Electrochemical Generation of Homogeneous Nickel(0) Catalysts for Butadiene Oligomerization

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Electrolytic reduction has been used successfully to prepare nickel catalysts which will convert butadiene to principally 4-vinylcyclohexene and 1,5-cyclooctadiene. The effects upon conversion and product distribution of (a) initial nickel compound, (b) added ligands, (c) solvent, (d) electrolyte, and (e) reduction potential were investigated. Of particular significance was a successful reduction in the absence of any supporting electrolyte. Evidence that the catalytic species contained nickel(0) was obtained by the isolation of $Ni(Ph_2PCH_2CH_2PPh_2)_2$ when the reduction was effected in the presence of this chelating phosphine. The electrochemically reduced species were also shown to undergo reactions typical of nickel(0) leading to organonickel derivatives.

Transition metals in low oxidation states (particularly zerovalent) are known to be the active species in a number of homogeneous catalytic reactions of unsaturated hydrocarbons.[1,2] In a number of cases, the action of a cocatalyst capable of acting as a reducing agent is necessary for catalyst formation. The objective of this research was to investigate the feasibility of *in situ* electrochemical reduction as a method of generating low-valent metal species capable of functioning, without isolation or further treatment, as homogeneous catalysts. We have chosen as a model system the oligomerization of butadiene by reduced nickel species.

Yamazaki and Murai have reported[3] that electrolysis of $[Ni(py)_4][ClO_4]_2$ or $NiCl_2$ in the presence of butadiene yields a red-brown complex which upon decomposition by sulfuric acid or heat yields *trans,-trans,trans-n*-hexadecatetraene. The tetraene presumably arises by tetramerization of the butadiene by a reduced nickel species. The reaction, however, was not catalytic. Shortly after completion of this work, a communication appeared describing the electrochemical synthesis of organonickel compounds.[4] It was also mentioned that the reduced nickel species would convert butadiene to cyclododecatrienes or (with triphenylphosphine present) to 4-vinylcyclohexene and 1,5-cyclooctadiene.

Results

The experimental procedure consisted of two phases: (1) catalyst generation and (2) reaction with butadiene. Catalyst generation involved the controlled-potential electrolysis of a solution of the nickel compound, electrolyte, and added ligand, if any, until the cell current decreased essentially to 0 mA. The initial current was arbitrarily limited to 100 mA. The reductions were generally accompanied by a series of striking color changes. Thus, in the system $NiCl_2\cdot$dimethoxyethane–Ph_3P–Bu_4NClO_4–*N,N*-dimethylformamide, the initially royal blue solution changed to dark green to red-brown to dark yellow-brown.

After completion of the electrolysis, the solution containing the reduced nickel species was transferred to a pressure vessel, butadiene was added, and the mixture was heated. The effect of a number of variables on the product distribution and per cent conversion were investigated and are discussed individually below. Under our experimental conditions, heating a mixture of butadiene and acetonitrile alone gave 3% of 4-vinylcyclohexene, a trace of 1,5-cyclooctadiene, and 2% of polymer. In some cases, the per cent VCH includes small amounts of octatrienes. The reduction potentials quoted below are referred to the $Ag|Ag^+$ couple.

Effect of Nickel Source.—Table I lists the results obtained with several types of nickel(II) compounds. The first three entries indicate that several combinations of nickel(II) chloride and triphenylphosphine may be used. Enhanced solubility in organic solvents makes nickel(II) chloride–tertiary phosphine complexes preferred sources of nickel (the phosphine is also necessary to prevent deposition of metallic nickel; *vide infra*). For convenience, prior preparation of the phosphine complexes can be circumvented by using the 1:1 complex of nickel(II) chloride and 1,2-dimethoxyethane (DME) which is also somewhat soluble in organic solvents. Addition of the appropriate phosphine results in the rapid *in situ* formation of the phosphine complex. The low conversions in experiments 1 and 4 are believed to be due to the very low solubilities of $NiCl_2$ and $NiCl_2(Cy_3P)_2$ resulting in a very low concentration of reduced nickel. The five-coordinate complex, $Ni(CN)_2(PhPMe_2)_3$, when reduced in acetonitrile gave an active catalyst; this reaction, however, was not analyzed quantitatively.

Effect of Added Ligand.—The effect of various added ligands on the catalyst system obtained from $NiCl_2\cdot$DME in acetonitrile is shown in Table II.

