(b) Stability of Thioketenes in a Nitrogen Atmosphere upon Irradiation. Thioketenes 1 and 2 did not undergo any noticeable change upon irradiation for 10 days with a 500-W tunsten lamp in a nitrogen atmosphere either in chloroform or in methanol. However, excitation to the higher excited singlet state by using a 450-W medium-pressure mercury lamp brought forth efficient reaction.[25]

(c) Stability of Sulfines. Both di-*tert*-butylthioketene *S*-oxide and 1,1,3,3-tetramethyl-2-(thiocarbonyl)cyclohexane *S*-oxide were found to decompose slowly to a polymeric material in about 10 days. However, both were found to be inert toward singlet oxygen. A chloroform or methanol solution of these thioketene *S*-oxides (100 mg) was irradiated in the presence of methylene blue (2 mg) in an aerated atmosphere for 2 days. The usual workup revealed no change. The thermal and photochemical behavior of thioketene *S*-oxides have been previously investigated.[26]

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Di-*tert*-butylsulfine is stable in aerated media both in the absence and presence of visible light. But 2,2,6,6-tetramethylcyclohexanethione *S*-oxide decomposes over a period of 10 days even in dark. However, these two sulfines were found to be stable toward singlet oxygen (dye sensitization).

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Registry No. 1, 16797-75-4; 2, 54440-00-5; 3, 16797-76-5; 4, 56956-25-3; 5, 10507-31-0; 6, 79265-24-0; 7, 39195-77-2; 8, 63702-87-4; 9, 63702-89-6; 10, 1195-93-3; 11, 88131-22-0.

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Intramolecular Trapping of Alkyl- and Arylrhodium Hydride Intermediates in the Decarbonylation of Aldehydes by Chlorotris(triphenylphosphine)rhodium

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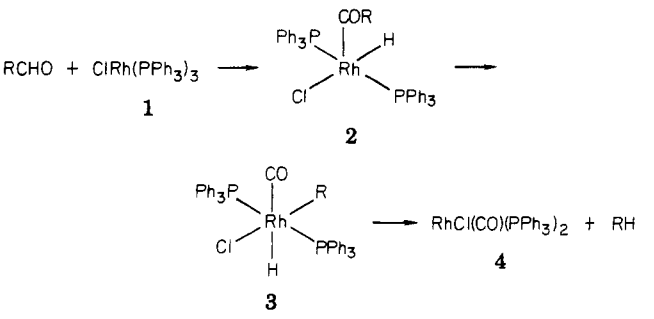
The reaction of 5-hexenal with $RhCl(PPh_3)_3$ (1) or $[RhCl(PPh_3)_2]_2$ (5) gives some cyclopentane. The reaction of 2-allylbenzaldehyde with 5 gives a good yield of indan. These cyclization reactions to give cyclopentanes, and other reactions of Δ^4-enals to give cyclopropanes, reveal the presence of intermediate alkyl- and arylrhodium hydride complexes on the pathway for decarbonylation of aldehydes. The formation of nortricyclene from *endo*-5-norbornene-2-carboxaldehyde shows that the alkylrhodium hydride must be formed with retention of stereochemistry at the α-carbon of the aldehyde.

The standard mechanism for the decarbonylation of aldehydes by chlorotris(triphenylphosphine)rhodium (1) proceeds in stepwise fashion via intermediate acylrhodium hydride (2) and alkylrhodium hydride (3) complexes (Scheme I).[1,2] Since the rate-determining step in this sequence is the initial oxidative addition,[2-4] the intermediate complexes, 2 and 3, cannot be observed directly. In fact, the mechanism and the intermediacy of 2 and 3 were originally based, in part, on analogy to the decarbonylation of acid chlorides where the intermediate acyl and alkyl complexes can be isolated.[1] Miller provided the first solid evidence[5] for the role of complex 2 by trapping the acylrhodium hydride from 4-pentenal by addition of the Rh–H bond to the double bond to give a six-membered-ring rhodium complex which decomposes to cyclopentanone. Suggs first isolated the oxidative addition product of an aldehyde and complex 1 by using 8-quinolinecarboxaldehyde, a substrate with an intramolecular ligand to trap the 5-coordinate acylrhodium hydride.[6] Most recently, Milstein isolated a 6-coordinate acylrhodium hydride from

