to the amount of olefin lost. The initial product distributions were obtained by extrapolating the product distribution to zero reaction time. The results of these studies are given in Table I.

Additions in methanol were conducted similarly to additions in acetic acid. The hydrogen chloride was bubbled into anhydrous methanol with cooling and the concentrations determined by titration with a standardized solution of sodium hydroxide. A few drops of 1,2-dimethylcyclohexene were added to the solutions of hydrogen chloride in methanol. Aliquots of the reaction solution were taken and added to a mixture of pentane–water. Separation and concentration of the organic layer followed by analysis on column A gave the percentages of TC and CC.

Reaction of 1,2-dimethylcyclohexene with hydrogen chloride in acetyl chloride was accomplished by saturating acetyl chloride with hydrogen chloride at room temperature. Portions of the saturated solution were removed, cooled to the indicated temperature, or diluted with additional acetyl chloride to the indicated concentration (Table III); a few drops of 1,2-dimethylcyclohexene were then added. Aliquots of the reaction solution were withdrawn and added cautiously to a mixture of ice-cold pentane–water with shaking. Extraction and concentration of the organic layer followed by analysis of glpc of the products gave the indicated percentages of TC. Additions in sulfolane were carried out in a similar manner.

Reactions in dichloromethane and pentane were carried out by bubbling hydrogen chloride through a solution of a few drops of 1,2-dimethylcyclohexene in pentane or dichloromethane at the indicated temperature. Although no rate measurements were attempted, the rate appeared to be slower at 25° than at 0° in pentane, and an increase in percentage of TC was noted at longer reaction times in dichloromethane. A solution of 73% CC and 27% TC in pentane at 0° was saturated with hydrogen chloride and allowed to stand for 2 hr; no detectable change in the product composition was observed.

Acknowledgments. We thank Mr. Wayne Borth for assistance with some of the experiments and Professors Charles Perrin and Daniel J. Pasto for helpful comments.

Substituent Effects on Silver–Olefin Complexation[1]

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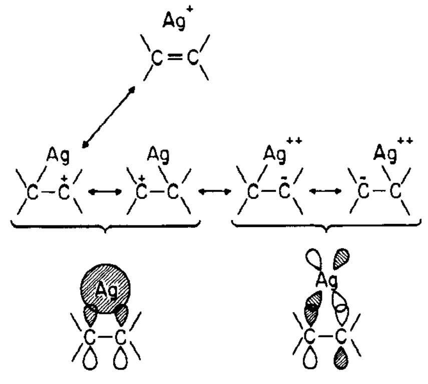
Abstract: The argentation constants in aqueous silver nitrate have been measured for several exo- and endo-substituted norbornenes as well as similarly substituted ethylenes. The constants are correlated by a modified Kirkwood–Westheimer cavity model. The validity of this model for argentation equilibria is discussed.

A classical technique for the study of reaction mechanisms is the determination of the effect of substituents. As the questions asked about transition states become finer it is essential that there be a parallel development in the precision of predictions of quantitative models of substituent effects. With this in mind, the stability of silver complexes of olefins holds promise of being a valuable addition to the physical organic chemists' arsenal of substituent-sensitive reactions because of the rapidity with which the complexes are formed and the ease of measurement.

Because of the well-known analogy of silver ion complexes to carbonium ions,[2] a study of substituent effects on complexation is particularly relevant to the broad area of carbonium ion chemistry. The argentation reaction, for example, might reveal (under easily controlled equilibrium conditions) the effect of structure on the solvation of charges embedded in a mixed hydrocarbon–aqueous environment analogous to that of a carbonium ion reaction.

A concern in studying substituent effects on argentation is the distribution of charge in the complex. The electronic structure of the complex has been described in terms of both resonance[2] and molecular orbital[3] symbolisms. These descriptions are summarized below (Chart I). The usual abbreviated resonance description has been augmented by the pair of right-hand structures in order to bring out the close parallel between the two descriptions.

Chart I



It can be seen that depending on the relative importance of the $2p\pi \rightarrow 5s$ charge transfer and $4d \rightarrow 2p\pi^*$ charge transfer (or equivalently the relative importance of the left-hand pair of resonance structures *vs.* the right-hand pair of structures) the argentation equilibrium might be either enhanced or diminished by electron-withdrawing substituents. Semiquantitative molecular orbital calculations based on a configuration interaction model suggest[4] that the charge-transfer contributions are both small and closely balanced so that the substituent effect should be largely determined by the uppermost structure (or its molecular orbital equivalent) in which the electron con-

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[1] Based in part on the Ph.D. Thesis of W. Gaal, Cornell University, Ithaca, N. Y., Sept 1968.

[2] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **60**, 836 (1938).

[3] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

[4] H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Jap.*, **37**, 249 (1964); T. Fueno, T. Okuyama, and J. Furukawa, *ibid.*, **39**, 2094 (1966). These articles describe quantitative treatments of silver complexation.

figuration is a singly charged silver ion adjacent to a neutral olefin.

Despite the long interest in olefin argentation, relatively little is known about the effect of substituents on the complex strength. Contrary to one's intuitive expectation, methyl substitution of olefins generally lowers the complex strength.[2,5] This was interpreted by Winstein and Lucas as an interference with the solvation of the cation rather than as a contribution of structures with negative charge on the olefin. The dominance of the solvation effect distorts the appearance of the underlying substituent effect. Fueno, Okuyama, Deguchi, and Furukawa have measured the argentation constants of a series of meta- and para-substituted styrenes.[6] These molecules present a constant immediate environment to the silver ion but they introduce the additional complication of resonance interaction between the substituent and the argentation center.

