Mechanism of Triarylchloroallene Solvolysis[1a]

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Abstract: A detailed study of the solvolysis of triarylchloroallenes is reported. The rate of disappearance of haloallene was found to equal the rate of appearance of HCl. An increase in solvent polarity results in a marked increase in the rate constant for solvolysis. The m value for triphenylchloroallene in aqueous acetone solutions is found to be 0.69 ± 0.06. No change in rate is observed with a 1250-fold excess of triethylamine added. Addition of 0.10 M LiCl results in a 29% rate depression while the addition of 0.10 M LiBr results in a slight rate enhancement. The exclusive product of solvolysis of triphenylchloroallene is 1,1,3-triphenylprop-2-yn-1-ol. Substituent effect data yield $\rho = -2.0$ against σ^+. The temperature dependence of the rate yields $\Delta H^{\ddagger} = 20.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -10.7$ eu. These data are interpreted in terms of a unimolecular reaction proceeding *via* a charge-delocalized allenyl cation.

The hydrolysis of the halogen-containing compounds prepared by reaction of $SOCl_2$, PCl_3, or PBr_3 with certain highly hindered tertiary propargyl alcohols, such as 1,1,3-triphenylprop-2-yn-1-ol, under neutral to slightly basic conditions is reported to result in the formation of the starting propargyl alcohol.[2,3a–e] Initially some workers took this result as strong evidence that these halogen-containing compounds had the same structure as the propargyl alcohol from which they had been prepared.[3a–e] Wotiz and Mancuso,[4] Jacobs and Fenton,[2] and Landor and coworkers[5] reexamined many of the compounds reported earlier and concluded, primarily on the basis of their ir spectra, that these products were haloallenes.

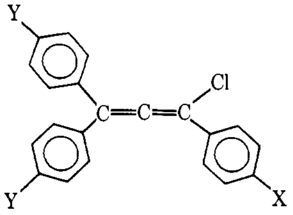
Our interest in this reaction stems from the current activity in the area of vinyl cations derived from unimolecular bond heterolysis of vinyl derivatives. Numerous reports concerned with the formation of these intermediates have appeared over the last few years.[6] In nearly every early report of a unimolecular reaction by a vinyl derivative the positive charge generated is stabilized by an appropriately situated π bond. Often an aromatic ring supplies the necessary delocalization of charge.

More recently, however, some workers have concentrated on reactions of simple alkyl-substituted vinyl derivatives. Only one report using an allylic double bond to stabilize the developing vinyl cation is to be found. Grob and Spaar reported that 2-bromo-4-methyl-1,3-pentadiene reacts 23 times faster than p-methoxy-α-bromostyrene in 80% ethanol at 100°.[7] On the other hand, 2-bromo-3-methyl-1,3-pentadiene reacts very slowly even at 110°, demonstrating the ability of the dimethylethylene group to stabilize an adjacent positive charge.

It should be noted that vinyl cations may be allylic to a double bond in two isomeric ways. While Grob and Spaar examined one such manner, the solvolysis reaction of haloallenes presents an alternative approach to the generation of a vinyl cation with such a double bond available for stabilization. This paper presents our work attempting to elucidate the mechanism of the solvolysis reaction of these compounds.

Results

A series of triarylchloroallenes (Ia–e) was prepared as described earlier.[1a] Other workers have reported that the treatment of 1,1,3-triphenylprop-2-yn-1-ol with $SOCl_2$ and pyridine in dry ether results in the formation of dimers or the cyclization of the expected triphenylchloroallene.[8] Jacobs and Fenton and others, however, reported that the chloroallene was indeed the product.[2,5] We have verified the results of these latter workers and suggest that in addition to the temperature the amount of solvent used in the preparation may be a critical parameter.



Ia, X = Y = H
b, X = Cl; Y = H
c, X = CH_3; Y = H
d, X = CH_3O; Y = H
e, X = H; Y = CH_3

Since there had been a considerable disparity of results from this synthetic route, it was decided that three criteria of purity would be employed where possible. In addition to a comparison of physical properties with those reported, it was necessary to assure that the compounds prepared exhibited the character-

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[1] (a) A preliminary account of this work has appeared: M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, **92**, 1082 (1970); (b) author to whom inquiries should be addressed; (c) National Science Foundation Undergraduate Research Participant, summer 1970.

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istic allenic stretching frequency and that no O-H or C=O absorption were to be found in the ir. Finally, cryoscopic molecular weights provided convincing evidence that the products were indeed the monomeric chloroallenes desired.

