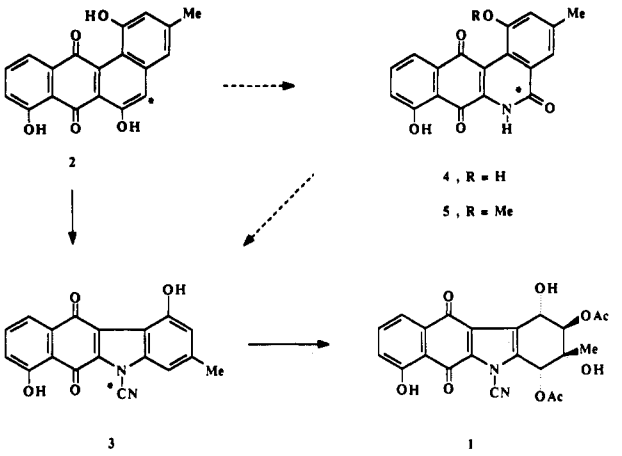
Scheme I



$(CF_3CO)_2O$ at 23 °C gave antibiotic WS 5995 A (7)[23] in quantitative yield,[9] while reaction with $[Me_3O]BF_4$[25] in THF at 23 °C gave known ester 16[9b] in 76% yield.

Finally, with a concise synthesis of 16 in hand, the conversion into 4 was readily accomplished by reaction with aqueous NH_4OH in MeOH under reflux for 48 h to give 5 in 55% yield,[26] followed by demethylation with BBr_3 in CH_2Cl_2 at −78 °C (47%).[26] This described method should be also useful for the preparation of related natural products such as the gilvocarcins, which contain the reduced 2-arylnaphthalene nucleus.[27] Further work directed toward the synthesis of prekinamycin and related targets is in progress.

Acknowledgment. We are grateful to the DGICYT (Project PB87-0201-C03-02), the SEUI (Project 87-090), and the CSIC for support of this work. N.T. acknowledges the receipt of a predoctoral fellowship by the Ministerio de Educación y Ciencia.

Supplementary Material Available: Characterization data for all new compounds and ^1H NMR spectra for 4, its diacetate, and 5 (10 pages). Ordering information is given on any current masthead page.

(25) Methylation with diazomethane in MeOH–Et_2O as previously reported[9a,b] was difficult to reproduce and gave 16 in lower yields.

(26) The yields were determined after acetylation (Ac_2O, cat. H_2SO_4, 23 °C, 2 h) of very insoluble benzo[*b*]phenanthridinones 4 and 5. Saponification (aqueous Na_2CO_3–MeOH, 23 °C) afforded pure 4 or 5 in quantitative yield.

(27) For recent lead references on the synthesis of these family of natural products, see: (a) Kwok, D.-I.; Farr, R. N.; Daves, G. D. *J. Org. Chem.* **1991**, *56*, 3711. (b) Parker, K. A.; Coburn, C. A. *J. Org. Chem.* **1991**, *56*, 1666. (c) Hua, D. H.; Saha, S.; Maeng, J. C.; Bensoussan, D. *Synlett* **1990**, 233.

An Unusual γ-Silyl Effect in $TiCl_4$-Catalyzed Arylation of 1,4-Benzoquinones

Thomas A. Engler* and Jayachandra P. Reddy

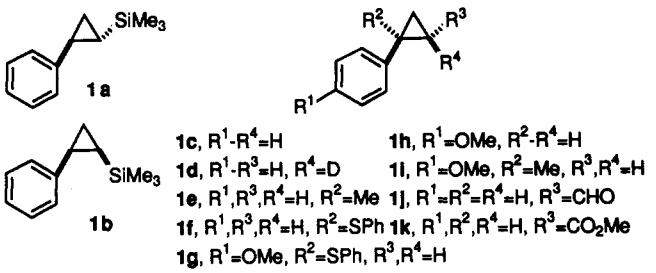
Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

Received August 9, 1991

Summary: Cyclopropylbenzene (1c) reacts with 2-methoxy-1,4-benzoquinone in the presence of $TiCl_4$ to give 2-(4′-cyclopropylphenyl)-5-methoxy-1,4-benzoquinone in moderate yield (46%). Considerable improvement in yield (69%) is observed in reactions of *trans*-2-phenyl-1-(trimethylsilyl)cyclopropane (1a) with the $TiCl_4$–quinone complex.

