

hydroxyethers identified as 1 and 2 in order of their appearance in the gas-liquid chromatogram.

A portion (approximately 100 mg.) of the crude product was dissolved in 5 ml. of acetone and oxidized at 0° with an excess of chromic acid. The reaction mixture was poured into water and extracted with three portions of ether. Evaporation of the solvent and analysis of the oxidized mixture by g.l.c. on a 30-ft. Carbowax column at 225° showed only a trace of 3-*t*-butylcyclohexanone.<sup>27</sup>

The remainder of the crude reaction mixture from the hydroboration of 4-*t*-butylethoxycyclohexene was chromatographed on a 25 × 2.5 cm. Florisil column set with 50% petroleum ether-benzene. Fractions 20 to 73, eluted with 90% benzene-petroleum ether to 20% chloroform-benzene, proved identical with hydroxyether 2 (VII). Recrystallization from petroleum ether gave colorless needles, m.p. 96.8–97.2°. The n.m.r. spectrum of hydroxyether (VII) displayed the following characteristic peaks: *t*-butyl at -51 c.p.s. (from tetramethylsilane); ethyl group as an A<sub>3</sub>XY pattern with  $\delta_{\text{CH}_3}$  -67,  $\delta_{\text{HX}}$  -205, and  $\delta_{\text{HY}}$  -207 c.p.s. with  $J_{\text{HXHY}} \approx 15$  and  $J_{\text{CH}_3\text{CH}_2} = 6.9$  c.p.s.; >CH-OC<sub>2</sub>H<sub>5</sub> at -194 c.p.s. with band half-width of 7.1 c.p.s. and >CHOH at -230 c.p.s. with band half width of 8.2 c.p.s.

*Anal.* Calcd. for C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>: C, 71.95; H, 12.08. Found: C, 72.04; H, 12.18.

Fractions 76 to 89, eluted with 40 to 60% chloroform-benzene, were identical with hydroxyether 1 (VIII). The fractions were combined and molecularly distilled at 70° at 0.20 mm. giving a viscous liquid. The n.m.r. spectrum of hydroxyether 1 displayed the following characteristic peaks: *t*-butyl at -53 c.p.s.; ethyl group as an A<sub>3</sub>XY pattern with  $\delta_{\text{CH}_3}$  at -71 (triplet),  $\delta_{\text{HX}}$  -206, and  $\delta_{\text{HY}}$  -222 c.p.s. with  $J_{\text{CH}_3\text{CH}_2} = 7.1$  and  $J_{\text{HXHY}} = 8.7$  c.p.s.; >CHOC<sub>2</sub>H<sub>5</sub> at -183 c.p.s. with band half-width of 24 c.p.s. and >CHOH at 201 c.p.s. with band half-width of 26 c.p.s.

*Anal.* Calcd. for C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>: C, 71.95; H, 12.08. Found: C, 72.25; H, 12.32.

The relative retention volumes of all components were determined and the yield of products was calculated. These values are listed in Table III, experiment 12.

**Oxidation of Hydroxyether VII.**—To a solution of 110 mg. of hydroxyether 2 in 10 ml. of acetone at 0° was added a slight excess of dichromate in 20% sulfuric acid. The reaction mixture was poured into 50 ml. of water and was extracted with two portions of ether. Evaporation of the solvent, after drying over magnesium sulfate, gave 100 mg. of a liquid (IX) which was purified by molecular distillation at 60–65° at 0.55 mm. The infrared spectrum of the product in carbon tetrachloride displayed very sharp carbonyl absorption at 5.82  $\mu$ . The n.m.r. spectrum displayed characteristic peaks at: *t*-butyl -56 c.p.s.; ethyl group as an A<sub>3</sub>X<sub>2</sub> pattern with  $\delta_{\text{CH}_3}$  -71 and  $\delta_{\text{CH}_2}$  -202 c.p.s. with

(27) The reliability of this method for the determination of 3- vs. 4-*t*-butylcyclohexanols in such mixtures was demonstrated by the oxidation of a mixture of 3- and 4-*t*-butylcyclohexanol of weight ratio 1.09 to a mixture of 3- and 4-*t*-butylcyclohexanone, weight ratio 1.10, as determined by g.l.c.

