carboxylic acid in acetone solution (Fig. 2) shows four peaks approximately in the weight 1:1:5:1, besides the strong absorption due to the solvent. The far right-hand peak is typical of a carboxyl group and the two small left-hand peaks are in about the correct positions for hydrogens located on a carbon carrying a chlorine and double bonds. The relative weights of the carboxyl and C–H peaks indicate that only one hydrogen is located on the carbon carrying the chlorine as at the 2-position of structure II. With III the C–H resonance absorption of the hydrogens at the 4-position would be expected to be twice the carboxyl absorption. It was expected from previous work,[3] if II is formed by ring-opening of I, that the hydrogen at the 2-position would come from the solvent. This has been shown to be the case by opening I to II in deuteroacetic acid. The reaction product showed only faint proton resonance absorption for the –CHCl– position (Fig. 2). Further decisive evidence that the carboxylic acid is not III was provided by its resolution into optically active forms through crystallization of the brucine salt. A sample of the acid with $[\alpha]^{23}\text{D}$ $-46.2°$ (*c* 4.06, acetone) was obtained having an infrared absorption spectrum identical with that given in Fig. 1.

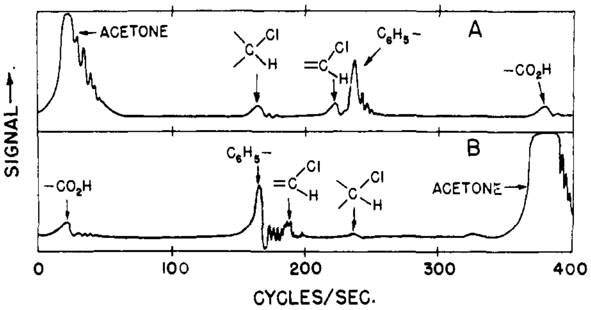

Fig. 2.—Nuclear magnetic resonance spectra of 5-mm. diameter samples at 40 mc. and 9040 gauss (12-sec. sweep) taken with Varian Associates Model V-4300 High Resolution Spectrometer: A, 50% solution of 2,4-dichloro-3-phenyl-3-butenoic acid in acetone solution, reverse sweep with higher magnetic field at the left; B, 50% solution of 2,4-dichloro-3-phenyl-3-butenoic-2-^{2}H acid in acetone, normal sweep with lower magnetic field at the left.

Experimental

2,4-Dichloro-3-phenyl-butenoic acid was prepared as described previously,[4] m.p. 111.8–113.0°.

2,4-Dichloro-3-phenyl-3-butenoic-2-^{2}H Acid.—A solution of 400 mg. of 2,4-dichloro-3-phenylcyclobutenone in 6.2 ml. of deuteroacetic acid (prepared by hydrolysis of acetic anhydride with deuterium oxide) was heated for 64 hours at 100°. One ml. of deuterium oxide was added and the mixture refluxed for an hour. An additional ml. of deuterium oxide was then added and the solvent removed in a stream of dry nitrogen at room temperature. The residue was crystallized from chloroform–hexane and yielded the deuterium-substituted acid with m.p. 111.8–113.2°. In the over-all purification process including the crystallization from chloroform containing the usual ordinary ethanol as a preservative, the carboxyl hydrogen underwent extensive exchange as shown by the *n-m-r* spectrum (Fig. 2).

Resolution of 2,4-Dichloro-3-phenyl-3-butenoic Acid.—The carboxylic acid (3.9 g.) and 6.7 g. of dry brucine were dissolved in 20 ml. of boiling, dry acetone. The resulting solution was kept in a refrigerator and after three days a considerable white precipitate separated. The mother liquor was decanted and the residual solid recrystallized from acetone. The resulting brucine salt was shaken with 100 ml. of ether and 100 ml. of 1.5 *M* hydrochloric acid. The ether layer was removed and washed successively with 75 ml. of 1.5 *M* hydrochloric acid, water and concentrated sodium chloride solution. The ether was then removed and the residual white solid recrystallized three times from chloroform–hexane. The final product had m.p. 113.0–114.0° and $[\alpha]^{23}\text{D}$ $-46.2°$ (*c* 4.06, acetone). Its infrared spectrum was indistinguishable from that of the optically inactive starting material (Fig. 1).

