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MERCURY IN ORGANIC CHEMISTRY. 27. π-ALLYLPALLADIUM SYNTHESIS VIA ORGANOPALLADIUM ADDITIONS TO NONCONJUGATED DIENES

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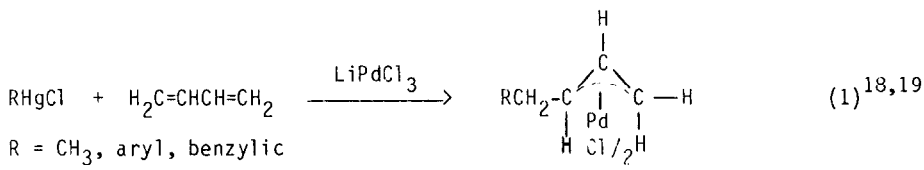
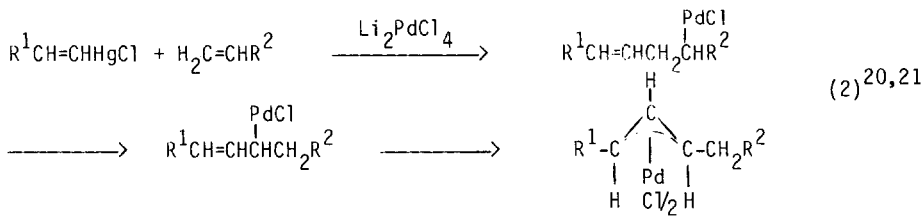
Summary: A variety of organomercurials react regioselectively with 1,4-, 1,5- and 1,6-dienes and Li_2PdCl_4 to form good yields of π-allylpalladium compounds. These reactions apparently proceed by organopalladium addition to one of the diene double bonds and subsequent palladium migration.

π-Allylpalladium compounds can be prepared by a number of procedures[2-6] the most important of which are the insertion of palladium(0) reagents into the carbon-halogen bond of allylic halides[7-11] and the direct allylic hydrogen substitution of alkenes by palladium salts.[12-17] Recently, the palladium-promoted addition of certain organomercurials to 1,3-dienes and vinylpalladium addition to alkenes have provided new routes to π-allylpalladium compounds (eqs. 1,2). With the great current interest in applications of π-allylpalladium



(1)[18,19]

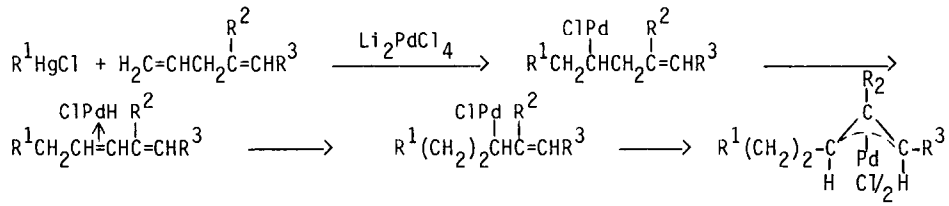


(2)[20,21]

compounds in organic synthesis,[22,23] we were interested in exploring whether this latter type of remote palladium migration could be extended to other systems, especially those in which the palladium was even further removed from the carbon-carbon double bond.

While our earlier work (eq. 2) indicated that homoallylic palladium compounds could cleanly rearrange via palladium hydride elimination-readdition to afford π-allylpalladium compounds,[20,21] we chose to prepare these same intermediates by a different pathway, namely organopalladium additions to 1,4-dienes, to see if π-allylpalladium compounds could also be generated in this manner (Scheme 1). Good to excellent yields can indeed be obtained in this