The effects of α- and β-silicon substitution on the control and rates of formation of carbocation centers has been well-documented; α-trimethylsilyl (TMS) groups retard, relative to C, and β-TMS groups dramatically accelerate solvolytic generation of carbocations.[1] There have been fewer demonstrations of the effects of silicon substituents γ to carbocation centers; however, the effects in terms of solvolysis rates are impressive in some cases (>10^4).[1,2] To date, reports of the γ-Si effect have been limited largely to studies of the rates of solvolysis of structurally well-defined esters and sulfonates. Herein, we report one of only a few examples of the utilization of the γ-Si effect as a control element in synthesis; in this case involving a Ti(IV)-mediated arylation of 1,4-benzoquinones.[3]

We prepared a number of substituted cyclopropanes 1 and studied their Lewis acid catalyzed reactions with 2-methoxy-1,4-benzoquinone, 2. The $TiCl_4$-promoted reaction of cyclopropanes 1a and 1c with quinone 2 at −78 °C



gave 7a and 8 in 69% and 46% isolated yields, respectively (Table I and Scheme I). The products 7a/8 apparently result from electrophilic aromatic substitution on the phenyl ring of 1a/c by the Ti(IV)-bound quinone complex 3 to give 5 which then undergoes oxidation by additional Ti(IV)–quinone complex 3[4] to yield 7a/8 and 2-methoxy-

(1) (a) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. For a listing of reviews of synthetic applications arising from these effects, see: (b) Larson, G. L. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; John Wiley and Sons, 1989; Vol. 1, Chapter 11. (c) See also: Bassindale, A. R.; Taylor, P. G. In ref 1b, Chapter 14.

(2) (a) Shiner, V. J., Jr.; Ensinger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842. (b) Davidson, E. R.; Shiner, V. J., Jr.; *J. Am. Chem. Soc.* **1986**, *108*, 3135. (c) Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804. (d) Bentley, T. W.; Kirmse, W.; Llewellyn, G.; Söllenböhmer, F. *J. Org. Chem.* **1990**, *55*, 1536. (e) Kirmse, W.; Söllenböhmer, F. *J. Am. Chem. Soc.* **1989**, *111*, 4127. (f) Grob, C. A.; Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502. (g) DeLucca, G.; Paquette, L. A. *Tetrahedron Lett.* **1983**, 4931.

(3) (a) During the preparation of this manuscript, a report on the effects of γ-Si substituents in Nef reactions appeared: Hwu, J. R.; Gilbert, B. A. *J. Am. Chem. Soc.* **1991**, *113*, 5917. (b) See also Davey, A. E.; Parsons, A. F.; Taylor, R. J. K. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1853.

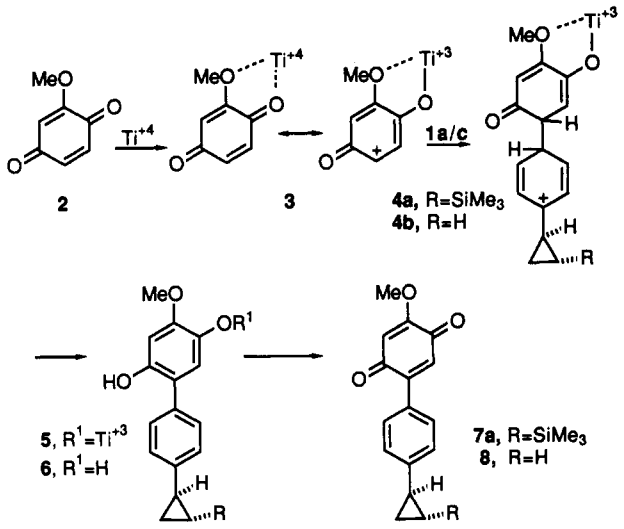
0022-3263/91/1956-6491$02.50/0

Table I. $TiCl_4$-Promoted Reactions of 2-Methoxy-1,4-benzoquinone with Mixtures of Cyclopropane 1a and Various Substituted Benzenes[a]

entry	coreactants	product(s) (% yields)[b]
1	1a only	7a (69)
2	1a:1b	7a (63)[c]
3	1a:1c	7a (48) + 8 (10)
4	1c only	8 (46)
5	1a:benzene	7a (54)
6	1a:toluene	7a (54)
7	1a:9a	7a (33)[d,e] + 10 (48)[e]
8	1a:9b	7a (61)
9	1a:anisole	11 (90)

