l* 0.5) for the pure chloride.

Several modifications were necessary in the run in *n*-butyl ether. Due to the slow rate of reaction in this solvent, 15 ml. of (+)-α-methylallyl chloroformate was employed and the reaction was taken to only 11% completion (6 days

(29) K. Hess and W. Wustrow, *Ann.*, **437**, 262 (1924).

(30) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughn, THIS JOURNAL, **58**, 146 (1936).

(31) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952, p. 545.

at 75°). Purified dioxane (25 ml.) was added to the product mixture. Flash distillation then gave a dioxane solution of the butenyl chlorides, which was fractionated as above.

Appropriate controls were run in order to establish the facts that the butenyl chlorides do not isomerize under the conditions of the distillation analysis and that α-methylallyl chloride is optically stable under the same conditions.

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Condensation of *t*-Butyl Esters with Organic Halides in the Presence of Alkali Amides

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The alkylation of *t*-butyl esters of acetic acid and its homologs with various organic mono- and dihalides has been effected with good yields by means of lithium or sodium amide in liquid ammonia. The resulting esters were hydrolyzed easily to give the corresponding free mono- and dibasic acids.

The possibility of direct alkylation of ethyl and *t*-butyl acetates was recently demonstrated by Hauser and Chambers[1] in the reaction with benzyl chloride and *n*-octyl bromide. This reaction constitutes a means of synthesizing higher esters and carboxylic acids along with the common malonic ester method. It was, however, unfortunate that few examples were published and the yields realized were not too good. Working independently on the same problem, the present authors have been able to gain fairly satisfactory yields in a number of the alkylations and the results have been summarized in Table I.

The reaction of *t*-butyl acetate and benzyl chloride was carried out under various conditions with lithium amide as a condensation agent in anhydrous ammonia and ether. Larger amount of ether decreased the yield, so that no condensation product could be isolated when the ammonia was completely substituted by ether prior to the addition of benzyl chloride to the suspension of the lithioacetate. When the volume ratio of ether to ammonia was less than 1:10, the treatment of equimolar mixture of *t*-butyl acetate and lithium amide with one mole of benzyl chloride gave a 31% yield of *t*-butyl hydrocinnamate, while the use of two equivalents each of lithium amide and ester increased the yield to 80% in contrast to the yield of 30% reported by Hauser and Chambers[1] in the benzylation of ethyl acetate by means of lithium amide.[2] Practically no *t*-butyl dibenzylacetate was isolated from the condensation mixture. Treatment of *t*-butyl acetate with two equivalents of benzyl chloride and sodium amide in place of the lithium compound resulted in the formation of *t*-butyl hydrocinnamate and *t*-butyl dibenzylacetate in yields of 19 and 61%, respectively, while attempted benzylation of *t*-butyl acetate by means of diethylaminomagnesium bromide[3] failed to give any desired product.

The alkylation of *t*-butyl acetate could successfully be extended to some primary alkyl halides. Thus ethyl, isobutyl, isoamyl, *n*-octyl and allyl bromides gave fair to good yields of the corresponding higher esters. Though the action of isopropyl iodide did not give the condensation product, the reaction of *t*-butyl α-bromoisobutyrate with *t*-butyl acetate gave a 71% yield of di-*t*-butyl α,α-dimethylsuccinate.

Benzylation of *t*-butyl ester of propionic, *n*-butyric and isovaleric acids gave the corresponding α-alkylhydrocinnamates in 90, 92 and 74% yields, respectively.[4]

Table II summarizes the condensation of *t*-butyl acetate with some dihaloalkanes. In view of the experimental difficulties in isolating the di-*t*-butyl esters thus formed, the reaction products were hydrolyzed directly to free dibasic acids.

While consistently higher yields of dibasic acids could be secured with tetra, hexa- and decamethylene bromides in the presence of lithium amide, ethylene chloride or bromide gave poor to fair yields of the normal condensation product, adipic acid. It should be noted that succinic acid has been isolated as a main product from the reaction using a higher mole ratio of ethylene bromide.[5]

Throughout these condensations of organic dihalides in the presence of lithium amide the sole isolable products were dibasic acids. Neither the ω-haloacid, which should be formed when only one of the halogen atoms of the dihaloalkanes was substituted with the enolate anion, nor the cycloalkanecarboxylic acid, *i.e.*, the cyclic alkylation product of the acetate, could be isolated. Since the use of sodium or potassium amide as the condensation agent appeared to afford the dialkylation products as mentioned above, the reaction was repeated in the presence of sodium amide in order to examine the possible formation of cyclopropane-

(1) C. R. Hauser and W. J. Chambers, *J. Org. Chem.*, **21**, 1524 (1956).

(2) Though the yield recorded by Hauser and Chambers is that of hydrocinnamic acid obtained on hydrolyzing the condensation product, the *t*-butyl hydrocinnamate is almost quantitatively hydrolyzed to the free acid so that these data are comparable with each other.

(3) K. Sisido, H. Nozaki and O. Kurihara, THIS JOURNAL, **74**, 6254 (1952).

(4) For the alkylation of tertiary esters of di-alkylacetic acids see C. R. Hauser and W. J. Chambers, *ibid.*, **78**, 3837 (1956).

(5) Though the origin of succinic acid is not certain, it is plausible that two moles of the lithium enolate of *t*-butyl acetate are coupled together by the oxidative action of ethylene bromide, *viz.*

$$2(CH_2COOR)^- + BrCH_2CH_2Br \longrightarrow ROOC—CH_2CH_2—COOR + CH_2{=}CH_2 + 2Br^-$$

This reaction may be analogous to the well-known formation of ethylene and bromide anion from ethylene bromide and magnesium.