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SOLVOLYSIS OF ALLENYLCARBINYL CHLORIDE AND ITS CYCLOPROPANATED HOMOLOGS

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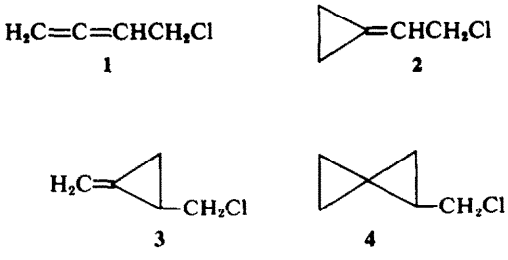
Abstract—Allenylcarbinyl, cyclopropylideneethyl, methylenecyclopropylcarbinyl, and spiropentylcarbinyl chloride were prepared and their solvolysis reactions in aqueous ethanol or aqueous dioxane or both were studied. Consideration of the solvolytic reactivity of these compounds and their products in aqueous dioxane indicate that all react, at least in part, *via* positive charge-delocalized transition states.

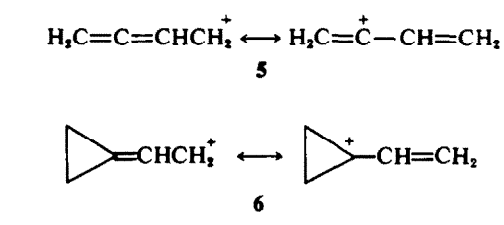
INTRODUCTION

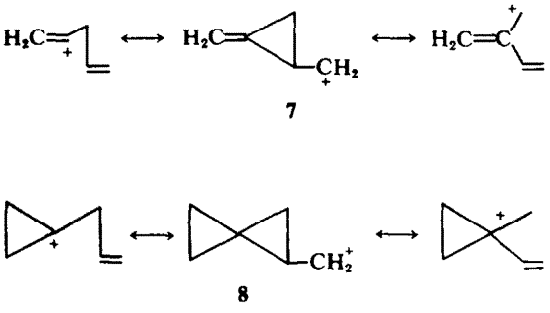
Allenylcarbinyl chloride (**1**) and its cyclopropanated homologs (**2–4**) constitute a useful series for assessing the ability of carbons with different degrees of unsaturation to accommodate positive charge.‡ Allylic-like resonance of allenylcarbinyl cation (**5**) and cyclopropylideneethyl cation (**6**) results in delocalization of charge, respectively, to a central allenic carbon and a carbon common to a double bond and a cyclopropane ring; and cyclopropylcarbinyl-like resonance of 2-methylenecyclopropylcarbinyl cation (**7**) or spiropentylcarbinyl cation (**8**) results in delocalization of charge to cyclopropyl carbons that differ in degree of unsaturation. We describe here the preparation of **1–4** and study of their solvolysis reactions.§

Synthesis. Allenylcarbinyl chloride (**1**) was prepared most conveniently by addition of hydrochloric acid to vinyl acetylene in the presence of calcium chloride,[7] and **2–4** were prepared by treatment of the corresponding alcohols with thionyl chloride in the presence of tri-n-butylamine. Allenylcarbinyl alcohol, obtained by treatment of 4 - chloro - 2 - butyn - 1 - ol with lithium aluminum hydride,[8] was converted to 2-methylenecyclopropylcarbinyl alcohol and spiropentylcarbinyl alcohol by treatment with Simmons–Smith reagent; the 2-methylenecyclopropylcarbinyl alcohol was contaminated with 10–15% cyclopropylideneethanol. The last alcohol was obtained in sufficient amounts by thermal rearrangement of its isomer.[‖] The equilibrium mixture at 200° of the alcohols corresponding to **2** and **3**, obtained starting with pure samples of both alcohols, contained 65% 2-methylenecyclopropylcarbinyl alcohol and 35% cyclopropylideneethanol. Interestingly, thermal rearrangement of **3** gave 3-methylenecyclobutyl chloride.

Kinetics. In Tables 1 and 2 are listed first-order







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‡For recent reviews of vinyl cations, see Refs 1–3.

§Studies have been reported recently of acid-catalyzed reactions of substituted allenylcarbinyl alcohols[4] and spiropentylcarbinyl alcohols[5] and deamination reactions of methylenecyclopropylcarbinylamine[6] and substituted spiropentylcarbinylamines.[5]

‖For a leading reference to thermal rearrangements of methylenecyclopropanes, see Ref 9.

