m/e 824.5109 (calcd for $C_{59}H_{68}O_3$ 824.5151), 826.5304 (M + 2). Anal. Calcd for $C_{59}H_{68}O_3$: C, 85.87; H, 8.31. Found: C, 85.71; H, 8.49.

Oxidation of 11. A solution was prepared by dissolving 0.002 g (2.54×10^{-6} mol) of 11 in 100 mL of dry degassed benzene. PbO_2 (0.002 g, 8.37×10^{-6} mol) was added, and the reaction was monitored by UV-visible spectroscopy. After about 1 h, the spectrum in Figure 2 was recorded. The absorption at 580 nm, attributed to 12, did not appear to follow a first-order decomposition pathway. The solution that was blue-green after 1 h was brown at the end of 3 h. A portion of the brown residue was analyzed by ESR spectroscopy and exhibited a weak paramagnetic signal. A UV-visible spectrum of the brown residue yielded a weak absorption at 580 nm and several absorptions below 450 nm.

Spectrophotometric Titrations of 6 and 10. Both compounds were titrated under similar conditions with DBU as a base and THF as a solvent. The results of the titrations are shown in Figures 3 and 4. Base was added to each solution as follows: 0.5 equiv was added to 6 in increments until a total of 2.0 equiv was added; 0.4 equiv of base was added in increments to 10 until a total of 2.0 equiv was added.

Anion Radical of 4. Into an ESR tube was placed about 0.2 mg of 4. Degassed THF was vacuum transferred, and the resultant solution was freeze-thaw degassed several times. A potassium mirror was formed above the solution level, and after the solution was brought into contact with the potassium, and orange solution developed. A strong signal developed and exhibited a triplet splitting pattern with a_H equal to 1.78 G (g = 2.0041). No other hyperfine splitting could be detected on using various modulation adjustments.

Cyclic Voltammetry of 4. An ASS 169 Electrochemistry system was used, composed of the following modules: A Princeton Applied Research Potentiostat/Galvanostat with a PAR 179 coulometer, a PAR Universal Programmer, a Houston 2000 X-Y recorder with time base, and a Tektronix 5103 N storage oscilloscope with a Polaroid camera. Positive feedback resistance compensation was employed. The measurement was carried out at room temperature (ca. 21 °C) in purified dichloromethane.

A three-electrode voltammetric cell was employed with a Pt disk working microelectrode, a Pt wire counter electrode, and an SCE reference. The sample solution was about 5×10^{-5} M, with 10^{-1} M tetrabutylammonium perchlorate as the supporting electrolyte.

The scan range was generally +0.5 to -0.5 V, and scan rates from 0.02 to 0.50 V/s were employed. The cathodic portion of E_1 was difficult to distinguish at fast scan speeds (greater than 0.2 V/s) and shifted anodically at slower scan rates. The anodic portion of E_1 was observable and did not change potential at the various scan rates. The E_2 couple remained reversible at all scan rates.

Acknowledgment. This work was supported by Grant CHE-8026714 from the National Science Foundation. We thank John Norman for some of the early thoughts concerning this project and Kim Stearley for helpful suggestions.

Registry No. 4, 87842-45-3; 4 radical anion, 87842-46-4; 5, 87842-41-9; 6, 87842-42-0; 6 dianion, 87842-50-0; 10, 87842-43-1; 10 dianion, 87842-51-1; 11, 87842-44-2; 12, 87842-49-7; i, 87842-47-5; ii, 87842-48-6; $AlCl_3$, 7446-70-0; $Ni(acac)_2$, 3264-82-2; DBU, 6674-22-2; 9-bromoanthracene, 1564-64-3; tetrachlorocyclopropene, 6262-42-6; trichlorocyclopropenium tetrachloroaluminate, 10438-65-0; 2,6-di-*tert*-butylphenol, 128-39-2; 3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenylmagnesium bromide, 54907-62-9; 4-bromo-2,6-di-*tert*-butyl-1-(trimethylsiloxy)benzene, 27329-74-4; 9-[3,5-di-*tert*-butyl-4-(trimethylsiloxy)phenyl]anthracene, 87842-40-8.

Carbonylation and Valence Isomerization of 1,3-Dihomocubane Derivatives by Chlorodicarbonylrhodium Dimer

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1,3-Dihomocubane and several analogous cage compounds react with $Rh_2(CO)_4Cl_2$ to give dinuclear acyl-rhodium complexes. These complexes are transformed into dicyclopentadiene and/or D_3-trihomocubanone derivatives either upon heating or by treatment with triphenylphosphine. 1,3-Ethanomethanocubane reacts analogously. The kinetics of these metal-induced transformations follow the second-order rate law. A linear relationship exists between the constants and the calculated strain energies of the starting cage compounds.

The interaction of transition-metal complexes with carbocyclic compounds containing strained structures has been the subject of both considerable research and controversy.[1] Rhodium complexes, e.g., were found to induce valence isomerization in cage compounds having three to six fused cyclobutane rings. The rearrangement of a system with *two* condensed cyclobutanes has been studied only in an open noncage system and was shown to proceed by an isomerization mechanism different from that of the more complicated polycyclobutane structures.[2] We thus found it warranted to investigate the effect of transition-metal complexes on the isomerization of a *cage* compound

(1) For some leading reviews, see: (a) Halpern, J. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P. Eds.; Wiley: New York, 1977; Vol. II, pp 705-730. (b) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461. (c) Mango, F. D. *Coord. Chem. Rev.* **1976**, *10*, 109.

(2) Sohn, M.; Blum, J.; Halpern, J. *J. Am. Chem. Soc.* **1979**, *101*, 2694.