The reduction must be carried out in the presence of a ligand capable of stabilizing the reduced nickel species. Thus, as indicated by expt 7, metallic nickel is precipitated when $NiCl_2\cdot$DME alone is subjected to electrolysis. Nickel metal was also formed when triphenylarsine and 1,5-cyclooctadiene were the added ligands (expt 8 and 9). Acrylonitrile prevented the formation of metallic nickel but did not give a catalytic system (expt 14). The triphenyl- and trialkylphosphines were effective in stabilizing the reduced nickel. The chelating phosphine, bis(1,2-diphenylphosphino)-ethane, gave a catalyst of low activity. The effect of varying the Ph_3P:Ni ratio from 2:1 to 4:1 is demonstrated by expt 10 and 11, respectively. A higher concentration of triphenylphosphine increases the conversion and the selectivity to VCH while decreasing the amounts of heavier materials, *i.e.*, CDT and poly-

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[1] I. Wender and P. Pino, "Organic Synthesis via Metal Carbonyls," Interscience, New York, N. Y., 1968.

[2] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.

[3] N. Yamazaki and S. Murai, *Chem. Commun.*, 147 (1968).

[4] H. Lehmkuhl and W. Leuchte, *J. Organometal. Chem.*, **23**, C30 (1970).

TABLE I[a]

EFFECT OF NICKEL SOURCE[b]

Expt no.	Nickel compd, mmol	Added ligand, mmol	C_4H_6, g	Yield, % VCH	COD	CDT	Polymer
1	$NiCl_2$, 0.4	Ph_3P, 4.6	11.5	7	0.5	~0	2
2	$NiCl_2 \cdot DME$,[c] 1.0	Ph_3P, 2.0	11.9	25	36	5	11
3	$NiCl_2(Ph_3P)_2$, 1.0	None	17.3	18	29	5	2
4	$NiCl_2(Cy_3P)_2$,[d] 0.4	None	10.1	6	3	2	3
5	$NiCl_2(Et_3P)_2$, 0.4	None	10.7	12	24	1	3
6	$NiCl_2(Bu_3P)_2$, 0.4	Bu_3P, 4.3	11.2	16	43	1	*e*

[a] The following abbreviations are used throughout the tables below: VCH = 4-vinylcyclohexene, COD = 1,5-cyclooctadiene, and CDT = cyclododecatrienes. The per cent yield is the chemical yield. [b] Conditions: CH_3CN (25 ml), Bu_4NClO_4 (0.1 *M*), −2.0 V. [c] DME = 1,2-dimethoxyethane. [d] Cy = Cyclohexyl. [e] Not determined.

TABLE II

EFFECT OF ADDED LIGAND[a]

Expt no.	Added ligand, mmol	C_4H_6, g	Yield, % VCH	COD	CDT	Polymer
7	None[b,c]		Metallic nickel			
8	Ph_3As,[b] 4.6		Metallic nickel			
9	1,5-COD,[b] 5.1		Metallic nickel			
10	Ph_3P,[d] 2.0	11.9	25	36	5	11
11	Ph_3P,[d] 4.0	11.6	40	43	3	8
12	Bu_3P,[d] 2.0	7.3	14	28	2	11
13	diphos,[e] 1.0	11.4	8	Trace	Trace	*g*
14	$CH_2{=}CHCN$,[d,f] 0.4	8.9	No catalysis			

[a] Conditions: CH_3CN (25 ml), Bu_4NClO_4 (0.1 *M*), −2.0 V. [b] 0.4 mmol of $NiCl_2 \cdot DME$. [c] Bu_4NBr as electrolyte. [d] 1.0 mmol of $NiCl_2 \cdot DME$. [e] diphos = bis(1,2-diphenylphosphino)ethane. [f] *N,N*-Dimethylformamide solvent. [g] Not determined.

mer. The substitution of tributylphosphine for triphenylphosphine enhances the selectivity to COD.

Effect of Solvent.—Several solvents were found to be suitable media both for the electrolytic reduction and the subsequent oligomerization reaction (Table III).

TABLE III

EFFECT OF SOLVENT[a]

Expt no.	Solvent[b]	Reduction V	Reduction Min	Yield, % VCH	COD	CDT	Polymer
15	CH_3CN	−2.0	40	25	36	5	11
16	DMF[c]	−2.0	42	17	32	8	7
17	DME[d]	−2.0	196	6	2	~0	13
18	DME[d]	−3.0	189	5	4	~0	*e*
19	DME[d,f]	−3.0	118	15	30	2	4

[a] Conditions: $NiCl_2 \cdot DME$ (1.0 mmol), Ph_3P (2.0 mmol), Bu_4NClO_4 (0.1 *M*). [b] 25 ml. [c] DMF = *N,N*-dimethylformamide. [d] DME = 1,2-dimethoxyethane. [e] Not determined. [f] 0.5 mmol of $NiCl_2 \cdot DME$.

