The Stereochemistry of Tris(triphenylphosphine)rhodium Chloride Decarbonylation of Aldehydes[1,2]

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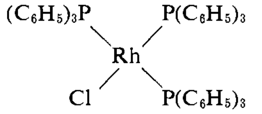
Abstract: A series of aldehydes differing in the hybridization of the carbon atom to which the carbonyl group is attached, *i.e.*, (−)-(*R*)-2-methyl-2-phenylbutanal (**2**), (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde (**3**), and (*E*)-α-ethylcinnamaldehyde (**4**), was decarbonylated using tris(triphenylphosphine)rhodium chloride (**1**). The products, (+)-(*S*)-2-phenylbutane (**5**), (+)-(*S*)-1-methyl-2,2-diphenylcyclopropane (**6a**), and (*Z*)-1-phenyl-1-butene (**7**), were formed with 81, 94, and 100% retention of optical activity, respectively. The optical purity in the decarbonylation of a series of 1-substituted cyclopropyl aldehydes varied from 83 to 6%. A cleavage radical pair disproportionation mechanism is proposed for the reaction on the basis of the stereochemical results. The decarbonylation of 1-methyl-2,2-diphenylcyclopropanecarboxaldehyde-*d* was used to demonstrate the intramolecularity of the reaction as well as to illustrate its application to the synthesis of specifically deuterium-labeled compounds.

In connection with another problem, it became necessary for us to find a stereospecific method for the removal of carbon monoxide from an aldehyde. Although there are a number of methods available for decarbonylation of aldehydes[4] most of them were not, nor did they show promise to be, stereospecific. It was only the decarbonylation of aldehydes by group VIII metal compounds which seemed to offer this promise. These reactions were known for some time[5] but it was the work of Tsuji and Ohno[6] which called our attention to the synthetically useful application of this reaction with tris(triphenylphosphine)rhodium chloride (**1**) as the reagent.



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Several aldehydes have been decarbonylated using reagent **1**. The reaction proceeds homogeneously in solvents such as benzene or dichloromethane in which **1** is moderately soluble. The reaction is sensitive to steric effects so that some aldehydes in which the carbonyl group is more hindered than a secondary alkyl carbon cannot normally be decarbonylated under the usual mild conditions. The more hindered aldehydes can, however, be smoothly decarbonylated using benzonitrile as the solvent.[6]

In order to evaluate the stereochemistry and stereoselectivity of the reaction, a number of aldehydes of known absolute configuration and varying in structure were decarbonylated. The aldehydes were selected so that the effect on the scope of the reaction of changing the hybridization of the carbon atom to which the carbonyl group is attached (sp^3, $sp^{2.28}$, sp^2) could be evaluated.

Syntheses and Absolute Configurations. The aldehydes selected for our study of the effect of change of hybridization were (−)-(*R*)-2-methyl-2-phenylbutanal (**2**), (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde (**3a**), and (*E*)-α-ethylcinnamaldehyde (**4**). The cyclopropyl system was selected to evaluate the effect of α substituents on the stereochemical course of the decarbonylation. Instead of the methyl group in **3a**, cyclopropyl systems were prepared, containing chloro (**3b**), fluoro (**3c**), and methoxy (**3d**) as substituents.

The absolute configuration of (−)-(*R*)-2-methyl-2-phenylbutanoic acid and (+)-(*S*)-2-phenylbutane (**5**) had previously been established[7] and, therefore, in order to prepare aldehyde **2** of known configuration it was only necessary to convert (−)-(*R*)-2-methyl-2-phenylbutanoic acid to aldehyde **2**. This proved to be quite difficult and, of the many methods tried,[8] only the reduction of the acid to the carbinol followed by oxidation with Jones reagent[9] in acetone produced the (−)-(*R*)-2-methyl-2-phenylbutanal (**2**) in acceptable yields (50–55%).

