Rhodium(I)-Catalyzed Rearrangements of Strained Molecules Containing Fused Cyclobutane Rings

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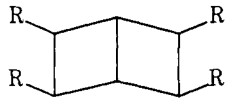
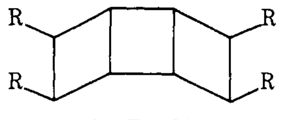
Abstract: [$Rh_2(NOR)_2Cl_2$] and [$Rh_2(COD)_2Cl_2$] catalyze the rearrangement of bicyclo[2.2.0]hexane (**1**) to cyclohexene; the corresponding rearrangement of *exo*-2,3,5,6-tetradeuterio-**1** yields 3,4,5,6-tetradeuteriocyclohexene. These observations are accommodated by a mechanistic scheme involving the initial rate-determining oxidative addition of the strained 1,4-carbon-carbon bond of **1** to Rh(I), followed by β-carbon-to-rhodium hydrogen migration and reductive elimination reactions of the resulting metallocyclic oxidative adduct. The stoichiometric reaction of [$Rh_2(CO)_4Cl_2$] with **1** yields an acyl oxidative adduct which is decomposed by PPh_3 to yield 3-cyclohexene-1-carboxaldehyde. The corresponding [$Rh_2(NOR)_2Cl_2$]-catalyzed rearrangement of *syn*-tricyclo[4.2.0.0^{2,5}]octane(**2**) yields a ca. 2:1 mixture of bicyclo[4.2.0]oct-2-ene and 1,5-cyclooctadiene, the former apparently arising from a pathway similar to that for the rearrangement of **1** to cyclohexene, while the latter arises from a parallel rearrangement of the common intermediate oxidative adduct. Both [$Rh_2(NOR)_2Cl_2$]-catalyzed rearrangements exhibited second-order rate laws, i.e., rate = k[**1** or **2**][$Rh_2(NOR)_2Cl_2$], with $k = 7.3 \times 10^{-2}$ and 7.6×10^{-2} M^{-1} s^{-1} for **1** and **2**, respectively, in $CDCl_3$ at 40 °C. The reactivity patterns for different substrates containing fused cyclobutane rings are interpreted and compared.

Introduction

The interaction of metal complexes, notably of rhodium(I) and silver(I), with strained carbocyclic compounds containing fused cyclobutane and cyclopropane rings has been a subject of considerable interest and controversy.[1] Complexes of these metals catalyze a variety of rearrangements of such compounds, which are thermally disallowed according to the rules of "orbital-symmetry conservation" and the course of which depends both on the nature of the organic compound and of the metal complex. In this paper we describe extensions of earlier studies[2] in our laboratory on the rhodium(I)-catalyzed rearrangements of cubane and its derivatives to related systems, notably bicyclo[2.2.0]hexane (**1**) and *syn*-tricyclo[4.2.0.0^{2,5}]octane (**2**). The objective of these studies was the systematic examination of the influence of structural features, notably the number and arrangement of fused cyclobutane rings, and the effect of cage constraints, on the rate and course of such rearrangements. Pertinent earlier publications, in addition to that on cubane (**3**), include those describing related studies on the rhodium-catalyzed rearrangements of other saturated compounds containing cyclobutane rings, notably quadricyclane,[3,4] tricyclooctanes,[5] hexamethylprismane,[6] homo-[7] and bishomocubanes,[8,9] and bicyclopentanes.[10,11]



1a, R = H
b, R = D



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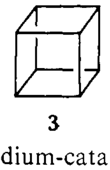

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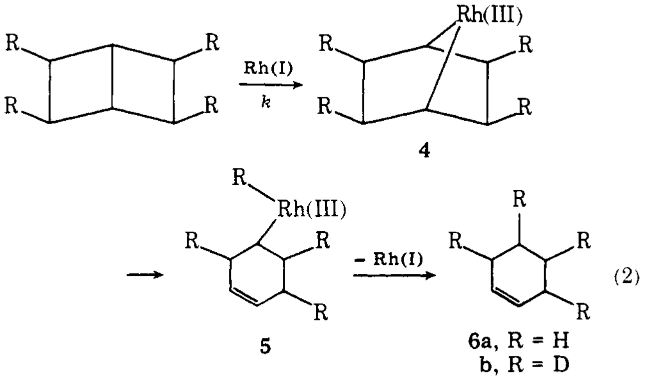
Results and Discussion

Bicyclo[2.2.0]hexane (1). Treatment of a benzene or chloroform solution of **1a** with catalytic amounts (ca. 0.01 M) of [$Rh_2(NOR)_2Cl_2$] (NOR = norbornadiene) resulted in quantitative conversion to cyclohexene in several hours. The kinetics of the reaction obeyed the second-order rate law, eq 1, with $k = 7.3 \pm 0.4$ M^{-1} s^{-1} in $CDCl_3$ at 40 °C, unaffected by variation of the concentration of **1** (0.16 to 0.39 M) or of [$Rh_2(NOR)_2Cl_2$] (4.5×10^{-3} to 9×10^{-3} M). [$Rh_2(COD)_2Cl_2$], where COD = 1,5-cyclooctadiene, catalyzed the same rearrangement, but at a significantly lower rate ($k \simeq 6.5 \times 10^{-3}$ M^{-1} s^{-1} at 120 °C in benzene).

