UV (C_6H_{12}) 234 (ϵ 3200) and 257 (800); IR ($CHCl_3$) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, J = 6.6 Hz) and 1.49 (d, J = 6.6 Hz) (total 3 H, NCMe), 1.56 (d, J = 6.4 Hz) and 1.62 (d, J = 6.6 Hz) (total 3 H, 4-Me), 3.3-3.4 (m, 1 H, 3-CH), 3.8-3.9 (m, 1 H, 4-CH), 3.9-4.0 (m, 1 H, 3-CH), 4.0-4.1 (q, J = 6.6 Hz, 1 H, NCH) and 7.2-7.4 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 23.3 (q, NCMe), 23.3 (q, NCMe), 24.3 (q, 4-Me), 24.4 (q, 4-Me), 32.3 (d, 4-C), 32.4 (d, 4-C), 52.3 (t, 3-C), 62.8 (d, N-C), 62.9 (d, N-C), 126.7 (d, Ph), 126.9 (d, Ph), 128.3 (d, Ph), 144.2 (s, Ph), 144.3 (s, Ph), 155.6 (s, C=N) and 155.7 (s, C=N). Anal. Calcd for $C_{12}H_{15}NS$: C, 70.19; H, 7.36; N, 6.82. Found: C, 69.88; H, 7.28; N, 6.75.

***cis*-*N*-Benzylthiocinnamamide (cis-1i)**: mp 74-76 °C; UV (C_6H_{12}) 220 (ϵ 16500), 284 (15000), 296 (13700) and 310 (10000); IR ($CHCl_3$) 3350 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.72 (d, J = 5.5 Hz, 2 H, N-CH_2), 6.41 (d, J = 12.1 Hz, 1 H, 2-CH), 6.53 (d, J = 12.1 Hz, 1 H, 3-CH) and 7.2-7.4 (m, 11 H, 2 Ph and NH); ^{13}C NMR ($CDCl_3$) δ 49.9 (t, NC), 128.0 (d), 128.4 (d), 128.6 (d), 128.7 (d), 128.8 (d), 130.0 (d), 132.0 (d), 134.7 (s), 135.3 (s), 141.9 (d), and 196.5 (s, C=S). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.96; N, 5.52. Found: C, 75.61; H, 5.88; N, 5.49.

An Unusual Doubly Substituted Product from the Phase-Transfer-Catalyzed Heck Reactions of *o*-Bromobenzaldehydes with Methyl Acrylate

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The reactions of *o*-bromobenzaldehydes with methyl acrylate under Heck conditions and with phase-transfer catalysis to yield significant amounts of doubly substituted deformylated products **1A-E** in addition to the expected *o*-formyl cinnamates **2A-E** are reported. X-ray crystallography of one such product (**4**) established that the bromine was replaced by a propionate and the formyl group by an acrylate residue. Employment of deuterium-labeled substrates showed that the hydrogen atom of the formyl group of the substrate was transferred intramolecularly and regiospecifically to the benzylic carbon of the propionate substituent of the product. A tentative hypothesis is advanced to explain these and other experimental findings.

The Heck reaction[1] of aryl bromides and various alkenes is a versatile and valuable synthetic process. A recent popular modification[2] that gives better results with thermally labile substrates involves the addition of a phase-transfer catalyst. In attempting to employ these new conditions in the reaction of 6-bromoveratraldehyde with methyl acrylate in DMF and with tetrabutylammonium chloride as the phase-transfer reagent, we observed the formation of a significant amount of an anomalous product (**1C**) in addition to the expected cinnamate (**2C**) (Table I). We have investigated the reaction with several *o*-bromoaryl aldehydes to establish its generality and now report our results.

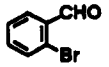
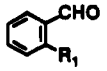
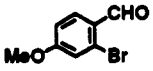
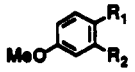
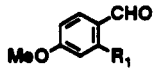
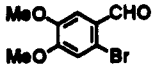
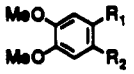
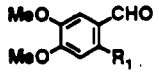
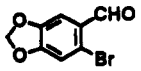
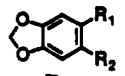
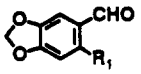
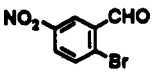
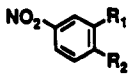
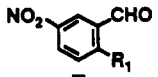
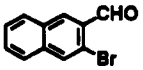
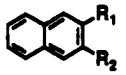
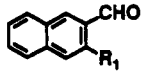
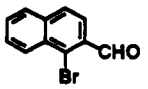
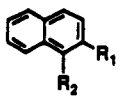
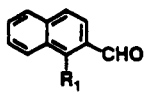
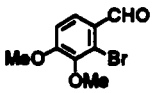
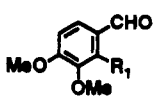
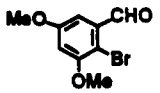
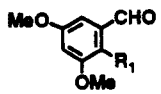
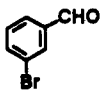
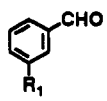
The reactions between ten bromoaldehydes and methyl acrylate were carried out under the general conditions described in the Experimental Section, with the results indicated in Table I. Total yields were moderate and very little of the bromoaldehyde substrate was recovered under these conditions. Polymerization of the methyl acrylate (employed in 5-fold excess) always took place and thin layer chromatograms of the reaction mixtures showed much streaking. The structures of the anomalous products were easily established by ^1H NMR, mass, and infrared data and confirmed in one instance (vide infra) by X-ray crystallography. The formation of **1** to any extent at all required (1) the aldehyde and bromine substituents to be ortho related (entry 10) and (2) the absence of a methoxy group ortho to the bromine (entries 8 and 9). The production of **1** was favored by an increase in the proportion of methyl acrylate used and by running the reaction in concentrated solution. Products **1** and **2** were not separable by TLC directly but could be separated by preparative TLC only after conversion of the aldehydes **2** to their dimethyl acetals by treating the reaction mixtures with trimethyl orthoformate, Dowex, and methanol under reflux. Decarbonylation of aromatic aldehydes[3] by Pd^0 catalysts does not usually occur under the mild conditions employed in these reactions and veratraldehyde itself was unaffected under such conditions. The normal Heck product **2** was also inert if re-subjected to the reaction after isolation, thus indicating that **2** is not an intermediate in the formation of **1**.