The present study is concerned with argentation constants in two aliphatic systems. The first is a set of exo and endo 5-substituted norbornenes. The second is a group of ω-substituted 1-alkenes. The substituent effects for these two groups have been determined and the results for the norbornenes are compared with the earlier styrene work and the results for the 1-alkenes. The applicability of an electrostatic field model for describing substituent effects in these systems is discussed.

Experimental Section

Preparation and Purification of Reagents. Carbon tetrachloride (Eastman Spectro Grade) and 2,2,4-trimethylpentane (Eastman Spectro Grade) were used without further purification. Standard silver nitrate and potassium nitrate solutions were prepared from analytical reagent grade salts and distilled water.

Allyl alcohol (Paragon Testing Laboratories) was dried over potassium carbonate and fractionally distilled through a 20-cm Vigreux column: bp 91–92° (745 mm); $n^{20}_{\rm D}$ 1.4133 [lit.[7] $n^{20}_{\rm D}$ 1.4135]; vpc analysis on a 5 ft $\times$ $^1/_8$ in. 5% FFAP on Chromosorb W column >99% peak purity.

3-Buten-1-ol (Chemical Procurement Laboratories) was dried over potassium carbonate and analysis on a 6 ft $\times$ $^1/_4$ in. sodium palmitate column showed only one peak. It was used without further treatment.

4-Penten-1-ol (City Chemical Co.) was dried over potassium carbonate and analysis on a 5 ft $\times$ $^1/_4$ in. 10% FFAP on Chromosorb W column showed only one peak. It was used without further treatment.

Crotonaldehyde (Eastman Chemical Co.) was fractionally distilled through a 20-cm Vigreux column and the fraction between 101.5 and 102.0 was collected. Gas-chromatographic analysis on a 10 ft $\times$ $^1/_4$ in. 20% FFAP on Chromosorb W column showed the aldehyde to have >98% peak purity.

Crotyl alcohol was prepared from the corresponding aldehyde with sodium borohydride in ethanol. The crude material was distilled through a 30-cm glass spiral column and further purified on a 5 ft $\times$ $^3/_8$ in. 5% FFAP on Chromosorb W column. Re-analysis on the same column showed it to have 97% peak purity. Its ir spectrum was superposable with that reported in the Sadtler Index (Spectrum 14583).

Norbornene (Enjay Chemical Co.) was purified by sublimation at 25° (5 mm) and collected in a Dry Ice–acetone trap. Gas chromatographic analysis on a 5 ft $\times$ $^1/_4$ in. 10% FFAP on Chromosorb W column showed one peak.

A mixture of *exo*- and *endo*-**5-norbornene-2-methanol** (Eastman Chemical Co.) was fractionally distilled through a 20-cm Vigreux column. Gas chromatography showed the distillate to be 80% endo and 20% exo. After three cycles through a 10 ft $\times$ $^3/_8$ in. 30% Carbowax 20M on Chromosorb P column the endo isomer was obtained in 98% peak purity and the exo isomer in 97% peak purity. The assignment of endo and exo was confirmed by comparison of the chemical shift for the endo 6-H with that reported in the literature.[8]

A mixture of *exo*- and *endo*-**5-norbornen-2-ol** (Aldrich Chemical Co.) was shown to be about 75% endo and 25% exo by analysis on a 20 ft $\times$ $^3/_8$ in. glass column packed with FFAP on Chromosorb P. This column was used to separate the isomers preparatively. After one cycle both had 98% peak purity.

1-Hexene (Aldrich Chemical Co.) was distilled through a 20-cm Vigreux column and the fraction (bp 63°) collected. Gas chromatography on a 15 ft $\times$ $^1/_{16}$ in. 2.5% FFAP on Chromosorb G column showed >98% peak purity.

2-Trimethylammoniomethyl-5-norbornene Nitrate. A sample of 5-norbornene-2-*N*,*N*-dimethylcarboxamide, prepared from commercial 5-norbornene-2-carboxylic acid by treatment of the acid chloride with dimethylamine, was provided by Mr. A. Zavadel. Using the method of Cope,[9] 9.3 g (0.062 mol) of the amide was reduced with lithium aluminum hydride in anhydrous ether. Without isolation the amine was methylated[10] with CH_3I in cyclohexane. The white solid formed was isolated by filtration and washed with cyclohexane to yield, after drying for 12 hr *in vacuo* at 55°, 9.5 g of product.

The iodide was converted to the hydroxide with silver oxide and an aqueous solution was neutralized to a pH of 6.3 with concentrated nitric acid. The crude solid remaining after all the solvent had been evaporated at 25° was light brown, but after several washings with anhydrous acetone, 5.6 g of a white crystalline material remained (dec 165–210°).

