of the natural product.[23] Since Nicolaou[6a] and Ley[6b] have already described the hydrolysis of 17 to 1, our work completes the third synthesis of this natural product.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM 26782) and National Cancer Institute (Training Grant No. T32-CA 09112). We are grateful to the Ayerst Laboratories for a postdoctoral fellowship to S.M.P. and to Dr. J. W. Westley of Hoffmann-La Roche, Inc., for providing a generous sample of natural X-14547A.

Registry No. 1, 66513-28-8; 3, 76566-87-5; (*Z*)-3, 76566-88-6; 5, 76584-28-6; 6, 91266-03-4; 6 iodoalkyne deriv., 91266-04-5; 7, 91266-05-6; 8, 83622-42-8; 9, 91266-06-7; 10, 15186-48-8; 11, 91266-07-8; 11 dihydro deriv., 91266-08-9; 11 dihydrotriol deriv., 91266-09-0; 11 dihydro acetate deriv., 91266-17-0; 11 dihydrotriol triacetate deriv., 91266-16-9; 12, 91326-64-6; 12 crotonate deriv., 91266-10-3; 13, 91266-11-4; 13 phosphonate deriv., 91266-12-5; 14, 91266-13-6; 15, 91266-14-7; (*Z*)-15, 91326-65-7; 16, 91280-61-4; 17, 76567-01-6; (*Z*)-$C_{10,11}$-17, 91326-66-8; triethyl 4-phosphonocrotonate lithium anion, 91266-15-8.

Supplementary Material Available: Spectroscopic data and physical constants for all synthetic intermediates (9 pages). Ordering information is given on any current masthead page.

(23) A sample of 17 prepared from natural X-14547A had $[\alpha]^{20}_D$ −308.2° (*c* 1.24, $CHCl_3$). Nicolaou has reported $[\alpha]^{25}_D$ − 170.6° (*c* 1.4, $CHCl_3$) for 17 (see ref 6a).

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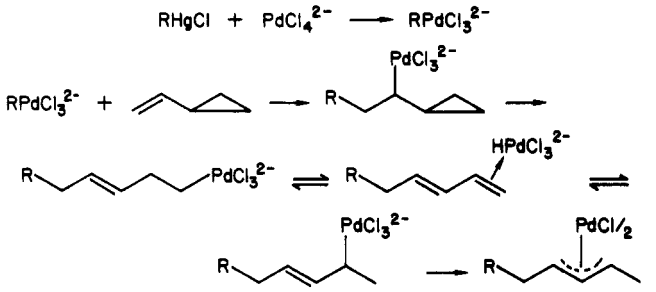
Mercury in Organic Chemistry. 30. Synthesis of (π-Allyl)palladium Compounds via Organopalladium Additions to Alkenyl- and Methylenecyclopropanes and Alkenyl- and Methylenecyclobutanes

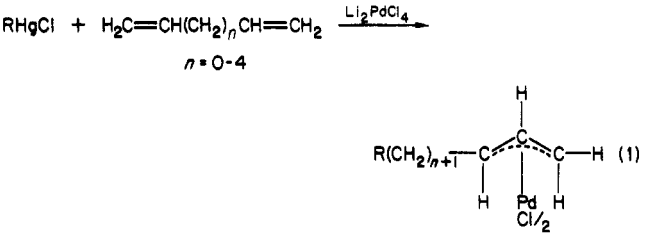
Summary: (π-Allyl)palladium compounds are readily available via organopalladium additions to alkenyl- and methylenecyclopropanes and alkenyl- and methylenecyclobutanes. This reaction apparently involves formation of a (cycloalkylcarbinyl)palladium intermediate which undergoes ring-opening and subsequent palladium migration to afford the (π-allyl)palladium product.