The question of relating the positions of the three-carbon substituents of the products **1** to the positions of the bromine and aldehyde of the starting material was investigated by examining the 500-MHz ^1H NMR of the nonsymmetric product **1E** (Entry 5). The aromatic signal at 8.3 (meta-coupled, J = 2.4 Hz) was the most downfield and assigned to H-6′ while the other two protons H-4′ and H-3′ were at 8.14 (dd, J = 8.5, 2.4 Hz) and 7.43 ppm (d, J = 8.5 Hz), respectively. The alkene protons at δ 7.95 and 6.51 were trans coupled (J = 16 Hz) doublets assigned to H-β and H-α, respectively, while the two methylene groups were triplets at δ 2.63 and 3.17 (J = 8 Hz). A difference NOE experiment with **1E** provoked an 8.3% enhancement of the olefinic proton at 6.51 ppm when H-6′ (δ 8.3) was irradiated. No other signal appeared in the difference spectrum. This compound unfortunately did not provide crystals good enough for an X-ray structure. We therefore synthesized 2-bromo-5-nitroanisaldehyde (**3**) and repeated the reaction with this substrate to obtain crystals of **4** suitable for an X-ray structure. The molecular plot diagram (Figure 1) confirms the results of the NOE experiment and unequivocally establishes that the bromine is

(1) Heck, R. F. *Org. React.* **1982**, *27*, 345-390.
(2) Jeffrey, T. *J. Chem. Soc., Chem. Commum.* **1984**, 1287. Hoffmann, H. M. R.; Schmidt, B.; Wolff, S. *Tetrahedron* **1989**, *45*, 6113-26.
(3) Hawthorne, J. O.; Wilt, M. H. *J. Org. Chem.* **1960**, *25*, 2215-7.

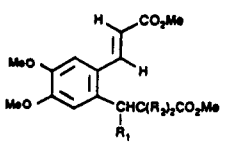
0022-3263/92/1957-2422$03.00/0

Table I. Reactions of Bromo Aldehydes with Methyl Acrylate[a]

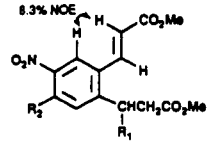
entry	substrate	reactn time, h	products 1	products 2	yield, % (ratio 1:2)
1		12	 A	 A	78 (2.1:1)
2		11	 B	 B	56 (0.8:1)
3		13	 C	 C	47 (0.6:1)
4		13	 D	 D	49 (0.73:1)
5		2	 E	 E	31 (1.3:1)
6		5	 F	 F	59 (1.9:1)
7		6	 G	 G	57 (1.6:1)
8		14		 H	53
9		9		 I	57
10		6		 J	63

[a] R_1 = *trans*-CH=CHCO$_2$Me; R_2 = $CH_2CH_2CO_2Me$.

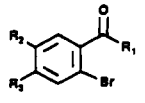
replaced by the saturated three-carbon substituent and the formyl group by the unsaturated substituent.



6 (R_1 = D, R_2 = H)
7 (R_1 = H, R_2 = D)



1E (R_1 = R_2 = H)
4 (R_1 = H, R_2 = OMe)
11 (R_1 = D, R_2 = H)



3 (R_1 = H, R_2 = NO_2, R_3 = OMe)
5 (R_2 = R_3 = OMe, R_1 = D)
8 (R_2 + R_3 = OCH_2O, R_1 = H)
9 (R_1 = R_3 = H, R_2 = NO_2)
10 (R_1 = D, R_3 = H, R_2 = NO_2)
12 (R_1 = D, R_2 = R_3 = H)
13 (R_1 = R_2 = H, R_3 = D)

The source of hydrogen for this reduction of one acrylate substituent was quickly identified as the formyl hydrogen of the aldehyde substituent of the substrate. This was evident when 6-bromoveratraldehyde-*formyl-d* (**5**) was subjected to the reaction. The ^{1}H NMR spectrum of the product now displayed a 50% decrease in intensity of the signal at δ 3.05 (t, J = 7.7 Hz) while the other methylene signal at δ 2.56 was a two-proton broadened doublet (J = 7.7 Hz). Sample **6** also showed a broad signal at δ 3.10 in its ^{2}H NMR spectrum and a molecular ion, the base peak, at 309.1335 (calculated for $C_{16}H_{19}O_6D$, 309.1322) in its high-resolution mass spectrum. The exact location of this single deuterium atom was determined by distinguishing the methylene groups of **1C** by treatment of the fully protonated compound (Table I entry 3) with methoxide and deuteriomethanol. The ^{1}H NMR spectrum, subsequently obtained, showed one methylene group at δ 3.05 now as a two-proton singlet but no signal for the methylene group at δ 2.56. The ^{2}H NMR spectrum (2.56, broad singlet) and the molecular ion 310.1386 (calculated for $C_{16}H_{18}O_6D_2$, 310.1380) of the product **7** confirmed that the