Acetonitrile and *N,N*-dimethylformamide are, however, the solvents of choice. The solubilities of the starting nickel complexes are much higher in these solvents. Much higher current densities can, therefore, be achieved in these solvents and the reductions can thus be effected much more rapidly (*cf.* expt 15 and 16 with expt 17–19). In acetonitrile and *N,N*-dimethylformamide, a lower Ph_3P:Ni ratio (2:1 *vs.* 4:1) was sufficient to obtain catalysts of satisfactory activity than was the case with 1,2-dimethoxyethane. It is likely that the former solvents are effective in stabilizing the reduced nickel species through coordination. Under the same experimental conditions, *N,N*-dimethylformamide gives a higher selectivity to COD than does acetonitrile. This is additional evidence that the solvent may be acting as a ligand in the catalytic nickel species. Sulfolane was also shown to be a suitable solvent, but the reaction was not analyzed quantitatively.

Effect of Electrolyte.—The results obtained with several different supporting electrolytes are shown in Table IV.

TABLE IV

EFFECT OF SUPPORTING ELECTROLYTE[a]

Expt no.	Supporting electrolyte[b]	C_4H_6, g	Yield, % VCH	COD	CDT	Polymer
20	Bu_4NClO_4	11.9	25	36	5	11
21	Bu_4NCl	12.3	10	17	5	13
22	Bu_4NBr	15.6	26	39	5	12
23	None[c]	13.6	26	34	5	9

[a] Conditions: $NiCl_2 \cdot DME$ (1.0 mmol), Ph_3P (2.0 mmol), CH_3CN (25 ml), −2.0 V. [b] 0.1 *M*. [c] Bu_4NClO_4 present in anode compartment.

Tetra-*n*-butylammonium perchlorate is a commonly used supporting electrolyte in electrochemical studies because of the poor coordinating ability of the perchlorate ion which minimizes interactions of the electrolyte with the metal-containing species. We have found that halide anions can be tolerated by the nickel catalyst systems (expt 21 and 22). The results obtained in the oligomerization reaction are very similar for the bromide and perchlorate salts; however, a lower conversion and a somewhat higher proportion of polymer resulted with the chloride derivative. Of significance, is the result of expt 23 in which supporting electrolyte was omitted. This could be useful in cases where interference from the electrolyte in subsequent reactions is a problem. With the exception of the Bu_4NCl system, essentially the same results are obtained with or without supporting electrolyte present.

Effect of Reduction Potential.—The reduction of a 2:1 Ph_3P:$NiCl_2 \cdot DME$ mixture in acetonitrile was carried out at several different potentials (Table V).

TABLE V

EFFECT OF REDUCTION POTENTIAL[a]

Expt no.	Reduction V	Reduction Min	C_4H_6, g	Yield, % VCH	COD	CDT	Polymer
24	−1.5	57	12.6	8	<1	Trace	10
25	−2.0	40	11.9	25	36	5	11
26	−2.5	78	12.2	14	25	2	16

[a] Conditions: $NiCl_2 \cdot DME$ (1.0 mmol), Ph_3P (2.0 mmol), Bu_4NClO_4 (0.1 *M*), CH_3CN (25 ml).

At −1.5 V a green solution and yellow solid were formed; this mixture exhibited lower activity for the oligomerization of butadiene (expt 24). At −2.0 V a dark red-brown solution resulted which showed high catalytic activity. A more negative potential (−2.5 V) had a deleterious effect on the catalyst system when employing acetonitrile as the solvent. It is likely that at −2.5 V some reduction of solvent is beginning to occur (the cathodic limit for acetonitrile has been reported[5] to be −2.84 V *vs.* $Ag|Ag^+$) which yields species that deactivated the catalyst.