$J = 7$  c.p.s., and >CHOC<sub>2</sub>H<sub>5</sub> at -206 c.p.s. with band half-width of 6.8 c.p.s.

*Anal.* Calcd. for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>: C, 72.68; H, 11.18. Found: C, 72.98; H, 11.37.

Treatment of 10 mg. of ketoether IX in 2 ml. of 10% sodium ethoxide in ethanol at room temperature for 10 min., followed by recovery of the organic material by ether extraction after dilution with water, produced a ketoether (X) with a retention time identical with that observed for the ketoether derived from hydroxyether VIII.

**Oxidation of Hydroxyether VIII.**—A 130-mg. portion of hydroxyether 1 was oxidized as described above for hydroxyether VII giving 117 mg. of a ketoether X which was purified by sublimation at 50° and 0.5 mm. giving colorless crystals with m.p. 54–56°. The infrared spectrum in carbon tetrachloride displayed carbonyl absorption at 5.78  $\mu$ . The n.m.r. spectrum displayed the following characteristic peaks: *t*-butyl at -44 c.p.s.; ethyl group as an A<sub>3</sub>XY pattern with  $\delta_{\text{CH}_3}$  -54,  $\delta_{\text{HX}}$  -157, and  $\delta_{\text{HY}}$  -179 c.p.s. with  $J_{\text{CH}_3\text{CH}_2} = 6.2$  and  $J_{\text{HXHY}} = 7.2$  c.p.s.; >CH-OC<sub>2</sub>H<sub>5</sub> at -174 c.p.s. with an apparent half-width of 17 c.p.s.

The gas-liquid chromatogram showed the presence of small amounts of two impurities. The analytical sample was purified by preparative gas-liquid chromatography.

*Anal.* Calcd. for C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>: C, 72.68; H, 11.18. Found: C, 72.73; H, 11.20.

**Treatment of the Hydroboration Product of 4-*t*-Butylethoxycyclohexene with Boron Trifluoride Etherate.**—A solution of 0.42 g. (2.30 mmoles) of olefin in 4 ml. of tetrahydrofuran was added to 1 ml. of 1.53 *M* borane in tetrahydrofuran at 0°. The reaction mixture was stirred for 10 min. and 0.42 g. (3 mmoles) of boron trifluoride etherate was added and allowed to stand for 3 min. The mixture was hydrolyzed, oxidized, and worked up as described above. The crude product was analyzed by g.l.c. and the results are presented in Table III, experiment 13.

In a separate experiment, aliquots of the reaction mixture, after addition of the boron trifluoride etherate, were periodically removed, hydrolyzed, oxidized, and the crude product analyzed by g.l.c. The results are presented in Fig. 5.

**Hydroboration of 4-*t*-Butylethoxycyclohexene in the Presence of Boron Trifluoride.**—To a solution of 2.02 g. (0.011 mole) of olefin and 1.57 g. (0.011 mole) of boron trifluoride etherate in 5 ml. of tetrahydrofuran at 0° was added 10 ml. of 0.74 *M* borane in tetrahydrofuran. The reaction mixture was stirred for 10 min., hydrolyzed, oxidized, and the crude product analyzed by g.l.c. The results are presented in Table III, experiment 14.

**Acknowledgment.**—The authors wish to thank Professor E. L. Eliel and his research collaborators for samples of authentic materials used in g.l.c. analysis in the *t*-butylcyclohexyl series. The authors also wish to thank the National Institutes of Health for a predoctoral fellowship to C. C. C. (fellowship number 1-F1-GM-21-333-01).

[CONTRIBUTION FROM THE BASIC RESEARCH LABORATORIES, TOYO RAYON CO., LTD., KAMAKURA, JAPAN]

## Organic Syntheses by Means of Noble Metal Compounds. VIII.<sup>1</sup> Catalytic Carbonylation of Allylic Compounds with Palladium Chloride

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The reaction of allyl chloride and allyl alcohol with carbon monoxide in ethanol to form ethyl 3-butenate by the catalytic action of palladium chloride was studied. Other allylic compounds react in the same way. It was found that in benzene solution allyl acetate forms 3-butenic acetic anhydride, and allyl ether yields 3-butenic anhydride by addition of carbon monoxide to the allylic carbon.

