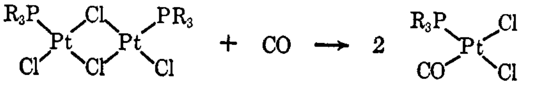
Organic Syntheses by Means of Noble Metal Compounds. XXXV.[1] Novel Decarbonylation Reactions of Aldehydes and Acyl Halides Using Rhodium Complexes

Kiyotaka Ohno and Jiro Tsuji

Contribution from The Basic Research Laboratories, Toyo Rayon Company Ltd., Kamakura, Japan. *Received June 12, 1967*

Abstract: It was found that aldehydes are decarbonylated by the reaction with chlorotris(triphenylphosphine)rhodium under mild conditions. Acyl halides are also decarbonylated to give olefins. Five-coordinate acylrhodium complexes were isolated as an intermediate of the reaction by oxidative addition of acyl halides to the complex. Several transformations of the acyl–rhodium complexes were carried out. Chlorocarbonylbis(triphenylphosphine)rhodium is an efficient catalyst of the decarbonylation of acyl halides and aldehydes; aromatic acid halides can be decarbonylated smoothly to give aromatic halides in the presence of a catalytic amount of this complex. The carbonylation of reactive alkyl halides to give acyl halides also is catalyzed by the complex. The mechanism of the decarbonylation and carbonylation reactions is discussed.

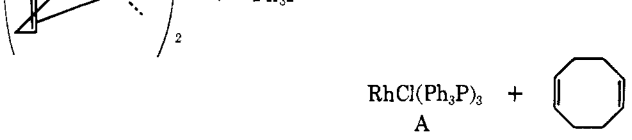
The decarbonylation of aldehydes and acyl halides to form olefins catalyzed by metallic palladium as a reverse reaction of the carbonylation of olefins has been reported.[1,2] Decarbonylation reactions would be very useful in organic chemistry if they can be carried out smoothly under mild conditions. In an effort to find a better catalyst than palladium for the decarbonylation reactions, we looked for a low valent noble metal complex catalyst. In order to find complexes which are active for the decarbonylation under mild conditions, several requirements should be satisfied from the consideration of the postulated mechanism of decarbonylation catalyzed by palladium. First of all, the complex should be a low valent one which is already reduced. Secondly, the complex should be coordinately unsaturated, so that it can undergo oxidative addition of acyl halides or aldehydes. Oxidative addition reactions have been a topic of recent extensive studies, and from these studies it has been made apparent that four-coordinate d^8 complexes are most suitable for the oxidative additions.[3] In addition, the complex should coordinate carbon monoxide more or less strongly to form a carbonyl complex. There are several noble metal complexes which seem to satisfy these requirements. For example, di-μ-chlorodichlorobis(trialkylphosphine)diplatinum is known to react with carbon monoxide at room temperature and atmospheric pressure to form dichlorocarbonyl(trialkylphosphine)platinum as shown below,[4] and the complex seemed to be a promising one to abstract carbon monoxide from aldehydes or acyl halides. However, it was found that this complex is completely inactive for the decarbonylation.



Recently, chlorotris(triphenylphosphine)rhodium (complex A) was synthesized by Wilkinson[5–7] and by Bennett.[8] Interestingly, this complex is easily converted into chlorocarbonylbis(triphenylphosphine)rhodium (complex B) by the reaction of carbon monoxide at room temperature and atmospheric pressure in solution. We found that this complex is extremely useful for the decarbonylations of aldehydes and acyl halides under mild conditions in homogeneous system.[9,10] In addition, it was found that the decarbonylation reactions can be carried out in the presence of a catalytic amount of chlorocarbonylbis(triphenylphosphine)rhodium (B) at higher temperature.[11,12] The decarbonylation reactions using the rhodium complexes described in this paper seem to be the best method of the decarbonylation and the method would have wide application in organic chemistry.[13] The rhodium complexes are stable and easy to handle. In this paper, scope, limitations, and mechanism of the useful decarbonylation reactions using the rhodium complexes A and B are discussed.

Results and Discussion

Decarbonylation of Aldehydes. In order to study the decarbonylation reaction, the complex A was synthesized by two methods. At first, di-μ-chlorobis(1,5-cyclooctadienyl)dirhodium was treated with a large excess of triphenylphosphine to give orange crystals of



---

[1] Part XXXIV, preceding paper.

[2] J. Tsuji, K. Ohno, and T. Kajimoto, *Tetrahedron Letters*, 4565 (1965).

[3] J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966).

[4] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

[5] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

[6] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

[7] F. H. Jardine and G. Wilkinson, *ibid., Sect. C*, 270 (1967).

[8] M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965).

[9] J. Tsuji and K. Ohno, *Tetrahedron Letters*, 3969 (1965).

[10] J. Tsuji and K. Ohno, *J. Am. Chem. Soc.*, **88**, 3452 (1966).

[11] J. Tsuji and K. Ohno, *Tetrahedron Letters*, 4713 (1966).

[12] J. Tsuji and K. Ohno, *ibid.*, 2173 (1967).

[13] An application of this method has already been reported (Y. Shimizu, H. Mitsuhashi, and E. Capri, *ibid.*, 4113 (1966).

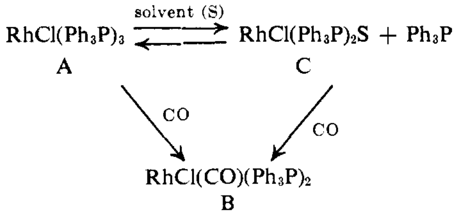
Table I. Decarbonylation of Aldehydes Using $RhCl(Ph_3P)_3$[a]

		Reaction				
Aldehyde	Solvent	Temp, °C	Time, min (hr)	Yield of complex B, %	Product	Yield,[b] %
Benzaldehyde	No	Reflux	5	80	Benzene	..
Benzaldehyde	No	120	30	72	Benzene	..
Benzaldehyde	No	Room temp	(24)	77	Benzene	..
Benzaldehyde	Toluene	Reflux	(1)	92	Benzene	83
n-Butyraldehyde	Benzene	Room temp	(2)	65	...	..
Isobutyraldehyde	Benzene	Room temp	(70)	83	...	..
Cinnamaldehyde	Benzene	Room temp	(12)	65	Styrene	..
Cinnamaldehyde	Benzene	Reflux	15	93	Styrene	77
Cinnamaldehyde	Dichloromethane	Room temp	(8)	65	Styrene	60
3-Phenylpropionaldehyde	Benzene	Reflux	10	90	Ethylbenzene	67
p-Chlorobenzaldehyde	Benzene	Reflux	(3)	90	Chlorobenzene	85
Salicylaldehyde	Toluene	Reflux	20	76	Phenol	70
n-Heptanal	Dichloromethane	Room temp	(24)	90	Hexane (86%) Hexene-1 (14%)	78
9,10-Dihydro-9,10-ethanoanthracene-11-carboxaldehyde	Benzonitrile	160	3	100	9,10-Dihydro-9,10-ethanoanthracene	67
1-Methyl-3-cyclohexene-1-carboxaldehyde	Benzonitrile	160	1	90	3-Methyl-1-cyclohexene	71
Cinnamaldehyde[c]	Benzene	Reflux	10	80	Styrene	89
trans-α-Methylcinnamaldehyde	Toluene	Reflux	5	90	β-Methylstyrene *cis* (91), *trans* (9)	88
trans-α-Methylcinnamaldehyde	Benzonitrile	160	1	91	β-Methylstyrene *cis* (96), *trans* (4)	86
trans-α-Ethylcinnamaldehyde	Benzonitrile	160	1	88	β-Ethylstyrene *cis* (94), *trans* (6)	82

[a] In all cases, 1–3 g of $RhCl(Ph_3P)_3$ and an excess of the aldehydes were used. [b] Yields based on the complex A. [c] $RhBr(Ph_3P)_3$ was used and $RhBr(CO)(Ph_3P)_2$ was formed.