Discussion

The distribution of products in the butadiene oligomerization reaction catalyzed by electrochemically reduced nickel species is generally in accord with the results obtained with chemically reduced catalysts. Thus, the catalyst obtained from the interaction of nickel(II) acetylacetonate and ethoxydiethylaluminum in the presence of triphenylphosphine gave (after 5 hr at 80°) 30% of VCH, 62% of COD, and 4% of CDT.[6] The results obtained in the electrochemical system $Ni(acac)_2$–pyridine–R_4NBr are comparable to those we have obtained. The above system gives 44% of VCH and 56% of COD.[4]

A number of zerovalent nickel compounds are known to catalyze the oligomerization of butadiene.[7] Direct evidence for the presence of nickel(0) species in the systems of this research was obtained by the following experiment. Reduction of a solution of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$ in acetonitrile at −2.0 V in the presence of 1 equiv of $Ph_2PCH_2CH_2PPh_2$ resulted in the precipitation of $Ni(Ph_2PCH_2CH_2PPh_2)_2$ in 89% yield.

The nickel(0) complexes, Ni(1,5-cyclooctadiene)$_2$, Ni(cyclooctatetraene), Ni(*all-trans*-cyclododecatriene), and $Ni(Ph_3P)_4$, were prepared by Lehmkuhl and Leuchte from $Ni(acac)_2$ and the appropriate ligand.[4] Recently, the electrochemical synthesis of two rhodium(0)–tertiary phosphine complexes has been described.[8]

Additional evidence for the presence of nickel(0) in our system was obtained by the following experiments. Reduction of $NiCl_2(Ph_3P)_2$ in acetonitrile followed by treatment of the solution with pentafluorobromobenzene gave $NiBr(C_6F_5)(Ph_3P)_2$. Similarly, a reduced solution of $NiCl_2(Et_3P)_2$ reacted with tetrachloroethylene to give $NiCl(CCl{=}CCl_2)(Et_3P)_2$. These organonickel(II) derivatives arise from the oxidative addition of the organic halide to a nickel(0) species.[9]

Experimental Section

Reagents.—The following chemicals were obtained from the source indicated in parentheses and used as received: $AgClO_4$ (K and K Laboratories), Bu_4NClO_4 (G. Frederick Smith), Bu_4NX(X = Cl, Br) (Eastman), Hg (National Zinc Co.), $NiCl_2 \cdot DME$ (Alfa Inorganics), Ph_3P and Bu_3P (Carlisle), and $Ph_2PCH_2CH_2PPh_2$ (Arapahoe). The following complexes were prepared by established literature methods: $NiCl_2(Bu_3P)_2$, $NiCl_2(Ph_2PCH_2CH_2PPh_2)$, $NiCl_2[(C_6H_{11})_3P]_2$, $NiCl_2(Et_3P)_2$, and $NiCl_2(Ph_3P)_2$. The Ph_3As (M and T) was recrystallized from MeOH. The COD (Columbia Carbon) and $CH_2{=}CHCN$ (Eastman) were distilled materials. The acetonitrile (Mallinckrodt) was dried over Davidson Type 4A molecular sieves. The DME (Eastman) and DMF (Mallinckrodt) were distilled from CaH_2. The solvents were degassed by sparging with prepurified nitrogen before use.

Apparatus.—All electrochemical work was carried out in a Vacuum Atmospheres Corp. Dry-Lab/Dry-Train containing an atmosphere of 96% nitrogen and 4% hydrogen.

Controlled-potential electrolyses were conducted in a U-shaped cell consisting of two compartments separated by a sintered-glass disk. One compartment (the cathode) was equipped with a ground-glass joint to hold the reference electrode assembly. Electrical contact with the cathode and anode compartments was made *via* platinum wires pinch-sealed through the base of the cell. The reference electrode assembly consisted of two parts: an upper tube containing a silver wire and a 0.001 *M* solution of $AgClO_4$ in 0.1 *M* Bu_4NClO_4 in CH_3CN and a lower tube containing 0.1 *M* electrolyte in the reduction solvent. The upper tube was separated from the lower and the lower tube from the catholyte by sintered-glass disks.

Controlled-potential electrolysis was effected with a Kepco Model 60-0.5 power supply used in conjunction with a Heath voltage reference source.

The butadiene reactions were conducted in Fisher–Porter aerosol compatibility bottles equipped with a pressure gauge and fitting for admitting gaseous butadiene. All equipment was dried at 105–110° before use.

Analysis.—The reactions were analyzed by glpc on a F & M Scientific Model 5750 chromatograph using a flame ionization detector. The analysis for VCH and COD was conducted on a 20 ft × $^1/_8$ in. column containing 20% tris(cyanoethoxy)propane on 35/80 mesh Chromosorb P at 120°. Analysis for cyclododecatrienes was carried out on a 6 ft × $^1/_8$ in. column containing 20% SE-30 on Chromosorb P at 120°. The polymer content of the reaction mixture was taken as the material which would not distil into a Dry Ice cooled receiver at 100° (0.075–0.1 mm). The VCH, COD, and CDT were isolated in an experiment using a catalyst obtained by reducing (at −2.0 V) 0.4 mmol of $NiCl_2 \cdot DME$ and 4.5 mmol of Ph_3P in 0.1 *M* Bu_4NClO_4-CH_3CN. They were identified by their ir and nmr spectra.