Sir: (π-Allyl)palladium compounds have recently become valuable intermediates in organic synthesis.[1,2] Two of the more useful methods of preparing these compounds involve the direct allylic hydrogen substitution of alkenes by palladium salts[3-8] and the insertion of palladium(0) reagents into the carbon–halogen or carbon–oxygen bond of allylic halides or acetates.[9-12] Recently, the reaction of

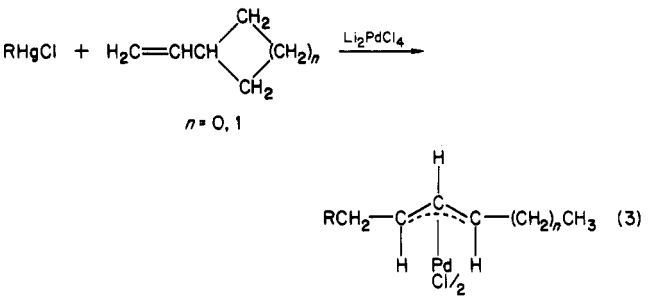
Scheme I



organomercurials, palladium salts, and either conjugated[13,14] or nonconjugated[15] dienes has provided a convenient new approach to (π-allyl)palladium compounds (eq 1).



Similarly, vinylmercurials may be reacted with palladium salts and simple olefins to afford (π-allyl)palladium compounds (eq 2).[16,17] We now report that the reaction of organomercurials, palladium salts, and alkenyl- or methylenecyclopropanes and alkenyl- or methylenecyclobutanes results in a novel ring-opening process and subsequent rearrangement, which affords a valuable, new, regioselective route to (π-allyl)palladium compounds (eq 3).



Our results to date are summarized in Table I. As can be seen in the table, aryl, methyl, vinyl and heterocyclic organomercurials can be employed in this reaction. With alkylmercurials bearing hydrogens beta to mercury, the (π-allyl)palladium product derived by palladium hydride addition to the olefin and subsequent rearrangement is isolated (entry 3).

A variety of olefins are observed to afford (π-allyl)palladium compounds by this procedure. Vinylcyclopropanes of various substitution patterns can be employed. Aryl substitution on the cyclopropane ring is observed to direct ring-opening toward the aryl group (entries 7 and 8).

(1) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.
(2) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag; New York, 1980.
(3) Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* **1964**, *86*, 4491.
(4) Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603.
(5) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630.
(6) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1975**, *97*, 2534.
(7) Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611.
(8) Trost, B. M.; Metzner, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3572.
(9) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.
(10) Sakakibara, M.; Takahashi, Y.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1969**, 396.
(11) Tsuji, J.; Iwamoto, N. *Chem. Commun.* **1966**, 828.
(12) Dent, W. T.; Long, R. British Patent 1 082 248, **1967**; *Chem. Abstr.* **1968**, *68*, 114748*j*.
(13) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5542.
(14) Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584.
(15) Larock, R. C.; Takagi, K. *Tetrahedron Lett.* **1983**, *24*, 3457.
(16) Larock, R. C.; Mitchell, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 180.
(17) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, *22*, 5231.

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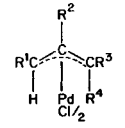
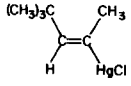
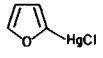
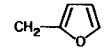
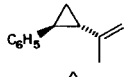
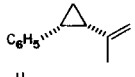
Table I. Synthesis of (π-Allyl)palladium Compounds