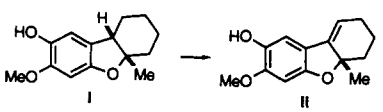
[a] A 2:2:1:1 ratio of $TiCl_4$–quinone 2–cyclopropane 1a–coreactant was employed in these reactions; in each case, a mixture of the coreactants in CH_2Cl_2 was added to a solution of $TiCl_4$ and quinone 2 in CH_2Cl_2 at −78 °C and the mixture stirred for 15 min followed by aqueous workup. [b] Isolated yields. [c] 100% of starting 1b was recovered in this experiment. [d] 50% of starting 1a was recovered in this experiment. [e] The ratio 7a:10 was determined by ^1H NMR.

Scheme I



hydroquinone[5] or undergoes protonolysis followed by oxidation of the resultant hydroquinone 6 on aqueous workup and purification. Evidence that the Ti(IV)–quinone complex 3 directly oxidizes 5 (or 6) in situ[4] comes from the stoichiometry of the reaction: 2 equiv of $TiCl_4$ and quinone 2, with respect to cyclopropanes 1a/c, are required to obtain good yields of 7a/8. Reaction of the *cis*-(trimethylsilyl)cyclopropane 1b is far less efficient; 7b is obtained on reaction with 2 equiv of the Ti(IV)–quinone complex 3 upon warming the reaction from −78 to −20 °C over 9 h, although a much lower yield (12%) is found. None of the other cyclopropanes reacted with the quinone in the presence of $TiCl_4$, mixtures of $TiCl_4$ and $Ti(OiPr)_4$, R_2AlCl (R = Cl or Et), $BF_3{\cdot}Et_2O$ or $ZnBr_2$ to give products in appreciable yields.

(4) In other studies we have found the $TiCl_4$–2 complex to be quite an effective oxidant. For example, dihydrobenzofuran i is oxidized to ii in 93% yield upon treatment with the $TiCl_4$–2 complex in CH_2Cl_2 at −78 °C followed by warming to room temperature: Naganathan, S. Unpublished results (see Naganathan, S. M.S. Thesis, University of Kansas, 1990).

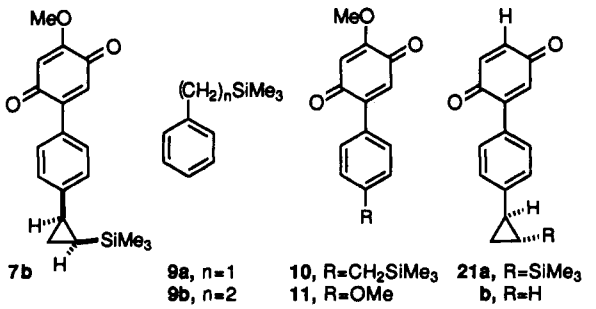


(5) 2-Methoxyhydroquinone is not isolated but reverts to starting 2 on separation from 7a/8 by silica gel chromatography.

Table II. Relative Rates of Solvolysis of γ-TMS Sulfonates and Trifluoroacetates

entry	comparative substrates			ref
1	Me3C, OBs (12)	Me3Si, OBs (13)		
	k_{rel} 1	~450		2a
2	Me3C, OBs	Me3Si, OBs		
	k_{rel} 1	~1		2a
3	OMs (14)	Me3Si, OMs (15)	Me3Si, OMs (16)	
	k_{rel} 1	~10^4	~50	2d
4	$CH_2OC(O)CF_3$ (17)	$CH_2OC(O)CF_3$, SiMe3	Me3Si, $CH_2OC(O)CF_3$ (18)	
	k_{rel} 1	~27	~25	2g
5	$Me_3CCH_2CH_2CH_2OBs$ (19)	$Me_3SiCH_2CH_2CH_2OBs$ (20)		
	k_{rel} 1	~130		2c

The higher yield found in reactions of 1a may be due to stabilization of the carbocation center in the presumed intermediate 4a by interaction with the γ-silicon–carbon bond. To ensure that cyclopropanes 1a–c were subjected to reaction with 2 under the same conditions, competition experiments involving the reaction of 2 equiv of the Ti(IV)–quinone complex 3 with 2 equiv of a 1:1 mixture of silylcyclopropane 1a and 1b or c were studied (Table I, entries 2–3). Reactions of silane 9b with 2 were also examined (entry 8). In each of these reactions, the major product was 7a; no products from 1b or 9b were isolated and only small amounts of 8 were found in reactions involving the mixture of 1a/c. The formation of 8 in entry 3 results from reaction of 1c and not from desilylation of 1a or 7a.[6a] This was demonstrated by reaction of a mixture of 1a and deuteriocyclopropane 1d[6b] with 3; the product quinone 8 contained the same amount of deuterium as in starting 1d. Reactions of 3 with silane 9b without 1a present also failed to produce a 1:1 adduct even upon warming the reaction mixture to room temperature.