The syntheses and determination of the absolute configurations of the cyclopropyl aldehydes **3a–d** and the cyclopropyl hydrocarbons **6a–d** that would be derived from them by decarbonylation have previously been accomplished.[10,11] Chart I lists the relative and absolute configurational assignments.

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[1] The support of this work by grants from the National Science Foundation and Public Health Service Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

[2] A preliminary account of this work has been reported: H. M. Walborsky and L. E. Allen, *Tetrahedron Lett.*, 823 (1970).

[3] In partial fulfillment of the requirements for the Ph.D. degree in Chemistry in the Graduate School of Syracuse University, July 1970.

[4] For a review, see W. M. Schubert and R. R. Kintner in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, Chapter 14.

[5] P. Sabatier and J. B. Senderens, *C. R. Acad. Sci. Paris*, **136**, 738, 921 (1903); Y. J. Suen and S. Fan, *J. Amer. Chem. Soc.*, **65**, 1243 (1943); H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **24**, 1369 (1959).

[6] J. Tsuji and K. Ohno, *Tetrahedron Lett.*, 3962 (1965); K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968); for a recent review, see J. Tsuji and K. Ohno, *Synthesis*, 157 (1969).

[7] D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1594).

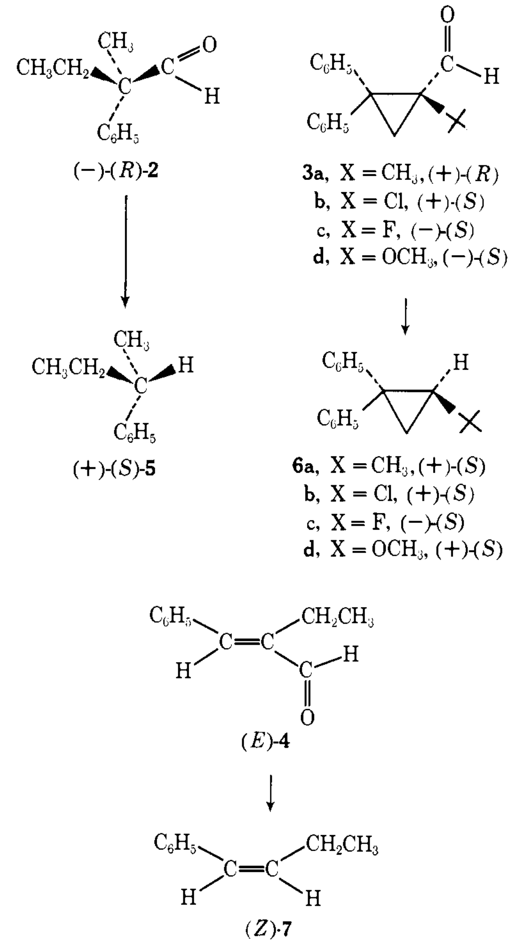
[8] Attempts to reduce the corresponding acid chloride, *N*,*N*-dimethylamide, and nitrile with a variety of aluminum hydrides failed. Oxidation of the carbinol with dicyclohexylcarbodimide and with acetic anhydride, or with lead tetraacetate, ceric ammonium nitrate, or chromic anhydride–pyridine, was also unsuccessful.

[9] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[10] H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Amer. Chem. Soc.*, **83**, 2517 (1961); H. M. Walborsky and C. G. Pitt, *ibid.*, **84**, 4831 (1962).

[11] H. M. Walborsky, L. E. Allen, H.-J. Traenckner, and E. J. Powers, *J. Org. Chem.*, **36**, 2937 (1971).

