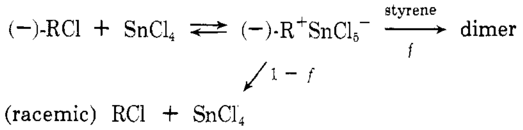
proposed by the authors where the mechanisms for racemization and hydrolysis were considered distinct.[5]

Ion-pair intermediates are also important in reactions promoted by $SnCl_4$. Thus, the $SnCl_4$-promoted racemization of optically active 1-phenylethyl chloride in CCl_4 containing excess styrene was reported by Heald and Williams.[11] Here, 1-phenylethyl chloride reacts with styrene to form styrene dimer *ca.* 36 times slower than it undergoes racemization, where the addition of styrene has no apparent effect on the rate of racemization. The authors described the reaction as proceeding by an ionization mechanism to produce a carbonium ion pair intermediate which regenerates racemic RCl more efficiently than it combines with styrene to form dimer. In this system, $1 - f$ is *ca.* 0.97.



$$\begin{tikzcd} (-)\text{-RCl} + SnCl_4 \arrow[r, shift left] & (-)\text{-R}^+SnCl_5^- \arrow[l, shift left] \arrow[r, "\text{styrene}", "f"'] \arrow[dl, "1-f"] & \text{dimer} \\ (\text{racemic})\ \text{RCl} + SnCl_4 & & \end{tikzcd}$$

Experimental Section

Optically active 1-phenylethyl chloride was prepared from the resolved carbinol[12] using thionyl chloride.[13] The reaction mixture was dissolved in pentane and the pentane solution of RCl was washed carefully with aqueous $NaHCO_3$. The solution was dried over K_2CO_3 and the pentane was evaporated at reduced pressure. The alkyl chloride was used as such without further purification, chloride analysis 99.9% Cl, $[\alpha]_{589}$ − 8.8.

Mercuric chloride was sublimed before use. Radiolabeled mercuric chloride was prepared using 0.25 *N* radiolabeled (^{36}Cl) hydrochloric acid as previously described.[3c] Reagent grade $CoCl_2 \cdot 6H_2O$ was dried over P_2O_5 in an Abderhalder drying apparatus at 110° (1 mm) before use. Radiolabeled cobalt(II) chloride was prepared by mixing 1 g of $CoCl_2$ with 0.1 ml of 0.25 *N* radiolabeled (^{36}Cl) hydrochloric acid in 10 ml of dry methanol. The methanol was next removed under reduced pressure and the recovered solid was dried at 110° (1 mm) for 2 days. The salt was neutral to Bromophenol Blue indicator in acetone. The activity of the sample was 2920 cpm/mg.

The solvents were prepared as previously described.[14]

The polarimetric rate measurements were made in a thermostated 1-dm all-glass cell using a Perkin-Elmer polarimeter, Model 141. The wavelengths used were 589 and 436 nm for runs with $HgCl_2$ and $CoCl_2$, respectively.

The exchange rate measurements were carried out using a sealed ampoule technique as previously described.[3c] The separation of organic chloride from inorganic chloride was afforded using pentane and water. Two-milliliter aliquots from each layer were delivered into 10 ml of Bray's solution[15] and the radioactivity level was measured using a Beckman LS100 Liquid Scintillation Counter.

The titrimetric rate measurements were carried out using a sealed-ampoule technique.[3c] Five-milliliter aliquots were titrated to the blue end point of Bromophenol Blue with 0.01095 *M* sodium methoxide in methanol solution.

Registry No.—$HgCl_2$, 7487-94-7; $CoCl_2$, 7646-79-9; 1-phenylethyl chloride, 72-65-1.

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Arene–Metal Complexes. VII. Stereoselective Catalytic Deuteration of *syn*-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium[1]

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The palladium on charcoal catalyzed deuteration of *syn*-(dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (1) in dioxane gave a high yield of *syn*-(dibenzobicyclo[2.2.2]octadiene)tricarbonylchromium which was predominantly a d_2 species with both of the deuteriums on the ethano bridge and anti to the tricarbonylchromium moiety. Deuteration of 1 and uncomplexed dibenzobicyclo[2.2.2]octatriene (2) was shown to go without rearrangement to the bicyclo[3.2.1]octane system or significant bridgehead hydrogen exchange. The predominantly anti addition of the deuteriums to 1 appears to be a result of the tricarbonylchromium moiety serving as a blocking group to shield one face of the carbon–carbon double bond.

