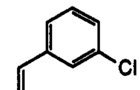

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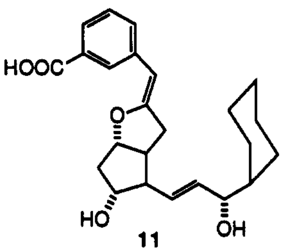

11

In summary, we have shown that dibenzyltitanocene (**2**) may serve as a convenient and synthetically useful reagent for the benzylidenation of ketones, esters, lactones, and amides. Substitution on the phenyl ring of the titanocene increases both the efficiency and the synthetic utility of the olefination. Further work with this and other titanocene derivatives and other types of substrates is currently under way.

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Supplementary Material Available: Detailed experimental procedures and ^{1}H and ^{13}C NMR spectra of titanium reagents and benzylidene products (49 pages). Ordering information is given on any current masthead page.

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Control of Chemoselectivity in the Rhodium(II)-Catalyzed Alkyne Insertion Reaction of α-Diazo Ketones

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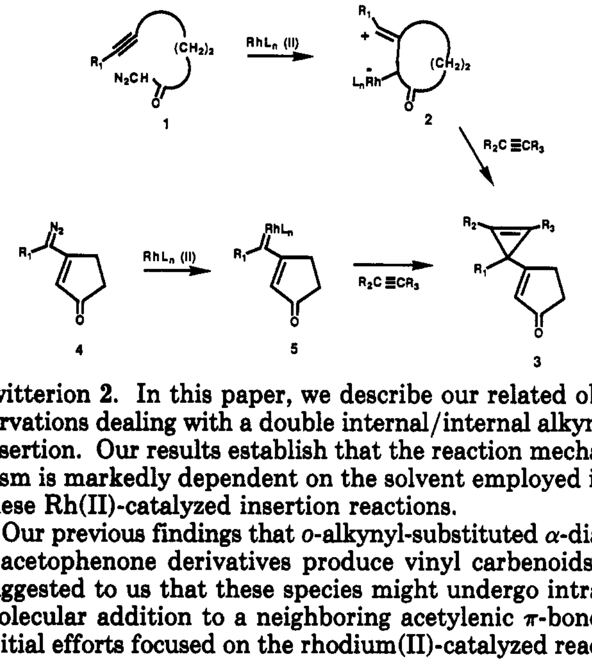
Summary: Chemoselectivity in the rhodium(II) catalyzed reaction of an acetylenic α-diazo ketone was found to be markedly influenced by the solvent used. Cyclopropenyl indenones are formed in pentane whereas alkenyl-substituted indenones are produced when CH_2Cl_2 is used as the solvent.

The insertion of alkynes into transition-metal–carbon bonds is a well-documented reaction and has been observed in nearly all of the triads of transition metals.[1-12] Recently, Hoye and Dinsmore reported on the Rh(II)-catalyzed double internal–external alkyne insertion reaction of an acetylenic α-diazo ketone.[13] The initially formed rhodium carbenoid intermediate was suggested to undergo internal insertion into the tethered alkyne unit followed by a second external addition to produce a cyclopropenyl-substituted cyclopentenone derivative (i.e., **3**). Migration of the rhodium metal to the remote alkyne carbon via a [2 + 2]-cycloaddition/cycloreversion path (i.e., **1** → **5**) was discounted on the basis that the distribution of products derived from **1** differed significantly from those obtained from the rhodium carbenoid species **5** generated from the vinylogous diazo ketone precursor **4**.[14] Instead, the results were rationalized via the intermediacy of zwitterion **2**. In this paper, we describe our related observations dealing with a double internal/internal alkyne insertion. Our results establish that the reaction mechanism is markedly dependent on the solvent employed in these Rh(II)-catalyzed insertion reactions.