Table 1. First-order rate constants for solvolysis in 80% aqueous ethanol

Compound	Temp., °	k, $sec^{-1} \times 10^6$	Purity, % VPC	Purity, % ∞titer
1	40	1·17	96	96
		1·22	96	95
	55	5·00	99	99
		5·17	99	97
	69·9	23·0	96	96
		23·7	96	96·5
3	40	0·195	93	—
		0·197	93	—
	55	1·34	93	80
		1·27	93	73
	69·9	6·50	93	71
		6·82	96	83
		6·88	96	81

Table 2. First-order rate constants for solvolysis in 50% aqueous dioxane

Compound	Temp, °	k, $sec^{-1} \times 10^6$	Purity, % VPC	Purity, % ∞titer
1	40	2·53	99	107[a]
	40	2·48	99	113[a]
	55	12·4	99	108[a]
	55	12·2	99	113[a]
	69·9	52·2	99	99·5
	69·9	53·5	99	99·5
2	40	56·2	45	100
	69·9	924	61	100
3	40	2·17	93	82
	40	2·12	86·5	—
	55	11·7	93	112[a]
	55	12·0	93	99
	69·9	55·5	93	90
	69·9	55·8	93	91
4	40	14·2	87	—
	40	13·3	87	—
	55	64·0	87	100·5
	55	70·8	87	95·5
	69·9	297	87	98·0
	69·9	345	87	97·7

[a] See the next to last paragraph under "*Kinetic runs*".

rate constants for solvolysis of **1** and **3** in 80% aqueous ethanol and of **1–4** in 50% aqueous dioxane. Activation parameters are given in Table 3.

Comparison of the solvolysis rate constants of **1–4** with those of the related allyl, crotyl, γ-methylpropargyl, and cyclopropylcarbinyl systems (Table 4) shows that the solvolytic reactivity of **1–4** is substantial and indicates that these compounds are reacting *via* positive charge-delocalized transition states. The nature of the solvolysis products from **1–4** give support to this inference.

Products. Solvolysis of allenylcarbinyl chloride (**1**) in 76% aqueous dioxane in the presence of calcium carbonate gave 8–11% vinyl acetylene, 10–11% chloroprene, 6% methyl vinyl ketone, and 73–77% of the corresponding alcohol, allenylcarbinyl alcohol. Heat-induced rearrangement of **1** was not a factor in its solvolysis reaction; this was shown by heating a neat sample of **1** at 80 ± 5° for 48 hr and observing no change in the VP chromatogram.

In the absence of calcium carbonate the same four products were formed, but the amount of the major product, allenylcarbinyl alcohol, decreased after 80–90 hr of heating due to reaction with the hydrochloric acid formed on solvolysis.

Solvolysis in the presence of excess calcium chloride gave no alcohol products but did give

Table 4. Relative rate constants

Chloride	k_{rel} in 80% C_2H_5OH at 69·9°	k_{rel} in 50% Dioxane at 25°[a]
Crotyl	1·00	1·00[b]
2	—	2·8
1	0·18[c]	0·042
γ-methylpropargyl	0·018	0·0098
allyl	0·034[d]	*ca* 0·001[e]
Cyclopropylcarbinyl	5·7	—
3	0·85	0·039
4	—	0·31

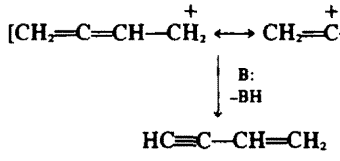
[a] Extrapolated values for **1–4**. [b] P. J. C. Fierens, G. Genskens and G. Klopman, *Bull. Soc. Chim. Belges* **68**, 177 (1959) reported $k = 7{\cdot}96 \times 10^{-6}$ sec^{-1}. [c] $k = 2{\cdot}33 \times 10^{-5}$ sec^{-1}. [d] Extrapolated from 50% ethanol ($Y = 1{\cdot}604$) at 44·6° using the Grunwald–Winstein equation and the Arrhenius equation ($E_a = 20{\cdot}4$ kcal/mole). [e] From Ref 17, p. 35.

Table 3. Activation parameters

Compound	Solvent	$\Delta H^{\ddagger}_{25°}$, kcal/mole	$\Delta S^{\ddagger}_{25°}$, e.u.
1	80% Ethanol	20·6 ± 2·0	−20 ± 6
1	50% Dioxane	21·1 ± 0·3	−17 ± 1
2	50% Dioxane	19·3 ± 0·6	−15 ± 2
3	80% Ethanol	24·6 ± 0·2	−10·6 ± 0·6
3	50% Dioxane	22·5 ± 0·1	−12·6 ± 0·3
4	50% Dioxane	21·8 ± 0·7	−11 ± 2

about 20% rearrangement to chloroprene plus < 1% vinylacetylene and methyl vinyl ketone. This observation rules out the possibility that the ketone is formed by an S_N2' reaction because the added chloride should not affect the rate of formation of ketone by such a mechanism.

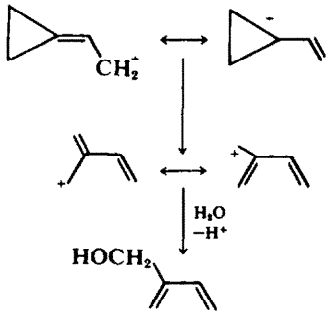
The most compelling evidence for an S_N1 mechanism in solvolysis of **1** is formation of the elimination product, vinylacetylene. It is difficult to rationalize the formation of this product in any way but from a resonance-stabilized ionic intermediate.