Chart I



(−)-(*R*)-**2**

3a, X = CH_3, (+)-(*R*)
b, X = Cl, (+)-(*S*)
c, X = F, (−)-(*S*)
d, X = OCH_3, (−)-(*S*)

(+)-(*S*)-**5**

6a, X = CH_3, (+)-(*S*)
b, X = Cl, (+)-(*S*)
c, X = F, (−)-(*S*)
d, X = OCH_3, (+)-(*S*)

(*E*)-**4**

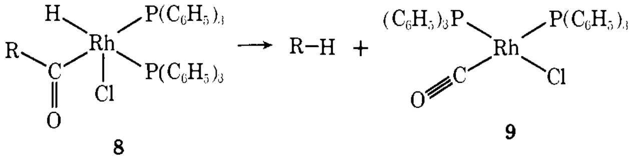
(*Z*)-**7**

The configuration of (*E*)-α-ethylcinnamaldehyde (**4**) was established by oxidizing it to the known (*E*)-α-ethylcinnamic acid[12] with silver oxide. The configuration of (*Z*)-1-phenyl-1-butene was assigned on the basis of nmr spectra in analogy to the work on the homologous 1-phenyl-1-propene.[13] The *Z* isomer has a shorter retention time in glpc than the *E* isomer and the nmr spectra clearly distinguish the two isomers on the basis of the signals observed for the vinyl protons.[13] The *Z* isomer shows a pattern of six lines centered at δ 5.48 which appears to be a pair of triplets, whereas the *E* isomer shows a multiplet of four sharp lines centered at δ 6.08.

Results and Discussion

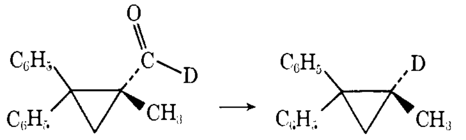
The decarbonylation of optically pure (−)-(*R*)-**2** required prolonged reaction at 160° in benzonitrile due most likely to the steric hindrance at the quaternary carbon atom. The *sec*-butylbenzene (**5**) isolated proved to be 81% optically pure and to have the (+)-(*S*) configuration, which corresponds to an overall retention of configuration. The decarbonylation of the cyclopropyl aldehyde (+)-(*R*)-**3a** proceeded smoothly in refluxing xylene to give a 70% yield of (+)-(*S*)-**6a** of 94% optical purity and retained configuration. The *E*-vinyl aldehyde **4**, when decarbonylated in refluxing benzene, produced only the *Z*-alkene **7**, corresponding to 100% retention of configuration. Under more vigorous conditions using benzonitrile[6] at 160° or no solvent and a catalytic amount of **1** at temperatures up to 260°, as much as 26% of the *E*-alkene **7** has been observed. In a blank experiment it has been shown (see Experimental Section) that the *Z*-alkene is converted to the *E*-alkene under the conditions of the reaction.

A mechanism has been proposed for the decarbonylation of aldehydes[6] which is similar to that proposed earlier for the decarbonylation of acid chlorides[6,14] The important intermediate is the acyl rhodium complex **8** which collapses to form hydrocarbon product, R–H, and complex **9**. It is this step in the reaction on which we will focus our discussion.



8 → R–H + **9**

That the reaction is clearly intramolecular, that is, that the aldehyde hydrogen is the one which becomes bonded to the carbon atom from which the carbonyl is removed, is shown by the results of the decarbonylation of 1-methyl-2,2-diphenylcyclopropanecarboxaldehyde-*d*. When the aldehyde containing 96 ± 3% deuterium at the aldehyde carbon is decarbonylated in xylene with **1**, the product hydrocarbon contains 93 ± 3% deuterium in the 1 position. This result is quite significant in that it demonstrates the synthetic utility of the decarbonylation reaction in the synthesis of specifically deuterated hydrocarbons. This mild procedure will make it possible to prepare hitherto inaccessible optically active deuterated hydrocarbons.



The high stereoselectivity observed and the lack of rearranged products militate against the incursion of a cationic alkyl intermediate as the migrating species. For if an alkyl cation was involved, one would have observed extensive racemization in **5** as well as ring-opened hydrocarbon in the decarbonylation of the cyclopropyl aldehyde **3a**.[15]

Based on our early results[2] a carbanionic intermediate seemed most attractive. Cram[16] has shown that in cleavage reactions generating a tetrahedral carbanion the result is high retention of configuration. Although vinyl anions have apparently not been generated in cleavage reactions, the ability of vinyllithium compounds to maintain their configuration is well documented.[16] This also holds equally true for the cyclopropyl anion such as the 1-methyl-2,2-diphenylcyclopropyl anion which when observed as the

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(12) N. E. Hoffman, A. T. Kanakkanatt, and R. F. Scheider, *J. Org. Chem.*, 27, 2687 (1962).