The rates of triarylchloroallene solvolysis were measured conductometrically or spectrophotometrically in triplicate. Excellent first-order rate plots were obtained to more than 90% reaction. The rate of disappearance of triphenylchloroallene measured spectrophotometrically was found to be equal to the rate of appearance of HCl as measured conductometrically in 90:10 ethanol-water at 25°. The results of these kinetic studies are compiled in Tables I, II, and III.

Table I. Solvolysis Rates of Triarylchloroallenes in 80:20 (v/v) Acetone-Water

Compd	Temp, °C	10^5k, sec^{-1}
Ia	24.98 ± 0.02	4.80 ± 0.051
	34.82 ± 0.02	14.6 ± 0.09
	45.00 ± 0.02	43.3 ± 0.33
Ib	25.00 ± 0.02	2.76 ± 0.036
	34.83 ± 0.02	9.16 ± 0.066
	45.07 ± 0.02	27.7 ± 0.04
Ic	24.99 ± 0.02	17.6 ± 0.34
Id	24.99 ± 0.02	180 ± 0.07
Ie	25.00 ± 0.02	17.7 ± 0.09[a]

[a] Measured in 90:10 acetone-water.

Table II. Solvent Dependency of Triarylchloroallene Solvolysis in Acetone-Water Solutions

Compd	$CH_3COCH_3:H_2O$ (v/v)	Temp, °C	10^5k, sec^{-1}
Ia	80:20	26.09 ± 0.02	5.41 ± 0.052
	70:30	26.09 ± 0.02	18.4 ± 0.21
	60:40	26.09 ± 0.02	56.5 ± 0.21
	80:20	44.99 ± 0.02	43.3 ± 0.33
	70:30	44.99 ± 0.02	138 ± 0.8
Id	90:10	26.09 ± 0.02	23.7 ± 0.42
	80:20	26.09 ± 0.02	195 ± 0.7

Table III. Salt Effects of Triphenylchloroallene[a] Solvolysis in 90:10 Ethanol-Water at 25.0°

LiCl	LiBr	10^4k, sec^{-1} [b]
		2.11 ± 0.037
		2.15 ± 0.005[c]
		2.07 ± 0.008[d]
	0.010	2.12 ± 0.031
	0.038	2.14 ± 0.058
	0.076	2.14 ± 0.03
	0.101	2.24 ± 0.004
0.010		1.88 ± 0.033
0.038		1.65 ± 0.043
0.075		1.52 ± 0.007
0.100		1.49 ± 0.008

[a] Solutions were 4.0-4.5 × 10^{-5} M in substrate. [b] Measured spectrophotometrically at 2750 Å. [c] Measured conductometrically; substrate concentration = 4 × 10^{-4} M. [d] 0.05 M $(C_2H_5)_3N$ added.

From the data in Table I, the activation parameters for the hydrolysis reaction are calculated to be $\Delta H^{\ddagger}$ = 20.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −10.7 eu[9] for Ia, and $\Delta H^{\ddagger}$ = 21.1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −8.80 eu[9] for Ib.

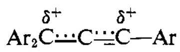
An increase in the solvent polarity results in a marked increase in the rate constant for solvolysis, as seen in Table II. When these data are plotted against the Grunwald-Winstein-Fainberg Y values for aqueous acetone mixtures m is calculated to be 0.69 ± 0.06 for Ia and 0.77 for Id at 26°.

Table III lists the data collected in ethanol-water solutions. When the rate of disappearance of triphenylchloroallene absorption at 2750 Å is measured at 25.0° in 90:10 ethanol-water in the presence of 0.05 M triethylamine, no meaningful change in the rate constant is detected. Furthermore the addition of 0.10 M LiCl results in a 29% depression of the rate of solvolysis while 0.10 M added LiBr results in a slight rate enhancement.

The exclusive product, isolated in 92% yield, from the solvolysis of triphenylchloroallene in 70:30 acetone-water at 27° is 1,1,3-triphenylprop-2-yn-1-ol. No evidence of carbonyl absorption is found in the ir spectrum of the crude material. Identical results were obtained when 1-(p-methoxyphenyl)-3,3-diphenyl-1-chloroallene was studied.

