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Allylic Fluorides. Solvolysis of 1,3,5,7,7,7-Hexafluoro-1-heptene

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Solvolysis of 1,3,5,7,7,7-hexafluoro-1-heptene in slightly aqueous formic acid leads to simultaneous allylic rearrangement (internal return) and hydrolysis, the *trans* isomer reacting approximately 20-fold faster than the *cis* at 30.15°. In addition, an acid-catalyzed reaction leading only to hydrolysis has been demonstrated. The importance of hydrogen bonding in both the rate-controlling and product-determining steps is apparent. An isomeric allylic fluoride, 2,3,5,7,7,7-hexafluoro-1-heptene, is inert to the reaction conditions. The reactivity sequence is considered in light of the electronegative and conjugative character of the fluorine atom.

While the literature concerning solvolysis reactions of allylic chlorides and bromides is voluminous, that dealing with allylic fluorides is virtually nonexistent.¹ We should like to report the first kinetic and product study of solvolysis of such a system.

Results.—In connection with another study, we have synthesized compounds of the type $\text{CF}_3(\text{VF})_n\text{I}$ by the reaction of vinyl fluoride with trifluoromethyl iodide.² From this reaction there was isolated, among others, the iodides 1,3,5,7,7,7-hexafluoroheptyl iodide, $\text{RCH}_2\text{FCH}_2\text{CHF}_2\text{I}$, and 2,3,5,7,7,7-hexafluoroheptyl iodide, $\text{RCH}_2\text{FCH}_2\text{FCH}_2\text{I}$ ($\text{R} = \text{CF}_3\text{CH}_2\text{CHFCH}_2-$), which upon treatment with triethylamine yielded the allylic fluorides, *cis*- and *trans*-1,3,5,7,7,7-hexafluoro-1-heptene, $\text{RCH}_2\text{FCH}=\text{CHF}$ (I), and 2,3,5,7,7,7-hexafluoro-1-heptene, $\text{RCH}_2\text{FCF}=\text{CH}_2$, respectively.

When dissolved in slightly aqueous formic acid, both *cis*- and *trans*-I led to the same two reaction products (II and III) as indicated by v.p.c. analysis. Compound II was also formed during attempted separation of *cis*- and *trans*-I by fractionation. This material gave the same elemental analysis as I as well as similar infrared and ultraviolet spectra. The F^{19} n.m.r. spectrum indicated CF_3 , CHF , and CHF_2 in ratio of 3:1:2 which indicates the structure to be that of the allylic rearrangement product 1,1,5,7,7,7-hexafluoro-2-heptene, $\text{RCH}=\text{CHCF}_2\text{H}$ (II). The other product was shown to be 5,7,7,7-tetrafluoro-2-heptenal, $\text{RCH}=\text{CHCHO}$ (III), as follows.

Addition of water to the solvolytic reaction mixture resulted in separation of an oil, the infrared spectrum of which indicated an α,β -unsaturated aldehyde in addition to peaks attributable to II. Addition of 2,4-dinitrophenylhydrazine reagent to an ethanolic solution of this oil resulted in formation of bright orange crystals which analyzed correctly for the hydrazone of III.

Kinetic data were obtained by periodically quenching samples of the reaction mixture in a large volume of water, extracting with ether, and analyzing by v.p.c. utilizing internal reference compounds. In 97.3% formic acid at 30.15°, solvolysis of *cis*- and *trans*-I occurred readily, exhibiting good first-order kinetics through at least 75% reaction with half-lives of the order of 1200 and 60 min., respectively. The isomeric allylic fluoride $\text{RCH}_2\text{FCF}=\text{CH}_2$ did not undergo re-

action under these conditions in 4 days. Kinetic data, most of which have been obtained with *trans*-I, are summarized in Table I.

