Notes

Novel Syntheses of 1,2-Diarylprop-2-en-1-ones

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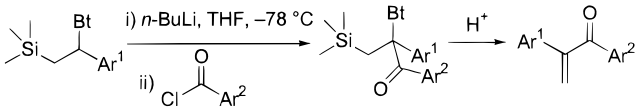
Introduction

1,2-Diarylprop-2-en-1-ones have found wide use in the synthesis of a variety of heterocyclic substrates, many of which show biological activity. The epoxides derived from 1,2-diarylpropenones show herbicidal activity;[1] 1,4-addition of nucleophiles produces fungicidal 1,2-diarylpropanones,[2] which also display central nervous system activity.[3] Nazarov cyclization of such propenones leads to indanones.[4] Pyrazolinecarboxamides[5] as well as other pyrazolines,[6] both classes used as insecticides, can be made via 1,2-diarylpropenones. 2,3-Diaryl-1-pyrroline 1-oxides are synthesized from 1,2-diarylpropenones.[7]

The direct insertion of an α-methylene group into ketones is the most often encountered approach to 1,2-diarylpropenones. Piperidine in the presence of formaldehyde,[8] *N*-methylaniline trifluoroacetate[9] in the presence of trioxane, and *N*,*N*,*N*′,*N*′-tetramethylmethanediamine[10] all produce 1,2-diarylpropenones starting from the corresponding deoxybenzoins.

The second largest group of methods consists of base-induced *β*-eliminations of a 3-heteroatom-substituted 1,2-diarylpropanone. These substrates are synthesized by one of the following approaches: (i) insertion of chloromethylcarbene into the C−H bond of deoxybenzoins;[11] (ii) conjugate addition of anions of protected cyanohydrins to *β*-nitrostyrenes followed by hydrolysis;[12] (iii) tin(II) induced α-bromomethylation of silyl enol ethers;[13] (iv) addition of methoxymethyl methyl sulfate to diarylalkynes;[14] (v) reduction of enamino ketones obtained from deoxybenzoins and *N*,*N*-dimethylformamide dimethylacetal;[15] (vi) a Prévost reaction performed upon 1,1-diarylallyl alcohols.[16]

Scheme 1



1a-f **2a-f** **3a-h**[a] **4a-h**[a]

1	Ar^1	**2**	Ar^2
a	2-MeC_6H_4	**a**	2-MeC_6H_4
b	4-MeC_6H_4	**b**	4-MeC_6H_4
c	2-FC_6H_4	**c**	4-ClC_6H_4
d	4-FC_6H_4	**d**	4-FC_6H_4
e	4-$MeOC_6H_4$	**e**	2,4,6-$Me_3C_6H_2$
f	2-ClC_6H_4	**f**	4-$MeOC_6H_4$

[a] See Table for the significance of Ar^1 and Ar^2 in **3** and **4**

Organometallic reagents have been used for the synthesis of 1,2-diarylpropenones: (i) Watanabe's coupling of aroyl chlorides with phenylketene in the presence of Pd(0) catalyst;[17] (ii) ruthenium-catalyzed alkylidene coupling of α-diazo ketones.[18] Several miscellaneous methods have been used to produce 1,2-diarylpropenones: (i) from aryllead tricarboxylates;[19] (ii) by the reaction of α-arylalkenyl Grignard reagents with nitriles;[20] (iii) hypervalent iodine oxidation of allenes.[21]

In connection with our use of benzotriazole as a synthetic auxiliary,[22] we have recently shown that 1,2-diarylpropenones can be obtained by fluoride ion vicinal elimination of silicon in substrates of type **3** (Scheme 1).[23] The synthetic value of this synthesis of **4** (Scheme 1)

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Table 1. Preparation of 2,3-Diarylpropenones 4