### Introduction

Extensive studies on catalytic carbonylation of allyl chloride with nickel carbonyl and its related reactions have been carried out by Chiusoli.<sup>2</sup> Later,  $\pi$ -allyl-


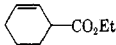
(1) Part VII: J. Tsuji, M. Morikawa, and J. Kiji, *J. Am. Chem. Soc.*, in press.

(2) G. P. Chiusoli, *Chim. Ind. (Milan)*, **41**, 503 (1959).

nickel halide, which is assumed to be an intermediate of the carbonylation of allyl chloride, was synthesized from an allyl halide and nickel carbonyl.<sup>3</sup> Its carbonylation was carried out in methanol, and

(3) E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **16b**, 77 (1961); *Chem. Ber.*, **94**, 2409 (1961).

TABLE I  
 REACTION OF ALLYLIC COMPOUNDS WITH CARBON MONOXIDE

Expt.	Allylic compd., g.	PdCl <sub>2</sub> , g.	Solvent, ml.	Reaction		Products	Yield, %
				Temp., °C.	Time, hr.		
1	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, 5.0	1.0	Ethanol, 50	120	40	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	47
2 <sup>e</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, 3.0	0.6	Ethanol, 15	130	22	CH <sub>3</sub> CH=CHCO <sub>2</sub> Et	5
						CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	9
3	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, 5.0	0.9	THF, 5 g.	80	24	CH <sub>3</sub> CH=CHCO <sub>2</sub> Et	5
			Benzene, 20			(CH <sub>3</sub> ) <sub>2</sub> CHCO <sub>2</sub> Et	13
						CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> Cl	88
4	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, 7.9	1.0 <sup>b</sup>	Ethanol, 50	120	21	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	19
5	CH <sub>2</sub> =CHCH <sub>2</sub> Cl, 15.0	1.8	Benzene, 50	80	20	CH <sub>2</sub> =CHCH <sub>2</sub> COCl	21
						CH <sub>3</sub> CH=CHCOCl	Trace
6	CH <sub>2</sub> =CHCH <sub>2</sub> OH, 10.4	3.5	Ethanol, 50	105	40	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	42
7 <sup>d</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> OH, 23.2	1.8	Benzene, 25	80	68	(CH <sub>2</sub> =CHCH <sub>2</sub> CO) <sub>2</sub> O	19
8	CH <sub>2</sub> =CHCH <sub>2</sub> OH, 50.0	3.5	None	130	22	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	39
						(CH <sub>3</sub> =CHCH <sub>2</sub> ) <sub>2</sub> O	30
9 <sup>c</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> OTs, 10.0	1.0	Ethanol, 20	80	2.5	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	24
						CH <sub>3</sub> CH=CHCO <sub>2</sub> Et	26
10	CH <sub>2</sub> =CHCH <sub>2</sub> OAc, 8.8	1.0	Ethanol, 20	80	2.5	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	80
11 <sup>d</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> OAc, 10.0	1.8	Benzene, 50	100	48	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Ac	ca. 58
12 <sup>c</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> OEt, 10.0	1.0	Ethanol, 20	80	4.5	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	57
						CH <sub>3</sub> CH=CHCO <sub>2</sub> Et	8
13 <sup>c</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> OPh, 13.4	2.0	Ethanol, 20	80	22.5	CH <sub>2</sub> =CHCH <sub>2</sub> CO <sub>2</sub> Et	18
						CH <sub>3</sub> CH=CHCO <sub>2</sub> Et	10
14 <sup>c</sup>	(CH <sub>2</sub> =CHCH <sub>2</sub> ) <sub>2</sub> O, 9.8	1.0	Ethanol, 20	100~105	4.5	CH <sub>2</sub> CHCH <sub>2</sub> CO <sub>2</sub> Et	73
15 <sup>d</sup>	(CH <sub>2</sub> =CHCH <sub>2</sub> ) <sub>2</sub> O, 9.8	1.8	Benzene, 50	80	50	(CH <sub>2</sub> =CHCH <sub>2</sub> CO) <sub>2</sub> O	ca. 19
16	CH <sub>3</sub> CH=CHCH <sub>2</sub> OH, 4.2	3.5	Ethanol, 46	130	20	CH <sub>3</sub> CH=CHCH <sub>2</sub> CO <sub>2</sub> Et	42
17	CH <sub>3</sub> CH=CHCH <sub>2</sub> OAc, 10.0	1.0	Ethanol, 50	100	13	CH <sub>3</sub> CH=CHCH <sub>2</sub> CO <sub>2</sub> Et	64
18 <sup>a</sup>	CH <sub>2</sub> =CHCH(CH <sub>3</sub> )OH, 7.2	1.8	Ethanol, 20	100	14	CH <sub>3</sub> CH=CHCH <sub>2</sub> CO <sub>2</sub> Et	39
19	CH <sub>3</sub> CH=CHCH(CH <sub>3</sub> )OAc, 9.0	1.8	Ethanol, 40	80	17	CH <sub>3</sub> =CHCHCH(CH <sub>3</sub> )CO <sub>2</sub> Et	39
20	 -Br, 8.1	1.8	Ethanol, 50	80	15		30