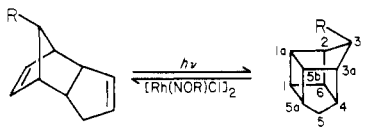
0022-3263/84/1949-0971$01.50/0

that has just *one* fixed bicyclo[2.2.0]hexane system.

In this paper we report a study on rhodium(I)-induced valence isomerization and carbonylation of 1,3-dihomocubane (octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene) (**2**, R = H) and of some of its derivatives. The study provides new information on the energy factors associated with the strained C–C bond and on the nature of the organometallic intermediates that are involved in this process.

Results

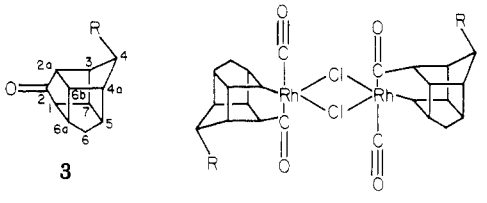
1,3-Dihomocubane (**2**, R = H), which is easily accessible by UV irradiation of dicyclopentadiene (**1**, R = H) (eq 1),[3-5]



(1)

1 **2**

proved to be thermally stable at 100 °C although, in analogy to many other strained compounds,[1] it could be readily converted into the starting material **1** (R = H), in the presence of catalytic amounts of dichlorobis(norbornadiene)dirhodium $[Rh_2(NOR)_2Cl_2]$. However, in contrast to bicyclo[2.2.0]hexane and to *syn*-tricyclo[4.2.0.0^{2,5}]octane,[2] the cage compound proved not to rearrange in the presence of $Rh_2(CO)_4Cl_2$ at 68 °C. Instead it formed a stable organometallic rhodium-carbonyl compound, which according to elemental analysis had the composition of $C_{12}H_{12}ClO_2Rh$.[4] The pure complex did not decompose on prolonged heating (24 h) in boiling benzene but was converted into D_3-trihomocubanone (octahydro-1,3,5-metheno-1*H*-cyclopenta[*cd*]pentalen-2-one) (**3**, R = H)[6] near its melting point, 169–170 °C. While the pyrolysis



3 **4**

led only to 30–50% of **3** (R = H) (depending on the rate of heating), the addition of 2 mol of triphenylphosphine per each equivalent of rhodium afforded this ketone in quantitative yield. [cf. ref 2].

Owing to the very low solubility of the organorhodium complex we were neither able to obtain a structure-indicative NMR spectrum nor to grow crystals suitable for X-ray analysis. However, the IR and mass spectra suggest **4** as a possible structure. The presence of acyl- and metal-carbonyl groups was deduced from the IR absorptions at 1720 and 2058 cm^{-1}, respectively. The 150-eV chemical ionization (CI) mass spectrum (reagent gas isobutane) in which the MH^+ ions appear at m/z 653/655/657 together with $[MH-nCO]^+$· peaks reveals that the complex is binuclearic. The EI spectrum (see paragraph at the end of the paper about supplementary material) indicates the gradual losses of all four CO groups as well

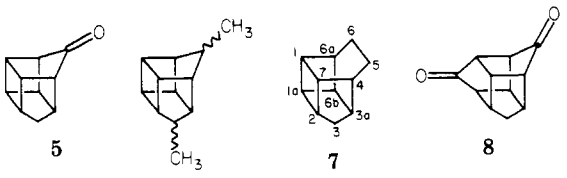
Table I. Distribution of GC-Isolated Products from the Reaction of Substituted 1,3-Dihomocubanes and $Rh_2(CO)_4Cl_2$[a]

starting compound	relative yield, % diene	ketone
2 (R = OH)	0	100
5	35	65
2 (R = $OCOCH_3$)	66	34
7	67	33
2 (R = Cl)	100	0
6[b]	100	0

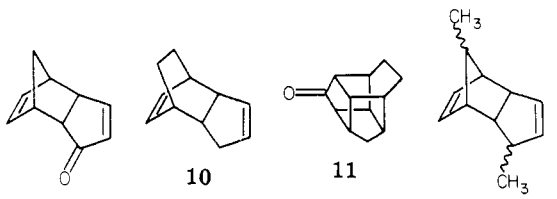
[a] Reaction conditions: 1.0 mmol of cage compound, 0.5 mmol of $Rh_2(CO)_4Cl_2$ in 4 mL of dry benzene in a sealed pressure tube under N_2 at 68 °C; reaction was stopped when the IR spectrum indicated total consumption of the starting rhodium complex. [b] Reaction temperature 110 °C.

as the formation of fragment ions formally corresponding to 2^{+}· amd 3^{+}·, respectively. The absence of chlorine-free dirhodium fragment ions suggests that the two metal atoms are linked via chlorine atoms rather than by a Rh–Rh bond.[7]

By analogy to **2** (R = H), *anti*-octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalen-3-ol (**2**, R = OH),[8] *anti*-3-acetyloxy- and *anti*-3-chlorooctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (**2**, R = $OCOCH_3$,[8] and **2**, R = Cl,[9] respectively), octahydro-1,2,4-metheno-3*H*-cyclobuta[*cd*]pentalen-3-one (**5**),[10] 3,5-dimethylocta-



5 **6** **7** **8**



9 **10** **11** **12**

hydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (**6**), and decahydro-1,2,4-methenocyclobut[*cd*]indene (1,3-ethanomethanocubane) **7**[11] were also reacted with $Rh_2(CO)_4Cl_2$. We found that the substituted analogues of **4** are less stable than the parent organorhodium complex. In fact, apart from the hydrocarbon **2** (R = H) only the carbinol **2** (R = OH) gave a pure derivative of **4** as the sole product by heating of equimolar amounts of the reactants in hot benzene (68 °C, 15 min). Prolonged heating (24 h) of **4** (R = OH) caused already partial decomposition of the complex into *anti*-4-hydroxyoctahydro-1,3,5-metheno-1*H*-cyclopenta[*cd*]pentalen-2-one (**3**, R = OH). Ketone **5** gave

