ICl_2). More surprising is the fact that a stable dichloride of iodomethyl 2-keto-10-camphyl sulfone could not be prepared. There is some spectrophotometric evidence that the dichloride has a transitory existence in solution, but it decomposes rapidly to liberate iodine monochloride and iodine. It is suggested that this dichloride may be unusually susceptible to decomposition because the carbonyl oxygen can serve (eq. 8) as a participating substituent in a process similar to that represented by eq. 3.

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Determination of Equilibrium Constants of Silver–Olefin Complexes Using Gas Chromatography

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Equilibrium constants for the formation of complexes of silver nitrate with compounds containing carbon–carbon unsaturation have been determined by a simple, rapid technique involving gas chromatography. The results indicate the strong influence of strain and steric effects on the values of these constants.

The weak interaction between silver ions and certain organic molecules containing carbon–carbon unsaturation was first quantitatively studied by Winstein and Lucas[1] in 1938. The complexes formed with these compounds and silver ion are generally quite unstable and studies on the equilibrium constants of these reactions have generally been carried out by measuring the partitioning of the olefin between an aqueous silver nitrate phase and carbon tetrachloride. This past work has been done principally by three groups: Lucas dealt chiefly with studies of aliphatic monoölefins[1,2] and some alkynes,[3] while Keefer and Andrews have been concerned with aromatic compounds,[4] and lately Traynham has investigated alicyclic olefins.[5]

This paper describes a new technique for the measurement of the equilibrium constants for the silver complex reaction that is more rapid and simpler to carry out than the older methods. This technique makes use of the relationship between the complexing equilibrium constants and retention times observed for olefins using silver nitrate–ethylene glycol gas chromatographic columns. By use of this method, new equilibrium data for the complexing reaction with silver nitrate in ethylene glycol have been obtained for a large number of aliphatic and alicyclic olefins as well as some alkynes and aromatic compounds. The equilibrium constants are found to be strongly affected by olefin structure and these variations are discussed in terms of steric, strain and electronic effects.

Development of Method

Varying retention times for different materials on a gas chromatography column are a reflection of the different partition coefficients for each material between the stationary liquid and the mobile vapor phase. The partition coefficient, H, is defined

$$H = \frac{\text{concn. of sample in liquid phase}}{\text{concn. of sample in carrier gas}}$$

This coefficient is obtained from measurable quantities by the equation[6]

$$H = \frac{3/2\left[\frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1}\right]F_c t_r}{V_L}$$

where

p_1 = absolute inlet pressure
p_0 = absolute outlet pressure
F_c = flow rate, corrected for temperature
V_L = volume occupied by liquid phase
t_r = time between air peak and sample peak

Evidence that this partition coefficient can be related to equilibrium processes has been given by Porter, Deal and Stross.[7] Furthermore, the obtainment of symmetrical peaks indicated that initial concentrations on the column were sufficiently low so that operation was near ideal.[7]

Next, consider what occurs when an olefin passes through a gas chromatographic column. For a column containing only a pure substrate, the following equilibrium is set up

$$(U)_V \rightleftarrows (U_L);\quad K_L = (U)_L/(U)_V = H$$

where

$(U)_L$ = concn. of olefin in liquid phase
$(U)_V$ = concn. of olefin in vapor phase
K_L = equilibrium constant for pure liquid substrate

Now if the stationary liquid phase contains a solute (*i.e.*, a metal salt), two effects are possible. One is a salting-out effect due to a reduction of solubility in the liquid phase of any substance in the vapor phase. When all other factors are

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(1) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(2) (a) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943); (b) H. J. Lucas, F. W. Billmeyer and D. Pressman, *ibid.*, **65**, 230 (1943): (c) F. R. Hepner, K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1333 (1952): (d) K. N. Trueblood and H. J. Lucas, *ibid.*, **74**, 1338 (1952).

(3) (a) W. S. Dorsey and H. J. Lucas, *ibid.*, **78**, 1665 (1956): (b) G. K. Helmkamp, F. L. Carter and H. J. Lucas, *ibid.*, **79**, 1306 (1957); (c) A. E. Comyns and H. J. Lucas, *ibid.*, **79**, 4341 (1957).

(4) (a) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 3113 (1950); (c) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950); (d) R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 640 (1952); (e) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 2210 (1956).

(5) (a) J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956); (b) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

(6) H. W. Johnson and F. H. Stross, *Anal. Chem.*, **30**, 1586 (1958).

(7) P. E. Porter, C. H. Deal and F. H. Stross, *J. Am. Chem. Soc.*, **78**, 2999 (1956).

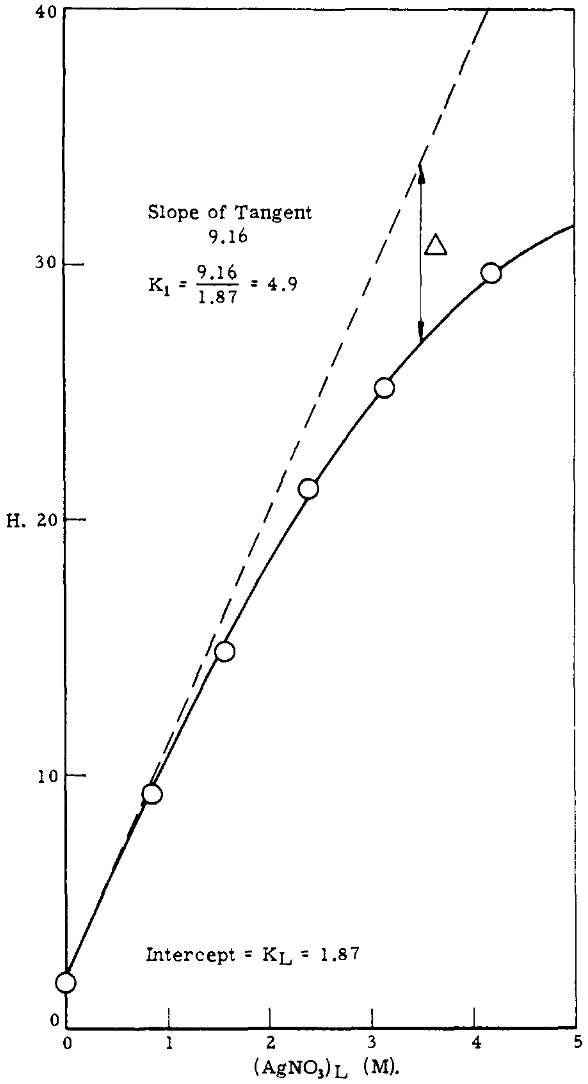

Fig. 1.—Variation of H with $(AgNO_3)_L$ for 1-pentene.

equal, an inert solute will cause retention times to be less. The other possible effect occurs when there is an interaction between the solute and material in the vapor phase (as is the case with silver nitrate solutions and olefins). This effect would tend to increase retention times for those compounds that interact.