Anal. Calcd for $C_{11}H_{20}N_2O_3$: C, 57.87; H, 8.83; N, 12.27. Found: C, 58.03; H, 9.00; N, 12.00.

exo- and *endo*-**2-Methoxycarbonyl-5-norbornene.** The exo and endo isomers were prepared from the purified carboxylic acid by the Fisher esterification procedure. The nmr spectra were identical with those reported in the literature for both the exo and endo isomers.[6]

Methyl *endo*-**Spiro[cyclopentane-1,7′-[5]norbornene]-2′-carboxylate.** This was prepared by the procedure of Wilcox and Craig.[11]

endo-**Spiro[cyclopentane-1,7′-[5]norbornene]-2-methanol.** A hydride reduction[11,12] of the methyl *endo*-spiro[cyclopentane-1,7′-[5]norbornene]-2′-carboxylate, after distillation of the product through a 30-cm glass spiral column, gave 3.0 g (85%) of alcohol: bp 95–96° (0.3 mm); vpc analysis on a 15 ft $\times$ $^1/_{16}$ in. 2.5% FFAP Chromosorb G column showed >95% peak purity.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18; O, 8.97. Found: C, 80.96; H, 10.18; O, 9.09.

Spiro[cyclopentane-1,7′-[2,5]norbornadiene]. A sample of *endo*-spiro[cyclopentane-1,7′-[5′]norbornene]-2′-trimethylammonium iodide[13] (32 g, 0.096 mol) was stirred with a twofold excess of silver oxide in aqueous methanol for 4 hr at 25°. The aqueous methanol was removed to yield 36 g of a dark yellow oil which was pyrolyzed at 140–170° to yield, after distillation, 4 g (29%) of diene.

Potentiometric Measurements. The apparatus consisted of a concentration cell fitted with silver metal electrodes (Sargent No. 30515-c), connected by an agar ammonium nitrate bridge. The potential difference was measured by balancing the cell against the emf provided by a Leeds and Northrup millivolt potentiometer using a Keithley 600A electrometer as a null detector. The side of the cell in which the titrations were performed was stirred mechanically. All measurements were performed inside a grounded Faraday cage. The silver metal electrodes were treated before each run by dipping them into diluted aqueous nitric acid (1 + 1) and washing for several minutes with distilled water.[14] The olefin solutions were prepared at either 1 or 0.1 *M* ionic strength in aque-

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(5) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

(6) T. Fueno, *et al.*, *ibid.*, **87**, 170 (1965).

(7) R. C. Weast and S. M. Selby, Ed., "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p c-511.

(8) R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967); J. C. Davis, Jr., and T. V. van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

(9) A. C. Cope and E. Ceganek, *Org. Syn.*, **39**, 19 (1959).

(10) K. Alder and B. Dortmann, *Syn. Meth. Org. Chem.*, 11, 919 (1966).

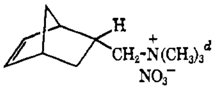
(11) C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

(12) A. C. Cope, *et al.*, *ibid.*, **81**, 2799 (1959).

(13) G. C. Whitney, III, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1966.

(14) E. Bishop and R. G. Dhaneshwar, *Analyst (London)*, **88**, 426 (1963).

Table I. Argentation Constants Determined Potentiometrically

Compound	$[Ag]_I$	$[O]_I$	K_1	Stand. dev	Lit. value
1. $CH_2{=}CHCH_2OH$	0.0331	0.0499	11.6	0.5	12,[a] 14,[b] 23[c]
2. $CH_2{=}CHCH_2CH_2OH$	0.0476	0.0581	23	2	
3. $CH_2{=}CHCH_2CH_2CH_2OH$	0.0031	0.0352	29.2	0.3	
4. $CH_3CH{=}CHCH_2OH$	0.0476	0.0570	5.6[b]	0.1	5.2[c]
5. $CH_3CH{=}CHCHO$	0.0467	0.585	2.1[b]	0.3	0.2[a]
6. 	0.0331	0.332	91,[e] 30[f]	3	

[a] 1.0 *M* ionic strength.[2] [b] 0.1 *M* ionic strength: R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **71**, 3906 (1949). [c] 2.0 *M* ionic strength. [d] 87% endo, 13% exo by nmr analyses; 0.13 *M* ionic strength. [e] Concentration constant. [f] Estimated thermodynamic constant; see Experimental Section.

ous potassium nitrate. The silver nitrate solution was brought to the same ionic strength with potassium nitrate. Strict temperature control was not maintained; all runs were performed between 25 and 28°. Because the ΔH for complex formation is small (*ca.* 7 kcal/mol)[2] this temperature variation introduces less than a 10% variation in *K* over this range.

The apparatus was checked by determining the emf's of a silver nitrate solution that was diluted successively with 1 *M* potassium nitrate to maintain constant ionic strengths. A plot of the observed change in potential for each dilution *vs.* the logarithm of the ratio of the final volume to the initial volume gave a straight line of slope, 59.4 V (σ = 0.8), which compares favorably with the theoretical Nernst slope of 59.2 at 25°.

The equilibrium constant for reaction of hydrated silver ion with olefin, eq 1, can be written as in eq 2 where the activity of water is

$$(m-n)H_2O + Ag(H_2O)_n^+ + O_{aq} \longrightarrow AgO^+(H_2O)_m \quad (1)$$

$$K_1 = \frac{[AgO^+(H_2O)_m]_{aq}}{[Ag+(H_2O)_n]_{aq}[O_{aq}]}\,\frac{f_{complex}}{f_{Ag}f_O} \quad (2)$$

taken as a constant and the quantities in brackets are the concentrations of the indicated species, while the activity coefficients, *f*'s, are collected in a separate factor.

