for 3 hours, then excess 2 *N* hydrochloric acid was added and the ether layer was separated. Distillation yielded methyl d_3-ethyl ketone in about 26% yield, which was readily reduced to the alcohol with lithium aluminum hydride.

d-**Butanol-2.**—*sec*-Butyl alcohol was resolved as described previously.[17] The sample used had $[\alpha]^{25}\text{D}$ +12.20°; it was therefore about 89% optically pure.

All chloroformates were made by the methods previously described; 2-butyl chloroformate had b.p. 39–40° (21 mm.). *sec*-Butyl chloride for gas chromatographic reference was made using the Lucas reagent on 2-butanol.

Rate measurements were made as previously described under conditions practically identical with those used for the undeuterated compound, done at the same time and described in reference 2. Thus most systematic errors disappear in considerations of isotope effects.

Substitution Stereochemistry.—Optically active 2-butanol, diluted with racemic 2-butanol, was converted to the chloroformate. In two experiments this was used directly in the gas phase flow apparatus; in two others it was diluted with racemic 2-butyl chloroformate. A very slow flow rate was used to obtain extensive decomposition. The effluent gas stream was passed through a trap containing methanol cooled in Dry Ice. After about 38 hours, the contents of the trap were distilled, first under vacuum at room temperature to remove butenes and hydrogen chloride, then at atmospheric pressure, yielding a fraction boiling 65–68°. The rotation of this fraction was measured and its purity estimated by vapor chromatography. In one case a 4% contamination of 2-butanol was found; in two others, a further dilution with racemic 2-chlorobutane was carried out. Results are expressed below by multiplying the observed rotation (varying from 8 to 0.2°) by factors given parenthetically for the various dilutions as follows: (a) dilution of the starting alcohol (3.66), (b) dilution of the chloroformate (5.52), (c) contamination of the product with impurities (assumed optically inactive) (1.04), (d) dilution of the 2-chlorobutane (6.87). In the following four experiments, the calculated rotations based on optically pure starting material are followed by some letters indicating which of the preceding corrections were applied. Experiment 1, corrn. a and c, $[\alpha]^{25}\text{D}$ +34.7°; exp. 2, corrn. a, $[\alpha]^{25}\text{D}$ +34.8°; expt. 3, corrn. a and b, $[\alpha]^{25}\text{D}$ +34.7°; expt. 4, corrn. a, b and d, $[\alpha]^{25}\text{D}$ +35.9°. Reference 9 gives for optically pure 2-chlorobutane $[\alpha]^{25}\text{D}$ 33.8°.

Elimination Stereochemistry.—The same apparatus was used to collect the elimination products in methanol at −80° as was used for the rate measurements and the optical result. The contents of the trap then were allowed to warm to room temperature and the gas phase was sampled in a 20-ml. syringe, which was then used to charge these products to the gas chromatography. The separated olefins were trapped in liquid nitrogen as they came off, and then analyzed for deuterium by mass spectra, kindly performed by Dr. R. Hunt of the Shell Oil Co., Deer Park, Tex. The recording on the gas chromatograph allowed the estimation of the contamination by neighboring olefins. The only contamination found was that of *cis*-olefin by *trans* and *vice versa*. The products from the *erythro* compound were separated on a 4-meter column at 0° with benzyl cyanide saturated with silver nitrate as the stationary phase. The products from the *threo* compound were separated on a 6-meter dioctyl sebacate column at 12° following a 2-meter dioctyl phthalate column at room temperature. Table III shows the results of these experiments, from which Table I was derived. The precision of the last column is not high, it varies both because of the nature of the column and because the point of changing receivers was arbitrary.

TABLE III

DEUTERIUM CONTENT OF SEPARATED OLEFINS

Stereoisomer	Butene	Atoms D/ molecule	Impurities %
erythro	1	1.01	0
erythro	*trans*	0.907	10
erythro	*cis*	0.29	22
threo	1	1.05	0
threo	*trans*	0.00	0
threo	*cis*	0.90	10

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[17] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 1744 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM M. RICE UNIVERSITY, HOUSTON, TEX.]

The Decomposition of Gaseous Chloroformates. III. Rearrangements in the Elimination Reaction[1]

BY EDWARD S. LEWIS AND WILLIAM C. HERNDON

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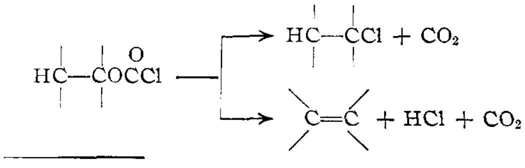
In the gas phase, the thermal decomposition of neopentyl chloroformate yields neopentyl chloride and methylbutenes, but no *t*-amyl chloride. From 1-butyl chloroformate, in addition to 1-chlorobutane and 1-butene, the 2-butenes are also produced. Evidence, based on retention of 1-deuterium, is presented to exclude the intermediacy of divalent carbon compounds. A polar mechanism for elimination is supported.