Catalyst Generation.—The following general procedure was used in all the experiments discussed above. The nickel compound, electrolyte, added ligand, and solvent were mixed (total volume 25 ml). The resulting solution or suspension was transferred to the cathode compartment of the elctrolysis cell. A solution (0.1 *M*) of electrolyte was placed in the anode compartment. Mercury was added to both compartments in an amount sufficient to cover the platinum wires sealed in the base. The reference electrode assembly was allowed to contact the solution in the cathode compartment. The mercury pool electrodes were stirred magnetically. Current was then passed through the cell at the desired reduction potential until a residual value of <5 mA was reached.

Butadiene Oligomerization.—After completion of the electrolysis, the mercury was drained from the cathode *via* a stopcock located in the base of the cell and the solution containing the reduced nickel species was transferred to a Fisher–Porter bottle. Butadiene was added at room temperature and the reaction mixture was stirred and heated to 130° over 2 hr. After an additional 3 hr at this temperature, heating was discontinued. The reaction mixture was cooled in an ice bath, then analyzed by glpc. A weighed quantity of VCH was added to the reaction mixture followed by reanalysis. The increase in area of the VCH peak (relative to the COD peak) was used to determine the quantities of these materials present.

Preparation of $Ni(Ph_2PCH_2CH_2PPh_2)_2$.—A solution of 0.26 g (0.49 mmol) of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$, 0.20 g (0.50 mmol) of $Ph_2PCH_2CH_2PPh_2$, and 0.86 g of Bu_4NClO_4 in 25 ml of CH_3CN was reduced at −2.0 V over an 18-min period. The solution changed from red-brown to yellow and a gold solid precipitated. The solid was recovered by filtration and washed with pentane to give 0.38 g. The infrared spectrum of this material was identical with that of a sample of $Ni(Ph_2PCH_2CH_2PPh_2)_2$ prepared by the procedure of Chatt and Hart.[10] A sample recrystallized from benzene–methanol gave orange crystals. *Anal.* Calcd for $C_{52}H_{48}P_4Ni$: C, 73.0; H, 5.7; Ni, 6.9. Found: C, 73.0; H, 5.7; Ni, 7.0.

Preparation of $NiBr(C_6F_5)(Ph_3P)_2$.—A solution of 1.30 g (2.0 mmol) of $NiCl_2(Ph_3P)_2$ in 50 ml of 0.1 *M* Bu_4NClO_4 in 1,2-dimethoxyethane was reduced at −3.6 V for 4.75 hr. Pentafluorophenyl bromide, 2.20 g (8.9 mmol), was added to the reduced

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[5] E. O. Sherman and D. C. Olson, *Anal. Chem.*, **40**, 1174 (1968).

[6] G. Wilke, H. Muller, and M. Kroner, *Angew. Chem.*, **73**, 33 (1961).

[7] G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).

[8] D. C. Olson and W. Keim, *Inorg. Chem.*, **8**, 2028 (1969).

[9] D. R. Fahey, *J. Amer. Chem. Soc.*, **92**, 402 (1970).

[10] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

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.

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Interaction of Silver Ion with Some Strained Olefins

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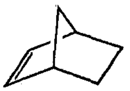
The interaction of silver ion with olefins that would have hindrance at the back of the complexed π orbital was studied. Hindrance causes a small decrease in complex formation indicating a slight dependance on solvation at the back of the complex.

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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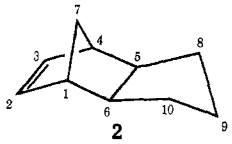

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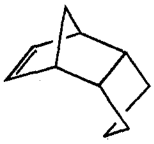

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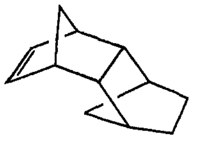

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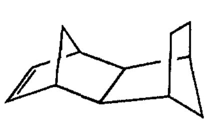

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The equilibrium constants determined by the Muhs and Weiss[1a] procedure (Table I) depend upon the difference in glpc retention time of olefin on an ethylene glycol column *vs.* its retention time on a silver nitrate impregnated ethylene glycol column.

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).