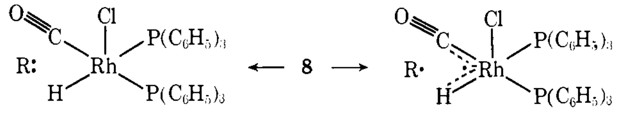
(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 238–240.

(14) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).

(15) C. H. DePuy, L. G. Schnack, J. W. Hanser, and W. Wideman, *ibid.*, **87**, 4006 (1965); P. v. R. Schleyer, D. W. van Diene, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(16) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 153.

lithium,[17] sodium,[18] or Grignard[19] reagent or when generated as the leaving group in Haller–Bauer cleavage reaction[20] has been shown to be configurationally stable.



anionic radical pair

Since the reaction has been shown to be intramolecular (*vide supra*), a free-radical mechanism can also accommodate the stereochemical results. An intramolecular reaction can, in a formal sense, be viewed as a cage reaction. Recent work has shown that radical cage disproportionation[21] as well as cage recombination reactions[22] can occur with a high degree of stereoselectivity. The work of Lansbury[23] and Schöllkopf[24] is a case in point. These authors have provided evidence that the Wittig rearrangement, which had previously been assumed to be an anionic reaction, involved not anions but radical pairs. Moreover, it should be noted that in the rearrangement of benzyl 2-phenylbutyl ether, the migrating 2-phenylbutyl radical involved in the cleavage–recombination reaction maintained its configuration to the extent of ~90% (~80% optical purity). This compares favorably to our observation on the decarbonylation of (−)-(*R*)-**2** in which the (+)-(*S*)-2-phenylbutane formed was of retained configuration with an optical purity of 81%. The radical pair mechanism becomes even more attractive when one examines the results of our study on the effect of α substituents on the stereochemistry of the decarbonylation of the cyclopropyl aldehydes **3a**–**d**, Table I. As can be seen the per cent of optical purity varies from 83% for the 1-chloro compound **3b** to 6% for the 1-methoxyl derivative **3d**. The optical purities are calculated by using the maximum rotations of **6b**–**d** which were obtained by the Haller–Bauer sodium amide cleavage[11] of their 1-benzoyl precursors. The Haller–Bauer reaction has been shown to proceed in a stereospecific manner[11] and to involve carbanion intermediates.[11,25] The stereoselectivity observed in the decarbonylation of aldehydes with tris(triphenylphosphine)rhodium chloride (**1**) is consistent with the radical pair mechanism proposed.

Table I. Decarbonylation of Optically Active 1-Substituted 2,2-Diphenylcyclopropanecarboxaldehydes

1 substituent	Config ($[\alpha]_{Hg}$, deg)[a]	Product, config ($[\alpha]_{Hg}$, deg)	% optical purity[c]
CH_3, **3a**	(+)-(*R*) (99)	**6a** (+)-(*S*) (141)	94
Cl, **3b**	(+)-(*S*) (153)	**6b** (+)-(*S*) (168)	83
F, **3c**[b]	(−)-(*S*) (164)	**6c** (−)-(*S*) (22)	73
OCH_3, **3d**	(−)-(*S*) (−49)	**6d**, (+)-(*S*) (75)	6

[a] Experiments were performed on incompletely resolved samples and corrected. [b] Enantiometer was used. [c] Based on optical purities previously determined for **6b**, **6c**, and **6d** (ref 11).