These results establish that the TMS group in 1a enhances the rate of the reaction with complex 3, and the

(6) (a) Electrophilic desilylation reactions of silylcyclopropanes with retention of the 3-membered ring have been reported, see references cited in: Paquette, L. A. *Chem. Rev.* **1986**, *86*, 733. (b) Prepared in 71% yield from *cis*-2-bromo-1-phenylcyclopropane by the sequence (1) *t*-BuLi/TMEDA/Et_2O, −78 °C → ~−45 °C; (2) D_2O. The % D content both in 1d and in the product 8 (R = D) was estimated at 84% by NMR spectroscopy.

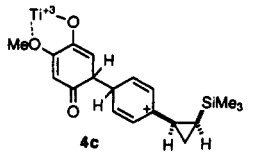
failure of **9b** to react suggests that the reactivity is not due to a "simple" γ-silicon effect. The role of the cyclopropyl group is presumably to properly position the γ-Si–C bond for interaction with the carbocation center **4a**. For comparison, representative relative rate data from solvolysis of several γ-TMS sulfonates and trifluoroacetates are shown in Table II.[2] The most dramatic rate accelerations are found in ring systems in which the back lobe of the C–Si bond is locked into a position pointing toward the back of the C–O bond undergoing cleavage (entries 1,3). Theoretical calculations on the 3-silylpropyl cation, $H_3SiCH_2CH_2CH_2^+$, show a strong geometric preference for stabilization favoring a "W" conformation in which the silyl group is antiperiplanar to the C_α–C_β bond and the plane of the carbocation moiety is perpendicular to the Si–C_γ–C_β–C_α mirror plane (a trans perpendicular conformation).[2b] A strong inductive effect of the Si on the γ-CH_2 is also indicated which results in a tendency of the negative γ-CH_2 to bond to the carbocation center. As a result, the C_γ–C_α distance is very short (1.75 Å) in the optimized structure. It has been suggested that this "hyperconjugative effect" should have an influence on the carbocation center as long as C_γ is close to C_α.[2b] A close match to the trans perpendicular orientation is found in the cation resulting from norbornyl system **15** (Table II, entry 3). However, the geometry about the C_1–C_2–C_3–Si portion of the 3-(trimethylsilyl)cyclohexyl cation (from **13**, Table II, entry 1) deviates significantly from a trans perpendicular arrangement in that the dihedral angle between a plane containing the p orbital of the carbocation, and a plane roughly containing C_1–C_2–C_3–Si is ~40°.[7a] This deviation may account for the smaller acceleration found in **13** vs **12** in comparison to that found in **15** vs **14**. The smaller acceleration in **20** vs **19** in comparison to **15** vs **14** may be due to unfavorable entropic factors. Nevertheless, the data from **13** vs **12** indicate that an ideal trans perpendicular orientation is not required, and considerable rate acceleration is still found in systems which cannot adopt a perfect trans-perpendicular geometry.

In **4a** and in the cyclopropylcarbinyl cation resulting from **18**, the back lobe of the Si–C bond can be pointed toward the p orbital of the carbocation center providing stabilization.[7b] Thus, the role of the cyclopropyl moiety in **4a** may be to restrict conformational flexibility and hold the back side of the C–Si bond near C_α.[9] A comparative study of the solvolysis of the cyclopropyl carbinyl systems **17**/**18** relative to the open chain systems **19**/**20** may be informative in this regard.[8,9]

To gain insight on the enhanced reactivity of the phenyl ring in **1a** relative to other aromatic systems, competition experiments involving the reactions of the $TiCl_4$–quinone complex **3** with 1:1 mixtures of cyclopropane **1a** and benzene, toluene, anisole, and silane **9a** were also conducted (Table I, entries 5–9). The results indicate that the *trans*-2-(trimethylsilyl)cyclopropyl group activates the ring to a greater extent than H, CH_3, $Me_3SiCH_2CH_2$, or cyclopropyl, comparable to Me_3SiCH_2, but not as much as OCH_3.[10]

