thiophene ring β proton), 2.8 (t, 2 H, CH_2Ar), 1.1–1.9 (broad m, 8 H, "central" methylene protons), 0.9 (t, 3 H, CH_3).

Anal. Calcd for $C_{14}H_{18}S$: C, 77.01; H, 8.31. Found: C, 76.88; H, 8.38.

14-(Benzothienyl-2)tetradecanoic Acid (3). This compound was prepared according to the following scheme (R = 2-benzothienyl).

$$RH \xrightarrow[2.\ Br(CH_2)_{12}Br]{1.\ BuLi} R(CH_2)_{12}Br \xrightarrow{(CO_2Et)_2CHNa} R(CH_2)_{12}CH(CO_2Et)_2 \xrightarrow[AcOH/H_2O]{H_2SO_4} 3$$

Alkylation of benzothiophene (6.6 g, 49 mmol) was carried out as above with BuLi (54 mmol) and 1,12-dibromododecane (16 g, 49 mmol). Since we found it difficult to separate the monobenzothienyl from the bisbenzothienyl derivative, the mixture was treated with sodium diethyl malonate in ethanol, and the resulting crude product was eluted with benzene on silica gel, to give 6.3 g (14 mmol) of 12-(benzothienyl-2)dodecylmalonate in 28% overall yield: n^{20}_D 1.5132; ^1H NMR as expected. Hydrolysis and decarboxylation of the latter with boiling 12% H_2SO_4 in an acetic acid–water mixture for 20 h gave **3** in 74% yield: mp 83–84.5 °C from MeOH; IR $\nu_{C=O}$ 1710 cm^{-1}.

Anal. Calcd for $C_{22}H_{32}O_2S$: C, 73.29; H, 8.95. Found: C, 73.06; H, 8.88.

[14](2,3)Benzothiophenophan-14-one (4). To a solution of **3** (0.40 g, 1.1 mmol) and 85% H_3PO_4 (0.26 g) in dry CH_3CN (220 mL), heated at 50 °C, was rapidly added 3.2 mL of $(CF_3CO)_2O$ under magnetic stirring. The resulting mixture was kept at 50 °C for 45 min, then worked-up with water–ether. The crude material was eluted on silica gel with benzene–light petroleum 2:1 to give 130 mg (0.38 mmol) of pure (TLC) **4** in 34% yield. For analytical purposes the compound was further purified by microdistillation with the ball tube under high vacuum. Compound **4** had: mp 21–23 °C; n^{19}_D 1.5503 (of the supercooled liquid); IR $\nu_{C=O}$ 1670 cm^{-1}; M^+ 342; ^1H NMR (CCl_4) δ 7.0–7.7 (m, 4 H, benzene ring protons), 2.85 (t, 2 H, $ArCH_2$), 2.70 (t, 2 H, CH_2COAr), 1.0–1.8 (broad m, 22 H, "central" methylene protons).

Anal. Calcd for $C_{22}H_{30}OS$: C, 77.14; H, 8.83. Found: C, 77.16; H, 8.94.

Further elution afforded 25 mg of a white crystalline material melting at 54.5–57.5 °C, to which the tentative structure of the dimeric cyclic can be assigned on the basis of the finding that its ^1H NMR spectrum is practically superposable to that of the monomeric cycle **4**.

Rate Measurements. These were carried out on a Beckman DB GT spectrophotometer fitted with a thermostated cell compartment and recorder. The kinetics solutions were prepared by placing the appropriate amounts of substrates and H_3PO_4 in CH_3CN in an all-quartz cell. After thermal equilibration at 50.0 ± 0.1 °C, the reaction was started by rapidly adding with a microsyringe a calculated amount of a standard solution of $(CF_3CO)_2O$ in CH_3CN. All operations were carried out under an argon atmosphere.

In the intermolecular model reaction between 2-methylthiophene and pentanoic acid, it was noted, in addition to the induction period, that the absorption rose significantly after the expected OD_∞ was reached. This behavior was attributed to the concurrent formation of an unknown byproduct whose strong absorption in the range of 300 to 600 nm superposed to that of the expected ketone. The addition of a drop of water at the end of the reaction caused the disappearance of the anomalous absorption and left an absorption consistent with a 75% yield of the expected ketone product. Similar behavior was also observed with thiophene and its 3-methyl derivative and with alkanoic acids other than pentanoic acid.