Introduction

The previous papers in this series[2,3] have been concerned with the kinetics and stereochemistry of the thermal, gas phase decomposition of alkyl chloroformates by the parallel courses 1 and 2.



$$\text{HC—COCCl} \longrightarrow \text{HC—CCl} + CO_2 \qquad (1)$$

$$\text{HC—COCCl} \longrightarrow \text{C=C} + HCl + CO_2 \qquad (2)$$

A transition state with significant charge separation, especially in the elimination reaction 2, was indicated from substituent and isotope effects, and the latter even suggested an intermediate. A dipolar transition state also has been suggested for the non-chain pyrolytic eliminations from alkyl bromides,[4] and intermediate ion-pairs have been proposed.[5]

In solution, extensive charge separation may be detected since certain carbonium ions rearrange when free or nearly so. Thus, carbonium ion intermediates may be accepted if rearrangement results in these special cases, and can be rejected if only unrearranged products are found. This criterion for the intermediacy of carbonium ions

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[1] From the Ph.D. thesis of W. C. Herndon, 1958; presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958.

[2] E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

[3] E. S. Lewis, W. C. Herndon and D. C. Duffey, *ibid.*, **83**, 1959 (1961).

[4] A. Macoll and P. J. Thomas, *Nature*, **176**, 392 (1955).

[5] C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).

is adaptable to gas phase reactions, in contrast to most other such criteria. In this paper the study of rearrangements in gas phase chloroformate decompositions is described.

Results

Neopentyl chloroformate, on decomposition in the gas phase in a flow system, yielded neopentyl chloride and a mixture of methyl butenes. *t*-Amyl chloride, shown to be stable and separable from the observed products, was absent. The composition of the product mixture was unaltered by a twenty-fold variation in flow rate and by smaller changes in the partial pressure of neopentyl chloroformate in the incoming gas stream. The extent of conversion to these products was consistent with a first-order course for each path. Table I gives the rate constants for several compounds also giving rearranged olefins and unrearranged alkyl chlorides.

TABLE I

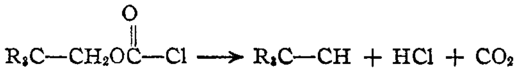
RATES OF DECOMPOSITION OF ALKYL CHLOROFORMATES WITH REARRANGEMENT

Alkyl group	Temp., °C.	Rate constants × 10^5, sec.$^{-1}$ k_s[a]	k_1	k_2	k_3	k_t[b]
$(CH_3)_3CCH_2$	240	1.85	3.99[c]	8.33[d]		14.1 ± 0.8
n-C_6H_{13}	279	8.67	(46.6)[e]			55.3 ± 1.7
n-$C_3H_7CH_2$	255	2.07	4.36[f]	0.985[g]	0.961[h]	8.38 ± 0.14
C_3H_7CHD	255	2.05	4.09[f]	0.997[g]	0.993[h]	8.13 ± 0.05
C_2H_5	255	2.99[i]				

[a] For unrearranged alkyl chloride. [b] Errors are standard deviations of from 3 to 12 runs. [c] 2-Methyl-1-butene. [d] 2-Methyl-2-butene. [e] Two olefinic peaks on chromatography, not identified and counted together. [f] 1-Butene. [g] *trans*-2-Butene. [h] *cis*-2-Butene. [i] Ref. 2.

It is seen that *n*-butyl chloroformate yields the 2-butenes in addition to 1-butene, and that *n*-hexyl chloroformate yields more than one olefin, both showing evidence of rearrangement analogous to that of the neopentyl compound. A carbonium ion intermediate is therefore suggested, although some alternative explanations need to be discussed.

It is conceivable that the electron-deficient intermediate which rearranges is a carbene produced by reaction 1. The most reasonable following step



$$R_3C{-}CH_2O\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \longrightarrow R_3C{-}CH + HCl + CO_2 \quad (1)$$

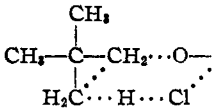
is the 1,2-shift of reaction 2, yielding 2-methyl-2-

$$R_3C{-}CH \longrightarrow R_2C{=}C^{R}_{H} \quad (2)$$

butene from neopentyl chloroformate. The formation of 2-methyl-1-butene from the same carbene is less clear, as is the formation of 2-butenes, but the decomposition of an excited cyclopropane resulting from an intramolecular insertion reaction is a conceivable course. The chemistry of gas phase carbenes is insufficiently understood to allow the exclusion of reaction 1 based upon the observed products alone.

