solution after transfer from the cell to a 7-oz bottle. After heating at 60° for *ca.* 10 min, the reaction mixture was filtered through alumina. Concentration of the filtrate gave a green oil. Extraction with pentane left a green gum. The addition of 30 ml of methanol resulted in the formation of a yellow solid, 0.19 g. An infrared spectrum of this material showed it to be $NiBr(C_6F_5)(Ph_3P)_2$.

Preparation of $NiCl(CCl{=}CCl_2)(Et_3P)_2$.—A solution of 0.3 g (0.8 mmol) of $NiCl_2(Et_3P)_2$ and 0.86 g of Bu_4NClO_4 in 25 ml of CH_3CN was reduced at −2.0 V over a 52-min period. The solution changed from dark red to brownish-gold. The solution was transferred to a 7-oz beverage bottle and treated with 1.82 g (11.0 mmol) of tetrachloroethylene. After standing overnight at room temperature, a 2-ml aliquot of the solution was chromatographed on alumina. Elution with 50% ether in pentane gave a yellow solid which had an infrared spectrum identical with that of authentic $NiCl(CCl{=}CCl_2)(Et_3P)_2$. Chromatography of the remainder of the solution on alumina gave, with pentane elution, 0.19 g of the yellow solid. Recrystallization from methanol-water gave gold crystals, mp 89–91° (lit.[11] mp 92–92.8°).

Registry No.—Butadiene, 106-99-0; $NiCl_2(Ph_3P)_2$, 14264-16-5; $NiCl_2(Cy_3P)_2$, 19999-87-2; $NiCl_2(Et_3P)_2$, 17523-24-9; $NiBr(C_6F_5)(Ph_3P)_2$, 14154-59-7.

Acknowledgment.—I am grateful to Dr. E. A. Zuech, Dr. D. R. Fahey, and Dr. D. L. Crain for helpful discussion and to Dr. Fahey for assistance in identifying the organonickel derivatives. The experimental assistance of Mr. B. L. Martin and Mr. G. R. Herrington is also appreciated.

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Interaction of Silver Ion with Some Strained Olefins

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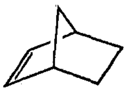
The interaction of silver ion with olefins that would have hindrance at the back of the complexed π orbital was studied. Hindrance causes a small decrease in complex formation indicating a slight dependance on solvation at the back of the complex.

Steric effects have long been recognized as an important factor influencing complex formation of silver(I) with olefins.[1] In an attempt to further elucidate the nature of steric effects in these complexes, a variety of olefins were investigated in which backside (the face of the double bond opposite to that complexed with silver) steric hindrance to the incipient complex was varied. Norbornene type ring systems were used for this because the relatively rigid ring system would prevent differences due to conformational variations. Silver ion has been shown to be largely complexed on the exo face of the norbornene ring[1c,d] so that substitution at the endo 5,6 positions would sterically block the back side of the complexed π orbital.

Conceivable blockage of solvation on the backside could drastically reduce complex formation. The interactions of silver(I) ion with norbornene (**1**), *exo*-5,6-trimethylene-2-norbornene (**2**), *endo*-5,6-trimethylene-2-norbornene (**3**), 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (**4**), and 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-*endo*,*exo*-dimethanonapththalene (**5**) were investigated by the Muhs and Weiss procedure[1a] and by the Winstein and Lucas method.[1b]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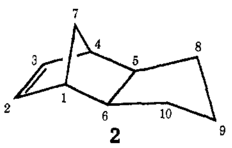

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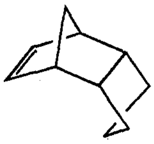
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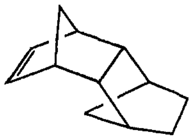
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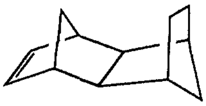
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The equilibrium constants determined by the Muhs and Weiss[1a] procedure (Table I) depend upon the difference in glpc retention time of olefin on an ethylene glycol column *vs.* its retention time on a silver nitrate impregnated ethylene glycol column.

TABLE I

EQUILIBRIUM CONSTANTS FOR SILVER COMPLEXES WITH OLEFINS BY MUHS AND WEISS TECHNIQUE AT 60°

Compd	K_L[a]	K_{eq}[b]	Rel K_{eq}
1	15.1	16.9[c]	1.0[c]
2	82.9	15.8	0.94
3	90.1	9.84	0.58
4	369	11.5	0.68
5	406	13.9	0.82
Norbornadiene	25.9	6.75	0.40[d]

[a] K_L is the partition coefficient for olefin on pure ethylene glycol. [b] K_{eq} is the equilibrium constant (l./mol) for formation of silver nitrate–olefin complex in ethylene glycol. [c] See discussion in Experimental Section. [d] Reference 1a gives 0.54 for this result at 40°.