Experimental Section

All melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 237 grating infrared spectrophotometer. Nmr spectra were obtained using either a Varian A-60 or a Bruker 90 MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained using a Nuclide 12-90 G 1.5 magnetic deflection mass spectrometer. Optical rotations were measured at either the 546.1-nm mercury line or at the 589.3-nm sodium line using a Bendix-Ericsson Model 987 ETL/NPL automatic polarimeter Type 143A equipped with a Texas Instrument Model FWS strip chart recorder. The instrument was equipped to read full scale 0 to ±0.500° with an error of approximately ±1.5%. Cell lengths were 0.2 or 0.4 dm.

Decarbonylation of (+)-(*R*)-1-Methyl-2,2-diphenylcyclopropanecarboxaldehyde. A solution of 0.60 g (2.5 mmol) of optically pure (+)-(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde,[18] $[\alpha]^{24}{}_{Hg}$ 98.6° (*c* 0.2, $CHCl_3$), and 2.50 g (2.5 mmol) of tris(triphenylphosphine)chlororhodium(I) in 75 ml of xylene was refluxed for 16 hr. Two volumes of ethanol were added to the cooled solution and the resulting precipitate of bis(triphenylphosphine)carbonylchlororhodium(I) (1.7 g, 84%; ir ($CHCl_3$) 1985 cm^{-1}). The solvent was removed and the product chromatographed on 30 g of alumina eluting with pentane to remove the major contaminants, then distilled at 0.2 mm (bath temperature 120°) to give 0.36 g (70%) of 1-methyl-2,2-diphenylcyclopropane which was homogeneous by glpc on five different columns. The nmr and ir spectra were identical with those of authentic samples. The rotation was $[\alpha]^{25}{}_{Hg}$ 141° (*c* 0.43, $CHCl_3$), 94% optically pure. An authentic sample, optically pure, has $[\alpha]^{25}{}_{Hg}$ 150.6°.

Decarbonylation of 1-Methyl-2,2-diphenylcyclopropanecarboxaldehyde-*d*. The deuterioaldehyde was prepared by the oxidation of the corresponding dideuteriocarbinol with chromic acid and pyridine.[10] The carbinol had been prepared from 1-methyl-2,2-diphenylcyclopropanecarboxylic acid using lithium aluminum deuteride. The aldehyde was decarbonylated following the procedure used for the protioaldehyde and the resulting 1-deuterio-1-methylcyclopropane had nmr (CCl_4): δ 0.91 (s, 3, CH_3), 1.06 (d, 1, *J* = 5 Hz, ring), 1.19 (d, 1, *J* = 5 Hz, ring), 7.04 (complex, 10, phenyl). The aldehyde contained 96 ± 3% deuterium and gave hydrocarbon containing 93 ± 3% deuterium as determined by mass spectrometry[26] at 8.5 and 9.0 eV, respectively.

Decarbonylation of 1-Methyl-2,2-diphenylcyclopropanecarboxaldehyde with Palladium. A mixture of 460 mg of aldehyde and 80 mg of 5% palladium on charcoal was heated at a bath temperature of 200–210° for 30 min. The carbon monoxide evolved was collected by displacement of water; the yield was approximately 80%. The product was an oil which was taken up in chloroform, filtered to remove the catalyst, evaporated, and separated from a small amount of starting material by preparative tlc. The product was mainly (90%) 1,1-diphenyl-1-butene, identified by comparison with the ir and nmr spectra of an authentic sample,[27] contaminated by at least four minor products as determined by glpc on EGIP at 200°. Nmr analysis indicated that neither 1-methyl-2,2-diphenylcyclopropane nor 2-methyl-1,1-diphenylpropene was present.

Decarbonylation of 1-Methyl-2,2-diphenylcyclopropanecarboxaldehyde with Bis(triphenylphosphine)carbonylchlororhodium (I). A mixture of 500 mg of aldehyde and 18 mg of complex was heated neat at a bath temperature of 230–250° for 3 hr. Approximately 50% of the theoretical amount of carbon monoxide was collected.

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(17) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964).

(18) H. M. Walborsky and J. B. Pierce, *J. Org. Chem.*, 33, 1962 (1968).

(19) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964).

