

alkyl complex **12**: mp 168–174°; $[\alpha]^{25}_D$ 5.8° (c 2, CHCl₃); ir (CHCl₃) 2070 cm⁻¹ (Ir¹¹¹CO). *Anal.* Calcd for C₄₅H₃₆Cl₂F₃IrOP₂: C, 55.45; H, 3.72. Found: C, 55.12; H, 4.01.

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Mechanism of Acid Chloride Decarbonylation with Chlorotris(triphenylphosphine)rhodium(I). Stereochemistry and Direction of Elimination

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Abstract: The decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chloride with chlorotris(triphenylphosphine)rhodium(I) gave exclusively *trans*- and *cis*-methylstilbene, respectively. These results are best explained either by an acyl-alkyl rearrangement with retention and a *cis* β -hydride elimination, or a concerted *cis* elimination. The rates of the decarbonylation of dichloro(3-perdeuteriophenyl-3,3-dideuteriopropionyl)bis(triphenylphosphine)rhodium(III) along with the undeuterated complex ($k_H = 3.34 \times 10^{-5} \text{ sec}^{-1}$, $k_D = 4.75 \times 10^{-6} \text{ sec}^{-1}$) showed a primary deuterium isotope effect of 7.04. Decarbonylation of 2-methylpentanoyl chloride, 2,2-dimethylpentanoyl chloride, 2-ethyl-3-methylbutanoyl chloride, and 2,3-dimethylbutanoyl chloride with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) showed that this olefin-forming reaction preferred the Saytzeff elimination.

The homogeneous decarbonylation of carboxylic acid halides with chlorotris(triphenylphosphine)rhodium(I) (**1**) takes place at room temperature.¹⁻⁴ When there is no β hydrogen on the acid halide, the product is an alkyl or aryl halide; when a β hydrogen is present, the products are the olefins and hydrogen halide. In the reaction, chlorotris(triphenylphosphine)rhodium(I) is converted to chlorocarbonylbis(triphenylphosphine)rhodium(I) (**4**) and the reaction is stoichiometric with respect to the former. Chlorocarbonylbis(triphenylphosphine)rhodium(I) also catalyzes the homogeneous decarbonylation, but at a higher temperature.^{3,5-9} The rhodium-catalyzed decarbonylation has the advantage over the palladium-catalyzed decarbonylation, since the major product from straight chain acid halides is the 1-olefin with small amounts of internal olefins resulting from isomerization. Palladium catalysis affords mainly internal olefins.^{10,11}

The mechanism for the decarbonylation of acid chlorides by chlorotris(triphenylphosphine)rhodium(I) has been proposed to involve both acyl- and alkyl- or arylrhodium complexes²⁻⁵ as shown in Figure 1. When catalytic amounts of **1** are used, the proposed mechanism involves the oxidative addition of an acid chloride to **4** at elevated temperatures to form **5**. In

the next step, **5** can lose carbon monoxide to give **2**, followed by acyl-alkyl rearrangement to produce **3**. Finally, olefins are obtained by a β -hydride elimination reaction with the regeneration of the complex **4**.

Results and Discussion

Stereochemistry. In order to study the overall stereochemistry of β -hydrogen elimination, the *erythro*- and *threo*-2,3-diphenylbutanoyl chloride (**6** and **7**) obtained from the corresponding acids¹² were treated with **1** to form the appropriate acylrhodium complexes (Figure 2).

When the *erythro* acyl complex (**8e**) was stirred in benzene for 5 days at 30°, a 90% yield of *trans*- α -methylstilbene was obtained. In the case of the *threo* acyl complex (**8t**), similar reaction conditions resulted in a 90% yield of α -methylstilbenes; *cis*- α -methylstilbene comprised 90% of this mixture and *trans*- α -methylstilbene the remaining 10%. Thus the elimination takes place stereospecifically with overall *cis* elimination occurring. In the decarbonylation of both *erythro* and *threo* acid chlorides either the acyl-alkyl rearrangement and the β -hydride elimination occur stereospecifically, or a concerted stereospecific *cis* elimination occurs.