In Table II are the equilibrium constants determined by distribution of olefin between carbon tetrachloride and an aqueous 1.0 *M* silver nitrate solution by the Winstein and Lucas[1b] treatment. The equilibrium constants are defined as follows.

$$K_0 = [\text{complex}]_{H_2O}/[\text{olefin}]_{CCl_4}[Ag^+]_{H_2O}$$

$$K_D = [\text{olefin}]_{CCl_4}/[\text{olefin}]_{H_2O}$$

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[1] (a) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962); (b) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (c) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970); (d) C. F. Wilcox and W. Gaal, *ibid.*, **93**, 2453 (1971).

TABLE II

EQUILIBRIUM CONSTANTS FOR FORMATION OF COMPLEXES OF SILVER WITH OLEFINS BY DISTRIBUTION BETWEEN AQUEOUS SILVER NITRATE AND CARBON TETRACHLORIDE AT 0.3°

Olefin	K_D	Std dev	K_0	Std dev	K_1	Std dev
1	4,696	±400	0.961	±0.041	4513	±430
2	131,625	±13100	0.033	±0.002	4396	±512
3	145,818	±13600	0.020	±0.002	2989	±408
4	>500,000		<0.005			
5	>500,000		<0.005			

This equals distribution of olefin between carbon tetrachloride and 1.0 *M* aqueous potassium nitrate.

$$K_1 = [\text{complex}]_{H_2O}/[\text{olefin}]_{H_2O}[Ag^+]_{H_2O}$$

$K_1 = K_0K_D$. In the discussion below it is K_1 that is used for the comparisons.

From Tables I and II it can be seen that steric blockage at the back side of the complex decreases the extent of complex formation slightly. Within the rather wide limits of error inherent in method II the relative equilibrium constants obtained by the two methods agree in the cases (**1**–**3**) where it is experimentally possible to compare them. The data in both methods support the conclusion that there is a small amount of charge developed on the vinyl carbon atoms which is stabilized by solvation. This is suggested by the lower value of K_{eq} for **3** when compared to the value found for **1** and **2** and the lower value of **4** when compared to **5**. The relatively small differences are in agreement with previous work suggesting little charge development on the olefinic carbons in the complex.[2,3]

In the Muhs and Weiss technique there appears to be one result that is inconsistent. The value of K_{eq} for **5** is a little lower than seems reasonable when compared to **1**. Conceivably this could be due to differences in solvation of the complex of **5** due to the much greater size of **5** compared to **1**. Perhaps a more reasonable model might be **4**. A comparison of **5** with **4** shows that blockage at the endo side of the double bond does decrease complex formation, which is consistent with the results found in a comparison of **1**–**3**.

Another aspect of interest is the use of silver ions as a means of purifying olefins. During the course of synthetic work involving norbornene type of ring systems, whose preparation utilizes Diels–Alder reactions, it is often necessary to separate 1:1 adducts from higher molecular weight materials. The value of K_0 from Table II is indicative of the amount of olefin that could be extracted from a carbon tetrachloride solution by aqueous silver nitrate when the olefin is largely insoluble in water. As the molecular weight increases the value of K_0 decreases very significantly. In **1**–**3** it is clear that this is very largely due to the partition coefficient (K_D) of olefin in carbon tetrachloride–water increasing in favor of carbon tetrachloride as the molecular weight of olefin increases. There are other factors but of much smaller magnitude such as the decrease due to blockage of solvation. Very probably for **4** and **5** the major factor is also an increase in K_D, but this is not proven since experimental evaluation of the extremely high K_D and extremely low K_0 was not considered reliable.

Experimental Section

General.—All near-infrared spectra were determined using a Cary 14 spectrophotometer. All glpc determinations were made on a Hewlett-Packard Model 5750 instrument with a flame ionization detector. Norbornene was purchased from Aldrich Chemical Co. and used without further purification. *exo*-5,6-Trimethylene-2-norbornene (**2**),[4] 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (**4**),[5] and 1,2,3,4,4a,5,8,-8a-octahydro-1,4,5,8-*endo*,*exo*-dimethanonaphthalene (**5**)[6] were known compounds and prepared essentially according to literature procedures. *endo*-5,6-Trimethylene-2-norbornene (**3**) was prepared essentially according to the procedure of Cristol[4] except that final purification to remove a small amount of **2** was carried out by repeated equilibration of an ether solution of **3** with 15% aqueous silver nitrate solutions. After three equilibrations no **2** could be detected in **3** by glpc on the silver nitrate column described below.

