(11) J. Kumamoto and F. H. Westheimer, *J. Am. Chem. Soc.*, **77**, 2515 (1955).
(12) D. W. C. Barnard, C. A. Bunton, D. R. Llewellyn, K. G. Oldham, B. L. Silver, and C. A. Vernon, *Chem. Ind.* (*London*), 760 (1955).
(13) C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).
(14) A. J. Kirby and A. G. Varvoglis, *J. Am. Chem. Soc.*, **88**, 1823 (1966).
(15) A. J. Kirby and A. G. Varvoglis, *J. Am. Chem. Soc.*, **89**, 415 (1967).
(16) A. J. Kirby and A. G. Varvoglis, *J. Chem. Soc. B*, 135 (1968).
(17) C. A. Bunton, E. J. Fendler, and J. H. Fendler, *J. Am. Chem. Soc.*, **89**, 1221 (1967).
(18) C. A. Bunton and J. M. Hellyer, *J. Org. Chem.*, **35**, 2798 (1970).
(19) C. A. Bunton, *Acc. Chem. Res.*, **3**, 257 (1970).
(20) C. A. Vernon, *Chem. Soc.*, *Spec. Publ.*, **No. 8**, 17 (1957).
(21) D. M. Brown and N. K. Hamer, *J. Chem. Soc.*, 1155 (1960).
(22) (a) G. DiSabato and W. P. Jencks, *J. Am. Chem. Soc.*, **83**, 4400 (1961); (b) A. J. Kirby and W. P. Jencks, *ibid.*, **87**, 3209 (1965).
(23) D. L. Miller and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 1507 (1966).
(24) (a) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969, pp 81–83, 103–105, and 112–115; (b) T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms", Vol. 2, W. A. Benjamin, New York, 1966, Chapters 5–7.
(25) D. G. Knorre, A. V. Lebedev, A. S. Levina, A. I. Rezvukhin, and V.F. Zavytova, *Tetrahedron*, **30**, 3073 (1974).
(26) G. W. Allen and P. Haake, *J. Am. Chem. Soc.*, **95**, 8080 (1973).
(27) J. Rebek and F. Gaviña, *J. Am. Chem. Soc.*, **97**, 3221 (1975).
(28) J. Rebek, F. Gaviña, and C. Navarro, *Tetrahedron Lett.* 3021 (1977).
(29) D. G. Gorenstein, Y. G. Lee, and D. Kar, *J. Am. Chem. Soc.*, **99**, 2264 (1977).
(30) J. P. Guthrie, *J. Am. Chem. Soc.*, **99**, 3991 (1977).
(31) M. Loew and W. R. MacArthur, *J. Am. Chem. Soc.*, **99**, 1019 (1977).
(32) C. H. Clapp and F. H. Westheimer, *J. Am. Chem. Soc.*, **96**, 6710 (1974).
(33) A. C. Satterthwait and F. H. Westheimer, *J. Am. Chem. Soc.*, **100**, 3197 (1978).
(34) S. Meyerson, E. S. Kuhn, F. Ramirez, J. F. Marecek, and H. Okazaki, *J. Am. Chem. Soc.*, **100**, 4062 (1978).
(35) J. A. Maynard and J. M. Swan, *Aust. J. Chem.*, **16**, 596 (1963).
(36) G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3561 (1966).
(37) (a) O. J. Scherer and N. Kuhn, *Angew, Chem.*, *Int. Ed. Engl.*, **13**, 811 (1974); (b) R. Breslow, A. Feiring, and F. Hermann, *J. Am. Chem. Soc.*, **96**, 5937 (1974).
(38) E. Niecke and W. Flick, *Angew. Chem.*, *Int. Ed. Engl.*, **13**, 134 (1974).
(39) J. Rebek and F. Gaviña, *J. Am. Chem. Soc.*, **97**, 1591 (1975), and references cited therein.
(40) S. Pohl, E. Niecke, and B. Krebs, *Angew. Chem.*, *Int. Ed. Engl.*, **14**, 261 (1975).
(41) S. H. D. Ko and F. J. Kezdy, *J. Am. Chem. Soc.*, **89**, 7139 (1967).
(42) D. R. Trentham and H. G. Gutfreund, *Biochem. J.*, **106**, 455 (1968).
(43) S. E. Halford, *Biochem. J.*, **125**, 319 (1971).
(44) S. E. Halford, D. A. Lennette, and M. J. Schlesinger, *J. Biol. Chem.*, **247**, 2095 (1972).
(45) S. E. Halford, M. J. Schlesinger, and H. G. Gutfreund, *Biochem. J.*, **126**, 1081 (1972).
(46) W. Bloch and M. J. Schlessinger, *J. Biol. Chem.*, **249**, 1760 (1974).
(47) M. A. Bleas, D. Turyn, R. Fernandez-Prini, and E. Baumgartner, *Nature* (*London*), **256**, 681 (1975).
(48) M. E. Carsten and H. N. Eisen, *J. Am. Chem. Soc.*, **75**, 4451 (1953).
(49) (a) D. Kumler and J. J. Eiler, *J. Am. Chem. Soc.*, **65**, 2355 (1943); (b) R. Phillips, P. Eisenberg, P. George, and R. J. Rutman, *J. Biol. Chem.*, **240**, 4393 (1965).
(50) H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1938).
(51) N. A. Izmailov and T. V. Mozharova, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **34**, 814 (1960).
(52) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966).
(53) J. F. Coetzee, *Prog. Phys. Org. Chem.*, **4**, 45 (1967).
(54) For example, the following pK_a values have been given for acetic acid: 4.8 (water), 9.6 (methanol), and 22.3 (acetonitrile) (ref 50, 53). For hydrochloric acid: −6.3 (water), 1.0 (methanol), and 8.9 (acetonitrile). The effect is not so marked for certain aminium acids, e.g., $C_5H_5NH^+$: 5.2 (water), 5.0 (methanol), and 12.3 (acetonitrile) (ref 51).
(55) C. A. Bunton and S. J. Farber, *J. Org. Chem.*, **34**, 3396 (1969).
(56) A. G. Weber and G. B. King, *Inorg. Synth.*, 1, 101 (1939).
(57) Although the rate data are quite approximate, the trends indicated by them are significant and reproducible. For a discussion of problems which arise in accurate kinetic studies of displacement reactions of esters in aprotic vs. protic solvents see ref. 58.
(58) Y. Pocker and D. L. Ellsworth, *J. Am. Chem. Soc.*, **99**, 2284 (1977), and references cited therein.
(59) Solvation effects in reactions of phosphate esters and anhydrides have been extensively discussed: P. George, R. J. Witonsky, M. Trochtman, C. Wu, W. Dorwart, L. Richman, W. Richman, F. Shurayh, and B. Lentz, *Biochim. Biophys. Acta*, **223**, 1 (1970).
(60) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969, p. 457.
(61) The basicity of X in $XP(O)(OH)_2$ should decrease as the acidity of XH increases, since factors which increase stability of X^-, and hence promote the dissociation $XH \rightleftharpoons X^- + H^+$, should also operate to lower X-basicity in the phosphate.
(62) F. R. Atherton, *Biochem. Prep.*, **5**, 2 (1957).