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(7) From the available data it is not possible to determine whether **4** has a syn or an anti structure. Similarly, the stereochemistry of the 3 and 3′ positions could not be assigned.
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Table II. Summary of Kinetic Data (eq 1)[a]

substrate	10^3k, M^{-1} s^{-1}
2 (R = H)	3.7 ± 0.02
2 (R = Cl)	0.083 ± 0.006
2 (R = OH)	6.6 ± 0.20
2 (R = $OCOCH_3$)	1.7 ± 0.15
5	10.0 ± 0.43
7	1.5 ± 0.03

[a] During the first 2 half-lives of the reactions the interaction of $Rh_2(CO)_4Cl_2$ with 1 to give $(diene)_2Rh_2Cl_2$ complexes was negligible. Therefore k_{obsd} is equal to k in eq 2.

in the best run a mixture of 40% of the corresponding rhodium adduct together with 32% of 8[12] and 18% of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (9).[10]

The rhodium complexes derived from 2 (R = $OCOCH_3$) and 7 proved to decompose readily into the rearranged compounds 1 (R = $OCOCH_3$) and 10, respectively, together with the corresponding carbonylation products 3 (R = $OCOCH_3$) and 11. The formation of 4 (R = Cl) could be traced only by infrared (1705, 2060 cm^{-1}) and mass spectra of the reaction mixture [m/z 720–728, $M^{+\cdot}$; 498–502 $(C_{12}H_{11}Cl_3O_2Rh_2)^{+\cdot}$], and by isolation of traces of RhCl(CO)$[P(C_6H_5)_3]_2$ upon addition of triphenylphosphine to the reaction mixture during its initial stages. Prolonged heating afforded pure 1 (R = Cl).[9]

Hardly any reaction took place when 6 and $Rh_2(CO)_4Cl_2$ were heated in benzene at 68 °C. A temperature of 110 °C was needed to induce rearrangement of 6 into 3,10-dimethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (12) (80% after 24 h) free of any trihomocubanone derivative.

The relative yields of ketones and dienes formed from the various cage compounds and chlorodicarbonylrhodium dimer are summarized in Table I.

It should be recalled that in analogy to $Rh_2(CO)_4Cl_2$ also $Ir_2(CO)_6Cl_2$ forms organometallic complexes with 1,3-dihomocubanes.[13] They too vary widely in stability. While the iridiocyclic compound from 2 (R = H)[13] could be heated without decomposition above 250 °C, the derivatives of substituted 1,3-dihomocubane proved to give dicyclopentadienes at, or even below, room temperature.

In spite of the fact that the product distribution of the reaction between $Rh_2(CO)_4Cl_2$ and the 1,3-dihomocubanes in benzene (68 °C) varies widely, their kinetics clearly obey the second-order rate law (eq 2), unaffected by variations of the concentration of the cage compounds and of $Rh_2(CO)_4Cl_2$ (0.065–0.194 M). The reaction constants are summarized in Table II.

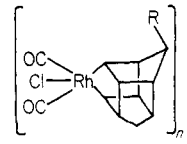
$$-d[C]/dt = k[C][Rh_2(CO)_4Cl_2] \quad (2)$$

C = starting cage compound

Discussion

Both the carbonylation and the rearrangement of the 1,3-dihomocubane derivatives were found to be associated with the selective cleavage of the C_1–C_{1a} bond. Several reasons have been given for similar selectivity observed in metal-assisted transformations of cage compounds. Excess strain around one C–C linkage,[14] elongation of a certain bond in the molecule,[15] and maximum gain in strain energy by conversion of the substrate into a specific product[6] have been suggested. These factors have been considered in our system.

In our preliminary study[13] we have shown that valence isomerization of 2 (R = H) by $Ir_2(CO)_6Cl_2$ is associated, in the rate-determining step, with the formation of a metallocyclic intermediate that has a D_3-trihomocubane-like structure (consider a metal atom instead of a CH_2 group). We presume that the reactions of the 1,3-dihomocubanes with $Rh_2(CO)_4Cl_2$ yield initially rhodiocyclic compounds having similar structural features. As due to limitations imposed by the available force field calculation methods the energies of such intermediates could not be calculated. However, by approximation of the metal insertion with a hypothetical introduction of a methylene group instead of that of a $Rh(CO)_2Cl$ fragment, one can assume that the transformation of 2 into 13 (R = H) is to



13

14

be favored over the formation of any isomeric $C_{10}H_{12}M$ cage compounds (M = metal-containing fragment). While the conversion of 2 (R = H) into D_3-trihomocubane (14, R = H) releases 33.8[16] to 35.7[17] kcal mol^{-1}, the release of strain energy by transformation of 2 (R = H) into any other $C_{11}H_{14}$ pentacycloundecane is substantially smaller (cf. the calculation given in ref. 6 and 16).

The specific insertion of the rhodium atom into the C_1–C_{1a} bond of 2 (R = H) emerges also from structural analysis.[18,19] For C_1 and C_{1a} the sum of itemized steric energies (stretch, bend, twist, nonbonded, out-of-plane, and stretch-bend) is 40.4 and 40.2 kcal mol^{-1}, respectively, whereas C_2, C_{5a}, C_{5b}, and C_6 have itemized steric energies substantially less, i.e., 24.5, 24.6, 25.8, and 25.7 kcal mol^{-1}, respectively. It is notable that most of the excess strain on C_1 and C_{1a} arises from bending and twist but not from stretching of the respective bond. As a consequence thereof the C_1–C_{1a} bond is not the longest one in 1,3-dihomocubane. In fact the molecular mechanics calculations reveal that the C_1–C_{5a}, C_1–C_6, C_{1a}–C_{5b}, C_2–c_6, C_{3a}–C_4, and C_4–C_6 bonds are longer than C_1–C_{1a} by 0.01–0.04 Å.