If the two-step process is followed, these results are consistent either with retention of configuration during the acyl to alkyl rearrangement (**2** \rightarrow **3**) to afford an alkyl complex (e.g., from the *erythro* isomer) followed by a *cis* β -hydrogen elimination or by inversion of configuration during this rearrangement to give alkyl complex (e.g., **10** from the *erythro* isomer) followed by a *trans* elimination. The same arguments apply to the *threo* isomer in which either retention, *cis* elimination

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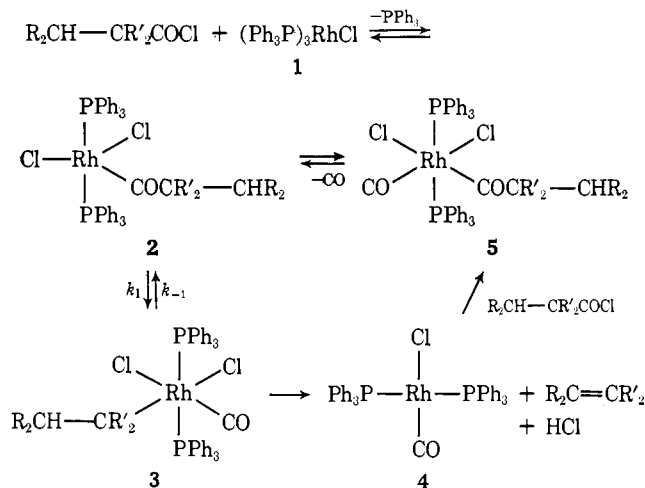


Figure 1. Mechanism of acid chloride decarbonylation.

or inversion, trans elimination explain the results. The intermediate alkyl complexes **9** and **10** cannot be detected conclusively by infrared during the course of the rearrangement, so that they are either present in relatively low concentrations or are not formed.

For the two-step mechanism, the retention, cis elimination pathway would be favored on the basis of the retention observed in the decarbonylation of aldehydes with rhodium¹³ as well as the evidence for cis metal-hydride elimination¹⁴⁻¹⁶ and retention in acyl-alkyl rearrangement (or the reverse reaction, carbonyl "insertion")¹⁷⁻²⁰ in other systems.

In an attempt to determine whether or not the step in which the alkyl group is released from the metal with the abstraction of a hydrogen is rate determining, 3-perdeuteriophenyl-3,3-dideuteriopropionyl chloride (**11**) was synthesized. Acyl complex **12** was prepared by the reaction of the acid chloride **11** with chlorotris(triphenylphosphine)rhodium(I), and its rate of decarbonylation along with that of the undeuterated complex were measured at 80°. The rate constants ($k_H = 3.34 \times 10^{-5} \text{ sec}^{-1}$ and $k_D = 4.75 \times 10^{-6} \text{ sec}^{-1}$) show a primary isotope effect of 7.04. These results are more consistent with a rate-determining concerted cis elimination reaction of **12** without the intervention of the intermediate alkyrhodium complex (**13**) than with the two-step mechanism (in which the decomposition of **13** is rate determining) for the following reasons. Although an isotope effect would be expected for a process in which an equilibrium between **12** and **13** is established prior to the rate-determining elimination reaction of **13** to afford styrene and **4**, the magnitude of the isotope effect would not be expected to be as large as was observed. With the conversion of **13** to products as the rate-determining step, a measurable concentration of **13** should be observed, yet neither could this intermediate

