funnel. After a solution of 0.50 g (1.3 mmol) of **3a** in 2 ml of the appropriate solvent was introduced to the flask, the addition funnel was charged with a solution of 0.75 g (2.6 mmol) of TBTH in 4 ml of the same solvent. Immediately after attaching the gas-measuring line (water displacement and dibutyl phthalate in a leveling buret were both used), the hydride solution was added at once to **3a**. Gas evolution began after a short (about 1 min) induction period; after correction to standard conditions, comparison was made with the amount of gas expected on the basis of the actual yield of 5 obtained (Table I). This evolved gas was shown to be hydrogen by gas-density measurements.¹⁴ A control reaction in which the evolved gas was passed through a sodium hydroxide solution of known strength showed that no significant amount of acidic material was lost from the reaction.

Glpc analyses were performed by withdrawing aliquots and quenching with one-fourth their volume of methyl iodide. Bromomesitylene was then added as internal standard. Besides consuming excess hydride, methyl iodide inhibited the thermal (wall-catalyzed) cyclization of **3a** upon contact with the hot injection part of the gas chromatograph. Combined yields of **6** and **5** were typically in the 95-100% range by glpc, with **6**:**5** ratios as reported in Table I.

In a large-scale run, 21.9 g (75.3 mmol) of TBTH was added at once to 15.0 g (37.5 mmol) of **3a** in 120 ml of dry benzene. After gas evolution was complete, solvent was removed and distillation afforded 4.9 g (90%) of material, bp 80-84° (14 mm), which glpc analysis indicated to be a 5:95 mixture of 6 and 5. 1-Benzyl-1-methylcyclopropane (5) had nmr (CDCl₃) δ 7.22 (s, PhH), 2.58 (s, PhCH₂), 0.80 (s, CH₃), and 0.38 (m, CH₂CH₂). A near-infrared spectrum of **3a** (Applied Physics Corp., Cary Model 14, 0.500 *M* **3a** in CCl₄) displayed an absorption maximum at 1.642 μ with a molar absorptivity (*A*) of 0.33 per cyclopropyl methylene group.²⁸

Measurement of Hydrogen Evolution from LiAlH, Treatment of 3a.—A flask and Claisen head assembly was fitted with a septum seal, stirring bar, and gas line to a leveling buret containing di-n-butyl phthalate. After 2 ml of a LiAlH₄ in ether solution (2.5 mequiv LiAlH₄/ml), the hydride was diluted with 20 ml more ether, and after the system had stabilized, 1.20 g (3.00 mmol) of 3a was introduced by syringe through the septum. Slow but steady gas evolution began immediately, leading to a total of 65.3 ml of gas (corrected to STP) over a 15-hr period (further standing led to a 5-ml *decrease* of volume over a 2-day period). Assuming that of 3a is converted to products in a typical ratio of 3:97 (6:5), this represents a quantitative yield of gas based on the amount of 5 formed.

Registry No.—3 (X = OMs), 40548-53-6; 3 (X = OH), 2109-99-1; 3a, 40548-52-5; 3b, 40548-55-8; 3c, 40548-56-9; 4 (X = OMs), 40548-57-0; 4 (X = OH), 2612-30-8; 4a, 40548-59-2; 4b, 35694-75-8; 4c, 40548-61-6; 5, 30836-86-3; 6, 1007-26-7; 7, 40548-64-9; 8, 538-93-2; 9, 1667-00-1; LiAlH₄, 16853-85-3; TBTH, 688-73-3; methanesulfonyl chloride, 124-63-0; potassium iodide, 7681-11-0; lithium bromide, 7550-35-8; lithium chloride, 7447-41-8; isobutyl 2-methylpropanoate, 97-85-8; isobutyl 2,2dimethyl-3-phenylpropanate, 40548-66-1; 2,2-dimethyl-3-phenyl-1-propanol, 13351-61-6.

(28) Compare $\lambda_{\max} = 1.638 \mu$ and A = 0.324 for the known 1-benzylcyclopropane; P. G. Gassman and F. V. Zalar, J. Org. Chem., **31**, 166 (1966).

Intermediates in the Reaction of Grignard Reagents with Nitromethane

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The reaction of *n*-butylmagnesium bromide with nitromethane formed *N*-*n*-butyl-*N*-methylhydroxylamine, *N*-*n*-pentyl-*N*-methylhydroxylamine, octane, and *n*-butyl alcohol. The same reaction in the presence of styrene gave a small amount of 2-butyl-5-phenylisoxazolidine. These results point to a complex between nitromethane and *n*-butylmagnesium bromide and to 2-butylnitrone as intermediates in the formation of the hydroxylamines isolated.