The product distributions in the solvolysis of methylenecyclopropylcarbinyl chloride (**3**) and spiropentylcarbinyl chloride (**4**) (see below), which solvolyze predominantly by S_N1 paths, indicate 5% and 18%, respectively, of unrearranged products. In these systems, S_N1 solvolysis gives less than 20% of direct substitution products. If the same factors can be assumed to be operative in the allenylcarbinyl system, distribution of the positive charge should favor the vinyl cation form, and less than 20% direct substitution of allenylcarbinyl alcohol by an S_N1 mechanism should occur.

The accumulated data demonstrates that **1** solvolyzes partially by an S_N1 pathway, which gives the three minor products. Most of the solvolysis in 76% aqueous dioxane, perhaps as much as 70–75%, proceeds by S_N2 displacement by solvent. A significant S_N2' pathway can be excluded.

Cyclopropylideneethyl chloride, in the presence of calcium carbonate in 80% aqueous dioxane, solvolyzed completely in 5 hr at 85° to give 8 products detectable by VPC. Two of these, subsequently identified as the corresponding alcohol, cyclopropylideneethanol, and 2 - hydroxymethyl - 1,4 - butadiene, were formed in near equal amounts and accounted for 80% of the products. Formation of the acyclic product seems best explained on the basis of ring opening of a resonance-stabilized cation to a more stable allylic cation, which undergoes attack by solvent. Cyclopropylideneethanol can also be formed *via* the cation that is formed initially, but analogy with the behavior of **3** and **4** leads us to believe that most of this alcohol is formed by an S_N2 pathway.

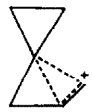


Solvolysis of methylenecyclopropylcarbinyl chloride under the usual reaction conditions gave fourteen products detected by VPC. The major product was 3-methylenecyclobutyl chloride, which accounted for 46% of the product. Also characterized were two alcohols, 3-methylenecyclobutyl alcohol (38%) and methylenecyclopropylcarbinyl alcohol (5%). Acetylcyclopropane, a product of the deamination of methylenecyclopropylcarbinylamine, could have been one of the unidentified minor products. In the absence of calcium carbonate, 3-methylenecyclobutyl alcohol was not detected and the relative amount of one of the lesser products was increased. Keefer and Roberts[10] reported that 3-methylenecyclobutyl alcohol reacts with acid or base to give only β-methylcrotonaldehyde and its condensation products. We can speculate that reaction of the cyclobutanol with the hydrochloric acid formed in this reaction must have occurred and the product found in increased amount was β-methylcrotonaldehyde.

Our findings are in agreement with the Japanese workers[6] who studied deamination of methylenecyclopropylcarbinylamine and found that 3-methylenecyclobutyl compounds made up most of the product mixture. The nature of the products and the fact that methylenecyclopropylcarbinyl chloride solvolyzes within an order of magnitude as rapidly as cyclopropylcarbinyl chloride indicate that the reaction occurs primarily by an S_N1 pathway and that the cyclopropyl ring carbon to which most of the positive charge is delocalized is the least saturated, *e.g.*,

The results from solvolysis of spiropentylcarbinyl chloride (**4**) were similar in kind to those obtained from solvolysis of methylenecyclopropylcarbinyl chloride (**3**). Fifteen products were detected by VPC, and three of these made up 75% of the product mixture. The major product, which accounted for 32% of the product mixture, was 5-chlorospirohexane. Also characterized were two alcohols, 5-spirohexanol and spiropentylcarbinyl alcohol, which made up 25% and 18%, respectively, of the product mixture. As with the reaction of **3**, the nature of the products from **4** and its reactivity comparable to cyclopropylcarbinyl chloride indicate that the major solvolysis pathway is an S_N1 reaction and that the cyclopropyl ring carbon which

assumes most of the positive charge is the least saturated, that is, the carbon common to both rings



EXPERIMENTAL

Temps are uncorrected. IR spectra were obtained with a Perkin Elmer 237B, Beckman IR-4, or Beckman IR-8 spectrophotometer. Spectra of small samples were obtained with the Beckman IR-8 equipped with a beam condenser. The micro samples were contained in a cavity cell supplied by Barnes Engineering Company. NMR spectra were obtained at 60 MHz with a Varian Associates A60A spectrometer; unless noted otherwise, spectra were taken of 10–20% solns in CCl_4, and resonance frequencies in NMR spectra were determined relative to internal TMS. VP chromatograms were obtained with either an Aerograph Model A-700 or a Varian-Aerograph Model 90-P. VPC columns used were: 15% Armene SD on HMDS treated Chromosorb W, 12-ft × ¼-in.; 20% Carbowax 20 M alkaline on acid washed, DMCS treated Chromosorb P, 10-ft × ¼-in.; 15% Diisodecyl phthalate on Chromosorb W, 12-ft × ¼-in.; 20% FFAP on DMCS treated Chromosorb P, 10-ft × ¼-in.; and 15% octyl phthalate on HMDS treated Chromosorb W, 12-ft × ¼-in. Unless stated otherwise, VPC analyses were based on relative areas rather than relative response factors. Elemental analyses were carried out by the Microanalytical Laboratory, University of California, Berkeley.