Scheme I



the reaction of 4-pentenal with chlorotris(trimethylphosphine)rhodium.[7] Thus, there is good evidence for the intermediacy of 2 on the pathway for the decarbonylation of aldehydes by Rh(I) complexes. In contrast, there is little evidence for complex 3, the aryl- or alkylrhodium hydride intermediate. The stereochemistries of the formation and decomposition of the alkylrhodium hydride intermediate will determine the overall stereochemistry of the decarbonylation of a chiral aldehyde since these are the steps in which bonds are made and broken to the chiral center. In the absence of observations on complex 3, it is not possible to assign stereochemistry to the individual bond making and bond breaking steps from a single observation of the net stereochemistry of decarbonylation. This paper

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0022-3263/84/1949-0621$01.50/0

Table I. Reaction of 5-Hexenal with Rhodium Complexes[a]

reagent	solvent (additive)	t, h	temp, °C	mol/mol of 5-hexenal consumed: pentene	cyclopentane	2-methylcyclopentanone	% RCHO recovered
1	$CHCl_3$[b]	45	25	0.22	0.09	0.49	c
1	CH_2Cl_2	46	25	0.17	0.13	0.53	42
1	CH_2Cl_2	10	40	0.08	0.06	0.11	c
5	CH_2Cl_2	37	40	0.46	0.02	0.53	c
5	CH_2Cl_2[d] (RCHO)	21	40	0.67	0.08	0.05	85
5	CH_2Cl_2[e] (CH_3CN)	31	25	0.34	0.10	0.65	17
5	CH_2Cl_2[f] (Ph_3P)	50	40	0.76	0.24	0.17	58
5	C_6H_6	24	80	0.72	0.03	0.08	c
5	CH_3CN	45	25	0.16	c	0.78	23

[a] [RCHO]/["Rh"] = 1. [b] Ethanol free. [c] None was detected. [d] [RCHO]/["Rh"] = 10. [e] [CH_3CN]/["Rh"] = 10. [f] [PPh_3]/["Rh"] = 10.

Table II. Reaction of 2-Allylbenzaldehyde with $[RhCl(PPh_3)_2]_2$

[ArCHO]/["Rh"]	solvent (additive)	t, h	temp, °C	% of products[a]: allylbenzene	β-methylstyrene	indan
6	CH_2Cl_2[b]	46	25	21	c	80
6	CH_2Cl_2[b]	43	40	28	25	47
1	CH_2Cl_2	48	40	36	22	43
10	CH_2Cl_2	48	40	47	c	53
10	CH_2Cl_2[d] (PPh_3)$_3$	76	25	71	1	28
6	C_6H_6[b]	48	54	26	13	62
5	C_6H_6	48	80	c	34	66
10	CH_3CN[e]	45	25	38	42	10
1[f]	CH_2Cl_2	29	40	27	43	30

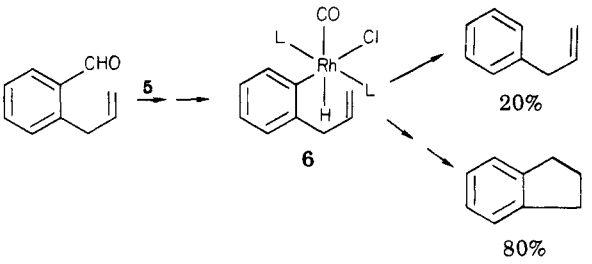
[a] 10^2 (moles of product)/total moles of product. [b] Analyzed by the internal standard method (see Experimental Section). [c] Not detected. [d] [PPh_3]/[RCHO] = 10. [e] 2-Methylindanone (10%) formed. [f] Reagent was $ClRh(PPh_3)_3$.

describes two different intramolecular trapping reactions of the alkyl and acylrhodium hydride complexes on the pathway for decarbonylation of aldehydes. The use of one of these trapping reactions allows us to distinguish between diastereomeric aldehydes and to assign the stereochemistry of the formation of the alkylrhodium hydride intermediate.