Anal. Calcd. $C_{10}H_8O_2Cl_2$: C, 51.97; H, 3.49. Found: C, 52.35; H, 3.63.

PASADENA 4, CALIFORNIA

[CONTRIBUTION FROM COATES LABORATORIES, LOUISIANA STATE UNIVERSITY]

Ring Size and Reactivity of Cyclic Olefins: Complexation with Aqueous Silver Ion[1,2]

BY JAMES G. TRAYNHAM AND MERLE F. SEHNERT[3]

RECEIVED FEBRUARY 27, 1956

Equilibrium constants for complex formation between aqueous silver ion and some cyclic olefins have been determined by a distribution method. The orders of equilibrium constants found were cyclopentene > cycloheptene > cyclohexene and bicycloheptene > bicyclooctene. For the monocyclic olefins, thermodynamic functions for the reactions have been evaluated. The inference is made that the relative reactivity of the olefin as an electron donor in π-complex formation is a function of ring strain: strain in a cyclic olefin facilitates complex formation.

Several recent investigations have provided correlations of ring size and reactivity among cycloalkane derivatives in displacement and carbonyl reactions.[4] Little systematic work with cyclic olefins has been described, however. Reported here are the results of an initial study of the effects of ring size on the reactivity of cyclic olefins.

Olefin complexes have been studied extensively,[5] but seldom have cyclic olefins been included. The complexes with aqueous silver ion are well known and have been studied quantitatively by Lucas and co-workers.[6] The equilibrium reaction for the formation in solution of the easily dissociable 1:1 complexes[6a] may be represented by equation 1

$$\text{olefin} + \text{Ag}^{\oplus} \rightleftarrows \text{complex}^{\oplus} \qquad (1)$$

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[1] Taken in part from the M.S. thesis submitted by M.F.S., January, 1956.

[2] Presented at the 11th Southwest Regional Meeting of the A.C.S., Houston, Texas, December 1, 1955.

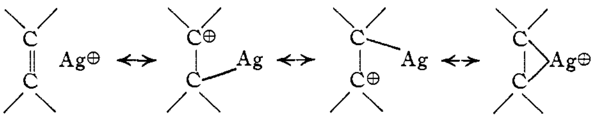
[3] Frederick Gardner Cottrell research assistant, 1954–1955.

[4] H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954), and references cited there.

[5] A recent review, with many leading references, is found in Chap. 8, by J. Chatt, and Chap. 9, by G. Salomon, "Cationic Polymerization and Related Complexes," P. H. Plesch, Ed., Academic Press, Inc., New York, N. Y., 1953.

[6] (a) S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938); (b) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).

The complex has been symbolized by various means. A resonance hybrid formulation has been used[6]



The complex has also been described[7] in terms of some double-bond character: donation of electrons from the occupied bonding π-orbital of the olefin to the unoccupied s-orbital of the $Ag^{\oplus}$ and donation from the occupied d-orbital of the $Ag^{\oplus}$ to the unoccupied antibonding π-orbital of the olefin. Since the complex is readily dissociated and no isomerization nor catalysis of hydration are observed,[6] little or no σ-bond character is to be attributed to the olefin–silver bond. It seems adequate, then, to regard the product of reaction as a π-complex in which only deformation of the π-orbital of the olefin is involved.

The relative availability of the π-electrons for complexation with an acceptor species (that is, the relative ease of deformation of the π-orbital) will be dependent upon several factors. Substituents, exerting both steric and polar effects, will be important; non-terminal olefins complex less extensively with metal ions than do terminal ones,[6,8] and highly halogenated olefins complex but little with iodine.[9] In the present study the effects of ring size on the complexing ability of some simple, relatively rigid cycloalkenes have been evaluated.

The method used was essentially that described by Winstein and Lucas.[6a] The olefin was distributed between known amounts of carbon tetrachloride and 1 molar aqueous potassium nitrate or 1 molar aqueous silver nitrate. The increased solubility of the olefin in silver nitrate solution over that in potassium nitrate solution was attributed entirely to complex formation; the concentrations of uncomplexed olefin in the two salt solutions were assumed to be equal. The reactants have been shown to form a 1:1 complex and the position of equilibrium has been shown to be essentially independent of the proportions of silver nitrate and potassium nitrate in a solution whose total salt concentration is 1 molar.[6a] Since there appeared to be no fruitful approach for evaluating activity coefficients of the species involved in the reaction, concentrations were used directly for calculating apparent equilibrium constants for complex formation by each olefin. Several determinations, with a usual variation of about ±1%, were used in evaluating the equilibrium constants for each olefin. With the monocyclic olefins, determinations of the distributions at three temperatures provided data from which thermodynamic functions for each reaction were calculated. The variations in K_{eq} led to a maximum uncertainty in $\Delta H°$ of approximately 0.5 kcal./mole.

