cis-7,8-Dicarbomethoxy-3,4-dimethyl-*anti*-tricyclo[4.2.2.0^{2,5}]-deca-3,9-diene (20d). A solution of 300 mg (1.3 mmol) of 3,4-dimethyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride[4] in 15 ml of dry methanol was heated at reflux for 5.5 hr, cooled to 0°, and treated with excess diazomethane in ether. The solution was kept overnight at room temperature and evaporated to leave a residue which was crystallized from aqueous methanol. Pure **20c** was obtained as white crystals: mp 61.5-63°; δ_{TMS} ($CDCl_3$) 5.96 (m, 2, olefinic), 3.52 (s, 6, methyl), 2.86 (br s, 2), 2.73-3.0 (m, 2), 2.5 (m, 2), 1.52 (br s, 6, methyl). Calcd *m/e* 276.1361; found 276.1366.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.54; H, 7.28.

Rearrangement of 16d with $PdI_2(PPh_3)_2$. Reaction of 11 mg (0.040 mmol) of **16d** with 3 mg (0.005 mmol) of catalyst in 0.5 ml of benzene for 600 hr at 80° returned 84% of unchanged **16d** and gave 5.9% of **17d**, 1.6% of **19d**, and 8.5% of **20d** (analysis on column d).[15]

Rearrangement of 16d with $PdCl_2(PPh_3)_2$. Reaction of 3 mg (0.011 mmol) of **16d** with 4 mg (0.009 mmol) of catalyst in 0.5 ml of benzene for 119 hr at 80° gave 100% of snoutane **17d** (analysis on column d).[15]

Rearrangement of 16d with $PdCl_2(PPh_3)_2$. Reaction of 3 mg (0.011 mmol) of **16d** with 3 mg (0.008 mmol) of catalyst in 0.5 ml of benzene for 120 hr at 80° gave 0.9% of **16d**, 96.6% of **17d**, 1.0% of **19d**, and 1.5% of **20d** (analysis on column d).[15]

Isomerization of 21 with $PdI_2(PPh_3)_2$. Heating 6 mg of **21**[4] with 0.5 ml of 0.0019 *M* catalyst solution in benzene at 79° for 119.5 hr gave 8% of snoutane **22**[4] and 92% of diene **23**; δ_{TMS} ($CDCl_3$) 5.70-6.15 (m, 2, olefinic), 5.83 (s, 2, cyclobutene), 3.73 and 3.67 (two s, 3 each, methyls), 2.58-3.30 (br m, 6).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.76.

Isomerization of 21 with [Rh(NOR)Cl]$_2$. A solution of 43.5 mg of **21** and 14 mg of catalyst in 1.4 ml of benzene was heated in a sealed ampoule at 40° for 44 hr. Work-up gave 26.9 mg of an oily product, vpc analysis of which on column f[15] showed it to be single substance. Isolation and pmr analysis gave proof that this material was uniquely **23**.

Acknowledgment. This research was supported in part with funds provided by the National Science Foundation.

References and Notes

(1) Part XXIX of the series dealing with Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. Part XXVIII is L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Amer. Chem. Soc.*, **97**, 1101 (1975).

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(15) (a) Column 10 ft × 0.125 in. 5% Carbowax 20 M on Chromosorb G; (b) 14 ft × 0.125 in. 3% UCON 50HB2000P on Chromosorb W; (c) 2 ft × 0.125 in. 5% Carbowax 20 M on Chromosorb P; (d) 16 ft × 0.125 in. 7.7% OV-25 and 5.8% Carbowax 20M on Chromosorb G; (e) 15 ft × 0.125 in. 4% OV-25 and 2% Carbowax 20M on Chromosorb G; (f) 6 ft × 0.25 in. 5% SE-30 on Chromosorb G; (g) 10 ft × 0.25 in. 8% Carbowax 20 M on Chromosorb G.

(16) We thank Dr. Denise Cottrell for this experiment.

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Rhodium(I)- and Palladium(II)-Promoted Rearrangements of Homocubanes. A Comparison of Kinetic Reactivity and Product Distribution with Substituent Alteration[1]

Leo A. Paquette,* Roger A. Boggs, and John S. Ward[2]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received August 3, 1974*

Abstract: The effect of varied 4-substitution of the homocubane ring system on the course of Rh(I) and Pd(II) catalyzed rearrangements was probed both by direct examination of product ratios and kinetically in the case of [Rh(NOR)Cl]$_2$. Comparison of the rate data with catalytic rate constants previously determined from Ag(I)-promoted bond switching reactions revealed a greatly diminished sensitivity of Rh(I) to the *electronic* nature of the substituent at C_4 but an increase in its response to *steric* factors. The range of k_{Rh} values, excluding those for the 4-*tert*-butyl and 4,5-dimethyl examples, is but a factor of 60 (compare Ag(I) where it is 500-fold). The rhodium norbornadiene chloride dimer promoted isomerization of 4-trideuteriomethylhomocubane shows essentially nil deuterium isotope effect (k_H/k_D = 1.011 ± 0.005). This behavior is attributed to the absence of carbonium ion character in the rate-determining transition state. The compatibility of these findings with an oxidative addition pathway is discussed, as are several additional quantitative relationships uncovered in this study.