5-Hexenal reacts with complex 1 to give mixtures of 2-methylcyclopentanone,[8] cyclopentane, and pentene.[9] Cyclohexanone was not formed. The chlorine bridged dimer $[RhCl(PPh_3)_2]_2$ (**5**) is also an effective reagent for reaction with 5-hexenal. In general, the distribution of the products, the rate of the reaction, and the mass balance are sensitive to the nature of the organometallic reagent, the solvent, and additives in complex ways which we do not fully understand. The reaction of 1 with 5-hexenal is very sensitive to temperature; the mass balance is reasonable at 25 °C, but consistently poor at 40 °C. These poor mass balances presumably reflect competing reactions which divert 5-hexenal from the reactions which give pentene, cyclopentane, and 2-methylcyclopentanone. These side reactions are less important with the chlorine-bridged dimer **5**, and the dimer is, therefore, a better choice of reagent. Added triphenylphosphine dramatically depresses the rate of reaction. Acetonitrile favors ketone. The results of these reactions under various conditions are given in Table I.

The three products of these reactions, 2-methylcyclopentanone, cyclopentane, and pentene, correspond most simply to intramolecular trapping of the acylrhodium hydride intermediate **2′** by the double bond, trapping of the alkylrhodium hydride **3′** by the double bond, and no trapping, respectively (Scheme II). Because both **2′** and **3′** are partitioned between competitive pathways, it may not be surprising that the product composition is a sensitive function of conditions, solvent, and additives.[10]

By changing the nature of the substrate, we were able to change the relative rate constants for the competitive processes in Scheme II and trap an arylrhodium hydride, **6**, in good yield. Thus, the reaction of 2-allylbenzaldehyde with $[RhCl(PPh_3)_2]_2$ in CH_2Cl_2 at 25 °C gave indan in 80% yield (eq 1). Reactions of 2-allylbenzaldehyde under



(1)

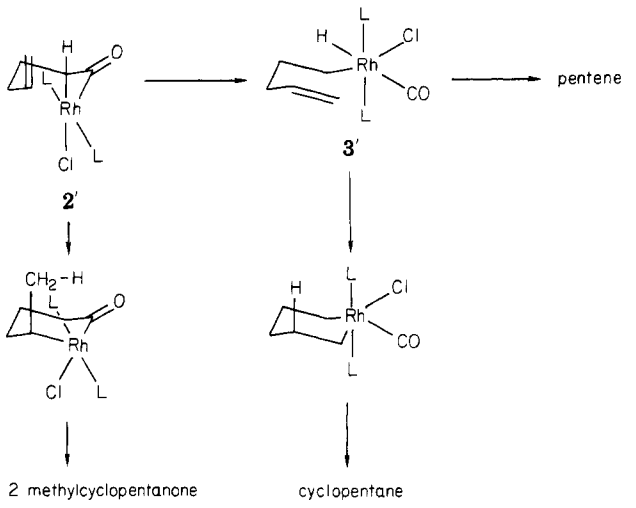
various conditions are reported in Table II. In general, mass balances were excellent with either 1 or **5** as the

(8) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190–197.

(9) The isomeric pentenes were not resolved under our GC conditions. We expect the pentenes to be isomerized under the reaction conditions.

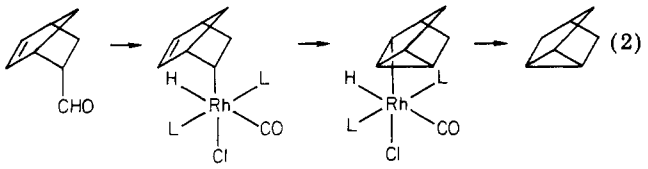
(10) An alternative explanation of the apparent complexities of the reaction is that 5-hexenal is partially isomerized to 4-hexenal under the reaction conditions and that 5-hexenal is the source of cyclopentane and 1-pentene while 4-hexenal is the source of the methylcyclopentanone. In this proposal, the variations in product yields reflect varying amounts of isomerization of 5-hexenal. We carefully monitored reactions of 5-hexenal by NMR for the presence of 4-hexenal, without success. Thus, if 4-hexenal is formed, it must be selectively consumed. In addition, we prepared 1-deuterio-5-hexenal. The deuterated aldehyde was reacted with **5** ([RCHO])/["Rh"] = 1) in CH_2Cl_2 for 24 h at 50 °C. Gas chromatographic analysis of the reaction mixture showed the formation of 2-methylcyclopentanone. The reaction mixture was concentrated to remove the more volatile products and analyzed by DNMR. The spectrum showed a strong signal at δ 0.98 (CH_2D) and no significant absorption between δ 1.5 and 2.5, corresponding to ring deuteration. Thus, 1-deuterio-4-hexenal is not the source of the 2-methylcyclopentanone.