The data are summarized in Tables I and II. The equilibrium constants reported are for complex formation.

TABLE I

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION AT 25°

Olefin	K_{eq}, l./mole
Cyclopentene	0.114
Cyclohexene	.0188[a]
Cycloheptene	.0217
Bicycloheptene	.270
Bicyclooctene	.098

[a] Winstein and Lucas[6a] report 0.0184.

TABLE II

THERMODYNAMIC DATA FOR COMPLEX FORMATION AT 25°

Olefin	$\Delta F°$, kcal./mole	$\Delta H°$, kcal./mole	$\Delta S°$, E. U.
Cyclopentene	1.29	−7.03	−27.9
Cyclohexene	2.36	−5.58[a]	−26.6
Cycloheptene	2.27	−6.61	−29.8

[a] Winstein and Lucas[6a] report −5.80.

Discussion of Results

Among these compounds, the effects of variations in ring size are small but definite. The differences in degree of ring strain, resulting from angle deformation and hydrogen–hydrogen repulsion, have been estimated through use of the data shown in Table III.

TABLE III

THERMOCHEMICAL DATA FOR SOME CYCLIC HYDROCARBONS[a]

Compound	ΔHc,[b] 25°	ΔHf,[c] 25°	ΔH_H,[d] 82°	ΔHf,[c] 82°
Cyclopentane	− 793.5,[e] −793.4[f]	−18.5[f]		−19.8[k]
Cyclohexane	− 944.4,[e] −944.8[f]	−29.4[f]		−31.0[k]
Cycloheptane	−1108.1[e]	−28.5[g]		−29.9[l]
Cyclopentene			−26.9[h]	7.1[m]
Cyclohexene			−28.6[i]	− 2.4[m]
Cycloheptene			−26.5[j]	− 3.4[m]

[a] All ΔH values are in kcal./mole. [b] ΔH_c = heat of combustion. [c] ΔH_f = heat of formation. [d] ΔH_H = heat of hydrogenation. [e] Sj. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 274 (1952). [f] A. P. I. Research Project 44, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons," Tables 6n, 23n, 6w, 23w, Ow. [g] Calculated from ΔH_c with $\Delta H_f(CO_2)$ = −94.05 kcal./mole and $\Delta H_f(H_2O)$ = −68.32 kcal./mole (reference *f*, this table). [h] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, THIS JOURNAL, **59**, 831 (1937). [i] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 137 (1936). [j] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *ibid.*, **61**, 1868 (1939). [k] Calculated from $d(\Delta H) = \int \Delta C_p dT$; ΔC_p calculated as function of T from values given in Tables Ov, 22v, 23v, reference *f*, this table. [l] Estimated from ΔH_f at 25° by consideration of $\Delta(\Delta H_f)$ 25° → 82° for cyclopentane and cyclohexane. [m] Computed: ΔH_f (cycloalkane) $-\Delta H_H$ (cycloalkene), both at 82°.

At 82°, the ΔH_f increment per CH_2 group in normal olefins is about −5.1 kcal./mole (reference *f*, Table III). The difference in heats of formation for cyclopentene and cyclohexene at 82° (−9.5 kcal./mole) indicates a strain of 4.4 kcal./mole for cyclopentene relative to cyclohexene. Similarly the difference in heats of formation for cyclohexene and cycloheptene (−1.0 kcal./mole) indicates a strain of 4.1 kcal./mole for cycloheptene relative to cyclohexene.[10] Although data for

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

(8) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

(9) J. A. A. Ketelaar and C. van de Stolpe, *Rec. trav. chim.*, **71**, 805 (1952).