Scheme 1



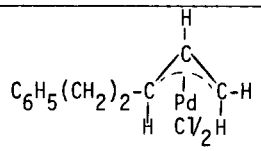
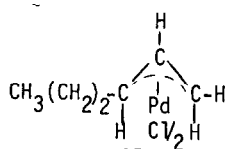
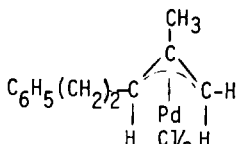
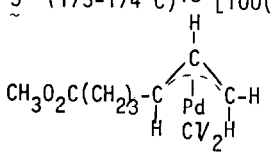
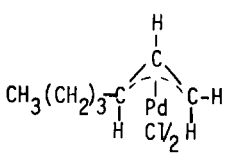
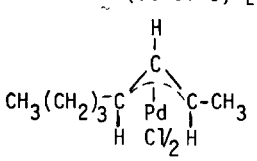
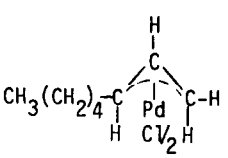
fashion (entries 1-3, Table I). These reactions appear to be highly regioselective (entry 3), attack occurring on the least substituted double bond exclusively.

A greater challenge lies in the reaction of 1,5-dienes with organopalladium compounds, since the palladium moiety in this situation is required to migrate two carbon atoms prior to π-allylpalladium formation.[24] Nevertheless, reasonably good yields of π-allylpalladium compounds are obtained from 1,5-hexadiene as illustrated by entries 4 and 5 in Table I. With 1,5-dienes, however, palladium hydride elimination becomes a significant side reaction. Rather than decompose, the palladium hydride apparently adds to the starting 1,5-diene generating a second π-allylpalladium complex. To generate the hydride-derived π-allylpalladium product cleanly, one simply needs to employ ethylmercuric chloride (entries 5-7). This approach to the generation of a palladium hydride has been used previously by Heck in his work on additions to 1,3-dienes.[19]

To determine if palladium can migrate three or more carbons, we have looked at the reactions of 1,6-heptadiene and 1,7-octadiene (entries 6 and 7). Ethylmercuric chloride reacts cleanly with 1,6-heptadiene and Li_2PdCl_4 to give a 61% yield of the expected π-allylpalladium compound **5**. No other π-allylpalladium compounds are observed. On the other hand, the analogous reaction with 1,7-octadiene gives approximately a 3:1 mixture of two π-allylpalladium compounds **6** and **7** in 92% isolated yield. Note that the major isomer is not **7** the compound expected from simple palladium hydride addition and migration. It is unclear at present how compound **6** is formed. We continue to explore the scope of this new approach to π-allylpalladium compounds.

In conclusion, organopalladium additions to 1,4-, 1,5- and 1,6-dienes provide a novel new method for the preparation of π-allylpalladium compounds. These reactions are regioselective and allow for the incorporation of functional groups as well. The majority of

Table I. Synthesis of π-Allylpalladium Compounds

entry	organomercurial	diene	product(s)[a] (mp) [% yield[b]]
1	C_6H_5HgCl	$H_2C{=}CHCH_2CH{=}CH_2$	 1 (124-125°C) [100(61)]
2	CH_3HgCl		 2 $(98\text{-}99°C)^{25}$ [87(44)]
3	C_6H_5HgCl	$H_2C{=}CHCH_2C(CH_3){=}CH_2$	 3 $(173\text{-}174°C)^{18}$ [100(51)]
4	CH_3O_2CHgCl	$H_2C{=}CH(CH_2)_2CH{=}CH_2$	 + 2 4 (79-80°C)[11] [43(24)] [3]
5	CH_3CH_2HgCl		2 [55(50)]
6		$H_2C{=}CH(CH_2)_3CH{=}CH_2$	 5 (60-61°C) [61(55)]
7		$H_2C{=}CH(CH_2)_4CH{=}CH_2$	 +  6 [69] 7 [23]

[a] All new compounds gave satisfactory IR and NMR spectral data and elemental analyses.

[b] Isolated yield (recrystallized yield).

results are most easily explained by initial organopalladium or hydridopalladium addition to the less hindered double bond of the diene, followed by a series of palladium hydride elimination-readdition reactions until an allylpalladium compound is formed.

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