Product Analyses. These were carried out on scaled-up kinetic experiments. The crude materials obtained after standard workup were analyzed by VPC on a "Erba Model G" instrument, fitted with a 5% methylsilicone SE-30 on Chromosorb column. In the case of product **2**, n = 15, the column was operated at 178 °C with eicosane as the internal standard, while in the case of the compound **4**, the temperature of the column was 230 °C and octacosane was the internal standard.

Registry No. **1**, n = 12, 21010-08-2; **1**, n = 13, 21010-09-3; **1**, n = 15, 21010-10-6; **1**, n = 17, 71948-92-0; **1**, n = 21, 26359-19-3; **2**, n = 12, 71948-93-1; **2**, n = 13, 886-42-0; **2**, n = 15, 6907-25-1; **2**, n = 17, 6907-40-0; **2**, n = 21, 6907-44-4; **3**, 71948-94-2; **4**, 71948-95-3; 2-hexylbenzothiophene, 71948-96-4; benzothiophene, 95-15-8; diethyl 12-(benzothienyl-2)dodecylmalonate, 71948-97-5.

Tests for Free-Radical Intermediates in the Decarbonylation of Aldehydes by Tris(triphenylphosphine)chlororhodium(I)

J. A. Kampmeier,* S. H. Harris,[1] and D. K. Wedegaertner

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received July 10, 1979

Wilkinson's catalyst [$RhCl(PPh_3)_3$ (**1**)] was reacted with phenylacetaldehyde (**5h**), phenylacetaldehyde-*d* (**5d**), *p*-methylphenylacetaldehyde (**6**), citronellal (**7**), and *exo*- and *endo*-5-norbornene-2-carboxaldehyde (**10x** and **10n**). The decarbonylation of mixtures of **5h** and **5d** shows an isotope effect (k_H/k_D) of 1.86 ± 0.07. No H–D crossover is observed when a mixture of **5d** and **6** is reacted with **1**. The reaction of citronellal (**7**) gives only 2,6-dimethyl-2-heptene. **10x** gives norbornene, and **10n** gives nortricycline; no crossover between the two systems is observed. These observations are consistent with concerted processes, intramolecular in aldehyde, for each step in the overall decarbonylation reaction; free-radical intermediates are excluded.

There is general agreement[2] on the overall mechanism (eq 1) for the decarbonylation of acid chlorides and aldehydes by tris(triphenylphosphine)chlororhodium(I) (**1**). However, the exact nature of the individual processes, i.e., oxidative addition (**1** + RCOX → **2**), acyl–alkyl migration (**2** → **3**), and reductive elimination (**3** → RX + **4**), is not clear. This reaction is a useful synthetic method and is a model for the discrete processes in other organometallic reactions. Therefore, a detailed knowledge of the mech-

$$\underset{\mathbf{1}}{RhCl(PPh_3)_3} + RCOX \rightarrow \underset{\mathbf{2}}{RCO(X)RhCl(PPh_3)_2} \rightarrow \underset{\mathbf{3}}{R(X)RhCl(CO)(PPh_3)_2} \rightarrow RX + \underset{\mathbf{4}}{RhCl(CO)(PPh_3)_2} \quad (1)$$

X = Cl, H

(1) Taken in part from the Ph.D. Thesis of Stephen H. Harris, University of Rochester, 1979; Sherman Clarke and Elon H. Hooker Fellow, University of Rochester.

(2) D. L. Egglestone, M. C. Baird, C. J. L. Lock, and G. Turner, *J. Chem. Soc., Dalton Trans.*, 1576 (1977); J. K. Stille and M. T. Regan, *J. Am. Chem. Soc.*, **96**, 1508 (1974), and references cited therein.