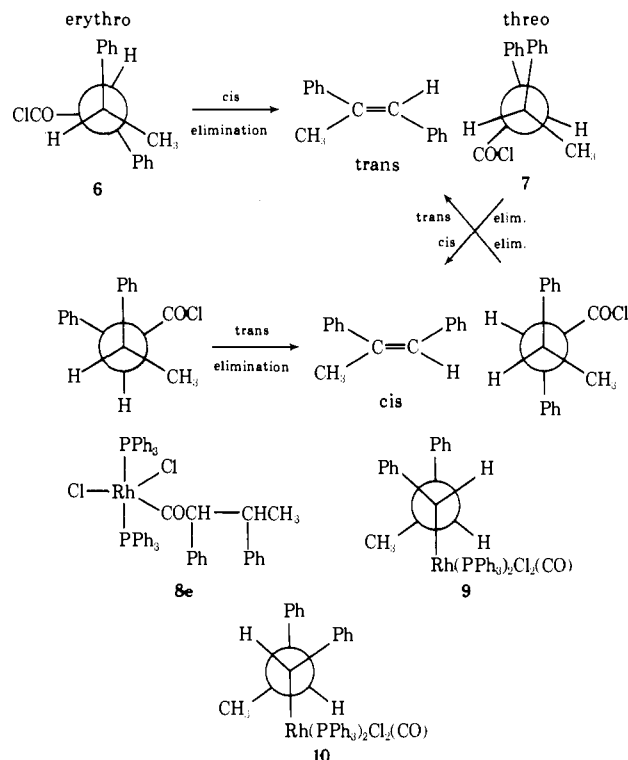
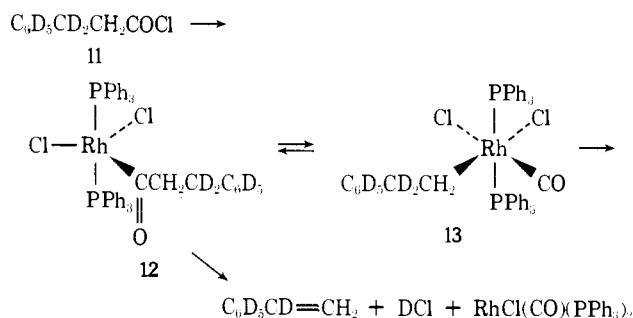


Figure 2. Stereochemistry of the decarbonylation-dehydrohalogenation of erythro- and threo-2,3-diphenylbutanoyl chloride.



nor the intermediate alkyl complex obtained from the decomposition of the erythro and threo complexes (**8e,t**) be detected by infrared. Mechanistic studies²¹ on the conversion of phenylacetyl rhodium complexes (of type **2**) to benzylrhodium complexes (of type **3**) show that this is an equilibrium process which favors the phenylacetyl species; the subsequent decomposition of the benzylrhodium complex to **4** has the fastest rate of the three. The racemization which accompanies the decarbonylation of optically active α -trifluoromethylphenylacetyl chloride to α -trifluoromethylbenzyl chloride and **4** has been attributed²² to this equilibrium step rather than the subsequent step, the conversion of the benzylrhodium complex to **4**. Thus, if an equilibration $2 \rightleftharpoons 3$ were established, a stereospecific reaction in the decarbonylation of the erythro and threo rhodium complexes (**8e,t**) would not be expected.

Direction of Elimination. In order to study the selectivity for the direction of elimination in the decarbonylation of acid chlorides containing β hydrogens, the

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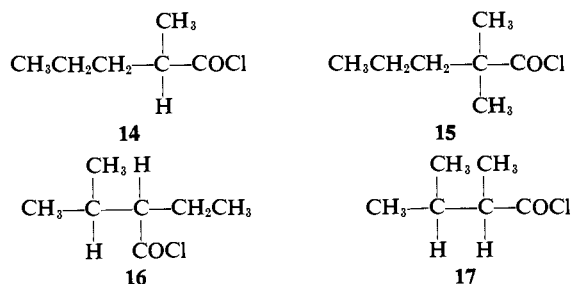
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Table I. Effects of Triphenylphosphine on the Catalytic Decarbonylation of Hexanoyl Chloride with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I) in Benzonitrile at 190°

Molar ratio Ph ₃ P/(Ph ₃ P) ₂ - RhCl(CO) ^a	Reaction time, hr	Yield, %	% product	
			1-Pentene	2-Pentene
0	4	62	66	34
1	6	58	86	14
2	16	65	90	10
5	18	57	95	5
10	24	10	96	4

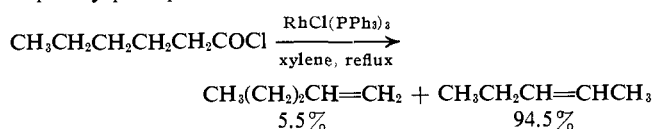
^a The reactions were carried out with 1.87 g of hexanoyl chloride and 100 mg of catalyst (molar ratio of hexanoyl chloride/catalyst = 96:1) in 10 ml of benzonitrile.

decarbonylation of several branched acid chlorides (14–17) having primary, secondary, and tertiary hy-



drogens was carried out, where two choices of types of hydrogens (primary *vs.* secondary, primary *vs.* tertiary, and secondary *vs.* tertiary) were available.