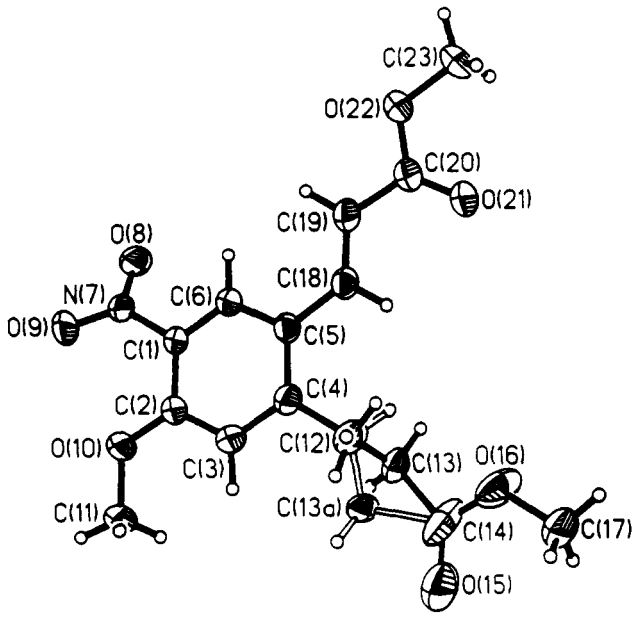


Figure 1. X-ray crystal structure of 4.

enolizable methylene group adjacent to the saturated ester (the signal at δ 2.56) had been deuterated. The location of the deuterium transferred from the formyl group in the first experiment was thus identified as the benzylic carbon of the saturated substituent. No evidence for deuterium scrambling or for the incorporation of deuterium onto the benzene ring was found. No deformylated product simply deuterated on the benzene ring could be detected either (vide infra). This hydrogen transfer from the formyl group was next shown to be an intramolecular process by carrying out the usual "crossover" experiment. Thus an equimolar mixture of 6-bromoveratraldehyde-*formyl-d* (**5**) and 6-bromopiperonal (**8**) was reacted with methyl acrylate under the standard conditions. After separation of the products by preparative TLC, **1D** and **6** were isolated. There was no transfer of deuterium from the *d*-formyl veratraldehyde **5** to **1D** and no transfer of hydrogen from bromopiperonal to **6**. This was established by ^{1}H and ^{2}H NMR of **1D** and **6** and by mass spectrometry. After allowing for the isotopic contribution to the M + 1 ion, no significant ion at m/z 293 was found for **1D** ($C_{15}H_{16}O_6$) or at m/z 308 for **6** ($C_{16}H_{19}O_6D$).

In the course of these reactions with deuterated aldehydes as substrates, we observed that the yields of the doubly substituted product were consistently lower than those for the protonated analogues. For further information about this apparent deuterium isotope effect, an equimolar mixture of 2-bromo-5-nitrobenzaldehyde (**9**) and its *d*-formyl analogue was **10** subjected to the reaction, the products, **1E** (entry 5) and its deutero analogue **11**, were separated, and an ^{1}H NMR spectrum of the mixture was determined. The integrals of the signals at δ 2.63 and 3.17 in the 200-MHz ^{1}H NMR spectrum were found to be in the ratio 8.61:7.12. From these numbers it can be calculated that a modest isotope effect of about 1.9 exists.

A plan to measure this more directly and accurately required the preparation of specifically ^{2}H labeled *o*-bromobenzaldehydes **12** and **13**. If an equimolar mixture of these compounds was subjected to the conditions of the reaction, mere integration of the four signals in the ^{2}H NMR spectrum of the crude reaction mixture should provide a simple and direct measure of the isotope effect. Unfortunately, this simple plan was foiled by the appearance of two extra ^{2}H signals at 4.64 and 5.78 ppm. By running reactions of the individual aldehydes **12** and **13** separately, it was established that these originated from the *d*-formyl compound **12** only and, furthermore, it was clear that no transfer of deuterium to the aromatic ring took place in **12** because no aromatic deuterium signal was found in this spectrum. The ^{2}H signal at 5.78 ppm would support the presence of methyl α-deuterioacrylate, but this could not be settled conclusively by the ^{1}H NMR spectrum of the reaction mixture because of overlap with signals from the products of the reaction. The second ^{2}H signal at δ 4.64 corresponds to a monodeuterated benzyl alcohol but here no evidence at all for its presence was evident in the ^{1}H NMR spectrum of the same sample or in any other sample of products listed in Table I. The only other ^{2}H signals were at 10.23 and 3.02 ppm as expected for deuterated **2A** and **1A**, respectively. These integrated in the ratio 5.04:1. With **13** the only ^{2}H signals were found in the aromatic region between 7 and 7.6 ppm but they were too close to each other and too broad for accurate integration.

In Scheme I we submit a proposal which attempts to rationalize the experimental evidence detailed above. The proximity of the formyl group in **14** presents this intermediate with an alternative pathway besides the reductive elimination that leads to the conventional products **2A–E**. It could evolve into **15** by two possible routes. The palladium(0) species generated in the formation of **2A–E** is delivered directly to the proximate C–H(D) bond of the formyl group for oxidative addition. Decarbonylation of simple aromatic aldehydes by palladium catalysis is known[3] but normally requires much more vigorous conditions. The inability of products **2A–E** to re-enter the cycle and transform into the doubly substituted materials **1A–E** must then be attributed to the difficulty of reversing the reductive elimination step (**14** → **2**) in the presence of excess potassium carbonate used in the reaction.

The second route to **15** involves oxidative addition of the Pd(II) of **14** to the C–H(D) bond to provide the Pd(IV) species, which undergoes β-elimination returning to Pd(II) in **15**. The chemistry of Pd(IV) has attracted much attention and its existence in many catalytic cycles has been proposed.[4] The involvement of the ortho substituents containing acidic hydrogen atoms in the Heck reactions of aromatic iodides has been observed.[5] recently.

The deuteration of the cinnamate double bond of **15** though formally a hydropalladation has a regiochemical outcome more in keeping with the transfer of deuteride (D^-) than that expected[6] for the four-center migratory insertion mechanism with a planar Pd(II) species such as **15**. Furthermore, if one of the byproducts of this reaction is in fact the α-deuterated methyl acrylate, the regiochemistry of deuterium transfer to the two double-bonded ligands in **15** is opposite, one to the other.