The actual mechanism for the formation of hydroxylamines from Grignard reagents and nitromethane is not known.² Semiquantitative studies of

$$\begin{array}{c} \mathrm{RMgX} + \mathrm{CH}_{\$}\mathrm{NO}_{2} \longrightarrow \mathrm{CH}_{\$}\mathrm{NOH} + \mathrm{RCH}_{2}\mathrm{NOH} \\ \downarrow \\ \mathrm{R} \\ \mathrm{R} \\ \mathrm{R} \end{array}$$

the reaction of ethylmagnesium bromide and *n*butylmagnesium bromide with nitromethane carried out in the present work gave results which point to certain intermediates in this reaction.

The reaction with ethylmagnesium bromide was used to follow the influence of the concentration of the Grignard reagent upon the ratio of the hydroxylamines produced. The hydroxylamines were converted into the *O*-trimethylsilyl derivatives and analyzed by vpc. The results are shown in Figure 1.

The reaction using *n*-butylmagnesium bromide with nitromethane gave information about the gases evolved and the neutral products formed. The amounts of butane and butenes generated with the addition of successive amounts of Grignard reagent are shown in Figures 2 and 3. This reaction also produced *n*-octane and *n*-butyl alcohol.



These results point to the following steps in the



and butenes are formed at this point. A similar complex has been proposed for the reaction product be-

⁽¹⁾ Abstracted in part from the Ph.D. Thesis of J. V. K., 1973.

⁽²⁾ S. Wawzonek and J. V. Kempf, Org. Prep. Proced. Int., 4, 135 (1972).



Figure 1.—Relative yields of ethylmethylhydroxylamine (O) and ethylpropylhydroxylamine (\bullet) with respect to benzene as an internal standard formed in the reaction of ethylmagnesium bromide with nitromethane.

tween molar amounts of ethylmagnesium bromide and nitroethane by Buckley.³

Complex 1 when treated with more *n*-butylmagnesium bromide reacts in two ways. Reduction to 2 occurs with the formation of *n*-octane, *n*-butyl alcohol, and butenes. The yield of *n*-octane corresponded to 15.6% based on the nitromethane used in a run involving 3 mol of Grignard reagent for 1 mol of nitromethane. This hydrocarbon could also be formed in the preparation of the Grignard reagent since the formation of the latter is reported to proceed in a yield of 94%.⁴ Based on this yield at least 6.6% of the *n*-octane is formed by the reduction of complex 1.

n-Butyl alcohol was isolated in an 8.8% yield, but vpc analysis directly on the ether extracted indicated a larger amount.

The reduction of complex 1 in this manner resembles that reported for dimethylaniline oxide by phenylmagnesium bromide; dimethylaniline, phenol, and biphenyl were reported as products.⁵

Reduction of 1 to 2 probably also occurs to a minor extent with the formation of butenes. This behavior would be similar to the reduction of ketones by Grignard reagents to alcohols. This type of reaction seems to be favored by excess Grignard reagents (Figure 3).

A more powerful reducing agent such as zinc and hydrochloric acid is reported to reduce the complex form ethylmagnesium bromide and nitroethane to diethylamine.³

The second reaction of complex 1 with excess Grignard reagent produces the nitrone 3 and butane. This reaction based on the results shown in Figure 1 proceeds at a slower rate than the reduction of 1. A similar evolution of ethane was reported for the reaction of ethylmagnesium bromide and nitroethane.⁸ Proof for the nitrone 3 was the formation of 2-butyl-5phenylisoxazolidine (4) in the reaction of nitromethane (1 mol) with *n*-butylmagnesium bromide (2 mol) in the presence of excess styrene. The yield (<0.2%) of 4 was low since the conditions using refluxing ether

(3) G. D. Buckley, J. Chem. Soc., 1492 (1947).

(4) H. Gilman, E. H. Zoellner, and J. B. Dickey, J. Amer. Chem. Soc., 51, 1576 (1929).

(5) V. Belov and K. K. Savich, J. Gen. Chem. USSR, 17, 262 (1947).

WAWZONEK AND KEMPF



Figure 2.—Moles of butane formed in the successive addition of *n*-butylmagnesium bromide to nitromethane.