Discussion

These results are consistent with a mechanism of solvolysis in which slow formation of an intermediate cation, II, is the rate-limiting step. While elimination-addition pathways in solvolysis of trisubstituted haloallenes are impossible, reasonable addition-elimination pathways may be formulated which result in the propargyl alcohols observed as products.[10] The lack of rate enhancement in the presence of 0.05 M triethylamine, however, speaks against the incursion of such a nucleophilic addition-elimination mechanism.



$$\mathrm{Ar_2\overset{\delta+}{C}\cdots C\cdots\overset{\delta+}{C}{-}Ar}$$

II

An electrophilic addition-elimination mechanism is also possible, but is considered unlikely under the conditions of this study. The calculated pH of the infinity kinetic solutions is 4.4 in 90:10 ethanol-water, and the absence of any change in kinetic behavior upon addition of triethylamine provides evidence against such a mechanistic pathway. Schubert and coworkers have noted that the hydrolysis of p-amino-α-bromostyrene in acidic media occurs by protonation of the alkene rather than by a unimolecular solvolysis reaction as reported earlier.[11] They further noted that hydration of this vinyl halide exhibits general acid catalysis. If such a mechanism were operative here, the addition of excess triethylamine would have been expected to decrease the rate of protonation even if triethylammonium ion acted as the general acid since the catalytic constant for hydronium ion is generally greater than that for other acids. If general acid catalysis were not operative, addition of excess triethylamine also would have been expected to decrease the rate of solvolysis by decreasing the hydronium ion concentration. No change in the rate constant for solvolysis was observed upon addition of a 1250-fold excess of triethylamine.

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(9) Calculated at 25.0°.

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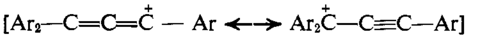
In addition, the rate constant for solvolysis in 90:10 ethanol–water at 25° at a substrate concentration of 4×10^{-5} *M* is 13.9 times greater than the rate constant for solvolysis at the same *Y* value (−0.747) in acetone–water at a substrate concentration of 4×10^{-4} *M*. This represents a tenfold increase in the acidity of the medium at infinity, yet results in a 14-fold decrease in the rate of solvolysis.

The effect of solvent composition on the rate of solvolysis compares favorably with studies on other vinyl substrates reported to undergo SN1 reaction such as 2-bromo-4-methyl-1,3-pentadiene (m = 0.81),[7] isopropenyl triflate (m = 0.52),[12] and trianisylvinyl tosylate (m = 0.41).[13] Furthermore these data are inconsistent with the solvent dependency generally observed for SN2 displacement reactions. When these results are compared with similar data on saturated systems which solvolyze by an SN1 mechanism, no discontinuity results. The solvolysis of benzhydryl chloride exhibits an *m* value of 1.11 in aqueous acetone at 25°,[14] that of α-methylallylchloride exhibits an *m* value of 0.70 in aqueous ethanol at 25°,[15] and that of dineopentylmethylcarbinyl chloride exhibits an *m* value of 0.70 in aqueous ethanol at 25°.[16] It was not surprising, therefore, to find that the rate of solvolysis of triphenylchloroallene in 90:10 ethanol–water does not fit the mY correlation line for aqueous acetone. Similar effects have been observed in a number of SN1 reactions.[17]

Unambiguous evidence of external return is provided by the common ion rate depression observed in aqueous ethanol. The selectivity ratio, k_{-1}/k_{H_2O}, calculated from these data is 5–13. This value compares favorably with those reported for the solvolysis of benzhydryl chloride, k_{-1}/k_{H_2O} = 10–16 in aqueous acetone,[14] and for 1-anisyl-2,2-diphenylbromoethylene,[18] k_{-1}/k_{H_2O} = 10 in aqueous DMF. The assignment of relative carbonium ion stabilities on the basis of such measurements is tenuous due to the fact that this interpretation of common ion rate depression data does not take into account the possibility of ion pair intermediates. Rappoport and Gal have addressed themselves to this problem and report substantial involvement of ion pairs in the solvolysis of 1,2-dianisyl-2-phenylbromoethylene based on a comparison of the rate of cis–trans isomerization with the solvolysis rate.[19] It should be noted, however, that although the present data yield no information about the incursion of ion pair intermediates in the solvolysis of triphenylchloroallene, such information is experimentally obtainable for other haloallenes. Further speculation thus seems unwarranted.