$$-d[\mathbf{1}]/dt = k[\mathbf{1}][Rh_2(NOR)_2Cl_2] \qquad (1)$$

The corresponding rearrangements of **1b** yielded exclusively 3,4,5,6-tetradeuteriocyclohexene (**6b**), identified by ^1H and ^{13}C NMR. These observations are readily accommodated by the mechanistic scheme of eq 2 involving rate-determining oxidative addition of a strained C–C bond, followed by β-hydrogen migration and reductive elimination.



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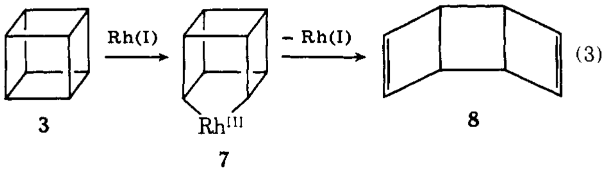
5

6a, R = H
b, R = D

(2)

All the steps of the above sequence are familiar processes in organometallic chemistry. The first step (i.e., oxidative addition) is similar to that previously postulated in the Rh(I)-catalyzed rearrangement of cubane (**3**) to *syn*-tricyclo[4.2.0.0]octa-3,7-diene (**8**) (eq. 3).[2] The different courses of rearrangement of cubane and bicyclo[2.2.0]hexane, beyond the common initial oxidative addition step, presumably reflect the barrier to β-hydrogen migration imposed by the cage structure of **7**, and the absence of a second strained car-



3 **7** **8** (3)

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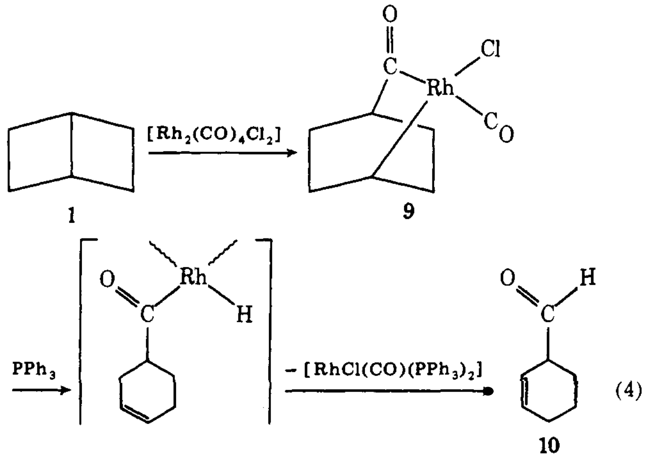
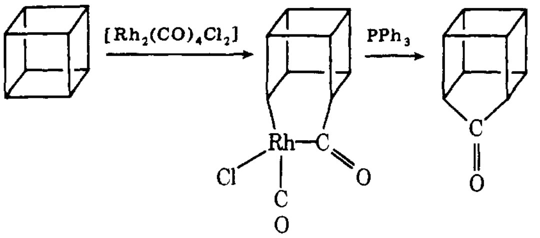
bon-carbon bond in the corresponding intermediate oxidative adduct, **4**, derived from bicyclo[2.2.0]hexane.

Corresponding parallels and differences between cubane and bicyclo[2.2.0]hexane were observed in the reactions of the two compounds with $[Rh_2(CO)_4Cl_2]$. Treatment of **1a** with a stoichiometric amount of $[Rh_2(CO)_4Cl_2]$ in carbon tetrachloride at 40 °C yielded a compound whose analytical composition and infrared spectrum (ν_{CO} 2028 and 1726 cm^{-1}) were consistent with the acyl compound, **9** (eq 4), which is



(4)

analogous to the product of the corresponding reactions of $[Rh_2(CO)_4Cl_2]$ with cubane (eq 5),[7] quadricyclane,[4] and cyclopropane.[12] However, in contrast to the corresponding reaction of the cubane adduct to yield homocubanone (eq 5),[2]



(5)

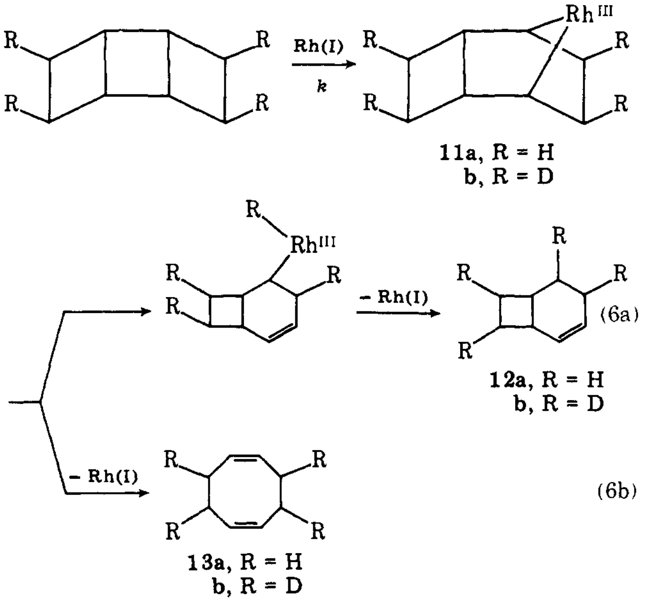
the bicyclohexane adduct **9** reacted with Ph_3P to yield 3-cyclohexene-1-carboxaldehyde (**10**). No 7-norbornanone could be detected by GLC.

