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CARBONYLATION OF PIPERYLENE IN THE PRESENCE OF PALLADIUM CHLORIDE

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Several recent publications have described the formation of carboxylic acid derivatives from the reaction between carbon monoxide and olefins in the presence of palladium chloride. Monolefin-palladium chloride complexes have been shown to give β-chloroacyl chlorides when reacted with carbon monoxide under pressure in aprotic solvents (1), while similar treatment of diolefins was found to give chloro-substituted unsaturated acyl chlorides in aprotic solvents and ethoxy substituted unsaturated esters in alcoholic solutions (2). The competition between reaction sites of unsymmetrical diolefins was shown by the production of variously substituted methylpentenoates from the carbonylation of isoprene at various temperatures (2).

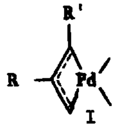
We wish to report an interesting and unusual example of the specificity observed during the carbonylation of piperylene. Treatment of ethanolic solutions of piperylene with carbon monoxide in the presence of catalytic amounts of palladium chloride gives ethyl 2-methyl-3-entenoate in 40-50% yields.

A typical example of this reaction is outlined below. Trans-piperylene (b.p. 42°, n_D^{25} .4290, 34 g. = 0.5 mole) and anhydrous palladium chloride (2.0 g.) are stirred under nitrogen in 60 ml. of absolute ethanol for one hour at room temperature, then placed in a steel reactor and rocked for 24 hours at 100-110° with carbon monoxide at a maximum pressure of 1700 psi. A pressure drop of 300 psi is observed during this period. The contents are chilled, filtered free of catalyst residue, and distilled, first at atmospheric pressure to remove unreacted piperylene and ethanol, then at reduced pressure to give 1) 1.0 g., b.p. 30-62°/20 mm, 2) 30 g., 43% yield of ester b.p. 62-69°/20 mm., and 3) 5.3 g. residue.

A similar reaction was performed using 3.0 g. palladium chloride to give 39 g. (55% yield) of ester after distillation. The catalyst residue, a mixture of black metallic palladium and light green palladium chloride complex (2), was recharged with piperylene and carbon monoxide as before to give 41 g. of material from which 14 g. (20% yield) of ethyl 2-methyl-3-pentenoate was isolated by distillation. The remaining material was a mixture of higher boiling esters (3).

The product, ethyl 2-methyl-3-pentenoate had the following properties: calculated for $C_8H_{14}O_2$: C, 67.57; H, 9.92; O, 22.50; found: C, 67.49; H, 10.00; O, 22.53. Vapor phase chromatography showed a single peak eluting in 7.7 minutes (12 ft. Carbowax column, helium 75 ml/min., programmed 6°/min). Infrared absorptions appeared at 1730 C=O, 1460 CH_3, 1160 OR, 970 cm^{-1} trans-CH=CH- which disappeared upon uptake of 1 mole hydrogen. No conjugation was apparent in the ultraviolet spectrum (λm = 225 mμ e 317, isooctane). Hydrolysis of the hydrogenated ester gave a carboxylic acid (b.p. 86°/8 mm (bath), n_D^{25} 1.4130) which was converted to an amide (m.p. 75-76°) and toluidide (m.p. 79-80°). Reported values (4) for 2-methylpentanoic acid are b.p. 192°/748 mm, n_D^{20} 1.4136, amide m.p. 79°, toluidide m.p. 80°. Reduction of the saturated ester with lithium aluminum hydride gave an alcohol (n_D^{23} 1.4176, 3,5-dinitrobenzoate m.p. 48-49°). Reported values for 2-methyl-1-pentanol are n_D^{20} 1.4190 and 3,5-dinitrobenzoate m.p. 50°. An NMR spectrum of the neat unsaturated acid shows an allylic methyl doublet centered at 1.34 (J=5 cps) and Me-CH doublet at 0.91 ppm (J=7 cps). One methinyl multiplet at 2.82, 1,2-disubstituted olefin multiplet at 5.26 (J=11 cps) and the carboxylic acid proton at 11.60 ppm are also observable.