With a solute like silver nitrate we then have the occurrence of two opposing effects on the retention times of olefins, and in order to determine equilibrium constants for the silver ion–olefin reaction, which is only a function of the second effect, the two must be resolved.

First let us consider the effect of silver nitrate and neglect the salting-out effect. The reaction between olefins and silver nitrate can be expressed as

$$(U)_L + (AgNO_3)_L = (U \cdot AgNO_3)_L$$

There is also a possibility of further reaction with silver nitrate to form the 1:2 complex, but this reaction goes to a much lesser extent than the formation of the 1:1 complex and generally only the latter shall be considered in this work.

The equilibrium constant for the above reaction in the solvent, L, (in this case ethylene glycol) is

$$K_1 = \frac{(U \cdot AgNO_3)_L}{(U)_L\,(AgNO_3)_L}$$

and the total amount of olefin present in the liquid phase is

$$\text{total olefin} = (U)_L + (U \cdot AgNO_3)_L$$

From this an expression can be set up for the partition coefficient, H, for a silver nitrate column

$$H = \frac{(\text{total olefin in liquid phase})}{(\text{total olefin in vapor phase})}$$

$$H = \frac{(U)_L + (U \cdot AgNO_3)_L}{(U)_L}$$

This can be rewritten as

$$H = \frac{(U)_L}{(U)_V} + \frac{(U \cdot AgNO_3)_L}{(U)_L(AgNO_3)_L} \times \frac{(U)_L}{(U)_V} \times (AgNO_3)_L$$

or

$$H = K_L + K_1K_L(AgNO_3)_L$$

In order to obtain valid equilibrium constants using this expression, a fast reaction between silver nitrate and olefin must be assumed. Although no quantitative date on the rate of the reaction has been reported, qualitative observation and comparisons with other π-complex reactions indicate the assumption is a valid one. Good complexers like 1,5-hexadiene and *trans*-cyclooöctene dissolve immediately on mixing with solutions of silver nitrate, and reactions of olefins with tetracyanoethylene and iodine have been reported to be essentially instantaneous.[8–10a]

This last expression indicates that if there were no salting-out effect a plot of H *vs.* silver nitrate concentration would give a straight line with a slope of K_1K_L and an intercept of K_L.

In practice a smooth curve is obtained with monoölefins which has a slope that decreases with increasing silver nitrate concentration. A typical curve obtained in this work is shown in Fig. 1. This decrease in slope is due to the effect of salting-out on H. As the salt concentration increases, the concentration of $(U)_L$ decreases and the value of H decreases from what it would be if there were no salting-out effect. At low concentrations of silver nitrate, the salting-out effect is small compared to the effect due to complexing and as $(AgNO_3)_L \rightarrow 0$, the situation developed above, which neglected salting-out, is approached. Therefore at $(AgNO_3)_L = 0$, the slope of the H *vs.* $(AgNO_3)_L$ plot is equal to K_1K_L and the intercept is equal to K_L. The difference (Δ) between this tangential line and the observed curve is due to the salting-out effect which is some function of the silver nitrate concentration.

In regard to the relationship between the salting-out effect and silver nitrate concentration, it was

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(9) B. C. McKusick and G. F. Biehn, *Chem. Eng. News*, **38**, No. 15, 114 (1960).

(10) D. Long and R. Neuzil, *Anal. Chem.*, **27**, 1110 (1955).

(10a) A recent note [E. Gil-Av and J. Herling, *J. Phys. Chem.*, **66**, 1208 (1962)] presents data on argentation stability constants which were obtained by a somewhat similar gas chromatographic technique. With the ten olefins studied in common we are in essential agreement, allowing for temperature differences. Furthermore, these authors have observed agreement in stability constants obtained by the gas chromatographic technique and the conventional distribution technique first used by Winstein and Lucas.[1]

empirically observed that a plot of log Δ *vs.* log $(AgNO_3)_L$ gave a straight line which can be expressed as

$$\log \Delta = \log S + n \log (AgNO_3)_L$$

where S is the intercept and n is the slope of the plot. This can be rewritten

$$\Delta = S(AgNO_3)_L{}^n$$

and the semi-empirical expression for the observed value of H is then

$$H = K_L + K_1K_L(AgNO_3)_L - S(AgNO_3)_L{}^n$$

The above is the expression used for the determination of the majority of the equilibrium constants observed. However, for some compounds with relatively high equilibrium constants, retention times on the gas chromatographic columns generally used were extremely long and an alternative procedure was used. This involved the use of a single dilute silver nitrate–ethylene glycol column, and a comparison of olefin behavior on it with that on a corresponding ethylene glycol column. Here the salting-out effect is neglected (it is insignificant at the low concentration of silver nitrate used, 0.32 M). The two points observed are then used to establish the straight line which is defined by the equation

$$H = K_L + K_1K_L(AgNO_3)_L, \text{ or}$$

$$K_1 = (H - K_L)/K_L(0.32)$$

for the particular silver nitrate concentration used.

Experimental

Equipment.—A Beckman GC-2 gas chromatography apparatus was used. This instrument had a modified inlet system so that the sample was injected directly into the end of the column. The pressure gauge was modified so that it measured the inlet pressure to the column.

Preparation of Columns.—The desired amount of finely pulverized silver nitrate was dissolved in ethylene glycol at 40°. Solutions were diluted to the mark at 40° and their density was also measured at this temperature. Mixtures containing 40% w. of solution and 60% w. of C-22 firebrick (60–80 mesh) were agitated on a shaker for 24 hours to obtain homogeneity. A weighed amount of packing was placed into a 6-foot stainless steel column with a 0.25″ o.d. Columns required 21–26 g. of packing. In addition to a column containing only ethylene glycol, five columns were prepared containing silver nitrate–ethylene glycol solutions of the following molarities: 0.85, 1.59, 2.38, 3.13 and 4.18. The packing for the columns used in the simplified technique with good complexers consisted of 40% w. of a 0.32 M solution of silver nitrate in ethylene glycol on 60% w. of C-22 firebrick (60–80 mesh). Two columns were prepared in 0.25″ o.d. stainless steel tubing, one of 6 feet and the other 1 foot. The column containing only ethylene glycol was 6 feet in length and was packed with a mixture of 22% ethylene glycol on C-22 firebrick. Columns were kept sealed when not being used and exhibited no change in behavior with time. They were used only at 40°.