The equilibrium constants were determined by addition of small volumes of aqueous olefin solutions (1 *M* in potassium nitrate for the neutral olefins; 0.1 *M* for the quaternary ammonium salt) to the concentration cell containing initially uncomplexed silver nitrate. The complexation constant is then derived by comparing the observed emf change with that expected from dilution alone.

Specifically, the value of K_1, the equilibrium constant, can be evaluated by plotting $X - 1$ *vs.* Q where $[O]_i$ = initial olefin concentration in titrant, $[Ag]_i$ = initial silver concentration in cell, ΔE_T = emf change on titration, ΔE_D = emf change expected for similar dilution with 1 *M* KNO_3, $\log X = (\Delta E_T - \Delta E_D)/59.2$, and $Q = [O]_i - [Ag]_i\,[(X-1)/X]$. From the observation that the theoretical Nernst slope is obtained over the concentration range used in the complexation study, it can be concluded that the activity coefficient of the silver ion is essentially constant and that the ratio of silver ion activities measured is equal to the ratio of concentrations. The activity coefficient of the olefin in the aqueous phase (referred to the gas phase as an ideal noninteracting standard state) is far from unity, but those factors leading to the deviation are largely reproduced in the complex and the combined activity coefficient factor should be approximately unity. This hypothesis parallels the Hammett-Zucker hypothesis for proton acid-base interactions.[15] For the same reason the ratio of two constants should approximate the value that would be found in the hypothetical gas-phase argentation.

A probable exception to this hypothesis might be the quaternary ammonium salt since in this complex the effective charge determining the activity coefficient will be intermediate between two separated and independent 1+ charges and a united 2+ charge. From the calculations of Tanford and Kirkwood[16] it can be estimated that the activity coefficient ratio of the quaternary ammonium salt will be enhanced by an additional factor of about three. In other words, this complex is less dissociated by a factor of three than the hypothetical substituted norbornene with the same substituent effect but without the charge.

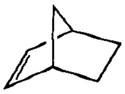
The equilibrium constants determined by this method are reported in Table I.

Distribution Experiments. The olefins were distributed between the organic solvent and 1 *M* potassium nitrate by shaking the solutions together in a constant temperature bath (25 ± 0.1°) for 1 hr. The two phases were separated in a separatory funnel. Each phase was centrifuged to ensure complete separation and then analyzed directly by glpc. When the concentration of olefin transferred to the aqueous phase was less than 10^{-2} *M*, an aliquot (5–15 ml) of the aqueous phase was extracted with 1 ml of fresh isooctane and the concentrated organic phase analyzed for olefin.

As a control on the completeness of the separations, dodecane was added to the organic phase of several representative olefin solutions. No trace of the dodecane could be detected in the aqueous phase after distribution either with or without the centrifugation step.

The distributions between the silver nitrate and organic solutions were done in exactly the same way. As the silver ion concentration was varied, the aqueous phase was maintained at constant 1 *M* ionic strength with potassium nitrate.

The glpc measurements were determined in triplicate and the distribution coefficients were determined for at least two different olefin concentrations; where trends were noted at least four different olefin concentrations were used. As a check on multicomplex formation, K_0's were determined at at least two different olefin and silver concentrations. Compounds **1**, **2**, **3**, **8**, and **9** were analyzed on a 5 ft × 1/8 in. 5% Carbowax 20M on Chromosorb W column. Compounds **4–7** were analyzed on a 15 ft × 1/16 in. 2.5% FFAP on Chromosorb G column.



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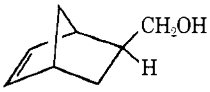

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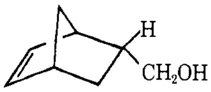

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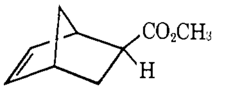

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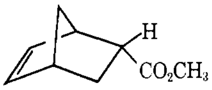

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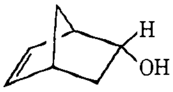

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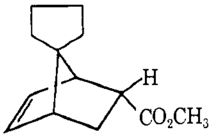

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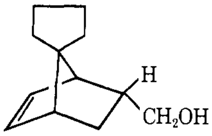

8

$CH_3(CH_2)_3CH{=}CH_2$

9

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(15) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 233 (1963).

(16) C. Tanford and J. G. Kirkwood, *J. Amer. Chem. Soc.*, 79, 5333 (1957).

The distribution method of Winstein and Lucas[2] was followed except that the concentrations of olefin were determined for both phases by glpc rather than for a single phase by bromine titration. The distribution coefficient of the olefin between the organic solvent and 1 M aqueous potassium nitrate is defined as eq 3. The heterogeneous equilibrium constant for the distribution of the olefin between the organic solvent and aqueous silver nitrate solution (brought to 1 M ionic strength) is defined as eq 4, where the concentration terms have their obvious meaning.

$$K_D = \frac{[O]_{org}}{[O]_{aq}} \qquad (3)$$

$$K_0 = \frac{[AgO^+]_{aq}}{[Ag^+]_{aq}[O]_{org}} \qquad (4)$$

With the assumption that the concentration of the olefin in the silver nitrate solution as uncomplexed olefin is $[O]_{aq}$ (uncomplexed) = $[O]_{org}/K_D$, and the further assumption that no 2:1 or 1:2 complex is formed, eq 5 follows.

$$K_0 = \frac{[O]_{aq}(\text{total}) - [O]_{org}/K_D}{\{[Ag]_{init} + [O]_{org}/K_D + [O]_{org} - [O]_{init\ org}[O]_{org}\}} \qquad (5)$$

The glpc analyses were carried out on either an Aerograph 200 or a Hi-Fi III (Varian Aerograph) instrument. The use of isooctane solvent for the organic rather than the traditional CCl_4 was dictated by the tendency of CCl_4 to corrode the flame ionization detector and thereby give erratic results. The relative responses of the different olefins were determined and appropriate corrections applied.