A Mechanistic Study of the Reactions of Methylallyl Chlorides with Silver Nitrate in Acetonitrile[1]

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Abstract: The reactions of α-, β-, and γ-methylallyl chlorides with silver nitrate in acetonitrile approximate to a 2.5-order kinetic pattern, first order in the allyl chloride and 1.5 order in silver nitrate. At 45.1 °C the relative rates are allyl (1.0), β-methylallyl (2.2), α-methylallyl (5.3), *cis*-γ-methylallyl (15), and *trans*-γ-methylallyl (19). In contrast, the accompanying silver ion assisted allylic rearrangements and the slower reactions with silver perchlorate are faster for the α-methylallyl chloride than for the γ-methylallyl chlorides. In reaction with 0.20 M silver nitrate, 0.30 M *trans*-γ-methylallyl chloride gives 88% *trans*-γ-methylallyl nitrate and 12% α-methylallyl nitrate and, during reaction, there is negligible rearrangement to α-methylallyl chloride. The *cis*-γ-methylallyl chloride gives essentially identical product ratios, again without any geometric isomerization. The α-methylallyl chloride leads to 66% α-methylallyl nitrate and 34% γ-methylallyl nitrates but, during reaction, appreciable isomerization to γ-methylallyl chlorides occurs and correction for products formed after isomerization leads to a true product ratio for direct formation from α-methylallyl chloride of 79% α-methylallyl nitrate and 21% γ-methylallyl nitrates. Mechanistic implications of the above results are discussed.

Several alkyl halides[2-6] have been studied in their reactions with silver nitrate in acetonitrile. Comparison of reaction rates with those for silver perchlorate provides a semiquantitative measure of the extent of nucleophilic participation in the rate-determining step and application of this principle to allyl bromide[7] indicated considerable nucleophilic assistance.

Extension to methylallyl chlorides is of interest since the α- and γ-substituted compounds show intermediate (borderline) mechanisms in their solvolyses.[8,9] Allyl systems have been included among those for which the borderline behavior has been postulated to involve rate-determining attack upon a preformed ion-pair intermediate[10,11] and a search for additional evidence for a mechanism of this type is included within this study.

The study has some parallels with a previous one carried out in water.[12] It has, however, several practical and theoretical

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Table I. Percentage Composition of "Unreacted" Methylallyl Chlorides after Completion of Reaction of an Acetonitrile Solution, Initially 0.300 M, with 0.200 M Silver Nitrate at 45.1 °C

		% composition[b]		
compd[a]	time, h	**1**	**3a**	**3b**
1	0	99	1[c]	
	38[d]	85	15[c]	
	57	82	18[c]	
	76	74	26[c]	
3a	0	1	98	1
	11.4[d]	7	92	1
	17.1	9	90	1
	22.8	9	90	1
3b	0	2	4	94
	11.4[d]	6	7	87
	22.8	9	7	84
	91.2	12	5	83

[a] **1** is α-methylallyl chloride, **3a** is *cis*-γ-methylallyl chloride, **3b** is *trans*-γ-methylallyl chloride. [b] By VPC; an equilibrium mixture would consist of about 55–75% **3** and 45–25% **1** (ref 9). [c] Sum of **3a** and **3b**. [d] Approximately 10 half-lives.

advantages over this previous study. Unlike the study in water, our system is initially homogeneous, allowing for quantitative kinetic data, and in acetonitrile,[4,7] unlike in water,[12,13] there is no appreciable autocatalysis by precipitated silver halide. In water a mixture of nitrate esters and alcohols results (with the added complication of the nitrate esters subsequently undergoing hydrolysis to provide an indirect route to the alcohol) but, in the weakly nucleophilic acetonitrile,[14] nitrate esters will be the only substitution products. Because of the increased nucleophilicity on transfer of the nitrate ion from water to acetonitrile,[15] there will be a greater tendency toward bimolecular character in the reaction of the preformed[16] allyl halide-silver ion complex.

Results and Discussion

Control Experiments. Vapor phase chromatography showed acetonitrile solutions (0.200 M) of each of the methylallyl chlorides to be unchanged even after 400 h at 45.1 °C. The addition of solid silver chloride, 0.100 M if it were to pass into solution, did not lead to any rearrangement. Silver chloride produced in situ, by reaction with silver nitrate, did lead to a very slow rearrangement of excess α- or γ-methylallyl chlorides[17] (Table I).