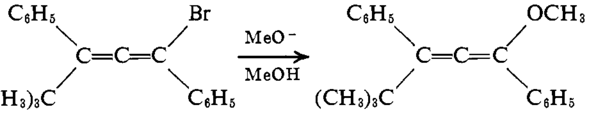
Charge Distribution in the Allenyl Cation

It has been reported that the allenyl cation structure contributes substantially to the cation formed (IIa) upon dehydration of certain tertiary propargyl alcohols.[20,21] The substituent effects observed here (ρ *vs.* $\sigma^+ = -2.0$) for the same cation may be interpreted as supporting this earlier work. It is interesting to note, however, that reaction with solvent occurs exclusively at the propargyl position of the cation even when a *p*-methoxyphenyl group is placed at the reaction center. Jacobs and Fenton have suggested that the formation of methyl 4,4-dimethyl-1,3-diphenyl-1,2-pentadienyl ether (IV) from the corresponding bromide (III) by treatment with MeO⁻ in methanol occurs by a SN1 process with attack at the propargyl position being sterically hindered.[2] They also reported the formation of 1,3,3-triphenyl-2-propen-1-one during recrystallization of triphenylbromoallene from aqueous methanol. We are exploring these discrepancies.



$$[Ar_2{-}C{=}C{=}\overset{+}{C}-Ar \longleftrightarrow Ar_2\overset{+}{C}{-}C{\equiv}C{-}Ar]$$

IIa



III IV

When attempts were made to prepare chloroallenes having substituents in the aromatic rings in the 3 position, highly colored products were often obtained. It appears that *p*-chloro or *p*-methoxy substituents activate the allene moiety presumably formed toward dimerization or cyclization. Other workers have reported similar results.[8,22,23] The enhanced solvolysis rate of Ie provides convincing evidence of charge delocalization to the propargyl position. Since the two rings at that end of cation are probably not able to achieve complete coplanarity, the effect of these substituents is diminished.

It may be concluded from this work that although substantial charge resides at the allenyl position, a large portion of the charge is most likely delocalized into the aromatic rings in the 3 position. Further structural modifications should provide more data in this area. No conclusion may yet be drawn regarding the ability of the "allylic" double bond in the allene moiety to stabilize a neighboring vinyl cation. Work is in progress to this end.

Experimental Section

All melting points are uncorrected. Ir spectra were obtained using a Perkin-Elmer Model 457 spectrophotometer. Nmr spectra were obtained using a Perkin-Elmer Model R-20B spectrometer. Acetone was purified according to Denoon[24] and stored over Linde 4A Molecular Sieves. Ethanol was purified according to Wiberg[25] and stored over Linde 3A Molecular Sieves. Microanalyses were performed by Atlantic Microlabs, Atlanta, Ga. Substituted phenylacetylenes were prepared according to the procedure of Cook.[26]

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1,1,3-Triphenyl-2-propyn-1-ol was prepared according to the procedure reported by Olah and Pittman.[21] The solid alcohol was recrystallized from petroleum ether in 66% yield: mp 80–81° (lit.[21] mp 82°); ir (CCl_4) 3599 (OH) and 2234 ($C\equiv C$) cm^{-1}; nmr (CCl_4) δ 2.70 (s, 1) and 7.40 (m, 15).

1,1-Diphenyl-3-(4-chlorophenyl)-2-propyn-1-ol was prepared in 76% yield according to the procedure described for 1,1,3-triphenyl-2-propyn-1-ol when *p*-chlorophenylacetylene was substituted for phenylacetylene: mp 74–75°; ir (CCl_4) 3600 (OH) and 2225 ($C\equiv C$) cm^{-1}.

1,1-Diphenyl-3-(4-methylphenyl)-2-propyn-1-ol was prepared as above in 75% yield: mp 64–66°; ir (CCl_4) 3600 (OH) and 2225 ($C\equiv C$) cm^{-1}.

1,1-Diphenyl-3-(4-methoxyphenyl)-2-propyn-1-ol was prepared in 70% yield as described above: mp 65–66°; ir (CCl_4) 3600 (OH) and 2225 ($C\equiv C$) cm^{-1}.

1,1-Di(4-methylphenyl)-3-phenyl-2-propyn-1-ol was prepared in 52% yield as described above: mp 82–84°; ir (CCl_4) 3600 (OH) and 2225 ($C\equiv C$) cm^{-1}.

1,3,3-Triphenyl-1-chloropropadiene (Ia) was prepared according to the procedure of Jacobs and Fenton.[2] Recrystallization from ether–ethanol afforded a 55% yield of the desired material: mp 69–70° (lit.[2] mp 70–71°); ir (CCl_4) 1964 ($C{=}C{=}C$) cm^{-1} (lit.[2] 1958 cm^{-1}); nmr (CCl_4) δ 7.30 (m); mol wt in benzene 926 (calcd, 302).

1-(4-Chlorophenyl)-1-chloro-3,3-diphenylpropadiene (Ib) was prepared according to the procedure described for Ia. Recrystallization from ether–ethanol gave the desired chloroallene in 80% yield: mp 84–85°; ir (CCl_4) 1926 ($C{=}C{=}C$) cm^{-1}.