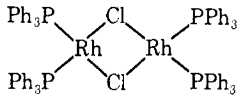
A. Later a more convenient method of preparation was reported by Bennett[8] and by Wilkinson.[6]

Wilkinson, *et al.*, found that the complex A forms a solvated, formally three-coordinate species (C) with liberation of one molecule of triphenylphosphine in solution (benzene or chloroform). This species C has a strong affinity for carbon monoxide and combines with carbon monoxide to form the stable complex B. In other words, this species C has vacant coordination sites which can be occupied by weakly bonded solvent molecules (S) or by other ligands. This is an essential property of the complex A for the decarbonylating activity. With the complex A, very smooth decarbonylation of aldehydes was observed even at room temperature with the elimination of one molecule of triphenylphosphine. The reaction can be expressed by eq 1. The decarbonylation of several aldehydes was carried out, and the results are shown in Table I. The reaction proceeds homogeneously in organic solvents such as benzene or dichloromethane, in which the complex A is moderately soluble. The progress of the reaction can be recognized easily by the color change from dark red to yellow. When the color of the solution turns to yellow, the decarbonylation reaction is complete. From the reaction mixture, triphenylphosphine is isolated by a proper work-up. Sometimes, triphenylphosphine oxide is formed by the reaction. Wilkinson, *et al.*, reported that the complex A absorbs oxygen reversibly and triphenylphosphine oxide is eliminated.[6]



$$RhCl(Ph_3P)_3 + RCHO \longrightarrow RhCl(CO)(Ph_3P)_2 + RH\ (\text{olefin} + H_2) + Ph_3P \quad (1)$$

Although no quantitative studies were carried out, it can be said that a steric effect has a large influence on the decarbonylation. Primary aldehydes are decarbonylated most easily at room temperature. When the decarbonylation is very slow at room temperature, it can be carried out more rapidly in boiling xylene or toluene. Under this condition, most secondary aldehydes can be decarbonylated. Aldehydes with larger steric hindrance, however, cannot be decarbonylated under this condition. Furthermore, when the aldehydes and the complex A are heated in xylene or toluene for a long period, the latter is converted into a brick red dimeric complex D, which is insoluble in xylene and precipitates, and hence the decarbonylation stops (eq 2). This difficulty can be overcome by using nitriles as the solvent. Benzonitrile or acetonitrile seems to solvate the three-coordinate species C(S–nitrile) strongly and prevent the formation of the dimer D completely. Thus, by using benzonitrile as the solvent, it is possible to decarbonylate highly hindered aldehydes. In benzonitrile, the formation of D is completely suppressed even at high temperature and the decarbonylation proceeds smoothly.

A or C $\longrightarrow$  $+ Ph_3P$ or S (2)

D

Benzonitrile or acetonitrile as the solvent has another advantage. As shown by eq 1, the decarbonylation with the complex A liberates one molecule of triphenyl-

Table II. Decarbonylation of Acid Halide by Complex A[a]

Acid halide	Solvent	Reaction Temp, °C	Reaction Time, min (hr)	Complex B,[b] %	Product	Yield,[b] %
Phenylacetyl chloride	Benzene	Reflux	10	97	Benzyl chloride	81
3-Phenylpropionyl chloride	Toluene	Reflux	30	71	Styrene	71
Phenylacetyl chloride	Dichloromethane	Room temp	(48)	95	Benzyl chloride	86
Benzoyl chloride	No	180	2	80	Chlorobenzene	61

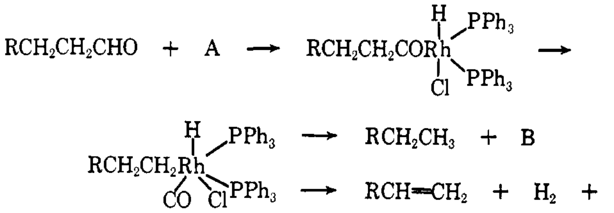
[a] An excess of the acyl halides was used. [b] Yields based on the complex A.

phosphine, the separation of which from decarbonylated products is not easy in some cases. It was found that the dimeric complex D is soluble in hot benzonitrile, forming the three-coordinate species C (S = benzonitrile) with solvated nitrile. Therefore, when the decarbonylation is carried out in benzonitrile or acetonitrile using the dimer D, it is possible to carry out the decarbonylation without liberating triphenylphosphine (eq 3).

$$\mathrm{D + S \longrightarrow \underset{C}{2RhCl(Ph_3P)_2S} \xrightarrow{RCHO} RH + RhCl(CO)(Ph_3P)_2 + S} \quad (3)$$

$$\mathrm{S = C_6H_5CN}$$

Although there is no direct evidence, it is probable that the decarbonylation proceeds through the formation of the acyl complexes, which are then converted into the alkyl complexes. The alkyl complexes decompose in two ways, namely, by forming olefins and hydrogen gas by the β-hydrogen abstraction or by coupling the coordinated hydrogen and alkyl group to form paraffins. In the rhodium-catalyzed decarbonylation, the products were mostly saturated compounds. However, when heptanal was decarbonylated, the formation of 1-hexene was confirmed as a minor product. The formation of the olefin can be explained reasonably by the above mechanism.



$$\mathrm{CH_3(CH_2)_5CHO \longrightarrow hexane\ (86\%) + 1\text{-}hexene\ (14\%)}$$

Based on this mechanism, it is expected that the reaction should proceed stereospecifically with respect to the carbon atom directly connected with the aldehyde group. Actually it was found that *cis*-β-substituted styrenes were formed predominantly from *trans*-α-alkylcinnamaldehydes (*trans* with respect to the phenyl and aldehyde groups). The result indicates that the decarbonylation of the aldehydes proceeds without interfering with the double bond.

The decarbonylation using the complex A consumes 1 mole of the complex for 1 mole of aldehydes and, after the reaction, the complex B is recovered. It is desirable to reconvert the complex B into the complex A, so that the complex can be used repeatedly. However, all attempts to convert the complex B into A were not successful under any conditions. For example, the complex B was heated to a temperature as high as 260° with an excess of triphenylphosphine as solvent for a long time. Only the complex B was recovered. So far there is no method of reconversion of B to A. The complex B is a very stable compound.