The decarbonylation of hexanoyl chloride with chlorotris(triphenylphosphine)rhodium(I) afforded predominantly 2-pentene, as a result of isomerization of 1-pentene under the reaction conditions. Addition of triphenylphosphine to the reaction mixture had no



effect on the isomer distribution ratio. The reaction was carried out such that the olefins and hydrogen chloride gas were removed from the reaction mixture as soon as they were formed, and were collected in a trap at -78° . These results possibly can be attributed to the fact that chlorotris(triphenylphosphine)rhodium(I) is a very active catalyst for the isomerization of 1-olefins to internal olefins.²³

The isomerization of olefins could also be catalyzed by a rhodium hydride formed from the addition of hydrogen chloride, which is generated from the reaction, to the rhodium(I) complexes. The addition of rhodium hydrides, L_nRhH, to alkenes followed by elimination leads to the isomerization of olefins.^{24,25} Chlorocarbonylbis(triphenylphosphine)rhodium(I), which does not isomerize the olefin,^{26,27} was chosen, therefore, as a catalyst for the study of β elimination *via* decarbonylation.

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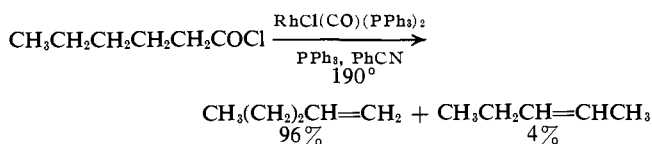
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Table II. The Catalytic Decarbonylation of Branched Acid Chlorides with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I) in the Presence of Triphenylphosphine^a

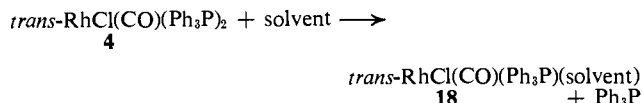
Acid chloride	Catalyst, (g)	Catalyst, mg	Product	% ^b	Yield, %
14	(0.94)	50	1-Pentene	30 (1)	52
			<i>cis</i> - and <i>trans</i> -2-Pentene	70 (3.5)	
15	(0.55)	50	2-Methyl-1-pentene	49 (1)	36
			2-Methyl-2-pentene	47 (3)	
16	(0.57)	50	<i>cis</i> - and <i>trans</i> -4-Methyl-2-pentene	4	80
			2-Methyl-1-pentene	10	
17	(1.14)	100	2-Methyl-2-pentene	44 (2)	75
			<i>cis</i> - and <i>trans</i> -4-Methyl-2-pentene	46 (1)	
			3-Methyl-1-butene	12.4 (1)	
			2-Methyl-1-butene	9.6	
			2-Methyl-2-butene	78.0 (19)	

^a These reactions were carried out at 190° in 10 ml of benzonitrile. The molar ratio of Ph₃P/catalyst = 10. ^b The statistically corrected ratios appear in parentheses.

The decarbonylation of hexanoyl chloride catalyzed by *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) (4) afforded 1-pentene as the predominant product; added triphenylphosphine suppressed the isomerization of 1-pentene to 2-pentene as shown in Table I. As the amount of added triphenylphosphine was increased, both the rates of decarbonylation and isomerization decreased. In the presence of a tenfold molar excess of triphenylphosphine over the catalyst, the suppression of isomerization was nearly complete and the ratio of 1- to 2-pentene was 96:4.



The decrease in the rate of the decarbonylation reaction caused by added triphenylphosphine suggests that the solvent-assisted dissociation of the carbonyl complex into the solvated species (18), the effective catalyst in the



decarbonylation,²⁷ is suppressed. Decarbonylations of the branched acid chlorides (14–17) were carried out in the presence of added triphenylphosphine, present in a molar ratio of 10:1 over the catalyst 4. In addition, the reaction was carried out such that the olefins and hydrogen chloride were removed from the reaction mixture as soon as they were formed and the evolved hydrogen chloride was neutralized. The products were collected in a trap at 0° containing excess pyridine-sodium hydroxide solution. In the absence of base in the trap, the evolved hydrogen chloride added to the branched olefin collected to give the corresponding alkyl chloride according to the Markovnikov rule. (Hydrogen chloride did not add to the straight chain olefin even in the absence of base in the trap.) The results of these decarbonylations (Table II) show the tendency toward Saytzeff elimination, in that secondary

hydrogen abstraction is preferred over primary (3:1) and tertiary over secondary (2:1) or primary (19:1).