Anal. Calcd for $C_{21}H_{14}Cl_2$: C, 74.79; H, 4.15; Cl, 21.06. Found: C, 74.69; H, 4.17; Cl, 21.10.

1-(4-Methylphenyl)-1-chloro-3,3-diphenylpropadiene (Ic) was prepared as above. Recrystallization from ether–ethanol gave the product in 70% yield: mp 127–128°; ir (CCl_4) 1926 ($C{=}C{=}C$) cm^{-1}.

Anal. Calcd for $C_{22}H_{17}Cl$: C, 83.42; H, 5.37. Found: C, 83.56; H, 5.53.

1-(4-Methoxyphenyl)-1-chloro-3,3-diphenylpropadiene (Id) was prepared as described above. Recrystallization from ether–ethanol gave a 67% yield of the desired product: mp 131–132°; ir (CCl_4) 1926 ($C{=}C{=}C$) cm^{-1}. This chloroallene exhibited marked instability. Attempts at analysis resulted in high C and H values and low Cl values. Those are consistent with rapid hydrolysis of the compound in air. Further support of this thesis comes from the observation of a $C\equiv C$ bond in the ir spectrum of material allowed to stand in air for 3 days. Consequently a sample of this compound was recrystallized and dried prior to each set of kinetic runs.

1-Phenyl-1-chloro-3,3-bis(4-methylphenyl)propadiene) (Ie) was prepared as described above. Recrystallization from ligroin gave the product in 67% yield: mp 81–82°; ir (CCl_4) 1923 ($C{=}C{=}C$) cm^{-1}.

Anal. Calcd for $C_{23}H_{19}Cl$: C, 83.50; H, 5.79; Cl, 10.71. Found: C, 83.52; H, 5.71; Cl, 10.68.

Product Studies. A 1.01-g sample of triphenylchloroallene was transferred to a solution of 700 ml of acetone and 300 ml of distilled water at 27.8° and stirred for 6 hr (ten half-lives). At the end of this period, 500 ml of water was added and the resulting solution extracted five times with 200-ml portions of ether. The organic layer was dried over $MgSO_4$ and evaporated. The solid product (92%) showed no absorption in the 1650–1750 cm^{-1} region. Recrystallization from ligroin yielded 0.78 g (83%) of 1,1,3-triphenyl-2-propyn-1-ol, mp 80–81°. A similar experiment utilizing Id gave 0.76 g (81%) of 1,1-diphenyl-3-(4-methoxyphenyl)-2-propyn-1-ol after recrystallization. No evidence of carbonyl absorption was found in the ir spectrum of crude product.

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Intramolecular Base-Catalyzed Imidazole Catalysis

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Abstract: A new two-step synthesis of 4(5)-(2′-hydroxyphenyl)imidazole (HPI) was utilized. Solvolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl toluate (PNPT) catalyzed by HPI and other related imidazole or phenol model compounds, such as 1-methyl-4-(2′-hydroxyphenyl)imidazole and 4(5)-(2′-methoxyphenyl)imidazole, indicated that reaction other than simple nucleophilic catalysis by the imidazole group and phenoxide ion function of HPI must operate during the catalyzed solvolysis. The favored geometry existing between the imidazole and phenoxide groups suggests an intramolecular bifunctional catalysis involving the phenoxide and imidazole groups. The rate constant of this intramolecular base-catalyzed imidazole catalysis was estimated to be 137.4 and 6.39 l./mole min for PNPA and PNPT, respectively. The compound 4(5)-[ω-(*p*-hydroxyphenyl)nonyl]imidazole (HPNI), which has an imidazole and phenol function joined by nine methylene units, was synthesized in seven steps from sebacic acid. The modest observed rate enhancement during the solvolysis of *p*-nitrophenyl acetate and *p*-nitrophenyl palmitate catalyzed by HPNI was attributed to a hydrophobic attraction between the substrates and the long chain model compounds.

Imidazole is known to be a nucleophilic catalyst for the solvolysis of *p*-nitrophenyl acetate (PNPA)[1] and related activated acyl compounds.[2] The simple nucleophilic catalytic process has been shown to be subject to base catalysis; the second base can be another imidazole molecule in a concentrated imidazole solution,[3] or could also be a hydroxide ion.[4] The object of this work was to introduce the second base and the imidazole group in the same molecule to test experimentally if this base-catalyzed imidazole catalysis can proceed intramolecularly in a dilute catalyst solution. Although many simple polyfunctional imidazole com-

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