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PALLADIUM CATALYZED TRANSFER OF ALLYLIC GROUPS

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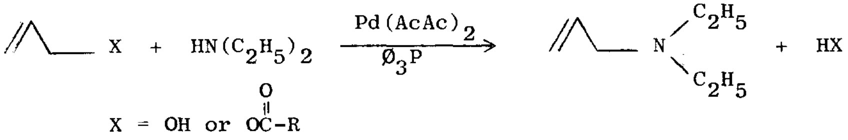
In a previous paper(1) we noted that an allylic ester (2,7-octadien-1-yl acetate) reacted smoothly with an amine (diethylamine) using a palladium complex catalyst to yield the corresponding N,N-diethyl-2,7-octadien-1-ylamine. This reaction has been reported independently in the patent literature(2). We now wish to report extension of the reaction to allylic functional moieties in general, including alcohols, ethers, esters and amines. Allylation of activated carbon atoms has also been observed.

Allylic alcohols, as well as esters and ethers, will react rapidly with primary or secondary amines to give allylic amines in high yield using a palladium-triphenylphosphine complex catalyst. Allyl alcohol (50 mmoles) reacted with diethylamine (50 mmoles) in the presence of palladium acetylacetonate (0.25 mmole) and triphenylphosphine (0.25 mmole) at 50° for 0.5 hour to yield 95% allyldiethylamine(3). Similar reactions using 2,7-octadien-1-ol yielded the corresponding



2,7-octadien-1-ylamine. When a primary amine, n-butylamine, was used as a reactant with 2,7-octadien-1-ol a mixture of mono and di octadienylated amines resulted. The products were identified by comparison of their nmr and infrared spectra with those of authentic materials.

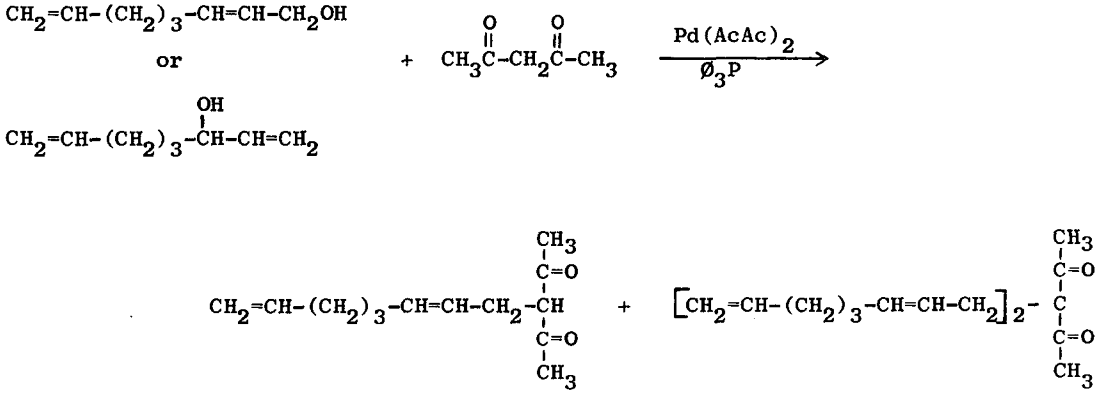
An allylic diol, 2-butene-1,4-diol (5.0 moles), reacted with diethylamine (3.1 moles), palladium acetylacetonate (0.011 mole) and triphenylphosphine

(0.033 mole) at 85° for 4 hours to yield 4-(N,N-diethylamino)-2-buten-1-ol (30%), bp 110°/9 mm.

The nmr and ir spectra of the product [(CCl_4) δ1.00 ppm, t, J = 7.0 Hz N-C-CH_3 (6H); 2.48, q, J = 7.0 Hz, N-CH_2- (4H); 3.03, m, =C-CH_2-N (2H); 4.0, m, O-CH_2 (2H); 5.08, s, H-O (1H); 5.7, m, -CH (2H)] [(neat) O-H 3.0µ, trans CH=CH 10.3µ] were consistent with the proposed structure. Analyzed for $C_8H_{17}NO$: %C, 66.81; %H, 11.80; %N, 9.52.

$$HOH_2CCH{=}CH{-}CH_2OH + HN(C_2H_5)_2 \xrightarrow[\emptyset_3P]{Pd(AcAc)_2} HOCH_2{-}CH{=}CH{-}CH_2{-}N(C_2H_5)_2$$

Allylic alcohols, amines and esters will react with compounds such as acetylacetone using catalytic amounts of a palladium-triphenylphosphine complex to give carbon allylated products in good yield. Reaction of acetylacetone (0.05 mole), allyl alcohol (0.043 mole), palladium acetylacetonate (0.25 mmole), and triphenylphosphine (0.75 mmole) at 85° for 3 hours yielded 70% of 3-allyl acetylacetone and 26% 3,3-bis-allyl acetylacetone. A similar reaction using 2,7-octadien-1-ol gave the corresponding octadienylated products. Interestingly, both 2,7-octadien-1-ol and 1,7-octadien-3-ol were found to yield the same monooctadienylated reaction product with acetylacetone, 3-(2,7-octadien-1-yl)acetylacetone. This is an indication that the reaction with both alcohols proceeds through a common



$$\begin{array}{l} CH_2{=}CH{-}(CH_2)_3{-}CH{=}CH{-}CH_2OH \\ \qquad\qquad \text{or} \\ CH_2{=}CH{-}(CH_2)_3{-}\overset{\overset{OH}{|}}{C}H{-}CH{=}CH_2 \end{array} + CH_3\overset{\overset{O}{\|}}{C}{-}CH_2\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[\emptyset_3P]{Pd(AcAc)_2}$$

$$CH_2{=}CH{-}(CH_2)_3{-}CH{=}CH{-}CH_2{-}\overset{\overset{\overset{CH_3}{|}}{\overset{C=O}{|}}}{\underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}}{CH}} + [CH_2{=}CH{-}(CH_2)_3{-}CH{=}CH{-}CH_2]_2{-}\overset{\overset{\overset{CH_3}{|}}{\overset{C=O}{|}}}{\underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{|}}}{C}}$$

keto and enol forms

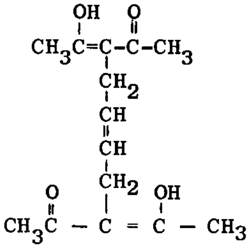
intermediate, a palladium π-allyl complex.