Operating Conditions.—Columns were operated at 40° with a helium flow of about 75 ml./min. The thermal conductivity detector was used at a current of 250 ma. Liquid sample sizes were in the 0.5-μl. region and gas samples were about 40 μl. No appreciable change in retention times was observed for small variations in sample sizes. The samples gave symmetrical peaks and the time elapsed between the maxima of the air and sample peaks was taken as the retention time. Column inlet pressure, atmospheric pressure and room temperature were also observed.

Observations for Calculation of K_1.—Values of retention times (and hence H) for the series of olefins were observed both on a pure ethylene glycol column and on the silver nitrate–ethylene glycol columns described previously. From the variation of H with silver nitrate concentration, K_1 can be calculated as described above.

Sources of Olefins.—Where available, API research samples or Phillips Petroleum Co. pure grade materials were used. Samples obtained from other commercial sources were checked for purity by gas chromatography and structures were consistent with observed infrared spectra.

The olefins that were synthesized for this study were prepared as follows:

α,ω-Dienes were prepared from the corresponding α,ω-diols which were available commercially. The diols were converted to the diacetates in greater than 90% yield by reaction with either acetic anhydride or acetyl chloride.[11,12] The diacetates were cracked to the α,ω-diolefins using the technique described by Bailey.[11] The diacetates were introduced to a vertical Vycor tube (15 × 2 cm.) filled with Pyrex helices at a rate of 5 ml./hr. The tube was held at a temperature of 525–550° and cracking was done under an atmosphere of nitrogen. The product was collected in a cooled container at the exit of the cracking tube. The oily product was washed thoroughly with water, dried and distilled. Yields of the pure diolefins varied from 50 to 75%: 1,6-heptadiene, b.p. 89–90°; 1,7-octadiene, b.p. 119–121°; 1,8-nonadiene, b.p. 143–144°; 1,9-decadiene, b.p. 168–169°. Infrared spectra and G.L.C. analysis indicated greater than 95% purity for each of the products.

Cyclopentadiene was freshly prepared by cracking of dicyclopentadiene.

1,3,5-Hexatriene was prepared from 1,5-hexadiene as starting material according to the method of Hwa, de Benneville and Sims.[13] The infrared spectrum and G.L.C. analysis of the product indicated that it was composed of 71% of the *trans* isomer and 29% of the *cis*.

Methylenecyclopentane was prepared from 1-cyclopentylacetonitrile in two steps according to the method of Arnold, Amidon and Dodson.[14] The infrared spectrum of the final product indicated it was principally methylenecyclopentane, but contained some 1-methylcyclopentene as impurity. G.L.C. indicated that the product was 81% methylenecyclopentane and 19% 1-methylcyclopentene.

Cycloöctadienes were prepared from cycloöctatetraene by reduction with sodium and alcohol.[15,16] The product was found to contain four components by G.L.C. on a 20-foot triethylene glycol column at 60°. The infrared spectra revealed the identity of each fraction: (a) *cis*-cycloöctene, 9%; (b) 1,3-cycloöctadiene, 7%; (c) 1,4-cycloöctadiene 43%; (d) 1,5-cycloöctadiene, 41%. The emergence times for the fractions identified as *cis*-cycloöctene and 1,5-cycloöctadiene agreed with those obtained from authentic samples. This mixture was used for the equilibrium studies of 1,3- and 1,4-cycloöctadiene.

***trans*-Cycloöctene** was prepared in several steps from cyclooctanone which was converted to the oxime which was reduced to cycloöctylamine using sodium in ethanol.[17] The amine was methylated with formaldehyde[18] and this was converted to the trimethylammonium iodide by reaction with methyl iodide.[19] The iodide was converted to the hydroxide which was thermally decomposed.[20] Analyses based on the infrared spectrum indicated the product contained 60% *trans*- and 40% *cis*-cycloöctene. The *trans* isomer could be isolated by extraction with aqueous silver nitrate.[20]

2-Methylenenorbornane was supplied by Dr. W. W. Spooncer of these laboratories. The acetate of 2-methanolbicyclo[2.2.1]heptane[21] was cracked to give a product with properties identical to those described by Diels and Alder.[22]

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[22] O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

TABLE I

VALUES OF K_1 AND K_L FOR COMPOUNDS STUDIED (40°)