Allenylcarbinyl chloride (1) was prepared by the method of Carothers *et al.*[7] From 330 g of monovinylacetylene* was obtained 140 g (25%) of 1 of 96% purity. Redistillation of 32·6 g of this material through a 60-cm Podbielniak column with tantalum wire spiral[11] gave 23·7 g of >99% pure 1, b.p. 88–89°, n_D^{21} 1·4768 (lit[7] b.p. 88°, n_D^{20} 1·4775). The NMR spectrum was in agreement with that reported by Ferguson.[12]

Methylenecyclopropylcarbinol and spiropentylcarbinol. Allenylcarbinol* (12·8 g, 0·18 mole) was treated with 146 g (0·55 mole) of diiodomethane and 60 g of powdered Zn–Cu couple[13] by the method of Le Goff.[13] After removal of the ether by distillation, the residue was examined by VPC on FFAP and found to consist of 73–76% methylenecyclopropylcarbinol, 22–24% spiropentylcarbinol, and 2–3% cyclopropylideneethanol. The residues from two runs were combined, and a rough separation of the principal carbinols was effected by distillation through the 60-cm Podbielniak column. The yield of methylenecyclopropylcarbinol was 14·6 g (47%), b.p. 75–81° (62 mm); that for spiropentylcarbinol was 3·4 g (9·5%), b.p. 67–71° (13 mm). Further purification was achieved by distilling the combined products from several runs through a Nester–Faust 0·8 × 60-cm polymer-coated spinning band column, and analytical samples of >99% purity were obtained by VPC on Carbowax 20 M alkaline.

Methylenecyclopropylcarbinol: b.p. 78–80° (54 mm); n_D^{21} 1·4670°, IR, 885 and 1740 cm^{-1} (C=C) [lit[14] b.p. 138–139°; n_D^{25} 1·4644; IR, 11·26 and 5·73 μ]; NMR, δ 5·38 (m, 2, $=CH_2$), 3·47 (AB part of ABX pattern, J_{AB} = 11 Hz, J_{AX} = 6 Hz, J_{BX} = 6 Hz, 2, CH_2O), 2·8–4·1 (conc dependent s, 1, OH), m centered at 1·3 ppm (3, cyclopropyl ring H's). Spiropentylcarbinol: b.p. 87° (50 mm); n_D^{21} 1·4645; NMR, δ 3·46 (d, 2, CH_2O), 2·8–3·6 (conc dependent s, 1, OH), m centered at 0·8 ppm (7, cyclopropyl ring H's). (Found: C, 73·35; H, 10·11. $C_6H_{10}O$ requires: C, 73·43; H, 10·27%).

Thermal rearrangement of methylenecyclopropylcarbinol. A 0·69-g sample of methylenecyclopropylcarbinol, which had been purified by VPC, was dissolved in 1 ml of PhH. The soln was sealed in a heavy-walled glass tube and heated for 1 hr at 220 ± 10° in a wax bath. Analysis by VPC on Carbowax 20 M alkaline showed the presence of a new substance in addition to PhH and starting alcohol with retention time similar to that of the latter compound and presumed to be cyclopropylideneethanol. Triplicate analysis by VPC indicated that the alcohol mixture was 63·6 ± 0·3% methylenecyclopropylcarbinol and 36·4 ± 0·3% cyclopropylideneethanol. The remaining sample was resealed, heated an additional 4 hr at 220 ± 10°, and again analyzed by VPC; the alcohol ratio was unchanged. An NMR spectrum of the soln was obtained. In addition to bands due to PhH and starting alcohol, bands were observed at δ 6·03 (m, =CH), 4·28 (d, J = 6 Hz, CH_2O), and 0·93 (apparent s, cyclopropyl H's). Comparison of band areas indicated the presence of 63% starting alcohol and 37% rearranged alcohol.

The equilibration procedure was repeated. Purified methylenecyclopropylcarbinol was heated in PhH solution for 1·5 hr at 220 ± 10°. Analysis by VPC on both Armene SD and FFAP indicated that the alcohol mixture was 66·3 ± 0·6% starting alcohol and 33·7 ± 0·6% cyclopropylideneethanol.