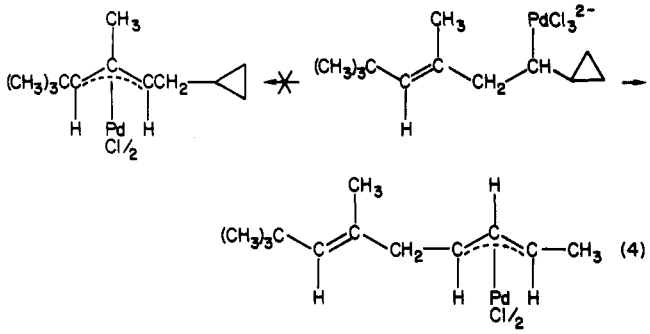


entry	organomercurial	olefin[a]	reaction conditions[b]	(π-allyl)palladium compounds R^1	R^2	R^3	R^4	compd no.[c]	isolated yield (%)
1	C_6H_5HgCl		0 °C, 2 h	CH_3	H	$CH_2C_6H_5$	H	**1**	79
2	CH_3HgCl		0 °C, 2 h	CH_3	H	CH_2CH_3	H	**2**[d]	52
				CH_3	H	CH_3	CH_3	**3**[d]	
3	C_2H_5HgCl		0 °C → 25 °C, 3 days	CH_3	H	CH_3	H	**4**	51
4			0 °C, 2 h	CH_3	H	(*E*)-$CH_2C(CH_3)$=$CHC(CH_3)_3$	H	**5**	87
5			0 °C, 2 h	CH_3	H		H	**6**[e]	63
				CH_3	H		CH_3	**7**[e,f]	
6	C_6H_5HgCl		0 °C, 2 h	CH_3	CH_3	$CH_2C_6H_5$	H	**8**[g]	55
				CH_3	CH_3	C_6H_5	CH_3	**9**[g]	
7			0 °C, 2 h	$C_6H_5CH_2$	H	$CH_2C_6H_5$	CH_3	**10**	44
8			0 °C, 2 h	$C_6H_5CH_2$	H	$CH_2C_6H_5$	CH_3	**10**	40
9			−78 °C → 0 °C, overnight	H	C_6H_5	CH_3	H	**11**	24
10			0 °C, 18 h	CH_3CH_2	H	$CH_2C_6H_5$	CH_3	**12**[h]	80
				CH_3CH_2	H	CH_3	$CH_2C_6H_5$	**13**[h]	
11			0 °C, 18 h	CH_3CH_2	H	C_6H_5	H	**14**	70

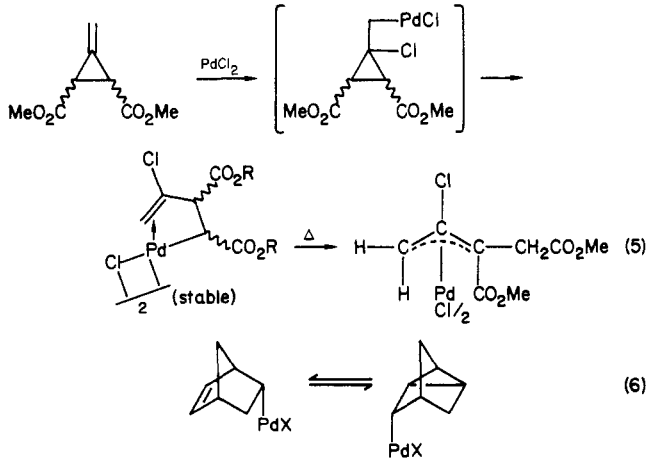
[a] Two or more (when the olefin was quite volatile and difficult to weigh) equiv of olefin were used in all cases. [b] All reactions were run in tetrahydrofuran. [c] All (π-allyl)palladium compounds gave appropriate spectral data and elemental analyses. [d] Ratio of **2** to **3** is 7:1. [e] Ratio of **6** to **7** is 2:1. [f] Compound **7** is a syn–anti mixture. [g] Ratio of **8** to **9** is 5:1. [h] Ratio of **12** to **13** is 5:1.

Methylenecyclopropane also undergoes this ring-opening process (entry 9). In view of the comparable strain energy of cyclopropanes and cyclobutanes,[18] we have examined analogous organopalladium additions to isopropenylcyclobutane (entry 10) and methylenecyclobutane (entry 11). Excellent yields of (π-allyl)palladium compounds were isolated in both cases.

The unique course of our reactions is best explained by the mechanism shown in Scheme I. The ease with which the cyclopropane ring opens can be seen by considering the reaction of (*E*)-2-(chloromercurio)-4,4-dimethyl-2-pentene and vinylcyclopropane (entry 4). In our previous work we have established that homoallylpalladium intermediates readily rearrange to the corresponding (π-allyl)palladium compounds.[15-17] The initial addition product from the above reaction contains both a homoallyl- and a (cyclopropylcarbinyl)palladium species, but the only (π-allyl)palladium product observed is that of cyclopropane ring-opening and not simple palladium migration to the original double bond (eq 4).