In the preceding paper of this series,[1] complexes of Rh(I) ($4d^8$) and Pd(II) ($4d^8$) were shown to promote the rearrangement of 1,8-bishomocubanes. In many instances, the isomerizations were observed to differ in type from the exclusive bond switching pathway catalyzed by Ag(I) ($4d^{10}$) salts,[3] dienes and not snoutanes arising as the major products. These diverse catalytic properties cannot be distinguished simply on the basis of the differing electronic configurations of the transition metals (d^8 *vs.* d^{10}) but are seemingly dependent to a greater extent on more subtle fac-

Table I. Metal Catalyzed Isomerizations of Homocubane

				Composition, %[a]				
Catalyst	Solvent	Temp, °C	Time, hr	**1**	**2**	**3**	**4**	Unidentified
$AgClO_4$	C_6H_6	40	40		100			
$[Rh(NOR)Cl]_2$	C_6H_6	40	40			100		
$PdI_2(PPh_3)_2$	$CHCl_3$	80	48		62.8	5.8	23.1	8.2
	C_6H_6	80	164	0.2	84.8	2.7	9.5	2.8
$PdCl_2(PPh_3)_2$	C_6H_6	80	164		97.0		2.1	0.9
$PdCl_2(PhCN)_2$	$CHCl_3$	80	48		69		31	
	C_6H_6	80	166		83		17	
$PtCl_2$	C_6H_6	80	166	89.5	10.3	Trace	0.2	
RuO_2	C_6H_6	80	164	96	4			
$[Ir(CO)_3Cl]_2$	C_6H_6	80	165	34.1	5.9	26.6	33.4	
(None)	$CHCl_3$	80	96		100			
(None)	C_6H_6	80	166	98.9	0.3			0.8

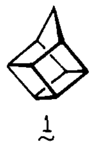
[a] Determined by vpc analysis on a 10 ft × 0.125 in. 15% PMPE 5-ring column heated to 70–80°.

tors. An important one of these is the nature of the attached ligands, particularly as they affect by their electronegativity, polarizability, and σ donor–π acceptor qualities the softness or hardness of the metal center.[1,4] The importance of steric factors at the reaction site has also manifested itself,[1] and is particularly recognizable when the bishomocubane is 4,5-disubstituted.

The present report details our study of the transition metal promoted isomerizations of homocubanes, molecules whose strain energies are intermediate between those of the structurally related 1,8-bishomocubanes and cubanes. The substrates chosen for investigation are the parent hydrocarbon, a wide range of 4-substituted derivatives, and the 4,5-dimethyl compound. Kinetic analysis of their $[Rh(NOR)Cl]_2$ promoted rearrangement has now provided convincing evidence that substantial electronic alteration at the reaction center in these strained molecules has little influence on rate. Additionally, evidence has been uncovered that implicates ring strain as an influential factor in controlling the relative levels of diene formation and bond switching. That such metal catalyzed valence isomerizations of homocubyl systems possess these additional intriguing features is of considerable mechanistic consequence.

Results

Homocubane Rearrangements. While exposure of **1** to anhydrous silver perchlorate in benzene leads exclusively and quantitatively to norsnoutane (**2**),[5] reaction with catalytic amounts of rhodium norbornadiene chloride dimer gives rise only to diene **3**. The palladium catalysts $PdI_2(PPh_3)_2$, $PdCl_2(PPh_3)_2$, and $PdCl_2(PhCN)_2$ promote isomerization of **1** chiefly to **2**, although appreciable amounts of **4** are also formed. The structural assignment to **4** was confirmed by spectral and vpc comparisons with an authentic sample prepared by rhodium dicarbonyl chloride dimer catalyzed rearrangement of norsnoutane (**2**) as described earlier by Katz.[6] That **4** is a secondary product formed from **2** was demonstrated (a) by isomerization of the latter under the actual experimental conditions using $PdCl_2(PhCN)_2$ as catalyst and (b) by noting its rate of appearance on a time *vs.* product distribution curve. Diene **3** is stable to further rearrangement. A change in solvent polarity from benzene to chloroform led to an enhancement in the levels of conversion to **4**. Table I lists the temperature, reaction times, and product distributions for these isomerizations.



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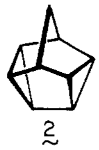

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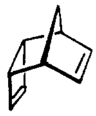

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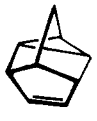

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In contrast to the behavior discussed above, platinum chloride and ruthenium dioxide showed little catalytic activity. On the other hand, the catalyst system most varied in its effect on homocubane proved to be $[Ir(CO)_3Cl]_2$. When reaction was allowed to proceed in dry benzene at 80° for 165 hr, conversion to diene **3** as well as to **2** and **4** was observed. On this basis, the iridium catalyst stands alone at being able to effect meaningful competitive isomerization of **1** along both possible reaction pathways. Also relevant were the findings that **1** in the absence of transition metals is essentially stable in benzene solution at 80° for 144 hr (0.3% conversion to norsnoutane observed), but is smoothly isomerized to **2** when heated in chloroform at the same temperature for 96 hr. The latter control experiment, further study of which has not been pursued, seemingly points up the possibility that the acid which is liberated from solvent under these conditions can likewise effect bond switching.

The present results provide the basis for certain interesting comparisons to be made. As concerns $[Rh(NOR)Cl]_2$ catalysis, both cubane[7a] and homocubane are isomerized exclusively to ring opened diene products. With 1,8-bishomocubane, however, small amounts of the dicyclopropane valence isomer also result.[5] The alternative mechanistic channel shows a similar trend. Thus, cubane has been reported to undergo only bond switching in the presence of catalytic quantities of Pd(II) complexes, although neither the nature of these catalysts nor the reaction conditions have been specified.[7b] As shown above, homocubane is similarly not predisposed toward diene production with the various palladium complexes examined (Table I), only $PdI_2(PPh_3)_2$ generating measurable quantities (2.7–5.8%) of **3**. With 1,8-bishomocubane, levels of diene as high as 29% have been noted.[1] In the last two series which were examined in these laboratories, careful attention was given to utilization of the identical batch of catalyst throughout. Reaction temperatures differ by only 5°. According to this, bishomocubane does not exhibit an exclusivity in product formation which is followed by its more strained congeners. As will be seen, this prevailing tendency is manifested as well in the 4-methyl derivative but not in the 4,5-dimethyl series where steric factors gain appreciable significance.