The equilibrium constant, K_1, for complexation of aqueous olefin is given as $K_1 = K_0K_D$. Table II summarizes the values of K_0, K_1, and K_D obtained in the distribution experiments.

Table II. Argentation Constants Determined by Distribution Method

Compd	K_D	Stand. dev	K_0	Stand. dev	K_1	Stand. dev.
1	1,730		0.52[a]		900	
2	1.68[b,c]	0.01	150	26	253	29
3	1.00[b,c]	0.05	330	40	330	44
4	266	21	1.30	0.13	346	44
5	76[c]		*d*		193	18
6	0.343	0.018[c]			*Ca.* 333	
7	*c*				3.6	0.5
8	*c*		*d*		15	5
9[e]	8,000		0.0092		74	

[a] Value determined independently = 0.51. [b] Limiting value as $[O]_{org}$ approaches zero. [c] Values with change in $[O]_{org}$. [d] Slight variation with changes in $[O]_{org}$ and [Ag]. [e] Based on one determination (CCl_4).

For several of the compounds studied a variation in the value of K_D for different olefin concentrations was observed. In these cases a plot of K_D *vs.* the equilibrium olefin concentration gave a good straight line. From these plots the appropriate K_D can be obtained for a given equilibrium concentration of olefin. The evaluate K_1, the K_D at a given olefin concentration, was multiplied by the K_0 at the same equilibrium olefin concentration. Table III summarizes these data.

Table III. Variations in K_D (Isooctane–Water) with Changes in Olefin Concentration

Compd	Slope	Intercept
2	19.2	1.68
3	17.2	1.00
5	94	76
7	2,600	3,800
8	1,188	48

For the *exo*- and *endo*-5-norbornene-2-methanol compounds the limiting value of K_D as $[O]_{org}$ approached zero was used because the K_0's for these substances were so large that the olefin equilibrium concentrations were of the order of 10^{-4} M. Analysis of *endo*-2-methoxycarbonyl-5-norbornene revealed slight trends in K_D and K_0. When the appropriate K_0's and K_D's were multiplied, a constant value of K_1 resulted. For the corresponding exo isomer K_0 and K_D both were constant within experimental error.

Methyl *endo*-spiro[cyclopentane-1,7′-[5]norbornene-2-carboxylate (**7**) showed trends in K_0 and K_D which were quite pronounced; however, K_1 was again a constant. *endo*-Spiro[cyclopentane-1,7′-[5]norbornene]-2′-methanol (**8**) also showed trends in K_0 and K_D, but when the appropriate constants were multiplied a constant K_1 was not obtained. An attempt to resolve this difficulty in terms of a hydrogen-bonded monomer–polymer equilibrium in the organic phase[17] did not improve the agreement.

Using the proper analytical expression[2] for dissection of the data into 1:1 and 1:2 complex stability constants also did not produce a good fit. It was concluded that the available data were not precise enough to quantitatively account for the trend in K_1. The recorded value is an average over the range of experiments.

When K_D for *endo*-norbornen-2-ol was determined at three different olefin concentrations, K_D was a constant. However, K_0 did show a trend, which indicated AgO_2^+ formation. Applying the proper analytical expression,[2] $K_{exp}[1 - K_1K_2'[O]_{uncomplexed}] = K_1 + 2K_1 \cdot K_2'[O]_{uncomplexed}$, to the data produced a parabolic curve instead of the expected straight line. Although the result may be explained by AgO_n^+ formation, quantitative dissection of the data was not accomplished. As an estimate of the stability constant for 1:1 complexation, the intercept of the limiting slope was taken.

Results and Discussion

The conventional method for measuring argentation constants by distribution of the olefin between an organic phase and an aqueous solution of silver nitrate is not suitable for water-soluble, hydrocarbon-insoluble charge olefins. For these a potentiometric technique involving a homgeneous aqueous phase was developed (see Experimental Section). This potentiometric method is also useful for highly water-soluble olefins like allyl alcohol, since these compounds in the distribution method have very small partition coefficients leading to large concentrations of uncomplexed olefin in the aqueous phase. The constant evaluated by the distribution method would in these cases be derived from the small difference between two large numbers. A further difficulty is that the amount of olefin remaining in the organic phase after the equilibration is consequently quite small and difficult to determine. An example of the first problem is provided by crotonaldehyde. As Winstein[2] has pointed out, the concentration of uncomplexed crotonaldehyde is almost equal to the total concentration in the aqueous phase and from his results he could not be certain that the olefin was complexing at all. An example of the latter problem, drawn from the present work, is provided by the *exo*- and *endo*-5-norbornene-2-methanol, where essentially all of the olefin was removed from the organic phase in a distribution experiment.

The equilibrium constants determined by the potentiometric method are collected in Table I. Where literature values are available for comparison they are included. It can be seen that in all cases, with the exception of crotonaldehyde, the agreement is good. For the reason already cited the literature value for crotonaldehyde is not to be given too much weight. Further, as will appear later in a comparison of the K's of the first five olefins in Table I, the higher K_1

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[17] A. Ens and F. E. Murray, *Can. J. Chem.*, 35, 170 (1957).

for crotonaldehyde reported here is consistent with the other olefin constants.