Experimental Section

Catalysts. Chlorotris(triphenylphosphine)rhodium(I) (1). This compound was prepared by a published procedure.²⁸ *Anal.* Calcd for $C_{37}H_{45}ClP_3Rh$: C, 70.10; H, 4.90. Found: C, 71.00; H, 5.05.

Chlorocarbonylbis(triphenylphosphine)rhodium(I) (4) was obtained from the carbonylation of 1.²⁹ *Anal.* Calcd for $C_{37}H_{30}ClOP_2Rh$: C, 64.32; H, 4.38. Found: C, 64.25; H, 4.44.

erythro- and threo-2,3-Diphenylbutanoyl Chloride (6 and 7). A solution of 0.912 g (3.8 mmol) of *threo*-2,3-diphenylbutanoic acid¹² and 4.83 g (3.2 ml, 0.038 mol) of oxalyl chloride in 4 ml of anhydrous benzene was stirred for 15 min at 30° and then heated to 70° for 2 hr. The excess oxalyl chloride and benzene were removed *in vacuo* at room temperature. The *threo*-2,3-diphenylbutanoyl chloride, 0.970 g (98%), was obtained as an oil. This oil was employed directly in the preparation of the corresponding acyl rhodium complex.

An analogous procedure was used for the preparation of the *erythro*-2,3-diphenylbutanoyl chloride. *Anal.* Calcd for $C_{16}H_{15}OCl$: C, 74.27; H, 5.84. Found: C, 74.41; H, 6.48.

Dichloro(erythro-2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) (8e) and Dichloro(threo-2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) (8t). To a solution of 1.074 g (1.16 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 50 ml of dichloromethane was added a solution of 0.368 g (1.42 mmol) of *erythro*-2,3-diphenylbutanoyl chloride in 5 ml of dichloromethane. The resulting mixture was stirred at 30° for 24 hr. An infrared spectrum of the reaction solution indicated that the acyl complex (1715 cm^{-1}) was contaminated with about 5% of chlorocarbonylbis(triphenylphosphine)rhodium(I) (4) (1969 cm^{-1}). The reaction solution was concentrated on a rotary evaporator at 30°. Upon the addition of 40 ml of pentane the desired acyl complex precipitated as yellow crystals. The crystals were washed with ether, and recrystallized at low temperature from acetone-pentane to yield 0.79 g (80%) of dichloro(*erythro*-2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) (8e); ν (CH_2Cl_2) 1715 cm^{-1} (RCORh). *Anal.* Calcd for $C_{44}H_{36}Cl_2OP_2Rh$: C, 67.76; H, 4.92. Found: C, 65.90; H, 4.94.

The *threo* acyl complex was prepared in an analogous manner; ν (CH_2Cl_2) 1720 cm^{-1} (RCORh).

Decomposition of Dichloro(erythro-2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) (8e) and Dichloro(threo-2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) (8t). A solution of 0.675 g (0.793 mmol) of the *erythro* acyl complex in 50 ml of benzene was stirred at 30° for 5 days. The benzene was removed on a rotary evaporator at 30°, and the residue was stirred in pentane overnight to extract the olefin product. The mixture was then filtered, and the filtrate was concentrated on a rotary evaporator. Glc analysis of the remaining liquid (5 ft \times 0.25 in. 20% SE-30-Chromosorb W) indicated the presence of a single component which had the same retention time as an authentic sample³⁰ of *trans*- α -methylstilbene. A 90% yield of *trans*- α -methylstilbene was obtained in this reaction.

Decomposition of the *threo* acyl complex (8t) resulted in a 90% yield of α -methylstilbenes. Glc analysis (5 ft \times 0.25 in. 20% SE-30-Chromosorb W) indicated the presence of *cis*- α -methylstilbene (90%) and *trans*- α -methylstilbene (10%) by comparison with the authentic samples.³⁰

3-Perdeuteriophenyl-3,3-dideuteriopropionic Acid. A solution of 8.0 g (0.80 mol) of toluene- d_8 (Stohler Isotope Chemicals, Inc.), 19.6 g (0.110 mol) of *N*-bromosuccinimide, and 0.2 g of benzoyl peroxide in 200 ml of carbon tetrachloride was heated to the reflux temperature for 4 hr. The succinimide was removed by suction filtration and washed with carbon tetrachloride, and the washing was combined with the filtrate. The solvent was removed under reduced pressure, and the residue was distilled at 50–58° (1.0 mm) to afford 10 g (70%) of benzyl- d_7 bromide.