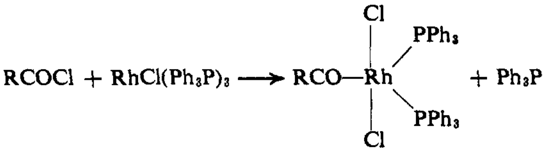
Decarbonylation of Acyl Halides. It was found that acyl halides can be decarbonylated with the complex A to form olefins and hydrogen halide (eq 4). For example, phenylpropionyl chloride was converted into styrene by refluxing in benzene with the complex A. When there is no hydrogen at the β position, the corresponding halides are formed (eq 5). The results of the decarbonylation of various acyl halides are shown in Table II.

$$\mathrm{RCH_2CH_2COX + RhCl(Ph_3P)_3 \longrightarrow RCH{=}CH_2 + RhCl(CO)(Ph_3P)_2 + Ph_3P + HX} \quad (4)$$

$$\mathrm{R'COX + RhCl(Ph_3P)_3 \longrightarrow R'X + RhCl(CO)(Ph_3P)_2 + Ph_3P} \quad (5)$$

$$\mathrm{R' = C_6H_5CH_2\text{–}, C_6H_5\text{–}}$$

The first step of the decarbonylation of acyl halides seems to be an oxidative addition ($d^8 \rightarrow d^6$) of acyl halides to the complex A; in fact, acyl complex (E) was actually isolated[10] (eq 6). This is the first example of an acyl metal complex isolated by the direct oxidative addition of acyl halides to a metal complex.



E (6)

Properties of the acyl complexes (E) are shown in Table III. Melting points shown in the table are not true melting points. The complexes begin to sinter at about 120° and finally melt at temperatures shown in the table. Probably the decarbonylation of the acyl complexes to form the complex B takes place before complete melting. The acyl complexes are air-stable yellowish brown crystals, easily soluble in chloroform, benzene, and dichloromethane, and moderately soluble in ether, but virtually insoluble in alcohol, hexane, and petroleum ether. They do not react with water and ethanol at room temperature. The complexes are isolated from benzene solution by addition of ethanol. However, it is not easy to obtain the complexes in a highly pure state. The complexes are easily transformed in solution. For example, when the complex A was heated with an excess of acyl halides in benzene for a long period of time, an orange-red complex containing phosphorus and chlorine in a ratio of 2:3 was formed. Therefore, the reaction of acyl halides and the complex A should be carried out carefully with purified acyl halides. Attempted purification through a silicic acid column caused extensive decomposition

Table III. Acyl–Rhodium Complexes ($RhCl_2RCO(Ph_3P)_2$)

R	Mp, °C	Yield,[a] %	Mol wt[b] Calcd	Mol wt[b] Found	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % P	Found, % C	Found, % H	Found, % Cl	Found, % P
$CH_3(CH_2)_4$	173–176	84	797	724	63.16	5.14	8.91	7.78	63.21	5.15	9.03	7.74
$CH_3(CH_2)_5$	165–166	80	811	806	63.60	5.31	8.75	7.52	63.30	5.22	9.37	7.1
$CH_3(CH_2)_{14}$	135–137	100	937	904	66.59	6.51	7.58	6.61	66.37	6.58	7.63	6.87
$CH_3(CH_2)_{16}$	120–126	96	965	942	67.20	6.73	7.36	6.43	66.39	6.50	8.27	6.1
$C_6H_5CH_2CH_2$	176–179	85	...	...	64.98	4.78	8.54	7.46	63.78	4.69	9.95	7.34
c-C_8H_{15}	179–182	88			63.90	5.25	8.79	...	64.40	5.08	8.42	...

[a] Yields based on the complex A. [b] Determined by a Mechrolab vapor pressure osmometer.

of the complexes. Usually long-chain acyl halides such as palmitoyl chloride form stable complexes.

The five-coordinate structure of the complexes is supported by elemental analyses and molecular weight determination as shown in Table III. Further confirmation of the structure was furnished by nmr spectra. As shown in Figure 1, the spectrum of dichloropalmitoylbis(triphenylphosphine)rhodium is consistent with the proposed structure, rather than with a possibility that one of the β-hydrogen atoms of the methylene group coordinates with the rhodium atom to form a six-coordinate hydride complex.[14] The spectrum of a β-phenylpropionyl complex showed absorption bands of all aliphatic protons at τ 6.84 (triplet, two protons due to $-CH_2CO-$) and 7.37 (triplet, two protons due to $C_6H_5CH_2-$); hence, no interaction with the rhodium atom is involved. The careful examination of the nmr spectra at higher field (up to τ 50) does not show any recognizable band characteristic of a proton coordinated to the metal. A strong infrared absorption band at 1715 cm^{-1} can be assigned to the acyl group. Thus the acetyl group in $[RhBr_2(COCH_3)(CO)(Et_2PhP)_2]$ absorbs at 1667 cm^{-1}.[15] Although our acyl complexes have somewhat higher absorption, they are still in a reasonable range. The stereochemistry of the complex B was not investigated.

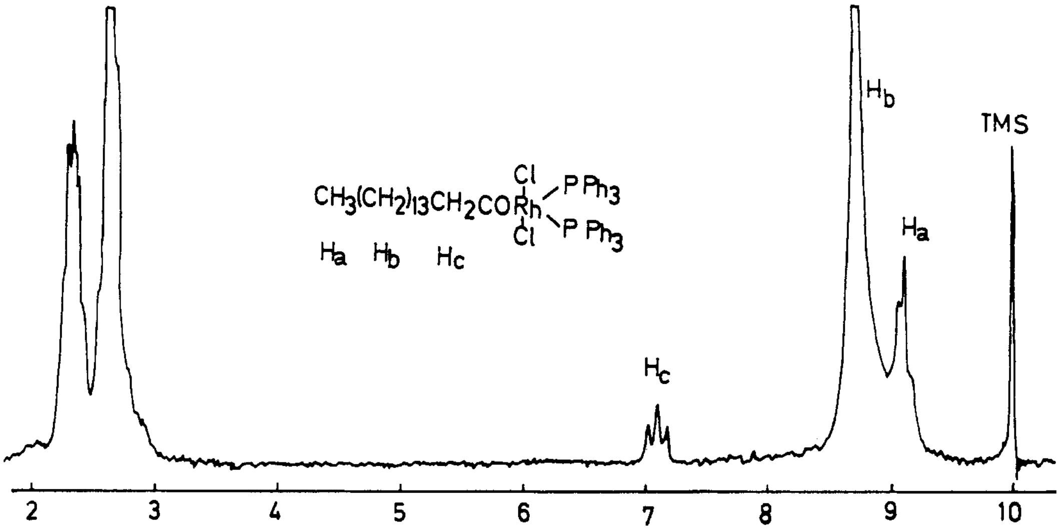


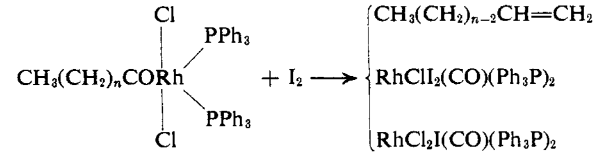
Figure 1. Nmr spectrum of dichloropalmitoylbis(triphenylphosphine)rhodium (100 Mc, in $CDCl_3$).

That the acyl complexes are intermediates in the decarbonylation was shown when dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium (E, R = $C_6H_5CH_2CH_2-$) was heated to 170° under reduced pressure (100 mm) to give the complex B and styrene.

$$\underset{E}{C_6H_5CH_2CH_2CORhCl_2(Ph_3P)_2} \longrightarrow \underset{77\%}{C_6H_5CH{=}CH_2} + \underset{99\%}{RhCl(CO)(Ph_3P)_2} + HCl$$

From dichloropalmitoylbis(triphenylphosphine)rhodium, *trans*-2-pentadecene was formed as a main product. The olefins obtained by heating the acyl complexes are a mixture of inner olefins formed by the isomerization of a 1-olefin produced initially by the β-hydrogen abstraction.