Similar analysis for the substituted 1,3-dihomocubanes, 2 (R = Cl), 2 (R = OH), 2 (R = $OCOCH_2$), as well as for 5 to 7 (Table III) indicates that the C_1–C_{1a} bond strain values for the different compounds are almost identical, which is not surprising, as the substituents are remote from the bond of interest. Thus, the bond strain alone cannot account for the differences in reaction rates of the derivatives of 2 (see Table II). When, however, the total strain energies (SE) of the cage compounds are considered (Table IV), a linear relationship between the experimentally derived rate constants, k_{obsd}, and SE is obtained (see Figure 1). The slight deviation observed for 2 (R = $OCOCH_3$) may be attributed to the fact that we calculated the energy data only for the cisoid conformation of the acetyl group.

The reason for the very low reactivity of the dimethyldihomocubane 6 (no measureable reaction was observed at 68 °C) is still to be investigated. A remote steric

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(15) E.g.: Sasaki, N. A.; Zunker, R.; Musso, H. *Chem. Ber.* **1973**, *106*, 2992.
(16) Based on force field calculations of Engler et al. (Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005).
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Table III. Bond Length and Strain at the C_1-C_{1a} Bond of Several Cage Compounds Calculated by Allinger 1973 Force Field (MM1)[a]

compd	bond length,[b] Å	energy, kcal mol^{-1} (25 °C, gas) stretch	nonbonded 1,4-interactions	bend and stretch-bend	torsional and torsional-bend	sum	bond strain[c]
2 (R = H)	1.5498	0.3762	0.8219	16.6652	2.964	20.8273	25.1873
2 (R = Cl)	1.5491	0.3624	0.8333	16.6831	2.949	20.8278	25.1878
2 (R = OH)	1.5499	0.3783	0.8228	16.6809	2.962	20.8440	25.2040
2 (R = $OCOCH_3$)	1.5501	0.3835	0.8175	16.6840	2.581	20.4660	24.8260
5	1.5466	0.3146	0.8526	16.8169	2.568	20.5521	24.9121
6	1.5490	0.3612	0.8908	16.6266	2.947	20.7764	25.1364
7	1.5570	0.5355	0.9182	17.5275	2.768	21.7492	26.1092

[a] See ref 21. [b] Standard value 1.5410 Å. [c] Bond strain energy = ΔH^b + 4.36 kcal mol^{-1} (see ref 19).

Table IV. Enthalpies and Strain Energies of Several Cage Molecules as Calculated by Allinger 1973 Force Field (MM1)[a]

compd	ΔH°_f, kcal mol^{-1} (25 °C, gas)	strain energy kcal mol^{-1} (25 °C, gas)
2 (R = H)	51.06	71.29
2 (R = Cl)	43.06	58.22
2 (R = OH)	12.64	72.89
2 (R = $OCOCH_3$)[b]	−38.47	71.66
5	30.52	76.62
6	37.82	71.85
7	42.79	68.60

[a] See ref 21. [b] Cis C—O—C=C conformation.

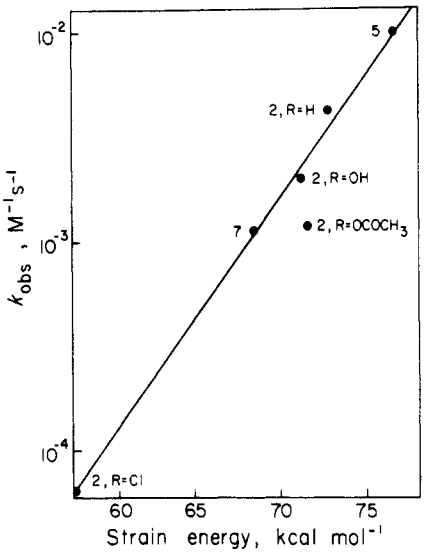
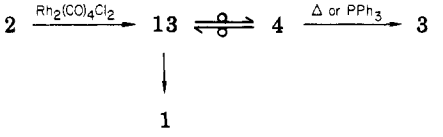


Figure 1. Reactivity–strain energy plot for various strained cage compounds.

effect such as that reported by Eaton and Patterson[20] may be of considerable importance in this system.

The kinetic measurements indicate one and the same reaction mechanism for $Rh_2(CO)_4Cl_2$-assisted conversion of the various 1,3-dihomocubane derivatives. The first step is assumed to involve an oxidative addition reaction in which **13** is formed. This complex may either undergo reductive elimination to give **1** or to rearrange with internal CO insertion. Complex **4**, so formed, leads then to ketone **3** by pyrolysis or by treatment with triphenylphosphine. Table I indicates that the mode of transformation of **13** depends greatly on the nature of the substituents in **2**.

Since the pure acyl–rhodium complex obtained from **5** and $Rh_2(CO)_4Cl_2$ proved to decompose in boiling benzene into a mixture of only **8** and **9** it can be concluded that the transformation **13** → **4** is reversible. The various possible steps are summarized in the following scheme:



Experimental Section

Melting points were taken on a Büchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 157 G spectrophotometer. Proton magnetic resonance were run by using HA-100D and WH-270 spectrometers. Chemical ionization (CI) mass spectra of the organometallic complexes were taken on a Varian MAT 311 mass spectrometer equipped with a combined CI/EI ion source at the following conditions: reagent gases for CI were hydrogen or isobutane; approximate ion source temperature 140–200 °C; direct insertion mode; accelerating voltage 3 kV; ionization energies 70, 25, and 12 eV, respectively, for EI; 150 eV for CI; emission current 300 μA (EI); 1 mA (CI). The mass spectra of the metal-free compounds were recorded with the aid of a Varian MS-GC MAT-111 instrument (80 eV). Gas chromatography was performed with a Varian 920 instrument equipped with a thermal conductivity detector or with a Varian-Aerograph 2800 with a flame ionization detector. All manipulations of metal complexes were performed under an inert atmosphere of nitrogen or argon.

Octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (2, R = H) was prepared by a modification of the synthesis of Schenck and Steinmetz.[3] A 24% yield of analytically pure **2** (R = H) was obtained when a solution of 17 g of **1** (R = H) (freshly chromatographed on alumina) in 250 mL of acetone (analytical reagent grade) was photolyzed under N_2 through quartz with a Hanovia 450-W medium-pressure mercury lamp (type 679A-36) for 12 h, followed by sublimation at 40–45 °C (1 mm) and column chromatography on silica gel (cyclohexane serving as eluent); mp 141–142 °C (lit.[5] mp 142–143 °C). The IR, NMR, and mass spectra were consistent with those reported previously.[22]

***anti*-Octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalen-3-ol (2, R = OH).** In the best run a solution of 10 g of **1** (R = OH)[23] in 400 mL of analytical reagent grade acetone was irradiated under N_2 in a 4.5 × 32 cm quartz tube of a Rayonet photochemical reactor fitted with 15 25-W low-pressure mercury lamps at a distance of 12 cm from the reaction vessel. After 5 days the solvent was removed and the yellow residue sublimed at 100 °C (0.5 mm). Recrystallization (2×) from hexane afforded 3.5 g (35%) of colorless crystals; mp 165–166 °C (lit.[8] mp 164–166 °C;[10] 171–172 °C). The compound proved to be analytically pure and further recrystallization of the sample had no effect on the melting point. The IR,[8] NMR[24] and mass spectra[25] were consistent

(20) Eaton, P. E.; Patterson, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 2573.
(21) See: Osawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1.
(22) For the preparation of (−)-**2** (R = H), see: Nakazaki, M.; Naemura, K. *J. Org. Chem.* **1977**, *42*, 2985.
(23) Woodward, R. B.; Katz, T. J. *Tetrahedron* **1959**, *5*, 70.
(24) Dilling, W. L. *J. Org. Chem.* **1975**, *40*, 2380.

with those reported in the literature. Several attempts to prepare **2** (R = OH) according to Dilling et al.[8] gave unsatisfactory results.

***anti*-3-(Acetyloxy)octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (2, R = $OCOCH_3$)** was obtained as a colorless liquid in 68% yield from **2** (R = OH) and acetic anhydride in pyridine according to Dilling et al.[8] followed by GC purification on 15% OV-101/Chromosorb W at 160 °C; ^1H NMR ($CDCl_3$) δ 1.25 (d, 1, J = 11 Hz), 1.66 (d, 1, J = 11 Hz), 1.94 (s, 3), 2.40–3.00 (m, 8), 5.06 (s, 1).[24]

Octahydro-1,2,4-metheno-3*H*-cyclobuta[*cd*]pentalen-3-one (5) was best prepared by irradiation of 7.0 g of **9**[10] in 200 mL of *n*-hexane in a Pyrex vessel for 50 h under N_2 with the aid of a 150 medium-pressure mercury lamp. After removal of some polymeric material and two successive sublimations [80 °C (3 mm)] there was obtained 5.0 g (72%) of colorless **5**: mp 125–126 °C (lit.[8] mp 126.5–127.5 °C); IR (CCl_4) 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.586 (d, 1, J = 10 Hz), 1.731 (d, 1, J = 10 Hz), 2.256 (br s, 1), 2.444 (t, 1, J = 6 Hz), 2.851–3.046 (m, 4), 3.118 (br s, 2).[24]

***anti*-3-Chlorooctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (2, R = Cl).** To a solution of 100 mg of **2** (R = OH) in 3 mL of dry benzene was added 0.5 mL of purified thionyl chloride in 3 mL of the same solvent. After 4 h at reflux the excess reagent and solvent were removed in vacuo. The residue was taken into methylene chloride, washed with water, dried, and concentrated. Preparative GC on 15% FFAP/Chromosorb W at 180 °C yielded 25 mg (23%) of **2** (R = Cl): mp 38–40 °C (lit.[9] oil). The IR, NMR, and mass spectra were consistent with the data for **2** (R = Cl) prepared by photocyclization of **1** (R = Cl).[9]

3,5-Dimethyloctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (6). A solution of 23.6 g of freshly distilled *endo*-3,10-dimethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (**12**) [Fluka AG, bp 73 °C (10 mm)] in 600 mL of analytical reagent grade acetone was placed in a quartz well and irradiated under N_2 at room temperature with 15 25-W Rayonett lamps (254 nm) located around the reaction vessel at a distance of 12 cm. After 6 days the solvent was removed and the residue distilled at 48–54 °C (2 mm) to yield 2.5 g (11%) of **6** as a colorless liquid. Further purification was accomplished by preparative GC on 15% OV-101 on Chromosorb W at 140 °C: ^1H NMR ($CDCl_3$) δ 1.03 (s, 3); 1.20 (s, 3), 1.30–1.58 (m, 5), 2.13–2.50 (m, 5); ^{13}C NMR ($CDCl_3$) δ 16.3 (J_{CH_3-H} = 126 Hz), 30.5, 32.1, 36.9, 40.7, 41.1; EI mass spectrum (80 eV, 25 °C), m/z (relative intensity) 160 (M^+·, 5), 145 (15), 122 (15), 105 (80) 91 (16), 81 (41), 80 (100), 79 (52), 77 (53), 59 (11), 44 (30). Anal. Calcd for $C_{12}H_{16}$: C, 90.0; H, 10.0. Found: C, 90.0; H, 10.2.