<sup>a</sup> Initial pressure of carbon monoxide, 100 kg./cm.<sup>2</sup> at room temp. <sup>b</sup> Palladium black. <sup>c</sup> In glass-coated 100-ml. pressure reactor. <sup>d</sup> Initial pressure of carbon monoxide 150 kg./cm.<sup>2</sup> at room temp. <sup>e</sup> In glass vessel.

methyl 3-butenolate was obtained.<sup>4,5</sup> In an effort to elucidate the mechanism of this reaction, the formation of 3-butenoylnickel dicarbonyl bromide as an intermediate of the reaction was spectroscopically confirmed by Heck,<sup>6</sup> and this intermediate was converted to 3-butenoyl bromide. Most recently, allyl 3-butenolate was obtained by catalytic carbonylation of allyl alcohol with tris[tris(*p*-fluorophenyl)phosphine]platinum.<sup>7</sup>

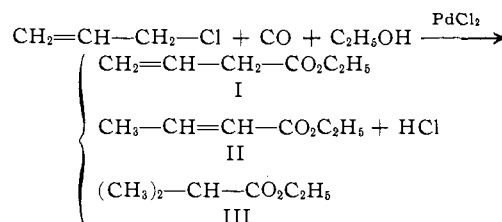
Palladium chloride is known to form several kinds of complexes with olefinic compounds. It was found that an olefin-palladium chloride complex reacts smoothly with carbon monoxide to give  $\beta$ -chloroacyl chloride.<sup>1,8</sup> Furthermore, we have confirmed the formation of 3-butenoyl chloride by the carbonylation of  $\pi$ -allylpalladium chloride in benzene.<sup>9</sup> In addition, it was found that only a catalytic amount of palladium chloride was necessary for the carbonylation of allyl chloride and allyl alcohol in ethanol.

### Results and Discussion

Since  $\pi$ -allylpalladium chloride is formed easily by the reaction of either allyl alcohol<sup>10</sup> or allyl chloride<sup>11</sup> with palladium chloride, carbonylation of allyl chloride and allyl alcohol without prior formation of  $\pi$ -allylpalladium chloride was studied. The reaction

proceeded smoothly. Other allylic compounds were also carbonylated in the same way. Results of the carbonylation of various allylic compounds are given in Table I.

**Carbonylation of Allyl Chloride.**—Ethyl 3-butenolate (I) was a main product in the carbonylation of allyl chloride in ethanol, but at the same time the formation of ethyl 2-butenolate (II) and ethyl isobutyrate (III) was confirmed. The reaction can be illustrated by the scheme



The amounts of these by-products varied with the reaction conditions; the reaction temperature and the concentration of hydrogen chloride generated during the reaction seem to be important factors; II was undoubtedly formed by double bond isomerization from I. Although there is no direct evidence, seemingly III was formed from propene produced by hydrogenolysis of allyl chloride by the reducing action of the palladium-ethyl alcohol system.<sup>12</sup> The formation of ethyl isobutyrate by carbonylation of propene in ethanol by the catalytic action of palladium chloride and hydrogen chloride is known.<sup>13</sup>

(12) B. B. Corson, "Catalysis," Vol. III, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p. 96.