3, **4**	Ar^1	Ar^2	yield **3** (%)	reacn conditions **3** → **4**: acid/solvent/time (h)	yield **4** (%)
a	4-MeC_6H_4	4-$MeOC_6H_4$	93	*p*-TsOH/MeOH/72	98
				TFA/CH_2Cl_2/0.3	99
b	2-MeC_6H_4	4-FC_6H_4	72	TFA/CH_2Cl_2/1	88
c	2-FC_6H_4	4-ClC_6H_4	83	TFA/CH_2Cl_2/6	76
d	4-FC_6H_4	4-$MeOC_6H_4$	86	TFA/CH_2Cl_2/1.1	94
e	2-ClC_6H_4	2-MeC_6H_4	98	*p*-TsOH/MeOH/2[a]	72
f	2-MeC_6H_4	4-MeC_6H_4	91	TFA/CH_2Cl_2/1	76
g	4-MeC_6H_4	2-MeC_6H_4	90	TFA/CH_2Cl_2/1	82
h	4-$MeOC_6H_4$	2,4,6-$(Me)_3C_6H_2$	88	TFA/CH_2Cl_2/0.5	75

[a] The reaction was performed at reflux.

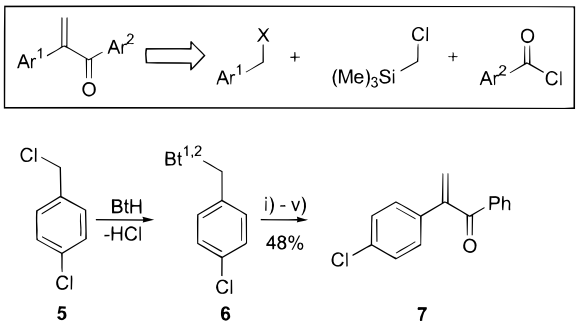
was limited by the formation of significant amounts of chalcone byproducts as a result of an anionic rearrangement.[23,24] We now show that the vicinal elimination of silicon in **3** can be accomplished under acidic conditions making this approach valuable for the synthesis of **4**.

Results and Discussion

Reagents **1a**−**d** were prepared as previously described.[23] Addition of the carbanions derived from **1** to acid chlorides afforded adducts **3a**−**h** in excellent yields, after the elimination of chloride anion, as the temperature of the reaction mixture rose from −78 °C to room temperature. The analogous reaction of esters or nitriles did not afford the desired ketones **3** (Scheme 1). All our attempts to utilize enolizable acyl halides failed to give the corresponding ketone probably due to the hardness of the anion derived from **1**. The reaction of the carbanions derived from **1** with aroyl chlorides works well regardless of the electronic character of the reagents **1** or the chlorides **2**. Thus, electron-rich **1e**, **2f** as well as electron poor **1c**, **2d** all give excellent yields of the corresponding **3a**−**h**. Steric effects, which are expected to play a role in the case of reagents **1a,f** and acid chlorides **2a**,**e**, do not influence the outcome of the reaction. It is worth mentioning that substrates **3a**−**h** did not undergo nucleophilic addition at the carbonyl when treated with *n*-BuLi probably due to the steric congestion. Ketones **3a**−**h** are all glassy compounds which tend to retain solvent and are therefore difficult to obtain in pure state. However, when these compounds were kept under high vacuum for 1 day, satisfactory NMR spectra and in some cases combustion analyses were obtained.

Vicinal elimination of silicon was accomplished by stirring adduct **3a**−**h** with acid in the appropriate solvent at room temperature (Scheme 1 and Table 1). The presence of a catalytic amount of *p*-toluenesulfonic acid in methanol promoted the elimination reaction in **3a** and afforded **4** in 98% yield. Under these conditions, the reaction was slow and complete transformation of **3a** required 72 h. Use of 2 equiv of trifluoroacetic acid (TFA) in methylene chloride accelerated the reaction, and **4a** was obtained in 99% yield after 0.3 h. The rate of the transformation **3** → **4** depends on the electronic character of Ar^1. Thus in the presence of TFA, electron-rich **3h** undergoes elimination in 0.5 h while electron deficient **3c** necessitates 6 h for the same transformation to be completed. Steric congestion due to a substituent in the *ortho* position of the phenyl group has little effect upon the elimination conditions as was the case with **3b,f**−**h**. The extreme case **3e,** where both phenyl groups possess a bulky *ortho* substituent, was reluctant to undergo elimination at room temperature in the presence of TFA. The transformation was accomplished in 72% yield upon reflux in methanol with catalytic amount of *p*-toluenesulfonic acid. After simple washing with water and extraction of the byproduct benzotriazole into dilute aqueous sodium hydroxide, the 1,2-diarylpropenones **4a**−**h** were obtained in high yields.