0022-3263/80/1945-0315$01.00/0

Table I. Reactions of Phenylacetaldehyde (5h), Phenylacetaldehyde-1-d (5d), and p-Methylphenylacetaldehyde (6) with $RhCl(PPh_3)_3$

entry no.	time, h	reactants,[a] mol × 10^4 5d[b]	5h	6	1	% of products 4[c]	RH(D)[c]	d_0[d]	d_1[d]
1	1.75	10.59	15.39		1.10	88	140[e,f]	72.4 ± 1.3	27.3 ± 1.5
2	2.75	17.77	8.38		0.96	83	93[e,g]	46.6 ± 0.6	53.3 ± 0.7
3	20.0	1.90			0.84	82	87[e]	1.3 ± 0.3	98.5 ± 0.3
4	1.5	10.52		10.14	1.03	89	44[e]	3.9 ± 1	95.9 ± 1
							64[h]	99.8 ± 0.3	0.2 ± 0.3

[a] All reactions are carried out under N_2 in 2.0 mL of CH_2Cl_2 at reflux. [b] 98.9 ± 0.5% d_1. Experiment 3 shows that no H/D exchange of the aldehyde proton occurs with the solvent. [c] Based on 1. [d] Obtained by linear least-squares analyses of multiple mass spectral determinations; errors are standard deviations. [e] Toluene. [f] $k_H/k_D = 1.86 \pm 0.15$. [g] $k_H/k_D = 1.86 \pm 0.05$. [h] p-Xylene.

anisms and stereochemistry for the individual steps is important. Because of reports of free-radical mechanisms[3] for oxidative addition, reductive elimination, and olefin insertion in other organometallic systems, we set out to definitively probe for the involvement of free radicals in the mechanism of decarbonylation of aldehydes by Wilkinson's catalyst (1). Appropriately functionalized aldehydes were used to test for free-radical intermediates.

Investigation of the mechanism of oxidative addition of aldehydes and acyl halides to metal centers poses a challenge since the sp^2-hybridized carbonyl carbon lacks chirality and, therefore, excludes the possibility of a stereochemical reaction probe. Baird, Nyman, and Wilkinson[4] investigated the kinetics of the decarbonylation of n-valeraldehyde by 1. No intermediates were observed by either IR or NMR spectroscopy, which led them to conclude that the oxidative addition of aldehydes to rhodium is probably rate determining. Also, these workers found that the more electrophilic pentafluorobenzaldehyde reacts 2.5 times faster than valeraldehyde. Previously,[5] it was observed that reductive eliminations involving phenyl groups are slower than those involving alkyl groups in acid chloride decarbonylations. The enhanced rate for pentafluorobenzaldehyde, then, implies that the rate-limiting step occurs before the reductive elimination step. This is consistent with the oxidative addition process being rate limiting. It should be noted that this interpretation is reasonable but not conclusive.

By using phenylacetaldehyde (**5h**), phenylacetaldehyde-1-d (**5d**), and p-methylphenylacetaldehyde (**6**), we have obtained further information about the oxidative addition process. When mixtures of **5h** and **5d** are decarbonylated with **1**, the primary kinetic isotope effect (k_H/k_D) is found to be 1.86 ± 0.07 (Table I). Attributing this result to the oxidative addition step implies that the transfer of hydrogen from the carbonyl carbon to rhodium or some other atom occurs either by a highly unsymmetrical, linear transition state[6] or by a nonlinear transition state.[7]

Decarbonylation of an equimolar mixture of **6** and **5d** with **1** shows no deuterium in the p-xylene produced or loss of deuterium from the toluene-α-d formed, at the 95% confidence level (Table I). Since **6** and **5d** were used in large excess, and comparable amounts of both the p-xylene and toluene-α-d products were obtained, all possible processes which are intermolecular in aldehyde can be excluded, regardless of mechanistic detail.[8] Thus, for example, a free-radical chain mechanism is ruled out for the oxidative addition of the aldehydes, or for any other transformation on the reaction path from aldehyde to hydrocarbon.