Benzyl- d_7 bromide (9.0 g, 50 mmol) was added dropwise to a stirred mixture of diethyl sodiomalonate (prepared from 9.0 g of diethyl malonate and 1.3 g of sodium) and 25 ml of absolute alcohol.

The reaction mixture was heated to the reflux temperature for 1 hr and then diluted with 25 ml of water. The organic product was extracted with ether and dried over magnesium sulfate, and the solvent was removed under reduced pressure to yield 10.0 g (78%) of the crude diethyl ester: ν (neat) 1728 cm^{-1} (ester); nmr ($CDCl_3$) δ 1.10 (m, 6 H), 3.26 (s, 1 H), 4.14 (q, 4 H) ppm.

To a solution of 8.6 g of potassium hydroxide in 10 ml of water was added 9.7 g (38 mmol) of deuterated diethyl ester. The solution was stirred and heated on a steam bath for 3 hr. The reaction mixture was then cooled by an ice bath, and 6 g of ice was added to lower the temperature to 20°. Hydrochloric acid was added until the reaction mixture was acid to Congo red paper. An excess of 1.5 ml of concentrated hydrochloric acid was added.

The crude deuterated benzylmalonic acid was extracted with ether and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude deuterated benzylmalonic acid (6.0 g) was heated at 180° for 30 min and the residue was distilled at 115–125° (0.5 mm) [lit.³¹ bp 125–126° (6 mm) for 3-phenylpropionic acid] to afford 3.0 g (60%) of the 3-perdeuteriophenyl-3,3-dideuteriopropionic acid: ν (neat) 1700 cm^{-1} (COOH); nmr ($CDCl_3$) δ 2.60 (s, 2 H), and 11.52 (s, 1 H) ppm.

3-Perdeuteriophenyl-3,3-dideuteriopropionyl Chloride (11). To 2.60 g (16.5 mmol) of 3-perdeuteriophenyl-3,3-dideuteriopropionic acid was added 4.20 g (33.0 mmol) of oxalyl chloride. The reaction mixture was heated to 65° for 2 hr. The resulting mixture was distilled under atmospheric pressure to remove excess oxalyl chloride and then under reduced pressure to yield 2.00 g (70%) of acid chloride at 54–58° (0.20 mm): ν (neat) 1795 cm^{-1} (COCl); mass spectrum m/e 139 ($M^+ - HCl$).

3-Phenylpropionyl Chloride. This acid chloride was prepared by the reaction of hydrocinnamic acid (Aldrich Chemical Co.) with oxalyl chloride as described above: yield, 93%; bp 61–65° (0.35 mm) [lit.³² bp 116° (15 mm)]; ν (neat) 1795 cm^{-1} (–COCl); mass spectrum m/e 132 ($M^+ - HCl$).

Dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III). To a solution of 0.843 g (5.00 mmol) of 3-phenylpropionyl chloride in 15 ml of dichloromethane was added 1.11 g (1.20 mmol) of chlorotris(triphenylphosphine)rhodium(I). The solution was stirred at room temperature for 24 hr. Upon precipitation with absolute alcohol, the orange crystals were washed with anhydrous ether and dried *in vacuo* to yield 1.10 g (87%) of acylrhodium complex: mp 205–207°; ν (KBr) 1710 cm^{-1} ($Rh^{111}COR$). *Anal.* Calcd for $C_{43}H_{39}Cl_2OP_2Rh$: C, 65.00; H, 4.73. Found: C, 65.14; H, 4.52.

Dichloro(3-perdeuteriophenyl-3,3-dideuteriopropionyl)bis(triphenylphosphine)rhodium(III) (12). This complex was prepared in an analogous manner to yield 87% of product: mp 204–208°; ν (KBr) 1710 cm^{-1} ($Rh^{111}COR$). *Anal.* Calcd for $C_{43}D_7H_{32}Cl_2OP_2Rh$: C, 64.46; H, 5.48. Found: C, 63.86; H, 4.84.