Scheme II



reagent. β-Methylstyrene was often formed; a simple control experiment showed that allylbenzene is isomerized to β-methylstyrene in CH_2Cl_2 at 40 °C in the presence of reacting 5-hexenal. We could not detect any isomerization of residual 2-allylbenzaldehyde by careful NMR analysis of actual reaction mixtures in which allylbenzene was isomerized to β-methylstyrene. Added phosphine slowed the reaction and also suppressed the formation of indan. Acetonitrile solvent facilitated trapping of the acylrhodium hydride intermediate to give a 10% yield of 2-methylindanone; the ketone was not formed under any other conditions. The major products from the reaction of 2-allylbenzaldehyde with 1 or 5 correspond to trapping of the arylrhodium hydride (indan) and simple decarbonylation (allylbenzene).

endo-5-Norbornene-2-carboxaldehyde reacts with 1 to give a high yield of nortricyclene.[3] The corresponding exo isomer gives only norbornene; the exo geometry precludes any interaction between rhodium and the double bond, and straightforward decarbonylation is observed. In the endo geometry, the alkylrhodium hydride **7** is trapped by a homoallylic rearrangement to the double bond (eq 2).


(2)

This rearrangement is well-known for several other alkyl–metal systems.[11] "Homoallylic trapping" of the alkylrhodium hydride intermediate also explains the formation[12,13] of cyclopropanes in the reaction of substituted 4-pentenals with 1.

The net stereochemistry of the decarbonylation of chiral aldehydes is retention.[14] As noted earlier, the mechanistic significance of this result is ambiguous and could correspond to either retention–retention or inversion–inversion sequences for the bond forming and bond breaking processes at the chiral center. The reactions of the *endo*- and *exo*-norbornenecarboxaldehydes show that the alkylrhodium hydrides must be formed with retention of stereochemistry. Had the alkylrhodium hydride been formed with inversion of stereochemistry, *exo*-aldehyde would have given *endo*-alkylrhodium hydride which would have been trapped by the double bond to give nortricyclene; conversely, the *endo*-aldehyde would have given norbornene. These observations on the norbornenecarboxaldehydes provide the first direct evidence that the alkylrhodium hydride intermediate in the decarbonylation of aldehydes is formed with retention of stereochemistry and, therefore, establish the stereochemistries of bond making and bond breaking as retention–retention. The stereochemistries of the individual steps had previously been deciphered[15] by analogy to other metal acyl–alkyl rearrangements.[16]

In summary, the experiments discussed in this paper show that the presumed aryl- or alkylrhodium hydride intermediates in the decarbonylation of aldehydes can actually be trapped by intramolecular addition to a double bond to give cyclopentanes or by homoallylic rearrangement to give cyclopropanes. Furthermore, the alkylrhodium hydride must form and decompose with retention of stereochemistry. These results, in connection with previous observations on the acylrhodium hydride intermediate, give us a solid description of the steps in the decarbonylation of aldehydes by Rh(I) complexes.

Experimental Section

Solvents were freshly distilled from drying agent in a nitrogen atmosphere. All reactions were conducted with exclusion of oxygen. NMR spectra were determined in $CDCl_3$ with Me_4Si as an internal standard on EM3 90-MHz and Bruker WH 400-FT NMR instruments. IR spectra were determined on a PE-467 instrument calibrated against the 1601-cm^{-1} absorption of polystyrene. Mass spectra were determined on a VG 7035 GC/MS/DS instrument.

Preparation of Complexes. $ClRh(PPh_3)_3$ (1) was prepared by the reaction of $RhCl_3 \cdot 3H_2O$ with triphenylphosphine/ethanol:[17] 133–135 °C dec (lit. 157–58 °C,[17] 134 °C,[18,19]). $[RhCl(PPh_3)_2]_2$ (5) was prepared by refluxing 1 in benzene.[20]

2-Hexenal Dimethylhydrazone.[19] Into a flame-dried, nitrogen-flushed, three-necked flask with a dropping funnel were added 100 mL of dry THF and 8.3 mL (60 mmol) of diisopropylamine. After this mixture was cooled to −78 °C, 25 mL of 2.4 M butyllithium in hexane (60 mmol) was added dropwise by a syringe. The solution was then warmed to 0 °C and stirred for 1.5 h at 0 °C. Acetaldehyde dimethylhydrazone[21] (5.16 g, 60