Compound	K_1[a]	K_L[b]	Calcd.[c]	Compound	K_1	K_L	Calcd
Ethylene	22.3	0.1	a	1,3-Butadiene	4.2	2.2	a
Propene	9.1	0.4	a	1,4-Pentadiene	10.2	2.9	a
1-Butene	7.7	0.9	a	1,5-Hexadiene	28.8	5.1	b
1-Pentene	4.9	1.9	a	1,6-Heptadiene	14.7	9.9	b
1-Hexene	4.3	3.5	a	1,7-Octadiene	11.3	19.4	b
1-Heptene	3.2	7.3	a	1,8-Nonadiene	10.4	36.5	b
1-Octene	2.6	13.1	a	1,9-Decadiene	7.8	76.3	b
3-Methyl-1-butene	5.1	1.5	a	*trans*-1,3-Pentadiene	3.5	5.1	a
3,3-Dimethyl-1-butene	3.6	2.2	a	*cis*-1,3-Pentadiene	4.4	6.1	a
3-Methyl-1-pentene	3.4	2.8	a	Isoprene	3.1	4.4	a
3-Ethyl-1-pentene	1.4	5.2	a	2,3-Dimethyl-1,3-butadiene	1.9	8.8	b
4-Methyl-1-pentene	2.8	2.7	a	2,4-Dimethyl-1,3-pentadiene	1.6	12.8	b
3-Methyl-1-hexene	2.7	5.3	a	2,5-Dimethyl-2,4-hexadiene	0.8	47.3	b
4-Methyl-1-hexene	2.3	6.0	a	2-Methyl-1,5-hexadiene	22.1	10.2	b
5-Methyl-1-hexene	3.1	5.9	a	2,5-Dimethyl-1,5-hexadiene	13.3	19.4	b
				trans-1,3,5-Hexatriene	5.1	19.4	b
cis-2-Butene	5.4	1.1	a	*cis*-1,3,5-Hexatriene	4.7	22.7	b
cis-2-Pentene	4.3	2.3	a	Methylenecyclobutane	5.8	5.3	a
cis-2-Hexene	3.1	4.3	a	Cyclopentene	7.3	5.8	a
cis-2-Heptene	2.6	8.1	a	1-Methylcyclopentene	1.9	8.9	a
cis-2-Octene	2.2	14.6	a	1-Methylcyclopentene	2.1	9.0	b
cis-3-Hexene	3.9	4.1	a	Methylenecyclopentane	4.0	10.2	a
cis-3-Heptene	2.7	7.6	a	1-Ethylcyclopentene	2.3	16.0	b
cis-4-Methyl-2-pentene	3.1	2.8	a	Ethylidenecyclopentane	0.7	21.8	a
cis-4,4-Dimethyl-2-pentene	2.7	5.3	a	Allylcyclopentane	3.9	24.9	b
cis-2,2-Dimethyl-3-hexene	2.5	8.9	a	Cyclopentadiene	4.6	10.7	b
				Cyclohexene	3.6	14.7	a
trans-2-Butene	1.4	1.0	a	1-Methylcyclohexene	0.5	21.3	a
trans-2-Pentene	1.1	2.3	a	3-Methylcyclohexene	3.5	16.5	a
trans-2-Hexene	0.8	4.0	a	4-Methylcyclohexene	3.8	14.2	a
trans-2-Heptene	.6	7.6	a	Methylenecyclohexane	6.0	18.7	b
trans-2-Octene	.4	14.6	a	1-Ethylcyclohexene	0.5	35.9	a
trans-3-Hexene	1.0	4.1	a	Ethylidenecyclohexane	1.6	39.6	a
trans-3-Heptene	0.6	7.6	a	Vinylcyclohexane	5.9	27.1	b
trans-4-Octene	.5	13.4	a	4,4-Dimethyl-1-cyclohexene	1.4	21.2	b
trans-4-Methyl-2-pentene	.7	3.4	a	Allylcyclohexane	3.2	46.7	b
trans-2-Methyl-3-hexene	.6	5.5	a	1,3-Cyclohexadiene	8.9	22.9	b
trans-4,4-Dimethyl-2-pentene	.4	4.4	a	1,4-Cyclohexadiene	4.9	33.2	b
trans-2,2-Dimethyl-3-hexene	.3	7.9	a	1-Methyl-1,4-cyclohexadiene	3.3	52.4	b
trans-2,5-Dimethyl-3-hexene	.2	6.5	a	4-Vinyl-1-cyclohexene	11.2	45.5	b
				Dipentene	5.9	126.	b
2-Methyl-1-propene	3.9	0.9	a	α-Phellandrene	5.1	108.	b
2-Methyl-1-butene	3.0	2.3	a	Cycloheptene	12.8	27.0	a
2-Methyl-1-pentene	2.1	3.7	a	Cycloheptene	12.7	27.0	b
2,3-Dimethyl-1-butene	2.4	3.2	a	Cycloheptatriene	7.6	89.2	b
2,3,3-Trimethyl-1-butene	1.8	5.4	a	*cis*-Cycloöctene	14.4	56.1	b
2-Ethyl-1-butene	3.5	4.2	a	*trans*-Cycloöctene	>1000	56.1	b
2-Ethyl-1-hexene	2.1	12.7	a	1,3-Cycloöctadiene	3.2	78.7	b
				1,4-Cycloöctadiene	14.4	90.7	b
2-Methyl-2-butene	0.8	2.2	a	1,5-Cycloöctadiene	75	144	b
2-Methyl-2-pentene	.6	4.2	a	Cycloöctatetraene	91	211	b
cis-3-Methyl-2-pentene	.7	4.2	a	2-Norbornene	62	17.7	b
trans-3-Methyl-2-pentene	.7	4.4	a	2,5-Norbornadiene	33.7	27.8	b
2,3-Dimethyl-2-butene	.1	4.5	a	2-Methylenenorbornane	4.3	35.1	b
				Camphene	3.1	61.2	b
2-Hexyne	2.0	18.3	a	α-Pinene	1.1	47.4	b
3-Hexyne	2.6	15.2	a	β-Pinene	3.7	84.5	b
2-Heptyne	1.6	34.0	a	Benzene	0.1	47.8	a
3-Heptyne	2.1	25.1	a	Toluene	.1	78.9	a
2-Octyne	1.2	65.2	a	*o*-Xylene	.1	183	a
4-Octyne	1.5	43.8	a	*m*-Xylene	.1	128	a
Allene	0.8	1.6	a	*p*-Xylene	.1	127	a
Methylallene	0.8	3.5	a	Ethylbenzene	.1	123	a

[a] K_1 = equilibrium constant (l./mole) for formation of silver nitrate–olefin complex in ethylene glycol. [b] K_L = partition coefficient for olefin on pure ethylene glycol column. [c] *Code for calculations:* a, 5 columns of varying $AgNO_3$ concentration used; b, 1 dilute $AgNO_3$ column used.

Results and Discussion

The values of K_1 and K_L for the compounds studied are listed in Table I. The values of K_1 and K_L are estimated to be reproducible to ±0.1 or 5%, whichever is larger. In cases where the two methods of calculation were used on the same compound, agreement was good. For example, with cycloheptene the values of K_1 are 12.8 and 12.7 and with 1-methylcyclopentene they are 1.9 and 2.1.

The nature of the bonding in complexes of unsaturated compounds with silver (and other transition metals with nearly filled d-orbitals) has been pictured by Dewar[23] to involve a σ-bond formed by overlap of the filled π-orbital of the olefin with (in the case of silver) the free s-orbital, and a π-bond formed by overlap of the vacant antibonding π-orbitals of the olefin with filled d-orbitals of the silver. The bonding in the complex will be affected by the availability of electrons in the filled orbitals and the ease of overlap of these orbitals as is determined by steric factors. With this picture it is difficult to make predictions on how electronic effects at the double bond will influence complex formation. For example, increasing the electron density at the double bond should enhance formation of the σ-bond and weaken the π-bond, while a decrease in electron density should have just the opposite effect. Although both types of bonds are important in complex formation, their relative importance is not known and this makes the influence of electronic effects on complex formation difficult to observe.