Tricarbonylchromium groups complexed to benzene rings have been shown to exert electronic and conformational effects.[1a] In this report we describe a study of an addition reaction to a double bond of an arene–tricarbonylchromium complex that has one of its faces shielded by the metal moiety. The results of this study indicate that the metal moiety exerts a steric effect and serves as a blocking group and thus addition occurs predominantly to the unshielded face of the carbon–carbon double bond.

Results

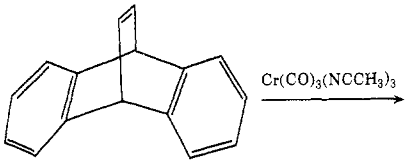
syn-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (1) was prepared in moderate yield by refluxing the

Table I
Deuterium Content of Dibenzobicyclo[2.2.2]octadiene Obtained from Deuteration of 1 followed by Decomplexation of the Purified Product 3[a]

Run	Yield of deuterated species, %: d_0	d_1	d_2	Deuterium incorporation, %
1	12.4	25.1	62.5	75.1
2	8.9	23.0	68.1	79.5
3	8.2	23.2	68.6	80.2

[a] Determined by mass spectroscopy with correction for normal isotopes.

free arene 2 with triacetonitriletricarbonylchromium in dioxane. Chemical analysis and the mass spectrum of 1 indicated that it contained only one tricarbonylchromium moiety. Oxidation of with ferric ion in 95% ethanol gave a high yield of 2, which shows that the arene did not rearrange upon complexation. The nmr spectrum of 1[2] confirms its constitution and the stereochemistry of 1 was indicated by the conversion of 1 to 3 by the addition of hydrogen to the etheno bridge. The nmr spectrum of 3[2] shows that the signals for the two sets of ethano hydrogen atoms are separated by 0.5 ppm (at δ 2.2 and 1.7). In order to get a shift this large, the tricarbonylchromium moiety must be syn to the ethano bridge.[3,4] The lower field signal (δ 2.2) was assigned to the protons syn to the tricarbonylchromium group, since protons which are closer to the tricarbonylchromium group are generally shifted downfield.[3,4]



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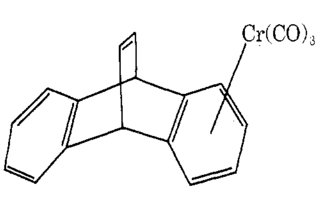
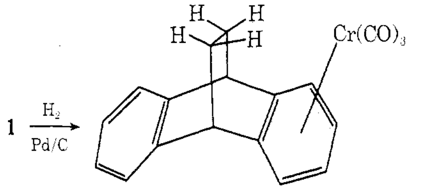
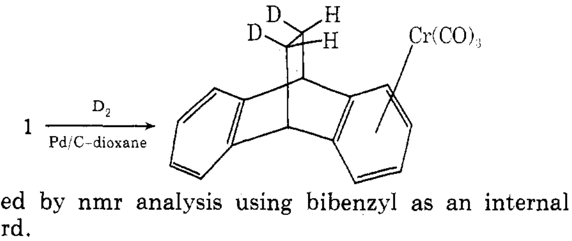


1



3

Catalytic hydrogenation of 1 in dioxane over palladium on charcoal (Pd/C) gave 87% of 3 and 13% of the uncomplexed dibenzobicyclo[2.2.2]octadiene (4). Yields were determined by nmr analysis using bibenzyl as an internal standard.



Catalytic deuteration of 1 under similar conditions followed by removal of decomplexed material by chromatography gave complex 3 which appeared, by nmr, to be largely dideuterated with both deuteriums on the ethano bridge anti to the metal moiety; the nmr spectrum of the product showed only small absorption at δ 1.7 (anti protons) and a board singlet at δ 2.2 (syn protons).[2]

Table II
Calculated and Measured R^a Values from the Deuteration of 1

Run	R, calcd[b]	R, measured[c]
1	4.0	5.0
2	4.9	7.2
3	5.1	7.4

[a] Defined as the ratio of syn bridge protons to anti bridge protons of 3. [b] From mass spectral data. [c] By nmr.

Quantitative determination of the ratio of syn to anti addition of deuterium was difficult for two reasons. First, a small amount of impurities in the complexed product of deuteration made integration of the signal due to the anti protons impossible. Therefore, the chromium was oxidatively removed from deuterated 3 and the amount of bridge protons relative to bridgehead protons of 4 was determined by nmr. The amount of anti photons of deuterated 3 was obtained by measuring the amount of syn protons to bridgehead protons of deuterated 3 and substracting this number from the total bridge protons determined from the nmr spectrum of deuterated 4.