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(13) Baird[15] proposed that the acylrhodium hydrides from 4-pentenals cyclize competitively to give both five- and six-membered-ring acylrhodium intermediates. Reductive elimination of rhodium with concomitant carbon–carbon bond formation converts the six-membered-ring acylrhodium complexes to cyclopentanones, as observed. Baird also proposed that the five-membered-ring acylrhodium complexes decarbonylate to give four-membered-ring cycloalkylrhodium intermediates which eliminate rhodium with carbon–carbon bond formation to give the cyclopropanes. Since 4-pentenals give neither cyclobutanone nor cyclobutane products,[8] there is no evidence for the five-membered-ring acylrhodium complex or for the decarbonylation of the six-membered-ring acylrhodium intermediate.

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mmol) in 100 mL of dry THF was added dropwise. After 2 h at 0 °C, the solution was cooled to −78 °C. 4-Bromobutene (6.75 g, 50 mmol, Aldrich) was added rapidly by syringe. This solution was stirred at −78 °C for 2 h and was kept at −10 °C in a refrigerator for 16 h. The solution was then poured into 200 mL of methylene chloride and 600 mL of water. The aqueous layer was removed and washed with methylene chloride (2 × 200 mL). The combined organic phases were then extracted with 100 mL of H_2O, dried with Na_2SO_4, and concentrated at reduced pressure to yield a yellowish liquid. Distillation gave 6.11 g (90%) of 5-hexenal dimethylhydrazone: bp 88 °C (27 mm); NMR δ 1.60 (overlapping triplets, J = 8 Hz, 2 H), 2.18 (m, 4 H), 2.72 (s, 6 H), 4.88 (br s, 1 H), 5.02 (br d, J = 8 Hz, 2 H), 5.80 (m, 1 H), 6.62 (t, J = 6 Hz, 1 H); IR (film 2899 (s, br), 1631 (m), 1460 (s), 1429 (s), 1245 (m), 1133 (m), 1028 (s), 995 (m), 912 (s) cm^{-1}.

5-Hexenal.[19] Into a flask were placed 5.3 g (39 mmol) of 5-hexenal dimethylhydrazone, 200 mL of ether, and 40 mL of 1.2 M HCl. The contents of the flask were stirred under nitrogen for 4 h at room temperature. The yellow aqueous layer was removed and washed with portions (2 × 100 mL) of pentane. The combined organic phase was extracted with 50 mL of water, 50 mL of saturated $NaHCO_3$, and 20 mL of brine. After the mixture was dried with Na_2SO_4, the solvent was removed by slow, careful distillation through an 18-in. Vigreux column. Careful distillation of the residue by using a receiver cooled to −78 °C gave 3.5 g (92%) of 5-hexenal: bp 50 °C (25 mm) [lit.[22] bp 118–118.5 °C (760 mm)]; NMR δ 1.78 (m, 2 H), 2.10 (m, 2 H), 2.46 (d, t, J = 1.5, 5 Hz, 2 H), 4.90 (br s, 1 H), 5.06 (br d, J = 6 Hz, 1 H), 5.75 (m, 1 H), 9.74 (t, J = 1.5 Hz, 1 H); IR (film) 3080 (m), 2940 (s), 2820 (s), 2720 (s), 1725 (s), 1640 (m), 990 (m), 910 (s) cm^{-1}; MS (70 eV), m/e (relative intensity 98 (2 M^+), 97 (4), 80 (38), 55 (53), 54 (100), 41 (94), 39 (71).

2-Bromobenzaldehyde Ethylene Acetal. To a solution of 10.0 g (54.4 mmol) of 2-bromobenzaldehyde (Aldrich) in 20 mL of benzene were added 4.02 g (64.8 mmol) ethylene glycol and 100 mg p-toluenesulfonic acid. The solution was heated in a Dean–Stark apparatus until no more water could be collected (5 h) and stored for 12 h at 25 °C. The solution was washed with 2 N NaOH (2 × 15 mL) and brine (3 × 15 mL) and dried over KOH. The solvent was removed at reduced pressure and the crude material distilled to give 11.2 g (90.5%) of the acetal: bp 96–100 °C (0.3 mm); ^1H NMR δ 4.1 (m, 4 H), 6.08 (s, 1 H), 7.2–7.5 (m, 4 H).

