carbazone deriv), 117604-62-3; **7**, 117527-63-6; **8**, 117604-61-2; cyclopentadiene, 542-92-7.

Supplementary Material Available: Computer-drawn structures of **7** and **8** and tables of atomic coordinates, bond lengths and angles, and displacement parameters (11 pages). Ordering information is given on any current masthead page.

Preparation of Hindered Styrenes and Arylacetylenes

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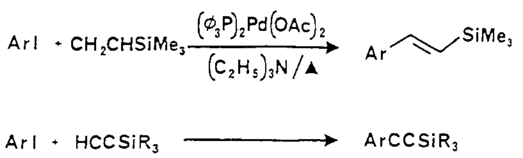
In connection with an approach to the synthesis of colchicine,[2] we required hindered, electron-rich styrenes and arylacetylenes such as **2**, **3**, and **5**. Recent reports by Karabelas and Hallberg[4] and by Stille et al.[5] prompt us to report our observations during the preparation of **2**, **3**, and **5**.

The preparation of simple styrenes and arylacetylenes is fraught with potential difficulties that have been previously discussed.[3-6] Furthermore, metal-catalyzed coupling reactions are often prevented by steric hinderance. These problems can be avoided by treatment of an aryl iodide[6] with vinyltrimethylsilane, catalytic palladium diacetate, and triphenylphosphine in refluxing triethylamine (Scheme I). From **1**, styrene **2** was formed in 93% isolated yield. This procedure is essentially that reported by Lau et al.[6] for the preparation of arylacetylenes. Iodide **1** was also converted into acetylenes **3a–c** with these conditions. (**3a**, >90% yield; **3b**, 92% yield; and **3c**, 95% yield, Table I).

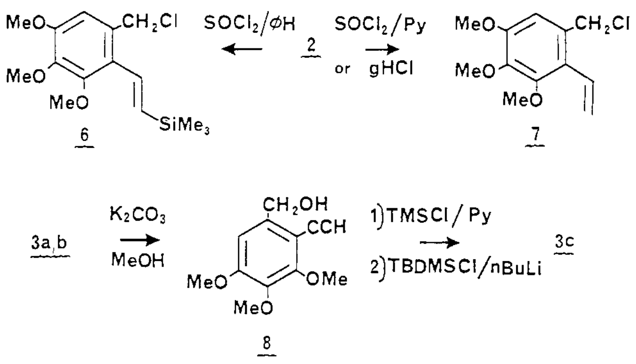
Conversion of malonate **4**[8] into styrene **5** (69% yield) required added cuprous iodide and reflux for 10 days. All TMS styrenes were exclusively the *E* isomer. Purification was effected by removal of the salts by filtration, by evaporation of the solvent, and by distillation of the residue in a Kugelrohr apparatus or filtration of the residue through silica gel. Unfortunately, the bromide corresponding to iodide **1** did not react with vinyltrimethylsilane under a variety of conditions with palladium(II) catalysts.

Removal of the silyl groups proceeded as expected to provide unsubstituted styrenes and acetylenes. The transformation of **2** into **6** could be accomplished by treatment with HCl gas (Scheme II). Exposure of **2** to thionyl chloride/pyridine also gave chloride **6**, while omission of pyridine afforded the benzyl chloride **7**. The silyl group of **3a,b** was readily cleaved with K_2CO_3 in methanol to yield **8**, which in turn could be transformed into **3c**.

Scheme I



Scheme II



This procedure for aryl substitution offers advantages over the recently published ones.[3-6] The aryl halide can be hindered and still yield the desired product, albeit slowly. This process can be used to prepare styrenes containing electron-donating groups. This procedure uses stable, readily available palladium(II) catalysts and does not require additional oxidants, such as silver. All reagents except the aryl iodide are commercially available. The byproducts of the reaction mixture are easy to remove. The requirement for an aryl iodide rather than a bromide may be a disadvantage in certain instances, but could permit selectivity. This method is an alternative to Stille's styrene synthesis,[5] which effects net direct displacement of tin in a vinyltin reagent. We believe this procedure offers a reasonable alternative for the preparation of certain hindered styrenes and arylacetylenes.