An attempt was made to detect this mechanism by studying the decomposition of 1-butyl-1-d_2 chloroformate, which could give olefins containing only one deuterium atom per molecule. Unfortunately, the extent of deuteration of the 1-butanol, prepared by the reduction of a butyric ester, was low. The chloroformate had 0.78 D atom per molecule, the 1-butene from the reaction had 0.71 D atom per molecule, representing a very minor loss of deuterium. The 2-butenes, found in smaller yield, were not analyzed for deuterium. If reaction 1 was the principal source of 1-butene, then it would be necessary to assume that the failure to lose deuterium must be attributable to a large intramolecular isotope effect in reaction 1. In this case, the loss of reactivity of about 39% of the available hydrogens would reduce the over-all rate of olefin formation by about this amount, not counting any secondary isotope effects. The observed reduction in total elimination rate is less than 4%, and the reduction in 1-butene rate alone is 6.2%, both in the range previously found for secondary effects.[3] We may then exclude reactions 1 and 2 as a major source of olefins.

Another type of intermediate is a substituted cyclopropane, produced in a one-step reaction such as is illustrated by the hypothetical transition state for the neopentyl compound by I. The



I

product of such a reaction, 1,1-dimethylcyclopropane, could break down to give the methylbutenes. When the reaction products were collected directly in a cold trap, conditions which were shown to lead to secondary reactions[2] but which also allowed the detection of minor components, a small peak on the gas chromatogram not attributable to an olefin was observed. Comparison of infrared spectrum and chromatographic behavior with a synthetic sample of 1,1-dimethylcyclopropane demonstrated identity. This peak was never observed when gas samples were taken before condensation. In the presence of hydrogen chloride, synthetic dimethylcyclopropane did yield (in the flow system) the methylbutenes and *t*-amyl chloride, but conversion was not extensive. Analysis of the liquid condensate from neopentyl chloroformate decomposition further revealed the presence of substantial amounts of *t*-amyl chloride, also never found in the gas samples. Since the cyclopropane derivative is found only under those conditions believed to be conducive to complex reactions, and would probably survive if formed in substantial amount, we may assume that dimethylcyclopropane is not an important intermediate in the gas phase reaction.

The exclusion of the neutral intermediates, the carbene and cyclopropane, supports more strongly a carbonium ion or ion-pair intermediate, which in turn naturally suggests the possibility that the reaction is heterogeneous. While we can not exclude this unequivocally, it appears improbable for the following reasons. Over a change in flow rate from 0.055 to 0.0049 ml./sec. the ratio of total olefin to neopentyl chloride was 6.67 with an average deviation of 0.22 in 12 runs, showing no trend with flow rate. Similarly the ratio of 2-methyl-2-butene to 2-methyl-1-butene was 2.09 with an average deviation of 0.07, also not correlated with flow rate. We may conclude that the kinetic law is the same for all these products. The rate constant for neopentyl chloride formation at 240° (k_s 1.8 × 10^{-5} sec.$^{-1}$) is similar to that of the ethyl compound at the same temperature (k_s 1.17 × 10^{-5} sec.$^{-1}$).[2] The mechanism suggested by the non-rearrangement in alkyl chloride formation would lead to the prediction that all primary chloroformates would react at comparable rates. Thus if the alkyl chloroformates studied previously[2,3] reacted homogeneously, then very likely the reactions in this paper are also homogeneous.

The mechanisms suggested by the data in these and the previous papers are: (1) A one-step reaction through a cyclic transition state of ROCOCl to give RCl does exist. When favorable, it has polar character in the direction R^+OCOCl^-, but the electron deficiency of R is not sufficient to promote rearrangement in the cases studied. This mechanism is supported by the relative reactivities of the different alkyl chloroformates,[2] the large negative entropy of activation,[2] the retention of configuration[3] and the absence of rearranged alkyl chlorides.

(2) An elimination reaction through a more polar transition state, probably leading to an intermediate of substantial charge separation. The intermediate is loosely bound (as shown by the near-zero entropy of activation), it can react by alternative routes to give different olefins[3] and rearranged products, but it does not dissociate enough to give stereochemically random products.[3] The presence of an intermediate is actually suggested only by the isotope effects[3] supported further in this paper by an analogous increase in the rate of formation of 2-butenes on 1-deuteration shown in Table I for *n*-butyl chloroformate.