The second reason that it was difficult to determine the ratio of syn to anti addition was that the deuterated product was not entirely the d_2 species, since some protons were also added to 1. In Table I are presented the amounts of the d_0, d_1, and d_2 species determined from the mass spectra of three runs of decomplexed deuterated 3. No species greater than d_2 were observed. From the data in Table I it is seen that only 75–80% deuterium was added. Evidently this reflects a large isotope effect[5] on the catalytic addition of hydrogen and deuterium, since the deuterium gas used was relatively pure and there was no other definite source of hydrogen, although traces of water or some hydrogen–deuterium exchange with solvent molecules could have increased the amount of hydrogen available. If it is assumed that no syn addition occurs, then the ratio of syn to anti bridge protons, R, is given by eq 1. In Table II are presented for three runs the R values

$$\frac{\text{syn H}}{\text{anti H}} \equiv R = \frac{2(\%d_0 + \%d_1 + \%d_2)}{2(\%d_0) + 1(\%d_1)} \qquad (1)$$

calculated from the mass spectral data and those determined from the nmr data. It is seen from these values that the observed values are actually higher than the calculated ones. Since the calculated values are maximum ones (because 100% anti addition was assumed), the larger measured values must reflect errors in the nmr measurements. The nmr measurements could easily be in error by 5% and if the integral of the signal for the syn protons is increased by 5% and that for anti protons is decreased by 5%, the R values for the three runs become 3.1, 3.8, and 4.9, respectively. These values are now below the calculated values but can be accounted for by only 1–8% syn addition.

In conclusion, then, we feel that our data clearly indicate that the addition of deuterium occurs mainly and possibly exclusively to the face of the carbon–carbon double bond which is anti to the tricarbonylchromium group.

For the sake of comparison, dibenzobicyclo[2.2.2]octatriene (2) was also deuterated under identical conditions. As shown in Table III, the distribution and per cent incorporation of deuterium compare favorably with the results obtained from the deuteration of complex 1. Small amounts of d_3 and d_4 species were observed from the deuteration of 2 but not from the deuteration of complex 1.

Table III
Deuterium Content of Dibenzobicyclo[2.2.2]octadiene Obtained from Deuteration of 2[a]

Run	Yield of deuterated species, %					Deuterium incorporation, %
	d_0	d_1	d_2	d_3	d_4	
1	16.7	17.8	62.2	2.9	0.4	76.3
2	15.8	20.1	58.7	4.7	0.7	77.3

[a] See Table I, footnote *a*.

Table IV
Nmr Data of Deuterated Dibenzobicyclo[2.2.2]octadiene Obtained from Deuteration of 1 and 2

Run	Number of protons		
	Aromatic[a]	Bridgehead	Bridge
1[b]	8.00	1.96	2.54
2[b]	8.00	1.97	2.44
3[b]	8.00	2.01	2.39
1[c]	8.00	1.98	2.49
2[c]	8.00	1.91	2.54

[a] Integration of the aromatic region was set equal to 8.00 protons. [b] Obtained from deuteration of **1** followed by decomplexation of **3**. [c] Obtained from deuteration of **2**.

This suggests that a small amount of bridgehead exchange occurs with **2** but not with **1**.

The nmr data of deuterated **4** obtained from deuteration of **1**—decomplexation of **3**—and deuteration of **2** are given in Table IV. These data indicate that the two routes are identical. The average value for the bridgehead protons obtained from **2** are slightly lower, as they should be if bridgehead exchange occurred, but within the range given by the error associated with measurement of an nmr integral.

The inflated number of bridge protons for each run given in Table IV is consistent with deuterium incorporation as determined from the mass spectra.

Discussion

There are three main results from this deuteration study. First, catalytic addition of hydrogen to the dibenzobicyclo[2.2.2]octatriene ring system, whether complexed or uncomplexed, was unaccompanied by rearrangement to the bicyclo[3.2.1]octane system. Second, no significant amount of bridgehead hydrogen exchanged occurred during the deuteration of either the complexed or uncomplexed arene. Third, the tricarbonylchromium group effectively shielded one face of the carbon–carbon double bond and resulted primarily in addition of deuterium from the other face of the double bond (anti addition).

The propensity of dibenzo[2.2.2]octatriene for rearrangement accompanying ionic addition[6] as well as free-radical addition[7] to the double bond is well known. The lack of rearrangement during the catalytic reduction[8] indicates that nothing special occurs with this system and the normal Horiuti–Polanyi mechanism[10] can be invoked.