The above reaction of **1** with $[Rh_2(CO)_4Cl_2]$ differs significantly from the corresponding reactions reported for bicyclo[2.1.0]pentanes,[10,11] which undergo *catalytic* rearrangement to cyclopentenes presumably by mechanisms analogous to that of eq 2 but (in contrast to the latter) with apparent extensive scrambling of deuterium labels. No intermediate acyl adducts (i.e., analogous to **9**) were reported for the bicyclopentane compounds. The origin of these differences between bicyclo[2.2.0]hexane and bicyclo[2.1.0]pentane is unclear.

***syn*-Tricyclo[4.2.0.0^{2,5}]octane (2).** As already noted, the different courses of rearrangement of cubane and bicyclo[2.2.0]hexane beyond the common initial oxidative addition step, as depicted by eq 2 and 3, respectively, presumably reflect the barrier to β-hydrogen migration imposed by the cage structure of **7** and the absence of a second strained carbon-carbon bond in the corresponding intermediate metallocyclic oxidative adduct **4**, derived from bicyclo[2.2.0]hexane. Accordingly, it was of some interest to examine the related chemistry of *syn*-tricyclo[4.2.0.0^{2,5}]octane, for which *both* pathways are possible. Some observations on the rhodium(I)- and silver(I)-catalyzed rearrangement of this compound have already been reported by Wristers, Brener, and Pettit.[5]

Treatment of a benzene or chloroform solution of *syn*-tricyclo[4.2.0.0^{2,5}]octane (**2a**) with catalytic amounts (ca. 0.05 M) of $[Rh_2(NOR)_2Cl_2]$ for about 2 h at 40 °C resulted in complete conversion to a mixture of the bicyclooctene (**12a**, ca. 70%) and 1,5-cyclooctadiene (**13a**, ca. 30%). These results are substantially in agreement with those of Wristers et al.,[5] although we were unable to detect the minor saturated product (ca. 2% tetrahydrosemibullvalene) reported by the latter authors. Essentially similar product distributions were obtained under the same conditions using $[Rh_2(COD)_2Cl_2]$ or $[Rh_2(CO)_4Cl_2]$ as catalysts.

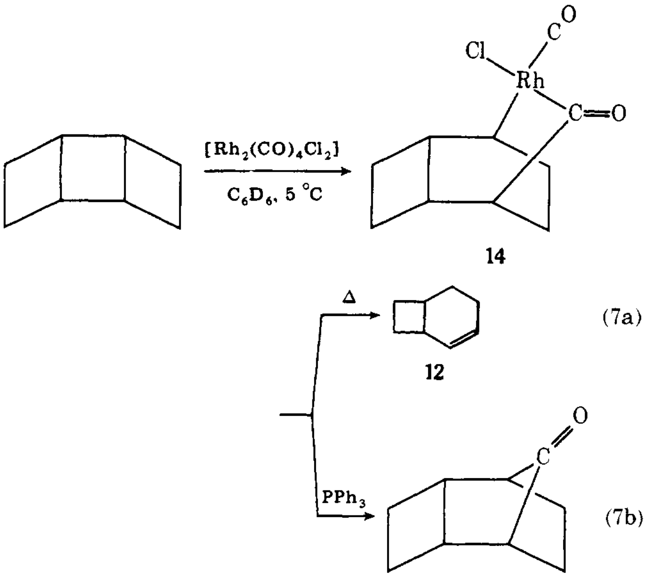
The corresponding rearrangements of the tetradeuterio compound, **2b**, yielded the products **12b** and **13b**. These observations can be accommodated by the mechanistic scheme of eq 6, which involves an initial rate-determining oxidative addition step, followed by partitioning of the rearrangement of the resulting metallocyclic oxidative adduct, **11b**, along parallel pathways (eq 6a and 6b) analogous to those previously



identified for cubane and for bicyclo[2.2.0]hexane, respectively.[13]

Kinetic measurements on the $[Rh_2(NOR)_2Cl_2]$-catalyzed reaction were complicated by exchange of the catalyst with the 1,5-cyclooctadiene product to form $[Rh_2(COD)_2Cl_2]$, which is a less effective catalyst, resulting in an apparent decrease in the catalytic rate constant as the reaction proceeded.[14] This complication was circumvented by the initial addition of an excess of norbornadiene to suppress the exchange. The rate law under these conditions was found to be similar to that for the rearrangement of **1**, i.e., eq 1, with $k = 7.6 \pm 0.3$ M^{-1} s^{-1} in $CDCl_3$ at 40 °C, unaffected by variation of the concentration of **2b** (0.14 to 0.29 M), of $[Rh_2(NOR)_2Cl_2]$ (3×10^{-3} to 6×10^{-3} M), or of added norbornadiene. The corresponding rate constant in benzene was significantly lower ($6.6 \pm 0.3 \times 10^{-3}$ M^{-1} s^{-1} at 50 °C) and the rate constant for the $[Rh_2(COD)_2Cl_2]$-catalyzed rearrangement was much lower (6.9×10^{-3} M^{-1} s^{-1} at 120 °C in benzene).