Cyclopropylideneethanol. A soln of 2·0 g of methylenecyclopropylcarbinol and 20 g of diphenylether was heated at 220 ± 5° for 4 hr. VPC on FFAP indicated that 36·6% rearrangement had occurred. Distillation through the spinning band column separated the alcohols from diphenylether. The alcohols (4·3 g) from 2 runs were combined and distilled through the spinning band column. A 1·5-g fraction consisting of 72% methylenecyclopropylcarbinol was collected at 73–78° (60 mm), and a 0·8-g fraction of cyclopropylideneethanol was collected at 56–61° (15 mm). A sample of >99% rearranged alcohol was collected by prep VPC on FFAP: n_D^{25} 1·4729; NMR, δ (m > 9 lines, 1, C=CH), 4·3 (conc dependent s, 1, OH), 4·17 (d, m, J = 6·5 Hz, 2, CH_2O), and 1·07 ppm (narrow m, 4, cyclopropyl H's). (Found: C, 70·86; H, 9·70. $C_7H_{12}O$ requires: C, 71·29; H, 9·59%).

Thermal rearrangement of cyclopropylideneethanol. A soln prepared from 24 μl of >99% pure cyclopropylideneethanol and 100 μl of PhH was sealed in a heavy-walled glass tube and heated at 220 ± 10° for 1·5 hr. Analysis of the pale yellow soln by VPC on FFAP indicated that the alcohol mixture was 65·5% methylenecyclopropylcarbinol and 34·5% cyclopropylideneethanol. This analysis was confirmed by NMR, which showed that the alcohol ratio was 65:35.

Methylenecyclopropylcarbinyl chloride (3). The procedure is patterned after one used for the preparation of cyclopropylcarbinyl chloride.[15] A soln of 12·0 g (0·142 mole) of 90% pure methylenecyclopropylcarbinol, 26·4 g (0·142 mole) of tri-n-butylamine, and 250 ml of ether was stirred and cooled to 4°. Thionyl chloride (17·0 g, 0·142 mole) was added dropwise in 1 hr at such a rate that the temp was maintained below 6°. Distillation through a 7-cm Vigreaux column gave 7·4 g (51%) of colorless liquid, b.p. 69–70° (200 mm), and analysis by VPC on Carbowax 20 M alkaline indicated that it consisted of a major component

*Gift of E. I. du Pont de Nemours and Co., Elastomers Division. Technical grade, diluted 50/50 with xylene, and contained in a one-quart steel cylinder.

(*ca* 88%) and 2 minor components (6% each). Redistillation through the spinning-band column gave a 1·65-g fraction, which was 96% pure **3**: b.p. 57° (200 mm); n_D^{23} 1·4622; IR, 890 and 1760 cm^{-1} (C=C); NMR, δ 5·45 (m, 2, =CH_2), 3·42 (AB part of ABX pattern, J_{AB} = 11 Hz, J_{AX} = 6 Hz, J_{BX} = 6 Hz, 2, CH_2Cl), and 1·5 ppm (broad m, 3, cyclopropyl H's). (Found: C, 58·71; H, 6·92; Cl, 34·38. C_5H_7Cl requires: C, 58·56; H, 6·88; Cl, 34·56%).

Spiropentylcarbinyl chloride (**4**). A procedure similar to that used to prepare **3** was employed. From 3·0 g (0·031 mole) of spiropentylcarbinol (92% pure by VPC) and equimolar amounts of tri-n-butylamine and thionyl chloride in 60 ml of ether was obtained 2·6 g (73%) of colorless spiropentylcarbinyl chloride, b.p. 69–71° (90 mm) and 42–70° (10–90 mm). The procedure was repeated to give 2·7 g (76%) of product. Analysis by VPC (Armene SD) indicated that the product consisted of 90% spiropentylcarbinyl chloride and two major and three minor impurities, including methylenecyclopropylcarbinyl chloride. The products were combined and redistilled through a polymer-coated spinning band column. The first fraction (0·9 g) was collected at 68–72° (90 mm) and was 51% **4**. In addition to bands due to **4**, it had IR 1630 cm^{-1} (C=C) and NMR δ 5·18 (br), 4·99 (br), 4·52 (pentet), 4·00 (s), 2·93 (d, J = 6 Hz), 2·51 (d, J = 7 Hz) and 0·47 ppm (s). The bands at δ 4·52, 2·51, and 0·47 ppm, with an approximate intensity ratio of 1:4:4, correspond to those reported[16] for 5-chlorospirohexane; the other bands are consistent with the 2 - (chloromethyl) - 1,4 - pentadiene structure. A sample of 95% **4** had $n_D^{23.5}$ 1·4601 and NMR δ 3·50 (AB part of ABX pattern, J_{AB} = 11 Hz, J_{AX} = 7 Hz, J_{BX} = 7 Hz, 2, CH_2Cl), 1·57 (m, 1, CH), and 0·77 ppm (m, 6, cyclopropyl H's). (Found: C, 61·80; H, 7·81; Cl, 30·58. C_6H_9Cl requires: C, 61·81; H, 7·78; Cl, 30·41%).