When a chloroform–ether solution of the complex was treated with an equivalent amount of iodine at room temperature in an attempt to prepare acyl iodide, the acyl complex was converted into an olefin and an iodine-containing complex, the structure of which was not well characterized. The complex has a sharp absorption at 2050 cm^{-1} due to an octahedral carbonyl complex, and analytical data indicate that the complex is a mixture of $RhClI_2(CO)(Ph_3P)_2$ and $RhCl_2I(CO)(Ph_3P)_2$. The olefin is a 1-olefin free of inner olefins and thus this procedure is useful for the conversion of long-chain acyl halides into 1-olefins with one less carbon atom. However, the acyl halides may be ob-



$$CH_3(CH_2)_nCORhCl_2(PPh_3)_2 + I_2 \longrightarrow \begin{cases} CH_3(CH_2)_{n-2}CH{=}CH_2 \\ RhClI_2(CO)(Ph_3P)_2 \\ RhCl_2I(CO)(Ph_3P)_2 \end{cases}$$

---

(14) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

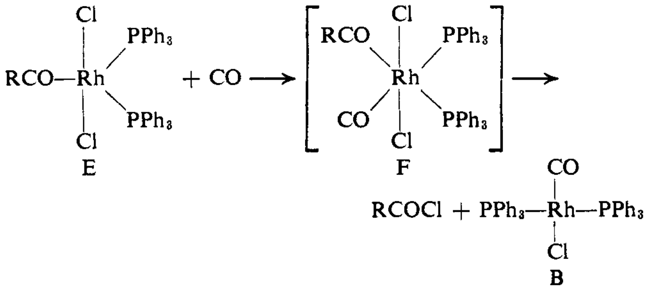
(15) J. Chatt and B. L. Shaw, *ibid., Sect. A*, 1437 (1966).

Table IV. Catalytic Decarbonylation of Acid Halides Using $RhCl(CO)(Ph_3P)_2$

Acid halide	Amt, g	Catalyst, g	Reaction Temp, °C	Reaction Time, hr	Product (% compn)	Yield,[b] %
Palmitoyl chloride	8	0.1	230	0.5	Pentadecene	54
Phenylacetyl chloride	8	0.1	200–220	2	Benzyl chloride	60
Heptanoyl bromide	4	0.1	200	0.5	1-Hexene (61), 2-, 3-hexene (39)	85
Octanoyl chloride	8	0.1	190–200	1	Heptenes	91
Octanoyl bromide	8	0.1	200	1	1-Heptene (71), *trans*-2-heptene (24), *cis*-2-heptene (5)	90
Sebacoyl chloride	35	0.3	210–220	3.5	1,7-Octadiene (25), 1,6-octadiene (34), 1,5-octadiene (13), other octadienes (28)	85
Benzoyl chloride	8	0.2	200	4	Chlorobenzene	85
Benzoyl bromide	8	0.2	220	1.5	Bromobenzene	87
p-Toluoyl chloride	8	0.25	230	8.5	*p*-Chlorotoluene	66
p-Toluoyl bromide	30	0.6	250	11	*p*-Bromotoluene	43
p-Toluoyl bromide	20	0.4[a]	250	13	*p*-Bromotoluene	29
p-Methoxybenzoyl chloride	5	0.27	240–250	12	*p*-Chloroanisole	46
3,4-Dichlorobenzoyl chloride	10	0.3	250	1.5	1,2,4-Trichlorobenzene	96
Isophthaloyl chloride	5	0.2	240–250	4	*m*-Dichlorobenzene (75), *m*-chlorobenzoyl chloride (25)	92
1-Naphthoyl chloride	5	0.2	240	2.5	1-Chloronaphthalene	77

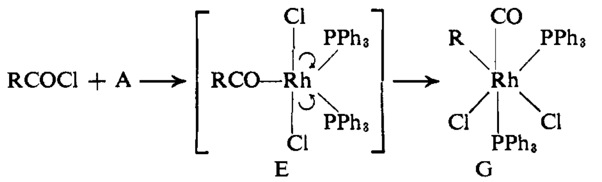
[a] $RhCl(CO)[(p\text{-}CH_3OC_6H_4)_3P]_2$. [b] Yields based on the acyl halides.

tained by treating the acyl complexes with carbon monoxide. Although the reaction of carbon monoxide at room temperature and atmospheric pressure with the complex E caused no appreciable change, under pressure (50 atm) at room temperature, dichloropalmitoylbis(triphenylphosphine)rhodium was converted into palmitoyl chloride and the complex B. The reaction can be explained by



The isolation of a complex F was attempted without success.

The acyl complexes E are most easily formed from acyl halides of a rather long carbon chain. Some acyl halides, however, behaved differently toward the complex A. For example, benzoyl chloride and acetyl chloride formed six-coordinate phenyl and methyl complexes (G), instead of stopping at the stage of the acyl complex formation. The same reaction was reported by Wilkinson, *et al.*[16]



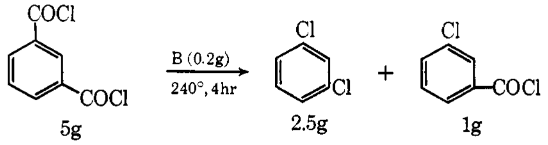
R = CH_3–, C_6H_5–

Catalytic Decarbonylation of Acyl Halides and Aldehydes. The complex B was found to be extremely efficient for the catalytic decarbonylation of acyl halides at 200° under homogeneous conditions, in contrast to the complex A which must be used in stoichiometric quantities at a lower temperature. Complex B is stable during the progress of the decarbonylation and the reaction system remains completely homogeneous, while evolution of carbon monoxide, hydrogen halide, and olefin proceeds smoothly. The results of the catalytic decarbonylation of acyl halides are shown in Table IV.

Benzoyl chloride and bromide were decarbonylated smoothly to give chlorobenzene and bromobenzene by heating at 200° in the presence of a catalytic amount of the complex B. The reaction proceeds so smoothly that when we try to distil benzoyl chloride slowly from a Claisen distilling flask by adding a catalytic amount of the complex B, we obtain chlorobenzene rather than benzoyl chloride as distillate.

$$C_6H_5COX \longrightarrow C_6H_5X + CO$$

The rate of the decarbonylation of aromatic acid halides varies with kinds of substituted groups on aromatic rings. Although no exact kinetic studies have been carried out, it can be said that an electron-donating group tends to decrease the rate of decarbonylation. For example, the decarbonylation of *p*-methoxybenzoyl chloride proceeded more slowly than that of benzoyl chloride under similar conditions, and the yield of *p*-chloroanisole was lower as shown in the table. On the other hand, the decarbonylation proceeds smoothly with an electron-withdrawing group on a benzene ring. Thus, isophthaloyl chloride was decarbonylated smoothly at 240–250° to give *m*-dichlorobenzene (yield, 69%) and *m*-chlorobenzoyl chloride (yield, 23%) in 4 hr.