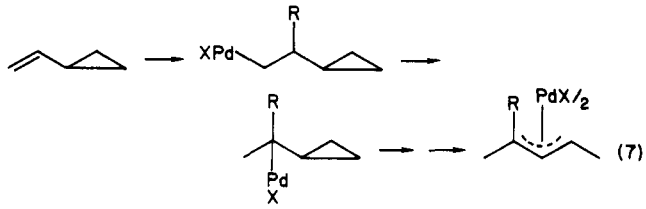


While organopalladium additions to unsaturated cyclopropanes and cyclobutanes have never been examined previously, vinylcyclopropanes have been ring-opened by palladium(0) reagents[19,20] and palladium dichloride.[21,22] Mechanisms entirely different from ours have been suggested here. The palladium dichloride ring-opening of 2,3-dicarbomethoxymethylenecyclopropane (eq 5)[23-25] and

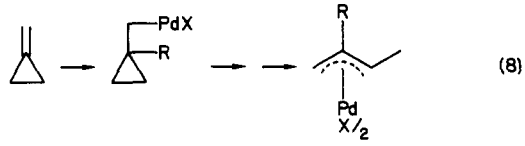


the observation of a nortricyclyl–norbornenyl palladium equilibrium (eq 6)[28] lend credence to our mechanism, however. It is noteworthy that other methylene cyclopropanes react with palladium dichloride[27-29] and palladium(0) reagents[30-35] in an entirely different fashion.

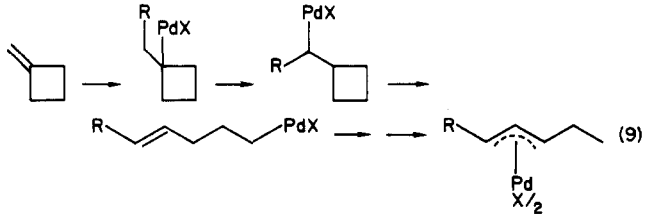
In some of our reactions (entries 2, 5, and 6), minor amounts of product derived from addition of the organic moiety to the internal carbon are observed. Apparently, the resulting intermediate subsequently rearranges to a (cyclopropylcarbinyl)palladium compound which then rearranges in the usual fashion (eq 7).



The major product isolated from the reaction of phenylmercuric chloride and methylenecyclopropane (entry 9) is that derived from phenyl addition to the internal olefin carbon (eq 8). This mode of addition contrasts with the usual regiochemistry observed in such reactions.



Isopropenylcyclobutane (entry 10) reacts in a manner analogous to vinylcyclopropane. Unlike methylenecyclopropane, methylenecyclobutane (entry 11) affords in 70% yield a (π-allyl)palladium compound which apparently arises by palladium addition to the cyclobutane carbon, rearrangement to a (cyclobutylcarbinyl)palladium intermediate, ring-opening, and palladium migration (eq 9). In



this extraordinary reaction, palladium at one time or another is bonded to every carbon of the original olefin. The ability of palladium to migrate considerable distances by β hydride elimination–readdition without formation of the corresponding olefin is quite remarkable.

We are continuing to explore the mechanism of these reactions, as well as the scope and limitations of this new (π-allyl)palladium synthesis. Recent work in our laboratories indicates that these reactions can be quite useful in

(18) Wilson, A.; Goldhamer, D. *J. Chem. Ed.* **1963**, *40*, 504.
(19) Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 2871.
(20) Chiusoli, G. P.; Costa, M.; Pallini, L.; Terenghi, G. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 304.
(21) Ketley, A. D.; Braatz, J. A. *J. Organomet. Chem.* **1967**, *9*, P5.
(22) Shono, T.; Yoshimura, T.; Matsumura, Y.; Oda, R. *J. Org. Chem.* **1968**, *33*, 876.
(23) Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1974**, 686.
(24) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880.
(25) Goddard, R.; Green, M.; Hughes, R. P.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1890.
(26) Ban, E.; Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1974**, *69*, 455.
(27) Hughes, R. P.; Hunton, D. E.; Schumann, K. *J. Organomet. Chem.* **1979**, *169*, C37.
(28) Noyori, R.; Takaya, H. *J. Chem. Soc. D* **1969**, 525.
(29) Dallas, B. K.; Hughes, R. P. *J. Organomet. Chem.* **1980**, *184*, C67.
(30) Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, *113*, 1063.
(31) Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, *113*, 3334.
(32) Binger, P.; Schuchardt, U. *Chem. Ber.* **1980**, *114*, 3313.
(33) Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325.
(34) Binger, P.; Cetinkaya, M.; Doyle, M. J.; Germer, A.; Schuchardt, U. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3.
(35) Binger, P.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 249.