Kinetics. A study has been carried out, in acetonitrile at 45.1 °C, of the kinetics of the reactions of α-methylallyl chloride (**1**), β-methylallyl chloride (**2**), *cis*-γ-methylallyl chloride (**3a**), and *trans*-γ-methylallyl chloride (**3b**) with silver nitrate. Analysis was in terms of the extent of precipitation of silver ion from solution as silver chloride and integrated 2.5-order rate coefficients,[4,7] first order in allyl chloride and 1.5 order in silver nitrate, were calculated (Table II). For **2, 3a,** and **3b** these remained essentially constant throughout each run and averaged values are reported. However, the values fall slightly with increasing initial concentration of silver nitrate, consistent with the behavior previously observed for the parent allyl halides.[7] Averaged values are also reported for **1** but the values within each individual run increased as reaction progressed, presumably owing to a silver ion assisted allylic rearrangement to the more reactive **3,** and for this compound initial values were obtained by extrapolation of a plot of 2.5-order rate coefficients against extent of reaction. Also for this substrate the values for the 2.5-order rate coefficient increase with increasing initial silver nitrate concentration, suggesting the possibility of a contribution from an alternative mechanism such as a contribution from the S_N1Ag^+-type mechanism observed with tertiary alkyl halides.[5b,6]

Table II. Average Values for the Integrated 2.5-Order Rate Coefficients for Reactions of Methylallyl Chlorides with Silver Nitrate and Silver Perchlorate in Acetonitrile at 45.1 °C

compd[a]	[C_4H_7Cl], M	[$AgNO_3$], M	$10^4k_{2.5}$, $M^{-3/2}$ s^{-1} [e]
1	0.0776	0.009 53	5.22 ± 0.21 (4.94)[b]
	0.0769	0.0185	5.30 ± 0.44 (4.72)[b]
	0.1552	0.0384	5.93 ± 0.57 (5.16)[b]
	0.0777	0.0399	5.55 ± 0.54 (5.00)[b]
	0.0770	0.0770	5.94 ± 0.31 (5.41)[b]
	0.0755	0.1533	6.53 ± 0.11 (6.33)[b]
2	0.0777	0.009 63	2.45 ± 0.06
	0.0777	0.009 63	2.60 ± 0.12
	0.0773	0.0190	2.24 ± 0.06
	0.1541	0.0375	1.97 ± 0.02
	0.0765	0.0376	2.08 ± 0.07
	0.0767	0.0377	2.14 ± 0.08
	0.0758	0.0758	2.01 ± 0.08
	0.0712	0.1490	1.61 ± 0.09
3a	0.0769	0.0769	14.7 ± 0.3
3b	0.0336	0.0336	19.6 ± 1.2
	0.0774	0.0774	17.3 ± 0.8
1	0.190	0.190[c]	0.67 ± 0.07 (0.78)[b]
3[d]	0.195	0.201[c]	0.35 ± 0.01

[a] **1, 2, 3a,** and **3b** are respectively the α, β, *cis*-γ-, and *trans*-γ-methylallyl chlorides. [b] Initial value. [c] Concentration of silver perchlorate. [d] Mixture of 21% **3a** and 79% **3b**. [e] Rate = $k_{2.5}[C_4H_7Cl][AgNO_3]^{3/2}$.

Table III. Product Composition[a] after Completion of Reactions of 0.300 M Methylallyl Chlorides with Silver Nitrate in Acetonitrile at 45.1 °C

			% composition			
compd	[$AgNO_3$]	method	**4**	**5**	**6a**	**6b**
1	0.200	VPC	64	0	36[b]	
1	0.400	NMR	67	0	33[b]	
2	0.200	VPC	0	100	0	0
3a	0.200	VPC	10	0	90	0
3a	0.400	NMR	12	0	88[b]	
3b	0.200	VPC	12[c]	0	0	88[c]
3b	0.400	NMR	13	0	87[b]	

[a] Remain essentially unchanged over from 10 to 80 half-lives. [b] Sum of **6a** and **6b**. [c] Corrected with the assumption (based upon the experimental observations) that an initially contained 4.2% **3a** will lead to 3.6% **6a** and 0.6% **4** in the product.

The last two entries in Table II represent 2.5-order rate coefficients measured for **1** and **3** (21% **3a**, 79% **3b**) when silver perchlorate is substituted for silver nitrate. No attempt was made to study the expected[18] variation of the values for the 2.5-order rate coefficient with varying initial concentrations of silver perchlorate. During the run with **3**, the integrated values for the coefficient remained essentially constant. For **1**, the values decreased with increasing extent of reaction and an initial value was obtained by extrapolation; this is undoubtedly due to the previously observed[19] silver ion assisted rearrangement to the now slower reacting **3.**

Vapor phase chromatography has been used to study the extent of rearrangement in "unreacted" methylallyl chloride during reaction of both **1** and **3b** with silver nitrate. For **1** appreciable rearrangement to **3** is observed but for **3** very little rearrangement to **1** occurs, consistent with a drift in the 2.5-order rate coefficients being observed during kinetic runs involving **1** but not during those involving **3.**

Product Studies. During the reactions with silver nitrate, elimination to form butadiene[19,20] or nucleophilic interaction with the solvent[21] would produce acid or a nitrilium ion (imidoyl cation), which would titrate as acid.[14] For each of the isomers, aliquots were removed from the reaction mixture and

Table IV. Relative Rates of Reaction of Allylic Chlorides under Various Conditions[a]

substituent	KI in acetone, 20 °C	NaOEt in EtOH, 50 °C	EtOH, 44.6 °C	$AgNO_3$ in CH_3CN, 45 °C	$AgNO_3$ in[b] EtOH, 25 °C	$AgClO_4$ in CH_3CN, 45 °C	HCOOH, 44.6 °C
α-methyl (**1**)	0.02	0.06	3.3	5.3	187	2230	5670
β-methyl (**2**)	1.6	1.03	1.3	2.2			0.5
cis-γ-methyl (**3a**)	8.4	5.2		15			
trans-γ-methyl (**3b**)	1.6	4.4	16[c]	19	321[c]	1000[d]	3550[c]
none (allyl)	1.0	1.0	1.0	1.0	1.0	1.0[e]	1.0