Decahydro-1,2,4-methenocyclobut[*cd*]indene (7).[11] Tricyclo[5.2.2.$0^{2,6}$]undeca-3,8-diene (**10**) was prepared in 40% yield according to Takaishi and Inamoto[26] [bp 58–62 °C (3 mm)] and subjected to column chromatography on alumina (*n*-hexane serving as eluent). The freshly purified diene (27.0 g) was irradiated in 1 L of analytical reagent grade acetone for 45 h with a Hanovia 450-W medium-pressure mercury lamp through a Vycor filter under N_2 at room temperature. The solvent was removed in vacuo and the residue chromatographed on silica gel impregnated with 3% silver nitrate (*n*-hexane serving as eluent). Sublimation of the first fraction [80 °C (1 mm)] afforded 4.05 g (15%) of colorless **7**; mp 112–114 °C (sealed tube); ^1H NMR ($CDCl_3$) δ 1.10–1.29 (m, 8), 2.00–2.30 (m, 6); ^{13}C NMR ($CDCl_3$) δ 18.3, 18.4, 30.9, 37.1, 38.0, 40.0, 40.3, 41.9, 42.2, 43.3; EI mass spectrum (80 eV, 25 °C), m/z (relative intensity) 146 (M^+·, 0.5), 91 (7.7), 80 (100), 79 (25.7). Anal. Calcd for $C_{11}H_{14}$: C, 90.4; H, 9.6. Found: C, 90.7; H, 9.7.

Octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene–Rhodium Dicarbonyl Chloride Adduct (4, R = H). A solution of 1.55 g of **2** (R = H) and 2.28 g of $Rh_2(CO)_4Cl_2$ in 40 mL of dry benzene was heated in a 100-mL pressure tube at 60 °C. After 50–60 min yellow crystals started to separate. After 24 h the adduct was filtered, washed with benzene and hexane to yield 3.80 g (99%) of pure **4** (R = H): mp 168–170 °C dec; IR (KBr) 2058 (C≡O), 1720 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{24}Cl_2O_4Rh_2$: C, 44.1; H, 3.7; Cl, 10.9. Found: C, 44.4; H, 3.7; Cl, 11.2.

Transformation of 4 (R = H) into Octahydro-1,3,5-metheno-1*H*-cyclopenta[*cd*]pentalen-2-one (3, R = H). Method A. A suspension of 65.3 mg of the acyl complex **4** (R = H) in 5 mL of CCl_4 and 105 mg of triphenylphosphine was heated at 60 °C for 15 min. The mixture was cooled and filtered to give 135 mg (98%) of $RhCl(CO)[P(C_6H_5)_3]_2$ of mp 195 °C [IR (Nujol) 1965 cm^{-1} (C≡O)]. The filtrate was concentrated and the residue was sublimed at 0.2 mm (100 °C) to yield 26 mg (99%) of **3** (R = H) that was identical in every respect with an authentic sample.[6]

Method B. A solution of 20 mg of **4** (R = H) in 2 mL of dimethyl sulfoxide was injected at 200 °C onto a GC column packed with 15% OV-101 on Chromosorb W, maintained at 140 °C. At the collector accumulated 4 mg (49%) of **3** (R = H) of the same physical properties as the sample obtained by method A.

Octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalen-3-ol–Rhodium Dicarbonyl Chloride Adduct (4, R = OH). As for **4** (R = H), a mixture of 43 mg of **2** (R = OH) and 68 mg of $Rh_2(CO)_4Cl_2$ in 1.5 mL of dry benzene was heated in a pressure tube at 68 °C. After 10 min, 92 mg (92%) of the yellow acyl complex **4** (R = OH) was collected by filtration: mp 135–137 °C dec; IR (Nujol) 3400 (OH), 2035 (C≡O), 1790 cm^{-1} (C=O); CI mass spectrum, m/z 684–689 (M^+· and MH^+), 657–661 [$(MH - CO)^+$], 629–633 [$(MH - 2CO)^+$], 573–577 [$(MH - 4CO)^+$], 177 ($C_{11}H_{13}O_2^+$). Anal. Calcd for $C_{24}H_{24}Cl_2O_6Rh_2$: C, 42.1; H, 3.5; Cl, 10.3. Found: C, 42.4; H, 3.7; Cl, 10.1.

4-Hydroxyoctahydro-1,3,5-metheno-1*H*-cyclopenta[*cd*]pentalen-2-one (3, R = OH). Treatment of 68.5 mg of **4** (R = OH) and 105 mg of triphenylphosphine in 5 mL of refluxing CCl_4 afforded after 15 min 13.8 mg (100%) of $RhCl(CO)(PPh_3)_2$ of mp 195 °C and 34 mg (100%) of **3** (R = OH): GC purification on 15% OV-101 on Chromosorb W; IR (CCl_4) 3450 (OH), 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.34 (d, 1, J = 10.5 Hz), 1.56 (d, 1, J = 10.5 Hz), 1.75 (m, 2), 2.14–2.57 (m, 6), 4.30 (s, 1); EI mass spectrum (70 eV, 70 °C), m/z (relative intensity) 176 (M^+·, 80), 174 (15), 158 (8), 157 (8), 154 (3), 153 (16), 152 (7), 150 (4), 133 (9), 132 (7), 131 (34), 130 (35), 129 (16), 117 (50) 91, (43), 82 (100), 66 (94), 51 (15). Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.8. Found: C, 75.1; H, 6.6.