the synthesis of a variety of heterocycles via intramolecular (π-allyl)palladium displacement processes.

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Registry No. 1, 84079-74-3; 2, 12090-69-6; 3, 43089-88-9; 4, 12245-05-5; 5, 91410-74-1; 6, 91410-75-2; 7, 91424-00-9; 8, 74312-72-4; 9, 91410-76-3; 10, 91410-77-4; 11, 31833-54-2; 12, 91410-78-5; 13, 91410-79-6; C_6H_5HgCl, 100-56-1; CH_3HgCl, 115-09-3; C_2H_5HgCl, 107-27-7; (*E*)-RHgCl (R = 4,4-dimethyl-2-penten-2-yl), 38010-69-4; RHgCl (R = 2-furanyl), 5857-37-4; vinylcyclopropane, 693-86-7; Li_2PdCl_4, 15525-45-8; 1-methyl-1-vinylcyclopropane, 16906-27-7; *trans*-2-(1-methylethenyl)-1-phenylcyclopropane, 41577-94-0; *cis*-2-(1-methylethenyl)-1-phenylcyclopropane, 91050-50-9; methylenecyclopropane, 6142-73-0; 1-methylethenylcyclobutane, 3019-22-5; methylenecyclobutane, 1120-56-5.

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Oxidation of Allylic Alcohols to Unsaturated Carbonyl Compounds by Ruthenium Dioxide and Dioxygen/Ruthenium Dixoxide

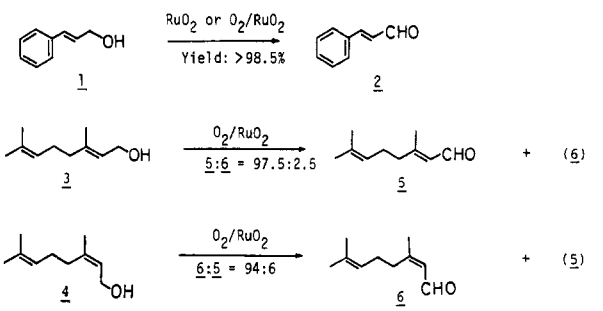
Summary: Ruthenium dioxide hydrate acts as an oxidant similar to MnO_2 and effectively catalyzes heterogeneous aerobic oxidation of allylic alcohols to yield unsaturated carbonyl compounds under mild conditons.

Sir: A variety of transition metals are well known to act as oxidant or catalyst in the dehydrogenation of alcohols to carbonyl compounds. For the oxidation of allylic alcohols to unsaturated carbonyls, the metal oxides of use have considerably been restricted because the allylic alcohols are in general more unstable than the saturated ones. Chromium(VI) compounds,[1] manganese dioxide,[2] and nickel peroxide[3] are usually chosen for stoichiometric oxidations. Platinum oxide and platinum on charcoal catalyze aerobic oxidation.[4] Cobalt oxide/dioxygen is also known to dehydrogenate allylic alcohols, though its efficiency is low.[5]

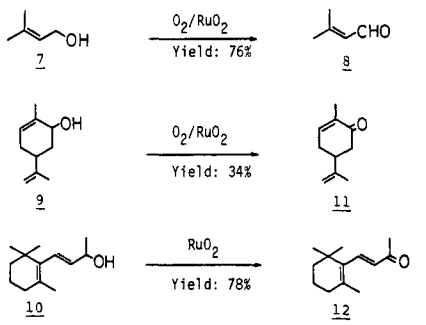
Among the oxides of ruthenium, RuO_4 is well-known as a powerful oxidant for alcohol dehydrogenation.[6] It is, however, too strong to be used for the selective dehydrogenation of allylic alcohols to the corresponding unsaturated carbonyls. We report here that ruthenium oxide with a lower oxidation state than RuO_4, namely, RuO_2 hydrate, acts as an oxidant with higher efficiency than MnO_2 and, furthermore, effectively catalyzes aerobic oxidation for allylic alcohols under mild conditions.