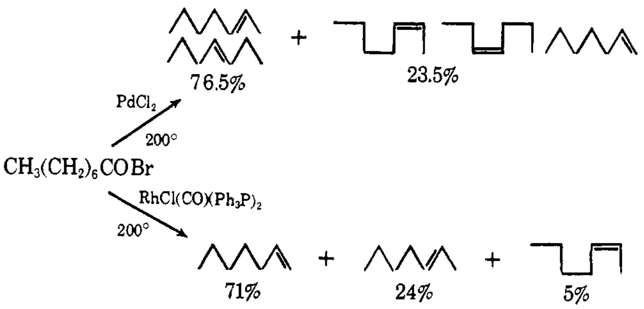
Although the palladium-catalyzed reaction gives a mixture of isomeric inner olefins, the double bond migration caused by the complex B is somewhat slower, though not completely negligible. When long-chain acyl halides are decarbonylated and olefins are dis-

---

(16) M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

tilled off as soon as they are formed, it is possible to isolate 1-olefins as main products rather than inner olefins. The decarbonylation of octanoyl bromide given in Scheme I shows results of the comparative studies using metallic palladium and the complex B.

Scheme I



The decarbonylation of chlorides of several aliphatic dicarboxylic acids was attempted. 3-(Methoxycarbonyl)propionyl chloride was converted into succinic anhydride under the reaction conditions, instead of giving expected acrylate. Dichlorides of adipic and suberic acid yielded only resinous material. On the other hand, a smooth decarbonylation of sebacoyl chloride was observed to give an octadiene mixture.

In addition to the complex B, the catalytic activity of chlorocarbonylbis(tri(*p*-methoxyphenyl)phosphine)-rhodium was tested and no difference in the catalytic activity was observed between these two complexes.

Of course the catalytic decarbonylation at high temperature can be carried out by using the complex A, which is easily converted *in situ* into the complex B by the stoichiometric reaction with the acid halides. When the present studies have been completed, Blum reported that the catalytic decarbonylation of aromatic acid halides is possible by using the complex A at 200°.[17]

The catalytic decarbonylation of aldehydes at 200° with the complex B proceeds smoothly and is especially effective with aromatic aldehydes. Some side reactions such as aldol condensation occurred when aliphatic aldehydes were decarbonylated. Some results are shown in Table V. In Table VI, the results of the catalytic decarbonylation of cinnamaldehyde derivatives by using the rhodium complex and palladium are shown. It is apparent that the rhodium catalyst gave higher ratio of the *cis*-styrene than palladium catalyst. Also the rhodium catalyst produced no saturated compound.

Table V. Decarbonylation of Aldehydes Using $RhCl(CO)(Ph_3P)_2$

Aldehyde	Amt, g	Catalyst, g	Reaction Temp, °C	Reaction Time, hr	Product	Yield,[a] %
p-Chlorobenzaldehyde	8	0.2	220	9	Chlorobenzene	71
Salicylaldehyde	5	0.1	210	8.5	Phenol	80
Cinnamaldehyde	8	0.1	230	4	Styrene	76

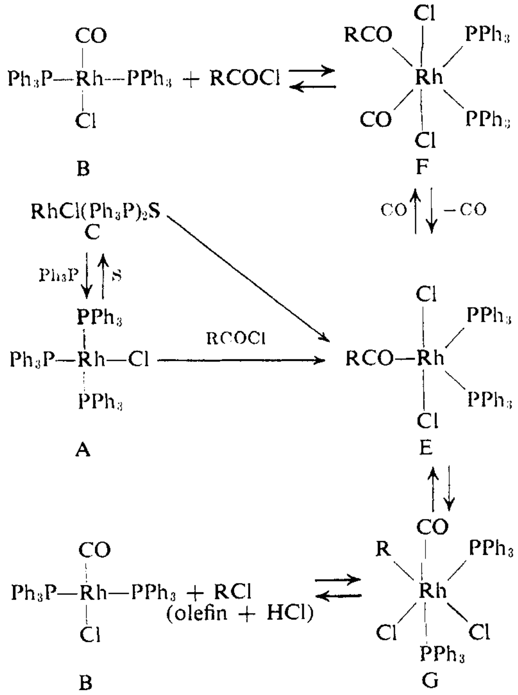
[a] Yield based on the aldehydes.

Catalytic Carbonylation of Halides with the Complex B. Based on the assumption of the reversibility of the decarbonylation, the carbonylation of allyl halides and benzyl halides in the presence of a catalytic amount of the complex B under carbon monoxide pressure was attempted. As shown below, benzyl halide was carbonylated in benzene to give phenylacetyl halides in a moderate yield.

$$C_6H_5CH_2X + CO \xrightarrow{B} C_6H_5CH_2COX$$

Mechanism of the Decarbonylation and Carbonylation. The first step of the reaction of the complex A with acyl halides is the oxidative addition to give the five-coordinate complex (E), which was isolated as a crystalline compound (Scheme II). When heated in the absence of carbon monoxide, the acyl complex (E) is converted into a six-coordinate alkylcarbonyl complex (G) by the acyl–alkyl rearrangement. Actually, when acetyl chloride and benzoyl chloride were treated with the complex A, the alkylcarbonyl complex (G, R = CH_3–, C_6H_5–) was isolated. Finally the alkylcarbonyl complex (G) is converted into olefin and the complex B by abstracting hydrogen at the β position. When there is no hydrogen at the β position, alkyl or aryl halides are formed. This is the reaction path of the decarbonylation of acyl halides using the complex A. The first step of the reaction, namely, the oxidative addition to form the complex E, is not reversible and decarbonylation by this complex is stoichiometric.

Scheme II

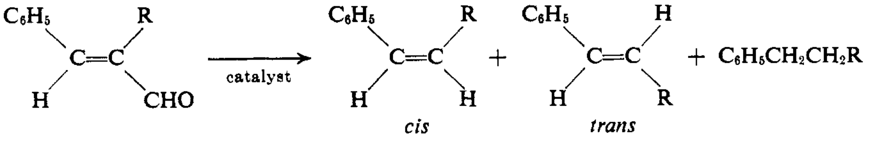


The catalytic decarbonylation using the complex B proceeds through the formation of an acyl complex (F) by the oxidative addition as the first step. When heated in the absence of carbon monoxide, 1 mole of carbon monoxide is lost to form the five-coordinate acyl complex (E). Then G is formed from E. Finally olefins or alkyl (aryl) halides are formed with the regeneration of the complex B. The reaction path (E → G → B + RX) was confirmed with aliphatic acid halides and some aromatic acid halides. However, a different type of decomposition of the complex G was observed with some aromatic acid halides. For example, the

---

(17) J. Blum, *Tetrahedron Letters*, 1605 (1966).

Table VI. Decarbonylation of Substituted Cinnamaldehydes



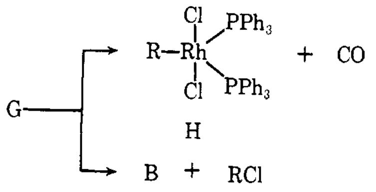
R	Amt, g	Catalyst	Amt, g	Reaction Temp, °C	Reaction Time, hr	Conversion, %	Yield, %	Product distribution, % cis	Product distribution, % trans	Product distribution, % A
CH_3	10	$PdCl_2$	0.2	250–260	4.5	80	78[a]	67	33	0
CH_3	10	$RhCl(CO)(Ph_3P)_2$	0.1	250–260	7	67	77[a]	88	12	0
CH_3	10	$RhCl(CO)[(p\text{-}CH_3OC_6H_4)_3P]_2$	0.25	250–260	4	87	87[a]	90	10	0
CH_3CH_2	10	$PdCl_2$	0.2	250–260	9	..	76[b]	38.5	49.3	12.2
CH_3CH_2	10	$RhCl(CO)(Ph_3P)_2$	0.3	250–260	3	91	87[a]	80	20	Trace

[a] Yield based on the converted aldehydes. [b] Yield based on the charged aldehyde.

complex G, derived from *p*-toluoyl chloride (infrared, 2080 and 800 cm^{-1}) was heated at 180° for 10 min without solvent, a new complex H was isolated, together with a small amount of the complex B. The complex H showed an absorption at 800 cm^{-1} due to the tolyl group and no carbonyl band. The complex was formed by the liberation of carbon monoxide. Therefore, the reaction cycle

$$(E \longrightarrow G \longrightarrow H \longrightarrow C + RX \xrightarrow{RCOX} E)$$

might be possible for some aromatic acid halides.