An 80–90% yield of **3** (R = OH) was obtained upon pyrolysis of the rhodium complex **4** [R = OH) on a 2-m long GC column packed with 15% OV-101/Chromosorb W at 180 °C (injection port 240 °C).

Reaction of *anti*-3-(Acetyloxy)octahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene with $Rh_2(CO)_4Cl_2$. A mixture of 40 mg of **2** (R = $OCOCH_3$), 60 mg of $Rh_2(CO)_4Cl_2$, and 3 mL of dry benzene was heated in a pressure tube at 80 °C for 12 h. A few crystals that separated proved by CI mass spectrometry to contain the labile adduct **4** (R = $OCOCH_3$): m/z 710–715 (M^+· and MH^+ ions). The solution was filtered through alumina and separated on a preparative GC column packed with 15% OV-101/Chromosorb W at 200 °C to give 58% of *endo*, *anti*-3-(acetyloxy)tricyclo[5.2.1.$0^{2,6}$]-deca-4,8-diene (spectral data identical with an authentic sample)[23] and 30% of 4-(acetyloxy)octahydro-1,3,5-metheno-1*H*-cyclopenta[*cd*]pentalen-2-one (**3**, R = $OCOCH_3$): mp 48-50 °C [lit.[27] oil; bp 115–120 °C (0.25 mm)]; IR (Nujol) 1765 and 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.46 (d, 1, J = 10.5 Hz), 1.68 (d, 1, J = 10.5 Hz), 1.89 (m, 1), 2.02 (s, 3), 2.20 (m, 1), 2.33–2.67 (m, 6), 5.06 (s, 1);[27] EI mass spectrum (70 eV, 25 °C), m/z (relative intensity) 218 (M^+·, 15), 190 (9), 177 (3), 176 (16), 175 (6), 158 (12), 148 (6), 147 (4), 131 (21), 130 (68), 129 (21), 124 (15), 119 (4), 117 (9), 115 (13), 93 (16), 92 (60), 91 (19), 82 (100), 66 (52), 43 (94). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5. Found: C, 71.4; H, 6.4.

Reaction of Octahydro-1,2,4-metheno-3*H*-cyclobuta[*cd*]pentalen-3-one with $Rh_2(CO)_4Cl_2$.[28] A pressure tube was charged with 150 mg of **5**, 200 mg of $Rh_2(CO)_4Cl_2$, and 4 mL of

(25) Dilling, W. L.; Plepys, R. A.; Kroening, R. D. *J. Am. Chem. Soc.* **1972**, *96*, 8133.

(26) Takaishi, N.; Inamoto, Y.; Aigami, K.; Tsuchihashi, K.; Ikeda, H. *Synth. Commun.* **1974**, *4*, 225.

(27) Slightly different physical properties were reported for **3** [R = $OCOCH_3$) by Nakazaki: Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *43*, 689.

(28) The reaction of **5** and $Rh_2(CO)_4Cl_2$ in diglyme-d_{14} or in diphenyl ether at 140 °C was reported to give >95% of **9** but no **8**: Jones, G., II; Ramachandran, B. R. *J. Org. Chem.* **1976**, *41*, 798.

dry benzene and heated at 68 °C for 24 h. Upon cooling, the corresponding yellow acyl-rhodium complex separated (140 mg, 40% yield), but it proved difficult to purify: IR (Nujol) 2035 (C≡O), 1760, 1705 cm^{-1} (C=O); EI mass spectrum (15 eV, 180 °C), *m/z* 680, 682, 684 ($M^{+\cdot}$), 652, 654, 656 [$(M - CO)^{+\cdot}$], 624, 626, 628 [$(M - 2CO)^{+\cdot}$], 617, 619 [$(M - CO - Cl)^{+}$]; (70 eV, 130 °C, *m/z* (relative intensity) 568, 570, 572 [$(M - 4CO)^{+\cdot}$, 0.7], 540, 542, 544 [$(C_{19}H_{30}O)Rh_2Cl_2^{+\cdot}$, 0.3], 478, 480, 482 [$(C_{12}H_{10}O_3)Rh_2Cl_2^{+}$, 8.7], 450, 452, 454 [$(C_{11}H_{10}O_2)RhCl^{+}$, 14], 414, 416 [$(C_{11}H_9O_2)$-$Rh_2Cl^{+\cdot}$, 2], 386 [$(C_{10}H_9)Rh_2Cl^{+\cdot}$, 13], 241, 243 ($RhCl^{+}$, 6), 174 ($C_{11}H_{10}O_2^{+\cdot}$, 48), 146 ($C_{10}H_{10}O^{+\cdot}$, 48), 118 ($C_9H_{10}^{+\cdot}$, 85), 117 ($C_9H_9^{+}$, 100), 91 ($C_7H_7^{+}$, 33), 78 ($C_6H_6^{+\cdot}$, 46), 77 ($C_6H_5^{+}$, 80), 66 ($C_5H_6^{+\cdot}$, 52).

A solution of 140 mg of the adduct in hot benzene was treated with 150 mg of triphenylphosphine, the yellow rhodium complex was filtered off, and the filtrate was separated on 15% OV-101/Chromosorb W at 165 °C to give 21 mg (35% from the adduct) of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**9**) (identical in all properties with those of an authentic sample[10]) and 46 mg of octahydro-1,3,5-methenocyclopenta[*cd*]pentalen-2,4-dione (**8**); mp 213-214 °C (lit.[12] 213-214 °C); IR and ^1H NMR spectra were consistent with those reported;[12] EI mass spectrum (70 eV, 25 °C), *m/z* (relative intensity) 174 ($M^{+\cdot}$, 40), 146 (20), 118 (85), 117 (100), 115 (30), 91 (35), 77 (25), 76 (25), 68 (40), 65 (30), 64 (25), 50 (30), 38 (55).