2-Allylbenzaldehyde. A solution of *sec*-BuLi in hexane (1.1 M) corresponsing to 2.75 mmol of reagent was added dropwise from a syringe to a solution of 0.477 g (2.08 mmol) of 2-bromobenzaldehyde ethylene acetal in 20 mL of dry THF at −78 °C. After 2.5 h at −78 °C, 0.373 g of hexamethylphosphoramide was added, and the solution was transffered under nitrogen into a solution of 0.429 g (2.08 mmol) of $CuBr{\cdot}Me_2S$ in 10 mL of THF at −50 °C.[23] After 30 min at −50 °C, the solution was warmed to −20 °C, and 1.1 mL (13.4 mmol) of freshly distilled allyl bromide was added rapidly by syringe. The solution was warmed slowly to 25 °C. After 1 h, 30 mL of saturated NH_4Cl solution was added and the product extracted into portions (4 × 50 mL) of ether. The ether solution was washed with concentrated NH_4OH (2 × 50 mL) and water, dried over Na_2SO_4, and concentrated to give crude 2-allylbenzaldehyde ethylene acetal: NMR δ 3.5 (dd, 2 H), 4.05 (, 4 H), 4.93 (br d, 1 H), 5.1 (br s, 1 H), 5.92 (m, 1 H), 5.93 (s, 1 H), 7.1–7.6 (m, 4 H).

The crude acetal was dissolved in a mixture of 6.5 mL of dioxane and 3.5 mL of H_2O, 50 mg of p-toluenesulfonic acid was added, and the solution was heated at 90 °C for 9 h. Brine (10 mL) was added and the solution extracted with ether (4 × 15 mL). The ether extract was washed with H_2O (2 × 10 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was distilled to give 0.29 g (80%) of 2-allylbenzaldehyde: bp 51–52 °C (0.35 mm); NMR δ 3.82 (d, J = 6.6 Hz, 2 H), 4.95, 5.01 (2 d, J = 13.3, 15.5 Hz, 2 H), 6.0 (m, 1 H), 7.29 (t, 1 H), 7.38 (t, 1 H), 7.5 (t, d, 1 H), 7.85 (dd, 1 H), 9.95 (s, 1 H); IR (film) 3090, 3005, 2980, 2920, 2860, 2740, 1695 (s), 1635, 1600 (s), 1575, 755 (s) cm^{-1}; MS (70 eV, 40 °C), m/e (relative intensity) 146 (21, M^+), 145 (28), 131 (54), 128 (25), 117 (39), 115 (39), 118 (23), 103 (19), 91 (25), 69 (56), 39 (28), 28 (100).

1-Deuterio-5-hexenal. 5-Hexenal (1.9 g, 19.4 mmol) was dissolved in 100 mL of $CHCl_3$ and 1.95 mL of 1,3-propanedithiol added. The solution was cooled to −3 °C and dry HCl gas passed in slowly for 10 min. The solution was stirred for 5 h at 0 °C and then added to 150 mL of H_2O. The $CHCl_3$ layer was washed with water (3 × 100 mL), 100 mL of 10% KOH solution, and 100 mL of water, dried over K_2CO_3, and concentrated. The residue was distilled [bp 92–94 °C (2 mm)] to give 2.8 g (76.8%) of the 2-(4-pentenyl)-1,3-dithiane: NMR δ 5.7 (m, 1 H), 4.95 (d, 1 H), 4.85 (s, 1 H), 3.95 (t, 1 H), 2.8 (m, 4 H), 2.0 (m, 4 H), 1.7 (m, 4 H). The dithiane (2.7 g, 14.4 mmol) was dissolved in 30 mL dry THF and the solution cooled to −40 °C. n-Butyllithium (5.8 mL, 2.6 M) was added slowly by syringe, and the solution was stirred for 3 h at −40 °C and for 2 h at −10 °C. Then, 10 mL of D_2O was added and the mixture extracted with ether. The ether solution was dried over K_2CO_3, the ether removed, and the residue distilled [bp 92–94 °C (2 mm)] to give 2.05 g of 2-(4-pentenyl)-2-deuterio-1,3-dithiane: NMR δ 5.7 (m, 1 H), 4.95 (d, 1 H), 4.85 (s, 1 H), 2.8 (m, 4 H), 2.0 (m, 4 H), 1.7 (m, 4 H). The deuterated dithiane (1.9 g, 10.1 mmol) was dissolved in 63 mL of CH_3CN/H_2O (9:1), and 1.3 g of $CaCO_3$ and 4.7 mL of CH_3I were added. The solution was stirred under N_2 for 7.5 h at 90 °C, cooled, poured into brine, and extracted five times with pentane. The pentane extracts were dried over $MgSO_4$ and carefully distilled through a Vigreux column by using a cooled receiver to give 0.250 g of 1-deuterio-5-hexenal, bp 46–50 °C (25 mm). The NMR spectrum was identical with that of the undeuterated 5-hexenal except for the intensity of the absorption at δ 9.74; the residual H signal showed the aldehyde to be about 90% deuterated.