(20) F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4838 (1962).

(21) H. M. Walborsky and J.-C. Chen, *ibid.*, **93**, 671 (1971).

(22) P. D. Bartlett and J. D. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969); F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970); These references contain excellent reviews of the literature pertaining to this point.

(23) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *ibid.*, **88**, 78 (1966).

(24) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970); in this review it is suggested that the ylide and Meisenheimer rearrangements also involve radical pairs.

(25) F. J. Impastato and H. M. Walborsky, *J. Amer. Chem. Soc.*, **84**, 4838 (1962); C. L. Bumgardner and K. G. McDaniel, *ibid.*, **91**, 6821 (1969).

(26) K. Bieman, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 202–224.

(27) H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *J. Amer. Chem. Soc.*, **90**, 5222 (1968).

Ethanol was added to ensure complete precipitation of any dissolved complex and glpc analysis indicated that the product was 1,1-diphenyl-1-butene contaminated with the same minor products as when formed using palladium; *vide supra*.

Preparation of (−)-(*R*)-2-Methyl-2-phenylbutanal. (−)-(*R*)-2-Methyl-2-phenylbutanoic acid,[28] $[\alpha]^{24}_{\mathrm{Hg}}$ −33.3° (*c* 2.0, C_6H_5), was reduced to (−)-(*R*)-2-methyl-2-phenyl-1-butanol, $[\alpha]^{25}_{\mathrm{Hg}}$ −9.7° (*c* 8.7, $CHCl_3$), using lithium aluminum hydride. To a solution of 3.4 g of the alcohol in 100 ml of acetone was added a solution of chromic anhydride in sulfuric acid (Jones reagent[29]) until the orange color persisted. The addition was carried out in a water bath at room temperature to prevent the mixture from getting too warm. The mixture was poured into ice water, extracted with ether, and dried over sodium sulfate, and the ether was removed to yield 3.0 g of crude aldehyde. Chromatography on neutral alumina using 9:1 benzene–ethanol as eluent gave 1.8 g of pure aldehyde: ir (CCl_4) 2805 and 2710 (aldehyde C–H) and 1730 cm^{-1} (C=O); nmr (CCl_4) δ 0.73 (t, 3, *J* = 7.5 Hz, CH_2CH_3), 1.34 (s, 3, $-CH_3$), 1.88 (q, 2, *J* = 7.5 Hz, $-CH_2CH_3$), 7.28 (s, 5, phenyl), 9.47 (s, 1, aldehyde); $[\alpha]^{25}_{\mathrm{Hg}}$ −12.7° (*c* 4.1, $CHCl_3$). The 2,4-dinitrophenylhydrazone had mp 123–124°; lit.[7] mp 122.8–124.2. The analytical sample was distilled at 0.5 mm (bath temperature 65°).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.60.

Decarbonylation of (−)-(*R*)-2-Methyl-2-phenylbutanal. A solution of 0.33 g (2.1 mmol) of aldehyde, $[\alpha]^{25}_{\mathrm{Hg}}$ −12.7° (*c* 4.1, $CHCl_3$), and 1.86 g (2.0 mmol) of tris(triphenylphosphine)chlororhodium (I) in 6 ml of benzonitrile was heated at 160° for 1.5 hr. The solution was cooled and decanted from the yellow precipitate of bis(triphenylphosphine)carbonylchlororhodium (I) which was rinsed with ethanol. The decantate and rinsings were chromatographed on 137 g of alumina using pentane as eluent and collecting 25-ml fractions. The contents of the eluent were monitored by glpc on a 10 ft × $^1/_4$ in. Carbowax-20M column of glass beads. The *sec*-butylbenzene was then distilled in a modified Hickman still at 30 mm. The product weighed 0.14 g (51%); nmr identical with that of authentic material,[30] $[\alpha]^{25}_{\mathrm{Hg}}$ 25.8° (*c* 2.8, C_2H_5OH), 81% optically pure; *vide infra*.