Cyclopropylideneethyl chloride (**2**). The method used for the preparation of methylenecyclopropylcarbinyl chloride was used. From 2·0 g (23·8 mmole) of 65% pure cyclopropylideneethanol, 4·4 g (23·8 mmole) of tri-n-butylamine, and 2·8 g (23·5 mmole) of thionyl chloride in 40 ml of ether at 0–5° was obtained 1·35 g (55%) of 55% pure **2**; the major fraction (0·60 g) had b.p. 52–53°/70–79 mm. A sample of **2** of >96% purity was obtained by prep VPC on FFAP at 120°: n_D^{22} 1·4770; no band in the 1650 cm^{-1} region; NMR, δ 5·98 (t, J = 7 Hz, 1, =CH), 4·17 (d, J = 7 Hz, 2, CH_2Cl), 1·17 ppm (narrow mult, 4, CH_2—CH_2) (from the fine splitting of the δ 5·98 and 4·17 ppm bands, it was estimated that $J_{CH_2—C=CH}$ = 2 Hz and $J_{CH_2—C=C—CH_2Cl}$ = 1 Hz). (Found: C, 58·26; H, 7·21; Cl, 34·32. C_5H_7Cl requires: C, 58·56; H, 6·88; Cl, 34·56%).

Kinetic runs. A weighed sample of the chloride to be solvolyzed was quickly pipetted into approximately 95 ml of solvent in a 100-ml volumetric flask which had been temperature equilibrated, and the timer was started. The soln was brought to 100 ml with additional solvent and shaken thoroughly. Aliquots of 5·00 ml were removed periodically and delivered into 10 ml of CCl_4 at about −10°. After addition of 20 ml of water and 3 drops of bromthymol blue indicator, the solns were titrated with 0·0238 or 0·0281 N NaOMe in MeOH. The solns were stirred magnetically during titration. Infinity titers were obtained after at least 10 half-lives. In all but two runs the reactions were followed to better than 50% completion, and in the majority of runs the reactions were followed to more than 80% completion. Duplicate runs were carried out; agreement between duplicate runs was within 5%. A plot of log (A/A_0) *vs* time, t, was made from the data obtained in each run, where A is the concentration of total chloride at any time t, and A_0 is the initial concentration. The first-order rate constant, k, was calculated from the initial slope using the equation $k = -2{\cdot}303\,\Delta \log(A/A_0)/\Delta t$. The initial concentration, A_0, was determined from the VPC purity where internal return to slowly solvolyzed chlorides occurred; otherwise, A_0 was determined from the infinity titer. Where the infinity titer method was used the initial concentrations agreed very closely with those determined by VPC purity. The initial concentration varied from 0·0162 to 0·0949 M but was generally between 0·032 and 0·071 M. The concentration, A, is equal to the initial concentration of reactant, A_0, less the concentration of HCl determined by titration. Rate constants are summarized in Tables 1 and 2.

In Table 2 are several infinity titers of > 100%. As the infinity titers were obtained by titration with standard base, excess acid, such as from decomposition of solvent impurities, results in high titers. Two different lots of Mallinckrodt Reagent Grade Dioxane were used to prepare the 50% dioxane solvent, and both gave positive blank titers. The blanks from one lot were small (0·02–0·08 ml) and increased only slightly at the infinity point. The other lot showed somewhat larger blanks (0·15–0·42 ml), and these increased to 0·59–1·81 ml at the infinity point. These blanks were subtracted from the kinetic titers for all runs of all compounds solvolyzed in aqueous dioxane. However, separate infinity blanks were not obtained in earlier determinations including the rate runs for solvolysis of allenylcarbinyl chloride at all three temperatures. Instead, initial blanks were subtracted, and this is the probable reason for the high infinity titers in Table 2. Blank titers in aqueous ethanol were negligible.

Activation parameters were calculated in the usual way[17] and are summarized in Table 3.

Products of solvolysis in 80% aqueous dioxane

(A) *From allenylcarbinyl chloride* (**1**). A soln was prepared from 10 μl of **1** (>99% pure by VPC) and 200 μl of 80% dioxane, and 25 μl aliquots together with solid Na_2CO_3 were sealed in m.p. capillary tubes with I.D. of 1·5–2·0 mm. The capillary tubes were heated in an oil bath at 90 ± 3°. At various intervals a capillary tube was removed and the contents were analyzed by VPC on FFAP. As time progressed four product bands appeared and gradually increased in size as the band due to **1** decreased. After 80 hr only about 5% of the starting material remained. The relative areas of the product bands were determined twice, and these expressed as mole percents are given in Table 5.

Table 5. Solvolysis products from allenylcarbinyl chloride

Product	Approximate mole % Run 1	Run 2
Vinylacetylene	8	11
Chloroprene	10	11
Methyl vinyl ketone	6	6
Allenylcarbinyl alcohol	77	73

The relationship between mole percent and relative band area was verified by analysis of mixtures of known composition. This was done for a mixture of methyl vinyl ketone and allenylcarbinyl alcohol and for a mixture of methyl vinyl ketone and **1**.