Our previous findings that *o*-alkynyl-substituted α-diazoacetophenone derivatives produce vinyl carbenoids[15] suggested to us that these species might undergo intramolecular addition to a neighboring acetylenic π-bond. Initial efforts focused on the rhodium(II)-catalyzed reaction of α-diazo ketone **6**. Treatment of **6** with a catalytic quantity of rhodium(II) octanoate in pentane at 25 °C afforded dimer **10** (51%) derived from a transient indenone intermediate (i.e., **9**). The structure of **10** was unequivocally established by an X-ray crystal structure analysis. That the reactive indenone **9** is the primary product of reaction follows from its interception by diphenylisobenzofuran (DPIBF). Cycloadduct **11** was obtained as the exclusive cycloadduct in 73% isolated yield. Formation of indenone **9** can be explained in terms of insertion of the initially formed rhodium carbenoid **7** (vide infra) onto the

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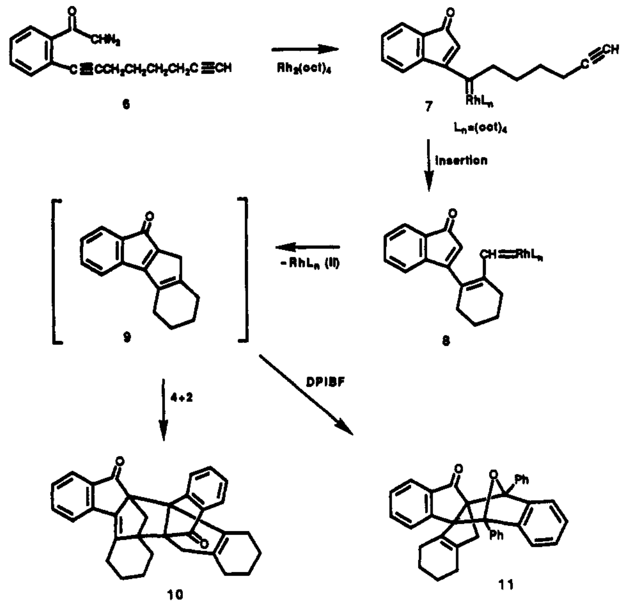
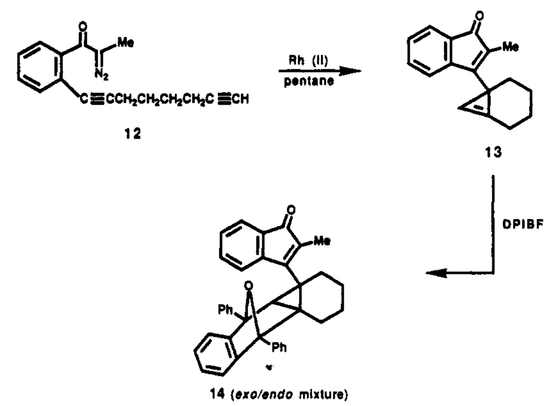
0022-3263/92/1957-1330$03.00/0

Scheme I



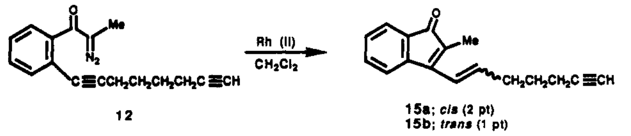
neighboring acetylenic π-bond with eventual formation of the cyclized dienyl carbenoid 8 (see Scheme I). Electrocyclization of 8 followed by reductive elimination of the rhodium species produces 9 which subsequently undergoes a [4 + 2]-cycloaddition to produce dimer 10.

Extension of the carbenoid cyclization/insertion reaction to α-diazo ketone 12 was next investigated. In this case it was possible to obtain cyclopropene 13 in 80% yield as an isolable but reactive intermediate from the $Rh_2(oct)_4$/pentane-catalyzed reaction.[16] Cyclopropene 13 readily undergoes Diels–Alder cycloaddition with DPIBF to give a 1:1 endo/exo mixture of cycloadducts in 67% isolated yield.[17]