Determination of the Maximum Rotation of (+)-(*S*)-*sec*-Butylbenzene in Solution. 2-Phenylbutanoic acid was resolved by the method of Gold-Aubert,[31] reduced to 2-phenyl-1-butanol using lithium aluminum hydride, converted to the *p*-toluenesulfonate ester, and reduced further, with lithium aluminum hydride, to the hydrocarbon. The distilled sample of *sec*-butylbenzene was shown to be chromatographically pure and to have ir and nmr spectra identical with authentic material. The rotation data were $\alpha^{23}\mathrm{D}$ 23.98° (neat, 1 dm); the literature value was $\alpha^{23}\mathrm{D}$ 24.3° (neat, 1 dm);[7] $[\alpha]^{24}_{\mathrm{Hg}}$ +31.8° (*c* 2.87, C_2H_5OH).

Decarbonylation of (*E*)-α-Ethylcinnamaldehyde. A mixture of 0.48 g of aldehyde (bp 115–116° (7 mm), $n^{26}\mathrm{D}$ 1.5840; lit.[32] bp 111–112° (7 mm), $n^{25}\mathrm{D}$ 1.5822), 2.66 g of tris(triphenylphosphine)chlororhodium(I), and 50 ml of benzene was heated at reflux for 90 min. Addition of ethanol caused the precipitation of 1.65 g (83%) of the yellow carbonyl complex. Analysis of the filtrate by glpc on an 8 ft × $^1/_4$ in. Dow 11 column at 120° indicated that the product olefin was pure (*Z*)-1-phenyl-1-butene.

A mixture of 7.85 g of aldehyde and 0.37 g of bis(triphenylphosphine)carbonylchlororhodium (I) was heated in a distillation apparatus at about 40 mm. The product distilled at 125–130° and it consisted of 74% (*Z*)- and 26% (*E*)-1-phenyl-1-butene as determined by integration of the glpc and nmr curves.

A sample of the alkene mixture (1.72 g) from above was heated at reflux with 0.07 g of bis(triphenylphosphine)carbonylchlororhodium (I) for 120 min. The mixture was analyzed by glpc and found to contain 63% *Z* isomer after 90 min and 50% *Z* isomer after 120 min.

Decarbonylation of (+)-(*R*)-1-Fluoro-2,2-diphenylcyclopropanecarboxaldehyde.[11] A solution of 165 mg (0.69 mmol) of aldehyde, $[\alpha]^{25}_{\mathrm{Hg}}$ +164° (*c* 0.56, dioxane), and 612 mg (0.66 mmol) of tris(triphenylphosphine)chlororhodium(I) in 4 ml of benzonitrile was heated at 165–170° for 1.5 hr. The solution was cooled, the solvent removed at less than 1 mm pressure, and the carbonyl complex precipitated with ethanol. The product was isolated by preparative thin-layer chromatography with benzene as developing agent; the yield was 87 mg (62%), $[\alpha]^{25}_{\mathrm{Hg}}$ +16.2° (*c* 1.0, $CHCl_3$).

Demonstration of the Configurational Stability of (+)-(*R*)-1-Fluoro-2,2-diphenylcyclopropane under Decarbonylation Conditions. A sample (49 mg, 0.23 mmol) of (+)-(*R*)-2,2-diphenylcyclopropyl fluoride, $[\alpha]^{15}_{\mathrm{Hg}}$ +16.2 (*c* 0.87, $CHCl_3$),[11] prepared above, 74 mg (0.08 mmol) of tris(triphenylphosphine)chlororhodium(I), and 114 mg (0.14 mmol) of bis(triphenylphosphine)carbonylchlororhodium(I) in 1 ml of benzonitrile was heated for 30 min at 165° and worked up as above. The recovered fluoride, 36 mg, had $[\alpha]^{25}_{\mathrm{Hg}}$ +14.2 ± 1° (*c* 0.72, $CHCl_3$) and was chromatographically pure.