Reactions of benzyltrimethylsilane (**9a**) and anisole with the $TiCl_4$–**2** complex in the absence of **1a** give **10** and **11**[11c] in 61% and 73% isolated yields, respectively. 1,4-Benzoquinone does react with cyclopropane **1a**/**c** in the presence of $TiCl_4$, and although the yields (as yet unoptimized) of the products **21a**/**b** are low (22% and 7%, respectively), the trend is the same as with quinone **2**. The reactions described herein represent a new method for selective arylation of 2-methoxy-1,4-benzoquinone.[11] In addition, because of the synthetic utility of the TMS,[1] TMS-cyclopropyl[6a] and quinone[11d] moieties, these reactions should also be useful for preparation of unsymmetrically substituted biaryls.[12] Finally, the results also demonstrate that properly positioned γ-Si substituents can be used to

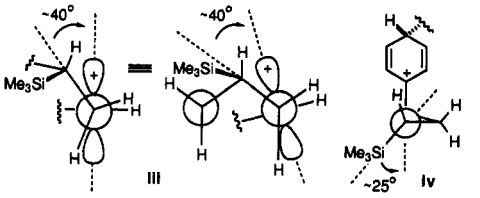
(7) (a) Estimated from examination of Drieding models. Two representations looking down the C_1–C_2 bond in the 3-(trimethylsilyl)cyclohexyl cation are shown in structure iii. (b) Ideal trans-perpendicular arrangement of the Si-C_γ-C_β-C_α^+ unit is not possible in **4a**, although the deviation from the preferred geometry appears to be less than in the 3-(trimethylsilyl)cyclohexyl carbocation. The dihedral angle formed between a plane containing the Si and C_1/C_2 of the cyclopropane in **4a** and a plane containing C_1/C_2 of the cyclopropane and the C^+ is estimated to be ~25°; see structure iv.



4c

(8) The enhanced rate of solvolysis of *cis*-[2-(trimethylsilyl)cyclopropyl]methyl trifluoroacetate (k = 45 relative to **17**) has been attributed to probable ground-state strain, see ref 2g.

(9) Stabilization by the back lobe of the Si–C bond is not possible with the intermediate **4c** which results from reaction of **1b**. The relatively mild rate acceleration found in solvolysis of *endo*-6-(trimethylsilyl)-*exo*-2-norbornyl mesylates (Table II, entry 3) is probably due again[8] to ground-state strain.



(10) Partial rate factors from protiodetritiation experiments show a relative activating trend of $TMSCH_2$– (f_p = 8.2 × 10^4) ≫ $TMSCH_2CH_2$– (f_p = 810) > CH_3 (f_p = 450) > H (f_p = 1); see data reproduced in ref 1c. In addition, the cyclopropyl group activates an aromatic ring to electrophilic substitution reactions to a greater extent than a CH_3 group.

(11) (a) Itahara, T. *J. Org. Chem.* **1985**, *50*, 5546. (b) Choudary, B. M. *Ind. J. Chem.* **1986**, *25B*, 1159. (c) Arylation of 1,4-benzoquinones by reaction with aromatic systems is accomplished with protic acid or $AlCl_3$; for leading references, see: Buchan, R.; Musgrave, O. C. *J. Chem. Soc., Perkin Trans. I* **1975**, 2185 and previous papers in this series. A survey of these reactions reveals that many times mixtures of mono- and isomeric diarylated quinones are produced in highly variable yields. The preparation of 2,5-diarylquinones by $AlCl_3$-catalyzed reactions of aromatics with 1,4-benzoquinone was first reported by Pummerer (Pummerer, R.; Dally, M.; Reissinger, S. *Chem. Ber.* **1933**, *66*, 793 and previous papers in this series). For a summary of other methods for arylation of quinones, see (d) Finley, K. T. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1988; Vol. 2, Part 1, p 537 and 1974; Vol. 1, Part 2, p 877 and references cited therein. Again, with substituted quinones, many of these methods give mixtures of isomeric arylated quinones in low to moderate yields. See also: (e) Cameron, D. W.; Feutrill, G. I.; Patti, A. F.; Perlmutter, P.; Sefton, M. A. *Aust. J. Chem.* **1982**, *35*, 1501. For reviews on naturally occurring aryl quinones, see: (f) Thomson, R. H. *Naturally Occurring Quinones-III*; Chapman and Hall: New York, 1987. (g) Gill, M.; Steglich, W. *Prog. Chem. Org. Nat. Prod.* **1987**, *51*, 1. (h) Pattenden, G. *Ibid.* **1978**, *35*, 133.