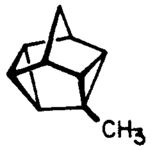
Isomerization Reactions of 4-Methylhomocubane. The perturbing effects of incremental alkyl substitution upon such homocubane rearrangements was first assessed with the 4-methyl derivative **5**. Complete specificity was again encountered with $AgClO_4$ and $[Rh(NOR)Cl]_2$ in benzene at 40°, the resulting isomeric hydrocarbons being **6** and **7**, respectively. With $PdI_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$, conver-

Table II. Metal Catalyzed Isomerizations of 4-Methylhomocubane

Catalyst	Solvent	Temp, °C	Time, hr	Composition, %[a] 5	6	7	8	9	Unidentified
$AgClO_4$	C_6H_6	40	24		100				
$[Rh(NOR)Cl]_2$	C_6H_6	40	30			100			
$PdI_2(PPh_3)_2$	$CHCl_3$	80	72		93				7
	C_6H_6	40	70	98	2				
	C_6H_6	80	23	81.9	15.5				3
	C_6H_6	80	93		88			1.8	10.2
$PdCl_2(PPh_3)_2$	$CHCl_3$	80	72		98.4				1.6
	C_6H_6	80	92		99.8				0.2
$PdCl_2(PhCN)_2$	$CHCl_3$	80	16		0.9		96.1	3.0	
	C_6H_6	80	45				97.4	2.6	
	C_6H_6	80	96				97.4	2.6	
$PtCl_2$	C_6H_6	80	49		92.6		1.4	6.0	
	C_6H_6	80	90		12.5		58.7	28.8	
	C_6H_6	80	264				98.2	1.8	
RuO_2	C_6H_6	80	96	96.1	3.9				
$[Ir(CO)_3Cl]_2$	$CHCl_3$	80	18	79.6	4.2	2.7	13.5		
	$CHCl_3$	80	76	51.9	1.8	3.6	37.2		5.5
	C_6H_6	80	50	95.8	0.2	0.4	2.9	0.7	
	C_6H_6	80	95	77.0	10.7	4.2	6.0	2.0	
	C_6H_6	80	264	14.8	4.6	30.0	45.2	5.4	
(None)	$CHCl_3$	80	96	19	18				
(None)	C_6H_6	80	118	95.2	4.5		0.3		
(None)	C_6H_6	80	144	94.0	6.0				

[a] Determined by vpc analysis on a 10 ft × 0.125 in. 15% PMPE 5-ring column heated to 70–80°.

5



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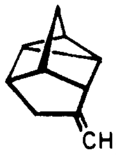

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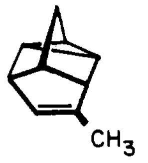

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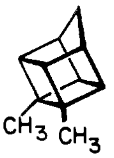
sion to norsnoutane **6** was again heavily favored, although small amounts of an unidentified component also were formed (Table II). When $PdCl_2(PhCN)_2$ was utilized, two new isomers made their appearance in relative ratios of 96–97% and 2.5–3%. The major component could be readily isolated by preparative vpc on an XF-1150 column. Its pmr spectrum (in $CDCl_3$) shows absorptions for an exocyclic methylene group at δ 4.83 (m, 1), and 4.68 (m, 1), three allylic protons at 2.43 (m, 1) and 2.28 (m, 2), and three cyclopropyl hydrogens at 0.90–1.25 (m, 3). Additional signals appear at 2.08 (m, 1), 1.80 (m, 1), and 1.52 (br s, 2). The infrared spectrum of a neat sample showed prominent peaks at 3070, 2975, 2940, 2865, 2840, 1660, 870, and 795 cm^{-1}. These characteristic spectral data serve as the basis for assignment of structure to **8**. Sufficient quantities of the minor isomer could not be obtained pure. However, the following evidence suggests the hydrocarbon to be **9**. When the progress of the rearrangement of **5** with $PdCl_2(PhCN)_2$ at 25° was followed by vpc, **9** was initially formed more rapidly than **8**, but gradually lost its concentration advantage to the exocyclic methylene compound. No further change was apparent when the relative percentage of **9** in this mixture dropped to approximately 3%. In addition, when a 99% pure sample of **8** (containing 1% of **9**) was exposed to $PdCl_2(PhCN)_2$ at 80° for 24 hr, the ratio of these isomers returned to the apparent equilibrium point of 96:4 in favor of **8**. Palladium-catalyzed isomerizations of olefins are well known and have been the subject of considerable study.[8] It may well be that the reaction follows a course involving insertion of Pd(II) into an allylic C–H bond, elimination to give a π-allyl metal complex, and subsequent addition of hydrogen at the alternative allylic terminus. Although we have no evidence on this point, the fact remains that the equilibrium lies heavily in the direction of **8** and signifies that this exocyclic olefin is thermodynamically more stable that its endocyclic isomer **9**. This behavior is contrasted nicely by the reversed thermodynamic preference of the **13–14** pair, the additional methyl group now providing sufficient stabilization to endocyclic isomer **13** to decrease its free energy relative to **14**.

As with **1**, RuO_2 showed no catalytic properties toward **5**, but $PtCl_2$ was now reactive and converted **5** to **8** (98.2%) and **9** (1.8%) after 264 hr at 80°. Iridium tricarbonyl chloride dimer maintained its position of promoting isomerization to all four products (Table II).