In contrast to its formation of stable adducts with cubane[2] and with bicyclo[2.2.0]hexane under the same conditions, $[Rh_2(CO)_4Cl_2]$ was found to catalyze the rearrangement of **2** to the same products as $[Rh_2(NOR)_2Cl_2]$ or $[Rh_2(COD)_2Cl_2]$ at temperatures above 20 °C. However, the formation of a stable, isolable adduct, whose infrared spectrum (ν_{CO} 1712 and 2000 cm^{-1}),^{1}H NMR spectrum, analytical composition, and chemical reactions (see below) all are consistent with the structure **14**, was achieved by reacting **2a** with a stoichiometric amount of $[Rh_2(CO)_4Cl_2]$ in benzene *at 5 °C*. Warming this compound until decomposition in benzene resulted in the formation of **12** in ca. 90% yield. Treatment of a methylene chloride or benzene-pentane solution of **14** with excess PPh_3 resulted in the formation of ca. 20-30% of *endo*-tricyclo[4.2.1.$0^{2,5}$]octan-9-one (**15**), together with varying amounts of **12**, **13**, and other unidentified products (eq 7).



14

12 (7a)

15 (7b)

In agreement with Wristers et al.,[5] no reaction of *anti*-tricyclo[4.2.0.$0^{2,5}$]octane (**16**) could be detected in benzene solutions containing 0.05 M $[Rh_2(NOR)_2Cl_2]$ at 63 °C after 20 h. However, in contrast to the report of these workers, we also detected no reaction of $[Rh_2(CO)_4Cl_2]$ with **16** in $CHCl_3$ (20 h at 25 °C or 5 h at 80 °C) following rigorous purification of **16** (including treatment with $AgClO_4$ in benzene at 50 °C for 3 h to decompose traces of the syn isomer). Although steric factors are clearly expected to contribute to this markedly lower reactivity of *anti*-tricyclo[4.2.2.$0^{2,5}$]octane, relative to the syn isomer, it has been suggested that electronic factors also may be involved.[15]

Discussion. The rhodium(I)-catalyzed rearrangements of bicyclo[2.2.0]hexane (**1**), *syn*-tricyclo[4.2.2.$0^{2,5}$]octane (**2**), and cubane all are accommodated by mechanistic schemes which have in common an initial rate-determining step involving the oxidative addition to rhodium(I) of a strained carbon-carbon bond shared by two fused cyclobutane rings. The subsequent rearrangement to cyclohexane, in the case of **1**, involves a β-hydrogen migration-reductive elimination sequence, whereas the rearrangement to *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene in the case of **3** (where β-hydrogen migration is precluded by the cage structure) is the consequence of cleavage of a second strained carbon-carbon bond of the intermediate metallocyclic oxidative adduct. The partitioning of the rearrangement of **2** to yield a ca. 2:1 mixture of the products **12** and **13** reflects comparable contributions from the two alternative rearrangement pathways of the oxidative adduct when the substrate is such that both pathways are accessible.

The kinetic data summarized in Table I permit direct comparison of the rate constants for the $[Rh_2(NOR)_2Cl_2]$-catalyzed rearrangement of all three substrates in $CDCl_3$ at 40 °C, i.e., 7.3×10^{-2}, 7.6×10^{-2}, and 14 $M^{-1}\ s^{-1}$, for **1**, **2**, and **3**, respectively. The rate constants for **1** and **2** are virtually identical, whereas that for **3** is ca. 200 times higher, presumably reflecting the enhanced strain and reactivity conferred by the cubane cage structure. (The corresponding rate constant for the $[Rh_2(NOR)_2Cl_2]$-catalyzed rearrangement of quadricyclane to norbornadiene is 2.2 $M^{-1}\ s^{-1}$.)[4] No reaction of cyclobutane was detected when the latter was treated with ca. 0.05 M $[Rh_2(NOR)_2Cl_2]$ at 120 °C for 20 h. Thus, bicyclo[2.2.0]hexane is the least strained cyclobutane derivative thus far reported to exhibit rhodium(I)-catalyzed rearrangements of this general type.