[a] Data for reactions in absence of silver ion from ref 8. [b] From ref 28. [c] Composition in terms of geometric isomers not determined. [d] A redistilled commercial sample which was found to be a mixture of 21% **3a** and 79% **3b.** [e] Calculated from data for allyl bromide, assuming a Br/Cl leaving-group ratio of 467 (the value for 2-halooctanes in reaction with silver nitrate in acetonitrile, from ref 4).

titrated to check for acid production. With **1** and **2** only trace amounts (<1%) of acid developed and no acid formation was observed during reaction of **3a** or **3b.** Consistent with a previous report,[22] **2** leads only to the corresponding β-methylallyl nitrate (**5**) but from **1, 3a,** or **3b** can be expected, in proportions depending upon the reaction mechanism, α-methylallyl nitrate (**4**), *cis*-γ-methylallyl nitrate (**6a**), and *trans*-γ-methylallyl nitrate (**6b**). Analysis was by vapor phase chromatography (VPC) or by nuclear magnetic resonance spectroscopy (NMR). The results are summarized in Table III.

As an aid to the analysis of the product studies, the extent of rearrangement of "unreacted" methylallyl chloride as a function of extent of reaction (as measured by silver chloride precipitation) can be used, in conjunction with the kinetic measurements of silver chloride precipitation for each methylallyl chloride, to correct for the relatively minor extent of product formation after allylic rearrangement. This allows determination of the true nitrate ester product ratios for direct reaction of **1** or **3** with silver nitrate.

Compound **3b** reacts with excess silver nitrate to give, throughout 90% reaction, negligible (<2%) rearrangement to **1.** Further, **1** is the slower reacting isomer with silver nitrate (Table II) and, if formed, it would have accumulated. It follows for **3b** (and, presumably, also for the similarly reacting **3a**) that the experimentally observed product ratios do reflect the true ratios for direct formation of nitrate esters.

At 94% reaction of **1** with excess silver nitrate, there is in the "unreacted" substrate 90% of **1** and 10% of **3.** The percentage of **3** shows an approximately linear relationship to the extent of silver chloride precipitation and at half reaction there is about 5.5% of **3** present. Also, **3** reacts with silver nitrate about 3.5 times as fast as **1** (Table IV) and appreciable amounts (ca. 19%) of methylallyl nitrates will be formed via **3.** This indirectly formed product will account for 2% **4** and 17% **6** within the experimentally determined 66% **4** and 34% **6** and the direct formation from **1** must, therefore, lead to 64 parts of **4** for each 17 parts of **6,** corresponding to a percentage composition of 79% unrearranged **4** and 21% allylically rearranged **6.**

Geometric isomerization during reaction, which would give **6b** from **3a** or **6a** from **3b,** is not observed. Such isomerization would not be predicted for S_N2 reaction and, while it is possible in principle for reactions proceeding through allylic carbonium ions, it was not observed in the study by Young, Sharman, and Winstein.[12]

Comparison with Earlier Studies. In Table IV, we have compiled our relative rate data for reactions in acetonitrile solutions of silver nitrate or silver perchlorate (from Table I) together with data from the literature[8] for substitutions under conditions varying from those strongly favoring S_N2 to those strongly favoring S_N1 reaction. It can be seen that, for reactions of **3** under S_N2 conditions, the cis isomer (**3a**) reacts faster than the trans isomer (**3b**) and both react considerably faster than the more sterically hindered **1.** Under conditions favorable to S_N1 reaction, **3a** and **3b** do not appear to have been separately studied but **3** reacts considerably faster than the parent allyl chloride and slightly slower than **1.** We find that, for reaction with silver nitrate in acetonitrile, **3b** reacts 1.3 times faster than **3a** and 3.6 times faster than **1.** For a similar study in 90% aqueous acetone at 50 °C, Prevost and Georgoulis[23] have found **3b** to react 3.5 times as rapidly as **3a** and at the same rate as **1.** For the heterogeneous reaction with silver nitrate in water, Young, Sharman, and Winstein[12] presented evidence from which we have estimated (based upon half-lives under identical conditions) that **3b** reacts twice as fast as **3a** and only half as fast as **1.** Results in these three solvents suggest decreasing S_N2 character and increasing S_N1 character as the silver nitrate reaction is transferred from acetonitrile to 90% aqueous acetone to water.

The relative rates for reaction with silver nitrate in acetonitrile almost exactly parallel those for solvolysis in ethanol[24] and these relative rates are intermediate in character between those for typical S_N2 processes, such as reaction with iodide ion in acetone[25] or ethoxide ion in ethanol[25] and solvolysis in moist formic acid,[24,26] which favors S_N1 reaction;[27] the relative rates presented for reaction with silver perchlorate in acetonitrile resemble quite closely those for solvolysis in moist formic acid. The values for reaction with silver nitrate in ethanol[28] show character intermediate between those for silver nitrate in acetonitrile and silver perchlorate in acetonitrile. It is clear that the surprise expressed by the authors[28] at finding **3** to react faster than **1** arose from their insistence upon a S_N1Ag^+ mechanism, whereas, although the reactions do lie over to the S_N1Ag^+ end of the spectrum, there is significant nucleophilic assistance involved in the rate-determining step.

A useful concept in studies of allylic systems is the product spread observed within the substitution products. DeWolfe and Young[8,9] define the product spread as the difference in the percentage of the primary substitution product contained in the mixture of substitution products formed by members of a primary-secondary (or primary-tertiary) pair of allylic isomers under identical reaction conditions. If a product spread is observed then there cannot be complete reaction in both cases through a common intermediate. We postulate appreciable nucleophilic assistance in the reactions of **1** and **3** with silver nitrate in acetonitrile and the large product spread of 67% is consistent with this viewpoint. The corresponding study of the heterogeneous reaction in water,[12] believed to lie toward the S_N1Ag^+ end of the mechanistic spectrum, had, in contrast, a product spread of only 14% within the alcohols formed and the spread of 4% for reactions with silver acetate in acetic acid[29] indicates a close approach to limiting S_N1Ag^+ conditions.