(10) A similar estimation of relative strains in some cyclopentane and cyclohexane derivatives has been described previously.[4] Because computation of ΔH_f (cycloheptene) had to be based on ΔH_H (cycloheptene) at 82°, all strain estimations here were made for 82°. An estimation of relative strains in cyclopentane and cyclohexane at 82° was identical with that at 25° reported by Brown, Brewster and Shechter.[4] We feel then that the relative strains estimated for the cycloalkenes at 82° are applicable in our study, although the temperatures used were 5°, 15° and 25°.

quantitative comparisons of the bicyclic olefins used are not available, bicycloheptene is regarded as being considerably more strained than is bicyclooctene.[11] Both are probably more strained than the monocyclic olefins used in this study.

The orders of relative strain then are cyclopentene $\geq$ cycloheptene $>$ cyclohexene and bicycloheptene $>$ bicycloöctene. Extent of complex formation with aqueous silver ion parallels relative ring strain among these olefins. That is, ring strain appears to lead to or facilitate deformation of the π-orbital for complex formation.

However, other factors are important too. Thus, although cyclopentene and cycloheptene are about equally strained relative to cyclohexene, cyclopentene complexed with silver ion far more extensively. An examination of the thermodynamic data (Table II) and of models affords some explanation for this departure from a simple ring strain relationship. A Fisher–Taylor–Hirschfelder model of cycloheptene can be constructed with both faces alike. The major plane of the π-electron cloud is perpendicular to that of the molecule. A hydrogen atom at position 4 then overlaps somewhat the π-electron cloud. Interference by this hydrogen with the complexed silver ion would make the complex less favored energetically.

Two alternate models may also be constructed—ones in which the two faces of the cycloheptene molecule are not alike—from a Fisher–Taylor–Hirschfelder kit and also from a LaPine–Stuart–Briegleb kit.[12] These two models may be regarded as chair and boat conformations. In neither is the major plane of the π-electron cloud perpendicular to the major plane of the molecule. One side of the π-electron cloud is freely exposed, but the other is virtually buried in one face of the molecule. It seems likely that the hydrogens surrounding that side of the π-electron cloud would impose a restraint on orbital deformation, necessary for complex formation.

All models of cyclopentene are essentially planar with both sides of the π-electron cloud completely exposed.

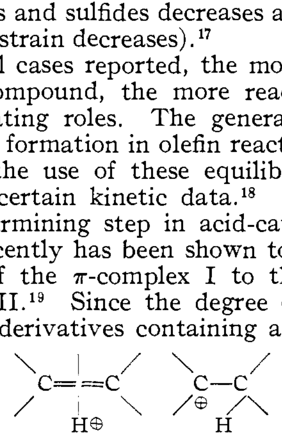
With all models, then, transannular hydrogens appear to be responsible for the less extensive complexation by cycloheptene compared to cyclopentene. In the "symmetrical" model for cycloheptene, the hydrogen interferes with the complexing silver ion; in the others, the hydrogens restrain orbital deformation. The thermodynamic data are in accord with these interpretations. Interference by hydrogen or restraint on orbital deformation would result in a less negative $\Delta H°$ value than would otherwise be expected. The small difference in $\Delta S°$ for cyclopentene and cycloheptene may not be significant, but it is gratifying that the difference is in the direction which is consistent with the interpretations based on models.

Related studies support the thesis that ring strain increases the availability of the π-electrons for complex formation. The rates of addition of phenyl azide,[13] of diethylaluminum hydride[14] and of hexachlorocyclopentadiene[14] to a series of cycloalkenes were essentially in the same order as the relative strains in the olefins. For the Diels–Alder reaction, relatively rapid complex formation between the diene and the olefin has been shown to precede product formation.[15]

cis- and *trans*-cycloöctene have been separated by their differences in reactivity toward silver nitrate; only the relatively more strained *trans*-isomer dissolved readily in the silver nitrate.[16] Similarly the *trans*-cycloöctene reacted immediately with phenyl azide, although the relatively unstrained *cis* isomer required weeks for the formation of a dihydrotriazole.[13]

Recent studies with heterocyclic compounds have shown that, for 4-, 5- and 6-membered rings, the electron density on the hetero atom in cyclic ethers, imines and sulfides decreases as ring size increases (ring strain decreases).[17]

Thus in all cases reported, the more strained is the cyclic compound, the more reactive is it in electron-donating roles. The general importance of π-complex formation in olefin reactions provides a basis for the use of these equilibrium data in interpreting certain kinetic data.[18] For example, the rate-determining step in acid-catalyzed olefin hydration recently has been shown to be the rearrangement of the π-complex I to the usual carbonium ion II.[19] Since the degree of I-strain in cyclobutane derivatives containing a trigonal carbon in the ring is considerable,[20] the faster rate observed[19] for hydration of methylenecyclobutane compared with isobutylene may well be a result of more extensive π-complexation with protons by the more strained methylenecyclobutane. A higher equilibrium concentration of the complexed species would result in a faster rate of rearrangement.