General Reaction Procedure. Into a Schlenk flask flushed with nitrogen were placed 0.10–0.05 mmol of $RhCl(PPh_3)_3$ or $[RhCl(PPh_3)_2]_2$ and the appropriate amount of aldehyde in 2.5–5.0 mL of solvent. The solution was deoxygenated with three freeze–pump–thaw cycles and closed in vacuo.

After the specified time at the specified temperature, the mixture was bulb-to-bulb distilled at reduced pressure. The residue was recrystallized from 1,2-dichloroethane to give $RhCl(CO)(PPh_3)_2$; the IR spectrum was superimposable with that of an authentic sample. The volatile fraction from the bulb-to-bulb distillation was analyzed by GC on a Hewlett-Packard 5710A thermal-conductivity gas chromatograph with a 10-ft column of 10% FFAP on Chromosorb PAW 60/80 or a 12-ft column of 20% Carbowax on Chromosorb P. Peak areas were determined by triangulation and were corrected for different thermal conductivities. The peaks were identified by coinjection with authentic samples on two different columns at two different temperatures. In the experiments with 5-hexenal, an internal GC standard was added before the bulb-to-bulb distillation. The GC traces were analyzed to give the number of moles of products of recovered aldehyde. The results in Table I, therefore, are reported as moles of product/mole of aldehyde consumed. Several reactions of allylbenzaldehyde were analyzed in the same manner (CH_2Cl_2, 25 °C; CH_2Cl_2, 40 °C; and C_6H_6, 54 °C). The other runs were analyzed without standard. Since the mass balances in the runs with standard were found to be >90%, the mass balances in the runs without standard were assumed to be >90% also, and the product composition was calculated as moles of product/total moles of product in all runs in Table II. No extraneous unidentified peaks were present in any of the GC traces.

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Registry No. 2′, 88180-28-3; 6, 88180-29-4; 7, 88180-30-7; $ClRh(PPh_3)_3$, 14694-95-2; $[RhCl(PPh_3)_2]_2$, 14653-50-0; $RhCl_3$, 10049-07-7; 2-allylbenzaldehyde, 62708-42-3; *endo*-5-norbornene-2-carboxaldehyde, 19926-90-0; nortricyclene, 279-19-6; allylbenzene, 300-57-2; indan, 496-11-7; *exo*-5-norbornene-2-carboxaldehyde, 19926-88-6; norbornene, 498-66-8; acetaldheyde

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dimethylhydrazone, 7422-90-4; 5-hexenal dimethylhydrazone, 88180-24-9; 2-bromobenzaldehyde ethylene acetal, 34824-58-3; allyl bromide, 106-95-6; 1-deuterio-5-hexenal, 88180-25-0; 1,3-propanedithiol, 109-80-8; 2-(4-pentenyl)-1,3-dithiane, 88180-26-1; 2-(4-pentenyl)-2-deuterio-1,3-dithiane, 88180-27-2; 5-hexenal, 764-59-0; 2-methylcyclopentanone, 1120-72-5; cyclopentane, 287-92-3; 4-bromobutene, 5162-44-7; 2-bromobenzaldehyde, 6630-33-7; pentene, 25377-72-4.