The lack of any significant amount of bridgehead hydrogen exchange is consistent with the mechanisms generally accepted for hydrogen–deuterium exchange reactions for olefins.[11-13] Catalytic deuteration of the bicyclo[2.2.1]heptene system has also been shown to go without exchange of bridgehead hydrogen atoms.[14]

A drawing of complex **1** was constructed from a Dreiding model of the uncomplexed arene **2** and the bond lengths and angles obtained from an X-ray diffraction study of (benzene)tricarbonylchromium.[15] Recently Mills reinterpreted the X-ray crystallographic data of several ortho-disubstituted complexed rings and concluded that the complexed rings are folded slightly (4° for six-membered rings) such that the two substituted ring carbon atoms are further away from the chromium than the other four ring atoms.[16] With or without the folding it is clear from our drawing that the tricarbonylchromium group shields one face of the carbon–carbon double bond; the distances between the midpoint of the etheno bridge and the carbonyl oxygen, the carbonyl carbon, and the chromium atoms are *ca.* 2.5, 2.5, and 3.5 Å, respectively (with the carbonyl group at its closest distance to the etheno bridge). The fact that the addition of the deuterium to complex **1** is predominantly anti indicates that the tricarbonylchromium moiety serves simply as a blocking group. Its presence prevents the catalyst from complexing with the syn face of the double bond.

Use of the tricarbonylchromium group as a blocking group could serve not only to force the stereoselectivity of a cis addition, but it is conceivable that it could force an addition reaction which is normally trans to become cis.

Experimental Section

Most equipment, materials, and methods have been previously described.[1a]

Dibenzobicyclo[2.2.2]octatriene (9,10-etheno-9,10-dihydroanthracene, 2) was prepared by the procedure of Cristol and Lim:[17] mp 118-120° (lit.[17] mp 119-120°); nmr (CDCl$_3$) δ 7.24 (m, 4), 6.98 (m, 2, -CH=CH-), 6.88 (m, 4), and 5.06 (d of d, 2).

Dibenzobicyclo[2.2.2]octadiene (9,10-ethano-9,10-dihydroanthracene, 4). A mixture of 0.49 mmol of **2** and 0.10 g of 10% palladium on charcoal in 20 ml of absolute ethanol was stirred under 1 atm of hydrogen until the hydrogen uptake ceased. A routine work-up gave a quantitative yield of white crystals, nmr (CDCl$_3$) δ 7.19 (m, 4), 7.04 (m, 4), 4.28 (poorly resolved quintet, 2), and 1.67 (t, 4), which agrees very well with the literature[18] nmr.

***syn*-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (1).** A quantity of 4 g of **2** and triacetonitriletricarbonylchromium, prepared[19] from 2.1 g of hexacarbonylchromium, in 15 ml of dioxane (distilled from LiAlH$_4$) was heated to reflux for 14 min in a Strohmeier apparatus.[20] The reaction mixture was cooled to 25° and filtered through Celite. The filtrate was washed with three 200-ml portions of water, dried (MgSO$_4$), and concentrated. The residue was triturated with five 50-ml portions of pentane (to remove **2**), dissolved in 10 ml of boiling methylene chloride, and crystallized by adding pentane to the methylene chloride solution. A quantity of 1.5 g (44%) of yellow needle crystals was obtained which was recrystallized from methylene chloride–pentane: mp 184.5-185.5° (lit.[21] mp 175°, 186° dec); nmr[2] (CDCl$_3$) δ 7.23 (m, 2), 6.98 (m, 4), 5.67 (m, 2), 5.02 (m, 2), and 4.83 (t, 2).

Anal. Calcd for C$_{19}$H$_{12}$O$_3$Cr: C, 67.06; H, 3.53. Found: C, 66.89; H, 3.51.

Procedure for Catalytic Deuterations in Dioxane. Dioxane was purified[22] and stored under nitrogen.

Into a clean, dry hydrogenation flask, a 50-ml erlenmeyer flask with a 4-ml addition funnel and stopcock attached to its side was placed a magnetic stirring bar, 0.135 g of 10% palladium on charcoal (Matheson Coleman and Bell), and 6-7 ml of dioxane. The flask was attached to the hydrogen apparatus[23] and the system was flushed with deuterium gas (Matheson Coleman and Bell) for 25 min. The catalyst was reduced by stirring and then a solution of 0.265 mmol of the olefin in 2-3 ml of dioxane was added *via* the side arm. A little more dioxane was added to the flask until the final volume was 12-13 ml. The mixture was then stirred vigorously until the uptake of deuterium ceased.