The decomposition of **16** with loss of carbon monoxide leads to the deuterated intermediate **17**, which undergoes a simple Heck reaction with more methyl acrylate to provide the doubly substituted products **1A–E** with the experimentally established positioning of the substituents. The lack of aromatic deuteration requires that the transfer of deuterium take place before the decarbonylation step. It is not clear why the presence of an *o*-methoxy group (entries 8 and 9, Table I) should prevent the formation of doubly substituted products. Attempts to extend the reaction to the direct preparation of dihydronaphthalenes

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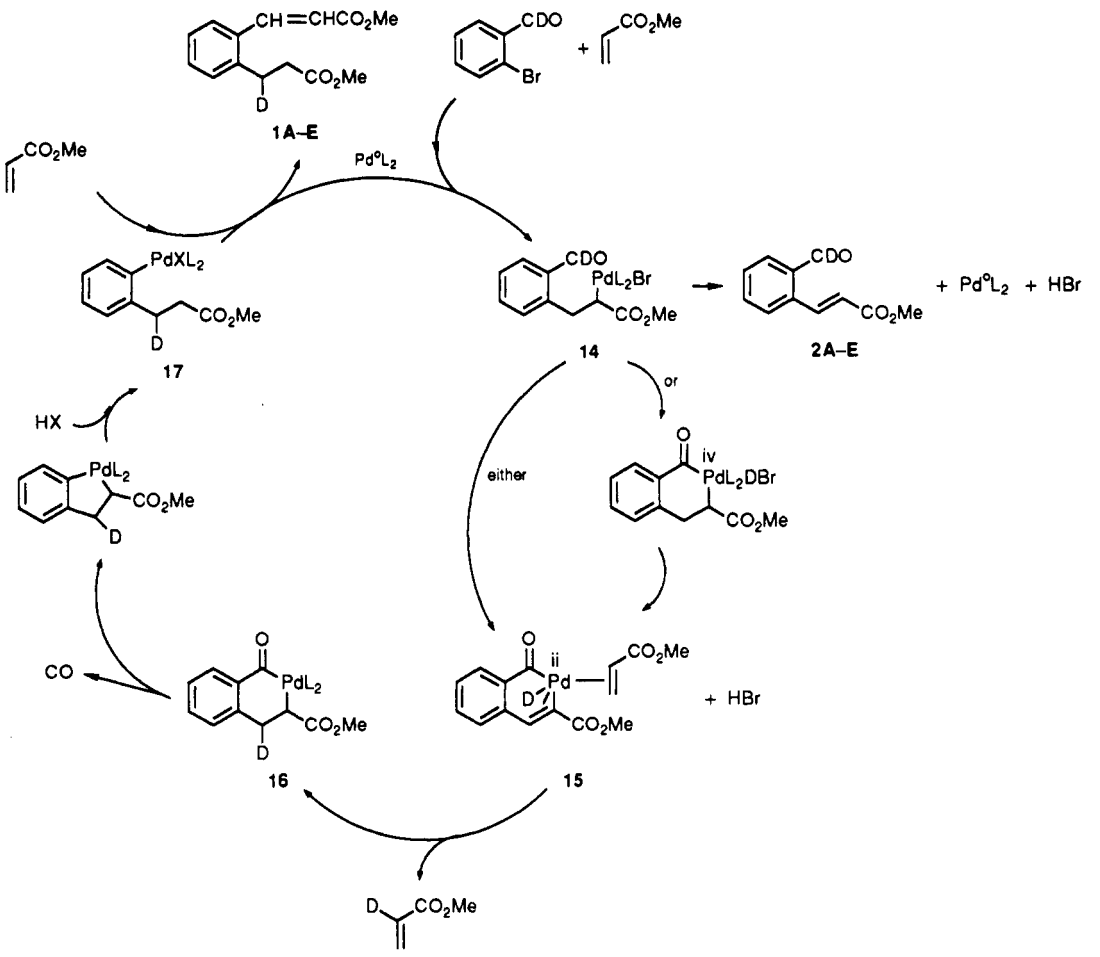
(5) Larock, R. C.; Yum, E. K. *Synlett* **1990**, *9*, 529–30.
(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 383–387.

Scheme I



by employing 2,3-dicarbomethoxy-1,3-butadiene as the substrate resulted only in polymerization of the diene and recovery of the bromo aldehyde.

Experimental Section

All the reactions were carried out in an Ar atmosphere. DMF was distilled over CaH_2 and deareated by bubbling Ar through the solution for 12 h. Methyl acrylate was distilled prior to use. Melting points are uncorrected. Low and high resolution mass spectra were obtained at at the South-Western Ontario Regional Mass Spectrometry Center at McMaster University, Hamilton, Ontario. ^1H NMR spectra were recorded in $CDCl_3$. Microanalyses were performed by MHW laboratories of Phoenix, AZ. Silica gel 60 (70–230 mesh) was used for flash chromatography. Preparative TLC was carried out on precoated 1000/μm 20 × 20 mm silica gel GF plates. Deuterium-labeled compounds **5**, **7**, **10**, **12**, and **13** are known as their protonated analogues and were not analyzed. They were judged to be >99% pure by ^1H NMR spectroscopy.

2-Bromo-4-methoxy-5-nitrobenzaldehyde (3). 2-Bromo-4-methoxybenzaldehyde (2.15 g) dissolved in acetic acid (8 mL) was treated with concd nitric acid (2 mL) and concd sulfuric acid (2.5 mL) at 0 °C. The solution was stirred and allowed to reach room temperature over 24 h. Water was added and the mixture extracted with ethyl acetate, the extracts were washed with water, and the solvent was removed. After chromatography on silica gel in ethyl acetate–hexane (1:5), the product was crystallized from the ethyl acetate–hexane (12%): mp 140–141°; IR (Nujol) 1670 cm^{-1}; ^1H NMR (80 MHz) δ 4.15 (s, 3 H, OMe), 7.35, 8.4 (s, 1 H each, 2 aromatic H), 10.3 (s, 1 H, CHO); MS (EI) m/z 259 and 261 (M^+); HRMS (EI) m/z 258.9574, calcd for $C_8H_6O_4N^{79}Br$, M^+, 258.9577. Anal. Calcd for $C_8H_6O_4NBr$: C, 37.06 H, 2.31. Found: C, 37.14; H, 2.35.