Thermal and Photochemical Reactions of 10-Oxabenzo-*syn*-sesquinorbornene (1,2,3,4,9,10-Hexahydro-9,10-*exo*-epoxy-1,4-*exo*-methanoanthracene)

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The chemical behavior of the title compound (**5**) is influenced both by the fused benzo group and by the oxa bridge. In thermal additions to the double bond **5** is from 1.3 to 13.7 times as reactive as the analogue **6** with CH_2 in place of the O bridge. Treatment of the oxa compound **5** with chloroform and 50% sodium hydroxide for 12 h yielded the crowded dichlorocarbene adduct to the double bond, while no way has been found to add dichlorocarbene to the methylene species **6**. The photochemical behavior of **5** in acetone resembles that of the parent *syn*-sesquinorbornene, **1**. The benzo group also enables **5** by direct photoexcitation to capture hydrogen from cyclohexane, which **1** cannot do without a sensitizer. As a consequence of this direct excitation, **5** undergoes rapid rearrangement which competes with its other photochemical reactions. X-ray crystallographic studies[9] of compound **5** and its dichlorocarbene adduct have been made and will be published separately.

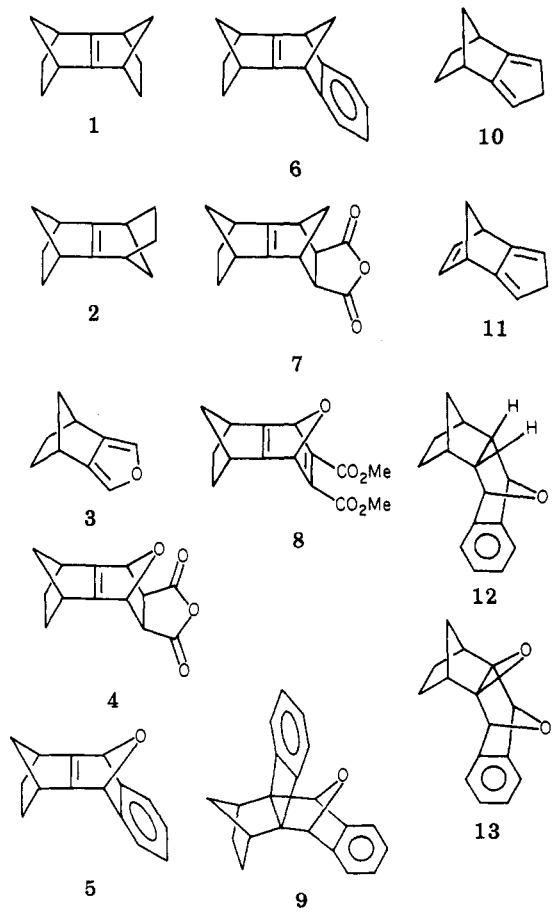
The reactivity of the carbon–carbon double bond responds to electronic effects of substituents in ways that are, in principle, fairly well understood. In addition, the double bond can be perturbed by geometric distortions of several kinds, each of which affects the chemical properties in particular ways. Incorporation in a small ring bends the system about the *z* axis (Figure 1); strained olefins with a double bond at a bridgehead exemplify, among other effects, torsion about the *x* axis.[1] Bending about the *y* axis is also enforced in 9,9′-dehydrodianthracene.[2]

The study of *syn*- and *anti*-sesquinorbornenes **1** and **2** (Chart I) has revealed a combination of some expected steric effects of the bridges[3] with newly discovered stereoelectronic properties of the π system. In the case of the syn isomer the double bond is bent like a hinge about the *x* axis 16–18° out of the normal planarity.[4] The readiness with which the sesquinorbornene system responds to small modifications of the environment of the double bond has prompted the present study[5] of some oxasesquinorbornenes in which the replacement of the CH_2 bridge by an oxygen atom has potential effects of both polar and steric kinds.

Vogel and co-workers[6] added maleic anhydride to norbornenofuran **3**, obtaining a single product, shown by X-ray crystallography to be the *syn*-oxasesquinorbornene anhydride **4**. We have compared furan with cyclopentadiene in addition to the dicarboxylic anhydrides of norbornene and norbornadiene.[7]

In this paper we report the preparation and properties of 10-oxabenzo-*syn*-sesquinorbornene (**5**) which proves to be a very favorable subject for X-ray crystallography and for comparisons of its chemical behavior with **4**, **6**, and **7**.

Chart I



Results

The starting norbornenofuran **3** was prepared by the method of Vogel.[8] Treatment of **3** with a single equivalent

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