On the other hand, the effects of steric hindrance and strain are more straightforward, and as can be seen in the ensuing discussion most of the effects observed can be rationalized using steric arguments. This does not imply that inductive effects do not also play an important role, but only indicates that these effects cannot be resolved while steric and strain effect are more apparent.

Influence of Alkyl Substituents.—In all of the olefinic classes of compounds studied (alkenes, dienes and cyclenes) it can be seen that increasing the number of substituents about the double bond system causes a reduction of K_1 for compounds within that class. This is illustrated for aliphatic monoölefins in Table II, and examples for the other classes of unsaturated compounds can be readily found in Table I. The data in Table II are in agreement with and extend the findings of Lucas.[1,2]

TABLE II

AVERAGE VALUES OF K_1 AS A PERCENTAGE OF THAT FOR α-OLEFINS

$RCH{=}CH_2$	100	$RCH{=}CHCH_3$ (*trans*	19
$RCH{=}CHCH_3$ (*cis*)	79	$RCH{=}C(CH_3)_2$	15
$R(CH_3)C{=}CH_2$	54	$(CH_3)_2C{=}C(CH_3)_2$	2

Another effect of substituents on the values of K_1 is seen with the homologous series of the various aliphatic olefins. The values of K_1 within any particular class decreases as the carbon number increases.

The introduction of a branched group on the alkyl chain of an olefin causes a reduction in the value of K_1. This decrease is greatest when the group is placed on the position beta to the double bond, and is somewhat less when the group is placed alpha to the double bond. When the substituent is placed further down the chain, the decrease is less than with α- or β-substituents. This is illustrated by examples given in Table III and holds generally for the various types of olefins studied.

TABLE III

VARIATION OF K_1 WITH METHYL SUBSTITUTION

	Compound	K_1
Reference	1-Hexene	4.3
α-Substitution	3-Methyl-1-hexene	2.7
β-Substitution	4-Methyl-1-hexene	2.3
γ-Substitution	5-Methyl-1-hexene	3.1
δ-Substitution	1-Heptene	3.2

With alkynes, substitution of an alkyl group on the carbon alpha to the triple bond has little effect on the value K_1. However, with both alkenes and alkynes the value of K_1 decreases as the number of substituents increases on the carbon beta to the unsaturated linkage. This can be seen from the lower values of K_1 for *cis*-2-hexene and 2-heptyne as compared to the corresponding 3-isomers.

In contrast to the alkenes and alkynes, substitution of methyl groups in the 3- or 4-position of cyclohexene has little effect on the values of K_1.

Another effect of substituents about the double bond on the values of K_1 is seen in the following series of olefins: $RCH{=}CH_2$, *cis*- or *trans*- $RCH{=}CHCH_3$, *cis*- or *trans* $RCH{=}CHC_2H_5$ and $R(CH_3)C{=}CH_2$. In each case as R varies in the order Me, Et, *i*Pr, *t*Bu, the value of K_1 decreases.

In the above series of olefins the decrease in K_1 parallels an increase in the bulkiness of the alkyl group added. However, this decrease in K_1 also parallels the increase in electron density at the double bond which would be expected in going from the methyl to the *t*-butyl group. Similarly the decrease in K_1 as the number of substituents about the double bond increases could be due to steric and/or inductive effects.

Effects that are most likely due to steric factors are the lowering of K_1 as the carbon number of a homologous series increases, and the introduction of a branched group in the molecule. Here, in most cases, the inductive effect of the various branched groups would be similar while the steric hindrance of the groups vary significantly. It can be seen with atomic models that a group placed on the carbon beta to the double bond will have a greater effect in blocking approach to the double bond than placing a similar group in the α-position. Groups further down the chain are too far removed from the reaction site to have any unique effect on K_1.

The difference between the effects of substituents on the α-carbon in alkenes and alkynes is also believed to be due to a spatial effect, since changes

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(23) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).

due to an inductive effect should be similar. The α-carbons of an alkyne are co-linear with the triply bonded carbons, and methyl groups substituted on them are held out of the region of the multiple bond where the silver ion complexes. With alkenes, the α-carbons are at an angle of about 120° with the doubly bonded carbons and here the substitution of a methyl group can cause more hindrance of the multiple bond.

The lack of effect of substituents away from the double bond in methylcyclohexenes is explained by the fact that the methyl groups in these positions would be in what is essentially an equatorial position and would not interfere with reactions at the double bond. In 4,4-dimethylcyclohexene, however, one methyl group has to be in what is essentially an axial position. A group in this position is above the "plane" of the ring and situated not far from the double bond. It then inhibits attack by silver ion on one side of the ring as is manifested by the marked lowering of K_1.

Variations between Compound Types.—A comparison of the values of K_1 of the alkynes with those for the corresponding alkenes shows that the alkyne values are intermediate between the values of the corresponding *cis*- and *trans*-olefins. It is not surprising to find K_1 values for alkynes less than for *cis*-olefins since the latter obtain added driving force for the reaction with silver ion due to relief of internal strain (see below) and such an effect would not play a role in reactions with alkynes. The higher values of K_1 for alkynes compared to those for the corresponding *trans*-olefins can be ascribed to the greater accessibility of the triple bond as compared to that of the double bond in the corresponding molecule. This follows the argument introduced earlier that carbons alpha to the triple bond are colinear with it and thus tend to make any further substituents more remote to the reaction site than would happen in the corresponding olefin.

While the presence of an extra pair of filled p-orbitals in alkynes appears to have little or no effect on the bonding with silver ion, such is apparently not the case with allenes. Allenes also contain two pairs of p-orbitals at right angles to each other, but they are distributed over three carbon atoms rather than being on the same two carbon atoms as with alkynes. In comparison with most olefins and alkynes, allenes are poor complexers with silver ion, as is seen in comparing the value of 0.8 for the K_1 of allene or methylallene with K_1 values of 9.1 and 7.7 for propylene and 1-butene. Steric factors should not play a role here and in some way these low values must be related to the arrangement of the p-orbitals (or the p-π-orbitals) in allenes.