Reaction of Decahydro-1,2,4-methenocyclobut[*cd*]indene with $Rh_2(CO)_4Cl_2$. A mixture of 520 mg of **7**, 680 mg of $Rh_2(CO)_4Cl_2$ and 25 mL of dry benzene was heated in a pressure tube at 80 °C. After 72 h the dark solution was filtered through alumina and separated on 15% OV-101/Chromosorb W at 200 °C to give 286 mg (56%) of **10**[26] and 171 mg (28%) of colorless decahydro-1,3,5-metheno-1*H*-cyclopent[*cd*]inden-2-one (**11**): mp 128-130 °C; IR (CCl_4) 1766 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.488-1.569 (m, H_4, $H_{4'}$, H_6, $H_{6'}$), 1.588 (7, H_{4a}), 1.685 (m, H_7, $H_{7'}$), 1.821 (m, H_5, H_{7b}), 1.970 (m, H_8), 2.144 (m, H_{7a}), 2.314 (m, H_{2a}, H_3), 2.562 (m, H_1). Anal. Calcd for $C_{12}H_{14}O$: C, 82.8; H, 8.1. Found: C, 82.8; H, 8.0.

Conversion of 3,5-Dimethyloctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (6) into *endo*-3,10-Dimethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (12). A mixture of 120 mg of **6**, 60 mg of $Rh_2(CO)_4Cl_2$, and 3 mL of benzene was heated in a pressure tube at 110 °C for 48 h. Preparative GC on 15% OV-101/Chromosorb W (130 °C) afforded 80% of diene **12** as the sole product (identical with the commercial compound).

Conversion of *anti*-3-Chlorooctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (2, R = Cl) into *endo,anti*-3-Chlorotricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (1, R = Cl). As in the previous experiment 20 mg of **2** (R = Cl), 26 mg of $Rh_2(CO)_4Cl_2$, and 1 mL of benzene were heated at 80 °C for 5 days. GC analysis indicated the formation of **1** (R = Cl)[9] as the only product.

Kinetic Measurements. Typically a solution of 38.5 mg (0.292 mmol) of **2** (R = H) in 0.5 mL of dry degassed benzene was heated under argon in a divided airless reaction tube with the aid of an oil bath regulated at 68 ± 0.05 °C. After 20 min the solution was admixed with a solution of 56.7 mg (0.292 mequiv) of $[Rh(CO)_2Cl]_2$ and 10 μL of *n*-decane (internal standard) in 1 mL of benzene that was preheated in the second part of the reaction vessel. Samples (1-2 μL) were withdrawn periodically from the reaction mixture and immediately frozen at -78 °C. GC analysis was performed on a Varian-Aerograph Model 2800/FID instrument equipped with a 10-cm glass precolumn (to avoid any reaction from taking place at the injection port) and a 10% FFAP/Chromosorb W capillary column. The initial rates were calculated in each case from the average of at least three experiments.

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Registry No. **1** (R = H), 1755-01-7; **1** (R = OH), 29846-26-2; **1** (R = $OCOCH_3$), 88669-65-2; **2** (R = H), 6707-86-4; **2** (R = Cl), 51965-71-0; **2** (R = OH), 15776-05-3; **2** (R = $OCOCH_3$), 55399-45-6; **3** (R = H), 56061-32-6; **3** (R = OH), 88669-66-3; **3** (R = $OCOCH_3$), 64706-13-4; **4** (R = H), 88669-69-6; **4** (R = OH), 88685-60-3; **4** (R = O), 88685-61-4; **5**, 15584-52-8; **6**, 88669-67-4; **7**, 62415-12-7; **8**, 57237-87-3; **9**, 5530-96-1; **10**, 54483-01-1; **11**, 88669-68-5; **12**, 10312-72-8; triphenylphosphine, 603-35-0; $Rh_2(CO)_4Cl_2$, 14523-22-9.

Supplementary Material Available: Table of mass spectral fragmentation data for complex **4** formed from **2** (R = H) and $Rh_2(CO)_4Cl_2$ (1 page). Ordering information is given on any current masthead page.

Sucrose Chemistry.† A Synthetically Useful Monoarenesulfonation[1a]

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The reaction of sucrose with 2,4,6-triisopropylbenzenesulfonyl chloride (tripsyl chloride) occurred preferentially at the 6'-OH group yielding crystalline 6'-*O*-tripsylsucrose (**2a**) in 39% yield without chromatography. The structure of **2a** was proven by the conversion of **2a** to the known 6'-amino-6'-deoxysucrose (**2d**) and by acid-catalyzed methanolysis which gave methyl 6-*O*-tripsyl-α- and -β-D-fructofuranoside. Also, ^1H-coupled ^{13}C NMR spectroscopy proved to be generally useful for determining substitution patterns at positions 6, 6', and 1' of sucrose. Kinetic studies of the tripsylation reaction revealed the relative reactivities of the primary OH groups at 6', 6, and 1' to be 3.5:1.0:0.16.

Selective reactions that distinguish between the hydroxyl groups of sucrose (**1a**) continue to be sought (see Chart I). The impetus for this search is derived from interest in the use of sucrose derivatives as noncaloric sweetening agents,[2] bacterial enzyme inhibitors,[3] surfactants,[4] food additives,[4] and resins,[4] and in other industrial applications.[4] Interest is still focused on selective derivatization of the three

† Dedicated to Professor Calvin L. Stevens on the occasion of his 60th birthday.

(1) (a) A preliminary account of some of this work has been presented: Taylor, K. G.; Doyle, R. J.; Singh, S.; Maynard, C. M. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March 29-April 3, 1981; American Chemical Society: Washington, D.C., 1981; CARB 33. (b) Department of Microbiology and Immunology.

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