TABLE I
KINETIC DATA FOR SOLVOLYSIS OF 1,3,5,7,7,7-HEXAFLUORO-1-HEPTENE (I) IN 97.3% FORMIC ACID AT 30.15°

Run	I	Added solute	$k \times 10^4$, min. ⁻¹	III/II ^a
<i>trans</i> -I				
1	0.0905	...	12.2	7.3
2	.0920	...	12.2	7.3
3	.0955	...	13.2	7.5
4	.1218	...	12.7	7.1
5	.1315	...	13.4	7.3
			Av.	12.7 ± 0.4
				7.3 ± 0.1
6	0.0920	[HCl], 0.0045 ^c	14.1	9.0
7	.1040	.1250	52.5	No I detectd.
8	.0980	.2000	79.0 ^b	No I detectd.
9	.1043	.5000	161.0 ^b	No I detectd.
10	.0960	[HF], 0.0830 ^d	16.0	7.5
11	.0910	.1250	15.4	9.8
12	.0990	.5100	22.2	11.2
13	.0955	[HCO ₂ Na], 0.1660	10.5	4.3
14	.0912	.1930	8.8	4.8
15	.1010	.2770	9.1	5.9
16	.1570	.3140	9.1	6.3
17	.0918	[NaF], 0.3720	9.9	4.5
18	.0776	[NaF], .1610, [HCO ₂ Na], 0.1630	8.9	.7
19	.0936	[NaCl], 0.3100	13.9	...
20	.0907	[LiClO ₄], 0.1000	14.7	9.3
21	.0635	[Na ₂ SO ₄], 0.0635	11.1	7.3
22	.0962	.0980	11.0	5.7
23	.0956	.2050	11.4	5.7
24	.500	[H ₂ O], 10.8%	6.5	7.5
25	.0560	10.8%	5.7	5.7
26	.0740	[HCO ₂ Na], 0.1450 [CH ₂ O], 10.8% [HCO ₂ Na], 0.1650	5.8	5.8
<i>trans</i> -I in 97.0% acetic acid				
27	0.0975	...	< 0.1	4-5
28	.0995	[NaOAc], 0.328	< .1	4-5
29	.1060 <i>trans</i> - .0606 <i>cis</i> -	...	< .1	4-5
<i>cis</i> -I in 97.3% formic acid				
30	0.1000	[HCO ₂ Na], 0.2080	0.56	~7
31	0.1620	0.3250	0.49	~7

^a Calculated from ratio of final areas multiplied by moles/area ratio of III/II. ^b Rate constant based on three points. ^c Water concentration varied from 3.1 to 5.4%. ^d Water concentration varied from 3.1 to 4.2%.

Under the above conditions, *trans*-I solvolyzes with a first-order rate constant of $12.7 \pm 0.4 \times 10^{-3} \text{ min.}^{-1}$ giving aldehyde III and rearrangement product II in approximately 7:1 mole ratio (runs 1-5). Increasing the water concentration to 10.8% resulted in a decrease in rate to $6.5 \times 10^{-3} \text{ min.}^{-1}$ (30.15°) with essentially no change in product distribution.

The rearrangement product II is not converted to aldehyde III under any of the conditions listed in

(1) (a) Several solvolytic studies of alkyl and aryl fluorides have been reported. See, for example: (b) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1677 (1950); (c) A. K. Coverdale and G. Kohnstam, *ibid.*, 3806 (1960); (d) C. G. Swain and R. B. Mosely, *J. Am. Chem. Soc.*, **77**, 3727 (1955); (e) C. G. Swain, T. E. C. Knee, and A. MacLachlan, *ibid.*, **82**, 6101 (1960); (f) C. G. Swain and R. E. Spalding, *ibid.*, **82**, 6104 (1960).
(2) T. J. Dougherty, *ibid.*, **86**, 460 (1964).

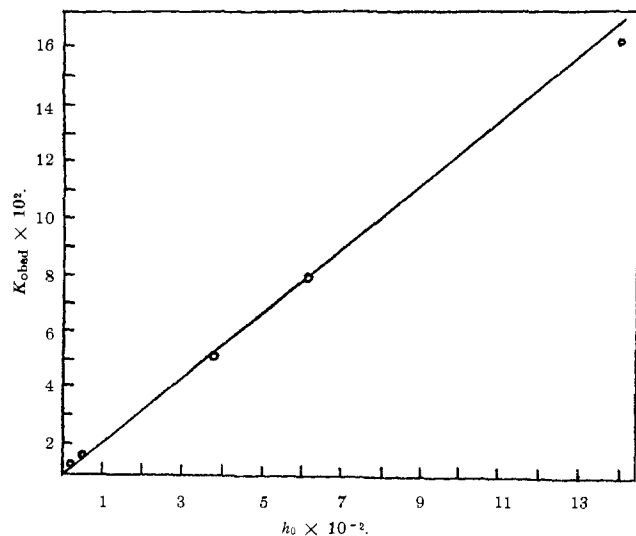


Fig. 1.—Acidity dependence of observed rate constant.

Table I. This was determined by the constancy of the final product distribution over several half-lives as well as by subjecting II to the initial solvolysis conditions.