I II

Further experiments to extend this study to other olefins and to other acceptor species are in progress.

Experimental

Materials.—Bicyclo[2.2.1]heptene-2 and bicyclo[2.2.2]-octene-2 were supplied by Professor H. M. Walborsky[11]; the samples were vacuum sublimed just before use.

Cyclopentene (b.p. 44–44.5°, n^{20}D 1.4250) and cyclohexene (b.p. 82.5–83°, n^{20}D 1.4470) were commercially available; they were redistilled just before use.

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[11] H. M. Walborsky and D. F. Loncrini, THIS JOURNAL, **76**, 5396 (1954), and references cited there.

[12] We were unable to make the "symmetrical" model from the LaPine–Stuart–Briegleb kit.

[13] K. Alder and G. Stein, *Ann.*, **485**, 211 (1931); **501**, 38–41 (1933).

[14] K. Ziegler and H. Froitzheim-Kuhlhorn, *Ann.*, **589**, 157 (1954).

[15] See M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., pp. 8–9 for a summary.

[16] A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

[17] H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *ibid.*, **76**, 4242 (1954), and references cited.

[18] The close relationship between complex formation and reaction rates in a similar system ($R-X + ICl \rightarrow RCl + IX$) has been discussed recently by R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953).

[19] R. W. Taft, Jr., *ibid.*, **74**, 4372 (1952); R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

[20] H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

Cycloheptene was prepared by the following sequence of reactions. Cyclohexanone was converted in 65% yield to 1-(nitromethyl)-cyclohexanol,[21] b.p. 100–102° (4 mm.), n^{20}D 1.4870. The nitro alcohol was reduced electrolytically[21] and the resulting acid solution of 1-(aminomethyl)-cyclohexanol was treated with sodium nitrite solution to give cycloheptanone[21] in 57% yield (from nitro alcohol), b.p. 70–71° (19 mm.), n^{20}D 1.4613. Cycloheptanone was reduced with lithium aluminum hydride[22] to cycloheptanol in 90% yield, b.p. 77–81° (14 mm.), n^{20}D 1.4764. Finally the cycloheptanol was dehydrated by distillation from hot phosphoric acid[23] to give a 50% yield of cycloheptene, b.p. 112–113°, n^{20}D 1.4561.

Determination of Equilibrium Constants.—The method, which involved distribution of olefin between carbon tetrachloride and aqueous silver nitrate, was virtually the same as that described by Winstein and Lucas.[6a] These authors showed that the two solvents did not react with each other under the conditions employed. They also presented an excellent discussion of the advantages of using the equilibrium constant for the reaction

$$\text{olefin}(\mathrm{CCl_4}) + \mathrm{Ag}^{\oplus}(\text{aq.}) \rightleftarrows \text{complex}^{\oplus}(\text{aq.}) \qquad (2)$$

rather than one for the reaction

$$\text{olefin}(\text{aq.}) + \mathrm{Ag}^{\oplus}(\text{aq.}) \rightleftarrows \text{complex}^{\oplus}(\text{aq.}) \qquad (3)$$

For olefins which are essentially insoluble in water, the equilibrium constant for reaction 2 is independent of the distribution ratio of olefin between CCl_4 and aqueous KNO_3, and the need for precise determinations of very small concentrations of olefin in the aqueous phase is obviated.[6a] All the olefins used in this study are essentially insoluble in water (the distribution ratios, C_{H_2O}/C_{CCl_4}, were all found to be quite small). The equilibrium constants reported herein are all for systems represented by equation 2.

Carbon tetrachloride solutions of the olefins were analyzed by an adaptation of a procedure which has been described[24]; 20 ml. of glacial acetic acid was added with the sulfuric acid to increase solubility of the organic species and the mercuric sulfate was omitted. With the monocyclic olefins, solutions approximately 0.5 and 1 *M* were used. With the bicyclic olefins, scarcity of samples required the use of more dilute solutions; bicycloheptene, 0.352 *M*; bicyclooctene, 0.097 *M*.