The heterogeneous stability constant, K_0, has been used for comparing silver ion complexation of olefins (see the Experimental Section for definitions of the different equilibrium constants).[18,19] Although this practice is acceptable for olefins with similar water solubility, in general it presents a distorted measure of the complexing ability. For example, from Table II the K_0 for norbornene is 0.52 and for *exo*-5-norbornene-2-methanol the K_0 is 150. The alcohol has a 300 times larger K_0 mostly because of the extra lowering of the free energy that occurs on transferring the $-CH_2OH$ group from a hydrocarbon environment to an essentially aqueous one. An approximate correction for this environmental effect is to multiply the K_0 by K_D to obtain the homogeneous K_1. This correction is, of course, unnecessary in the potentiometric evaluation of K_1. When the K_0's for this pair of olefins are corrected, the corresponding K_1's are found to be 900 and 253 (see Table II), which correctly reflects the poorer complexing ability of the alcohol with its electron-withdrawing $-CH_2OH$ group.

The value for K_1 found in a distribution experiment might not have been precisely equal to K_1 determined by the potentiometric method because the former refers to complexation with aqueous silver nitrate *saturated* with organic solvent. Reference to the common entries of Tables I and II reveals that this difference is apparently smaller than the experimental errors of the measurements. It was found in early control experiments that use of aqueous solutions saturated with CCl_4 did not change the potentiometric results derived from a totally aqueous solvent. The combination of this control experiment and the good agreement of the common data in Tables I and II indicates that it is valid to compare the K_1's of different workers without regard to the organic solvent employed as long as the solvent has a low water solubility. A further example is work of Menon and Pincock[20] who found a value of 0.39 ($\sigma = 0.04$) for norbornene using pentane as solvent compared to values of 0.52 and 0.51.

A priori it is possible for norbornene to form silver complexes with the cation on either the exo or the endo face of the double bond. In order to compare the relative K_1's of the endo-substituted olefins with norbornene it is important to know the fraction of the norbornene complex with an endo silver ion. It is presumed that in the absence of a compelling electronic interaction the bulk of an endo substituent would exclude endo argentation. Even in the absence of endo substituents it is well known that norbornene is attacked preferentially from the exo side by electrophilic reagents.[20-22]

An indication that endo argentation is a minor process is obtained by comparing the two exo derivatives in Table II with the corresponding endo isomers. Were the complex largely endo the two endo compounds would have particularly small K_1's and the exo/endo ratios would be very large. Further evidence is obtained by comparing the endo-substituted olefins containing a 7-spirocyclopentane group with the corresponding olefins containing only hydrogen atoms at the 7 position. Space-filling models show that a 7-spirocyclopentane group seriously inhibits complexation on the exo side of the double bond. As Table I shows, introduction of the 7-spiro group reduces the K_1's by factors of 20 and 50. Since some small residual complexation from the exo side might be envisioned it can be concluded that endo argentation is less than 2–5%. The exo-substituted olefins bearing a 7-spiro group unfortunately could not be isolated in sufficient quantity for measurement; however, the combined weight of analogy and direct measurement suggests strongly that endo argentation is a minor process for all of the olefins except possibly those with a bulky 7-spiro group.

Recent semiquantitative measurements by Brown and Kawakami[23] support this conclusion. These workers found that the glpc retention time of norbornene increased by a factor of about five in going from an ethylene glycol column to one prepared from a solution of silver nitrate in ethylene glycol. In contrast they found that within their experimental error the ratio of retention times of 7,7-dimethylnorbornene on the same pair of columns was the same as the ratio for 7,7-dimethylnorbornane. If an uncertainty in retention time of 0.1 min is assumed, these measurements indicate that exo argentation is preferred over endo argentation by a factor of at least 100. In the calculations that follow exo argentation is assumed.

Substituent effects on the ionization of carboxylic acids can be calculated with fair precision using the Kirkwood–Westheimer cavity model.[24] The model is an electrostatic one in which the effective dielectric constant of the medium is calculated from (1) the size of the (assumed) spherical cavity containing the substituent, the reaction site, and the connecting framework, (2) the dielectric constant of the material in the cavity, and (3) the bulk dielectric constant of the medium external to the cavity. The dielectric constant of the material in the inner cavity is generally taken as 2.0, a value typical of hydrocarbon-like materials. The only remaining parameters are the radius of the spherical cavity and the locations of substituent and reaction site within the cavity. Although the use of realistic values for these parameters generally leads to reasonable values for the substituent effects, the parameters can be treated as unknowns and adjusted to give the best fit. Tanford has examined much pK data for amines and carboxylic acids and developed a prescription that yields physically plausible parameters that fit the entire range of data.[25] Despite this and many other successes with the Tanford parameterization,[26] it remains essentially empirical and there is no *a priori* reason to expect the prescription to be

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(18) J. G. Traynham and M. F. Sehnert, *J. Amer. Chem. Soc.*, **78**, 4024 (1956).

(19) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(20) B. C. Menon and R. E. Pincock, *Can. J. Chem.*, **47**, 3327 (1969).

(21) For a related example see: A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607, 2614 (1968); H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **89**, 1525 (1967).

(22) With radical reagents exo attack is preferred also. See C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968), for leading references.

(23) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).