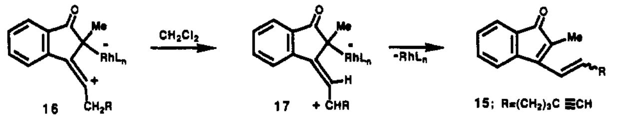


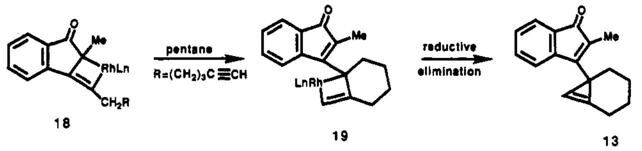
14 (exo/endo mixture)

During the course of our studies, *we found that the choice of solvent markedly influences the product distribution obtained from 12*. This is illustrated by the treatment of α-diazo ketone 12 with a catalytic quantity of rhodium(II) acetate at 25 °C in CH_2Cl_2 which resulted in a 2:1 mixture of the *cis*- and *trans*-alkenyl-substituted indenones 15 (85% combined yield). No signs of cyclopropene 13 (<2%) could be detected in the crude reaction mixture by NMR spectroscopy. When $Rh_2(oct)_4/CH_2Cl_2$ was used as the catalyst/solvent combination, a 2:3 mixture of cyclopropene 13 and indenone 15 was obtained. Use of pentane instead of CH_2Cl_2 with $Rh_2(OAc)_4$ resulted in the exclusive formation of cyclopropene 13 (80%). *What is so remarkable about these results is the degree to which chemoselectivity can be achieved by simply changing the solvent from CH_2Cl_2 to pentane.*



A reasonable explanation to account for the formation of indenone 15 involves stepwise cyclization of the initially formed carbenoid in accord with the Hoye–Dinsmore proposal.[14] A 1,2-hydrogen shift from 16 would result in the formation of 17, and this is followed by collapse to 15 and regeneration of the rhodium catalyst.[18] The intermediates involved in the formation of 15 are dipolar, which would explain why the generation of 15 is strongly inhibited in pentane.[19] When pentane is used as the solvent, metal migration occurs via the metallocyclobutene intermediates 18 and 19 so as to avoid charge buildup.





In summary, we have discovered an interesting and useful solvent effect in the rhodium(II)-catalyzed cyclizations of α-diazo-substituted alkynes. Further studies in this area are currently in progress.

Acknowledgment. We wish to thank the National Science Foundation for generous support of this research.

Supplementary Material Available: Spectroscopic data for new compounds and X-ray data (18 pages). Ordering information is given on any current masthead page.

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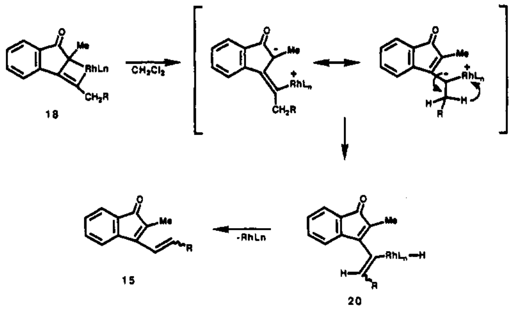
[16] Presumably an intermediate related to 13 is involved in the conversion of 7 → 8 → 9. The presence of the methyl group in 13 significantly retards the electrocyclization reaction.

[17] Bicyclo[4.1.0]hept-1(7)-ene has recently been isolated and shown to readily undergo [4 + 2]-cycloaddition with DPIBF; see: Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969. Billups, W. E.; Lee, G. A.; Arney, B. E.; Whitmire, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 7980.

[18] Another conceivable path suggested by a reviewer for the conversion of 12 into 15 involves formation of the rhodium hydride species 20 which then undergoes reductive elimination to give 15 and regeneration of the catalyst.



[19] For other examples of product control of a rhodium catalyzed process being influenced by solvent, see: Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, 6299. Davies, H. M. L.; Saikali, E.; Young, W. B. *J. Org. Chem.* **1991**, *56*, 5696. Davies, H. M. L.; Clark, T. J.; Kimmer, G. F. *J. Org. Chem.* **1991**, *56*, 6440.