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Palladium catalyzed reaction of α-chloromethylnaphthalene with olefins

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Abstract

The reaction of α-chloromethylnaphthalene with various olefins in the presence of palladium acetate produces three different kinds of products. The coupling products with the olefinic bond conjugated to the naphthalene ring are the major products for the reactions of most olefins. An unusual rearrangement product formed via a cyclopalladation intermediate is isolated from the reactions of the two *N*-vinyl olefins. © 2000 Elsevier Science Ltd. All rights reserved.

The palladium-catalyzed alkylation of olefins by alkyl halides is one of the important aspects of the Heck reaction.[1–4] We[5] have reported the palladium-catalyzed reactions of various benzyl halides with a variety of olefins. Recently, we[6] have also found that benzylic quaternary ammonium salts could serve as a benzyl donor in the palladium-catalyzed alkylation of olefins. As part of our continuing efforts in the study of palladium catalyzed reactions of alkyl halides with olefins, we report here the reaction of α-chloromethylnaphthalene with various olefins in the presence of palladium acetate.

In a typical experimental procedure a mixture of α-chloromethylnaphthalene (1 equiv), olefin (1.1 equiv), tributylamine (2 equiv) and $Pd(OAc)_2$ (1 mol%) was refluxed in DMF under a nitrogen atmosphere. It was found that α-chloromethylnaphthalene has similar reactivity to benzyl halides. Three different products, which depended largely on the structure of the olefin used, were isolated or detected as shown in Scheme 1. The results are summarized in Table 1. Among the three products, compound **2** is the usual coupling product of the Heck reaction. Compound **1** is the olefinic isomer of **2**; compound **1** is generally thermally more stable than the compound **2** because of the stability of the conjugated system. Compound **3** is a totally new kind of rearrangement product.

For acrylonitrile, acrylamide, styrene and *N*-allylphthalimide (entries 2–5), only the coupling products **1**, with the olefinic bond conjugated to the naphthalene ring, were isolated. For methyl acrylate (entry 1) two olefinic isomers (**1** and **2**) were obtained. For 1,1-di(4-methoxyphenyl)ethylene (entry 8), only **2** was isolated. Reactions of the two *N*-vinyl olefins, *N*-vinylsuccinimide and *N*-vinylphthalimide, with α-chloromethylnaphthalene (entries 6 and 7) produced the unexpected rearrangement products **3**, in

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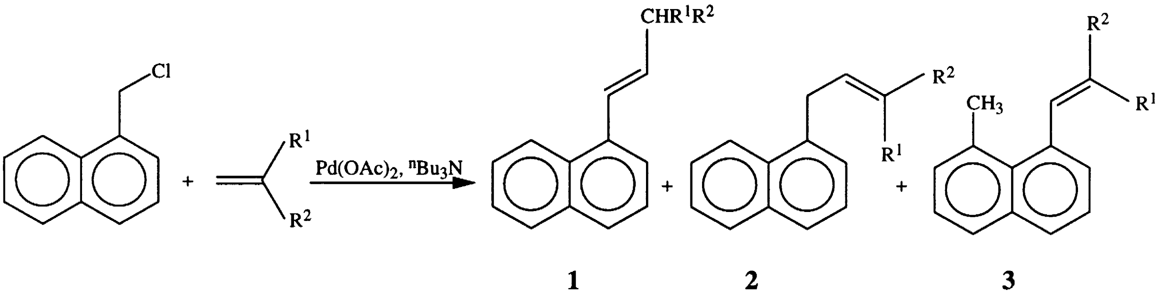
Table 1
Palladium-catalyzed reactions of α-chloromethylnaphthalene with olefins

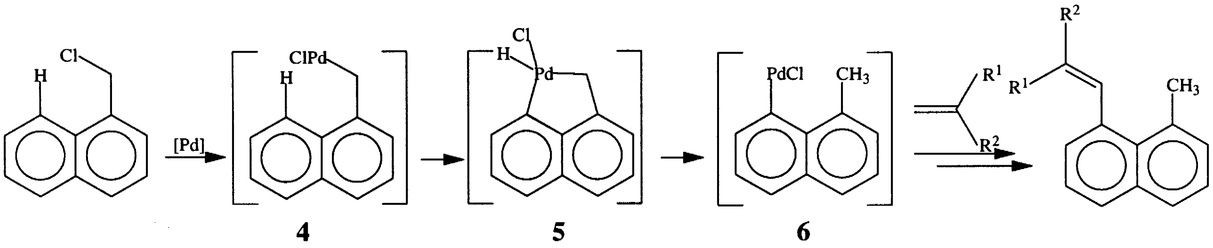
Entry	R^1	R^2	Product	Temp, °C	Time, h	Yield[a], %
1	H	$COOCH_3$	**1a, 2a**	130	10	75 (3:1)[b]
2	H	Ph	**1b**	130	10	70
3	H	$CONH_2$	**1c**	130	10	49
4	H	CN	**1d**	130	10	45
5	H	phthalimidomethyl	**1e**	130	10	47
6	H	succinimido	**1f/3f**[c]	140	15	20/25
7	H	phthalimido	**1g/3g**[d]	140	15	20/26
8	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	**2h**	130	10	22
9	H	$OCOCH_3$	α-$C_{10}H_7CH_2OAc$	130	10	50

a. Yields based on α-chloromethylnaphthalene. b. Ratio of 1a to 2a was determined by ^{1}HNMR spectrum. c. ^{1}H NMR data for 3f (500 MHz, $CDCl_3$): δ = 8.50 (d, J(H,H) = 17.0 Hz, 1H, =C*H*), 7.80-7.00 (m, 6H, *H*-Aromat.), 6.80 (d, J(H,H) = 17.0 Hz, 1H, =C*H*), 2.83 (s, 4H, CH_2), 2.73 (s, 3H, CH_3). d. ^{1}H NMR data for 3g (500 MHz, $CDCl_3$): δ = 9.60 (d, J(H,H) = 18.0 Hz, 1H, =C*H*), 7.92-7.26 (m, 10H, *H*-Aromat.), 7.02 (d, J(H,H) = 18.0 Hz, 1H, =C*H*), 2.96 (s, 3H, CH_3).



Scheme 1.

which the olefinic species are attached directly to the *peri* position of the naphthalene ring, together with the formation of products **1**. The unusual rearrangment products **3** were considered to form via the cyclopalladation intermediate. A simplified mechanism is proposed in Scheme 2.



Scheme 2.

So far as we know, this is the first example of the catalytic rearrangement vinylation of organic halides in the Heck reaction, although Heck[7] reported a similar rearrangement of neophyl mercury acetates with styrene in the presence of stoichiometric palladium acetate. Observation of the similar cyclopalladation of naphthalene related palladium complexes[8] could give support to the present hypothesis. The fact that the unusual rearrangement products **3** were isolated only in the reactions of the two *N*-vinylimides suggests that the nitrogen containing olefins may be involved in the stabilization of the intermediates as coordinative ligands to ensure that the intermediate **4** has time to undergo cyclopalladation. This obviously needs to be investigated further. For the reaction of α-chloromethylnaphthalene with vinyl acetate (entry 9), only α-naphthalenemethyl acetate was isolated.

Acknowledgements

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