When the same reaction was carried out in the absence of $CaCO_3$ the same four product bands developed. The relative area of the major product peak (due to allenylcarbinyl alcohol) started to decrease after 80–90 hr. This was shown to be due to reaction of the alcohol with the hydrochloric acid generated in the reaction.

The solvolysis was also carried out in the presence of calcium chloride. A soln of 10 μl of **1** in 200 μl of 80% aqueous dioxane was divided into 25-μl aliquots and sealed in capillary tubes together with solid $CaCl_2$. The tubes were heated at 80 ± 5°. No alcohol was detected by VPC after 65 hr, but about 20% of the chloride rearranged to chloroprene and small bands (< 1% yield) appeared due to vinylacetylene and methyl vinyl ketone.

As the above runs were carried out on a small scale, there were insufficient quantities of the products available for complete identification. Therefore, a large-scale run was carried out with 10·0 g (0·113 mole) of > 99% pure **1** and 13·0 g (0·130 mole) of $CaCO_3$ in 200 ml of 76% aqueous dioxane. The mixture was stirred for 138 hr at 95 ± 5° and worked up. The presence of vinylacetylene, chloroprene, methyl vinyl ketone, and allenylcarbinyl alcohol was shown by means of IR and NMR spectroscopy and by comparison of VPC retention times with authentic samples.

Thermal stability of **1** was assessed by heating a sealed sample at 80 ± 5° for 48 hr. Analysis by VPC showed that the sample was still > 99% pure.

The stability of allenylcarbinyl alcohol was also assessed by dissolving 10 μl in 100 μl of 80% aqueous dioxane, sealing 25 μl of this soln in each of two capillary tubes, and heating at 80 ± 5° for 96 and 168 hr. Neither sample showed any change from the original soln.

(B) *From cyclopropylideneethyl chloride* (**2**). The same micro procedure as described above was carried out with 95% pure **2** and a bath temp of 85 ± 2°. VPC bands due to products were noted early in the reaction, and after 5 hr only a trace of **2** remained. There were 8 bands due to products, and the retention times on FFAP at 143° and the approximate percent of total product are summarized in Table 6. Note that the two products with longest retention times accounted for 80% of the product; these compounds were subsequently identified as 2 - hydroxymethyl - 1,3 - butadiene and cyclopropylideneethyl alcohol.

Table 6. Solvolysis products from cyclopropylideneethyl chloride

Product	Retention time on FFAP at 143°, min	Approximate mole %
A	1·2	1
B	1·7	1
C	2·4	8
D	3·3	3
E	7·0	trace
F	9·8	7
G[a]	11·9	38
H[b]	14·0	42

[a]2-Hydroxymethyl-1,3-butadiene. [b]Cyclopropylideneethyl alcohol.

When the reaction was carried out in the absence of $CaCO_3$, bands due to the major products and product F were greatly diminished in size and a new band developed with a retention time slightly less than that of **2**. After 100 hr at 85 ± 2°, this band accounted for > 90% of the product. This product did not have the same retention time of methylenecyclopropylcarbinyl chloride (**3**).

Only a small amount of **2** was available for a larger scale run, and this was contaminated with about 60% methylenecyclopropylcarbinyl chloride (**3**). Fortunately, solvolysis of **2** is considerably faster than solvolysis of **3**, and the reaction was stopped before much **3** had reacted. From 0·35 g (3·40 mmole) of impure **2** and 0·35 g (3·50 mmole) of $CaCO_3$ in 5 ml of 75% aqueous dioxane was obtained 2 - hydroxymethyl - 1,3 - butadiene and cyclopropylideneethyl alcohol by distillation followed by prep VPC; identity of the two major products was established by comparison of their IR and NMR spectra and VPC retention times with authentic samples. (Preparation of 2 - hydroxymethyl - 1,3 - butadiene is described below.)

(C) *From methylenecyclopropylcarbinyl chloride* (**3**). The micro procedure described under part A above was carried out with 99% pure **3** and a bath temperature of 85–90°. After 43 hr, the starting material had all reacted and there were 14 bands due to products. The retention times on FFAP at 144° and the approximate percent of total product are summarized in Table 7. Note that the three major products accounted for nearly 90% of the product, and these were subsequently identified as 3-methylenecyclobutyl chloride, methylenecyclopropylcarbinyl alcohol and 3-methylenecyclobutyl alcohol. When the reaction was carried out in the absence of $CaCO_3$, the band due to 3-methylenecyclobutyl alcohol was not present.