Table I. Summary of Kinetic Data

substrate	catalyst	temp, °C	solvent	k, M^{-1} s^{-1}
1b	$[Rh_2(NOR)_2Cl_2]$	40	$CDCl_3$	7.3×10^{-2}
	$[Rh_2(COD)_2Cl_2]$	120	C_6D_6	6.4×10^{-3}
2b	$[Rh_2(NOR)_2Cl_2]$	40	$CDCl_3$	7.6×10^{-2}
	$[Rh_2(NOR)_2Cl_2]$	50	C_6D_6	6.6×10^{-3}
	$[Rh_2(COD)_2Cl_2]$	120	C_6D_6	6.9×10^{-3}
	$[Rh_2(CO)_4Cl_2]$	50	$CDCl_3$	4.6×10^{-3}
3[a]	$[Rh_2(NOR)_2Cl_2]$	40	$CDCl_3$	14
3	$[Rh_2(NOR)_2Cl_2]$	40	CCl_4	2.6×10^{-1}

[a] Data for cubane from ref 2. Other data from this work.

Among the features of these rhodium(I)-catalyzed rearrangements that remain to be explained is the marked influence of ligand variation on the catalytic activities of different rhodium(I) complexes. Even modest ligand variations such as that involved in going from $[Rh_2(NOR)_2Cl_2]$ to $[Rh_2(COD)_2Cl_2]$ can markedly influence the catalytic activity to an extent that depends strikingly on the substrate. Thus, the ratio of the catalytic rate constants for these two complexes (k_{NOR}/k_{COD}) is only ca. 3.5 for 1,4-dimethylcubane,[2] but very much larger for **1** and **2** (Table I), as well as for quadricyclane.[14] The origin of these differences is presently unclear.

Experimental Section

General Methods. Melting points were taken with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR10 spectrometer and are reported in wavenumbers (cm^{-1}) calibrated relative to the 1602-cm^{-1} line of polystyrene. ^1H magnetic resonance spectra were recorded on a Varian A-60A or a Bruker HX-270 spectrometer, and are reported in parts per million (δ) from internal Me_4Si. ^{13}C magnetic resonance spectra were obtained with a JEOL FX-60Q spectrometer using Me_4Si as standard. Preparative VPC was performed with a Varian 920 chromatograph equipped with a thermal conductivity detector using the following columns: (A) 10 ft × 0.25 in. 18% OV 101 on 60/80 mesh Chromosorb W; (B) 7 ft × 0.25 in. 20% Carbowax 20M on 60/80 mesh Chromosorb P; (C) 10 ft × 0.25 in. 20% FFAP on 60/80 mesh Chromosorb W. Elemental analyses were performed by Galbraith Labs, Inc. All manipulations of metal complexes were performed under an inert atmosphere of nitrogen or argon.

Materials. $[Rh_2(CO)_4Cl_2]$ was purchased from Strem Chemical Co. and sublimed or recrystallized from benzene prior to use. $[Rh_2(NOR)_2Cl_2]$ and $[Rh_2COD)_2Cl_2]$ were prepared as described[16] from rhodium trichloride hydrate and the corresponding diene. Cyclobutane and 3,4-dichlorocyclobutene were obtained from Chemical Samples Co. and 3-cyclohexene-1-carboxaldehyde was purchased from Aldrich Chemical Co.

Bicyclo[4.2.0]oct-2-ene (12a) was prepared by the method of Cope.[17] The pyrolysis of the *S*-methyl xanthates of the isomeric bicyclo[4.2.0]octan-2-ols yields **12a**.

***endo*-Tricyclo[4.2.1.$0^{2,5}$]nonan-9-one (15)** was synthesized, following the procedure of Sakai,[18] from bicyclo[4.2.1]nona-2,4,7-trien-9-one,[19] which was prepared by the reaction of lithium cyclooctatetraenide and dimethylcarbamoylchloride.

Bicyclo[2.2.0]hexane (1a and 1b). These compounds were prepared by a modification of the synthesis of Dewar benzene as described in the literature.[20]

***syn*-Tricyclo[4.2.0.$0^{2,5}$]octane (2a and 2b).** *syn*-Tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene was prepared according to the literature procedure[21] by coupling 3,4-dichlorocyclobutene with 0.5% sodium amalgam. The resultant diene was purified by preparative VPC (column A at 70 °C). A mixture of *syn*-tricyclooctadiene (430 mg, 4.1 mmol) in 10 of pentane at 25 °C was reduced with hydrogen at low pressure in the presence of platinum oxide (100 mg). The catalyst was removed by filtration, and the residual solution was reduced in volume by fractional distillation and purified by preparative VPC (column A, 70 °C) to yield 0.40 g (88%) of pure **2a**: NMR (270 MHz,

C_6D_6) δ 2.30 (t of multiplets, $J = 0.9$ Hz, 4 H), 2.56 (d, $J = 0.9$ Hz, 4 H), 2.96 (br s, 4 H). When the reduction was performed using deuterium, **2b** was isolated: NMR (C_6D_6) δ 1.86 (br s, 4 H), 2.30 (br s, 4 H). Anal. ($C_8H_8D_4$) C, H + D.