Work-up for Measuring the Syn to Anti Addition of Deuterium to 1. The reaction mixture was filtered through Celite with gentle suction and the filter was then washed with dioxane. The solvent of the filtrate was removed on a rotary evaporator and the yellow solid was chromatographed on 26 g of silica gel using methylene chloride to transfer the solid to the column and pentane, and 10 and 50% methylene chloride–pentane mixtures as the eluents. An nmr spectrum of the yellow complex **3** was taken after the solvent was removed under vacuum. The complex was then transferred to a flask using methylene chloride, the solution was concentrated, and the residue was dissolved in 5 ml of 95% ethanol. To this solution was added 1.59 mmol of ferric chloride in 5 ml of ethanol. The solution was allowed to stand overnight and then a routine ether extraction gave **4** as a white solid, which was then analyzed by mass spectroscopy and nmr.

Work-up for Measuring the Absolute Yield of Products from 1. The reaction mixture was filtered and to the filtrate was added 0.124 mmol of bibenzyl[24] as an nmr standard. The solvent was comcarefully removed on a rotary evaporator.[25] The residue was completely dissolved in $CDCl_3$ and analyzed by nmr.

Work-up for Uncomplexed Materials. After filtration, a routine ether extraction was carried out and the residue was analyzed by mass spectroscopy and nmr.

Acknowledgment. We wish to thank Professor M. D. Rausch and Dr. G. A. Moser for making their results available to us prior to publication.

Registry No.—**1**, 51286-77-2; **2**, 2734-13-6; **3**, 51286-78-3; **3**-d_2, 51349-37-2; **4**, 5675-64-9; $Cr(CO)_3(NCCH_3)_3$, 22736-49-8.

Supplementary Material Available. The 100-MHz pmr spectra in $CDCl_3$ of **1**, **3**, and the tricarbonylchromium complexed products from the deuteration of **1** (mainly **3**-d_2 with the deuteriums on the ethano bridge anti to the tricarbonylchromium group) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1920.

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(24) When 1,1,2,2-tetrachloroethane was used as the standard, it caused decomposition of the complex.

(25) When the dioxane was removed by washing an ether solution of the complex several times with water followed by drying with $MgSO_4$, the complex unexplainably decomposed upon removal of the ether on the rotary evaporator.

Phase-Transfer Catalyzed Synthesis of Dimethylvinylidenecyclopropane Derivatives in Aqueous Medium[1]

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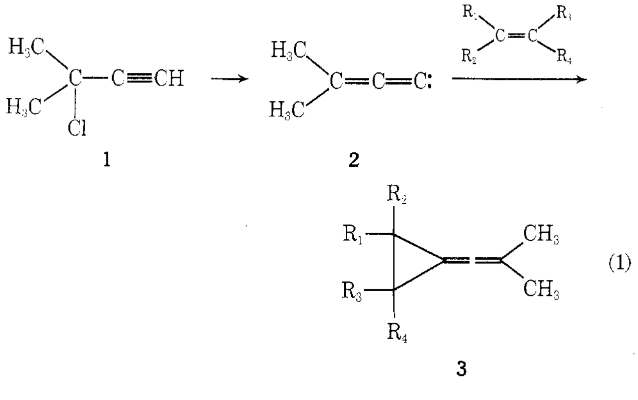
Phase-transfer catalyzed synthesis of dimethylvinylidenecyclopropane derivatives in aqueous medium from 3-chloro-3-methyl-1-butyne (**1**) and various olefins are described. Slow addition of **1** to a stirred mixture of 51% aqueous potassium hydroxide, benzene, and an appropriate substrate olefin (3-molar excess to **1**) in the presence of benzyltriethylammonium chloride as a catalyst afforded the corresponding dimethylvinylidenecyclopropane in moderate yields.

Since Hartzler's report on the generation of dimethylvinylidenecarbene (**2**) from 3-chloro-3-methyl-1-butyne (**1**) or 1-chloro-3-methyl-1,2-butadiene *via* base-catalyzed γ- or α-eliminations of hydrogen chloride, and on its reaction with some simple olefins (eq 1),[2-4] his procedure has been used widely for preparation of alkenylidenecyclopropane derivatives.[5] However, cyclopropanation of olefins with this carbene generally proceeds in low yield owing to the relatively low electrophilic reactivity of the carbene.[2,6] Furthermore, Hartzler's procedure requires rigorously anhydrous conditions for generation of the carbene **2**. This paper describes a convenient method for the generation of **2** in aqueous medium by the phase-transfer technique, and its wide applicability to the synthesis of various dimethylvinylidenecyclopropane derivatives.[7,8]



Results and Discussion

Reaction with Styrene under Various Conditions. In order to find the optimum conditions for the cyclopropanation of olefins with **2**, **1** was added to a stirred mixture of 51% aqueous potassium hydroxide[9] and styrene under several conditions (eq 2). The results are given in Table I. The best yield of the adduct 1-dimethylvinylidene [or -(2-methylpropenylidene)] -2-phenylcyclopropane (**4**)[2a] was