Scheme 2



Reaction conditions: i) *n*-BuLi, −78 °C; ii) Me_3SiCH_2Cl, −78 °C→rt iii) *n*-BuLi, −78 °C; iv) C_6H_5COCl, −78 °C→rt; v) TFA, 2 equiv, rt.

This new approach to structures of type **4** possesses significant advantages when compared to the previously described methods. Thus, a large pool of readily available starting materials allows for a wide diversity of the two aryl groups by combining arylmethyl halides, aroyl chlorides, and (chloromethyl)trimethylsilane (Scheme 2). To demonstrate this concept, a 9:1 mixture of ((1- and ((2-benzotriazolyl)methylene)arene **6** was prepared in almost quantitative yield by the displacement of halogen in 4-chlorobenzyl chloride (**5**) (Scheme 2). The mixture **6** was deprotonated and reacted with (chloromethyl)trimethylsilane at −78 °C, allowed to reach room temperature and cooled to −78 °C, deprotonated, and reacted with benzoyl chloride. The crude mixture after work up was subjected to acid hydrolysis with TFA in methylene chloride to afford **7** in 48% overall yield. Thus, benzotriazole acts as an useful auxiliary for building **7** from a large variety of **2** and **5** without the need for separation of intermediates.

In summary a new and general method for the synthesis of 1,2-diarylprop-2-en-1-ones has been presented. This new approach allows for the use of a large pool of available reagents, utilizes mild reaction conditions, is insensitive to electronic and steric effects, and proceeds in high yields.

Experimental Section

General Methods. Melting points were determined with a capillary melting point apparatus equipped with a digital

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thermometer. ^{1}H and ^{13}C NMR spectra were collected on a 300 MHz NMR spectrometer (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Tetrahydrofuran (THF) was distilled under nitrogen immediately before use from sodium/benzophenone. (Chloromethyl)trimethylsilane was purchased from Gelest, Inc. Column chromatography was conducted with silica gel grade 230−400 mesh. The chromatographic technique was flash chromatography as described by Still[25] with a 3:1 hexanes/ethyl ether mixture unless otherwise stated. All organometallic reactions were carried out under argon in oven-dried glassware. All other reagents were reagent grade and were used without purification.

General Procedure for the Preparation of Compounds 3a−h. *n*-BuLi in hexanes (1.43 M, 2.14 mL, 0.003 mol) was added to the appropriate **1a−e** (0.003 mol) dissolved in THF (50 mL), and the mixture was cooled at −78 °C. After 30 min the appropriate aroyl chloride **2a−f** (0.003 mol) was added, and the reaction mixture was allowed to reach room temperature in 16 h. Aqueous ammonium chloride saturated solution was added (40 mL), and the mixture was stirred at room temperature for 1 h. The aqueous layer was extracted with ethyl ether (2 × 30 mL), and the combined organic layers were washed with brine (2 × 30 mL), dried ($MgSO_4$), and had the solvent removed to give a residue which was subjected to flash column chromatography.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-[4-(methyloxy)phenyl]-2-(4-methylphenyl)-3-(trimethylsilyl)propan-1-one (3a): the physical data for this compound have been previously reported.[23]