(13) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Letters*, No. 22, 1437 (1963).

(4) E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **17b**, 484 (1962).

(5) G. P. Chiusoli and S. Merzoni, *ibid.*, **17b**, 850 (1962).

(6) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 2013 (1963).

(7) G. W. Parshall, *Z. Naturforsch.*, **18b**, 772 (1963).

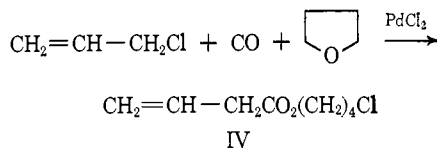
(8) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Letters*, No. 16, 1061 (1963).

(9) J. Tsuji, J. Kiji, and M. Morikawa, *ibid.*, No. 26, 1811 (1963).

(10) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

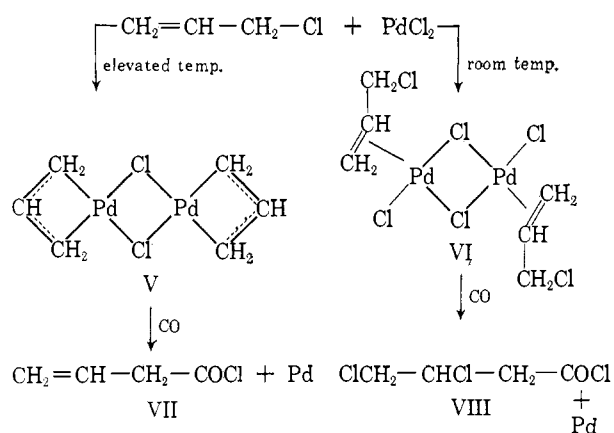
(11) R. Hüttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

The formation of these by-products was suppressed by carrying out the reaction in a mixed solvent of benzene and THF, instead of in alcohol. In this reaction, 3-butenoyl chloride, initially formed, reacted with THF giving 4-chloro-1-butyl 3-butenate (IV).



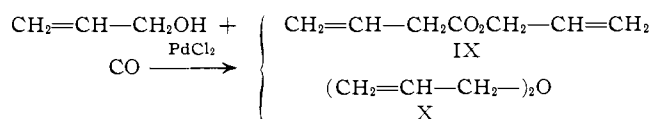
In this way, since 3-butenoyl chloride reacts with THF to give the chloroester without generating hydrogen chloride, the formation of by-products was completely suppressed.

As reported before, 3-butenoyl chloride was the product of the carbonylation of  $\pi$ -allylpalladium chloride in benzene. When allyl chloride in benzene was treated with carbon monoxide in the presence of palladium chloride, the same product was formed. Interestingly, the carbonylation of allyl chloride in benzene at room temperature and at an elevated temperature proceeds differently. While the reaction of allyl chloride in benzene with carbon monoxide at an elevated temperature leads to 3-butenoyl chloride (VII), the reaction at room temperature gives 3,4-dichlorobutanoyl chloride (VIII).<sup>1,5</sup> In the former, only a catalytic amount of palladium chloride is necessary, while in the latter, an equimolecular amount of palladium chloride is consumed. The difference of reactions can be explained in the following way. The structures of the intermediate palladium chloride complexes are different. At room temperature, allyl chloride reacts as a simple olefin, not as an allylic compound, forming an olefin-palladium chloride complex (VI), which is converted to VIII. The formation of  $\beta$ -chloroacyl chlorides by carbonylation of simple olefins with palladium chloride is a general reaction.<sup>1,8</sup>