Experimental Section[9]

(*E*)-3,4,5-Trimethoxy-2-[2-(trimethylsilyl)ethenyl]benzenemethanol (2a). Palladium acetate, 0.0538 g (2.40×10^{-4} mol, 2.2 M %), was added to a room-temperature solution containing 2.40 g (2.40×10^{-2} mol, 220 M %) of vinyltrimethylsilane, 0.1164 g (4.44×10^{-4} mol, 4.1 M %) of triphenylphosphine, and 3.55 g (1.10×10^{-2} mol, 100 M %) of the iodide **1a**[7] in 25 mL of deaereated triethylamine. The reaction was then heated at reflux under argon for 3 days. The reaction yielded 3.01 g of 93% yield of (*E*)-styrene (**2a**) after workup: IR 3600–3200, 2950, 1590, 1490, 1400, 1330, 1245, and 1120 cm^{-1}; NMR δ 0.18 (s, 9 H), 3.68 (s, 3 H), 3.78 (s, 6 H), 4.67 (2, 2 H), 6.13 (d, $J \sim 20$ Hz, 1 H), 6.83 (s, 1 H), and 7.92 (d, $J \sim 20$ Hz, 1 H); mass spectrum, m/z 296 (M$^+$).

The styrene **2a** converted to bis(β,β,β-trichloroethyl) [(2-ethenyl-3,4,5-trimethoxyphenyl)methyl]propanedioate by sequential treatment with thionyl chloride to provide **3b**, which was reacted with bis(β,β,β-trichloroethyl) propanedioate. This compound was identical with material prepared by an alternate route.[10]

The silyl ether **1b** was converted into the silyl ether **2b**. From 0.113 g (5.05×10^{-5} mol, 2 M %) of palladium(II) acetate, 1.00 g (2.53×10^{-3} mol, 100 M %) of the aryl iodide **1b**, 0.38 g (3.79×10^{-3} mol, 150 M %) of vinyltrimethylsilane, and 0.0245 g (9.34×10^{-5} mol, 3.7 M %) of triphenylphosphine in 6 mL of triethylamine, at reflux for 2 days, 0.86 g (93% yield) of the (*E*)-styrene **2b** was isolated: NMR δ 2.00 (s, 18 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 4.67 (s, 2 H), 6.14 (d, $J \sim 20$ Hz, 1 H), 6.86

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[2] (a) Taken from the Ph.D. Thesis of Bill J. McBride, University of California, San Diego, 1984. (b) Garst, M. E.; McBride, B. J. Abstract no. 49, Organic Division; 192nd American Chemical Society Meeting, Anaheim, CA, 1986.

[3] (a) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985. (b) Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691.

[4] Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286–5290 and references cited therein.

[5] (a) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422–424. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478–5486.

[6] Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280–2286.

[7] Ziegler, F. E.; Schwartz, J. A. *J. Org. Chem.* **1978**, *43*, 985–991.

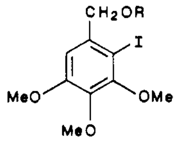
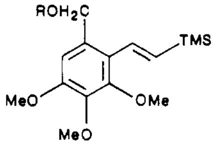
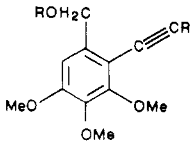
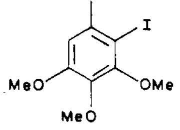
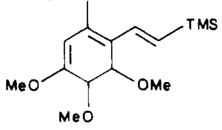
[8] Prepared from iodide 4 by sequential treatment with thionyl chloride and di-*tert*-butyl malonate (see ref 2a).

[9] See: Garst, M. E.; Frazier, J. D. *J. Org. Chem.* **1987**, *52*, 446–448 for general experimental details.