2-Bromo-4,5-dimethoxybenzaldehyde-*formyl*-*d* (5). The title compound was prepared by the Swern oxidation[7] of the corresponding deuterio bromo alcohol which was obtained by Superdeuteride reduction of the corresponding methyl ester. The methyl ester was prepared by the CH_2N_2 methylation of the corresponding bromo acid. **5**; IR ($CHCl_3$) 1660, 1596 cm^{-1}; ^1H NMR (250 MHz) δ 3.95 and 4.0 (s, 3 H each, OMe), 7.1 and 7.5 (s, 1 H each, aromatic H); MS (EI) m/z 247, 245 and 245, 243 (M^+, M^+ – D and M^+, M^+ – D); HRMS (EI) m/z 244.9797 calcd for $C_9H_8DO_3{}^{79}Br$, M^+, 244.9797.

2-Bromo-5-nitrobenzaldehyde-*formyl*-*d* (10). Swern oxidation of the deuterio bromo alcohol which was prepared by the Superdeuteride reduction of methyl *o*-bromobenzoate gave *d*-formyl bromobenzaldehyde which gave the title compound upon nitration with concd H_2SO_4/HNO_3: IR (Nujol) 1696 cm^{-1}; ^1H NMR (250 MHz) δ 7.88 (1 H, d, J = 9 Hz, aromatic H), 8.29 (1 H, dd, J = 9, 2.8 Hz, aromatic H), 8.73 (1 H, d, J = 2.8 Hz, aromatic H); MS (EI) m/z 232, 230 and 230, 228 (M^+, M^+ – D and M^+, M^+ – D); HRMS (EI) m/z 229.9437 calcd for $C_7H_3O_3DN^{79}Br$, M^+, 229.9436.

2-Bromobenzaldehyde-*formyl*-*d* (12). The title compound was prepared as described above: ^1H NMR (250 MHz) δ 7.35–7.55 (2 H, m, aromatic H), 7.6–7.7 (1 H, m, aromatic H), 7.88–7.99 (1 H, m, aromatic H); MS (EI) m/z 187, 185, 183 (M^+ and M^+ – D); HRMS (EI) m/z 184.9585 calcd for $C_7H_4OD^{79}Br$, M^+, 184.9591.

4-Deuterio-2-bromobenzaldehyde (13). The title compound was prepared by the bromination of 4-deuterio-2-lithiobenzaldehyde dimethyl acetal with 1,2-dibromoethane followed by acid hydrolysis. 4-Deuteriobenzaldehyde dimethyl acetal was prepared by the reaction of D_2O with 4-lithiobenzaldehyde dimethyl acetal which was prepared by the Li–halogen exchange of 4-bromobenzaldehyde dimethyl acetal: IR (Nujol) 1660 cm^{-1}; ^1H NMR (80 MHz) δ 7.42 (1 H, d, J = 7.2 Hz, aromatic H), 7.68 (br s, 1 H, aromatic H), 7.96 (d, J = 7.2 Hz, aromatic H); MS (EI) m/z

(7) Heck, R. F. U.S. Pat. 3,783,140 (Cl 260–330.5; C 07c); *Chem. Abstr.* **1973**, *78*, p71699f.

187, 186 and 185, 184 (M^+, $M^+ - H$ and M^+, $M^+ - H$); HRMS (EI) m/z 184.9586 calcd for $C_7H_4OD^{79}Br$, M^+, 184.9585.

General Procedure for the Phase-Transfer-Catalyzed "Heck" Reaction. Bu_4NCl (1.67 mmol), K_2CO_3(2.07 g, 15 mmol), $Pd(OAc)_2$ (62.7 mg, 0.28 mmol), and methyl acrylate (2.7 mL, 30 mmol were stirred for 5 min under Ar. To the resulting brown solution was added the *o*-bromobenzaldehyde (6 mmol) in deareated DMF (0.75 mL), and the mixture was stirred at 65–70 °C for 2–14 h (see Table I). The reaction mixture was diluted with EtOAc (20 mL) and the resulting dark solution was filtered through a thin pad of Celite. The filtrate was diluted with water and extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under vacuum. The dark thick oil obtained was chromatographed on silica (EtOAc/hexane) to obtain a mixture of compounds **1** and **2**. This mixture was dried in vacuo for 3 h and was dissolved in dry MeOH (5 mL) and trimethyl orthoformate (5 mL). The resulting solution was refluxed for 12 h with Dowex (100 mg). The reaction mixture was filtered and concentrated to obtain a viscous oil. The oil was subjected to preparative TLC on silica (multiple elution) to obtain double substitution products **1A–G** and dimethyl acetals of **2A–J** which were dissolved in THF (10 mL) and stirred with 2 N HCl (5 mL) for 2 h. The resulting solutions were subjected to usual workup followed by appropriate purification to give aldehydes **2A–J**.

Methyl 3-[2′-(2-Carbomethoxyethyl)phenyl]-2-propenoate (1A). Preparative TLC (EtOAc–hexane, 1:6, triple elution) of the oil obtained from the reaction of *o*-bromobenzaldehyde and methyl acrylate gave a viscous oil, (**1A**) and dimethyl acetal of **2A** (78%, 2.1:1).