The tendency, within acetonitrile, for silver nitrate to favor S_N2-type reaction and silver perchlorate to favor S_N1-type reaction can be used as a measure of the susceptibility of substrates with halide-ion leaving groups toward nucleophilic assistance in their substitution reactions. Data from the present investigation plus data from the literature are brought together within Table V. The silver nitrate/silver perchlorate reactivity ratios show a reasonable trend, with the higher values for reactions one would expect to be S_N2 in nature and lower values (unity in the extreme case) as substrates show increasing S_N1 (plus E1) character. Consistent with this interpretation, the

Table V. Relative Reactivities of Silver Nitrate and Silver Perchlorate with Various Substrates in Acetonitrile and Comparison with Grunwald-Winstein *m* Values

substrate	temp, °C	[AgX]	$k_{2.5}AgNO_3/k_{2.5}AgClO_4$	ref	$m^{a,b}$
allyl bromide	45	0.04	1600	7	0.46^c
$C_6H_5C_6H_4COCBr(CH_3)_2$	74	0.16	130	30	
2-bromooctane	45	0.03	80	4, 18	0.58^d
γ-methylallyl chloride[e]	45	0.20	48	this work	0.66
α-methylallyl chloride	45	0.20	8.1	this work	0.88
tert-butyl chloride	35	0.16	2.0	6	1.00^f
tert-butyl chloride	35	0.01	1.1	6	1.00^f

[a] Values for allyl chlorides from ref 8. [b] In aqueous ethanol at 25.0 °C. [c] For allyl chloride. [d] For 2-bromopropane at 50 °C, from ref 31, p 68. [e] Mixture of 21% cis and 79% trans isomers. [f] By definition.

values for the ratio are in exactly the reverse order to that observed for the Grunwald-Winstein *m* values for solvolyses in aqueous ethanol, an analysis in which a value of unity for *tert*-butyl chloride (by definition) is reduced as increasing amounts of nucleophilic assistance from the solvent occurs.[31]

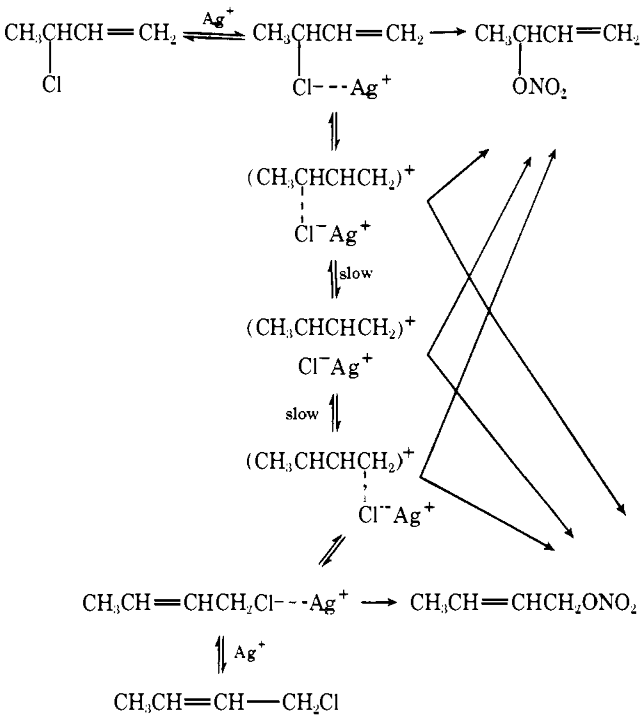
The ratios of 48 and 8.1, respectively, for **3** and **1** indicate borderline (intermediate) mechanisms for these substrates in their reactions with silver nitrate. If the silver perchlorate reaction is assumed to be S_N1Ag^+ in character, then about 2 and 12%, respectively, of the reactions with 0.2 M silver nitrate are proceeding by a mechanism not involving nucleophilic assistance by nitrate ion in the rate-determining step.[32] When the values for these ratios are compared with the value of in excess of 10^3 for allyl bromide, they demonstrate the considerable shifting of the mechanism toward the S_N1Ag^+ end of the spectrum by either an α- or γ-methyl substituent.

Reaction Mechanism. Since it is estimated from the kinetic measurements that the *maximum* S_N1Ag^+ contribution is 2% for **3** and 12% for **1**, the observation of a 67% product spread cannot be due to concurrent S_N1Ag^+ and S_N2Ag^+ processes, which would lead to roughly equal amounts of both allylic isomers in the unimolecular mechanisms and only direct substitution product in the bimolecular mechanism. It appears either that carbonium ions are also implicated in the reactions proceeding with nucleophilic assistance in the rate-determining step[10,11] or that, in the presence of silver-ion assistance, a synchronous S_N2' reaction becomes more important than previously indicated[33] for similar anionic substitutions in its absence. Consistent with attack upon a carbonium ion intermediate (presumably within an ion triplet) is the observation by Bordwell and Mecca[34] of an enormous retardation of nucleophilic attack, even by powerful nucleophiles, when a γ hydrogen of α-methylallyl chloride (**1**) is replaced by an electron-withdrawing arylsulfonyl group. Such a substitution would hinder the ionization favorable to carbonium ion mechanisms but should increase the susceptibility of the molecule to any synchronous S_N2' reaction.

A mechanism involving carbonium ion containing intermediates in a nucleophilically assisted reaction has previously been proposed for reactions of silver nitrate in acetonitrile with several primary and secondary alkyl halides[3,4] and with the unsubstituted allyl halides.[7] On the other hand, the reactions of methyl iodide with silver arenesulfonates in acetonitrile[35] have considerable bonding between the nucleophile and the methyl carbon in the transition state and it is believed that these reactions approximate to a classical S_N2Ag^+ reaction.