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-fluorophenyl)-2-(2-methylphenyl)-3-(trimethylsilyl)propan-1-one (3b): colorless glass; ^{1}H NMR δ −0.24 (s, 9H), 2.11 (s, 3H), 2.40−2.45 (m, 2H), 6.89 (t, J = 8.1 Hz, 2H), 7.02−7.04 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.24−7.31 (m, 4H), 7.56 (t, J = 5.7 Hz, 2H), 8.03 (d, J = 6.6 Hz, 1H); ^{13}C NMR δ −0.1, 22.0, 27.6, 78.7, 113.0, 115.1 (d, J = 21.9 Hz), 120.0, 123.9, 125.5, 127.2, 128.0, 128.7, 132.2 (d, J = 8.9 Hz), 133.3, 133.4, 137.3 (d, J = 38.5 Hz), 146.8, 164.7 (d, J = 255.4 Hz), 195.0. Anal. Calcd for $C_{25}H_{26}FN_3OSi$: C, 69.57; H, 6.07; N, 9.74; found, C, 69.32; H, 6.44; N, 10.07.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(4-chlorophenyl)-2-(2-fluorophenyl)-3-(trimethylsilyl)propan-1-one (3c): colorless glass; ^{1}H NMR δ −0.19 (s, 9H), 2.44 (d, J = 14.7 Hz, 1H), 2.55 (d, J = 14.8 Hz, 1H), 6.66 (t, J = 7.4 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 7.12−7.20 (m, 4H), 7.30−7.35 (m, 5H), 8.10 (d, J = 5.9 Hz, 1H); ^{13}C NMR δ −0.0, 27.5, 75.6 (d, J = 4.0 Hz), 112.6, 116.8 (d, J = 23.4 Hz), 120.2, 123.8, 124.3, 126.6 (d, J = 12.0 Hz), 127.8, 127.9 (d, J = 3.3 Hz), 128.6, 130.3, 130.6 (d, J = 9.0 Hz), 133.1, 133.4, 138.9, 146.9, 160.1 (d, J = 248.6 Hz), 192.7. Anal. Calcd for $C_{24}H_{23}ClFN_3OSi$: C, 63.77; H, 5.31; N, 9.30; found, C, 63.53; H, 5.24; N, 9.20.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(4-fluorophenyl)-1-[4-(methyloxy)phenyl]-3-(trimethylsilyl)propan-1-one (3d): colorless glass; ^{1}H NMR δ −0.18 (s, 9H), 2.49 (d, J = 15.0 Hz, 1H), 3.73 (s, 3H), 6.66 (d, J = 9.0 Hz, 2H), 6.99−7.05 (m, 3H), 7.22−7.33 (m, 4H), 7.50 (d, J = 9.3 Hz, 2H), 8.02−8.04 (m, 1H); ^{13}C NMR δ 0.2, 31.0, 55.3, 76.8, 112.0, 113.5, 115.0 (d, J = 21.6 Hz), 120.0, 123.9, 127.4, 130.0 (d, J = 7.8 Hz), 131.9, 133.2, 135.1, 146.7, 162.2 (d, J = 247.0 Hz), 163.1, 193.9. Anal. Calcd for $C_{25}H_{26}FN_3O_2Si$: C, 67.09; H, 5.85; N, 9.39; found, C, 66.97; H, 6.11; N, 9.32.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(2-chlorophenyl)-2-(2-methylphenyl)-3-(trimethylsilyl)propan-1-one (3e): colorless glass; ^{1}H NMR δ −0.11 (s, 9H), 2.33 (s, 3H), 2.77 (d, J = 14.8 Hz, 1H), 2.95 (d, J = 15.0 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 7.20−7.30 (m, 4H), 7.40−7.46 (m, 3H), 7.61 (d, J = 7.9 Hz, 1H), 8.20 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ −0.1, 19.9, 25.6, 78.9, 113.8, 119.9, 124.1, 124.4, 126.3, 126.8, 127.3, 129.0, 129.5, 130.3, 131.6, 131.8, 132.7, 133.1, 135.4, 136.3, 138.3, 146.8, 196.8. Anal. Calcd for $C_{25}H_{26}ClN_3O_2Si$: C, 67.02; H, 5.85; N, 9.38; found, C, 66.60; H, 6.04; N, 9.39.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-1-(2-methylphenyl)-2-(4-methylphenyl)-3-(trimethylsilyl)propan-1-one (3f): colorless glass; ^{1}H NMR δ −0.20 (s, 9H), 2.04 (s, 3H), 2.29 (s, 3H), 2.54 (s, 2H), 6.66−6.71 (m, 3H), 6.99 (br s, 2H), 7.13−7.27 (m, 5H), 7.34−7.38 (m, 1H), 7.92 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ −0.3, 20.2, 21.8, 28.0, 80.5, 113.1, 119.8, 123.6, 124.1, 125.8, 125.9, 126.7, 128.7, 128.9, 129.8, 131.1, 133.3, 133.5, 135.6, 136.9, 137.1, 137.7, 146.8, 201.4. HRMS (EI) (*m*/*e*): calcd for $C_{26}H_{29}N_3OSi$, 427.2080; found, 427.2094.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-2-(2-methylphenyl)-1-(4-methylphenyl)-3-(trimethylsilyl)propan-1-one (3 g): colorless glass; ^{1}H NMR δ −0.18 (s, 9H), 2.35 (s, 3H), 2.44 (s, 3H), 2.35−2.62 (m overlapped, 2H), 6.51 (d, J = 7.7 Hz, 1H), 6.72−6.81 (m, 2H), 7.06−7.10 (m, 2H), 7.18−7.32 (m, 6H), 8.03 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ −0.1, 20.2, 21.0, 30.7, 78.8, 112.9, 119.8, 123.5, 125.3, 126.6, 128.1, 129.0, 129.8, 130.9, 133.4, 134.5, 136.7, 137.3, 138.5, 146.6, 201.8. HRMS (EI) (*m*/*e*) calcd for $C_{26}H_{29}N_3OSi$, 427.2080; found, 427.2195.