The Behavior of 4,5-Dimethylhomocubane. As previously noted,[5] addition of catalytic amounts of silver perchlorate to anhydrous benzene solutions of **10** results in exclusive conversion to **11**. Importantly, positioning of two alkyl groups



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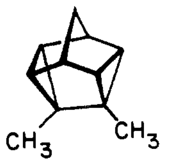

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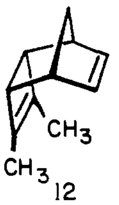

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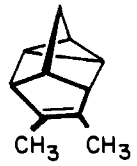

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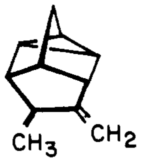

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Table III. Isomerizations of 4,5-Dimethylhomocubane by Derivatives of Transition Metals

Catalyst	Solvent	Temp, °C	Time	Composition, %[a] 10	11	12	13	14
$AgClO_4$	C_6H_6	40	24 hr		100			
$[Rh(NOR)Cl]_2$	$CDCl_3$	50	7 days		12	54	33.5	0.5
$[Rh(NOR)Cl]_2$	C_6H_6	40	184 hr		15	64	19	2
$PdI_2(PPh_3)_2$	C_6H_6	80	7 weeks	93	(35)[b]	(12)[b]	(52)[b]	(1)[b]
$PdCl_2(PPh_3)_2$	C_6H_6	80	7 weeks	70	(33)[b]	(10)[b]	(56)[b]	(1)[b]
$PdCl_2(PhCN)_2$	C_6H_6	80	11 hr	50	(70)[b]	(0)[b]	(28)[b]	(2)[b]
		80	592 hr		67		32	1
(None)	C_6H_6	80	7 weeks	98	1.5		0.5	

[a] Determined by vpc analysis on a 10 ft × 0.125 in. 15% PMPE 5-ring column heated to 70°. [b] Values normalized to 100%.

Table IV. Isomerization Rate Data for Various 4-Substituted Homocubanes and **10** ($[Rh(NOR)Cl]_2$, anhydrous C_6H_6, 40.0°)

Compd	R	k_{Rh}, M^{-1} sec^{-1}	k_{rel} *vs.* **1**	k_{Ag},[a] M^{-1} sec^{-1}	k_{rel} *vs.* **1**[a]
1	—H	1.36×10^{-2}	1.0	7.36×10^{-4}	1.0
5	$—CH_3$	3.41×10^{-2}	2.5	7.15×10^{-3}	9.7
15a	$—CH_2OCH_3$	3.23×10^{-2}	2.4	1.10×10^{-3}	1.5
15b	$—CH_2OH$	8.74×10^{-2}	6.4	8.49×10^{-3}	11.5
15c	$—C(CH_3)_3$	4.05×10^{-5}	0.0030	2.88×10^{-4}	0.4
15d	$—C_6H_5$	3.24×10^{-3}	0.24	1.66×10^{-2}	22.6
15e	—◁	2.90×10^{-2}	2.1	2.53×10^{-2}	34.4
15f	$—OC_2H_5$	1.4×10^{-3}	0.1	3.69×10^{-1}	500
10		1.06×10^{-3}	0.078	6.44×10^{-3}	8.7

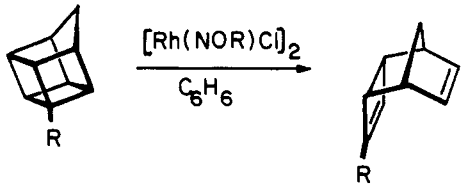
[a] Data taken from ref 5.

at the pair of remote corners does not alter the course of rearrangement usually promoted by Ag^+. Furthermore, **10** rearranges 8.7 times faster than homocubane under these conditions. As shown in Table III, we have observed that the $[Rh(NOR)Cl]_2$-promoted reaction does not afford diene **12** exclusively. Rather, hydrocarbon **12** is formed to the extent of only 64%. In addition, the product mixture contained 15% of the norsnoutane and a rather large amount of isomer **13** (19%). The structure proof for **13** rests upon its spectral features (pmr ($CDCl_3$) δ 2.33 (m, 2, allylic), 1.80 (m, 1, bridgehead), 1.50–1.70 (m, 1, cyclopropyl bridgehead), 1.67 (s, 6, methyls), 1.43 (m, 2, methylene), and 1.27 (d, J = 4.5 Hz, 2, cyclopropyls)) and its formation from **11** in the presence of $[Rh(NOR)Cl]_2$. A fourth product (2%), which also appears in low yield in the Pd(II) catalyzed isomerizations, was not available in quantities sufficient for characterization. Because it is produced in small amounts (1–2%) when **13** is exposed to complexes of Rh(I) and Pd(II), we have tentatively assigned to this substance the structure **14** by analogy with the rearrangement of **9** to **8**. Since **13** and **14** are formed by secondary rearrangement of **11**, the response of **10** to this rhodium catalyst can be summed up as 64% diene formation and 36% bond switching. The related 1,8-bishomocubane derivative experiences 72.5% diene formation and 27.5% bond switching under comparable conditions.[5] In this example, the usually enhanced proclivity of homocubanes to furnish larger amounts of diene product is clearly not prevailing.

The reactivity of **10** toward palladium catalysts is decreased relative to the parent system and conversion to diene becomes reasonably competitive with norsnoutane formation when $PdI_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$ are employed. It will be recalled that these complexes produce no detectable diene with **1** and **5**.

Kinetic Evaluation of Substituent Effects. The qualitative indications that 4-methylhomocubane (**5**) is more reactive toward $[Rh(NOR)Cl]_2$ than homocubane (**1**) were confirmed by quantitative measurements (Table IV). This pair of rearrangements, studied kinetically in anhydrous benzene at 40.0°, revealed a 2.5-fold acceleration to result upon introduction of the corner methyl group. This rate increase in diene production is somewhat less than that seen for Ag(I) catalysis where **5** undergoes structural reorganization to the isomeric snoutane 9.7 times faster than **1**. Similar comparison of the reactivity of 4,5-dimethylhomocubane (**10**) toward the two catalyst systems has given evidence of more dramatic effects. With silver perchlorate in benzene, **10** experiences exclusive bond switching 8.7 times faster than **1** at 40°. When treated with $[Rh(NOR)Cl]_2$ under analogous conditions, **10** isomerizes a factor of 12.8 times more slowly than **1**. Factoring of the catalytic rate constant (k_{Rh}) by that percentage of the reaction which proceeds by the bond switching mechanism (36%) gives a value of 3.8×10^{-4} M^{-1} sec^{-1}. Consequently, the response of **10** to Rh(I)-promoted bond switching is 17 times less rapid than it is toward Ag(I) under these circumstances.