A strongly acid-catalyzed reaction is shown by runs 6–9 in which various amounts of hydrochloric acid have been added to the solvent. Addition of acid also strongly favors hydrolysis over allylic rearrangement. The observed rate constant was found to increase nearly linearly with increasing concentration of HCl. Because of difficulties in obtaining accurate rate constants in the more strongly acidic solutions, these data should be considered approximate. Additionally, it was found that within this range of HCl concentration in 97.3% formic acid, h_0 is proportional to $[\text{HCl}]$ (Fig. 4). Thus, a plot of h_0 vs. k_{obsd} also is linear³ (Fig. 1).

Additions of HF resulted in small rate increases, slightly favoring III.

Sodium formate resulted in small rate retardation and a generally lower proportion of hydrolysis product, although the data are quite scattered. Sodium fluoride had a similar effect.

In all runs in which base was added (HCO_2Na or NaF) there was detected an additional product (by v.p.c.). This material appeared as a shoulder on the peak for III, gradually decreasing relative to III as the reaction proceeded. After 4–5 half-lives, this material had converted to III. This conversion could also be brought about rapidly by adding HCl. In the more aqueous solvent, the second peak was barely detectable even at early stages in the reaction.

Small salt effects were noted with NaCl and LiClO_4 . Sodium sulfate caused an unusual effect in that it resulted in a small but apparently real decrease in rate ($\sim 10\%$) which was independent of concentration within the range studied.

The formation of products II and III could also be followed by v.p.c. techniques and compared with decrease in starting material. In runs 13–18 containing added base, good material balance was obtained throughout the entire reaction. In all other cases, material balance was poor (low in aldehyde) except

(3) Swain (ref. 1f) has observed that the rate of acid-catalyzed solvolysis of benzyl fluoride in 90% water–10% acetone solution follows h_0 , but not $[\text{H}_3\text{O}^+]$.

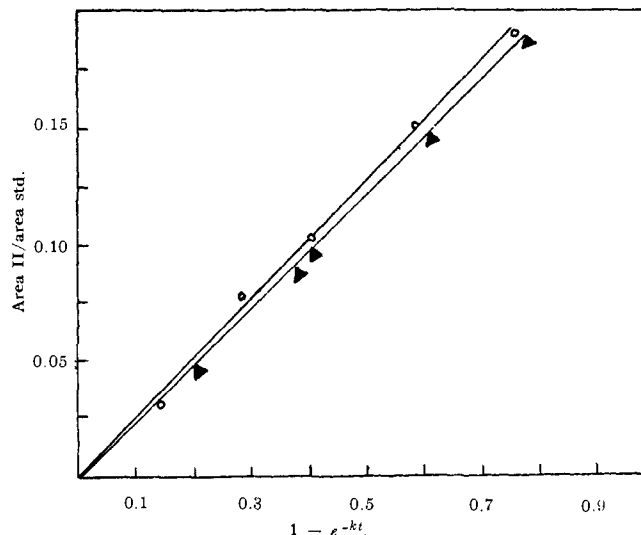


Fig. 2.—Rate of formation of II: ▲, no base added; ○, in presence of 0.1930 M sodium formate.

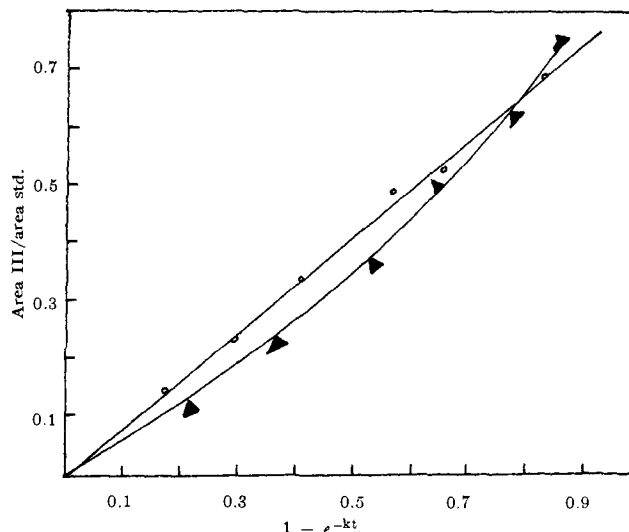
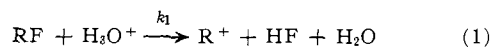


Fig. 3.—Rate of formation of III: ▲, no added base; in ○, presence of 0.1930 M sodium formate.

at the final stages of reaction, as indicated in Fig. 2 and 3. Rate of disappearance of I, however, in no case deviated from first order.