Rates of Decomposition of Dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) and Dichloro(3-perdeuteriophenyl-3,3-dideuteriopropionyl)bis(triphenylphosphine)rhodium(III) (12). Two reaction flasks containing the same concentration of acylrhodium complex were placed in an oil bath which was maintained at 80°. Samples of the reaction solution were withdrawn by a syringe through a serum cap, and the formation of product was determined by gas chromatography. One reaction flask contained 0.665 g (0.800 mmol) of dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) and 92.2 mg of toluene (internal standard), and was diluted with benzene to 6 ml; the second flask contained 0.671 g (0.800 mmol) of dichloro(3-perdeuteriophenyl-3,3-dideuteriopropionyl)bis(triphenylphosphine)rhodium(III) and 103 mg of toluene (internal standard), and was diluted with benzene to 6 ml.

2-Methylpentanoyl Chloride (14). To a solution of 167 g (1.40 mol) of thionyl chloride was added 94.0 g (0.700 mol) of 2-methylpentanoic acid (Aldrich Chemical Co.) at 50° over a period of 1 hr. The solution was allowed to stand overnight. The unchanged thionyl chloride was removed at atmospheric pressure and the residue was distilled to afford 83 g (88%), bp 138–140° (lit.³³ bp 140°), of product; ν (neat) 1795 cm^{-1} (COCl).

2,2-Dimethylpentanoyl chloride (15) was prepared in an analogous method from 2,2-dimethylpentanoic acid (Matheson Coleman and Bell) in a yield of 86%: bp 150–152°; ν (neat) 1795 cm^{-1} (–COCl).

2,3-Dimethylbutanoyl chloride (17) was prepared in an analogous

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(33) W. A. Quebedeaux, G. Wash, W. O. Ney, W. W. Crouch, and H. L. Lochte, *J. Amer. Chem. Soc.*, **65**, 767 (1943).

method from 2,3-dimethylbutanoic acid (K & K Laboratories Inc.) in a yield of 61%: bp 136–138° [lit.³⁴ bp 135.9–136.6° (751 mm)]; ir (neat) 1795 cm⁻¹ (–COCl).

2-Ethyl-3-methylbutanoic Acid. To 450 ml of water in a 1-l. flask fitted with a mechanical stirrer and cooled in an ice bath was added 58 ml (107 g) of concentrated sulfuric acid. When the temperature had fallen to 15°, 72 g (0.50 mol) of 2-ethyl-3-methylbutyraldehyde (Eastman Kodak Co.) was added, followed by 57 g (0.36 mol) of potassium permanganate in 2.5-g portions. The permanganate was added at such a rate that the temperature of the solution did not rise above 20°. When the addition was completed, sodium bisulfite was added until the solution became clear. The oil layer was separated, washed with water, and distilled from a Claisen flask. The foreruns were separated from any water and redistilled. The combined fractions were redistilled at atmospheric pressure to afford 55 g (85%) of product, bp 140°.

2-Ethyl-3-methylbutanoyl Chloride (16). To 54.5 g (0.500 mol) of thionyl chloride was added 55 g (0.42 mol) of 2-ethyl-3-methylbutanoic acid at 50° over the course of 1 hr. When the addition was completed, the solution was heated on a water bath for 30 min. Distillation of the solution afforded a crude acid chloride, bp 110–156°, which was purified by redistillation, bp 150–152°, to yield 40 g (64%) of product; ir (neat) 1795 cm⁻¹ (COCl).

Stoichiometric Decarbonylation of Hexanoyl Chloride with Chlorotris(triphenylphosphine)rhodium(I). To a solution of 0.210 g (1.50 mmol) of hexanoyl chloride (Matheson Coleman and Bell) in 10 ml of xylene was added 1.3 g (1.5 mmol) of chlorotris(triphenylphosphine)rhodium(I). The solution was heated to the reflux temperature for 2.5 hr and the olefins were collected in a trap at –78°. Glc analysis (20 ft × 0.375 in. 20% SE-30 Chromosorb W column) indicated the presence of 1-pentene (5.5%) and 2-pentene (94.5%) by comparison with authentic samples.