(12) For a recent review and leading references on the synthesis, uses and biological activity of biaryls, see: (a) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977. (b) Yogo, M.; Ito, C.; Furukawa, H. *Chem. Pharm. Bull.* **1991**, *39*, 328. (c) Fu, J.-m.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665. (d) Manthey, M. K.; Pyne, S. G.; Truscott, R. J. W. *J. Org. Chem.* **1990**, *55*, 4581. (e) Iihama, T.; Fu, J.-m.; Bourguignon, M.; Snieckus, V. *Synthesis* **1989**, 184. (f) Tilley, J. W.; Clader, J. W.; Zawoiski, S.; Wirkus, M.; LeMahieu, R. A.; O'Donnell, M.; Crowley, H.; Welton, A. F. *J. Med. Chem.* **1989**, *32*, 1814. (g) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989**, 1711. (h) Huth, A.; Beetz, I.; Schumann, I. *Tetrahedron* **1989**, *45*, 6679. (i) Petrillo, G.; Novi, M.; Dell'Erba, C. *Tetrahedron Lett.* **1989**, 6911. (j) Finet, J.-P. *Chem. Rev.* **1989**, *89*, 1487. (k) Negishi, E.; Takahashi, T.; King, A. O. *Organic Synthesis* **1987**, *66*, 67. (i) Harusawa, S.; Miki, M.; Hirai, J.-i.; Kurihara, T. *Chem. Pharm. Bull.* **1985**, *33*, 899. See also refs 11f–h.

enhance reactions in systems in which the unsubstituted analogs perform in mediocre fashion.

Acknowledgment. This research was supported financially by the National Institutes of Health (GM 39820). T.A.E. acknowledges a granteeship from Eli Lilly and Company and a fellowship from the Alfred P. Sloan Foundation.

Supplementary Material Available: Spectral data and experimental procedures for the preparation of **1a/b, 7a/b, 8, 10, 11**; ^1H and ^{13}C NMR spectra of **1a/b** (and their bromocyclopropane precursors), **7a/b, 8, 10, 11**, and **21a**; experimental procedures for the competition experiments; and summaries of NOE data for **1a/b** and their bromocyclopropane precursors (31 pages). Ordering information is given on any current masthead page.

Transmetalation Reactions of Alkylzirconocenes: Copper-Catalyzed Conjugate Addition to Enones

Peter Wipf* and Jacqueline H. Smitrovich

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

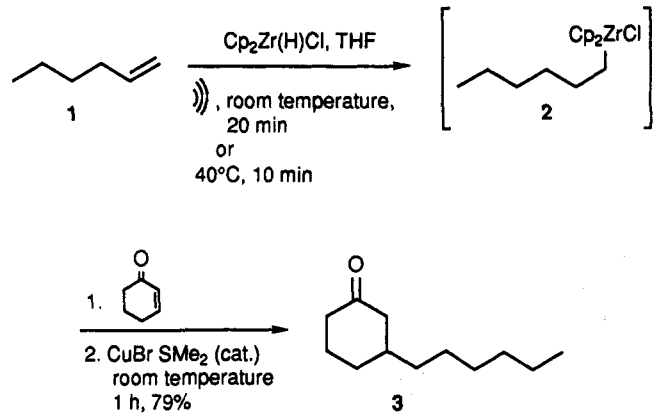
Received August 23, 1991

Summary: Rapid hydrozirconation of alkenes by zirconocene hydrochloride, followed by addition of 1 equiv of enone and catalytic amounts of Cu(I) salts, led to the corresponding 1,4-addition products in moderate to high yields and provided the first protocol for in situ preparation of alkyl cuprates from alkenes.

