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CARBOCYCLIZATION OF *E,E*-1,4-DIPHENYL-1,3-BUTADIENE WITH DICHLOROALKANES MEDIATED BY RIEKE METALS

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Abstract: The Rieke metal complexes of barium and strontium readily react with *E,E*-1,4-diphenyl-1,3-butadiene to form metal-diene reagents. Upon treatment with 1,*n*-dichloroalkanes, these metallocycles are transformed into ring derivatives in excellent chemical yield.

We have previously reported that Rieke magnesium[1] and Rieke calcium[2] readily react with 1,3-dienes to form substituted (2-butene-1,4-diyl)magnesium and calcium complexes. These complexes function as bis-nucleophiles when treated with electrophiles. Reactions of these bis-allylic organometallic reagents with organic dihalides have been shown to yield 4-, 5-, or 6-membered ring carbocycles.[3] Since both strontium and barium have significantly different redox potentials, larger ionic radii, and are more electropositive compared to magnesium and calcium, we envisioned that the corresponding strontium- and barium-diene complexes would function differently than their calcium and magnesium

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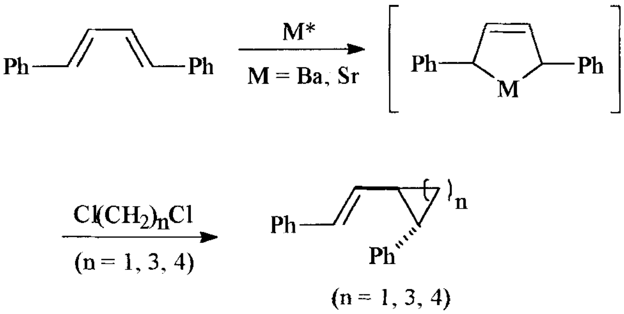
counterparts. We decribe here the first reported diene complexes of M(1,4-diphenyl-1,3-butadiene) (M = Ba and Sr) and an improved method for the formation of carbocyclization products upon the reaction of these complexes with 1,*n*-dichloroalkanes.[4]

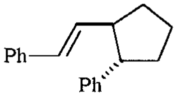
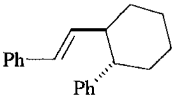
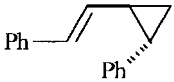
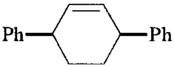
Rieke barium and Rieke strontium were prepared by the reduction of BaI_2[5] and $SrBr_2$,[6] respectively, in THF solution with preformed lithium biphenylide under an argon atmosphere at room temperature.[7] Both of these metals were soluble[8] and homogeneous in THF and reacted smoothly with *E,E*-1,4-diphenyl-1,3-butadiene to form the metallocycles in 2 h at ambient temperature.



These bis-organometallic reagents were found to readily undergo alkylation reactions with 1,*n*-dichloroalkanes in excellent chemical yield.

As shown in Table 1, *trans*-1-phenyl-2-*trans*-β-styrenylcyclopentane was formed in excellent chemical yield when the carbocyclization was mediated by Ba* and Sr* (Table 1, entries 1 and 2). Similarly, entries 4 and 5 demonstrate that the highest yields in the formation of *trans*-1-phenyl-2-*trans*-β-styrenylcyclohexane were obtained using Ba* and Sr*. Conversely, in the

Table 1. Reactions of 1,4-Diphenyl-1,3-butadiene with 1,*n*-Dichloroalkanes Mediated by Rieke Metals.

Entry	Metal	Electrophile	Product[a]	% Yield[b]
1	Ba*	Cl-$(CH_2)_3$-Cl		99
2	Sr*	"	"	93
3	Mg*	"	"	81
4	Ba*	Cl-$(CH_2)_4$-Cl		97
5	Sr*	"	"	90
6	Mg*	"	"	51
7	Ba*	Cl-CH_2-Cl		67
8	Sr*	"	"	55
9	Mg*	"	"	76
10	Ca*	"	"	47
11	Ba*	Cl-$(CH_2)_2$-Cl		--
12	Sr*	"	"	--
13	Mg*	"		59
14	Ca*	"	"	80

a) All products are known and match the reported ^1H NMR, ^{13}C NMR, FTIR, and mass spectra data. b) Isolated yield.

examples employing methylene chloride as the electrophile, the magnesium-diene complex afforded the cyclopropane ring product most efficiently (Table 1, entry 9). Finally, when the metallocycles derived from Ba* and Sr* were treated with 1,2-dichloroethane, only the diene was recovered (Table 1, entries 11 and 12). However, it is interesting that when the Mg* and Ca* metallocycles were utilized, *cis*-3,6-diphenyl-1-cyclohexene was afforded in 59% and 80%, respectively (Table 1, entries 13 and 14).