Table II. Reaction of Citronellal with Benzoyl Peroxide and $RhCl(PPh_3)_3$

citronellal[a] (7)	reactant	solvent (°C)	7[b]	8[c]	9
10.0	BP[d] (1.0)	none (80)	7.3	1.47	<0.1
1.0[e]	BP (0.2)	C_6H_6 (100)	0.66	0.19	<0.01
0.1[f]	1 (0.1)	C_6H_6 (80)	<0.001	<0.001	0.09[g]

[a] All values are in mmol. Reactions are performed for 24 h. [b] The remaining product is isopulegol and neoisopulegol, formed by a thermal ene reaction. [c] Menthone/isomenthone = 2. [d] Benzoyl peroxide. [e] 0.5 M. [f] 0.3 M. [g] 0.075 mmol of $RhCl(CO)(PPh_3)_2$.

The possibility of intramolecular free-radical mechanisms for the individual steps in the decarbonylation process was tested by using unsaturated aldehyde substrates. Citronella (**7**) reacts with benzoyl peroxide to give a mixture of menthone and isomethone (**8**) as the only free-radical products (Table II). No product from the decarbonylation of the acyl radical is observed, and it follows that the cyclization/decarbonylation ratio from the common acyl intermediate is >100:1. Therefore, the rate constant ratio must also be >100:1. Since the decarbonylation rate constant for a primary acyl radical[9] is $1–10^3$ s^{-1}, the rate constant for this intramolecular cyclization of the acyl radical from citronellal can be estimated at $10^2–10^5$ s^{-1}.

In contrast to these results, 2,6-dimethyl-2-heptene (**9**) is the only observable product in the reaction of citronellal with **1**. If an acyl radical were involved in the oxidative addition step, it would have to be captured by a rhodium complex with a rate at least 100 times greater than that for the cyclization process in order that no menthones be formed. Therefore, radicals of significant lifetime cannot be involved in the oxidative addition mechanism.

The deuterium isotope effect predicts a nonlinear or unsymmetrical, linear pathway for the oxidative addition process. The acyl radical, which is expected to be formed by a linear bond-breaking transition state, has been ex-

(3) (a) J. A. Osborn, "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, 1975, p 65; (b) J. Norton, *Acc. Chem. Res.*, **12**, 139 (1979); (c) S. J. Tremont and R. G. Bergman, *J. Organomet. Chem.*, **140**, C12 (1977).

(4) M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. A*, 348 (1968).

(5) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967).

(6) (a) L. Melander, "Isotope Effects in Reaction Rates", Ronald Press, New York, 1960, pp 24–32; (b) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(7) (a) W. Chiao and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **100**, 2802 (1978); (b) W. H. Saunders, Jr., *Chem. Scr.*, 8, 27 (1975).

(8) H. M. Walborsky and L. E. Allen, *J. Am. Chem. Soc.*, **93**, 5465 (1971), have previously shown that when 2,2-diphenyl-1-methylcyclopropanecarboxaldehyde-d is decarbonylated with 1 in xylene, 1-deuterio-1-methyl-2,2-diphenylcyclopropane is produced. Thus, processes which would lead to H/D exchange with the solvent were excluded.

(9) M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 297 (1974).

Table III. Decarbonylation of *endo*- and *exo*-5-Norbornene-2-carboxaldehyde (10) with $RhCl(PPh_3)_3$ at 85 °C

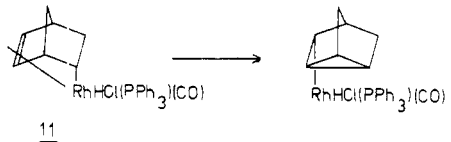
run no.	reactants[a]			products[a]	
	1	10n	10x	NTC[b]	NB
1	0.27	0.24	0.01	0.201	0.002
2	0.27	0.012	0.238	0.010	0.056
3	0.108	0.138	0.112	0.104	<0.001

[a] All values are in mmol. Reactions are performed for 24 h. The volume of the solution is 4 mL (benzene solvent). With acetonitrile or chloroform as the solvent, isomerization of the starting material occurs. [b] The amount of volatile products and $RhCl(CO)(PPh_3)_2$ agrees within 5%.

cluded by the results above. Therefore, a nonlinear process is implied, consistent with a concerted insertion of the metal into a C–H bond.[10]