Discussion.—The following series of steps accounts for the experimental data. Steps 1 and 2 are considered to be rate determining, *i.e.*, $k_{\text{obsd}} = k_1[\text{H}_3\text{O}^+] + k_2$. The rate of formation of the ion pair (eq. 2) in 97.3% formic acid can be estimated from Fig. 1⁴ by extrapolation to $h_0 = 0$ which gives $k_2 = 10 \times 10^{-3} \text{ min.}^{-1}$.



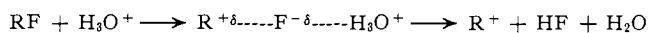
(4) Since $k_1[\text{H}_3\text{O}^+] = k_1 h_0$, either k_{obsd} vs. $[\text{H}_3\text{O}^+]$ or h_0 may be used to determine k_2 . It is easier experimentally, however, to determine h_0 than $[\text{H}_3\text{O}^+]$ for slightly aqueous formic acid solution (see Experimental).

Thus, the rate of the acid-catalyzed portion of the reaction, $k_1[\text{H}_3\text{O}^+]$, is $2.7 \times 10^{-3} \text{ min.}^{-1}$ in 97.3% formic acid containing no added bases. Under these conditions, therefore, the major portion ($\sim 80\%$) of the reaction proceeds *via* the ion pair mechanism (eq. 2). In 0.125 *M* HCl in formic acid this pathway accounts for less than 20% of the reaction. The ratio k_3/k_4 , which describes the partitioning of the ion pair between solvolysis and internal return (rearrangement), may be determined from k_1 , k_2 , and the product distribution III/II since

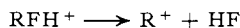
$$\frac{\text{III}}{\text{II}} = \frac{k_1[\text{H}_3\text{O}^+] + k_2k_3/k_3 + k_4}{k_2k_4/k_3 + k_4}$$

This equation leads to $k_3/k_4 = 5.5$ which is in good agreement with the product ratio in solutions containing sodium formate where the acid-catalyzed reaction becomes insignificant.⁵

Acid-catalyzed solvolytic reactions of fluoro compounds are not uncommon. Triphenylmethyl,^{1c} benzyl,^{1f} *t*-butyl,^{1b} *t*-amyl,^{1b} and cyclohexyl^{1b} fluorides have been shown to exhibit acid catalysis which may be attributed to the strong hydrogen bonding between hydronium and the incipient fluoride ion in the rate-determining step.



Swain^{1f} favors rate-determining dissociation of the conjugate acid for solvolysis of triphenylmethyl and benzyl fluoride based on the observed h_0 dependence.



In the allylic fluoride solvolysis under consideration, the former mechanism appears most feasible at least within the range of acidity studied.

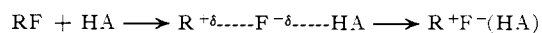
An increase in rate might have been expected in the more aqueous solvent, 89.2% formic acid, on the basis of its increased acidity. This is apparently offset, however, by the decrease in rate of formation of the ion pair intermediate (eq. 2) as evidenced in runs 25 and 26 in which this is essentially the only reaction path.⁵ It appears, therefore, that the formic acid molecule itself is required in the rate-determining process for formation of the ion pair. This is a reasonable result based on the relatively strong hydrogen bonding interaction expected between formic acid and the incipient fluoride ion. In this connection it is instructive to examine the effect of added HF on the reaction rate. The increases observed are much greater than expected, simply on the basis of dissociation to hydronium ions which participate in the acid-catalyzed reaction.⁷ Clearly, HF is able to function in the ion pair-forming step in much the same way as does formic acid, but even more effectively. Thus, an increase in HF concentration of approximately 0.4 *M* results in a near doubling of total rate (from 12.7×10^{-3} to $22.2 \times 10^{-3} \text{ min.}^{-1}$), whereas an increase in formic acid concentration of approximately 2 *M* (from 89.2 to 97.3% formic acid) is required to bring about a

(5) An estimate of the $\text{p}K_a$ of 97.3% formic acid based on the h_0 vs. [HCl] plot is 4.2–4.3 ($\text{p}K_a$, anhydrous formic acid = 6.2,⁶ dilute formic acid = 3.75⁶). In slightly aqueous formic acid containing 0.1 *M* sodium formate the rate of the acid-catalyzed reaction is within experimental error.

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 256, 260.