R = p-$CH_3C_6H_4$–

The carbonylation reaction of alkyl halides using the complex B can be expressed exactly by the reverse process of the decarbonylation and starts with the oxidative addition of alkyl halides to the complex B to form G. The complex B is regenerated at the end of the carbonylation. As related reactions, Chatt and Shaw reported the formation of $RhCl_2(CO)(COCH_3)(Et_2PhP)_2$ by the oxidative addition of acetyl chloride to $RhCl(CO)(Et_2PhP)_2$. This reaction corresponds to ($B + RCOCl \rightarrow F$) in the above mechanism. Also, Heck reported the addition of methyl iodide to $RhCl(CO)(R_3P)_2$ to form a six-coordinate alkyl complex, which, in turn, is converted into an acetyl complex by carbon monoxide insertion.[18] These reactions correspond to ($B + RCl \rightarrow G \rightarrow F$) in the mechanism proposed above.

The decarbonylation of aldehydes can be explained in the same way. Instead of acyl halides, aldehydes undergo the oxidative addition and the whole process can be expressed by replacing the chlorine atom with hydrogen in the mechanism shown for acyl halides. However, the oxidative addition of aldehydes is not known and the isolation of an acyl complex by the reaction of the complex A with aldehydes was attempted without success. The acyl hydride complex, supposedly formed by the oxidative addition of aldehydes, is not stable and decarbonylation proceeds very easily. The stereochemistry of the intermediate complexes postulated in this mechanism was not considered.

Finally it should be noted that the mechanisms of palladium catalyzed and rhodium complex catalyzed decarbonylation reactions are quite similar. The only difference is that rhodium forms definite complexes with stabilizing ligands, while palladium has no such well-characterized ligands.

Experimental Section

Materials. Commercially available rhodium trichloride trihydrate was used without further purification. Most of the aldehydes used in the decarbonylation reaction were commercial products and they were purified by distillation right before use. 9,10-Dihydro-9,10-ethanoanthracene-11-carboxaldehyde[19] and 1-methyl-3-cyclohexene-1-carboxaldehyde[20] were prepared by the Diels–Alder reaction by following the given procedure. α-Substituted cinnamaldehydes were prepared by the method of Kraft[21] and the products were found to be homogeneous by gas chromatography. The *trans* structure of these aldehydes was confirmed by the method of Hoffman.[22] Acyl halides were prepared from the corresponding acids by the reaction with thionyl chloride. Acyl bromides were prepared by the action of hydrogen bromide on the corresponding chlorides.

Preparation of the Complex A. Di-μ-chlorobis(1,5-cyclooctadienyl)dirhodium (0.971 g) was dissolved in 2 ml of dry benzene and triphenylphosphine (3.2 g), dissolved in 10 ml of benzene, was added. The solution was left to stand for 15 hr, during which time the yellow solution turned dark red. Most of the benzene was removed under vacuum and 40 ml of ethanol was added. Precipitated orange crystals were collected (yield, 1.8 g). The crystals began to melt partially at 100° and finally decomposed at 130–135°. The complex A can be prepared more conveniently by the method given by Wilkinson and by Bennett.

Decarbonylation of Aldehydes Using the Complex A. Only typical examples are shown.

A. Decarbonylation of Benzaldehyde. The complex A (1.848 g), benzaldehyde (1.3 g), toluene (5 ml), and ethylbenzene (0.262 g, for gas chromatographic determination of benzene formed by the decarbonylation) were mixed in a 25-ml round-bottom flask and the solution was refluxed for 1 hr. The dark red solution turned yellow and yellow crystals of the complex B deposited on the bottom of the flask. Gas chromatographic analysis of the solution showed the formation of benzene (0.1294 g, 83% based on the complex A). Most of the solvent was removed under reduced pressure and 15 ml of ethanol was added to ensure the precipitation of the complex B, 1.27 g of the complex being collected by filtration.

---

(18) R. F. Heck, *J. Am. Chem. Soc.*, **86**, 2796 (1964).

(19) P. F. Weiss and R. Rusch, *Bull. Soc. Chim. France*, 550 (1963).

(20) H. Pines, F. J. Pavlik, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **73**, 5740 (1951).

(21) W. M. Kraft, *ibid.*, **70**, 3569 (1948).

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

B. 9,10-Dihydro-9,10-ethanoanthracene-11-carboxaldehyde. The complex A (2.49 g, 0.0027 mole) and the aldehyde (1.4 g, 0.006 mole) were dissolved in 20 ml of benzonitrile in the flask. The solution was heated in an oil bath kept at 165° for 3 min, during which time the dark red solution turned yellow. Most of the solvent was removed under reduced pressure (100°, 3 mm) and 10 ml of ethanol was added. The precipitated yellow crystals were collected by filtration and 1.8 g (*ca.* 100%) of the complex B was obtained. The ethanolic solution was concentrated and the residue was dissolved in chloroform and passed through an alumina column. The first fraction (0.37 g, 67%) was identified as 9,10-dihydro-9,10-ethanoanthracene by analysis and nmr and infrared spectra, mp 142–143° (lit.[23] 142°). *Anal.* Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.97; H, 6.79.

C. Decarbonylation of Heptanal. A mixture of heptanal (0.5 g) and the complex A (0.462 g) in 10 ml of dichloromethane was left to stand at room temperature for 1 day, during which time the dark red solution turned yellow. Gas chromatographic analyses (PEG 1000 column at 45° and phenylacetonitrile–silver nitrate column at 50°) showed that the product consisted of hexane (86%) and 1-hexene (14%). Total yield was 78% based on the complex A. The complex B was obtained in 95% yield.

Preparation of the Acyl–Rhodium Complexes (E). The acyl complexes were prepared by the following two methods: A, a slight excess of acyl halides was dissolved in dry benzene with the complex A and the solution was refluxed for 10–30 min; B, a large excess of acyl halides was dissolved in dichloromethane with the complex A and the solution was left for 1–2 days at room temperature. Crude crystals were dissolved in benzene and precipitated by the addition of ethanol to give pure crystals. Some examples are shown below.

A. Dichloropalmitoylbis(triphenylphosphine)rhodium. The complex A (9.24 g, 0.01 mole) was dissolved in 30 ml of dry benzene and 3.025 g (0.011 mole) of freshly distilled palmitoyl chloride was added. The system was swept with nitrogen. The solution was refluxed for 20 min. The dark red solution turned instantly orange. Benzene was removed under reduced pressure. When 30 ml of hexane was added, yellow precipitate appeared, which was collected by filtration to give 9.2 g (99%) of the acyl complex. The crude complex was dissolved in benzene and reprecipitated by careful addition of ethanol to give platelike crystals. The same purification procedure was repeated twice. The analyses are shown in the table.