The acyl–alkyl rearrangement is generally accepted to be concerted.[11] Therefore, this step was not studied individually but as a byproduct from the investigation of the reductive elimination step. The fact that cyclized, decarbonylated products from the reaction of citronellal with **1** are not observed implies that alkyl radicals are not formed; 1-(2-propyl)-3-methylcyclopentane is not produced, although it would be expected[12] if 2,6-dimethyl-2-heptene were formed via an alkyl radical. A more discriminating study of the possible role of alkyl free radicals was performed using *exo*- and *endo*-5-norbornene-2-carboxaldehydes (**10x** and **10n**). The norbornenyl radical has been studied extensively,[13] and the rate constant for the intramolecular cyclization to the nortricyclyl radical is one of the fastest known, 10^8 s^{-1}. In addition, equilibrated mixtures of norbornenyl and tricyclyl radicals invariably give mixtures of products. Thus, both norbornene (NB) and nortricycline (NTC) should be formed from either the endo (**10n**) or exo (**10x**) aldehyde, if radical processes were occurring.

Table III shows the results of the reactions of the two isomeric aldehydes with **1**. Qualitatively, the data support the hypothesis that **10n** gives NTC and **10x** gives NB. The formation of norbornene from **10x** is a straightforward decarbonylation reaction. The formation of NTC from the endo isomer can be rationalized on the basis of a rapid homoallylic rearrangement[14] of **11**.



11

It is also observed that the endo isomer reacts faster than the exo isomer. A crude competition experiment (Table III, entry 3) shows that the rate constant for the reaction of **10n** is >83 times larger than that for **10x**. This difference can be explained by the hypothesis that π complexes are favored over coordination of the aldehyde moiety[4] and that only the endo aldehyde group can react intramolecularly with a π-complexed rhodium species.

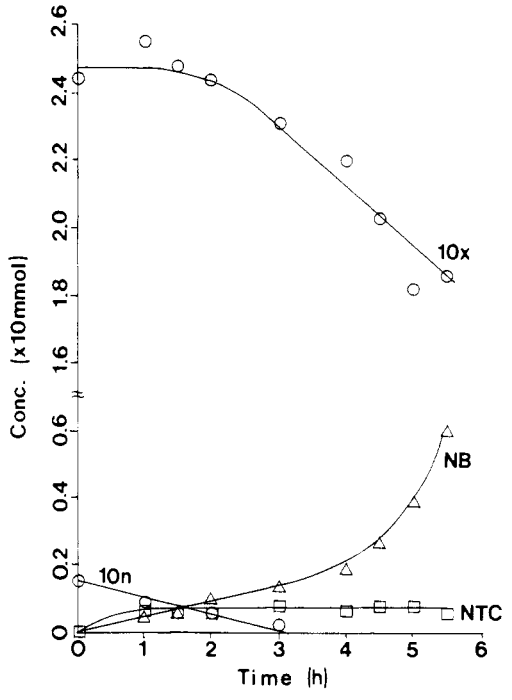


Figure 1. Decarbonylation of excess **10** (**10x**:**10n**, 95:5) with $RhCl(PPh_3)_3$ in benzene.

Also, the chelation of the endo aldehyde and olefin could lead to a more rapid reaction. The competition experiment also provides data useful in determining the extent of product crossover. The data in entry 3 in Table III show that no detectable NB is formed when an excess of **10n** and **10x** reacts with **1**. Therefore, less than 1% of **10n** is converted into NB. A similar result is obtained from entry 1.

The extent of possible crossover products from **10x** was determined by following the concentration of the reactants and products as a function of time (Figure 1), since the reaction of the exo isomer is slow. The increase in NB from 2.0–5.5 h is 0.05 mmol, with a decrease in **10x** of 0.058 mmol. During this time, less than 0.002 mmol of NTC was produced, based on error limits. This corresponds to less than 3.4% crossover of **10x** to give NTC.