(7) Even assuming that HF is as strong an acid in 97.3% formic acid as it is in water ($\text{p}K_a = 3.14$), the total rate increase would be less than 10% in these runs (10–12).

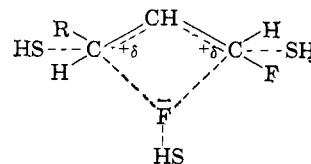
similar increase. The transition state for ion pair formation may be visualized in much the same manner as that for the acid-catalyzed reaction; in the latter case, of course, ion pair formation is precluded. Further, it is expected that the degree of carbon-fluorine bond breaking in the transition state will become progres-



sively less as the hydrogen bonding reagent interacts more strongly with the incipient fluoride ion.

The intramolecular nature of the rearrangement reaction is indicated by the small effect on product distribution of added fluoride ion and by the absence of an autocatalytic effect in the rate of formation of II. Sodium fluoride appears to act as a base in decreasing the rate of the acid-catalyzed reaction in much the same way as does sodium formate.

In considering the structure of the ion pair R^+F^- the runs in 97% acetic acid (27–29) are particularly interesting. Although the total rate of reaction is at least a factor of two hundred slower, the product distribution is remarkably close to that in formic acid. It may have been expected that a greater fraction of the ion pair would tend to undergo dissociation (rather than internal return) in the more strongly solvating medium, formic acid.⁸ Most of the information can be accommodated by an ion pair involving several molecules of solvent functioning in two ways, *i.e.*



Thus, the competition between solvolysis and internal return derives from the combined hydrogen bonding ability and nucleophilic character of the solvent *vs.* recapture of the fluoride ion by the cationic member of the ion pair. In acetic acid the nucleophilic character is expected to be somewhat enhanced, but the hydrogen bonding ability decreased compared to formic acid. This results in a near canceling of effects with net retention of product distribution compared to formic acid.⁹

A similar rationalization of the constancy of product distribution can be made for the results in 89.2% formic acid since water is more nucleophilic but less strongly hydrogen bonding than the acidic solvents. When HF is the hydrogen bonding species, the tendency for removal of the fluorine atom to form HF_2^- would be expected to be very strong, resulting in more solvolysis as is found (runs 10–12).

The ability of internal return to compete favorably with solvolysis is no doubt in part a result of the strong driving force to formation of the C–F bond, particularly in the CF_2H moiety. Internal return to starting material is not detected in this system, but would be expected to be considerably less important than allylic rearrangement.¹⁰

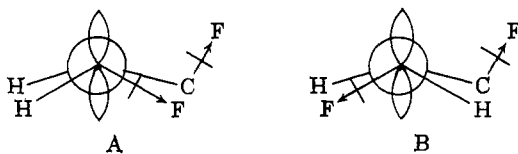
(8) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952), have shown that the ratio of internal return to solvolysis decreases from 3.59 in acetic acid to 0.18 in formic acid for the 3-phenyl-2-butyl-*p*-toluenesulfonate system.

(9) The author thanks Prof. C. D. Ritchie for suggesting this interpretation.

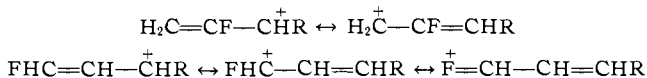
(10) The carbon-fluorine bond energies in fluoromethanes become progressively greater as more fluorine atoms are added: C. R. Patrick, "Ad-

The second solvolysis product (other than III) formed in formic acid containing added base is not the same as the second solvolysis product formed in acetic acid (by v.p.c.). These materials are probably the corresponding esters, although the possibility that one of them may be the unrearranged alcohol $RCH(OH)CH=CHF$ which undergoes acid-catalyzed rearrangement to III cannot be excluded at this time.

The slower rate of solvolysis for *cis*-I compared to *trans*-I (approximately 20-fold) may be attributed to an unfavorable alignment of C-F dipoles between the allylic and vinylic fluorine atoms in its transition state. Thus in the conformation preferred for removal of the allylic fluorine atom (C-F approximately parallel to adjacent π -orbitals) the two C-F dipoles interact in an approximately additive manner (A), whereas, a near canceling effect obtains in the case of the *trans* isomer (B). Thus, in addition to direct dipole-dipole interactions, a greater degree of charge separation is required in the transition state for the *cis* isomer.



The very low reactivity of the isomeric allylic fluoride, $RCHFCF=CH_2$, can be attributed to the extreme energy requirements expected for generating a positive charge β to highly electronegative fluorine (where no conjugation can occur) compared to that required to develop a positive charge α to fluorine where the inductive effect is offset by conjugation.