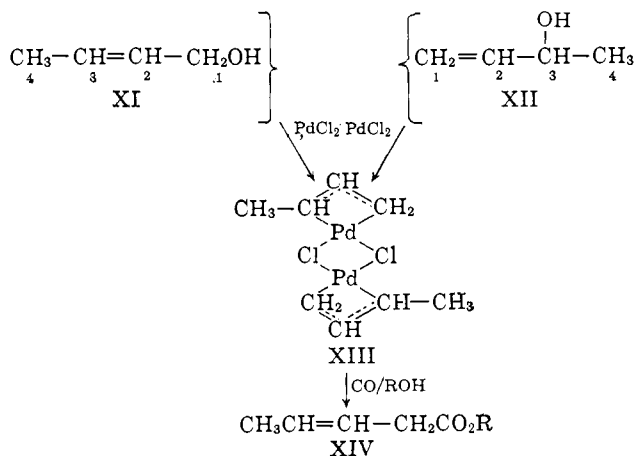
**Carbonylation of Allylic Alcohols.**—Carbonylation of allylic alcohols in ethanol gave ethyl esters of  $\beta, \gamma$ -unsaturated carboxylic acids, as shown in Table I. However, in the carbonylation of corresponding steroids, such as  $\Delta^4$ -cholesten-3- $\beta$ -ol or its acetate, the elimination of water or acetic acid to form 3,5-diene was observed instead of the expected carbonylation. When the carbonylation of allyl alcohol was carried out without solvent, allyl 3-butenate (IX) was obtained.

In this case, a considerable amount of diallyl ether (X) was formed.

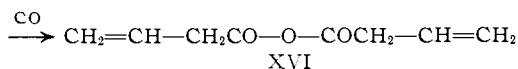
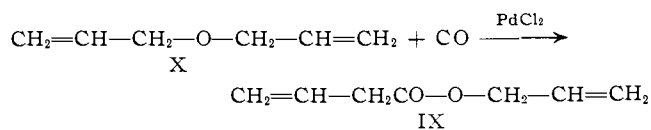
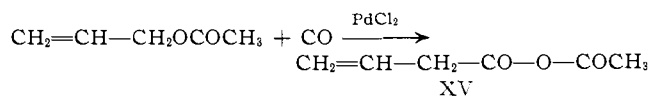


Palladium chloride undoubtedly acted as a catalyst for the ether formation. Recently, it was reported that hexachloroplatinic acid is an effective catalyst for allyl ether formation from allyl alcohol.<sup>14</sup>

Allylic rearrangements often occur when allylic compounds are treated with various reagents and the possibility of such rearrangements in this carbonylation was investigated. Both 2-buten-1-ol (XI) and 1-buten-3-ol (XII) were carbonylated in ethanol to form ethyl 3-pentenoate (XIV). This can be explained in the following way. When the complex is formed from XI and XII, the double bonds are delocalized between C-1 and C-3, giving the same complex (XIII) from both allylic alcohols, and 3-pentenoate (XIV) is formed as the sole product.



**Carbonylation of Allylic Esters and Ethers.**—Ethyl 3-butenate and 2-butenate were obtained by carbonylation of an allyl ester and an allyl ether in ethanol. The relative ratios of these two esters were different depending on group attached originally to the allyl carbon as shown in Table I. Then the reaction was carried out in benzene. From allyl acetate, the mixed anhydride of acetic and 3-butenic acid (XV) was formed. A more interesting reaction is that of diallyl ether (X). By the first insertion of carbon monoxide, allyl 3-butenate (IX) was formed. Insertion of a second molecule of carbon monoxide gave 3-butenic anhydride (XVI). This is a simple method for synthesizing anhydrides of  $\beta, \gamma$ -unsaturated acid.



(14) J. Milgrom and W. H. Urry, *Proc. Intern. Conf. Coordination Chem.*, 7th, Stockholm, 264 (1962).

Other noble metal compounds such as rhodium chloride, palladium nitrate, palladium oxide, or a mixture of hexachloroplatinic acid and stannous chloride<sup>15</sup> were also found to be effective for the carbonylation of allyl chloride. Even metallic palladium such as palladium-carbon or that obtained by reduction of palladium chloride can be used as a catalyst for the carbonylation of allyl chloride. However, their activities were somewhat lower than that of palladium chloride. It should be mentioned that  $\pi$ -allylpalladium bromide is formed by the reaction of metallic palladium and allyl bromide,<sup>16</sup> and it is reasonable to consider that  $\pi$ -allylpalladium chloride is formed from metallic palladium as an intermediate of the carbonylation of allyl chloride catalyzed by metallic palladium.