Figure 3.—Moles of butenes formed in the successive addition of n-butylmagnesium bromide to nitromethane.

and a 6.5-hr reaction time were less rigorous than those required to prepare a good yield of an authentic sample from N-butylnitrone and styrene; the latter required heating in toluene for 24 hr.

The last step involving the formation of a hydroxylamine (5) by the addition of a Grignard reagent to a nitrone is well documented in the literature.²

$$C_4H_9MgBr + CH_8NO_2 \longrightarrow CH_2 = N + C_4H_{10}$$

The formation of the aci derivative of nitromethane by the Grignard reagent occurs to a slight extent in this reaction; about 0.075 mol of butane was liberated during the addition of the first mole of Grignard reagent. This intermediate is responsible for the small amount of oxime formed in this reaction; addition of the Grignard reagent would form a complex **6** which

$$C_{4}H_{9}MgBr + CH_{2} = NOMgBr \longrightarrow C_{4}H_{9}CH_{2}N(OMgBr)_{2}$$

would hydrolyze to the oxime. Evidence for the presence of valeraldoxime was obtained in the present

GRIGNARD REAGENTS WITH NITROMETHANE

work by a nmr study of the products obtained by decomposing the Grignard product solely with water.

The conversion of nitromethane into the aci derivative becomes more important with increasing amounts of Grignard reagent since the yield of hydroxylamines drops with more than 3 mol of Grignard reagent (Figure 1) and the yield of butane (Figure 2) increases.

Experimental Section⁶

Preparation and Gas Chromatographic Analysis of O-Tri-methylsilyl Derivatives of N-Ethyl-N-methylhydroxylamine and N-Ethyl-N-propylhydroxylamine.—Ethylmagnesium bromide (0.25 mol) in ether (150 ml) was added dropwise with stirring to nitromethane (5.4 ml, 0.1 mol) in ether (200 ml) at 0°. The reaction mixture was gently refluxed for 12 hr and then decomposed by addition of water. Hydrochloric acid was added to adjust the solution to a pH of 9-10, and the reaction mixture was subjected to steam distillation. The distillate was collected in dilute hydrochloric acid, a total of 2.5 l. being collected. The acidic steam distillate was reduced to a small volume in vacuo, made basic with concentrated aqueous sodium hydroxide, and extracted four times with 75-ml portions of ether. The ether solution was dried (CaSO₄) and filtered, and the ether was distilled from the mixture through a 20-in. zigzag column until only 15-20 ml of solution remained. The concentrated ether solution was transferred to a 50-ml glass-stoppered flask and treated with 6.0 ml of pyridine and 6.0 ml of trimethylchlorosilane at 0°. The mixture was brought to room temperature and allowed to stand for several hours. Then, 2.00 ml of benzene was added; the solution was thoroughly mixed and subjected to gas chromatographic analysis using a 6 ft by $1/_8$ in. column of 10% W-98 silicon rubber on 100-200 mesh Chromsorb P with an injection port temperature of 250° , column temperature programmed to start at 50° and rise to 200° at 10° /min, detector temperature of 360° and gas flow of 50 ml/min at 50 psi. The retention times follow: benzene, 2.6 min; N-ethyl-N-methyl-O-trimethylsilylhydroxylamine, 4.4 min; N-ethyl-N-propyl-O-trimethylsilyl-hydroxylamine, 7.2 min. In the manner described above, ethylmagnesium bromide was added to nitromethane in mole ratios of 1.50, 2.10, 2.25, 2.50, 2.75, 3.00, 3.50, 4.00, and 4.50 and analyses were by gas chromatograph. The mixture of 3 mol of ethylmagnesium bromide with I mol of nitromethane using normal addition was also analyzed. The yields of hydroxylamines were less than those obtained by the inverse method. The use of a known quantity of benzene in the gas chromatography sample made it possible to calculate relative yields of the trimethylsilanated dialkylhydroxylamines with respect to nitromethane by comparing the area of their signals to that of benzene. The results are shown in Figure 1.