Experimental

Synthesis of Allylic Fluorides.—The compounds used in this work were obtained by elimination of HI with triethylamine from the corresponding iodides, obtained through the reaction of trifluoromethyl iodide with vinyl fluoride as previously described.²

The olefins were separated and purified by preparative v.p.c. and identified by infrared and n.m.r. spectra. The F^{19} n.m.r. (56.4 Mc.) spectrum of *cis*-1,3,5,7,7,7-hexafluoro-1-heptene indicated: CF_3 ($\phi = 65.5$, area = 3), $=CHF$ ($\phi = 123$, area = 1; 4 peaks of equal intensity separated by 38–39 c.p.s.), allylic F (2 peaks, $\phi = 177, 180$, combined area = 1), and $-CHF-$ ($\phi = 185$, area = 1). The *trans* isomer exhibited: CF_3 ($\phi = 65.0$, area = 3), $=CHF$ ($\phi = 124$, area = 1, 3 peaks of relative areas of 1:2:1, separated by 76 c.p.s.), allylic F (2 peaks, $\phi = 172, 176.5$, combined area = 1), and $-CHF-$ ($\phi = 185.5$, area = 1). The *cis* compound showed medium absorption at 775 cm^{-1} and the *trans* isomer, strong absorption at 918 cm^{-1} in the infrared. The C=C stretching vibration occurred strongly at 1670 and 1677 cm^{-1} for the *cis* and *trans* isomers, respectively. *Anal.* Calcd. for $C_7H_5F_6$: C, 40.7; H, 3.89; F, 55.4. Found: *cis*-, C, 41.1; H, 4.13; F, 55.2; *trans*-, C, 41.1; H, 4.07; F, 55.1.

The isomeric 2,3,5,7,7,7-hexafluoro-1-heptene has been previously identified.² Its F^{19} n.m.r. spectrum indicated: CF_3 ($\phi = 65.5$, area = 3), $=CF$ ($\phi = 116$, area = 1), and $-CHF-$ ($\phi = 186, 190$, area = 2). Upon ozonization this olefin yields 2,4,6,6,6-pentafluorohexanoic acid (an α -fluoro acid)² which is the same acid obtained from ozonization of *cis*- and *trans*-1,3,5,7,7,7-hexafluoro-1-heptene.

1,1,5,7,7,7-Hexafluoro-2-heptene (II) obtained as indicated above was analyzed. *Anal.* Calcd. for $C_7H_5F_6$: C, 40.7; H, 3.89; F, 55.4. Found: C, 41.2; H, 3.93; F, 54.2. The F^{19}

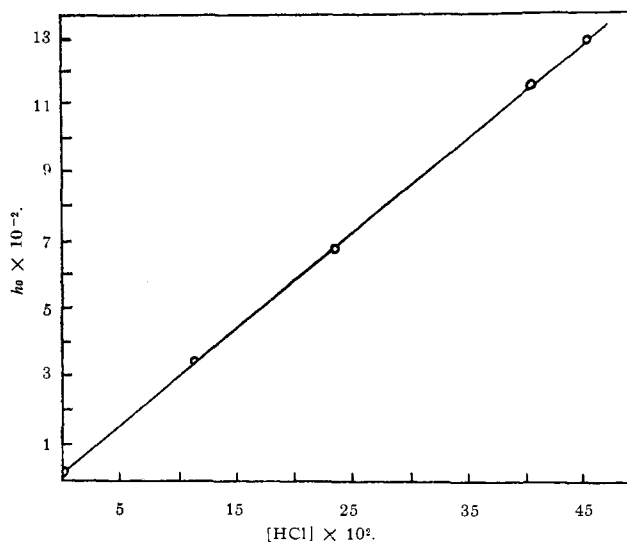


Fig. 4.—Concentration of HCl in slightly aqueous (3.0 to 5.0% H_2O) formic acid vs. h_0 .

n.m.r. spectrum (neat except for 5–10% Freon 11 as reference) exhibited: CF_3 ($\phi = 65.6$, area = 3.0), $-CHF_2$ ($\phi = 113$, area = 2.0) and $-CHF-$ ($\phi = 185.3$, area = 1). The CF_3 group consisted of 2 sets of triplets ($J = 10.6$ c.p.s.) separated by 7.7 c.p.s. and the $-CHF_2$ was a doublet ($J = 60.2$ c.p.s.).