1A: IR (neat) 1733, 1712, 1630 cm^{-1}; ^1H NMR (250 MHz) δ 2.59 and 3.09 (t, 2 H each, J = 8 Hz, CH_2), 3.66 and 3.81 (s, 3 H each, CO_2Me), 6.37 (d, 1 H, J = 16 Hz, alkene H), 7.36 (m, 4 H, aromatic H), 7.99 (d, 1 H, J = 16 Hz, alkene H); HRMS m/z 248.1034, calcd for $C_{14}H_{16}O_4$, M^+, 248.1048. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45. Found: C, 67.53; H, 6.72.

Methyl 3-[2′-(2-Carbomethoxyethyl)-4′-methoxyphenyl]-2-propenoate (1B). Preparative TLC (EtOAc–hexane, 1:5, triple elution) of the oil obtained from the reaction of 2-bromo-4-methoxybenzaldehyde and methyl acrylate gave a viscous oil (**1B**) and dimethyl acetal of **2B** (56%, 0.8:1).

1B: IR (neat) 1737, 1715, 1630 cm^{-1}; ^1H NMR (250 MHz) δ 2.58 and 3.09 (t, 2 H each, J = 7.6 Hz, CH_2), 3.76 and 3.81 (s, 3 H each, CO_2Me), 3.79 (s, 3 H, OMe), 6.27 (d, 1 H, J = 15.6 Hz, alkene H), 6.77 (m, 2 H, aromatic H), 7.53 (d, 1 H, J = 9 Hz, aromatic H), 7.9 (d, 1 H, J = 15.6 Hz, alkene H); HRMS (EI) m/z 278.1143, calcd for $C_{15}H_{18}O_5$, M^+, 278.1154. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.47. Found: C, 64.74; H, 6.52.

Methyl 3-(2′-formyl-4′-methoxyphenyl)-2-propenoate (2B): IR (neat) 1730, 1688, 1618 cm^{-1}; ^1H NMR (80 MHz) δ 3.83 (s, 3 H, CO_2Me), 3.95 (s, 3 H, OMe), 6.45 (d, 1 H, J = 15.8 Hz, alkene H), 6.75 (dd, 1 H, J = 8.6, 2.5 Hz, aromatic H), 7.1 (d, 1 H, J = 2.5 Hz, aromatic H), 7.8 (d, 1 H, J = 8.6 Hz, aromatic H), 8.55 (d, 1 H, J = 15.8 Hz, alkeneH), 10.12 (s, 1 H, CHO); HRMS (EI) m/z 220.0920, calcd for $C_{12}H_{12}O_4$, M^+, 220.0924. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.34; H, 5.52.

Methyl 3-[2′-(2-Carbomethoxyethyl)-4′,5′-dimethoxyphenyl]-2-propenoate (1C). Preparative TLC (EtOAc–hexane, 1:5, double elution) of the oil obtained from the reaction of 6-bromoveratraldehyde and methyl acrylate gave **1C** and the dimethyl acetal of **2C** (47%, 0.6:1). **1C** was crystallized (ether–hexane).

1C: mp 62–63 °C; IR (Nujol) 1732, 1704, 1626, cm^{-1}; ^1H NMR (200 MHz) δ 2.56 and 3.04 (t, 2 H each, J = 8 Hz, 2 CH_2), 3.66 and 3.89 (s, 3 H each, CO_2Me), 3.80 and 3.86 (s, 3 H each, OMe), 6.37 and 8.30 (d, 1 H each, alkene H), 6.72 and 7.05 (s, 1 H each, aromatic H); HRMS (EI) m/z 3.08.1236, calcd for $C_{16}H_{20}O_6$, M^+, 308.1259. Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.32, H; 6.49. Found: C, 62.15; H, 6.59.

Methyl 3-[2′-(2-Carbomethoxyethyl)-4′,5′-(methylenedioxy)phenyl]-2-propenoate (1D). Preparative TLC (EtOAc–hexane, 1:5) of the oil obtained from the reaction of 6-bromopiperonal (**8**) and methyl acrylate gave **1D** and the dimethyl acetal of **2D** (49%, 0.73:1). **1D** was crystallized (ether–CH_2Cl_2–hexane).

1D: mp 108–109 °C; IR (Nujol) 1744, 1726, 1647 cm^{-1}; ^1H NMR (200 MHz) δ 2.54 and 3.02 (t, 2 H each, J = 7.6 Hz, CH_2), 3.76 and 3.8 (s, 3 H each, CO_2Me), 5.98 (s, 2 H, OCH_2O), 6.23 (d, 1 H, J = 15.7 Hz, alkene H), 6.07 and 7.03 (s, 1 H each, aromatic H), 7.96 (d, 1 H, J = 15.7 Hz, alkene H); HRMS (EI) m/z 292.0967, calcd for $C_{15}H_{16}O_6$, M^+, 292.0967. Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.46. Found: C, 61.51; H, 5.51.

Methyl 3-[2′-(2-Carbomethoxyethyl)-5′-nitrophenyl]-2-propenoate (1E). Preparative TLC (ether–hexane) of the oil obtained from the reaction of **9** and methyl acrylate gave **1E** and the dimethyl acetal of **2E** (31%, 1.3:1). **1E** was crystallized (ether–hexane).

1E: mp 78–79 °C; IR (Nujol) 1721, 1710, 1636 cm^{-1}; ^1H NMR (200 MHz) δ 2.63 and 2.17 (t, 2 H each, J = 7.8 Hz, CH_2), 3.67 and 3.85 (s, 3 H each, CO_2Me), 6.51 (d, 1 H, J = 16 Hz, alkene H), 7.4 (d, 1 H, J = 8.5 Hz, aromatic H), 7.96 (d, 1 H, J = 16 Hz, alkene H), 8.14 (dd, 1 H, J = 8.5, 2.4 Hz, aromatic H), 8.3 (d, 1 H, J = 2.4 Hz, aromatic H); HRMS (EI) m/z 293.0889, calcd for $C_{14}H_{15}O_6N$, M^+, 293.0888. Anal. Calcd for $C_{14}H_{15}O_6N$: C, 57.33; H, 5.11. Found: C, 57.33; H, 5.30.