***anti*-Tricyclo[4.2.0.0^{2,5}]octane (16).** *anti*-Tricyclo[4.2.0.0^{2,5}]-octa-3,7-diene was obtained by coupling 3,4-dichlorocyclobutene using 0.5% lithium amalgam following the literature procedure.[21] The *anti*-tricyclooctadiene was then hydrogenated by the same method as used for the reduction of the syn isomer. Purification by VPC (column A, 70 °C) yielded **16** (90%): NMR (270 MHz, C_6D_6) δ 1.91 (m, 4 H), 2.46 (m, 4 H), 2.71 (m, 4 H).

Bicyclo[2.2.0]hexane–Rhodium Dicarbonyl Chloride Adduct (9). A solution of **1a** (50 mg, 0.61 mmol) and $[Rh_2(CO)_4Cl_2]$ (58 mg, 0.15 mmol) in 1 mL of carbon tetrachloride was heated for 10 h at 40 °C. The reaction mixture was cooled to room temperature, and the resulting yellow precipitate was separated by filtration and washed with carbon tetrachloride. This yellow solid was recrystallized from benzene and *n*-pentane. Light orange crystals of **9** (65 mg, 88%) were isolated: mp 105–107 °C dec; IR (CCl_4) ν(terminal CO) 2028 cm^{-1} (vs), ν(inserted CO) 1726 cm^{-1} (vs); NMR (C_6D_6) δ 0.8–3.1 (br m). Anal. ($C_8H_{10}ClO_2Rh$) C, H, Cl.

Triphenylphosphine-Induced Decomposition of the Acyl Rhodium Complex (9). A solution of triphenylphosphine (53 mg, 0.20 mmol) in 1 mL of methylene chloride was added by syringe to 2 mL of a methylene chloride solution of **9** (27 mg, 0.10 mmol). The solution was stirred for 4 h at room temperature. The precipitate of $[Rh(PPh_3)_2(CO)Cl]$ was removed by filtration, and the residual methylene chloride solution was subjected to VPC separation on column B at 100 °C. The only product isolated was **10** (7.0 mg, 65%). No peak was detected with the same retention time as an authentic sample of 7-norbornanone.[22]

Thermal Decomposition of the Acyl Rhodium Complex (9). The acyl complex **9** (25 mg, 0.09 mmol) was dissolved in 1 mL of benzene. The solution was heated at 60 °C for 16 h. The only product isolated by VPC using column C at 35 °C was cyclohexene (65%).

***syn*-Tricyclo[4.2.0.0^{2,5}]octane–Rhodium Dicarbonyl Chloride Adduct (14).** A solution of **2a** (100 mg, 0.93 mmol) and $[Rh_2(CO)_4Cl_2]$ (150 mg, 0.39 mmol) in 5 mL of dry benzene was stored at 5 °C for 24 h. The solvent was removed in vacuo from the resultant yellow solution. The residue was recrystallized twice from benzene and *n*-pentane. Light orange crystals of **14** (154 mg, 65%) were isolated: mp 138–140 °C dec; IR (nujol mull) ν(terminal CO) 2000 cm^{-1} (vs), ν(inserted CO) 1712 cm^{-1} (vs); NMR ($CDCl_3$) δ 1.4–2.6 (br m, 10 H), 4.3 (m, 2 H), Anal. ($C_{10}H_{12}ClO_2Rh$) C, H, Cl.

Triphenylphosphine-Induced Decomposition of the Acyl Rhodium Complex (14). Compound **14** (304 mg, 1.0 mmol) was dissolved in a 1:1 mixture of benzene and *n*-pentane (7 mL). The solution was cooled to −30 °C. Triphenylphosphine (2.1 g, 8.0 mmol) was added and the mixture was warmed to room temperature. Following removal of the solvent in vacuo, the residue was extracted with *n*-pentane. The pentane solution, subjected to VPC separation using column B at 150 °C, yielded 26 mg (19%) of *endo*-tricyclooctan-9-one (**15**) identified by comparison with an authentic sample. (Some of the other products were **12a** and **13a**.)

Thermal Decomposition of the Acyl Rhodium Complex (14). A benzene solution (0.5 mL) of **14** (25 mg, 0.08 mmol) was heated at 140 °C in a sealed ampule for 1 h. The product was collected by VPC using column A at 85 °C. The only detectable product was **12a.**

The Rhodium(I)-Catalyzed Isomerization of Bicyclo[2.2.0]hexane (1). $[Rh(NOR)Cl]_2$ (30 mg, 0.07 mmol) and **1a** (100 mg, 1.25 mmol) in 1 mL of benzene were heated at 50 °C for 4 h in a sealed ampule. The solution was cooled to room temperature and a sufficient quantity of *n*-pentane was added to precipitate the rhodium complex. Preparative VPC of the residual pentane solution after filtration, using column C at 30 °C, yielded cyclohexene (>90%) as the only product of this rearrangement. This procedure was repeated using **1b** and $[Rh(NOR)Cl]_2$ at 50 °C and **1b** and $[Rh(COD)Cl]_2$ at 120 °C. In the presence of both catalysts starting material **1b** could be recovered without any scrambling of deuterium labels during the rearrangement of **1b** to **6b.** Compound **6b** was isolated by preparative VPC (column C at 30 °C) from the reactions of **1b** with both rhodium catalysts: ^1H NMR ($CDCl_3$) δ 1.6 (m, 2 H), 1.9 (m, 2 H), 5.6 (d, $J = 1.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.3 (t, $J = 19.5$ Hz, 2 C), 24.9 (t, $J = 19.5$ Hz, 2 C), 127.4 (s, 2 C).