Conjugated dienes are somewhat poorer complexers than the corresponding monoölefins as can be seen by comparing values of K_1 for 1,3-butadiene and the 1,3-pentadienes with those of 1-butene and 1-pentene. A similar effect can be noted in comparing the K_1-values of 1,3,5-hexatrienes and 1,5-hexadiene. The reaction of these conjugated dienes with one silver ion is believed to involve reaction at one particular double bond (not with the whole conjugated π-system) and the weakening of the bonding (compared to a mono-olefin) can be ascribed to delocalization. This effect of conjugation on K_1 is also observed with most of the alicyclic compounds studied. Cyclopentadiene, cycloheptatriene and 1,3-cycloöctadiene have lower values of K_1 than the respective corresponding mono-unsaturated cycloalkenes. While the effects of conjugation in five, seven and eight-membered rings fit the above generalization, an exception is 1,3-cyclohexadiene which has a much higher value of K_1 than cyclohexene.

Earlier published work with olefins and transition metals[24,25] indicated that stable chelate compounds could be prepared from dienes whose double bonds were separated by two methylene groups (*i.e.*, 1,5-cycloöctadiene, dicyclopentadiene, dipentene and 1,5-hexadiene.) In order to establish whether this particular diene structure was unique for stability of complexes, the argentation equilibrium constants were obtained for the homologous series of α,ω-dienes from C_4 through C_{10}. A plot of K_1 for these compounds *vs.* the number of methylene groups separating the double bonds is given in Fig. 2. This shows that while all the dienes are relatively good complexers, the 1,5-diene is far superior to all others studied. The 1,5-diene system appears to possess the optimum configuration for chelation and hence forms a strong complex with silver ion. The shorter systems can only form a chelate with difficulty (probably not at all with butadiene) and in the longer systems there is more freedom of motion of the chain and less likelihood of positioning the double bonds for chelation.

When the 1,5-diene system is held rigidly in a ring, such as 1,5-cycloöctadiene, the value of K_1 is extremely high (75). With the exception of cyclooctatetraene the value of K_1 for 1,5-cycloöctadiene is the highest observed in the current studies. This is a result of optimum positioning of the two double bonds and then using the ring structure to hold them firmly in place. Cycloöctatetraene has an even higher value of K_1 (91), but a portion of this may be due to an unresolved contribution from the reaction of a second silver ion with the alternate 1,5-diene system.[26] The contribution of this second reaction might be sufficiently large, even at 0.32 M $AgNO_3$ concentration, that it would contribute to the value of K_1.

Another compound that has its double bonds held in a good position for chelation is 2,5-norbornadiene which has a K_1 value of 34. This system is not as good as the rigid 1,5-diene system (*i.e.*, 1,5-cyclooctadiene) but it is still a good complexer. The methyl bridge puckers the six-membered ring which increases the chelation tendency as compared to that of the essentially planar 1,4-cyclohexadiene.

A comparison of the behavior of endocyclic olefins with aliphatic olefins is difficult since ring size has a strong effect on the value of K_1. The order of K_1 observed in this work is: *cis*-cycloöctene > cycloheptene > cyclopentene > cyclohexene.

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(24) J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 2496, 3413 (1957).

(25) J. Chatt and L. M. Venanzi, *ibid.*, 4735 (1957).

(26) A. Nakamura and N. Hagihara, *Bull. Soc. Chem. Japan*, **32** 880 (1959).

This differs markedly from the order reported by Traynham[5] ($C_5 > C_7 > C_6 > C_8$) and does not follow the trend of heats of hydrogenation ($C_6 > C_7 \geq C_5 > C_8$).[27]

The equilibrium constants obtained by Traynham differ in two respects from those obtained here: (1) equilibrium constants are for the reaction

$$(\text{Olefin})_{CCl_4} + (AgNO_3)_{H_2O} \rightleftarrows (\text{Olefin}\cdot AgNO_3)_{H_2O}$$

and such a constant is the product of the distribution constant for the olefin between the two solvents and the equilibrium constant for the argentation reaction in water; and (2) the values are for the reaction in water rather than in ethylene glycol. These differences may be the cause for the different orders observed for cyclic olefins.

Traynham has indicated that the formation constants for silver ion complexes of the cycloalkenes are in essentially the same order as the estimated relative strains in the olefins. The observed order for strain energy in cycloalkanes is $C_8 > C_5 > C_7 > C_6$,[28] and although the difference between C_8 and C_5 will be decreased, the order for cycloalkenes will remain the same. Thus, while the values observed by Traynham for the three lower members of this series fall in line with strain energy, the value for *cis*-cyclooöctene is at the wrong end of the series. The values of K_1 observed in this work fail to follow the above strain energy order in that K_1 for cycloheptene is much greater than that for cyclopentene while the strain energies of the two are similar. For these reasons it is felt that strain energy of the cycloalkenes is not the predominant factor in determining the argentation constant.

Heat of hydrogenation data for cycloalkenes parallels neither the argentation constant order obtained in this work nor that obtained by Traynham. While Gardner, Brandon and Nix[29] have found some correlation between heats of hydrogenation of olefins and their aqueous argentation equilibrium constants, attempts to extend the relationship to other olefins studied by Lucas (*i.e.*, *cis*- and *trans*-2-pentene and 1-hexene)[1,2a] do not succeed. There is evidence of some parallelism between hydrogenation and argentation—for example, the heats of hydrogenation and values of K_1 for the different olefin types fall in the same order. However, the nature of complex formation, with the type of bonding pictured and the involvement of the large silver ion, indicates that steric and electronic effects should be of much more importance here than in the hydrogenation reaction. Thus, while the complete explanation of the variation of K_1 with olefin structure is not at hand, it is felt that in all cases (and particularly with the cycloalkenes) a parallelism with the hydrogenation reaction is not to be expected.

Bridging also has an effect on the behavior of endocyclic olefins. α-Pinene, which contains an endocyclic double bond in a six-membered ring, has a value of K_1 considerably higher than that for 1-methylcyclohexene, particularly if we expect some hindrance from the bridging group. The bridge apparently constricts the six-membered ring so that the environment about the double bond approaches that of 1-methylcyclopentene. The better complexing power of five-membered rings has already been shown, and presumably α-pinene tends to behave in this manner.