Methylallyl derivatives are compounds for which a mechanism involving rate-determining attack upon a preformed carbonium ion[10,11,36] (S_N2C^+ reaction[37]) could very well operate. The simplest scheme which can accommodate the observed kinetic orders, the rate ratios for reaction with silver nitrate and silver perchlorate, the relative rates of reaction of several allyl halides with silver nitrate, the relatively slow rate of allylic isomerization within "unreacted" methylallyl chloride, and the product spread for the α and γ isomers is shown in Scheme I (with the final stage always involving nucleophilic attack by nitrate ion).

Scheme I



One could imagine a simplified scheme with only one (symmetrical) ion-pair intermediate. Such a scheme would be capable of explaining the product spread within the nitrate ester products but, in order to have nitrate ion participation within the rate-determining step, return to allyl halide-silver ion complex would have to be relatively rapid. The scheme would then provide a facile route for allylic isomerization within unreacted methylallyl chloride and, since this rearrangement process is actually relatively slow, it is necessary to introduce a barrier to this isomerization; this is easiest accomplished by introducing the concept of initially formed unsymmetrical ion pairs which return to precursor or react with nitrate ion faster than they equilibrate. Sneen and Bradley[11,38] have previously proposed a scheme of this type for reactions of α,γ-dimethylallyl chloride on the basis of stereochemical studies with optically active substrate.

Experimental Section

Materials. Acetonitrile and silver perchlorate were purified as described previously.[6] Fractional distillation of α-methylallyl chloride (Aldrich) gave material of at least 96% purity (VPC), with γ-methylallyl chloride as the major impurity; repeated distillation through a short-path condenser raised the purity to 99%. One fractional distillation of β-methylallyl chloride (Matheson Coleman and Bell) gave material of 99.6% purity (VPC). Commercial samples of γ-methylallyl chloride were found after fractional distillation to be of at least 98% purity (VPC), with α-methylallyl chloride as the sole impurity; however, the material contained 70–80% trans and 20–30% cis isomer and the individual geometric isomers were synthesized as described below.

***trans*-γ-Methylallyl Chloride.** The *trans*-γ-methylallyl alcohol was prepared by reduction of crotonaldehyde using sodium borohydride in aqueous ethanol.[39] The crude product was converted to the chloride by treatment[40] with pyridine and phosphorus trichloride at 0 °C. The product mixture was distilled and the distillate washed with water and dilute Na_2CO_3 and dried over anhydrous $MgSO_4$. Analysis by VPC indicated about 18% α-methylallyl chloride. Repeated distillation through a short-path condenser gave material of 94% purity, contaminated with 4% of the cis-γ isomer and 2% of the α isomer. Preparative VPC gave a pure sample for spectral analysis: IR[40] includes 6.06, 8.04, 10.3 (trans-olefinic C–H), 13.5 μ; NMR δ 1.71 (d, 3, CH_3, J = 4.8 Hz), 4.01 (d, 2, CH_2, J = 5.2 Hz), 5.69 (m, 2, vinyl).

***cis*-γ-Methylallyl Chloride.** The *cis*-γ-methylallyl alcohol was prepared by semihydrogenation of 2-butyn-1-ol (Pfaltz and Bauer) using a 5% palladium on barium sulfate catalyst, poisoned toward double-bond reduction by addition of powdered sodium hydroxide.[41] The product was contaminated with less than 3% of the trans-γ isomer (VPC). Triphenylphosphine–carbon tetrachloride reagent[42] converted the alcohol to the cis-γ chloride. Final purification was by preparative VPC: IR[40] includes 6.03, 7.90, 12.9, 15.0 (cis-olefinic C–H) μ; NMR δ 1.67 (d, 3, CH_3, J = 5.0 Hz), 3.97 (d, 2, CH_2, J = 6.8 Hz), 5.51 (m, 2, vinyl).

β-Methylallyl Nitrate.[22] This compound was prepared by refluxing for 1 h β-methylallyl chloride with pulverized silver nitrate.[12] Purification was by preparative VPC: IR includes 6.08, 7.91, 11.7, 13.2 μ; NMR δ 1.80 (s, 3, CH_3), 4.87 (s, 2, CH_2), 5.10 (s, 2, vinyl).

α- and γ-Methylallyl Nitrates. A mixture was prepared either by the method of Patterson and Brown[43] or by the method of Young, Sharman, and Winstein.[12] The latter method gave from α-methylallyl chloride at room temperature a mixture of 41% α-methylallyl nitrate and 59% of a mixture of *cis*- and *trans*-γ-methylallyl nitrates, with the trans isomer predominating. Pure samples of α-methylallyl nitrate and *trans*-γ-methylallyl nitrate were obtained by preparative VPC.

The α-methylallyl nitrate includes in the IR spectrum peaks at 6.08, 7.93, 10.2, 11.3, 11.7, and 13.2 μ and the ^{1}H NMR spectrum consists of δ 1.43 (d, 3, CH_3, J = 6.2 Hz) and ca. 5.6 (complex, 4, CH plus vinyl protons). The *trans*-γ-methylallyl nitrate includes in the IR spectrum peaks at 6.00, 6.09, 7.90, 10.4 (trans-olefinic C–H), 11.7, and 13.2 μ and the ^{1}H NMR spectrum consists of δ 1.78 (d, 3, CH_3, J = 6.1 Hz), 4.87 (d, 2, CH_2, J = 6.0 Hz), and 5.8 (m, 2, vinyl).

Rearrangement Studies. Analysis was by VPC using a 20 ft × ¼ in. 15% TCEP on Chromosorb W column at 45–66 °C. The retention times for a typical experiment at 66 °C were 367 s for α-methylallyl chloride (**1**), 625 s for *trans*-γ-methylallyl chloride (**3b**), and 666 s for *cis*-γ-methylallyl chloride (**3a**).