Radical processes occurring in the acyl–alkyl migration or reductive elimination steps are, therefore, unlikely since the norbornenyl radical would have to be trapped 30–100 times faster than its cyclization to the nortricyclyl radical ($k = 10^8$ s^{-1}) in order to be consistent with the observed product distribution. A norbornenyl cation intermediate is also excluded since it rapidly rearranges to give mainly nortricyclyl products.[15]

In conclusion, decarbonylation of a mixture of deuterated and undeuterated aldehydes (**5d** and **6**) with **1** gives no crossover products. This excludes all possible mechanistic steps intermolecular in aldehyde. Sensitive tests for acyl and alkyl free radicals, provided by the decarbonylation of citronellal, **10x**, and **10n** with **1**, give no evidence for any free-radical intermediates. The mechanism most consistent with the observed data is one involving concerted processes for all of the steps in the decarbonylation reaction (eq 1, X = H).

Experimental Section

Boiling points and melting points are uncorrected. NMR spectra were performed on a JEOL-JNM-MH 100 or a JEOL-

(10) R. G. Pearson, *Acc. Chem. Res.*, **4**, 152 (1971).
(11) (a) L. F. Hines and J. K. Stille, *J. Am. Chem. Soc.*, **94**, 485 (1972); (b) P. L. Block, D. J. Boschetto, J. R. Rosenblum, J. P. Dimers, and G. M. Whitesides, *ibid.*, **96**, 2814 (1974); (c) A. Wojicicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).
(12) R. J. Kinney, W. D. Jones, and R. G. Bergman, *J. Am. Chem. Soc.*, **100**, 7902 (1978).
(13) J. K. Kochi, "Free Radicals", Wiley, New York, 1973, pp 466–477.
(14) (a) R. P. Hughes and J. Powell, *J. Organomet. Chem.*, **34**, C51 (1972); (b) D. R. Coulson, *J. Am. Chem. Soc.*, **91**, 200 (1969); (c) J. K. Stille and L. F. Hines, *ibid.*, **92**, 1798 (1970).
(15) S. J. Cristol, J. C. Morrill, and R. A. Sanchez, *J. Am. Chem. Soc.*, **88**, 3087 (1966).

C60HL instrument in $CDCl_3$ solution with tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 137 or 467 instrument, calibrated to 1601 cm^{-1}. Mass spectra were performed on a DuPont 490B mass spectrometer. Analytical gas chromatography (VPC) was performed on a Perkin-Elmer Model 900 instrument with flame ionization detectors. Preparative VPC was done on a Varian Aerograph Model 90-P instrument.

The columns used are: column A, $^1/_8$ in. × 10 ft 10% Apiezon L on Chromosorb W (AW-DMCS), 80–100; column B, $^1/_8$ in. × 10 ft 20% SE-30 on Chromosorb W, 80–100; column C, 0.25 in. × 10 ft 10% SE-30 on Chromosorb W, 60–80; column D, $^1/_8$ in. × 10 ft 10% DNDP on Chromosorb P, 60–80. Solvents are purified by literature methods[16] and are distilled under nitrogen before use. Unless specified otherwise, all experiments are performed under nitrogen. IR and NMR spectra have been recorded for all compounds used in this study and are consistent with the assigned structures.

Preparation[17] of $RhCl(PPH_3)_3$ (1). Compound 1 is prepared by the reaction of triphenylphosphine with $RhCl_3$ in greater than 95% yield for several preparations: IR (KBr) 3030 (w), 1600 (w), 1480 (w), 1440 (s), 1075 (m), 740 (s), 690 (s), 525 (s), 510 (s), 300 (w) cm^{-1}.

Preparation of Phenylacetaldehyde-1-*d* (5d). 2-Benzyl-1,3-dithiane[18] in THF is converted to the 2-lithio derivative by excess *n*-BuLi.[19] Subsequent treatment with excess D_2O gives 2-benzyl-1,3-dithiane-*2-d*. Its treatment[18] with $HgCl_2$–HgO in refluxing 95% aqueous methanol gives 1-deuterio-1,1-dimethoxy-2-phenylethane, which is hydrolyzed at 50 °C for 1 h with 3:1 dioxane–1 M aqueous HCl to give phenylacetaldehyde-*1-d*: bp 60–62 °C (5 mm), in 37% overall yield; IR (film) 2070 (m), 1710 (s), 747 (m), 700 (m) cm^{-1}; NMR δ 3.55 (2 H, s), 7.22 (5 H, m); MS (20 eV), although fragmentation was observed (even at lower IP) no M − 1 peak was observed with undeuterated phenylacetaldehyde. The deuterium content of this sample of phenylacetaldehyde-*1-d*, using a linear least-squares analysis (7 MS repetitions), is 98.9 ± 0.5% d_1.