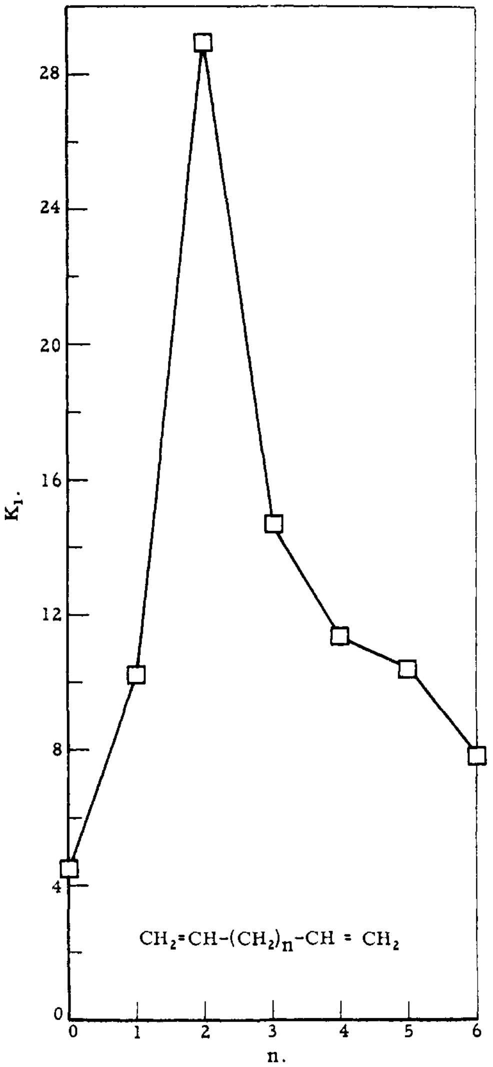

Fig. 2.—Variation of K_1 of α,ω-diolefins with chain length.

Results of studies on aromatics indicate very low values of K_1 for all compounds studied. This is in agreement with the findings of Ogimachi, Andrews and Keefer.[4] These workers have postulated that the silver ion coördinates preferentially above and between two adjacent unsubstituted ring carbons when such positions are available. Presumably, delocalization of the π-electrons from any particular two-carbon site is the reason for the relatively weak complexing power of aromatics.

Relief of Strain.—With disubstituted olefins of the type RCH=CHR the *cis* isomers always have a larger value of K_1 than the corresponding *trans*-isomers. This difference between *cis* and *trans* isomers can be explained on the same basis as is the difference in their heats of hydrogenation.[30]

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[27] R. B. Turner, W. R. Meador and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

[28] V. Prelog, *Bull. soc. chim. France*, 1433 (1960).

[29] P. D. Gardner, R. L. Brandon and N. J. Nix, *Chemistry & Industry* 1363 (1958)

[30] R. B. Turner, D. E. Nettleton and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

A major factor involved in the hydrogenation of alkenes is the relief of strain due to bond oppositions present in the *cis* isomers (*i.e.*, between the two rigidly held alkyl groups on the same side of the planar molecule), but not in the *trans* isomers. In the formation of silver–olefin complexes, it can be assumed that there is just sufficient twisting of the olefin p-orbitals to relieve partially the bond oppositions in the planar *cis*-alkenes by permitting a slight rotation about the double bond. The large spherical 5s-orbital of Ag(I) should be capable of accommodating this twisting.[29] Thus, the gain in energy in going from a strained *cis*-structure to a complex where strain is relieved is greater than the energy obtained in going from a non-strained *trans* structure to a complex having energy similar to that of a *cis* complex.

The formation of silver complexes with compounds containing exocyclic double bonds is strongly influenced by ring size. Methylene- and ethylidenecyclopentane have values of K_1 that are essentially the same as their aliphatic analogs (*i.e.*, isobutene and 2-methyl-2-butene), while the values for the corresponding six-membered compounds are appreciably higher.

The larger values of K_1 for the six-membered ring compounds with exocyclic double bonds as compared to those for the corresponding five-membered ring compounds is in agreement with the findings of Brown.[31] It was observed that reactions involving a six-membered ring with a trigonal carbon had a greater tendency to form a 4-coördinated center than the corresponding compound with a five-membered ring. This is due to the relief of bond oppositions in going from a six-membered ring with a trigonal carbon to one with all tetrahedral carbons. The former is more nearly planar and hence bond oppositions are greater. With the corresponding compounds with five-membered rings, the introduction of tetrahedral carbon for a trigonal carbon causes little change in the planarity of the molecule and hence little change in the bond opposition. Consequently no extra driving force is obtained. Thus one would expect the five-membered ring exocyclic olefins to behave like their aliphatic analogs while six-membered ring exocyclic olefins would show higher values of K_1.

Methylenecyclobutane, like methylenecyclohexane, exhibits an enhancement in the value of K_1 over that observed for their aliphatic analogs. Here the increase in the argentation equilibrium constant is ascribed to relief of Baeyer strain in the four-membered ring by the introduction of some sp^3-character to the carbons in the double bond.

2-Methylenenorbornane, with its bridged six-membered ring, has a value of K_1 very similar to that for methylenecyclopentene, rather than one similar to methylenecyclohexane. This is because the bridging methylene group causes this compound to maintain a rigid configuration, and there is little or no alleviation of bond opposition when the trigonal center tends toward the tetrahedral. Other bridged compounds such as camphene and β-pinene are seen to behave in a similar manner if some allowance is made for steric hindrance of the added methyl groups.

2-Norbornene has one of the highest values of K_1 observed in the present studies. In this mono-olefin, the high value of K_1 is ascribed to the large amounts of strain at the double bond. This has been supported by physical data such as an abnormally large heat of hydrogenation[27] and the position of the C=C and C—H stretching bands in the infrared spectrum which are comparable with those of cyclobutene.[32,33] Schleyer[34] has discussed the nature of this strain and has attributed it principally to the considerable amount of angle strain in the rigid bicyclic molecule. Apparently this angle strain is relieved to some extent by complex formation with silver ion. The best example of complex formation being related to relief of angle strain has been reported by Wiberg and Bartley.[35] They found that cyclopropene (a compound that possesses about the maximum in angle strain) was quantitatively removed from a mixture with nitrogen when it passed through an aqueous silver nitrate solution. They also found that cyclopropene is quantitatively removed from a mixture with nitrogen by an ammoniacal silver nitrate solution. From this they concluded that the cyclopropene–silver nitrate complex must have a formation constant of about 10^7. Complex formation may impart some sp^3-character to the double bond and angle strain could then be relieved by some lengthening of the double bond. Conceivably this is what occurs with cyclopropene and to a lesser extent with norbornene where the angle strain is less. The extra strain in cyclopropene has been estimated to be at least 9 kcal./mole and possibly considerably greater[35] while that for 2-norbornene is estimated to be about 5 kcal./mole (judging from the heats of hydrogenation of 2-norbornene and bicyclo[2,2,2]octene.[27]

Another example of the importance of strain in forming complexes with silver nitrate is the strong complex formed with *trans*-cycloöctene. The *trans* isomer has 9.3 kcal./mole of extra strain over that of *cis*-cycloöctene as judged by heat of hydrogenation data.[36] The strong complexing power of *trans*-cycloöctene allows its easy separation from the *cis* isomer by extraction with aqueous silver nitrate.[20] In the present work, *trans*-cycloöctene was never observed to emerge from any of the silver nitrate columns and based on the times its behavior was observed a value of $K_1 >$ 1000 is estimated. Here the relief of strain is presumably due to complex formation allowing some twisting of the double bond.