(24) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); J. G. Kirkwood and F. H. Westheimer, *ibid.*, **6**, 506, 513 (1938); F. H. Westheimer, W. A. Jones, and R. A. Lad, *ibid.*, 10, 478 (1942).

(25) C. Tanford, *J. Amer. Chem. Soc.*, **79**, 5348 (1957).

(26) Two representative applications are: C. F. Wilcox, Jr., and J. S. McIntyre, *J. Org. Chem.*, 30, 777 (1965); F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967).

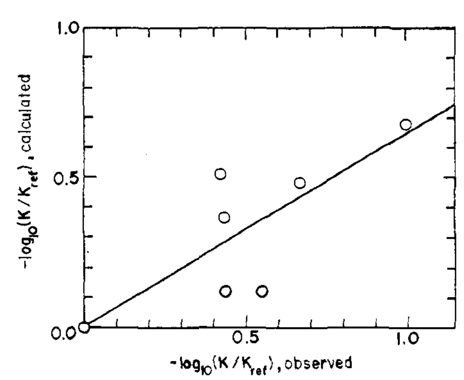

Figure 1. Comparison of observed substituent effects with those calculated by the conventional Kirkwood–Westheimer–Tanford cavity model.

transferable to the calculation of other types of ionization processes without modification.

In the analysis of our argentation data the expected substituent effect was not calculated directly, but instead was equated to the substituent effect observed in the corresponding 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids multiplied by the ratio of the theoretical effects calculated for the acid dissociation and the argentation equilibria. This procedure was followed because it tends to compensate for errors inherent in the use of a point dipole approximation for substituents as well as for variations in the effective depth of the group below the cavity surface. Such a procedure has been applied to closely related pairs of substituted acids[27] and gave calculated ratios almost within the error of measurement.

The ratio procedure does not take into account possible alteration in the parameterization that should accompany the change from proton ionization to argentation equilibria. However, the distances between the substituent dipoles and the proton of the bicyclo[2.2.2]octanecarboxylic acids are similar to the corresponding distances in the silver complexes and it would be expected that substituent effects calculated for the complexes using the Tanford proton ionization parameters, even if inappropriate, should be approximately correct. Any systematic deviation would be a guide for designing new parameters appropriate to argentation equilibria.

A possible complication is the difference in rotational constraints in the two series. In the bicyclo[2.2.2]octanecarboxylic acids the bond from the skeleton to substituent is nearly coaxial with the vector pointing toward the ionizing proton, whereas in the argentated olefins varying angles are found between this bond and the vector to the silver atom. The ambiguity in geometry is complicated further by the differences in solvation of the different conformers. The equilibrium mixture of conformations, each with a different combination of substituent and solvent dipoles, need not be the same in the presence and absence of the bound silver atom. While all of the substituents studied in the present work might be affected to some extent, the three worst potential offenders are the *exo*- and *endo*-methylol compounds and the quaternary ammonium ion since each of these groups has one skeleton–methylene bond. Actually the quaternary ammonium ion should present no complications because, as models show clearly, the bulk of the three methyls holds this side chain in an extended position in both the olefin and the complex.

In Table IV are recorded the log (K/K_0) observed for the substituted olefins and the values calculated on the basis of free rotation of the substituent.[28] The one exception is the trimethylammonium derivative for which the preferred extended form was used (see above). The calculated value for this ion includes the estimated activity coefficient correction described in the Experimental Section. These data are shown graphically in Figure 1 with the size of the circles representing the estimated uncertainty in the *observed* values.

Table IV. Observed and Calculated Argentation Constants

	$-\log(K/K_{\mathrm{ref}})$		
Compd	Obsd	Calcd[a]	Calcd[b]
1	[0.0]	[0.0]	[0.0]
3	0.44	0.12	0.14
2	0.55	0.12	0.15
6	0.43	0.37	0.44
5	0.67	0.48	0.58
4	0.42	0.52	0.63
Quaternary salt	1.00	0.69	1.05

[a] Using Tanford parameters appropriate to proton ionization. [b] Using modified parameters developed in text.

The line drawn in Figure 1 is the least-squares fit to an equation of the form $\log(K/K_{\mathrm{ref}}) = m\sigma_{\mathrm{calcd}}$ where σ_{calcd} is the calculated substituent effect. By definition the line passes through the origin. The value of m obtained is 0.65 ($\sigma_{\mathrm{slope}} = 0.12$).[29]

It is obvious from Figure 1 that the correlation is only marginally satisfactory. However, the two worst offenders, the methylol points, deviate in the direction anticipated by the discussion above. For example, the methylol points would be brought very close to the regression line if it were assumed that these substituents occupied three equal energy conformations in the hydrocarbon but only two in the complex. The restriction on accessible conformations would introduce a negative contribution to the calculated value of log (K/K_{ref}) of $-\log(^3/_2)$. Such restriction of accessible conformations is unlikely to show up in the more rigid systems commonly used to establish substituent effects. The strongest conclusion to be drawn is that the effect is possible and deserves to be explored further in other ways.

An alternative explanation of the deviations of the methylol points would be to appeal to some form of model error. An obvious possibility is charge transfer from the olefin to the silver ion. Explicit calculations using the Kirkwood cavity model did not yield an improved fit. The essential difficulty remains the large observed substituent effects for the methylol points compared to much smaller calculated effects.

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(27) C. F. Wilcox, Jr., and C. Leung, *J. Amer. Chem. Soc.*, **90**, 336 (1968).