B. Dichlorohexanoylbis(triphenylphosphine)rhodium. The complex A (1.85 g) was dissolved in 10 ml of dichloromethane in a flask which was swept with nitrogen. Then 1.3 g of hexanoyl chloride was added. Ten minutes after the addition of the acyl chloride, the solution turned orange. The solution was left for 1 day. Dichloromethane was removed by distillation and *n*-hexane (30 ml) was added to give yellowish brown crystals (1.54 g, 84%). The crystals were purified as described above: nmr spectrum, τ 9.25 (triplet, CH_3–), 8.5–9.1 (multiplet, $(CH_2)_4$), 7.07 (triplet, two protons, –CH_2CO–), 2.30 (12 ring protons (*ortho*)), 2.58 (18 ring protons (*meta* and *para*)).

C. Dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium. The complex A (1 g) was dissolved in a mixture of dichloromethane (10 ml) and benzene (10 ml) in a flask, which was swept with nitrogen. Freshly distilled 3-phenylpropionyl chloride (1 g, a large excess) was added. The solution was left to stand at room temperature for 12 hr. The solution was concentrated under reduced pressure to about 5 ml and 20 ml of *n*-hexane was added to give yellowish brown crystals (0.765 g, 85%). The crystals were purified by reprecipitation, but analytically pure sample was not obtained and analysis showed higher halogen content. An infrared spectrum showed an absorption band at 1715 cm^{-1} due to the rhodium carbonyl: nmr spectrum, τ 7.34 (triplet, 2 protons due to –$CH_2C_6H_5$), 6.85 (triplet, 2 protons due to –CH_2CO–), 2.88 (5 ring protons), 2.58 (18 ring protons of *meta* and *para* positions of the phosphines), 2.32 (12 ring protons of *ortho* positions of the phosphines).

Reaction of the Acyl–Rhodium Complex with Carbon Monoxide. Dichloropalmitolylbis(triphenylphosphine)rhodium (1.83 g) was dissolved in 10 ml of benzene in a glass vessel equipped with a gas inlet capillary. The vessel was placed in an autoclave and carbon monoxide (50 atm) was introduced. The reaction was carried out at room temperature for 3 hr. After the reaction, yellow crystals precipitated on the bottom of the vessel. An infrared spectrum of the benzene solution showed the formation of acyl halide (1800 cm^{-1}). The acyl halide was converted into the corresponding ester by the addition of ethanol. The solvent was removed under reduced pressure and *n*-hexane (10 ml) was added to ensure the precipitation of yellow crystals, which were collected by filtration (0.735 g, 92%). The crystals were identified as the complex B by melting point (190–195°) and infrared spectrum. The hexane solution was concentrated and the residue was subjected to chromatography (silica gel–hexane) to give 0.23 g (69%) of liquid. The liquid was identified as ethyl palmitate by analysis, molecular weight, and infrared spectrum (1735 cm^{-1}). *Anal.* Calcd for $C_{18}H_{38}O_2$: C, 76.0; H, 12.65; mol wt, 284. Found: C, 75.79; H, 12.61; mol wt, 284.

Reaction of the Acyl Complex with Iodine. Dichlorostearoylbis(triphenylphosphine)rhodium (1.930 g, 0.002 mole) was dissolved in 10 ml of chloroform. An ethereal solution of iodine (0.5588 g, 0.0022 mole in 20 ml) was added dropwise in 20 min. The solution was stirred for 7 hr at room temperature. Gradual precipitation of chocolate brown crystals was observed. After standing overnight at room temperature, the precipitation of the crystals was complete and the solution became yellowish brown. The crystals were collected by filtration (1.325 g). They are slightly soluble in chloroform and dichloromethane and insoluble in benzene, ethanol, ether, and ethyl acetate. Its infrared spectrum showed a strong band at 2050 cm^{-1}. The filtrate was concentrated and the residue was subjected to chromatography (silicic acid, hexane) to give 0.19 g (40%) of liquid, which was identified as 1-heptadecene by the following data: infrared spectrum, 1645, 990, 910 cm^{-1}; nmr spectrum showed the presence of a terminal olefin. *Anal.* Calcd for $C_{17}H_{34}$: C, 85.63; H, 14.37; mol wt, 238; Found: C, 85.45; H, 14.21; mol wt, 238.

Dichloropalmitoylbis(triphenylphosphine)rhodium (4.685 g) was treated with iodine (1.27 g) in a manner described above and 0.686 g (60%) of 1-pentadecene was isolated by column chromatography: infrared spectrum, 1630, 990, 906 cm^{-1}. *Anal.* Calcd for $C_{15}H_{30}$: C, 85.71; H, 14.28; mol wt, 210; Found: C, 85.98; H, 14.31; mol wt, 210.

Thermal Decomposition of the Acyl Complex. A. Dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium (1.918 g, 0.00230 mole) was placed in a 10-ml Claisen distilling flask and the system was evacuated to 100 mm. The flask was heated in an oil bath kept at 170°. The yellowish brown complex turned gradually yellow and liquid distilled off slowly. The liquid was collected (0.15 g) and identified as styrene by gas chromatography and infrared spectrum. Yellow residue in the flask was collected and dissolved in chloroform. Precipitation by the addition of ethanol gave 1.23 g (77%) of the complex B.

B. Dichloropalmitoylbis(triphenylphosphine)rhodium (2 g) was decomposed as described above under reduced pressure (2 mm). After 15 min, 0.377 g of liquid was collected. The liquid gave three peaks by gas chromatography, which were separated by preparative gas chromatography. The main component (80%) was identified as *trans*-2-pentadecene by infrared spectrum (960 cm^{-1}, *trans* olefin) and ozonization to give acetaldehyde. From the residue in the flask, 1.31 g of the complex B was obtained.

Catalytic Decarbonylation of Acyl Halides with the Complex B. A. **Octanoyl bromide** (8 g) and the complex B (0.1 g) were placed in a 25-ml Claisen flask and the flask was heated in an oil bath at 200°. Soon evolution of carbon monoxide and hydrogen bromide began and heptene began to distil off after about 20 min. After 1 hr, the distillation of heptene stopped and almost no residue was left in the flask, 3.7 g (92%) of heptene being collected. Isomer distribution was determined by gas chromatography (squalane and phenylacetonitrile–silver nitrate column). The mixture consists of 1-heptene (71%), *trans*-2-heptene (24%), and *cis*-2-heptene (5%).

B. **3,4-Dichlorobenzoyl chloride** (10 g) and the complex B (0.3 g) were placed in the distilling flask and heated at 250° under nitrogen for 1.5 hr, during which time 8 g (96%) of liquid was collected by distillation. The distillate was identified as 1,3,4-trichlorobenzene by infrared and nmr spectra and analysis.

C. **1-Naphthoyl chloride** (5 g) and 0.2 g of the complex B were heated in the flask for 2.5 hr at 240°. After the evolution of gas stopped, the residue was distilled under reduced pressure, bp 137–138° (30 mm), to give 3.28 g (77%) of liquid product, which was identified as 1-chloronaphthalene by infrared spectrum, molecular weight determination, and analysis. *Anal.* Calcd for $C_{10}H_7Cl$: C, 73.9; H, 4.30; Cl, 21.85; mol wt, 162.5. Found: C, 73.76; H, 4.39; Cl, 21.60; mol wt, 159.