Since the reaction was carried out in the pressure reactor, no identification of reaction intermediates was possible. It is nevertheless reasonable to assume that the reaction proceeds through the formation of acylpalladium dicarbonyl halide, by analogy with carbonylations catalyzed by nickel carbonyl.<sup>6</sup>

### Experimental

The n.m.r. spectra were determined on a Varian high resolution spectrometer Model DP 60 and HR 100 using tetramethylsilane as an internal standard. Gas chromatographic analyses were carried out on a silicon DC 550 on Celite column, 2 m. in length, at 180° for higher boiling products or at 100° for lower ones. The molecular weights were determined in benzene using the Mechrolab vapor pressure osmometer. All boiling points are uncorrected.

Commercially available anhydrous palladium chloride was used without further purification. Carbon monoxide (99.5% pure) was purchased from the Matheson Co. 2-Buten-1-ol, obtained commercially, was purified by preparative gas chromatography. Commercially available allyl phenyl ether was used without further purification. The following were synthesized by known methods: allyl *p*-toluenesulfonate,<sup>17</sup> diallyl ether,<sup>14</sup> 3-penten-2-ol,<sup>18</sup> 1-buten-3-ol,<sup>19</sup> 3-bromocyclohexene.<sup>20</sup> Allyl acetate and 2-acetoxy-3-pentene were synthesized by the usual method of acetylation of the corresponding alcohols with acetic anhydride in the presence of pyridine. Allyl ethyl ether was prepared by the standard method from allyl bromide and sodium ethoxide.

**Reaction of Allyl Chloride with Carbon Monoxide.** (a) **Reaction in Ethanol (Expt. 1).**—To a mixture of 50 ml. of ethanol, 5 g. of allyl chloride, and 1 g. of palladium chloride in the 100-ml. stainless steel pressure reactor, carbon monoxide was charged up to 100 kg./cm.<sup>2</sup>. The reaction mixture was stirred at 120° for 40 hr. After palladium was separated, the reaction mixture was poured into five times its volume of water and the solution was extracted several times with ether. The ethereal solution was dried over anhydrous sodium sulfate. Distillation under reduced pressure gave 3.9 g. of mixed esters, b.p. 43–47° (43 mm.). Gas chromatographic analysis of the mixed esters showed two peaks which were separated by preparative gas chromatography. One of them was identified by n.m.r. and infrared spectra with authentic ethyl 3-butenate,<sup>21</sup> and the other with commercially available ethyl 2-butenate. The amount of ethyl isobutyrate was negligibly small.

(b) **Reaction in Ethanol (Expt. 2).**—To avoid an effect of metal surface of the pressure reactor, the reaction was carried out

in a glass vessel having a gas inlet capillary. The vessel was set in the pressure reactor. After the reaction, the mixture was gas chromatographically analyzed and the formation of ethyl isobutyrate, ethyl 3-butenate, and ethyl 2-butenate was confirmed.

(c) **Reaction in a Mixed Solvent of Benzene and THF (Expt. 3).**—The reaction was carried out in a 50-ml. stainless steel pressure reactor. After the initial rapid gas absorption, carbon monoxide was recharged up to 100 kg./cm.<sup>2</sup> and the mixture was stirred for 24 hr. 4-Chloro-1-butyl 3-butenate, b.p. 103–104° (13 mm.) (10.2 g.), was obtained and identified by n.m.r. spectrum, which showed peaks at: 8.22 (—CH<sub>2</sub>—), 6.93 (—CH<sub>2</sub>—CO—), 6.42 (—CH<sub>2</sub>—Cl), 5.94 (—O—CH<sub>2</sub>—), 4.89 (CH<sub>2</sub>=), 4.12  $\tau$  (—CH—).

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>O<sub>2</sub>Cl: C, 54.40; H, 7.41; Cl, 20.12; mol. wt., 176.6. Found: C, 54.39; H, 7.35; Cl, 19.92; mol. wt., 179.5.