[10] Prepared from bis(β,β,β-trichloroethyl) 3,4,5-trimethoxybenzylpropanedioate by formylation with dichloromethyl methyl ether and stannic chloride followed by Wittig olefination (see ref 2a).

0022-3263/89/1954-0249$01.50/0

Table I

entry	aryl iodide	product	method	yield, %
1	 **1a**: R = H	 **2a**: R = H	*a*	93
2	**1b**: R = TMS	**2b**: R = TMS	*a*	93
3	**1a**	 **3a**: R = H; R′ = TMS	*b*	90
4	**1b**	**3b**: R = R′ = TMS	*b*	92
5	**1b**	**3c**: R = TMS; R′ = TBDMS	*c*	95
6	 **4**	 **5**	*d*	69

Z = COOtBu

[a] Pd(OAc)$_2$, Ph$_3$P, (CH$_3$CH$_2$)$_3$N, CH$_2$CHTMS, Δ, 2 days. [b] Pd(OAc)$_2$, Ph$_3$P, CHCTMS, (CH$_3$CH$_2$)$_3$N, Δ, 2 days. [c] Pd(OAc)$_2$, Ph$_3$P, CHCTBDMS, (CH$_3$CH$_2$)$_3$N, Δ, days. [d] Pd(OAc)$_2$, Ph$_3$P, CH$_2$CHTMS, (CH$_3$CH$_2$)$_3$N, CuI, Δ, 6 days.

(s, 1 H), and 6.95 (d, $J \sim 20$ Hz, 1 H).

2-[2-(Trimethylsilyl)ethynyl]-3,4,5-trimethoxybenzenemethanol (3a). Palladium(II) acetate, 0.0063 g (2.8×10^{-5} mol, 5.6 M %), was added to a room temperature solution containing 0.0126 g (4.80×10^{-5} mol, 9.5 M %) of triphenylphosphine, 0.07 g (8×10^{-4} mol, 1.5 M %) of (trimethylsilyl)acetylene, and 0.20 g (5.05×10^{-4} mol, 100 M %) of the aryl iodide **1a** in 5.0 mL of dry, degassed triethylamine. The reaction mixture was then heated at reflux for 2 h. Over the course of the reaction, a black precipitate of triethylammonium iodide was formed. The reaction was processed to give the product **3a** cleanly and in high yield, >90%: IR 3750–3300 (broad), 2980, 2140, 1600, 1500, 1470, 1410, 1335, 1250, 1195, and 1130 cm^{-1}; NMR δ 0.27 (s, 9 H), 3.82 (s, 3 H), 3.85 (s, 3 H), 3.94 (s, 3 H), 4.72 (brs, 2 H), and 6.78 (s, 1 H); mass spectrum, *m/z* 294 (M$^+$).

The silyl ether **3b** was prepared from the ether **1b** as follows: 5.62 g (1.42×10^{-2} mol, 100 M %) of iodide **1b**, 0.0639 g (2.85×10^{-4} mol, 2 M %) of palladium(II) acetate, 0.1270 g (4.84×10^{-4} mol, 3.4 M %) of triphenylphosphine, 2.10 g (2.14×10^{-2} mol, 130 M %) of (trimethylsilyl)acetylene, and 30 mL of triethylamine was refluxed for 4.5 h, cooled to room temperature, poured into 100 mL of anhydrous ether, and filtered through Celite. The crude product was distilled in a Kugelrohr oven 60 °C under high vacuum (~0.05 mmHg) to give 4.78 g (92% yield) of the TMS ether **3b**: IR 2960, 2150, 1595, 1485, 1455, 1405, 1330, 1250, 1195, and 1130 cm^{-1}; NMR δ 0.20 (s, 9 H), 0.28 (s, 9 H), 3.82 (s, 3 H), 3.88 (s, 3 H), 3.96 (s, 3 H), 3.78 (s, 2 H), and 6.87 (s, 1 H); mass spectrum, *m/z* 366 (M$^+$).