Table 7. Solvolysis products from methylenecyclopropylcarbinyl chloride

Product	Retention time on FFAP at 144°, min	Approximate mole %
A	1·3	1·2
B	1·5	2·1
C	1·7	0·3
D	2·0	0·8
E	2·3	0·1
F	2·8	0·8
G[a]	3·0	45·8
H	3·5	3·0
I	5·0	0·8
J	5·4	0·5
K	6·1	trace
L	6·9	1·8
M[b]	10·0	5·0
N[c]	12·0	37·9

[a]3-Methylenecyclobutyl chloride. [b]Methylenecyclopropylcarbinyl alcohol. [c]3-Methylenecyclobutyl alcohol.

From 3·0 g (0·0292 mole) of 97% pure methylenecyclopropylcarbinyl chloride and 3·5 g (0·035 mole) of $CaCO_3$ in 75 ml of 75% aqueous dioxane was obtained by distillation followed by prep VPC: 3-methylenecyclobutyl chloride, NMR δ 4·83 (pentet, J = 2 Hz, 2, =CH_2), 4·37 (pentet, J = 7 Hz, 1, CHCl), and 3·08 ppm (narrow multiplet, 4, CH_2—C—CH_2); methylenecyclopropylcarbinyl alcohol, identical with authentic material; and 3-methylenecyclobutyl alcohol, NMR δ 4·83 (pentet, J = 2 Hz, 2, =CH_2), 4·30 (pentet, J = 7 Hz, 1, CHO), 4·0 (s, 1, OH), and 2·79 ppm (narrow multiplet, 4, CH_2—C—CH_2). (Found: C, 71·58; H, 9·30. C_5H_8O requires: C, 71·39; H, 9·59%).

(D) *From spiropentylcarbinyl chloride* (4). The micro procedure described under part A above was carried out with 97% pure 4 and a bath temp of 90–95°. After 17·5 hr, the starting material had all reacted and there were 11 bands due to products present in more than trace amounts. The retention times on Armene SD at 112° and the approximate percent of total product of these products are summarized in Table 8. Note that the five major products accounted for nearly 90% of the product, and four of these were subsequently identified as 2 - chloromethyl - 1,3 - butadiene, 5-chlorospirohexane, spiropentylcarbinyl alcohol, and 5-spirohexanol.

From 1·3 g (0·0112 mole) of 90% pure spiropentylcarbinyl chloride and 1·3 g (0·013 mole) of $CaCO_3$ in 30 ml of 75% aqueous dioxane was obtained by distillation followed by prep VPC the four products listed above. 5-Spirohexanol had NMR δ 4·47 (pentet, J = 7 Hz, 1, C<u>H</u>O), 4·36 (s, 1, O<u>H</u>), 2·21 (d, J = 7 Hz, 4, cyclobutyl H's), and 0·38 ppm (s, 4, cyclopropyl H's); identity of the other three was established by comparison of IR and NMR spectra and VPC retention times with the compounds prepared in other ways.

2-Hydroxymethyl-1,3-butadiene. The procedure of Aufdermarsh[18] was used to convert 8·0 g (0·09 mole) of allenylcarbinyl chloride and 2·4 g (0·099 mole) of Mg to the Grignard reagent. Formaldehyde, generated by heating 20 g of paraformaldehyde at 180°, was run into the mixture over a period of 30 min. Water (10 ml) was added dropwise followed by 40 ml of 2 M H_2SO_4. The phases were separated and distillation of the dried ether soln gave 0·9 g of product with b.p. 42–66° (0·5 mm), which proved to be a 3 : 1 mixture of 2 - hydroxymethyl - 1,3 - butadiene and 1,2 - pentadiene - 5 - ol. The former compound had NMR δ 6·39 (4 lines, X part of ABX pattern, $J_{AX} + J_{BX}$ = 29 Hz, 1, C_3—<u>H</u>), 5·18 (m, 4, =C<u>H</u>$_2$), 4·24 (s, 2, C<u>H</u>$_2$O), and 4·1 ppm (s, 1, OH). (Found: C, 71·01; H, 9·89. C_5H_8O requires: C, 71·39; H, 9·59). The latter product had NMR δ 4·72 (narrow mult, 3, <u>H</u>$_2$C=C<u>H</u>), 4·1 (s, 1, O<u>H</u>), 3·60 (m, 2, C<u>H</u>$_2$O) and 2·27 ppm (sym mult, 2, =C—C<u>H</u>$_2$—C).

Table 8. Solvolysis products from spiropentylcarbinyl chloride

Product	Retention time on FFAP at 144°, min	Approximate mole %
A	1·8	1
B[a]	4·5	7·5
C[b]	4·9	32·1
D	6·1	2·7
E	7·0	1·6
F	7·4	1·1
G	9·4	1·0
H[c]	10·0	17·7
I[d]	10·9	25·1
J	12·8	2·5
K	13·4	7·5

[a] 2-Chloromethyl-1,3-butadiene. [b] 5-Chlorospirohexane. [c] Spiropentylcarbinyl alcohol. [d] 5-Spirohexanol.

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