5,7,7,7-Tetrafluoro-2-heptenal (III) obtained from the solvolysis as described above showed infrared peaks at 2950 and 2720 ($-CHO$), 1695 (conjugated $-CHO$), and 1640 cm^{-1} ($C=C$).

The 2,4-dinitrophenylhydrazone, recrystallized from ethyl acetate, m.p. $177-178^\circ$ was analyzed. *Anal.* Calcd. for $C_{13}H_{12}F_4N_2O_4$: C, 42.9; H, 3.3; N, 15.4; F, 20.9. Found: C, 43.0; H, 3.3; N, 15.4; F, 20.7. The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone in ethanol solution showed λ_{max} 368 $m\mu$, $\epsilon \approx 30,000$, characteristic of this type of structure.

Formic acid, 97%, was slowly fractionated through a 4-ft. helix-packed column. A center cut which analyzed for 0.4% H_2O was used for the kinetic runs with the appropriate amount of distilled water added.

Acetic acid, 99.9%, was diluted to 97.0% with distilled water.

Kinetic data were obtained by v.p.c. techniques using 2,3,5,7,7,7-hexafluoro-1-heptene as an internal reference as follows. The allylic fluoride (*cis*- or *trans*-I) was dissolved in the formic acid solvent (3.0 ml.) to which the various solutes had been added. Hydrochloric acid and HF were added in the form of concentrated aqueous solutions of known concentration.

Polypropylene test tubes closed with serum caps were used as reaction vessels. After immersing the tubes in a constant temperature bath at $30.15^\circ (\pm 0.05^\circ)$, samples (0.2–0.4 ml.) were periodically removed with a syringe and quenched by squirting into a mixture of 3.0 ml. of ether and 3.0 ml. of water. The aqueous layer was washed with ether (2×3.0 ml.), the ether layer washed with water (5×5.0 ml.), and dried ($CaCl_2$). The contents of the ether solution were analyzed by injection of a sample (0.3–0.6 ml.) into a gas chromatograph equipped with an 8-ft. stainless steel column packed with 10% Carbowax 1500 on Chromosorb and operated at 125° with a helium flow rate of 150 ml./min. After exactly 16 min., the temperature was programmed for 35–40 min. at the rate of $4.6^\circ/\text{min}$. The area of the olefin was then compared to the reference compound in order to calculate concentration. A sample at $t = 0$ gave the relationship of moles of olefin and reference compared to areas. The concentration of olefin in moles/liter could then be calculated for each sample by relating its area to that of the reference. Retention times for each component under these conditions are: ether, 0.5–4 min.; 2,3,5,7,7,7-hexafluoro-1-heptene, 5 min.; *cis*-1,3,5,7,7,7-hexafluoro-1-heptene, 8 min.; *trans*-1,3,5,7,7,7-hexafluoro-1-heptene, 10 min.; 1,1,5,7,7,7-hexafluoro-2-heptene, 12 min.; 5,7,7,7-tetrafluoro-2-heptenal, 32 min.

The moles/area ratios of the various compounds were determined in independent experiments for use in measuring rates of formation of products II and III. The ratios for I and II were essentially identical and that for III approximately 50% greater. In the kinetic runs, however, a large degree of variability in the moles/area ratio was found. This offered no difficulty for

determining rates of loss of I since the ratio was determined at zero time for each run. In calculating rates of formation of II and III, it was assumed that the ratios varied in the same way as that for I.

As indicated above, material balance in runs not containing either sodium formate or sodium fluoride was poor in early stages of reaction. This is illustrated in Fig. 2 and 3 for rates of formation of products both in the presence and absence of added base. In both cases, the rate of loss of I is first order through at least 75% reaction.

Determination of H_0 .—Measurements were carried out by the usual indicator method.¹¹ The necessary value of extinction coefficient for the free base in 97.3% formic acid was obtained in

(11) Reference 6, pp. 266–271.

solutions saturated with sodium formate. For the acid form, obtained in solutions containing *p*-toluenesulfonic acid, $\epsilon \approx 0$. Calculations were made using

$$H_0 = -\log h_0 = pK_a + \log C_B/C_{BH^+}$$

where pK_a = indicator constants for either 4-chloro-2-nitroaniline or 4-nitrodiphenylamine, and C_B/C_{BH^+} is obtained from $\epsilon/\epsilon_B - \epsilon$ where ϵ = extinction coefficient of acidic solution and ϵ_B = extinctive coefficient for the indicator base in the solvent. Figure 4 shows the plot of $[HCl]$ vs. h_0 .