The allylated and octadienylated acetylacetones(4) were identified by comparison of their nmr and infrared spectra with those of authentic materials.

Allylic esters such as allyl acetate and 2,7-octadien-1-yl acetate react more slowly than allylic alcohols with acetylacetone. However, when a tertiary amine was added to the reaction mixture a more rapid rate was attained. For instance acetylacetone (0.05 mole), 2,7-octadien-1-yl acetate (0.025 mole), palladium acetylacetonate (0.25 mmole), and triphenylphosphine (0.75 mmole) gave a 33% yield of 3-(2,7-octadien-1-yl) acetylacetone after one hour at 85°. When N-methyl morpholine (0.025 mole) was present in an identical reaction, 73% of this product was realized in one hour. A similar effect was noted when allyl acetate was used as the reactant.

Allyldiethylamine (0.5 mole) was reacted with acetylacetone (0.6 mole), palladium acetylacetonate (2.4 mmoles) and triphenylphosphine (7.2 mmoles) at 85° for 20 hours to give 70% of 3-allyl acetylacetonate and 20% 3,3-bis-allyl acetylacetone. N,N-Diethyl-2,7-octadien-1-ylamine reacted in a similar fashion to yield carbon octadienylated products.

2-Buten-1,4-diol (1.0 mole) was reacted with acetylacetone (5.0 moles), palladium acetylacetone (0.012 mole), and triphenylphosphine (0.036 mole) at 85° for three hours to yield compound I (30%), bp 157-162°/0.3 mm.



I

The nmr spectrum [(CDCl$_3$) δ2.09, s, CH$_3$ (12H); 2.97, d, J = 3.5 Hz =C-CH$_2$-C= (4H); 5.44, m, =CH (2H); 16.68, s, =C-OH (2H)] was consistent with the proposed structure. The singlet at 2.09 ppm represents the four methyl groups because of the rapid exchange of enolic protons among the four carbonyl groups. Analyzed for $C_{14}H_{20}O_4$: %C, 66.84; %H, 7.92.

A somewhat broader range of activated carbon compounds can be allylated by these palladium catalysts than might be expected by analogy to published reports of butadiene reactions with activated carbon compounds (4). Phenylacetone and phenylacetonitrile react with butadiene or allylic alcohols to give the corresponding C-allyl derivatives. Octadienylation of phenylacetonitrile with 2,7-octadien-1-ol yielded 2-phenyl-4,9-decadienenitrile, b.p. 127°/0.35 mm. This structure was assigned on the basis of nmr and ir spectra [δ1.5 ppm, m, -CH$_2$- (2H); 2.0, m, =C-CH$_2$ (4H); 2.5, m, =C-CH$_2$-C-C$_6$H$_5$ (2H); 3.74, t, J = 7.0 Hz, -CH(O)CN (1H); δ4.8-6.1, m, HC=CH and HC=CH$_2$ (5H); δ7.27, s, -C$_6$H$_5$ (5H)] [(neat) CN, 4.45μ, C=C 6.09, 6.22, 10.05, 10.3 and 10.95μ] and elemental analyses.

Anal. Calcd. for C$_{16}$H$_{19}$N: %C, 85.27; %H, 8.18; %N, 6.21. Found: %C, 85.28; %H, 8.18; %N, 6.16.

Phenylacetone was octadienylated with 2,7-octadien-1-ol to yield 3-phenyl-5,10-undecadiene-2-one, b.p. 118°/0.35 mm. The structure assigned is based on nmr and ir spectra [δ1.5, m, -CH$_2$- (2H); δ1.95, s, CH$_3$ (3H); δ1.9, m, -C-CH$_2$ (4H); δ3.60, t, J = 7.5 Hz, -CH(C$_6$H$_5$)CO (1H); δ4.7-6.1, m, HC=CH and HC=CH$_2$ (5H); δ7.21, s, -C$_6$H$_5$ (5H)] [(neat) C=O 5.85μ, C=C 6.1, 6.25, 10.05, 10.3 and 10.98μ] and elemental analyses.

Anal. Calcd. for C$_{17}$H$_{22}$O: %C, 84.25; %H, 9.15. Found: %C, 84.12; %H, 9.15.

Further work is planned to use this new allylation reaction to synthesize compounds of interest and to further investigate the catalytic effect of tertiary amines. A full paper will be published when this work is completed.

References

1. R. M. Manyik, W. E. Walker, K. E. Atkins, and M. L. Farmer - see preceding communication.

2. T. S. Shryne, E. J. Smutny, and D. P. Stevenson, U. S. Patent 3,493,617 (February 3, 1970).

3. All reactions were performed in a nitrogen atmosphere. All solvents were nitrogen purged before use.

4. G. Hata, K. Takahashi, and A. Miyake, Chem. Indus. (London) 1836 (1969).