N-Ethyl-N-methyl-O-trimethylsilylhydroxylamine.-In a 250ml flask were placed 100 ml of ether, 10.0 ml of triethylamine, and 5.0 ml of N-ethyl-N-methylhydroxylamine. The solution was cooled in ice and 5.0 ml of trimethylchlorosilane was added. The flask was stoppered and cooled in ice with occasional shaking for 2 hr; it was then allowed to stand at room temperature for 2 hr. Water (70 ml) was added to the nearly solid reaction mixture. The ether layer was separated, washed with four 100-ml portions of water, and dried (CaSO₄). The ether upon removal under reduced pressure gave 1.5 ml of liquid. A sample of the desired product was isolated by preparative gas chromatography using a 10 ft by 1/8 in. column of SE-30 on 100-120 mesh Chromosorb P with an injection port temperature of 175°, column temperature of 90°, detector temperature of 175°, and a gas flow of 170 ml/ min at 30 psi. The retention time was 7.8 min; micro bp 117° min at 30 psi. The recention time was 1.5 min, micro S_P 1.7. (740 mm); n^{24} D, 1.3995; mmr (DCCl₃, HCCl₃ as internal stan-dard) δ 2.67 (q, 2, J = 7 Hz, NCH₂), 2.67 (s, 3, NCH₃), 1.02 (t, 3, J = 7 Hz, CH₃CH₂); ir (neat) 3.36, 3.47, 6.96, 7.27, 8.05, 9.58, 9.78, 10.77, 11.46; 11.87; 1313, 13.35, 14.65 µ.

Anal. Calcd for C₆H₁₇NOSi: C, 48.92; H, 11.64; N, 9.51. Found: C, 48.66; H. 11.67; N, 9.33.

N-Ethyl-N-propyl-O-trimethylsilylhydroxylamine.—N-Ethyl-N-propylhydroxylamine (10 ml) was converted into the O-trimethylsilyl ether (4.08 g) by the method described for the N-ethyl-N-methyl derivative: bp 65-65.5° (30 mm); n^{24} D 1.4128; retention time on column described for the ethylmethyl derivative 14.9 min; nmr (DCCl₃, HCCl₃ as internal standard) δ 2.67 (m, 4, N(CH₂)₂), 1.49 (sextet, 2, J = 7 Hz, CH₃CH₂CH₂), 1.02 (t, 3, J = 7 Hz, NCH₂CH₃), 0.90 (t, 3, J = 7 Hz, CH₃CH₂-CH₃); ir (neat) 3.36, 3.45, 6.25, 7.25, 8.05, 10.53, 10.56, 10.91, 11.09, 11.45, 11.94, 13.35, 14.26, and 14.66 μ .

Anal. Calcd for CsH21NOSi: C, 54.79; H, 12,07; N, 7.99. Found: C, 54.71; H, 11.89; N, 7.86.

2-Butyl-5-phenylisoxazolidine. A.—n-Butylmagnesium bromide (2 mol) in ether (500 ml) was added with stirring to a solution of nitromethane (1 mol) and styrene (2 mol) in ether (630 ml) during a period of 2.5 hr. The resulting solution was refluxed with stirring for an additional 4 hr and then hydrolyzed by addition of 150 ml of water; the magnesium salts were filtered from the mixture. Extraction of the ether solution with 4 N hydrochloric acid followed by basification of the acid extract gave an oil which by nmr analysis did not contain aromatic material. The magnesium salts from the reaction were continuously extracted with benzene for 2.5 days. The benzene was removed at reduced pressure and the resultant oil taken up in 300 ml of ether. The ether solution was extracted with four 100-ml portions of 6 Nhydrochloric acid. The acid solution was diluted with 200 ml of water and made basic with concentrated aqueous sodium hydroxide. The solution was then extracted with five 150-ml portions of benzene. The benzene solution was dried (CaSO₄) and the benzene upon removal *in vacuo* gave 11.4 g of oil. The oil was chromatographed on a 2.5 ft \times 2.0 in. column of silica gel using hexane and hexane-ether as the developing solvent. The fraction, which by nmr analysis contained aromatic material, was rechromatographed on a 2.5 ft \times 1 in. column of silica gel using 2.5% ether in hexane as the eluent. The fraction which contained aromatic material was purified by preparative thin layer chromatography using a silica gel plate and chloroform as the The material was removed from the silica developing solvent. gel with methylene chloride. Removal of the methylene chloride in vacuo at room temperature gave 0.40 g of 2-butyl-5-phenyloxazolidine: n²⁵D, 1.5178; nmr (DCCl₃) δ 7.28 (m, 5, C₆H₅), 4.99 (t, 1, J = 7 Hz, C₆H₅CH), 2.80 (poorly resolved t, 4, J = 7 Hz, N(CH₂)₂), 1.1–1.85 (m, 6, CH₂CH₂, CH₂CHPh), 0.92 (t, 3, J =7 Hz, CH₃); ir (neat) 3.38, 6.68, 6.85, 7.30, 9.70, 13.21, and 14.37 µ.