Aqueous solutions of silver nitrate and potassium nitrate, each 1.0000 *M*, were prepared from weighed amounts of reagent grade salts.

The distributions of olefin between carbon tetrachloride and aqueous salt solution were carried out in flasks equipped with mechanical stirrers. The flasks were immersed in an insulated water-bath whose temperature was controlled with a Bronwill unit-type thermoregulator. The thermoregulator was set at 25, 15 and 5° with the aid of a calibrated thermometer and the temperature was maintained within ±0.02° of the setting.

A mixture of 30 ml. of olefin–CCl_4 solution with 400 ml. of potassium nitrate solution or with 100 ml. of silver nitrate solution was stirred for an hour to establish equilibrium. After the phases had separated, two 10-ml. samples were withdrawn from the CCl_4 phase with a pipet. The olefin concentration in each of these samples was then determined by bromine titration.[24] The olefin concentration in the aqueous phase was calculated from the change in concentration in the CCl_4 phase. These equilibrium concentrations were then used to calculate the equilibrium constant for complex formation

$$K_{\text{eq}} = \frac{[\mathrm{BAg}^+]}{[\mathrm{B}][\mathrm{Ag}^+]}$$

where

$[\mathrm{BAg}^+]$ = equilibrium concentration of complex
$[\mathrm{B}]$ = equilibrium concentration of olefin in CCl_4 phase
$[\mathrm{Ag}^+]$ = equil. concn. of uncomplexed $\mathrm{Ag}^{\oplus}$ = init. concn. of $\mathrm{Ag}^{\oplus}$ − (total concn. of olefin in $AgNO_3$ − total concn. of olefin in KNO_3)

TABLE IV

DATA FOR OLEFIN–SILVER ION COMPLEX FORMATION[a]

Olefin	Temp., °C.	Init. concn. olefin in CCl_4	Concn. olefin in 1 *M* KNO_3	Equil. concn. of olefin in CCl_4	Equil. concn. of olefin 1 *M* $AgNO_3$	*K*eq, l./mole
Cyclopentene	25	1.0950	0.0024	0.8155	0.0839	0.109
	25	0.4370	.0001	.3146	.0367	.119
	15	1.1000	.0016	.7381	.1094	.164
	15	0.4370	.0006	.2860	.0453	.164
	5	1.1070	.0013	.6255	.1445	.267
	5	0.4430	.0007	.2401	.0610	.267
Cyclohexene	25	1.0200	.0003	.9443	.0182	.0193
	25	0.5070	.0002	.4776	.0088	.0183
	15	0.9820	.0002	.8905	.0220	.0250
	15	0.4040	.0001	.3640	.0095	.0261
	5	1.0160	.0004	.9076	.0325	.0366
	5	0.3640	.0002	.3234	.0122	.0376
Cycloheptene	25	.8500	.0003	.7940	.0168	.0212
	25	.4300	.0002	.4000	.0090	.0222
	15	.8520	.0003	.7660	.0258	.0342
	15	.4360	.0002	.3930	.0129	.0328
	5	.8620	.0003	.7390	.0369	.0515
	5	.4520	.0002	.3930	.0177	.0453
Bicyclo[2.2.1]heptene-2	25	.3520	.0003	.1890	.0489	.270
Bicyclo[2.2.2]octene-2	25	.0970	.0001	.0730	.0072	.098

[a] All concentrations are in moles/liter.

Each reported value of K_{eq} represents an average of at least two runs with two determinations each, with the systems olefin-KNO_3 and olefin–$AgNO_3$. The approximate variation in similar determinations of K_{eq} was ±1-2%. The experimental data are summarized in Table IV.

Acknowledgments.—We are happy to express our appreciation for generous financial support received from Research Corporation and for olefin samples given by Professor Harry M. Walborsky, The Florida State University.

BATON ROUGE, LOUISIANA

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[21] F. F. Blicke, N. J. Doorenbos and R. H. Cox, THIS JOURNAL, **74**, 2924 (1952).

[22] J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 2928 (1949).

[23] W. M. Dehn and K. E. Jackson, *ibid.*, **55**, 4284 (1933).

[24] H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938); S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33–37.