The effect of 4-CH_2OCH_3, 4-CH_2OH, and 4-cyclopropyl substituents is to produce a 2.1–6.4-fold rate enhancement relative to **1**. Such quite small accelerations again contrast with the behavior of these molecules toward silver ion (Table IV). Particularly striking, however, are the reactivities of **15c**, **15d**, and **15f**. The 4-*tert*-butyl group in **15c** exerts a far greater steric impediment toward $[Rh(NOR)Cl]_2$- than toward $AgClO_4$-promoted rearrangement. To argue the 100-fold decrease on the basis of the differing molecular dimensions of the catalysts and a mechanistic changeover which may require the rhodium reagent to approach C_4 in more intimate fashion appears reasonable. The rate decelerations caused by the 4-phenyl and 4-ethoxy groups are best ascribed to the absence of carbonium ion character in the rate determining transition state. When the reverse is true and some charge development does materialize as in the case of Ag(I) catalysis,[5] then these



15 **16**

a, R = CH_2OCH_3
b, R = CH_2OH
c, R = $C(CH_3)_3$
d, R = C_6H_5
e, R = —◁
f, R = OC_2H_5

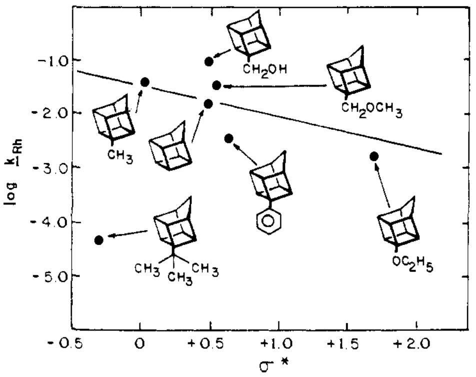


Figure 1. Correlation of log k_{Rh} with σ^* for various 4-substituted homocubanes. The kinetic data are taken from Table IV.

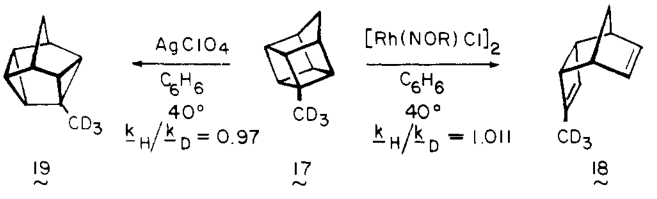
substituents accelerate valence isomerization. Close examination of the data summarized in Table IV reveals the kinetic difference between the two catalysts to be on the order of 100 for **15d** and 5000 for **15f.**

Since homocubanes **15a–f** are cleanly ring opened to **16a–f** under the conditions employed, the small accelerating effects of electron-donating groups such as methyl, methoxymethyl, hydroxymethyl, and cyclopropyl, in conjunction with the decelerating consequences of phenyl and ethoxy substitution at C_4, can be most reasonably accounted for in terms of dominant inductive effects to the exclusion of possible resonance contributions in the transition state of kinetic consequence.

Some attention was also given to 4-vinyl, 4-acetoxymethyl-, and 4-carbomethoxyhomocubanes. For unknown reasons, the first two compounds did not rearrange *via* pseudo-first-order kinetics. Isomerization of the ester was exceedingly slow; at 150°, rearrangement to form products was noted, several of which appeared to arise from secondary reactions.

When the logarithmic values of k_{Rh} are plotted against the appropriate Taft σ^* constants as in Figure 1, a good straight line is not defined. With the exclusion of the data for **15c** because of the obvious intrinsic steric complications, the correlation coefficient of the other six points comes only to 0.705. One reasonable way to interpret these data is to assume that $[Rh(NOR)Cl]_2$ catalysis is especially subject to small alterations in the steric size of the 4-substituent.

Secondary Deuterium Isotope Effect Data. Additional mechanistic insight was provided by the isomerization of **17** to **18** with $[Rh(NOR)Cl]_2$. Previously, **17** had been found to isomerize in the presence of silver perchlorate to **19** with a very small and somewhat inverse isotope effect of 0.97 ± 0.03.[5] In the present study, tandem experiments involving **17** and its nonlabeled counterpart **5** were carried out simultaneously under identical conditions. The average of several such sets of experiments showed the fractionation factor to be again negligible, although now slightly positive in direction ($k_H/k_D = 1.011 \pm 0.005$). This finding agrees with the earlier inferences that no meaningful hybridization changes operate at C_4 in the rate determining step. Any mechanism involving positive charge development at C_4 which would open the possibility for hyperconjugative interaction of the C–D bonds with the adjacent homocubyl orbital is convincingly ruled out.



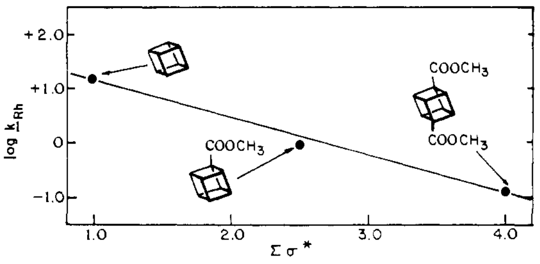


Figure 2. Plot of log k_{Rh} with $\Sigma\sigma^*$ for several cubane derivatives (data taken from ref 7a).