B.—A solution of N-butylhydroxylamine (2.12 g), paraformaldehyde (1.07 g), and styrene (2.73 g) in toluene was refluxed for 24 The water (0.6 ml) which formed immediately was removed hr. using a Dean-Stark trap. One-half of the toluene was distilled from the reaction mixture, and the remainder of the solution was extracted with three 100-ml portions of 3 N hydrochloric acid. The acid solution was made basic with concentrated aqueous sodium hydroxide and extracted with four 100-ml portions of The ether solution was dried (CaSO₄) and upon removal ether. of the solvent gave 3.53 g of an oil. Fractionation of the material gave 2.60 g (25.0%) of a pale yellow oil distilling at 97–99° (0.92 mm): n^{25} D 1.5128; nmr (DCCl₈) δ 7.25 (m, 5, C₆H₅), 4.95 (t, 1, J = 7 Hz; C₆H₅CH), 2.77 (poorly resolved t, 4, J = 7 Hz, N(CH₂)₂), 1.1–1.85 (m, 6, CH₂CH₂, CH₂CHC₆H₅), 0.92 (t, 3, $J = 7 \text{ Hz}, \text{CH}_3$).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.26; H, 9.48; N, 6.81.

A yellow solid was formed by treating 2-butyl-5-phenylisoxazolidine with chloroplatinic acid. Two recrystallizations from ethanol containing a drop of concentrated hydrochloric acid gave a solid which decomposed at 168–71° when the heating rate was $12^{\circ}/\text{min}$. The sample prepared from the product isolated from the Grignard reaction decomposed at 167–70°. A mixture of the two decomposed at 167–171°. The actual structure of this material is not known.

Anal. Caled for $C_{12}H_{21}Cl_4NOPt$: C, 28.68; H, 3.89; N, 2.57. Found: C, 28.54; H, 3.80; N, 2.51.

⁽⁶⁾ Melting points are corrected and boiling points are not corrected. Ir data were recorded using a Perkin-Elmer Infracord double beam recording spectrometer and nmr data on a Varian A-60 spectrometer. Analytical gas chromatography was carried out using an F & M Model 5750 dual column gas chromatograph equipped with Disc chart integrator. Peak areas were measured either by counting the integrator trace or using a compensating polar planimeter. Preparative gas chromatography was carried out using an F & M Model 500 gas chromatograph with a Model 720 oven.

Gaseous Products from the Reaction of *n*-Butylmagnesium Bromide with Nitromethane.—A 500-ml three-necked flask was equipped with a 50-ml buret containing $0.505 \ M$ *n*-butylmagnesium bromide, a stirrer, and a condenser. The condenser was fitted with a small cold finger cooled by a liquid nitrogen-

isopropyl alcohol slush. The entire system was purged with nitrogen which was saturated with ether. A solution of 2.442 g (0.040 mol) of nitromethane in 150 ml of ether was placed in the reaction vessel. The solution was refluxed with stirring, and aliquots of Grignard solution were added. After each addition, the solution was allowed to continue refluxing for about 20 min. The cold trap was then warmed to room temperature and the gases were collected in a gas-measuring buret containing water. After measurement, the gases were analyzed using a 11 ft by 1/4in. column of 33% 2,4-dimethylsulfolane on 60-80 mesh Chromosorb P with an injection port temperature of 125°, column temperature of 50°, detector temperature of 270°, and a gas flow of 33 ml/min at 40 psi. Retention times follow: air, 1.7 min; butane, 3.55 min; 1-butene, 4.6 min; cis-2-butene, 5.2 min; and trans-2-butene, 5.8 min. A trace amount of unidentified material with a retention time of 2.5 min was also detected. The results are shown in Figures 2 and 3.

Neutral Products from the Reaction of *n*-Butylmagnesium Bromide with Nitromethane.—The ether used in this experiment was dried over sodium wire and distilled immediately before use. The *n*-butyl bromide was filtered through a 5 in. \times 1 in. column of alumina to remove all traces of *n*-butyl alcohol. Its purity was assured by gas chromatographic analysis. All phases of the reaction were conducted under nitrogen which was purified by passage through two bottles of Fieser's solution, two bottles of concentrated sulfuric acid, solid sodium hydroxide, and solid calcium chloride.