2-(1*H*-1,2,3-Benzotriazol-1-yl)-2-[4-(methyloxy)phenyl]-1-(2,4,6-trimethylphenyl)-3-(trimethylsilyl)propan-1-one (3h): colorless glass; ^{1}H NMR δ −0.04 (s, 9H), 2.11 (s, 6H), 2.22 (s, 3H), 2.75 (d, J = 14.8 Hz, 1H), 2.85 (d, J = 14.8 Hz, 1H), 4.05 (s, 3H), 6.63 (br s, 2H), 6.75 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.34−7.38 (m, 2H), 8.13 (d, J = 7.9 Hz, 1H); ^{13}C NMR δ −0.1, 20.3, 20.5, 31.6, 55.2, 80.3, 113.5, 113.8, 119.4, 123.0, 125.7, 127.9, 128.0, 129.2, 133.2, 133.4, 136.5, 138.0, 146.4, 159.6, 207.8. Anal. Calcd for $C_{28}H_{33}N_3O_2Si$: C, 71.30; H, 7.05; N, 8.91; found, C, 71.75; H, 7.06; N, 8.79.

General Procedure for the Preparation of Compounds 4a−h. *p*-Toluenesulfonic acid monohydrate (0.1 mmol) or trifluoroacetic acid (2 mmol) was added to a solution of **3** (1 mmol) in methanol (5 mL) or methylene chloride (4 mL), and the mixture was stirred at room temperature or heated under reflux for the time indicated in Table 1. In the case of **4a,e** methanol was removed under reduced pressure, and the residue was dissolved in methylene chloride (20 mL). In all cases the solution in methylene chloride was washed with water, extracted with aqueous sodium hydroxide solution (5%, 2 × 20 mL) and brine (2 × 20 mL), and then dried ($MgSO_4$). The residue was subjected to flash chromatography.

1-[4-(Methyloxy)phenyl]-2-(4-methylphenyl)prop-2-en-1-one (4a): the physical data for this compound have been previously reported.[23]

1-(4-Fluorophenyl)-2-(2-methylphenyl)prop-2-en-1-one (4b): colorless oil; ^{1}H NMR δ 2.19 (s, 3H), 5.98 (s, 1H), 5.99 (s, 1H), 7.07−7.18 (m, 3H), 7.20−7.28 (m, 3H), 7.89−7.93 (m, 2H); ^{13}C NMR δ 20.3, 115.3 (d, J = 21.9 Hz), 126.0, 127.4, 128.3, 129.6, 130.2, 132.2 (d, J = 9.2 Hz), 133.3 (d, J = 3.0 Hz), 135.4, 138.1, 149.0, 165.3 (d, J = 254.3 Hz), 194.6. Anal. Calcd for $C_{16}H_{13}FO$: C, 79.98; H, 5.45. Found: C, 79.58; H, 5.64.