(d) **Synthesis of Acid Chloride (Expt. 5).**—After the reaction, precipitated palladium was removed and the reaction mixture was distilled under reduced pressure. A considerable amount of a forerun consisting of benzene and acid chloride was distilled. Then the acid chloride boiling at 42–45° (75 mm.) was obtained (2.3 g.) whose infrared spectrum showed a band at 1800 cm.<sup>-1</sup> caused by the carbonyl group. An n.m.r. spectrum showed the peaks: two doublets at 6.63 (—CH<sub>2</sub>CO) and 4.86 (CH<sub>2</sub>=C), and a multiplet centered at 4.36  $\tau$  (—CH—). The forerun and the acid chloride were combined and esterified with ethanol to form ethyl 3-butenate. The yield of the acid chloride was determined by gas chromatography based on the amount of the ester. A small amount of ethyl 2-butenate was also detected.

**General Procedure for Reactions of Various Allylic Compounds with Carbon Monoxide to Form  $\beta,\gamma$ -Unsaturated Esters.**—The amounts of material used and the reaction conditions are shown in Table I. Reactions were carried out in the glass vessel mentioned above, in the stainless steel pressure reactor, or in the glass-coated pressure reactor. Initial carbon monoxide pressure at room temperature was adjusted to 100 kg./cm.<sup>2</sup>. In the case of the reactions giving both ethyl 3-butenate and ethyl 2-butenate, or allyl 3-butenate and diallyl ether, yields of these products were determined gas chromatographically using calibration curves. Separation of the products, if necessary, was carried out by preparative gas chromatography and the structures of the products were confirmed by comparing the n.m.r. and infrared spectra of the products with those of authentic samples. Other higher boiling esters were isolated by distillation under reduced pressure. These esters have the following boiling points and n.m.r. spectra: ethyl 3-pentenoate, b.p. 68–71° (44 mm.); n.m.r. spectra: 8.82 and 5.88 (O—CH<sub>2</sub>CH<sub>3</sub>), 8.30 (CH<sub>3</sub>—C=), 7.06 (—CH<sub>2</sub>—CO), 4.44  $\tau$  (—CH=CH—); ozonolysis gave acetaldehyde, identified as the 2,4-dinitrophenylhydrazone (m.p. 164°); ethyl 2-methyl-3-pentenoate, b.p. 72–74° (42 mm.); n.m.r. spectra: 8.77 and 5.90 (O—CH<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>—C), 8.35 (CH<sub>3</sub>—C=), 6.97 (>CH—CO), 4.46  $\tau$  (—CH=CH—); ozonolysis gave acetaldehyde; ethyl cyclohexene-3-carboxylate, b.p. 75–77° (11 mm.); n.m.r. spectra: 8.75 and 5.92 (O—CH<sub>2</sub>CH<sub>3</sub>), 7.03 (>CH—CO—), 4.26 (—CH=CH—), and complex multiplet for (—CH<sub>2</sub>—)<sub>3</sub> around 8.2  $\tau$ . Hydrogenation gave ethyl cyclohexanecarboxylate.

**Synthesis of 3-Butenoic Acetic Anhydride (Expt. 11).**—After the reaction, precipitated palladium was separated and distillation of the solution gave 7.6 g. of a fraction boiling at 55–90° (15 mm.). The infrared spectrum of this fraction showed absorption bands at 1820 and 1760 cm.<sup>-1</sup> characteristic of anhydride carbonyl. When the anhydride was treated with excess ethanol and a few drops of sulfuric acid, the formation of ethyl acetate and ethyl 3-butenate was confirmed by gas chromatography. In this case, the amount of ethyl 2-butenate was negligibly small.

**Synthesis of 3-Butenoic Acid Anhydride (Expt. 15).**—The reaction mixture was distilled under reduced pressure. After a considerable amount of a mixture consisting of allyl 3-butenate and 3-butenic anhydride, 2.9 g. of pure anhydride boiling at 91–96° (20 mm.) was obtained. The anhydride showed infrared absorption bands at 1820 and 1760 cm.<sup>-1</sup> owing to anhydride carbonyl and at 1645 cm.<sup>-1</sup> owing to olefinic unsaturation. Further confirmation of the anhydride was obtained by converting it to ethyl 3-butenate by treatment with ethyl alcohol. Hydrogenation of the anhydride gave butyric anhydride.

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