(34) M. Hommelen, *Bull. Soc. Chim. Belg.*, **42**, 245 (1933).

Stoichiometric Decarbonylation of Hexanoyl Chloride with Chlorotris(triphenylphosphine)rhodium(I) in the Presence of Triphenylphosphine. The reaction was carried out as above except with the presence of 1 molar excess of triphenylphosphine. Glc analysis showed no change in the product ratio.

Catalytic Decarbonylation of Acid Chlorides with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I). **A. General Procedure for the Decarbonylation of Hexanoyl Chloride.** To a solution of hexanoyl chloride (Matheson Coleman and Bell) in 10 ml of benzonitrile was added 100 mg (0.27 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) and an appropriate amount of triphenylphosphine (Table I). The solution was heated to 190° for a period of 4–24 hr, and the product olefins were collected in a cold trap at –78°. The isomer distribution was analyzed by glc using a 20 ft × 0.375 in. 20% SE-30–Chromosorb W column.

B. Decarbonylation of the Branched Acid Chlorides. A typical decarbonylation was carried out as follows. A solution of 570 mg (3.83 mmol) of 2-ethyl-3-methylbutanoyl chloride, 190 mg (1.36 mmol) of triphenylphosphine, and 50 mg (0.14 mmol) of *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) in 10 ml of benzonitrile was heated to 190° for 24 hr. The products were collected by distillation and absorbed in a pyridine–sodium hydroxide solution. Gas chromatography (20 ft × 0.375 in. 20% SE-30–Chromosorb W column) and mass spectral analysis showed: *cis*- and *trans*-4-methyl-2-pentene (46%), *m/e* 84 (M⁺); 2-methyl-1-pentene (10%), *m/e* 84 (M⁺); and 2-methyl-2-pentene (44%) *m/e* 84 (M⁺); yield, 80%.

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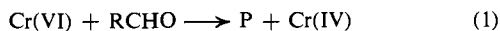
Chromium(IV) Oxidation of Aliphatic Aldehydes

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Abstract: The oxidation of aliphatic aldehydes in aqueous solution by chromium(IV) generated *in situ* from chromium(VI) and vanadium(IV) has been studied. Propionaldehyde is oxidized in a practically quantitative yield to propionic acid. Pivaldehyde gives a mixture of pivalic acid, *tert*-butyl alcohol, and isobutylene. The aldehydes seem to react in their hydrated forms; the value of the ρ constant for the oxidation of aldehyde hydrates is –0.96. The reaction exhibits a moderate deuterium isotope effect ($k_H/k_D = 1.7$ for propionaldehyde and $k_H/k_D = 2.1$ for pivaldehyde), which is consistent with a hydrogen atom transfer in the rate-limiting step from the aldehydic carbon atom to the oxidant. A mechanism for the chromium(IV) oxidation analogous to that earlier suggested for the oxidation of alcohols is proposed, and conclusions concerning the overall mechanism of the chromic acid oxidation of aldehydes are presented.

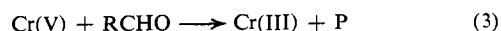
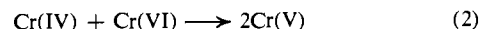
The first step in the chromic acid oxidation of aldehydes is generally thought of as involving a two-equivalent change to give the organic product and chromium(IV). This contention is supported by the



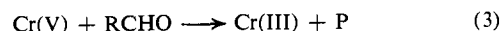
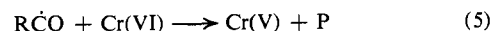
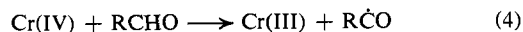
work of Chatterji and Mukherjee,¹ which showed an induction factor of 0.5 in the formaldehyde induced oxidation of manganese(II). However, the fate of chromium(IV) after the initial step has been open to question. Two most frequently cited routes for the fate of chromium(IV) are shown in Scheme I and

(1) A. K. Chatterji and S. K. Mukherjee, *J. Amer. Chem. Soc.*, **80**, 3600 (1958).

Scheme I



Scheme II



Scheme II. For a long time, these two schemes were also considered to be possible mechanisms in the oxidation of alcohols. However, recent studies in our laboratory have clearly shown the activity of chromium-