***p*-Methylphenylacetaldehyde (6).** A THF solution of 2-lithio-1,3-dithiane is reacted with *p*-methylbenzyl bromide yielding 2-(*p*-methylbenzyl)-1,3-dithiane.[18,19] It is treated with $HgCl_2$–HgO in refluxing 95% aqueous methanol to give 1,1-dimethoxy-2-(*p*-methylphenyl)ethane, which is in turn hydrolyzed with 3:1 dioxane–10% aqueous HCl and distilled, bp 70–72 °C (4 mm) [lit.[20] bp 96–98 °C (10 mm)], to give **6** in 30% overall yield.

Preparation of Menthone (8). Menthone and isomenthone are prepared by the hydrogenation of pulegone[21] with 10% Pd/C in ethanol and are used as a mixture (63% menthone; 37% isomenthone by NMR): IR (film) 2941 (s), 1706 (s), 1443 (s) cm^{-1}.

Preparation of 2,6-Dimethyl-2-heptene[22] (9). Citronellal is refluxed with 10% Pd/C at 200 °C bath temperature until the vapor temperature drops to 170 °C. Distillation and preparative VPC (column C, 90 °C) yields 6.3% of 2,6-dimethyl-2-heptene: NMR δ 0.90 (6 H, d, J = 6 Hz), 0.90–1.30 (3 H, m), 1.64 (3 H, s), 1.72 (3 H, s, br), 1.99 (2 H, m), 5.16 (1 H, m).

***endo*- and *exo*-5-Norbornene-2-carboxaldehyde (10n and 10x).** 5-Norbornene-2-carboxaldehyde (Aldrich), 30 g, in 20 mL of methanol is stirred for 30 min with 2 mL of 40% methanolic Triton-B. The solution is poured onto 100 mL of water and extracted with ether (3 × 50 mL). After being dried and concentrated, the aldehyde is distilled on a Nester-Faust Adiabatic Annular Teflon Spinning Band Column, yielding 5.6 g (19%) of the exo aldehyde, bp 54 °C (10 mm) [lit.[23] bp 62.3 °C (17 mm)], in 95% isomeric purity by VPC (column D, 125 °C): NMR δ 1.32 (3 H, m), 1.94 (1 H, d, t, J = 12.4 Hz), 2.30 (1 H, m), 2.95 (1 H, s, br), 3.08 (1 H, s, br), 6.10 (2 H, m), 9.69 (1 H, d, J = 3 Hz).

After a center cut, the endo aldehyde is obtained in a 23% yield (7.0 g): bp 58 °C (10 mm) [lit.[23] bp 65–66 °C (17 mm)]; NMR δ 1.42 (3 H, m), 1.80 (1 H, m), 2.98 (2 H, m), 3.25 (1 H, s, br), 6.03 (1 H, d, d, J = 3.6 Hz), 6.26 (1 H, d, d, J = 3.6 Hz), 9.50 (1 H, d, J = 3 Hz). By VPC (column D, 125 °C), the aldehyde is 96% endo.

Preparation of Nortricycline (NTC). *exo*-2-Norbornyl tosylate[24] is treated with potassium *tert*-butoxide by the method of Stille.[25] The distillate is poured onto water and extracted with pentane. VPC collection of the NTC from the pentane layer (column C, 90 °C) gives an 11% yield of product, mp 54–56 °C (lit.[26] mp 56 °C).