Reaction, within sealed ampules at 45.1 °C, of 4 mL of an acetonitrile solution 0.300 M in **1**, **3a**, or **3b** and 0.200 M in silver nitrate was allowed to proceed for in excess of 10 half-lives and the "unreacted" allyl chloride was analyzed (Table I). Also, for **1** and **3b**, the extent of allylic rearrangement during reaction at 45.1 °C of a 0.200 M acetonitrile solution with 0.300 M silver nitrate was investigated. Sealed ampules containing 2 mL were removed at appropriate time intervals, quenched in dry ice–acetone slush, and partitioned between 2 mL of cold ether and 2 mL of cold aqueous 0.44 M sodium bromide (to remove silver ion), and the ether layer was then removed and analyzed by VPC at 45 °C. Simultaneous with the removal of ampules for VPC analysis, other samples were removed and analyzed for unprecipitated silver ion by potentiometric titration.

Product Studies. Analyses for the nitrate esters were carried out by VPC using a 5 ft × ¼ in. 15% Carbowax 20M on Chromosorb W column at 69 °C. Alternatively, for situations where the allyl chlorides were completely consumed, analysis was by NMR spectroscopy. The regions in which the methylene protons of γ-methylallyl nitrate give a doublet (intensity D) and the allylic proton of α-methylallyl nitrate plus the vinylic protons of both isomers give a multiplet (intensity M) are away from the strong interference caused by the methyl protons of the solvent. If x is the fraction of γ-methylallyl nitrate (*cis*- plus *trans*-), then

$$\frac{D}{M} = \frac{2x}{2x + 4(1 - x)} = \frac{x}{(2 - x)}$$

and from the integration the product ratios can be calculated.

A sample of α-methylallyl nitrate was used to prepare two solutions in acetonitrile, one 0.200 M in nitrate ester and the other 0.100 M in nitrate ester and 0.100 M in silver nitrate. After 72 h at 45.1 °C, VPC showed no evidence for rearrangement to γ-methylallyl nitrate (or other reaction).

The analysis by VPC (Table III) was after reaction for in excess of 10 half-lives in sealed ampules at 45.1 °C of 4 mL of a solution which was 0.300 M in **1**, **2**, **3a**, or **3b** and 0.200 M in silver nitrate. The resultant product ratios were found to remain unchanged over at least 80 half-lives.

The analysis by NMR (Table III) was after reaction in sealed ampules at 45.1 °C of 2 mL of a solution which was 0.400 M in silver nitrate and 0.300 M in **1**, **3a**, or **3b**. After in excess of 10 half-lives, the contents was filtered directly into a NMR tube and a drop of tetramethylsilane was added. The product ratio was shown to remain unchanged over at least 20 half-lives.

Kinetic Procedures. Potentiometric titration to determine the concentration of silver ion remaining in solution and titration of developed acid, in the presence of silver ion, were carried out as described previously.[4] All studies were made at 45.11 ± 0.06 °C. The integrated 2.5-order rate coefficients were calculated using the appropriate form of the integrated rate equation.[4,7]

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References and Notes

(1) (a) Abstracted, in part, from the Ph.D. Thesis of C.R.D., Northern Illinois University, Dec 1975. (b) Presented, in part, at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstract No. ORGN-193.

(2) F. G. Donnan and H. E. Potts, *J. Chem. Soc.*, **97**, 882 (1910).

(3) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960).

(4) Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4760 (1965).

(5) (a) Y. Pocker and W. H. Wong, *J. Am. Chem. Soc.*, **97**, 7097 (1975); (b) *ibid.*, **97**, 7105 (1975).

(6) D. N. Kevill and R. F. Suthoff, *J. Chem. Soc., Perkin Trans. 2*, 201 (1977).

(7) D. N. Kevill and L. Held, *J. Org. Chem.*, **38**, 4445 (1973).

(8) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(9) R. H. DeWolfe and W. G. Young in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, 1964, Chapter 10.

(10) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970).

(11) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).

(12) W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(13) P. S. Walton and M. Spiro, *J. Chem. Soc. B*, 42 (1969).

(14) D. N. Kevill and G. M. L. Lin, *Tetrahedron Lett.*, 949 (1978).

(15) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(16) D. N. Kevill, V. V. Likhite, and H. S. Posselt, *J. Chem. Soc., Perkin Trans. 2*, 911 (1975).

(17) C. Prevost and E. Melendez, *An. R. Soc. Esp. Fiz. Quím., Ser. B*, **57**, 51 (1961), have previously shown that colloidal silver chloride can cause relatively slow allylic chloride isomerizations; *Chem. Abstr.*, **55**, 25726*i* (1961).

(18) Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4771 (1965).

(19) D. N. Kevill and C. R. Degenhardt, *J. Chem. Soc., Chem. Commun.*, 662 (1974).

(20) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

(21) J. J. Ritter and P. Minieir, *J. Am. Chem. Soc.*, **70**, 4045 (1948).

(22) A. F. Ferris, K. W. McLean, I. G. Marks, and W. D. Emmons, *J. Am. Chem. Soc.*, **75**, 4078 (1953).

(23) C. Prevost and C. Georgoulis, *C. R. Acad. Sci.*, **248**, 3450 (1959).

(24) Reference 8, p 786.

(25) Reference 8, p 765.

(26) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(27) For further discussion of nucleophilic substitution reactions of allyl halides, see also P. B. D. de la Mare and C. A. Vernon in "Studies on Chemical Structure and Reactivity", J. H. Ridd, Ed., Methuen, London, 1966, Chapter 2.

(28) S. Oae and C. A. VanderWerf, *J. Am. Chem. Soc.*, **75**, 2724 (1953).

(29) J. D. Roberts, W. G. Young, and S. Winstein, *J. Am. Chem. Soc.*, **64**, 2157 (1942).

(30) D. N. Kevill and N. H. Cromwell, *J. Org. Chem.*, **29**, 499 (1964).