Discussion

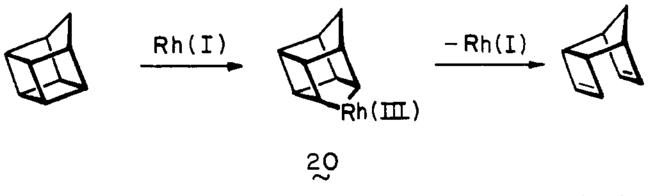
The present results disclose that Rh(I)-catalyzed rearrangements of homocubanes to dienes are insensitive to the electronic nature of the C_4 substituent but affected kinetically by steric compression at that site. 4-*tert*-Butylhomocubane (**15c**) is an extreme example of the latter category. 4,5-Dimethyl derivative **10** is also encumbered but to a lessened extent. Least-squares treatment of the kinetic data plotted in Figure 1, excluding the point for **15c**, gives a ρ^* value of −0.87. Significantly, this value compares closely to the small negative ρ^* value observed for the $[Rh(NOR)Cl]_2$-promoted isomerization of cubane, carbomethoxycubane, and 1,4-biscarbomethoxycubane when the appropriate log k_{Rh} values[7a] are plotted against $\Sigma\sigma^*$[9] (see Figure 2). Viewed from a different perspective, the rate constants measured for the Rh(I)-promoted isomerizations of the homocubanes are seen to differ by a factor of only 60 (excluding **10** and **15c**, Table IV).

In contrast, the k_{Ag} values for these same homocubanes vary by a factor of 500.[5] Thus, that bond reorganization which operates to give snoutane products is appreciably more sensitive to the electronic characteristics of the corner substituent. This is also reflected nicely in the more negative ρ^* value of −2.33 (r = 0.995) for these reactions.[5] Similarly, the rates of Ag(I) catalyzed isomerization of various cubanes[7b] generate a ρ^* value of −1.35 (r = 0.987).[10] This kinetic behavior can most reasonably be taken to mean that development of positive charge does not take place in the rate-limiting step of the Rh(I) reactions. The small negative ρ^* values could arise from a preequilibrium process,[11] but a kinetic dependence of the Michaelis-Menten type

$$-\frac{d[\text{homocubane}]}{dt} = \frac{kK[\text{homocubane}][\text{Rh(I)}]}{K[\text{homocubane}] + 1}$$

remains to be determined at the experimental level.

The combined evidence can be satisfied by the proposal of Cassar, Eaton, and Halpern[7a] that ring opening reactions promoted by Rh(I) catalysts which give diene products proceed stepwise through an intermediate such as **20** where the



transition metal has entered into oxidative addition in the rate-determining step. What can be claimed additionally at this time is that the insertion process which leads to **20**, does not entail charge development at C_4. The real possibility exists that this condition arises because oxidative addition into the nonadjacent C_2C_5 bond is kinetically favored. That one of the less substituted edge bonds enters more readily into oxidative addition might be inferred from the relative rates of rearrangement of **5** (k_{rel} = 2.5) and **10** (k_{rel} = 0.078).[12] However, this single correlation should not be considered as establishing the point since the impact of steric effects at C_4 and C_5 on the preequilibrium, if one does operate,[11] has yet to be determined. Thus, the question remains open.

Two final quantitative comparisons warrant mention. Firstly, the distribution of snoutane products from reaction of the various cubyl hydrocarbons with the several Pd(II) catalyst systems parallels increasing strain, barring the presence of an excessive level of steric congestion. Using $PdI_2(PPh_3)_2$ as an example, 1,8-bishomocubane is seen to undergo rearrangement with formation of much less snoutane (4.5%) than is evidenced by homocubane (94.3% norsnoutane). With the introduction of a 4-methyl group, these percentages become 46.1 and 89.8, respectively.

Secondly, the catalytic activity of Ag(I) and Rh(I) toward homocubanes is dissimilar not only in product formation but also in sensitivity to electronic factors. Analysis of the product and rate data reveals that the diene forming reaction is relatively substituent insensitive, whereas the bond switching process is particularly responsive to substitution at C_4. These observations may prove to be generally characteristic of those features which distinguish isomerizations proceeding by way of oxidative addition from those involving generation of transient carbonium intermediates.

Experimental Section

Proton magnetic resonance spectra were obtained on Varian A60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative and analytic vpc work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Kinetic measurements were achieved with the aid of a Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator.

General Rearrangement Procedure. The homocubane (3–45 mg) and appropriate catalyst (3–14 mg) were taken up in a small volume of the indicated solvent (0.3–2 ml) and the resulting solutions were divided among three precleaned tubes which had been previously flushed with nitrogen. For those reactions conducted at 80°, the tubes were sealed under nitrogen. The contents of each tube were processed by shaking with 1 ml of saturated aqueous potassium cyanide solution and 0.2 ml of pentane. The organic layers so obtained were analyzed directly by vpc.

***endo*-3-Methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (7).** A 100-mg sample of **5** was dissolved in 2 ml of anhydrous benzene which was 1.08×10^{-2} *M* in $[Rh(NOR)Cl]_2$. After 7 days at room temperature, the reaction mixture was treated as above with KCN. The organic phase was dried and carefully evaporated and the only product was purified by preparative scale vpc on a 12 ft × 0.25 in. column packed with 25% PMPE 6-ring on Chromosorb W (110°) to give 50 mg (50%) of **7** as a colorless liquid: δ_{TMS} (CCl_4) 5.85 (m, 2), 5.65 (m, 1), 2.7 (m, 4), 1.9 (br d, 1), 1.55 (m, 4).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.86; H, 9.08.

8-Methylenetetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (8). A solution of 50 mg of **5** and 10 mg of $PdCl_2(PhCN)_2$ in 0.25 ml of chloroform was heated at 85° for 24 hr and processed as before. Isolation of the major product from a 6 ft × 0.25 in. 5% XF-1150 column at 65° gave pure **8** as a colorless liquid: δ_{TMS} ($CDCl_3$) 4.83 (m, 1), 4.68 (m, 1), 2.43 (m, 1), 2.28 (m, 2), 2.08 (m, 1), 1.80 (m, 1), 1.52 (br s, 2), 0.90–1.25 (m, 3).