The oxidation of cinnamyl alcohol (1) to cinnamaldehyde (2) is used for the measurement of activity of MnO_2.[7] The oxidation of 1 by MnO_2 (MnO_2/1 = 10) leads to 2 in ca. 70% yield.[8] We chose 1 as a substrate to examine the oxidation activity of RuO_2 in the dehydrogenation of allylic alcohols. Treatment of alcohol 1 (95 mg) with hydrated RuO_2 (Nippon Engelhard or Alfa) (500 mg) in 1,2-dichloroethane (2 mL) under an argon atmosphere at room temperature for 4 h gave quantitatively *trans*-cinnamaldehyde (2) after chromatographic purification (Scheme I). Under these conditions, this ratio of 1 to hydrated RuO_2 was optimal. However, the ratio of oxide to substrate could be decreased by raising the reaction temperature and prolonging the reaction time. For example, when a mixture of equal quantities of 1 and RuO_2 hydrate was stirred at 70 °C for 15 h in 1,2-dichloroethane under an argon atmosphere, 2 was produced quantitatively. These results show that hydrated RuO_2 effects the dehydrogenation of allylic alcohols with greater efficiency than MnO_2.

Scheme I



Scheme II



When the argon atmosphere was replaced by oxygen, the efficiency of the reaction was improved. Thus, alcohol 1 was oxidized to 2 in a yield of 98.5%, when 1 (1.0 g) was stirred with RuO_2 hydrate (0.1 g) and 2,6-di-*tert*-butyl-*p*-cresol (0.025 g) under an oxygen atmosphere (1 atm) in 1,2-dichloroethane (3.8 mL) at 70 °C for 26 h. The hindered phenol was added to prevent the autoxidation of the aldehyde formed in the reaction. Without the phenol, the yield of the aldehyde was significantly decreased after high conversion (>50%) of the alcohol.

To study the stereochemical course of the dehydrogenation described here, oxidations of geraniol (3) and its stereoisomer, nerol 4 were carried out. Catalytic aerobic oxidation of the *E* isomer 3 (3/RuO_2 = 4/1, 70 °C, 6 h) gave 90.3% (conversion 95%, selectivity 95%) of citral consisting of 97.5% of the *E* isomer 5 and 2.5% of the *Z* isomer 6. Similar oxidation of the *Z* isomer 4 afforded a mixture of the aldehyde including 94% of the *Z* isomer 6 and 6% of the *E* isomer. These results show that the RuO_2-catalyzed aerobic oxidation proceeds with retention of olefin stereochemistry. Anaerobic oxidation of these

(1) For a review, see: Wiberg, K. B. "Oxidation in Organic Chemistry", Academic Press: New York, 1965; Part A, p 69.
(2) For a review, see: Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 636.
(3) (a) Nakagawa, K.; Konaka, R.; Nakata, T. *J. Org. Chem.* **1962**, *27*, 1597. (b) Clement, W. H.; Selwitz, C. M. *Ibid.* **1964**, *29*, 241.
(4) Rylander, P. N. "Organic Synthesis of Nobel Metal Catalysts"; Academic Press: New York, 1973; p 101.
(5) Belew, J. S.; Garza, C.; Marhieson, J. W. *J. Chem. Soc. D* **1970**, 634.
(6) Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3838.
(7) Maruyama, K. "Shin-Jikken Kagaku Koza"; Maruzen: Tokyo, 1976; Vol. 15, [I-1], p 72.
(8) Attenburrow, J.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094.

0022-3263/84/1949-3435$01.50/0 © 1984 American Chemical Society