(28) These calculated values represent the interaction at a single average angle and distance. Representative calculations of the average of the several interactions for different conformations gave essentially the same results. The vastly simpler procedure of averaging the angles and distances before calculating the interaction was followed here.

(29) If the methylol points are excluded the remaining four points yield a better looking line (slope = 0.77) but the standard deviation is not improved significantly because of the reduced number of points.

The value of 0.65 derived above for m is the ratio between the calculated and observed substituent effects. It differs from unity, in part, because of the inappropriateness of transferring the Tanford parameterization, developed for proton dissociation, to silver cation dissociation. By trial and error it is found that, if the Tanford depths, d, are replaced by 1.5 Å for charges and 2.0 Å for dipoles, m becomes 1.0 with $\sigma_m = 0.13$. The 0.5-Å increase is consistent with the larger ionic radius of a silver cation.[30] The increased depths constitute a new cavity model, one designed specifically for treating silver-olefin complexation. It should be employed cautiously, however, because of the limited data set that went into its construction. In this calculation it was assumed that the formal 1+ charge of silver was localized on the silver cation.

The argentation constants of substituted styrenes in water measured by Fueno and coworkers were well correlated by a Hammett $\rho\sigma$ equation which yielded a $\rho = -0.766$. The substituent effects were interpreted qualitatively[6] and quantitatively[31] in terms of the variation in π density at the vinyl site induced by the substituent. It is noteworthy that application of the new cavity model described above leads to a calculated ρ of -1.1. Given that the styrene complexes are probably a blend of electrostatic (polarization) and resonance (charge transfer) effects the agreement is satisfactory and demonstrates once again that a major contribution to a substituent effect can be accounted for in terms of a simple electrostatic cavity model.

It is revealing to consider the argentation data for the substituted 1-alkenes. These constants, recorded in Table I, when plotted as a function of the appropriate σ^* values based on ethylene as the reference structure give a good fit with $\rho = -0.93$. A point for acrylaldehyde was included in the correlation by multiplying our measured value for crotonaldehyde by 2.0, the measured argentation ratio between 2-propen-1-ol and 2-buten-1-ol.[32] The conformational flexibility of the substituents of the 1-alkenes represents a formidable problem for cavity model calculations and they have not been attempted. However, the value of the modified cavity model can be seen by the good (surely fortuitous in part) agreement between the calculated log (K/K_0) of -1.75 for 1-hexene and allylammonium perchlorate compared to the observed value of -1.8.[33] If the allylammonium perchlorate constant is used to define the regression line for the argentation of the substituted 1-alkenes, then the flexible substituents tend to show larger than expected substituent effects just as with the bicyclic olefins.

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[30] E. A. Moelwyn-Hughes, "Physical Chemistry," 2nd revised ed, Pergamon Press, Elmsford, N. Y., 1961, p 875.

[31] T. Fueno, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **39**, 2094 (1966).

[32] The correction factor was obtained from our measurements on allyl alcohol and crotyl alcohol and is consistent with other measurements[5] of the effect of methyl groups on argentation equilibria.

[33] F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. A*, 335 (1967).

Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. III. The Synthesis and Degenerate Thermal Valence Isomerization of Pentacyclo[$3.3.2.0^{2,4}.0^{3,7}.0^{6,8}$]dec-9-ene[1]

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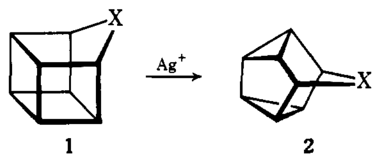
Abstract: Exposure of *cis*-dimethyl pentacyclo[$4.4.0.0^{2,5}.0^{3,10}.0^{4,7}$]decane-8,9-dicarboxylate (**7**) to silver fluoroborate in an inert solvent results in skeletal isomerization *via* a ${}_{\sigma}2_a + {}_{\sigma}2_a$ electrocyclic mechanism to give the isomeric ester **8**. Hydrolysis of **8** and electrolytic decarboxylation afford pentacyclo[$3.3.2.0^{2,4}.0^{3,7}.0^{6,8}$]dec-9-ene (**3**). When the hydrolysis is performed in NaOD–D_2O and the deuterium labeled diacid is decarboxylated in analogous fashion, dideuteriohydrocarbon (**9**) is obtained. Gas phase pyrolysis of **9** in the 500° temperature range is seen to result in a highly specific degenerate rearrangement which effectively scrambles uniquely the vinyl and remote cyclopropyl protons. Mechanistic schemes are presented to account for this unprecedented behavior. At slightly higher temperatures, **3** gives rise to *cis*-9,10-dihydronaphthalene (**10**), together with further transformation products of this latter hydrocarbon. Interestingly, **9** affords **10** in which the deuterium label is completely scrambled. Mechanisms which accommodate the observed isotopic distribution are discussed.

Recently, the unprecedented [${}_{\sigma}2_a + {}_{\sigma}2_a$] electrocyclic skeletal isomerization of homocubyl[3] and 1,1′-bishomocubyl systems[3,4] to pentacyclic derivatives of general structure **2** under unusually mild conditions (Ag^+, ambient temperature) was reported. Significantly, such metal ion catalyzed molecular rear-



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[1] For paper II of this series, note L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

[2] National Institutes of Health Postdoctoral Fellow, 1969–1970.

[3] L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

[4] W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970).