(3) A one-step elimination reaction not involving polar intermediates is suggested by the different reaction products from 1- and 2-butyl chloroformates, the former yielding a mixture richer in 1-butene. Since the rearranged ion-pairs from the two sources probably would be the same, the excess 1-butene may be formed by a direct route analogous to an alkyl acetate pyrolysis. This mechanism is not demonstrated, but it is by no means excluded for a portion of the reaction.

Experimental

Materials.—Neopentyl alcohol (2,2-dimethyl-1-propanol) was prepared by the lithium aluminum hydride reduction of trimethylacetic acid. The reduction of ethyl butyrate by sodium in acetic acid-*d*[6] yielded 1-butanol-1-*d*. Chloroformates were made from the alcohols by the previously described procedure.[2] Neopentyl chloroformate boiled at 43–45° (20 mm.); *n*-butyl chloroformate had b.p. 51–52° (28 mm.). Commercial *n*-hexyl chloroformate was redistilled, b.p. 43° (9 mm.). For chromatographic comparison, *t*-amyl chloride was prepared from *t*-amyl alcohol and concentrated hydrochloric acid; neopentyl chloride (contaminated with *t*-amyl chloride) was prepared from neopentyl alcohol, thionyl chloride and quinoline.[7] Butenes were commercially available and the isomeric methylbutenes were prepared by dehydration of *t*-amyl alcohol and then distillation. The preparation of 1,1-dimethylcyclopropane followed the method of Shortridge.[8]

The deuterium content of 1-butene was determined by Mr. R. Hunt of Shell Oil Co. by mass spectra. The deuterium content of the 1-butyl-1-*d* chloroformate was determined by converting it to 1-butene by the following rearrangement-free sequence. 1-Butyl-1-*d* chloroformate→ 1-butanol-1-*d* (with water) → 1-butyl-1-*d* acetate (with acetyl chloride) → 1-butene-1-*d* (on pyrolysis). It contained 0.78 atom deuterium per molecule. The decomposition of 1-butyl-1-*d* chloroformate yielded butenes, separated and collected as described before,[3] and the 1-butene contained 0.71 atom deuterium per molecule. In this experiment, the smaller yields of 2-butenes did not allow analysis.

The kinetic measurements and treatments followed the previously described methods.[2] Products from neopentyl chloroformate were identified not only by comparison of retention time, but in several cases also by comparison of the infrared spectrum of the separated components in the gas phase with those of synthetic materials and with the American Petroleum Institute spectra.

The same flow system was used to show that *t*-amyl chloride, neopentyl chloride, *n*-butyl chloride, 2-butyl chloride and *cis*-2-butene were not decomposed or isomerized to as much as 1%, in agreement with the literature.[9,10]

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[6] D. G. Hill, W. H. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **74**, 5599 (1952).

[7] W. Gerrard and P. Tolcher, *J. Chem. Soc.*, 3640 (1954).

[8] R. W. Shortridge, *J. Am. Chem. Soc.*, **70**, 946 (1948).

[9] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 2039 (1951), and earlier papers by Barton and co-workers.

[10] W. W. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *J. Am. Chem. Soc.*, **80**, 2384 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIF.]

The Effect of Geometry in the Allyl Group on the Rate of the Claisen Rearrangement

BY LAURENCE D. HUESTIS AND L. J. ANDREWS

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The *cis* and *trans* isomers of γ-methylallyl phenyl, γ-phenylallyl phenyl and γ-methylallyl 2,6-dimethylphenyl ethers have been prepared. The reaction rates of each pair of isomers have been determined in the neighborhood of 200° using diphenyl ether as the solvent. In general the *trans* compounds were found to be more reactive, but only slightly so, than the *cis*. Apparently the carbon of the migrating allyl group does not approach the *ortho* ring carbon atom sufficiently closely in the activation process so that the reaction rate is sterically sensitive to the geometric configuration about the β,γ-double bond. The rearrangement of *cis*-γ-methylallyl 2,6-dimethylphenyl ether, but not of its *trans* isomer, is accompanied by partial *cis–trans* isomerization of the ether. Presumably the dienone intermediate in these *para* rearrangements can revert to ether by a process in which the *trans* isomer is formed stereoselectively.

The proposal of Hurd and Pollak[1] that the *ortho*-Claisen rearrangement of phenyl allyl ethers is intramolecular in character is now quite generally accepted.[2] It seems likely that a similar cyclic mechanism is operative in the initial phase of the *para*-Claisen rearrangement, a process in

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[1] C. D. Hurd and M. A. Pollak, *J. Org. Chem.*, **3**, 550 (1939).

[2] For a recent discussion of the confirming evidence see Chapter 5 by D. J. Cram in the book edited by M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 295–303.