A solution of *n*-butylmagnesium bromide was prepared from 19.4 g (0.80 mol) of magnesium and 80.5 ml (0.75 mol) of n-butyl bromide in 300 ml of ether. The Grignard flask was attached to a 1-l. three-necked flask equipped with mechanical stirrer, heating mantle, and reflux condenser. A solution of 13.5 g (0.25 mol) of nitromethane in 150 ml of ether was placed in the reaction vessel and the n-butylmagnesium bromide solution was added dropwise with stirring at a rate which maintained constant reflux. After addition was complete, the reaction mixture was refluxed with stirring for an additional 4 hr. The Grignard solution was decomposed by the dropwise addition of 125 ml of 6 N hydrochloric acid. After an additional 30 ml of concentrated hydrochloric acid was added to the solution, the ether was separated and the aqueous solution was extracted with three 100-ml portions of ether. The combined ether solutions were dried $(CaSO_4)$ and distilled using a spinning band column. The fraction boiling from $80-118^{\circ}$ weighed 6.78 g and by gas chromatographic analysis using a Carbowax column consisted of ether (0.60 g), *n*-octane (4.55 g), and n-butyl alcohol (1.63 g). Gas chromatographic analysis was carried out using a 6 ft by 1/8 in. column of 15% Carbowax 4000 on 100-120 mesh Chromosorb P with an injection port temperature of 165°, column temperature of 100°, detector temperature of 225°, and a gas flow of 30 ml/min at 40 psi. The retention times follow: ether, 0.3 min; n-octane, 0.5 min; and *n*-butyl alcohol, 2.3–2.5 min, depending on sample size.

Registry No.-4, 40548-43-4; nitromethane, 75-52-5; ethyl bromide, 74-96-4; trimethylchlorosilane, 75-77-4; N-ethyl-N-methyl-O-trimethylsilylhydroxylamine, 40548-44-5; N-ethyl-Nmethylhydroxylamine, 13429-36-2; N-ethyl-N-propyl-O-trimeth-ylsilylhydroxylamine, 40548-46-7; N-ethyl-N-propylhydroxyl-amine, 40548-47-8; n-butyl bromide, 109-65-9; N-butylhydroxylamine, 5080-24-0; chloroplatinic acid, 17083-70-4.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. IX. The Hydration of Enol Acetates in Wet Acetic Acid¹

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The rate expression for hydration of vinyl acetate to acetaldehyde was found to be rate = $k[\text{Li}_2\text{Pd}_2\text{Cl}_3]$ - $[C_{2}H_{a}OAc][H_{a}O]^{n}/[LiCl]$ where n has a value of between 1 and 2. The rate expression is consistent with attack of external water on a dimeric palladium(II) vinyl acetate π complex to give a hydroxypalladation adduct which decomposes to acetaldehyde and Li₂Pd₂Cl₈. The decomposition of this adduct is not by simple acetate elimination to give vinyl alcohol since this mechanism would predict that 1-cyclopenten-1-yl acetate would not react. In fact this enol acetate is rapidly saponified. Formation of a palladium(II)-substituted acet-aldehyde which then reacts with acetic acid solvent to give CH₃CHO seems to be the most likely mechanism. The determination of the rate expression is complicated by the fact that water is not only a reagent but affects the various equilibria present in the system. As with previous exchanges, substitution on vinyl carbon retards the rate of exchange. The nonintegral order in $[H_2O]$ is believed to be due to preferential solvation of the reactive metal ion species.

Previous papers of this series have considered exchange of vinyl³ and allylic⁴ ester with acetic acid, allylic esters with chloride,⁵ and vinylic chlorides with radioactive chloride⁶ and acetic acid.⁷ A general feature of these exchanges is that they involve attack of acetate or chloride on a dimeric palladium(II) π complex to give a palladium(II) σ -bonded intermediate, 1. For vinylic exchange the reaction scheme would be given by eq 1 (X and Y = Cl or OAc). Exchange is completed by elimination of Y to give back the olefin. When X is acetate, attack occurs only from outside the coordination sphere of the palladium(II);

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 (3) P. M. Henry, J. Amer. Chem. Soc., 93, 3853 (1971).

 - (4) P. M. Henry, ibid., 94, 1527, 5200 (1972).
 - (5) P. M. Henry, *Inorg. Chem.*, **11**, 1876 (1972).
 (6) P. M. Henry, J. Org. Chem., **37**, 2443 (1972)
 - (7) P. M. Henry, J. Amer. Chem. Soc., 94, 7311 (1972).



when X is chloride, attack can occur from either outside or inside the coordination sphere.

This paper will describe the palladium(II) chloride catalyzed reaction of vinyl acetate with a third and

⁽¹⁾ Paper VIII: P. M. Henry, J. Org. Chem., 38, 1140 (1973).