Conditions for Glpc Determinations.[1a]—The ethylene glycol column was a 6-ft (0.25-in. o.d.) aluminum column packed with 40.0% by weight of ethylene glycol on Chromosorb P (60–80 mesh). The silver nitrate column was a 1.5-ft (0.25-in. o.d.) aluminum column packed with 40.0% by weight of 0.325 *M* silver nitrate in ethylene glycol on Chromosorb P (60%). Determinations were carried out at 60°. To check for deterioration of the column with time, the retention time of norbornene was checked at various intervals. No change in retention time for norbornene was found in either ethylene glycol or the silver nitrate column after 72 hr at 60°. The samples were dissolved in pentane and the retention time was measured as the time from the solvent to the sample peak. The values of K_{eq} are reproducible to 5%. We could not reproduce the absolute values of K_{eq} for norbornene reported by Muhs and Weiss at 40°. We could not obtain C-22 firebrick used by Muhs and Weiss and perhaps this is the cause of the differences. We obtained similar results on Chromosorb W and also using a stainless steel column with Chromosorb P and W. However, relative values for K_{eq} were very similar to relative values reported by Muhs and Weiss. These values did not change after heating at 60° for 72 hr. Some comparisons of relative K_{eq} at 40° are given below.

	Rel K_{eq} (this study)	Rel K_{eq} (Muhs and Weiss)
Norbornene	1.0	1.0
2,5-Norbornadiene	0.47	0.54
Camphene	0.046	0.050

Conditions for Carbon Tetrachloride–Aqueous Silver Nitrate Method.[1b,7]—The aqueous phase was maintained at 1.0 *M* ionic strength by using 1.0 *M* potassium nitrate or 1.0 *M* silver nitrate. The olefin in carbon tetrachloride was varied from 0.1 to 1 *M*. No variation in the values for the equilibrium constant could be detected in this range of concentrations. Equilibration was carried out by shaking 10.0 ml of aqueous phase with 4.0 ml of organic phase at 0.3° for 1 hr with a mechanical shaker. A sample of the olefin was shaken with silver nitrate solution and an identical sample was shaken with 1.0 *M* potassium nitrate. The difference in the concentration of olefin in the carbon tetrachloride phase equilibrated with silver nitrate and that equilibrated with potassium nitrate was evaluated and K_0 was determined as described by Traynham and Olechowski.[7] In cases where K_0 was less than 0.005 no complex formation could be detected. A value of 0.005 for K_0 could have been detected. All of the compounds were examined by ir, nmr, and glpc before and after treatment with aqueous silver nitrate. In each case the compounds were homogeneous and the spectral properties were

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(2) (a) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970); (b) T. Fueno, T. Okuyama, T. Deguchi, and J. Furukawa, *ibid.*, **87**, 170 (1965).

(3) R. G. Parker and J. D. Roberts, *ibid.*, **92**, 743 (1970).

(4) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *ibid.*, **82**, 2351 (1960).

(5) S. B. Soloway, *ibid.*, **74**, 1027 (1952); J. K. Stille and D. R. Witherell, *ibid.*, **86**, 2188 (1964).

(6) J. K. Stille, P. R. Kasper, and D. R. Witherell, *J. Org. Chem.*, **28**, 682 (1963); J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959); K. Alder and H. F. Rickert, *Justus Liebigs Ann. Chem.*, **543**, 1 (1939).

(7) J. G. Traynham and J. R. Olechowski, *J. Amer. Chem. Soc.*, **81**, 571 (1959).

completely in agreement with the proposed structures. No change in properties could be detected after treatment with silver nitrate.

The value of K_D was determined largely by the procedure of Wilcox and Gaal.[1d] Olefin was dissolved in 2.00 ml of carbon tetrachloride and shaken with 100.0 ml of 1.0 *M* potassium nitrate at 0.3° for 1 hr. The layers were separated in a separatory funnel and the aqueous layer was centrifuged and then filtered through a Whatman No. 5 filter paper. A 90.00-ml aliquot of aqueous solution was cooled in an ice bath and extracted with 2.00 ml of ice-cold pentane. The pentane solution was then evaluated by gas chromatography on a 10-ft (0.25-in. o.d.) column of 10% UCC-W-982 Silicone on Chromosorb W (60–80). The values for **4** and **5** were greater than five times the value for **3**. However, we do not feel that a reliable estimate could be made for the absolute value of K_D. The extremely high value of K_D for **4** and **5** leads to a high susceptibility to error due to traces of impurities and through incomplete separation of the phases. We obtained variations in the results for these two compounds which we attribute to these factors.

Registry No.—**1**, 498-66-8; **2**, 10466-50-9; **3**, 2826-19-9; **4**, 15914-93-9; **5**, 15914-93-9; silver ion, 14701-21-4.