The Rhodium(I)-Catalyzed Isomerization of *syn*-Tricyclo-[4.2.0.0^{2,5}]octane (2). $[Rh_2(NOR)_2Cl_2]$ (35 mg, 0.08 mmol) and **2a** (135 mg, 1.25 mmol) in 1 mL of benzene were heated at 50 °C in a sealed ampule for 3 h. The solution was cooled to room temperature, and a sufficient quantity of *n*-pentane was added to precipitate the rhodium catalyst. The solution was then filtered and concentrated by fractional distillation. VPC analysis (column A at 70 °C and B at 85 °C) showed that a mixture of ~19% norbornadiene (displaced from the catalyst by the product **13**), ~12% **13a,** and ~67% **12a** (identical with authentic samples) was formed.

This experiment was repeated, in the manner described above, with compound **2b.** The products were separated using preparative VPC (column C at 85 °C). The first peak (~19%) was identical with an authentic sample of norbornadiene. The second peak (~67%) was identified as **12b:** NMR (270 MHz, CCl_4) δ 1.50 (m, 2 H), 1.73 (m, 1 H), 2.02 (br s, 1 H), 2.57 (m, 1 H), 5.69 (br s, 2 H). Anal. ($C_8H_8D_4$) C, H + D. The third peak (12%) was identified as **13b:** NMR (270 MHz, CCl_4) δ 2.31 (br s, 4 H), 5.47 (br s, 4 H).

When the reaction mixture was prepared with a 10 M excess of norbornadiene relative to $[Rh_2(NOR)_2Cl_2]$, **13b** was isolated (~33%).

A solution containing $[Rh_2(COD)_2Cl_2]$ (40 mg, 0.08 mmol) and **2b** (208 mg, 1.86 mmol) in 1 mL of benzene was heated in a sealed ampule for 6 h at 120 °C. After cooling the solution to room temperature, *n*-pentane was added to precipitate the rhodium catalyst. The resulting mixture was filtered and the products were separated using preparative VPC (column B at 85 °C). The first peak (~66%) corresponded to **12b.** The second peak (~34%) corresponded to a mixture of **13a** and **13b:** NMR ($CDCl_4$) δ 2.31 (br s, 1.3 H), 5.47 (br s, 1 H).

A solution of **2b** (40 mg, 0.36 mmol) and $[Rh_2(CO)_4Cl_2]$ (18.5 mg, 0.05 mmol) in 0.5 mL of benzene was stored at 5 °C for 24 h. The solution was then treated with *n*-pentane. The only product isolated from this reaction corresponded to **12b** (18%).

In the presence of $[Rh(NOR)Cl]_2$ and $[Rh(COD)Cl]_2$ starting material **2b** could be recovered without scrambling of deuterium during the rearrangement of **2b.**

Kinetics. All kinetic measurements were performed on VPC purified hydrocarbons, in dried NMR spectral grade deuterated solvents. The reaction solutions were prepared in a nitrogen atmosphere in NMR tubes which were sealed and inserted into a variable temperature Varian A-60A NMR probe. About 10 min was allowed for temperature equilibration prior to measurement of the rates of rearrangement. At 5–15-min intervals, the spectrum was integrated and compared to a measured internal standard of undeuterated solvent. Rates of rearrangement of **1b** and **2b** were monitored by following the decrease of the absorption at lowest field. First-order rate plots (i.e., plots of the logarithm of the concentration of the organic substrate vs. time) remained linear for at least 3 half-lives. The measured rate constants are reported in Table I.

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(13) The absence of a significant deuterium kinetic isotope effect for the $[Rh_2(CO)_4Cl_2]$-catalyzed rearrangement of **2** (i.e., $k_{2a} = k_{2b} = 8.6 \pm 0.4 \times 10^{-3}\ M^{-1}\ s^{-1}$ in C_6D_6 at 50 °C) is consistent with this interpretation.

(14) The equilibrium constant for the substitution reaction, $(1/2)[Rh(NOR)Cl]_2 + COD \rightleftharpoons (1/2)[Rh(COD)Cl]_2 + NOR$, is approximately 1 (J. Halpern and M. Takagi, unpublished results).