Organocuprates are among the most versatile organometallic derivatives applied in organic synthesis. However, most of the ligands that are transferred via both higher and lower order cuprates originate from organolithium or organomagnesium species.[1] The involvement of highly reactive and strongly basic first- and second-column derivatives in the preparation of cuprates complicates the experimental protocol and limits the range of functionality that is tolerated in the starting material. Therefore, alternative preparations of copper complexes that do not originate in alkyl or alkenyl halides considerably extend the synthetic scope of organocopper chemistry beyond present limitations. In a preliminary study, we have shown that *alkenyl* alanes undergo an in situ exchange process with a bisalkynylcopper complex.[2] As precursors to *alkyl* cuprates, however, we considered zirconium derivatives, because alkylzirconocenes are easily prepared by treatment of alkenes with zirconocene hydrochloride ($Cp_2Zr(H)Cl$,[3] Schwartz Reagent).[4,5]

Contrary to previous observations,[5a,6] addition of 0.10 equiv of $CuBr \cdot SMe_2$ to a solution of 1 equiv of 1-hexylzirconocene (**2**) and 2-cyclohexenone in THF led to rapid 1,4-addition. After the reactants were stirred at room temperature for 1 h, product **3** was isolated in 79% yield. Commercially available[7] $Cp_2Zr(H)Cl$ was used for the preparation of zirconocene reagent **2** from 1-hexene (**1**). Sonication or warming of the reaction mixture to 40 °C considerably increased the rate of hydrozirconation of alkenes.[8,9]

Scheme I



Besides $CuBr \cdot SMe_2$, other Cu(I) and Cu(II) salts such as CuBr, CuI, CuCN, $(C_4H_9C_2)_2CuCNLi_2$, $Cu(acac)_2$, and $Cu(OTf)_2$[10] catalyzed the 1,4-addition of zirconocene **2** to cyclohexenone, presumably via a transmetalation process related to the Cu(I) catalyzed 1,4-addition of Grignard reagents to α,β-unsaturated carbonyl compounds.[11,12]

Table I shows the results of the initial investigation of the scope of this novel in situ transmetalation and conjugate addition process.[13,14] As expected,[3] hydrozirconation

(1) (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980 (c) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (d) Lipshutz, B. H. *Synthesis* **1987**, 325. (e) Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225.

(2) (a) Ireland, R. E.; Wipf, P. *J. Org. Chem.* **1990**, *55*, 1425. (b) Wipf, P.; Moon, C.-W.; Smitrovich, J. H. Manuscript in preparation.

(3) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115.

(4) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd.: New York, 1986.

(5) For preparation and use of *alkenyl*zirconocenes, see: (a) Yoshifuji, M.; Loots, M.; Schwartz, J. *Tetrahedron Lett.* **1977**, 1303. (b) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. (c) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (d) Negishi, E.; Swanson, D. R.; Miller, S. R. *Tetrahedron Lett.* **1988**, *29*, 1631. (e) Lipshutz, B. H.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 7440. (f) Babiak, K. A.; Behling, J. R.; Dygos, J. H.; McLaughlin, T. K.; Ng, J. S.; Kalish, V. J.; Kramer, S. W.; Shone, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 7441.

(6) *Alkyl* groups did not transmetalate from Zr to Cu(I) under the conditions reported by Schwartz and co-workers for *alkenyl*zirconocenes.[5a] The significant decrease in reactivity from alkenyl- to alkylzirconocenes is likely due to the superior bridging capabilities of systems with π-bonds adjacent to the metal–carbon bond, which increase transferability; see: (a) Negishi, E. I. *Pure Appl. Chem.* **1981**, *53*, 2333. (b) Zweifel, G.; Miller, J. A. *Org. React.* **1984**, *32*, 375. (c) Alexakis, A.; Hanaizi, J.; Jachiet, D.; Normant, J.-F.; Toupet, L. *Tetrahedron Lett.* **1990**, *31*, 1271.

(7) Aldrich Co., Milwaukee, WI, and Alfa Products, Ward Hill, MA. Material from several different batches of Schwartz's reagent obtained from these companies was used and gave consistent results throughout this study.

(8) Bremner, D. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; J. Wiley & Sons: New York, 1989; Vol. 5, p 3.

(9) Hydrozirconation of unfunctionalized alkenes with $Cp_2Zr(H)Cl$ proceeds slowly at room temperature in aprotic solvents: Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 638.

(10) At present time, we are unable to decide if indeed it is Cu(II) that catalyzes this process (see, for example: Sakata, H.; Aoki, Y.; Kuwajima, I. *Tetrahedron Lett.* **1990**, *31*, 1161), or if, more likely, the Cu(II) salt is rapidely reduced to Cu(I) by excess alkylzirconocene.

(11) Beard, C.; Wilson, J. M.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc.* **1964**, *86*, 269.

(12) In the absence of copper salts, no reaction between alkylzirconocene and enone was detected.

0022-3263/91/1956-6494$02.50/0