2-[2-[(1,1-Dimethylethyl)dimethylsilyl]ethynyl]-3,4,5-trimethoxybenzenemethanol TMS Ether (3c). Palladium(II) acetate, 0.0160 g (7.12×10^{-5} mol, 2 M %), was added to a room-temperature solution containing 0.0318 g (1.21×10^{-4} mol, 3.4 M %) of triphenylphosphine, ~0.54 g of (*tert*-butyldimethylsilyl)acetylene (3.9×10^{-3} mol, 110 M %), and 1.41 g (3.56×10^{-3} mol, 100 M %) of **1b** in 10 mL of degassed triethylamine. The reaction was then heated at reflux for 4 h. After the standard workup and distillation in a Kugelrohr oven, the reaction gave 1.38 g (95% yield) of the product **3c**: NMR δ 0.20 (s, 9 H), 0.22 (s, 6 H), 1.02 (s, 9 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 3.97 (s, 3 H), 4.80 (s, 2 H), and 6.89 (s, 1 H).

Alcohol **3b** was converted into the silyl ether **3c** by treatment with K$_2$CO$_3$ in methanol, which afforded **8**. Compound **8** was reacted with TMSCl–pyridine and then BuLi–TBDMSiCl to yield **3c**.

Bis(1,1-dimethylethyl) (*E*)-[[3,4,5-Trimethoxy-2-[2-(trimethylsilyl)ethenyl]phenyl]methyl]propanedioate (5). A solution containing 1.95 g (3.74×10^{-3} mol, 100 M %) of the iodomalonate **4**,[8] 0.0252 g (1.12×10^{-4} mol, 3 M %) of palladium(II) acetate, 0.0682 g (2.24×10^{-4} mol, 6 M %) of tri-*o*-tolylphosphine, 0.75 g (7.47×10^{-3} mol, 200 M %) of vinyltrimethylsilane, and 0.0249 g (1.31×10^{-4} mol, 3.5 M %) of cuprous iodide in 5.0 mL of triethylamine was heated to reflux under argon for 10 days. The reaction turned dark brown, and a precipitate was formed. After 2 days 5.0 mL of triethylamine was added. The crude reaction was placed in ~100 mL of anhydrous ether and filtered through silica (~10 g). The solvent was removed at reduced pressure to afford 1.27 g (69% yield) of styrene: IR 2970, 2935, 1725, 1595, 1490, 1455, 1370, and 1250 cm^{-1}; NMR δ 0.14 (s, 9 H), 1.41 (s, 18 H), 3.05–3.23 (m, 2 H), 3.28–3.45 (m, 1 H), 3.66–3.87 (m, 9 H), 6.26 (d, $J \sim 2$ Hz, 1 H), 6.52 (s, 1 H), and 6.85 (d, $J \sim 20$ Hz, 1 H); mass spectrum, *m/z* 494 (M$^+$).

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Registry No. **1a**, 64490-45-5; **16**, 117370-30-6; **2a**, 117370-31-7; **2b**, 117370-32-8; **3a**, 117370-33-9; **3b**, 117370-34-0; **3c**, 117370-35-1; **4**, 117407-47-3; **5**, 117370-36-2; **8**, 117370-37-3; vinyltrimethylsilane, 754-05-2; bis(β,β,β-trichloroethyl) [(2-ethenyl-3,4,5-trimethoxyphenyl)methyl]propanedioate, 117370-38-4; bis(β,β,β-trichloroethyl)propanedioate, 18833-38-0; (trimethylsilyl)acetylene, 1066-54-2; (*tert*-butyldimethylsilyl)acetylene, 86318-61-8.

Homochiral Ketals in Organic Synthesis. Diastereoselective Cyclopropanation of α,β-Unsaturated Ketals Derived from (*S*,*S*)-(−)-Hydrobenzoin[1]

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Not long ago we described a general and stereochemically predictable diastereoselective cyclopropanation of

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