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Anomalous Rates of Proton Transfer to and from Nitrogen and Carbon in the Reactions of Amines with 1,1-Dinitro-2,2-diphenylethylene

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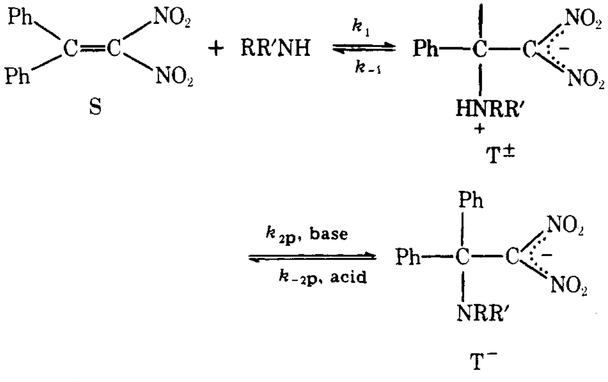
Abstract: Two kinetic processes are observed in the reactions of 1,1-dinitro-2,2-diphenylethylene with piperidine, morpholine, *n*-butylamine, and aniline in 50% aqueous dimethyl sulfoxide. The first, relatively fast and reversible, refers to nucleophilic addition of the amine to the 2 position of 1,1-dinitro-2,2-diphenylethylene to form a zwitterionic addition complex ($T^\pm$), which is subsequently deprotonated to the anionic addition complex (T^-). In the piperidine and *n*-butylamine reactions proton transfer is fast and nucleophilic attack is rate determining; in the morpholine and aniline reactions proton transfer is partially rate limiting. The second kinetic process, which is relatively slow, refers to protonation of T^- on carbon to form T^0, followed by rapid and irreversible cleavage of T^0 into $Ph_2C{=}O$ and $^-CH(NO_2)_2$. The rate constants for the various elementary steps were evaluated. They show a dramatic steric effect not only on the nucleophilic attack step but also on the proton transfer rates. For example, deprotonation by *N*-methylmorpholine of $T^\pm$ derived from morpholine has a rate constant of $2 \times 10^3\ M^{-1}\ s^{-1}$ instead of the 10^8–$10^9\ M^{-1}\ s^{-1}$ expected for a diffusion-controlled reaction. Rates of protonation of T^- on carbon by water and several general acids are as expected for similar dinitro compounds, but protonation by H^+ is 10^3–10^4 times faster than expected. This high rate is tentatively attributed to an intramolecular proton switch mechanism, $T^\pm \rightarrow T^0$.

This is the first paper in a series in which we will explore mechanistic features and structure-reactivity problems which not only relate to nucleophilic additions to olefins[1] but which are relevant to other classes of reactions such as nucleophilic vinylic substitutions,[2] ElcB eliminations,[3] and proton transfer reactions involving "normal" acids[4] as well as carbon acids.[5] The present paper deals with the reactions of piperidine, morpholine, *n*-butylamine, and aniline with 1,1-dinitro-2,2-diphenylethylene in 50% aqueous dimethyl sulfoxide (v/v). Two kinetic processes were observed. The first ($1/\tau_1$), relatively fast and reversible, was studied most thoroughly and is consistent with eq 1:



(1)

where k_{2p} and k_{-2p} refer to proton transfer and are defined as:

$$k_{2p} = k_{2p}{}^{w} + k_{2p}{}^{OH}[OH^-] + k_{2p}{}^{A}[RR'NH] + k_{2p}{}^{B}[B] \qquad (2)$$

$$k_{-2p} = k_{-2p}{}^{H}[H^+] + k_{-2p}{}^{w} + k_{-2p}{}^{AH}[RR'NH_2{}^+] + k_{-2p}{}^{BH}[BH^+] \qquad (3)$$

with $k_{2p}{}^{w}$, $k_{2p}{}^{OH}$, $k_{2p}{}^{A}$, and $k_{2p}{}^{B}$ being the rate coefficients for the deprotonation of $T^\pm$ by the solvent, hydroxide ion, amine, and another base (buffer), which sometimes was added to the reaction solution, respectively, and $k_{-2p}{}^{H}$, $k_{-2p}{}^{w}$, $k_{-2p}{}^{AH}$, and $k_{-2p}{}^{BH}$ being the rate coefficients for the protonation of T^- on nitrogen by the hydronium ion, the solvent, and the conjugate acids of the amine and of B, respectively.

The second process ($1/\tau_2$), which is relatively slow and irreversible, refers to the cleavage of T^- yielding benzophenone and dinitromethane anion.

Equation 1 can be regarded as a model for the initial two steps in the mechanism of base-catalyzed nucleophilic vinylic substitutions by amines;[6,7] in a "real" vinylic substitution reaction the substrate would have a nucleofugic leaving group (e.g., $Ph(X)C{=}C(NO_2)_2$) and there would be product-forming steps in which the leaving group departs from T^- (and possibly from $T^\pm$). A question of great relevance to the mechanism of base-catalyzed nucleophilic vinylic substitutions is whether proton transfer can always be assumed to be a rapid equilibrium step[6a-d] ($k_{2p} \gg k_{-1}$ in eq 1) or whether proton transfer may become rate limiting ($k_{2p} \ll k_{-1}$ in eq 1) under certain conditions.[7] Our results show the latter to be the case.

Results

General Features. When 1,1-dinitro-2,2-diphenylethylene (henceforth called S) is mixed with an amine in 50% aqueous

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