Methyl 3-(2′-formyl-4′-nitrophenyl)-2-propenoate (2E): mp 145–147 °C (Ether–hexane); IR 1727, 1680, 1617 cm^{-1}; ^1H NMR (250 MHz) δ 3.86 (s, 3 H, CO_2Me), 6.49 and 8.49 (d, 1 H each, J = 15.8 Hz, alkene H), 7.82 (d, 1 H, J = 8.5 Hz, aromatic H), 8.41 (dd, 1 H, J_1 = 8.5, 2.3 Hz, aromatic H), 8.71 (d, 1 H, J = 2.3 Hz, aromatic H), 10.34 (s, 1 H, CHO); HRMS (EI) m/z 235.0741, calcd for $C_{11}H_9O_5N$, M^+, 235.0748. Anal. Calcd for $C_{11}H_9O_5N$: C, 56.17; H, 3.82. Found: C, 56.14; H, 3.88.

2-(2′-Carbomethoxyethenyl)-3-(2′-carbomethoxyethyl)-naphthalene (1F). Preparative TLC (EtOAc–hexane, 1:4, double elution) of the oil obtained from the reaction of 3-bromo-2-naphthaldehyde and methyl acrylate gave **1F** and the dimethyl acetal of **2F** (59%, 1.9:1). **1F** was crystallized from (EtOAc–CH_2Cl_2–hexane).

1F: mp 102–103 °C; IR (Nujol) 1732, 1694, 1612 cm^{-1}; ^1H NMR (250 MHz) δ 2.68 and 3.24 (t, 2 H each, J = 8 Hz, CH_2), 3.67 and 3.84 (s, 3 H each, CO_2Me) 6.51 and 8.08 (d, 1 H each, J = 16 Hz, alkene H), 7.46 and 7.78 (m, 2 H each, aromatic H), 7.66 and 8.04 (s, 1 H each, aromatic H); HRMS (EI) m/z 298.1190, calcd for $C_{18}H_{18}O_4$, M^+, 298.1205. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.23; H, 6.17.

2-Formyl-3-(2′-carbomethoxyethenyl)naphthalene (2F): mp 81–83 °C (CH_2Cl_2–hexane); IR (Nujol) 1730, 1681, 1618 cm^{-1}; ^1H NMR (80 MHz) δ 3.81 (s, 3 H, CO_2Me), 6.4 and 8.45 (d, 1 H each, J = 15.7 Hz, alkene H), 7.4–7.8 (m, 4 H, aromatic H), 7.91 and 7.98 (s, 1 H each, aromatic H), 10.32 (s, 1 H, CHO); HRMS (EI) m/z 240.0934, calcd for $C_{15}H_{12}O_3$, M^+, 240.0930. Anal. Calcd for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 75.08; H, 5.02.

1-(2′-Carbomethoxy-1′-ethyl)-2-(2′-carbomethoxy-1′-ethenyl)naphthalene (1G). Preparative TLC (EtOAc–hexane, 1:5, double elution) of the oil obtained from the reaction of 1-bromo-2-naphthaldehyde and methyl acrylate gave **1G** and dimethyl acetal of **2G** (57%, 1.6:1).

1G: IR (neat) 1730, 1716, 1620 cm^{-1}; ^1H NMR (200 MHz) δ 2.63 and 3.57 (t, 2 H each, J = 8 Hz, CH_2), 3.71 and 3.83 (s, 3 H each, CO_2Me), 6.47 and 8.25 (d, 1 H each, J = 16 Hz, alkene H), 7.68 (m, 6 H, aromatic H); HRMS (EI) m/z 298.1208, calcd for $C_{18}H_{18}O_4$, M^+, 298.1205. Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.48; H, 6.04. Found: C, 72.51; H, 6.21.

1-Formyl-2-(2′-carbomethoxyethenyl)naphthalene (2G): IR (neat) 1729, 1688, 1617 cm^{-1}; ^1H NMR (80 MHz) δ 3.79 (s, 3 H, CO_2Me), 6.45 and 8.41 (d, 1 H each, J = 15.8 Hz, alkene H), 7.3–7.9 (m, 6 H, aromatic H), 10.33 (s, 1 H, CHO); HRMS (EI) m/z 240.0933, calcd for $C_{15}H_{12}O_3$, M^+, 240.0930. Anal. Calcd for $C_{15}H_{12}O_3$: C, 75.00; H, 5.00. Found: C, 75.04; H, 5.08.

Methyl 3-(6′-Formyl-2′,3′-dimethoxyphenyl)-2-propenoate (2H). Flash chromatography (EtOAc–hexane, 1:5) of the oil obtained from the reaction of 2-bromo-3,4-dimethoxybenzaldehyde and methyl acrylate followed by recrystallization (EtOAc–hexane) gave colorless needles of **2H** (53%): mp 72–73 °C; IR (Nujol) 1730, 1683, 1619 cm^{-1}; ^1H NMR (250 MHz) δ 3.81 (s, 3 H, CO_2Me), 3.83 and 3.97 (s, 3 H each, OMe), 6.38 and 8.17 (d, 1 H each, J = 16.1 Hz, alkene H), 7.04 and 7.7 (d, 1 H each, J = 8.6 Hz, aromatic H), 10.05 (s, 1 H, CHO); HRMS (EI) m/z 250.0885, calcd for $C_{13}H_{14}O_5$, M^+, 250.0881. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.46; H, 5.62.