(31) For a discussion, see, for example, P. R. Wells, "Linear Free Energy Re-

lationships", Academic Press, New York, 1968, pp 59–68.
(32) Insofar as the reaction with silver perchlorate could involve nucleophilic participation in the rate-determining step, the percentages reported must be regarded as maximum values.
(33) (a) B. D. England and E. D. Hughes, *Nature (London)*, **168**, 1002 (1951); (b) B. D. England, *J. Chem. Soc.*, 1615 (1955).
(34) F. G. Bordwell and T. G. Mecca, *J. Am.Chem. Soc.*, **94**, 5829 (1972).
(35) D. N. Kevill and A. Wang, *J. Chem. Soc., Chem. Commun.*, 618 (1976).
(36) (a) F. G. Bordwell and G. A. Pagani, *J. Am. Chem. Soc.*, **97**, 118 (1975); (b) F. G. Bordwell and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 123 (1975); (c) *ibid.*, **97**, 127 (1975); (d) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *ibid.*, **97**, 132 (1975).
(37) The S_N2C^+ terminology for this type of reaction was introduced by E. Gelles, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2918 (1954). While they assumed rate-determining attack on free carbonium ions, we feel that the terminology can logically be applied to any situation where the rate-determining attack is upon a carbonium ion, even when it is within an ion pair or an ion triplet (as in silver ion assisted reactions) or associated with a neutral molecule (with an initially positively charged leaving group).
(38) R. A. Sneen and W. A. Bradley, *J. Am. Chem. Soc.*, **94**, 6975 (1972).
(39) M. R. Johnson and B. Rickborn, *J. Org. Chem.*, **35**, 1041 (1970).
(40) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950).
(41) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965, pp 69–71 and 152.
(42) E. I. Snyder, *J. Org. Chem.*, **37**, 1466 (1972).
(43) F. L. M. Patterson and G. M. Brown, *Can. J. Chem.*, **34**, 879 (1956).

High Pressure Nuclear Magnetic Resonance Kinetics. 3. Proton Nuclear Magnetic Resonance Study of the Effect of Temperature and Pressure on the Exchange of Acetonitrile on Nickel(II)

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Abstract: The effect of temperature and pressure (up to 200 MPa) on the solvent exchange of $[Ni(CH_3CN)_6](ClO_4)_2$ in acetonitrile has been studied utilizing ^1H FT NMR chemical shifts and T_2 measurements of both free and bound resonances at 60 MHz. It is found that, in order to obtain reliable values of ΔH^* and ΔS^*, the full Swift-Connick equation must be used, whereas for ΔV^* a simplified analysis may be adopted. Values of the exchange parameters are $k_{298.1} = 2840 \pm 50\ s^{-1}$, $\Delta H^* = +64.3 \pm 0.9$ kJ mol^{-1}, $\Delta S^* = +37.0 \pm 2.8$ J mol^{-1} K^{-1}, $\Delta V^*_{294\ K} = +9.6 \pm 0.4$ cm^3 mol^{-1}. They are in accord with a dissociative interchange mechanism I_d.

1. Introduction

Ever since the pioneering work of Eigen and Wilkins,[1] which showed that, for aqueous solutions, the rates and activation parameters for ligand substitution were closely similar to those of solvent exchange, the study of the latter process has assumed fundamental importance. The correlations have since been extended to nonaqueous solutions[2] and, although deficiencies in the theory have been discussed in terms of solvent structure,[3] a basic tenet of all such ideas is that the mechanism usually has a dissociative activation mode. Direct evidence as to this point is by no means easy to obtain since, in such studies, the solvent concentration cannot be varied at will. As discussed by Swaddle,[4] although there are severe theoretical limitations in regarding the entropy of activation as a measure of "the increase in randomness", comparisons of ΔS^* for closely related systems such as solvent exchange for different ions and/or solvents should give useful mechanistic information. The fast exchange of solvent bound to a transition ion with bulk solvent has been widely studied ever since the work of Swift and Connick[5] using NMR line broadening, i.e., T_2 (sometimes coupled with chemical shift and T_1) measurements, but it is disappointing to note that the precision and reproducibility of such results is considerably less than those obtained using classical techniques. Particularly disturbing is the fact, not infrequently mentioned, that the experimental data obtained by different researchers are often closely similar and yet the derived activation parameters are often so different.[6]

The pressure dependence of a reaction rate may be discussed in terms of transition-state theory through ΔV^*, the volume of activation. Stranks[7] has discussed how this parameter should also yield useful diagnostic information. For reactions involving no charge separation or neutralization going from reactants to the transition state and hence, when electrostriction changes should be negligible, ΔV^* can be directly related to the partial bond formation, rupture, or stretching during the activation process. In principle, the volume of activation defined as

$$\Delta V^* = -RT(\partial \ln k/\partial P)_T \qquad (1)$$

should be considerably less prone to error than ΔS^* since increasing rate with increasing pressure implies a negative ΔV^* and vice versa.

No such simple relation applies for ΔS^*, but it is readily shown that

$$\Delta S^*/R = \underbrace{\ln (k/T) - \ln (k_B/h)}_{-\Delta G^*/RT} \underbrace{-(1/T)\ \partial \ln (k/T)/\partial(1/T)}_{+\Delta H^*/RT} \qquad (2)$$

Errors in k produce only very small errors in ΔG^* owing to the logarithmic relationship. However, a reliable estimate of ΔH^* requires the knowledge of a differential term which is more difficult. This term is usually large and never changes sign. Furthermore, ΔS^*, a small term which may be of either sign, is obtained as the difference of two terms of similar magnitude and this accounts for the important error problem associated with ΔS^* determinations.

An alternative way of looking at the error problem on ΔS^* is to note that the first and last terms on the right-hand side of eq 2 represent the extrapolation of the tangent to the ln (k/T) vs. $1/T$ curve to $1/T = 0$. For "ideal" Eyring behavior, they simply represent the extrapolation of the straight line plot to

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