Calcd for $C_{10}H_{12}$ *m/e* 132.0939; found 132.0942.

8,9-Dimethyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (13). A solution of 25 mg (0.17 mmol) of **10** and 10 mg (0.026 mmol) of $[Rh(CO)_2Cl]_2$ in 0.3 ml of chloroform was sealed under argon in an nmr tube. After 3 hr at 50°, pmr analysis indicated approximately 30% rearrangement to **13**, after 9 hr 25% of **10** remained, and after 23 hr the conversion to **13** was complete. The spectrum remained unchanged after 5 days of additional heating (50°). Work-up as before and isolation from a 12 ft × 0.25 in. 10% PMPE 6-ring column (90°) gave pure **13**: δ_{TMS} ($CDCl_3$) 2.33 (m, 2), 1.80 (m, 1), 1.50–1.70 (m, 1), 1.67 (s, 6), 1.43 (m, 2), 1.27 (d, *J* = 4.5 Hz, 2).

Calcd for $C_{11}H_{14}$ *m/e* 146.1095; found 146.1098.

***endo*-3-Methoxymethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16a).** A 50-mg (0.37 mmol) sample of **15a** was dissolved in 2 ml of 0.015 *M* $[Rh(NOR)Cl]_2$ in benzene. After 24 hr at 40°, the reaction was arrested with aqueous potassium cyanide solution and the lone product was isolated from a 6 ft × 0.25 in. 20% Carbowax 20 M column (Chromosorb W) at 110°. There was obtained 19 mg (38%) of **16a:** δ_{TMS} (CCl_4) 5.75 (m, 3), 3.55 (s, 2), 3.20 (s, 3), 2.75 (m, 4), 1.85 (d, *J* = 8 Hz, 1), 1.5 (d, *J* = 8 Hz, 1).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.31; H, 8.73.

***endo*-3-Hydroxymethyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16b).** Reaction of 50 mg (0.35 mmol) of **15b** with 5 mg (0.01 mmol) of $[Rh(NOR)Cl]_2$ in 0.5 ml of benzene for 6 hr at 40° gave rise upon isolation from a 7 ft × 0.25 in. 10% Carbowax column (135°) to pure diene; ν_{max} (neat) 3350, 3055, 2965, 2930, 2865, 1655 cm^{-1}; δ_{TMS} (C_6D_6) 5.83 (m, 3), 3.77 (m, 2), 2.82 (m, 2), 2.42–2.65 (m, 2), 1.87 (d, *J* = 8 Hz, 1), 1.52 (s, 1), 1.38 (d, *J* = 8 Hz, 1). Calcd *m/e* 148.0888; found 148.0889.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.92; H, 8.32.

***endo*-3-*tert*-Butyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16c).** Reaction of 17 mg (0.10 mmol) of **15c** with 5 mg (0.01 mmol) of $[Rh(NOR)Cl]_2$ in 0.4 ml of benzene for 12 days at 60°, quenching with KCN solution, and isolation from the Carbowax column (85°) gave **16c:** δ_{TMS} (C_6D_6) 5.85 (m, 2), 5.65 (m, 1), 2.40–2.95 (m, 4), 1.94 (d, *J* = 8 Hz, 1), 1.38 (d, *J* = 8 Hz, 1), 0.87 (s, 9). Calcd *m/e* 174.1408; found 174.1411.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.59; H, 10.37.

***endo*-3-Phenyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16d).** Reaction of 10 mg (0.095 mmol) of **15d** with 11 mg (0.024 mmol) of $[Rh(NOR)Cl]_2$ in 2 ml of benzene for 20 hr at 40° furnished pure **16d** after work-up and purification on the Carbowax column: δ_{TMS} (C_6D_6) 7.10 (s, 5), 6.11 (br s, 1), 5.50–5.84 (m, 2), 3.16 (m, 1), 2.84 (m, 2), 2.58 (m, 1), 1.88 (d, *J* = 9 Hz, 1), 1.52 (d, *J* = 9 Hz, 1). Calcd for $C_{15}H_{14}$ *m/e* 194.1095; found 194.1099.

***endo*-3-Cyclopropyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16e).** Reaction of 15 mg (0.095 mmol) of **15e** with 3 mg (0.007 mmol) of $[Rh(NOR)Cl]_2$ in 0.5 ml of benzene for 17 hr at 40° and vpc purification on the Carbowax column (90°) afforded **16e:** ν_{max} (neat) 3085, 3060, 3040, 3010, 2965, 2925, 2865, 1625 cm^{-1}; δ_{TMS} (C_6D_6) 5.86 (m, 2), 5.68 (s, 1), 2.62 (m, 2), 2.38 (m, 2), 1.88 (d, *J* = 8 Hz, 1), 1.32 (d, *J* = 8 Hz, 1), 0.78–1.38 (m, 3), 0.14–0.48 (m, 2). Calcd *m/e* 158.1095; found 158.1097.

Anal. Calcd for $C_{14}H_{12}$: C, 91.08; H, 8.92. Found: C, 90.97; H, 9.06.

