CHEMISTRY LETTERS, pp. 835-836, 1991.

Palladium(0)-catalyzed Dimerization/Allylation of 1-Alkynes with Allyl Carbonate

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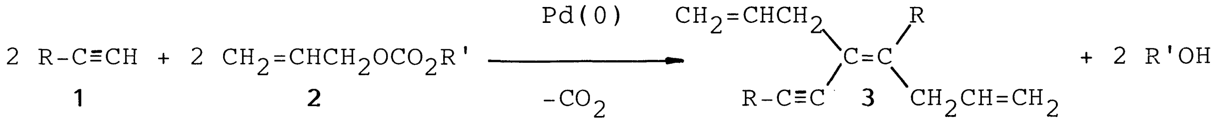
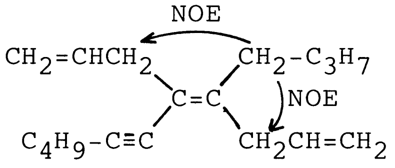
Palladium(0) complexes catalyzed a dimerization/allylation of 1-alkynes with allyl carbonate in which three carbon-carbon bonds were formed regio- and stereoselectively.

Linear dimerization of 1-alkynes is known to be catalyzed by a wide variety of transition metal complexes including those of rhodium and palladium. Head-to-head and/or head-to-tail dimers are the normal products.[1] Allyl carbonates have been used as the efficient allylating agents for the palladium-catalyzed allylation of nucleophiles under neutral conditions.[2] Representative nucleophiles are acetoacetates and malonates. Now we have found that palladium(0) catalyzes the dimerization/allylation of 1-alkynes **1** with allylic carbonate **2**. Three carbon-carbon bonds are formed in this reaction regio- and stereoselectively.



$$2\ \underset{\mathbf{1}}{R\text{-}C\equiv CH} + 2\ \underset{\mathbf{2}}{CH_2{=}CHCH_2OCO_2R'} \xrightarrow[-CO_2]{Pd(0)} \underset{\mathbf{3}}{(CH_2{=}CHCH_2)(R\text{-}C\equiv C)C{=}C(R)(CH_2CH{=}CH_2)} + 2\ R'OH$$

Typically, equimolar amounts of 1-hexyne (**1**; $R=C_4H_9$) and allyl carbonate (**2**; $R'=CH_2CH=CH_2$) were reacted in an autoclave in the presence of 2 mol% of $Pd(dba)_2$ (dba=dibenzylideneacetone) and PPh_3 (P/Pd=2) at 100 °C for 6 h in acetonitrile. The product, (Z)-5-allyl-4-butyl-1,4-undecadien-6-yne (**3**; $R=C_4H_9$), was obtained directly from the reaction mixture by distillation at 112-115 °C/0.25 mmHg in 85% yield.[3] This was identified by selective hydrogenation of the terminal double bonds on osmium black followed by ozonolysis of the resulting enyne to yield 4-octanone. The Z configuration rests on the NOE measurement (Scheme 1). Several 1-alkynes and allyl methyl carbonate also took part in this reaction (Table 1). Extention of this approach to **1** with R=Ph, CH_2OH, and CO_2CH_3 resulted in the formation of **4** of the former or polymeric products of the latter two.



Scheme 1.

$R-C≡C-CH_2CH=CH_2$
4

Table 1. Reaction of 1-alkyne **1** with allylic carbonate **2** in the presence of $Pd(dba)_2$-2 PPh_3

1	2	Temp/°C	Time/h	Yield of **3**/%
$R=CH_3$	$R'=CH_2CH=CH_2$	120	10	55 (Z)
C_4H_9	CH_3	reflux	4	46 (Z)
	$CH_2CH=CH_2$	70	5	56 (Z)
	$CH_2CH=CH_2$	100	6	85 (Z)
C_6H_{13}	CH_3	70[a]	1	78 (ND)[b]
$C(CH_3)_2OH$	$CH_2CH=CH_2$	reflux[a]	2	37 (ND)[b]

Reaction conditions: **1** 5 mmol, **2** 5 mmol, CH_3CN 10 cm^3, $Pd(dba)_2$ 0.1 mmol, PPh_3 0.2 mmol.
a) The solvent was toluene. b) The configuration was not determined.

The generally accepted mechanism for the allylation with allyl carbonate involves the oxidative addition of palladium(0) to this carbonate to generate (π-allyl)palladium alkoxide after facile decarboxylation. The alkoxide anion thus generated in situ picks up the active hydrogen of a nucleophile to produce the corresoponding carbanion which in turn attacks the (π-allyl)palladium to yield the allylated compound.[2] According to this mechanism, a possible intermediate may be a 1-en-4-yne compound **4**, which might sustain further alkynylation and allylation to yield the observed product. However no appreciable amount of **4** ($R=C_4H_9$) was detected throughout the 1-hexyne-allyl carbonate reaction. Moreover introduction of 1-undecen-4-yne (**4**; $R=C_6H_{13}$) to the reaction resulted in no participation of this compound. These observations do not indicate the intermediacy of **4**. Further studies on the scope and the mechanism are underway.

References

1) For reviews, see P. N. Rylander, "Organic Syntheses with Noble Metal Catalysts," Academic Press, New York (1973), p. 191; J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, California (1987), p. 608.
2) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, and K. Takahashi, J. Org. Chem., **50**, 1523 (1985).
3) IR (neat) 1640, 1050, 915 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H), 0.92 (t, 3H), 1.25-1.55 (m, 8H), 2.07 (t, 2H), 2.33 (t, 2H), 2.90 (d, 2H), 3.08 (d, 2H), 4.96-5.10 (m, 4H), 5.74-5.92 (m, 2H). ^{13}C NMR (15 MHz, CD_3COCD_3) δ 13.5, 14.0, 19.3, 22.0, 23.0, 30.7, 30.8, 31.3, 37.0, 39.9, 81.0, 92.7, 114.9, 115.2, 117.1, 136.1, 136.3, 144.3.

(Received February 13, 1991)