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Autoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide and Chromium(III) Acetylacetonate

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The system chromium(III) acetylacetonate-*tert*-butyl hydroperoxide has been used to initiate autoxidation of cyclohexene in 1-chlorooctane solvent in the temperature range 30–60°. Oxygen absorption rates and peroxide decomposition rates are presented and contrasted to a similar study of 1-octene. Disappearance rates of chromium(III) acetylacetonate could not be determined spectrophotometrically because of the rapid appearance of an interfering absorption.

In connection with a study of the effectiveness of chromium(III) acetylacetonate and *tert*-butyl hydroperoxide as a free-radical initiator system,[2] an investigation of the autoxidation of cyclohexene initiated by this system has been undertaken. Some kinetic data for the autoxidation and for *tert*-butyl hydroperoxide decomposition in the temperature range 30–60° are presented and compared to that reported earlier for 1-octene.[2]

Experimental Section

Chemicals.—Eastman "White Label" cyclohexene was distilled under nitrogen prior to use. Samples of autoxidized cyclohexene were prepared by bubbling oxygen through cyclohexene (neat) at 30° in the presence of azobisisobutyronitrile for 3 days and analyzed[3] for peroxide content (2.9×10^{-2} *M*). No attempt was made to purify the peroxide formed. Aliquots of this autoxidized cyclohexene were added to solutions of pure cyclohexene in chlorooctane prior to chromium(III) acetylacetonate-*tert*-butyl hydroperoxide initiated autoxidation. All other chemicals have been described previously.[4]

Kinetics.—All kinetic measurements have been described previously.[4] Attempts to study chromium(III) acetylacetonate disappearance rates spectrophotometrically[2] were foiled by the rapid appearance of an absorption of unknown origin in the 336-mμ region. No absorption peak was observed in the 438–440-mμ region [Cr(VI)] during the course of this work, although at higher initial concentrations ($\sim 10^{-3}$ *M*) of chromium(III) acetylacetonate, Cr(VI) was detected in reaction mixtures.

Products.—Products were identified by comparison with gas chromatographic retention times of previously analyzed reaction mixtures[5] or with authentic samples of known reaction products. Analyses were performed on a Perkin-Elmer Model 154D gas chromatograph using a 6-ft stainless steel column packed with silicone grease on "GC-20" (Perkin-Elmer column type O). Helium flow was 8.0 psi, column temperature 148°. Gas chromatograph analyses were performed on three reaction mixtures: one cyclohexene sample was autoxidized by chromium(III) acetylacetonate-*tert*-butyl hydroperoxide at 50°; one cyclohexene sample was autoxidized by azobisisobutyronitrile at 50° similar to the procedure of Mayo, *et al.*;[5] one cyclohexene sample was permitted to react at 50° in the presence of chromium(III) acetylacetonate-*tert*-butyl hydroperoxide *in vacuo*.

Results and Discussion

Tables I and II present initial oxygen absorption rates and *tert*-butyl hydroperoxide decomposition rates

TABLE I

CYCLOHEXENE AUTOXIDATION[a,b] RATES IN THE PRESENCE OF CHROMIUM(III) ACETYLACETONATE AND *tert*-BUTYL HYDROPEROXIDE

$[\mathrm{Cr(acac)_3}]_0 \times 10^5$ *M*	[*tert*-BuOOH]$_0$, *M*	[Cyclohexene]$_0$, *M*	Rate × 10^6 *M* sec^{-1} 30°	40°	50°
0.00	0.00	4.95	0.0	0.0	0.0
0.00	0.99	4.95	5.26	28.9	56.3
1.35	0.99	4.95	6.76	n[c]	n
2.69	0.00	4.95	0.0	n	n
2.69	0.50	4.95	6.80	n	n
2.69	0.99	0.99	1.29	n	n
2.69	0.99	1.98	3.76	n	n
2.69	0.99	4.95	9.05	n	n
2.69	2.97	4.95	13.5	n	n
2.69	3.96	4.95	14.5	n	n
3.92	0.99	4.95	10.0	17.9	29.2
5.38	0.99	4.95	11.2	n	n
6.10	0.99	4.95	6.66	n	n
7.83	0.50	4.95	n	22.9	25.3
7.83	0.99	1.98	n	21.4	51.9
7.83	0.99	4.95	3.91	35.4, 28.0,[d] 5.50[e]	46.9
7.97	0.00	4.95	0.0	n	n
15.66	0.99	4.95	5.95	28.2	46.8

[a] 1-Chlorooctane solvent. [b] Oxygen pressure = 1 atm. [c] n = no data. [d] Autoxidized cyclohexene added. [e] 1.0×10^{-2} *M* cyclohexenone added.

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[1] Brooklyn College of Pharmacy, Long Island University.

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