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Dehalogenation of Propargyl and Allenyl Halides. II.^{1,2}

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Reaction of lithium aluminum hydride with 3-chloro-3-methyl-1-butyne and 1-chloro-3-methyl-1,2-butadiene (I) involves two independent reactions. Displacement of chlorine by hydrogen occurred with complete acetylene-allene rearrangement to yield 3-methyl-1,2-butadiene and 3-methyl-1-butyne, respectively. Addition yielded organoaluminum derivatives which underwent further reactions; hydrolysis yielded 3-methyl-1-butene, 3-methyl-2-butene, 3-methylbutane, and 1,1-dimethylcyclopropane. The course of the addition to I was examined by deuterolysis which gave 3-methyl-1-butene-3-*d*₁, 2-methyl-2-butene-4-*d*₁, 2-methylbutane-4,4-*d*₂ (containing appreciable amounts of another dideuterio isomer), and 1,1-dimethylcyclopropane-2-*d*₁. Addition of lithium aluminum deuteride was also studied. Displacement predominated with the propargyl chloride and addition with I. Similar reactions were observed with chloroallene and bromoallene. Propargyl chloride gave mainly displacement, but propyne predominated over allene among the products. For the synthesis of allenic hydrocarbons by dehalogenation of propargyl halides, zinc-copper couple is a better reagent than lithium aluminum hydride.

It was established earlier² that dehalogenation of propargyl halides with zinc-copper couple gives the same mixture of allenic and acetylenic hydrocarbons as similar dehalogenation of the corresponding allenyl halides. Dehalogenation with lithium aluminum hydride gave very different results.^{2,4} Tertiary propargyl halides, $RR'CX\equiv CH$, gave allenic hydrocarbons, $RR'C=C=CH_2$, which appeared to contain no more than traces of the acetylenic isomers. The corresponding allenyl chloride gave mainly olefins and saturated hydrocarbons; small amounts of acetylenic hydrocarbons were also formed. Allenic hydrocarbons were not found, but small amounts would have escaped detection. 1-Bromo-3-methyl-1,2-butadiene gave a hydrocarbon mixture in 70% yield distributed as follows: 61% 3-methyl-1-butyne, 36% isopentane, 3% olefinic material (mainly 3-methyl-1-butene). Both bromoallene and propargyl bromide gave mainly propyne in this dehalogenation.

Gas-liquid chromatography has made possible a more exact study of lithium aluminum hydride dehalogenation of these halides. This paper presents the results with 1-chloro-3-methyl-1,2-butadiene (I) (Table I), 3-chloro-3-methyl-1-butyne (Table II), and with three-carbon halides (Table III).

(1) This paper is taken in part from the Ph.D. thesis of R. D. Wilcox, U.C.L.A., 1962. Part of the material was presented at the XIXth International Congress of Pure and Applied Chemistry, London, July, 1963 (Abstracts of the Congress, A, p. 23). The research was supported largely by a contract with the Office of Ordnance Research, U. S. Army.

(2) For Part I, see T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955). References to earlier work on dehalogenation of substituted propargyl halides are given there.

(3) U. S. Rubber Co. Fellow, 1959–1960.

(4) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963).

Results and Discussion

Reactions of halides with lithium aluminum hydride were carried out in two ways. Method A involved addition of the halide to the hydride suspension at room temperature or below followed by heating to 100°. Method B involved addition at the reaction temperature which was maintained throughout the reaction period. Acid hydrolysis gave mixtures of hydrocarbons which were separated by g.l.c. and the components identified by retention times (comparison with authentic specimens) and by infrared and mass spectra. The course of the reaction with I was followed by hydrolysis of reaction mixtures with deuterium oxide and by use of lithium aluminum deuteride.

The complex mixtures of products are believed to result from two independent reactions: the first is displacement of the halogen by hydride; the second involves addition of the reagent to the propargyl or allenyl halide system. The latter forms organoaluminum compounds which mainly react further and eventually yield, by hydrolysis, olefins and saturated hydrocarbons. Further complications are introduced by reduction of at least one of the displacement products (3-methyl-1-butyne) by hydride species produced in the reaction mixture.

The displacement reaction is unique because it involves complete acetylene-allene rearrangement with both 3-chloro-3-methyl-1-butyne and 1-chloro-3-methyl-1,2-butadiene; the propargyl chloride yields only dimethylallene and the allenyl chloride yields only 3-methyl-1-butyne. As would be expected, displacement is more important with the more reactive chloride