Decarbonylation of (−)-(*S*)-1-Methoxy-2,2-diphenylcyclopropanecarboxaldehyde. A solution of 0.30 g (1.2 mmol) of aldehyde,[11] 82% optically pure, $[\alpha]^{26}_{\mathrm{Hg}}$ −40° (*c* 1.0, $CHCl_3$), and 1.1 g (1.2 mmol) of tris(triphenylphosphine)chlororhodium(I) in 6 ml of benzonitrile was heated at 160–165° for 1.5 hr. The solution was cooled, the solvent removed *in vacuo*, and the carbonyl complex precipitated with ethanol; the yield was 0.68 g (84%). The filtrate was chromatographed on silica gel to remove nonvolatile contaminants and the (+)-(*S*)-1-methoxy-2,2-diphenylcyclopropane[11] was isolated by glpc on a 4 ft × $^1/_4$ in. CES column at 145°. Its purity was checked by glpc and 90-MHz nmr and its rotation was $[\alpha]^{25}_{\mathrm{Hg}}$ +4.4° (*c* 1.2, $CHCl_3$), 5.9% optically pure.

Demonstration of the Configurational Stability of (+)-(*S*)-1-Methoxy-2,2-diphenylcyclopropane under Decarbonylation Conditions. A sample of (+)-(*S*)-1-methoxy-2,2-diphenylcyclopropane, $[\alpha]^{30}_{\mathrm{Hg}}$ +54° (*c* 0.65, $CHCl_3$), was treated with a mixture of tris(triphenylphosphine)chlororhodium(I) and bis(triphenylphosphine)carbonylchlororhodium(I) in benzonitrile at 160–165° for 1.5 hr. The recovered (+)-(*S*)-1-methoxy-2,2-diphenylcyclopropane had $[\alpha]^{28}_{\mathrm{Hg}}$ +53° (*c* 0.75, $CHCl_3$).

Decarbonylation of (±)-(*R*,*S*)-1-Chloro-2,2-diphenylcyclopropanecarboxaldehyde. A solution of 0.520 g (2.03 mmol) of aldehyde[11] and 1.83 g (1.98 mmol) of tris(triphenylphosphine)chlororhodium (I) in 10 ml of benzonitrile was heated at 160–165° for 1.5 hr. The mixture was cooled, the benzonitrile distilled *in vacuo*, and ethanol added to the residue to precipitate the carbonyl complex. The yellow precipitate, 1.23 g (90%), was filtered and the filtrate subjected to preparative tlc on silica gel developing first with benzene to remove the remaining benzonitrile, then with pentane to give two products. The product with the higher R_f amounted to 98 mg (25%) and was identified as 1,1-diphenylpropene: mp 49–50°; reported[33] mp 52°; nmr (CCl_4) δ 1.74 (d, 3, *J* = 7 Hz, $-CH_3$), 6.10 (q, 1, *J* = 7 Hz, –CH), 7.14 (m, 10, phenyl). The second product weighed 183 mg (40%) and proved to be 1-chloro-2,2-diphenylcyclopropane:[11] mp 73–74°; nmr (CCl_4) δ 1.71 (d, 2, *J* = 6 Hz, $-CH_2-$), 3.70 (t, 1, *J* = 6 Hz, –CHCl–), 7.37 (m, 10, phenyl). Both products were homogeneous by glpc on SE-30 at 200°.

Anal. Calcd for $C_{15}H_{13}Cl$: C, 78.80; H, 5.73. Found: C, 78.69; H, 5.69.

The above procedure was repeated using (+)-(*S*)-1-chloro-2,2-diphenylcyclopropanecarboxaldehyde, $[\alpha]^{24}_{\mathrm{Hg}}$ +56.9° (*c* 1.0, $CHCl_3$), 37.2% optically pure. The (+)-(*S*)-1-chloro-2,2-diphenylcyclopropane isolated had $[\alpha]^{24}_{\mathrm{Hg}}$ +62.4° (*c* 1.0, $CHCl_3$), 28.8% optically pure.

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