The production of 2-methylpentenoate with the high selectivity observed in this instance may shed some light upon the mechanism of palladium catalyzed carbonylations of diene systems. It is noted that both butadiene and isoprene react at terminal positions with carbon monoxide to give pentenoates (2). It is also found that propylene is attacked in a terminal position rather than the more substituted central position (1,5).

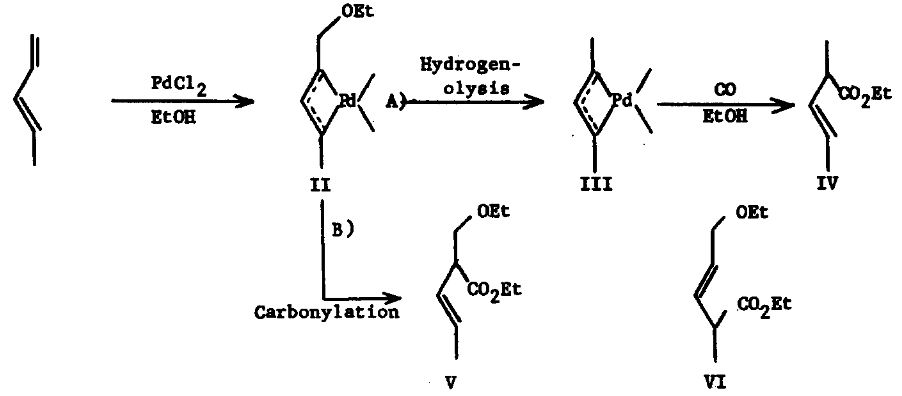


$R = H, CH_3$

$R' = X, CH_3, XCH_2$

Since these materials are thought to be carbonylated through a complex of the type it follows that carbon monoxide attack occurs preferentially at the terminal position. The isolation of 5-ethoxy-3-methyl-3-pentenoate from the carbonylation of isoprene in ethanol supports the existance of an ethoxy π-allyl palladium complex R = CH_3, R' = $EtOCH_2$- (2) proposed by Robinson and Shaw (6). Furthermore the isolation of ethyl 3-pentenoate and ethyl 4-methyl-3-pentenoate from carbonylation of butadiene and isoprene, respectively, shows that hydrogenolysis of a hetero group and carbonylation occurred in the system (2). It was not possible, however, to determine the relative order of these two reactions.

Considering the reaction of piperylene to give the 2-methylpentenoate, it is apparent that both carbonylation at a secondary position and hydrogenolysis took place. The following mechanism might be proposed to explain this result.



The initial step is reasonably expected to be the formation of the ethoxy π-allyl complex II (7), followed by hydrogenolysis of the labile allyl ether group (2,6) and finally insertion of carbon monoxide (2). In this case, hydrogenolysis as the first step gives the symmetrical intermediate III, which then can react at either <u>secondary</u> position to give the 2-methyl derivative IV, shown in A. Carbonylation to the ethoxy acyl derivative followed by hydrogenolysis cannot be absolutely precluded on the basis of this result; however, such a course would require the less favorable hydrogenolysis of the species V and VI derived by path B.

REFERENCES

(1) J. Tsuji, M. Morikawa, J. Kiji, Tetrahedron Letters, No. 16, 1061(1963).

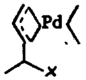
(2) J. Tsuji, S. Hosaka, J. Am. Chem. Soc. 87, 4075(1965).

(3) Vapor phase chromatography and infrared analysis of this material indicated a complex mixture of higher molecular weight esters from which only a single compound ($C_9H_{16}O_2$) was isolated.

(4) Huntress and Mulliken, Identification of Pure Organic Compounds, Order I, p. 193, Wiley and Sons, N. Y. (1941).

(5) J. Tsuji, J. Kiji, M. Morikawa, Tetrahedron Letters, No. 26, 1811(1963).

(6) S. D. Robinson, B. L. Shaw, J. Chem. Soc., 4806(1963).

(7) Robinson and Shaw state that piperylene and sodium chloropalladite gave a mixture of palladium complexes in alcohol. Structures such as  might be proposed; however, no evidence for the formation of the hexenoate could be found.