Once the importance that relief of strain has on the values of K_1 has been considered, the value of K_1 of 34 for 2,5-norbornadiene seems low. This molecule has strain similar to that of 2-norbornene, yet it has a K_1 value of about one-half of that of the latter. (Once again it must be noted that

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[31] H. C. Brown, J. H Brewster and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

[32] H. B. Henbest, G. C. Meakins, B. Nichols and R. A. L. Wilson, *J. Chem. Soc.*, 997 (1957).

[33] R. C. Lord and R. W. Walker *J Am. Chem. Soc.*, **76**, 2518 (1954).

[34] P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

[35] K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6374 (1960).

[36] R. B. Turner and W. R. Meador, *ibid.*, **79**, 4113 (1957).

Traynham's K_0 values for these compounds are 2,5-norbornadiene, 0.572, and 2-norbornene, 0.270.[5] The qualifications about comparing our values with his, that were discussed earlier, also apply here.) It appears, from our work, that 2,5-norbornadiene acts as a good chelater (with a fairly high K_1) and that in the formation of the complex there is little relief of strain. A picture of bonding of the chelated complexes has not been established with the definitiveness that has been done for monoölefins, and the bonding here may indeed be sufficiently different that no relief of strain in the double bond occurs.

Formation of Olefin·$(AgNO_3)_2$ Complex.—In the discussion on the development of this method, it was assumed that the formation of a 1:2 olefin–silver nitrate complex was generally negligible. This was borne out for monoölefins where the plot of H *vs.* $AgNO_3$ concentration has a decrease in slope with increasing $AgNO_3$ concentration (see Fig. 1). This same type of plot was also obtained with aromatics, alkynes and allenes which indicated that these compounds formed no appreciable amount of the 1:2 complex although they contained two or more pairs of free p-orbitals.

Although the values of K_1 for most of the diolefins studied were determined by the short one-column technique, those for four conjugated 1,3-diolefins (butadiene, isoprene, *cis*- and *trans*-1,3-pentadiene) and one non-conjugated diolefin (1,4-pentadiene) were determined by the long method involving observations on five silver nitrate columns. When H was plotted against silver nitrate concentration it was found that the slope increased with increasing silver nitrate concentration. This can be explained by assuming the presence of an appreciable reaction of these dienes with a second molecule of silver nitrate, presumably at the second double bond. This would lead to the following relationship between H and $(AgNO_3)$ for dienes

$$H = K_L + K_1K_L(AgNO_3) + K_1K_2K_L(AgNO_3)^2 - S(AgNO_3)^n$$

where K_2 is the equilibrium constant for the reaction with the second molecule of silver nitrate. Since the value of n for monoölefins has been observed to be about 2 and if we assume a similar salting-out effect for dienes, the slope of the H–$(AgNO_3)$ plot will increase if $K_1K_2K_E > S$. Since the value of S for 1-butene is 0.1 (and a similar value is expected for 1,3-butadiene since S is observed to be mainly a function of boiling point), and the value of K_1K_E for butadiene is about 10, the value of K_2 must be greater than 0.01. If the same salting-out constants are assumed for 1,3-butadiene as for 1-butene the value of K_2 for 1,3-butadiene calculates to be 0.05.

The presence of this second reaction does not interfere with the determination of K_1, since the value of $dH/d(AgNO_3)$ as $(AgNO_3)$ approaches zero for the above equation will still be equal to K_1K_L as with the first equation.

[CONTRIBUTION FROM THE EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

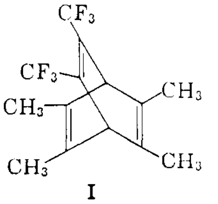
Organometallic Chemistry of the Transition Metals. I. Metal Complexes of a Bicyclo[2,2,2]octatriene Derivative

BY R. B. KING[1]

RECEIVED JULY 12, 1962

The reactions of the bicyclo[2,2,2]octatriene derivative (I), obtained from durene and hexafluorobutyne-2, with iron pentacarbonyl, cyclopentadienylcobalt dicarbonyl and molybdenum hexacarbonyl have been found to yield the complexes $C_{14}H_{14}F_6Fe(CO)_3$, $C_5H_5CoC_{14}H_{14}F_6$ and $C_{14}H_{14}F_6Mo(CO)_4$, respectively, analogous to known diene complexes of these metals. Proton and F^{19} n.m.r. data on the iron and cobalt complexes suggest the existence of isomers which involve different pairs of the three double bonds of the ligand I bonding to the metal atom.

Recently the hydrocarbon, bicyclo[2,2,2]octatriene (II)[2] ("barrelene") and certain of its substitution products such as I[3] have been reported. Since hydrocarbons with a similar arrangement of double bonds such as bicyclo[2,2,1]heptadiene (III) and 1,5-cycloöctadiene (IV) readily form diene complexes, it seemed possible that bicyclo[2,2,2]octatriene derivatives would form similar complexes utilizing two of their three double bonds in complex formation. It will be noted that there are three possible pairs of double bonds that bicyclo[2,2,2]octatriene derivatives can use in the formation of a diene complex. The existence of isomeric compounds differing only in the pair of double bonds bonded to the metal atom is therefore possible in the cases of sufficiently asymmetrical bicyclo[2,2,2]octatriene derivatives. It should be possible to distinguish such isomers



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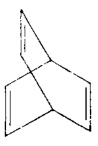

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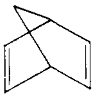
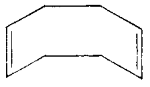


III



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(1) Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Penna.

(2) H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

(3) C. G. Krespan, B. C. McKusick and T. L. Cairns, *ibid.*, **82**, 1515 (1960); **83**, 3428 (1961).