General Decarbonylation Procedure. Into either a flask with a side-arm and condenser or a reaction tube is placed $RhCl(PPh_3)_3$. The flask or the tube is evacuated and flushed with nitrogen twice. The aldehyde and solvent are added by a syringe. The reaction tubes are sealed. After the mixture is heated for an appropriate time, the solution is bulb-to-bulb distilled and analyzed by VPC.

a. Decarbonylation of 5h, 5d, and 6 (Table I). Yields of $RhCl(CO)(PPh_3)_2$ (4) are determined gravimetrically after cooling the reaction solution (−20 °C), filtering, and washing with ether: IR (KBr) 1964 (s), 1480 (m), 1434 (s), 1093 (s), 745 (s), 690 (s), 595 (m), 535 (s), 520 (s), 320 (w) cm^{-1}. Yields of toluene and *p*-xylene are determined using column A at 90 °C. The internal standard was added before bulb-to-bulb distillation in runs 1 and 4, Table I. Some internal standard is lost in the bulb-to-bulb distillation leading to high yield values, especially in run 1. The internal standard is added after the bulb-to-bulb distillation in runs 2 and 3. Samples of toluene and *p*-xylene are collected (entire peak) by preparative VPC (column C, 60 °C) and are then analyzed for deuterium content by mass spectrometry at low ionization potential to eliminate fragmentation.

b. Decarbonylation of Citronellal, 10n, and 10x. The residue from the bulb-to-bulb distillation is recrystallized from ca. 2 mL of 1,2-dichloromethane to yield **4**. A VPC standard is added before the bulb-to-bulb distillations, and the solutions are analyzed by VPC with the following conditions: 2,6-dimethyl-2-heptene, column A, 90 °C; menthone and isomethone, column B, 110 °C; NB and NTC, column A, 90 °C; **10n** and **10x**, column D, 125 °C.

c. Decarbonylation Time Study of 10x. A solution of 0.108 mmol (100 mg) of $RhCl(PPh_3)_3$ and 30 μL (0.25 mmol) of **10x** (95% exo) in 2 mL of benzene is maintained at 70 °C while 50-μL aliquots are removed at appropriate time intervals. The aliquots are quenched at −78 °C and are kept frozen until VPC analysis.

Peroxide Cyclization of Citronellal. A reaction tube is charged with benzoyl peroxide and freshly distilled citronellal; benzene, if used, is added at this time. The tube is flushed with nitrogen and then sealed. After heating, a VPC standard is added, and the solution is filtered through alumina to destroy the excess peroxide. The products are analyzed by VPC (column B, 110 °C).

Acknowledgment. We are grateful to Matthey-Bishop Industries for a generous loan of $RhCl_3$ and to the National Science Foundation, NSF-7308798, for financial support.

Registry No. **1**, 14694-95-2; **4**, 13938-94-8; **5d**, 71964-68-6; **5h**, 122-78-1; **6**, 104-09-6; **7**, 106-23-0; **8**, 89-80-5; **9**, 5557-98-2; **10n**, 19926-90-0; **10y**, 19926-88-6; 2-benzyl-1,3-dithiane, 31593-52-9; 2-benzyl-1,3-dithiane-*2-d*, 71964-69-7; 1-deuterio-1,1-dimethoxy-2-phenylethane, 71964-70-0; *p*-methylbenzyl bromide, 104-81-4; 2-(*p*-methylbenzyl)-1,3-dithiane, 71964-71-1; 1,1-dimethoxy-2-(*p*-methylphenyl)ethane, 42866-91-1; isomenthone, 491-07-6; *exo*-2-norbornyl tosylate, 959-42-2; NB, 498-66-8; NTC, 279-19-6.

(16) D. P. Perrin, W. L. F. Armarego, and D. F. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, New York, 1966.
(17) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(18) E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971).
(19) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975).
(20) E. Spath, *Chem. Ber.*, **47**, 766 (1914).
(21) J. Read, G. J. Robertson, and A. M. R. Cook, *J. Chem. Soc.*, 1276 (1927).
(22) H. E. Eschienazi, *Bull. Soc. Chim. Fr.*, 967 (1952).
(23) D. K. Freeman and K. B. Desai, *J. Org. Chem.*, **36**, 1554 (1971).
(24) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).
(25) F. M. Sonnenberg and J. K. Stille, *J. Org. Chem.*, **31**, 3441 (1966).
(26) E. R. Lippincott, *J. Am. Chem. Soc.*, **73**, 2001 (1951).