---

(23) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74,** 2193 (1952).

D. Sebacoyl chloride (35 g) and the complex B (0.3 g) were placed in a 100-ml Claisen flask and heated at 210°. Soon evolution of carbon monoxide and hydrogen chloride was observed. Diolefins formed were distilled off as soon as possible and, after 3.5 hr, 17 g of liquid was collected. Redistillation of the liquid product afforded 14.1 g of colorless liquid (bp 119–125°). Part of the liquid product was hydrogenated with palladium on carbon with uptake of 2 moles of hydrogen. The reduced product was found to be homogeneous by gas chromatography and identified as *n*-octane by infrared spectrum, molecular weight determination by mass spectroscopy (114, C_8H_{18}), and gas chromatography. The liquid product was subjected to preparative gas chromatography and four fractions were isolated. The first fraction (25.2%) was identified as 1,7-octadiene; infrared spectrum, 990, 910 cm^{-1}; nmr spectrum, τ 8.36 (4 protons due to methylene group), 8.0 (4 allylic protons), 4–5.17 (6 olefinic protons); and analysis. *Anal.* Calcd for C_8H_{14}: C, 87.19; H, 12.81; mol wt, 110. Found: C, 87.04; H, 12.55; mol wt, 110. The second fraction (46.3%) was shown to be a mixture of 1,5- and 1,6-octadienes by the relative intensity of the infrared absorption bands (900, 965, 910, 695 cm^{-1}) and nmr spectrum (τ 9.03, triplet due to CH_3; 8.3–8.8, multiplet due to methyl and methylene protons; 8.0, broad multiplet due to allylic protons; 4.0–5.2, olefinic protons). The nmr spectrum showed no band due to biallylic proton, indicating that no 1,4-octadiene was contained. The third and fourth fractions were found to be a mixture of various inner dienes.

Catalytic Decarbonylation of Aldehydes with the Complex B. A. Salicylaldehyde (5 g) and the complex B (0.1 g) were placed in the 25-ml Claisen distilling flask and the mixture was heated at 210°. After 5 hr, phenol (3.1 g, 80%) was isolated by distillation.

B. ***trans*-α-Methylcinnamaldehyde** (10 g) and chlorocarbonylbis(tris(*p*-methoxyphenyl)phosphine)rhodium (0.25 g) were placed in the flask and the flask was heated at 250–260° for 1.5 hr under nitrogen. β-Methylstyrene was removed by distillation as soon as it was formed. After 4 hr, 7.78 g of liquid product was obtained. Redistillation of the product gave β-methylstyrene [bp 110° (120 mm), yield 6 g (87% based on the consumed aldehyde)] and the starting aldehyde [bp 145° (40 mm), 1.336 g]. β-Methylstyrene showed two peaks in gas chromatogram, which were separated by preparative gas chromatography. These peaks were found to be due to the *cis* (90%) and *trans* (10%) isomers. The infrared spectra of both isomers showed the same absorption bands described in a literature.[24] Also the nmr spectra support the structure shown: *cis*-β-methylstyrene, τ 2.88 (5 ring protons), τ_A 3.64 (1 proton, $C_6H_5CH{=}$), τ_B 4.48 (1 proton, $=CH$), τ_C 8.22 (3 methyl protons); coupling constants, J_{AB} = 11.5 cps, J_{BC} = 7 cps, J_{CA} = 1.5 cps; *trans*-β-methylstyrene, τ 2.92 (5 ring protons), τ 3.9 (2 protons), τ 8.2 (3 protons, doublet).

Carbonylation with the Complex B. Carbonylation of Benzyl Chloride. Benzyl chloride (10 g), complex B (0.2 g), and dry benzene (20 ml) were mixed in a glass vessel equipped with a gas inlet capillary. The vessel was placed in a 200-ml stainless steel autoclave. The reaction was carried out at 180° under pressure (CO, 150 atm) for 20 hr. After the reaction, the solution was yellow and homogeneous. The infrared spectrum of the solution showed the presence of acyl halide (1800 cm^{-1} strong) and complex B (1980 cm^{-1}, weak). Ethanol (10 ml) was added to the solution to convert the acyl halide into the corresponding ester. By distillation 2 g of ethyl phenylacetate was obtained. Ethyl phenylacetate was identified by infrared spectrum (1735 cm^{-1}) and nmr spectrum (τ 8.88, triplet, and 6.02, quartet; ethyl group: τ 6.58, $-CH_2-$; τ 2.88, ring protons).

Carbonylation of Allyl Bromide. Allyl bromide (5 g) in benzene (20 ml) was carbonylated with 1 g of bromocarbonylbis(triphenylphosphine)rhodium for 15 hr at 120–140° under pressure (CO, 100 atm). After the reaction, the catalyst was decomposed. The formation of an acyl bromide was confirmed by infrared spectrum (1770 cm^{-1}) and the acyl bromide was converted into the corresponding ethyl ester. After the usual work-up, 1.41 g of ethyl crotonate was collected by distillation.

---

[24] R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

The Synthesis and Study of Pseudo-Aromatic Compounds. VI. The Synthesis of 6,7-Dihydrocyclohepta[*d,e*]naphthalene and a Conformational Analysis of 1,2-Benzoheptafulvene[1]

Domenick J. Bertelli, J. T. Gerig, and John M. Herbelin[2]

Contribution from the Department of Chemistry, The University of California at Santa Barbara, Santa Barbara, California. *Received February 27, 1967*

Abstract: The synthesis of 6,7-dihydrocyclohepta[*d,e*]naphthalene is described. The analyses of the nmr coupling constants of 1,2-benzoheptafulvene, 2H-benz[*c,d*]azulene, 6,7-dihydrocyclohepta[*d,e*]naphthalene, 2,3-benzotropone, 4,5-benzotropone, and benzotropenium ion are reported. The data lead to the conclusion that 1,2-benzoheptafulvene is rapidly inverting between two nonplanar forms, while 2,3-benzotropone is apparently planar.

In order to describe adequately the π-electronic interactions in seven-membered ring pseudo-aromatic compounds, it is necessary to establish the conformation of the system. Several theoretical treatments of heptafulvene derivatives have been described,[3] but have necessarily relied upon assumed molecular geometries. To help elucidate this problem, we have undertaken a program to describe as accurately as possible the conformational characteristics of heptafulvene systems and herein report a study involving the 1,2-benzoheptafulvene π system. The present data combined with existing data for 2H-benz[*c,d*]azulene[4] should provide a sound basis for a theoretical treatment of the 1,2-benzoheptafulvene system.

We have previously described the synthesis and ultraviolet spectrum of 1,2-benzoheptafulvene[5] which

---

[1] Presented before the Organic Division, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967.

[2] NSF Undergraduate Research Participant, Summer 1966.

[3] N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966); T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan*, **35**, 910 (1962); J. Koutecky, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); A. Julg, *J. Chim. Phys.*, **59**, 759 (1962); E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lauie, M. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. Chim. France*, **18**, 684 (1951).

[4] V. Boekelheide and C. D. Smith, *J. Am. Chem. Soc.*, **88**, 3950 (1966).