General Procedure for Kinetic Measurements. All kinetic experiments were run in oven-dried 1-dr vials (except for **15c** where sealed tubes were used) which had been washed sequentially with nitric acid, distilled water, ammonium hydroxide, and distilled water. Fresh solutions of $[Rh(NOR)Cl]_2$ in anhydrous benzene were prepared immediately before use. After addition of the homocubane, the solutions were allowed to equilibrate at 40.0° for 5–10 min. An accurate timer was started and aliquots were removed at suitable time periods. Each aliquot was quenched in 1 ml of saturated aqueous potassium cyanide solution and analysis of the organic layer was made on a Hewlett-Packard 5750 gas chromatograph. The areas of the relevant peaks were measured electronically and by planimetry. Least-squares treatment of the plots of ln $a/(a - x)$ *vs.* time (sec) provided the data in Table IV, which values represent the average of at least two runs. Reproducibility within ±5% was observed throughout. For those homocubanes which rearranged rapidly, reaction was generally followed to 2–3 half-lives. The slower rearrangements were analyzed kinetically to 0.2–1 half-lives. Good linearity prevailed under both sets of circumstances.

Acknowledgment. This research was supported in part with funds provided by the National Science Foundation.

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(11) Dauben and Kielbania[3] have advanced the suggestion that rearrangement proceeds *via* bidentate interaction of the strained hydrocarbon system with the transition metal complex. We view Ag(I) catalysis to be the result of edge argentation without subsequent oxidative addition.[3a]

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9-Thia[4.2.1]nonabicyclic System. Synthesis and Selected Transformations

A. G. Anastassiou,* J. C. Wetzel, and B. Y-H. Chao

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210.

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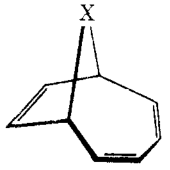
Abstract: The preparation of C_8H_8S, $C_8H_{10}S$, and $C_8H_{12}S$ 9-thia[4.2.1]bicycles and the stereoisomeric pairs of the corresponding sulfoxides is described. The synthetic design necessitated the development and subsequent use of three highly selective reactions: (i) oxidation of the 9-thia[4.2.1]bicycle with *m*-chloroperbenzoic acid to yield a single isomeric sulfoxide which, regardless of degree of saturation, incorporates the SO group invariably syn to the C_2 bridge; (ii) exclusive catalytic hydrogenation of the π appendage located anti to the SO dipole with marked affinity for ethylene over butadiene; and (iii) high-yield regiospecific diimide reduction of the π segment positioned syn to the SO function. Under conditions of thermal activation, C_8H_8SO sulfoxides **2** and **4** and their dihydro counterparts **5** and **7** interconvert, while the tetrahydro analogs **8** and **11** fail to do so. Mechanistically, all the evidence accumulated thus far from a measurement of activation constants suggests that directional transposition of the SO dipole results from scission of the C–SO bond bridging the molecule. Moreover, examination of specifically tagged **4**, namely **18**, in this connection established that the **4** $\rightleftharpoons$ **2** process is attended by bridge migration. Attention is also drawn to the absence of by-products in the **2** $\rightleftharpoons$ **4** and **5** $\rightleftharpoons$ **7** interconversions which is clearly indicative of strong interaction between the reactive sites, sulfinyl radical ($\dot{S}$=O) and monoallylic or diallylic carbon center, of the species intermediating the isomerizations.

Because of their inherent rigidity and well-defined shape, 9-heterobicyclo[4.2.1]trienes (**1**; X = heteroatom) are ideally structured as models for the purpose of assessing (i) the practical merits of nonbonded π interaction and, ultimately, of such intriguing concepts as bicycloconjugation and bicycloaromaticity and (ii) the scope and limitations of the influence exerted by orbital symmetry on the course of pericyclic (sigmatropic, cheletropic, electrocyclic, etc.)[1] transformations. Thus far, our recorded work in the area has dealt chiefly with photoinduced bond relocations[2,3] and dimerization,[4] thermal cheletropy,[5] reagent chemistry,[6] and photoelectron spectroscopy[7] of the nitrogen member of the family.[8] Recently, we also briefly touched upon the sulfur analog (**1**; X = S, SO), describing its preparation[9] and photoinduced response.[10] In an effort to probe the π electronics of this intriguing thiabicycle by photoelectron spectroscopy[11] and also to further assess its pericyclic response, we recently prepared a variety of key derivatives and are now offering a full account of the synthetic aspect of this work. In part, the present report also deals with mechanism, its chief emphasis along these lines residing on the inversion of the rigidly held sulfoxide bridge.



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Synthesis and Characterization

Synthetic entry into the general 9-thiabicyclo[4.2.1]nona-2,4,7-triene skeleton was gained by the addition of SO, thermally generated from ethylene sulfoxide, to cyclooctatetraene at 110°.[12] The white crystalline sulfoxide thus prepared (nmr, Figure 1a) was shown to constitute a single stereoisomer, **2**, by conversion to its invertomer **4**. This was accomplished efficiently (*ca.* 40% overall yield) in two steps, (i) careful $LiAlH_4$ reduction of **2** to the corresponding sulfide **3** (nmr, Figure 1b) and (ii) oxidation of **3** with *m*-chloroperbenzoic acid (MCPBA) at *ca.* −40° to produce sulfoxide **4** contaminated with only *ca.* 5% (nmr) of stereoisomer **2**. Compound **4** was effectively separated from its stereoisomeric contaminant by means of column chromatography at *ca.* −15° (nmr, Figure 1c). Chemically, the [4.2.1] frame of **4** was established by its conversion to sulfide **3** on treatment with $LiAlH_4$, while the stereoisomeric relationship between the two sulfoxides was confirmed by the conversion of **2** to **4** on exposure to trimethyloxonium fluoroborate. The specific stereochemical assignments shown in **2** and **4** were made on the basis of nmr spectral information. Specifically, brief comparison of the nmr spectra depicted in Figures 1a and 1c reveals that the "ethylene" protons are displaced to higher field and the "butadiene" hydrogens to lower field on going from **4** to **2**. Bearing in mind the well-documented deshielding effect experienced by protons positioned syn to the SO group,[13-15] it is readily seen that the observed chemical shifts are best accommodated by the stereochemical assignments shown in **2** and **4**.