Methyl 3-(2′-formyl-4′,6′-dimethoxyphenyl)-2-propenoate (2I). Flash chromatography (EtOAc–hexane, 1:5) of the oil ob-

tained from the reaction of 2-bromo-3,5-dimethoxybenzaldehyde and methyl acrylate followed by recrystallization (EtOAc–hexane) gave colorless needles of **2I** (57%): mp 103–105 °C; IR (Nujol) 1731, 1686, 1619 cm^{-1}; ^1H NMR (80 MHz) δ 3.79 (s, 3 H, CO_2Me), 3.81 and 3.99 (s, 3 H each, OMe), 6.39 and 8.15 (d, 1 H each, J = 15.9 Hz, alkene H), 6.7 and 7.1 (d, 1 H each, J = 2.5 Hz, aromatic H), 10.1 (s, 1 H, CHO); HRMS (EI) m/z 250.0884, calcd for $C_{13}H_{14}O_5$, M^+, 250.0881. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.46; H, 5.64.

Methyl 3-(3′-Formylphenyl)-2-propenoate (2J). Flash chromatography (EtOAc–hexane, 1:5) of the oil obtained from the reaction of *m*-bromobenzaldehyde and methyl acrylate followed by recrystallization (EtOAc–hexane) gave colorless needles of **2J** (63%); mp 55–56 °C; IR (Nujol) 1740, 1680, 1617 cm^{-1}; ^1H NMR (80 MHz) δ 3.81 (s, 3 H, CO_2Me), 3.86 (s, 3 H, OMe), 6.54 (d, 1 H, J = 15.9 Hz, alkene H), 7.55–8.03 (m 5 H, aromatic H + alkene H), 10.04 (s, 1 H, CHO); HRMS (EI) m/z 190.0630, calcd for $C_{11}H_{10}O_3$, M^+, 190.0630.

Methyl 3-[2′-(2-Carbomethoxyethyl)-4′-methoxy-5′-nitrophenyl]-2-propenoate (4). The title compound was prepared from 2-bromo-4-methoxy-5-nitrobenzaldehyde according to the general procedure (29%): mp 114–115 °C (CH_2Cl_2–hexane–ether); IR (Nujol) 1730, 1716, 1620 cm^{-1}; ^1H NMR (200 MHz) δ 2.62, 3.14 (t, 2 H each, J = 7.4 Hz, CH_2), 3.68, 3.82, (s, 3 H each, CO_2Me), 3.98 (s, 3 H, OMe), 6.37, 7.83 (d, 1 H each, J = 15.7 Hz, alkene H), 6.98, 8.10 (s, 1 H each, aromatic H); HRMS (EI) m/z 323.1003, calcd for $C_{15}H_{17}O_7N$, M^+, 323.1005. Anal. Calcd for $C_{15}H_{17}O_7N$: C, 55.38; H, 5.26. Found: C, 55.30; H, 5.21.

Crystal Structure Analysis of 4. Crystals of $C_{15}H_{17}NO_7$, M = 323.3 are triclinic, space group $P\bar{1}$, a = 7.820 (2), b = 9.418 (2), and c = 11.337 (2) Å, α = 99.83 (1)°, β = 100.97 (1)°, γ = 100.87 (1)°, V = 786.3 (2) Å^3, with Z = 2, D_c = 1.365 g cm^{-3}, $F(000)$ = 340, λ = 0.71073 Å, T = 295 K, μ (Mo Kα) = 1.02 cm^{-1}. Data were collected on a Siemens R3m/V diffractometer from a crystal of dimensions 0.48 (100, $\bar{1}$00) × 0.32 (010, 0$\bar{1}$0) × 0.36 ($\bar{1}$11, 1$\bar{1}\bar{1}$) mm. From 3105 independent data measured by the ω scan method, ($2\theta \leq 52°$), 1863 (with $F \geq 6\sigma(F)$) were considered observed and used in the structure solution and refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods to R and R_w values of 6.15 and 8.02% (Siemens SHELXTL PLUS software). Full details of the X-ray analysis are listed in the supplemental data. In the molecular plot (Figure 1), one of the side chains is illustrated as disordered at C(12) and C(13) such that the methylene unit C(13) occupies two distinct sites and four proton positions were located in a difference map associated with the methylene carbon C(12). The disorder was estimated to be 65:35. The remainder of the side chain appears quite ordered.

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Supplementary Material Available: ^1H NMR spectra of **5**, **7**, **10**, and **13** and X-ray crystallographic data for **4** (14 pages). Ordering information is given on any current masthead page.

A Study on the Reducing Abilities of Tris(alkylthio)silanes[1]

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Tris(methylthio)silane and tris(isopropylthio)silane effectively reduce a variety of organic substrates via free radical mechanisms. These silanes can also be used as hydrosilylating agents for alkenes having electron-donating substituents. The bond dissociation energy of the Si–H bonds have been measured by photoacoustic calorimetry and found to be around 83 kcal mol^{-1}. The absolute rate constants for the reaction of the *tert*-butoxyl radical with $(RS)_3SiH$ have been measured by a laser flash photolysis technique and the optical absorption spectra of the corresponding radicals have been obtained. Multiple scattering X_α calculations showed that the dominant absorption detected in the UV–vis region was due to $\sigma_{Si-S}(e) \rightarrow$ SOMO and SOMO $\rightarrow \sigma^*_{Si-S}(e)$ transitions.

Introduction

In organic synthesis, the most useful types of free radical reactions are (i) reductions of a variety of functional groups and (ii) the formation of carbon–carbon bonds, either inter- or intramolecularly.[4] Such chain processes have been carried out by using tri-*n*-butyltin hydride[5] and, more recently, tris(trimethylsilyl)silane.[6-8] One of the most important considerations in selecting different reducing agents for these processes concerns the relative hydrogen-donor abilities of the hydrides,[9] viz., eq 1. Tri-

$$R^\bullet + X_3MH \rightarrow RH + X_3M^\bullet \quad (1)$$

alkylgermanium hydrides are less reactive donors than their tin analogues, while the corresponding germyl radicals are at least as reactive as stannyl radicals in reactions with organic substrates.[12] However, due mainly to the high cost

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