Since barium and strontium are more electropositive than calcium and magnesium, the resulting metallocycles act more efficiently as electron transfer reagents and only the diene resulting from electron transfer was afforded. Also consistent with this trend of electrochemical reduction potentials was when Mg* and Ca* were treated with 2,3-dihexyl-1,3-butadiene, neither metal reacted with the diene to form the metallocycle after stirring 2 h at room temperature. However, when Ba* was utilized, the diene was transformed into (2,3-dihexyl-2-butene-1,4-diyl)barium in 55% after 30 min at room temperature.[9] The Ba*, due to its higher electrochemical reduction potential, was the only Rieke metal found to react with this diene. Moreover, the effective reduction potential and resulting reactivity can be increased by using alkylated biphenyls. For example, when 4,4'-di-*tert*-butylbiphenyl was utilized to complex with the barium atom, the barium metallocycle formed in quantitative yield.[9]

In summary, Rieke barium and Rieke strontium have been shown to undergo direct metallation with *E,E*-1,4-diphenyl-1,3-butadiene, and the resulting metallocycles underwent dialkylation with 1,*n*-dichloroalkanes in excellent yield when n = 3 and 4. Significantly, these cyclizations are both highly stereoselective and regioselective. Studies are currently underway to develop novel diene-metal complexes using Rieke barium which may find utility in organic synthesis.

A representative procedure for the preparation of the known products reported here is outlined as follows.

***trans*-1-Phenyl-2-*trans*-β-styrenylcyclopentane**[10]: (Table 1, entry 1). Lithium (3.1 mmol) and biphenyl (3.2 mmol) in freshly distilled THF (5 mL) were stirred under argon until the lithium was completely consumed (ca. 2 h). To a well-suspended solution of BaI_2 (1.5 mmol) in freshly distilled THF (5 mL), the preformed lithium biphenylide was transferred via cannula at room temperature. The reaction was stirred for 30 min at room temperature, and the resulting brown suspension of Rieke barium was ready for use. To the barium solution was added *E*,*E*-1,4-diphenyl-1,3-butadiene (0.158 g, 0.77 mmol) in THF (10 mL) at room temperature. After being stirred at room temperature 2 h, the reaction mixture was cooled to -78 °C and excess 1,3-dibromopropane (0.245 g, 2.17 mmol) was added via a disposable syringe. After stirring 2 h at -78 °C, the mixture was warmed to room temperature and stirred 2 h, followed by the addition of 3 M HCl at 0 °C. The aqueous layer was extracted with diethyl ether (3 X 20 mL). The combined organic phases were washed with 1 N sodium thiosulfate solution (20 mL) and dried over $MgSO_4$. Removal of solvent and flash chromatography on silica gel afforded *trans*-1-phenyl-2-*trans*-β-styrenylcyclopentane (190 mg, 99 % yield): ^{1}H NMR δ 7.26-7.19 (m, 8H), 7.17-7.11 (m, 2H), 6.23-6.09 (m, 2H), 2.84-2.62 (m, 2H), 2.19-2.03 (m, 2H), 1.89-1.62 (m, 4H); ^{13}C NMR δ 144.5, 137.7, 133.5, 129.2, 128.3, 128.2, 127.5, 126.7, 125.9, 125.9, 52.7, 51.6, 34.9, 33.2, 24.2; IR (neat) 3082, 3058, 3025, 2952, 2869, 1600, 1494, 1448, 964, 744, 698 cm^{-1}; HRMS calcd for $C_{19}H_{20}$ 248.1565, found 248.1565.

***trans*-1-Phenyl-2-*trans*-β-styrenylcyclohexane**[10]: (Table 1, entries 4-6).

***trans*-1-Phenyl-2-*trans*-β-styrenylcyclopropane**[10]: (Table 1, entries 7-10).

***cis*-3,6-Diphenyl-1-cyclohexene**[10]: (Table 1, entries 13 and 14).

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References

1. (a) Sell, M. S.; Klein, W. R.; Rieke, R. D. *J. Org. Chem.* **1995**, *60*, 1077. (b) Sell, M. S.; Xiong, H.; Rieke, R. D. *Tetrahedron Lett.* **1993**, *34*, 6007. (c) Sell, M. S.; Xiong, H.; Rieke, R. D. *Tetrahedron Lett.* **1993**, *34*, 6011.

2. Wu, T. C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045.

3. Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.

4. The crystal structures of M(2,3-dimethyl-1,4-diphenyl-1,3-butadiene)$(THF)_4$ (M = Ca and Sr) have recently been reported: Mashima, K.; Sugiyama, H.; Kanehisa, N.; Kai, Y.; Yasuda, H.; Nakamura, A. *J. Am. Chem. Soc.* **1994**, *116*, 6977.

5. The preparation of Rieke barium has been reported: (a) Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 6130. (b) Corey, E. J.; Noe, M. C.; Shieh, W. *Tetrahedron Lett.* **1993**, *34*, 5995.

6. For the preparation of Rieke Strontium, see: Rieke, R. D.; Chen, T. *Chem. Mater.* **1994**, *6*, 576.

7. When the reduction of BaI_2 was performed using preformed lithium naphthalenide, the metallocycle did not form.

8. These metals presumably form complexes with biphenyl M(biphenyl)$_2$ (M = Sr or Ba) and hence are soluble in THF.

9. This is a gas chromatography ratio of the dihydro product versus the unreacted diene after acidic hydrolysis.

10. ^{1}H NMR, ^{13}C NMR, IR and HRMS for all these known compounds were in agreement with the reported data given in references 2 and 3.

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