Tetrahedron Letters, Vol 32, No 33, pp 4167-4168, 1991
Printed in Great Britain

0040-4039/91 $3 00+
Pergamon Press plc

PALLADIUM-CATALYZED TANDEM BOND FORMING REACTION LEADING TO AROMATIC RING THROUGH DIENE-YNE SYSTEM

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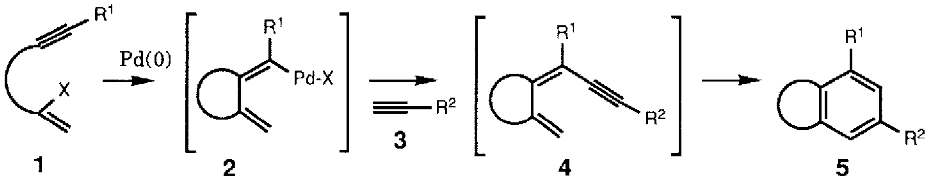
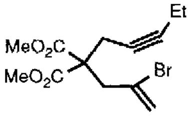
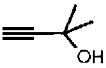
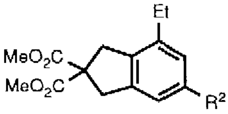
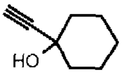
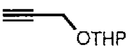
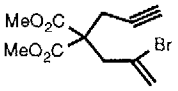
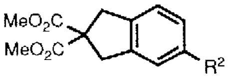
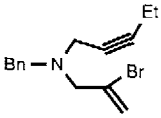
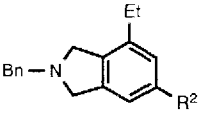
Summary; A double cyclization involving palladium-catalyzed intramolecular followed by intermolecular carbon-carbon bond formations starting from vinyl bromides with acetylenes produced aromatic compounds through diene-yne system in high yields.

In the context of our researches on the synthesis of highly conjugated systems which are often observed as indispensable functionalities in several intriguing natural products, the encountered problem is a lack of a simple method on constructing such a conjugated system under mild conditions. We envisioned a palladium-catalyzed tandem insertion and alkylation sequence of acetylenes to organopalladium species. Several recent reactions concerning the concurrent formation of carbon-carbon bonds[1] prompted us to report our preliminary results along the scheme shown below. The vinyl bromides **1** involving acetylene moiety in the same molecule reacted with another acetylenes **3** in the presence of palladium catalysts. The initial products were diene-ynes **4**, which cyclized to the aromatic compounds **5** in good yields.

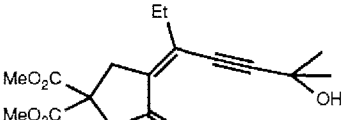


The general procedure is as follows. A mixture of vinyl iodide **1**, acetylene **3** (1.2 equiv.), palladium acetate (5 mol%), triphenylphosphine (20 mol%), copper(I) iodide (5 mol%), and triethylamine (1.5 equiv.) in acetonitrile (3 ml) was refluxed under argon atmosphere for 10~14 h. After usual workup and purification, the cyclized compounds were obtained in the indicated yields in Table 1. The aromatic products **5** were obtained in good yields with a variety of terminal acetylenes. Since the reaction can be performed under mild conditions, various functional groups such as hydroxy, amine, THP, and ester can tolerate. When the reaction is carried out at room temperature, the reaction is slow. However, the substrates utilized in Entry 1 afforded the diene-yne compound **4a** in 67% yield, which cyclized to **5a** on further stirring.

Table 1. Palladium-catalyzed Cyclization Leading to Aromatic Ring

Entry	1	3 ($\equiv$—R^2)	5 (%)	
1	 1 a	 3 a	 5 a	79
2	1 a	 3 b	5b	97
3	1 a	 3 c	5c	84
4	1 a	$\equiv$—C$_6$H$_{13}$ 3 d	5d	73
5	 1 b	3 a	 5 e	77
6	1 b	3 b	5 f	92
7	1 b	3 c	5 g	76
8	1 b	3 d	5 h	70
9	 1 c	3 a	 5 i	81
10	1 c	3 d	5 j	61

All products showed consistent spectra (IR, ^{1}H NMR, and ^{13}C NMR).



4 a

We are grateful to the SC-NMR Laboratory of Okayama University for taking high resolution NMR.

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(Received in Japan 11 April 1991)