1-(4-Chlorophenyl)-2-(2-fluorophenyl)prop-2-en-1-one (4c): colorless oil; ^{1}H NMR δ 5.89 (s, 1H), 6.14 (s, 1H), 7.04 (t, J = 8.5 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.30−7.43 (m, 4H), 7.83 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 115.7 (d, J = 21.6 Hz), 124.4 (d, J = 3.5 Hz), 126.0, 128.6, 130.0 (d, J = 3.3 Hz), 130.4 (d, J = 8.3 Hz), 135.1, 139.2, 143.3, 159.4 (d, J = 247.3 Hz), 194.6. Anal. Calcd for $C_{15}H_{10}ClFO$: C, 69.11; H, 3.87. Found: C, 68.78; H, 3.75.

2-(4-Fluorophenyl)-1-[4-(methyloxy)phenyl]prop-2-en-1-one (4d): colorless oil; ^{1}H NMR δ 3.86 (s, 3H), 5.55 (s, 1H), 5.96 (s, 1H), 6.92 (d, J = 8.9 Hz, 2H), 7.03 (t, J = 8.7 Hz, 2H), 7.38−7.43 (m, 2H), 7.90 (d, J = 8.9 Hz, 2H); ^{13}C NMR δ 55.4, 113.6, 115.4 (d, J = 21.7 Hz), 119.1, 128.6 (d, J = 8.2 Hz), 129.6, 132.3, 133.2 (d, J = 3.3 Hz), 147.1, 162.6 (d, J = 247.9 Hz), 163.7, 195.9. Anal. Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11. Found: C, 74.84; H, 5.29.

2-(2-Chlorophenyl)-1-(2-methylphenyl)prop-2-en-1-one (4e): colorless oil; ^{1}H NMR δ 2.46 (s, 3H), 5.98 (s, 1H), 6.13 (s, 1H), 7.19−7.40 (m, 7H), 7.58 (d, J = 7.5 Hz, 1H); ^{13}C NMR δ 20.1, 124.9, 126.9, 129.4, 129.5, 129.6, 130.5, 131.2, 131.3, 133.0, 137.0, 137.8, 148.9, 197.2. HRMS (EI) (*m*/*e*) calcd for $C_{16}H_{13}OCl$, 256.0655; found, 256.0672.

2-(2-Methylphenyl)-1-(4-methylphenyl)prop-2-en-1-one (4f): white prisms, mp 43.3−44.0 °C; ^{1}H NMR δ 2.27 (s, 3H), 2.43 (s, 3H), 5.99 (s, 1H), 6.10 (s, 1H), 7.12−7.28 (m, 6H), 7.35 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H); ^{13}C NMR δ 19.9, 20.2, 124.9, 125.7, 128.1, 128.4, 129.6, 130.0, 130.1, 131.0, 131.6, 135.8, 136.9, 137.4, 138.2, 150.4, 198.3. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.32; H, 7.02.

1-(2-Methylphenyl)-2-(4-methylphenyl)prop-2-en-1-one (4 g): colorless oil; ^{1}H NMR δ 2.34 (s, 3H), 2.45 (s, 3H), 5.66 (s, 1H), 6.10 (s, 1H), 7.15−7.23 (m, 4H), 7.32−7.34 (m, 3H),

(25) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

7.43 (d, J = 7.4 Hz, 1H); ^{13}C NMR δ 20.2, 21.1, 125.2, 125.8, 127.7, 129.0, 129.3, 130.5, 131.1, 133.9, 137.3, 138.1, 138.5, 149.4, 199.6. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.09; H, 7.24.

2-[4-(Methyloxy)phenyl]-1-(2,4,6-trimethylphenyl)prop-2-en-1-one (4h): light yellow prisms, mp 84.8−85.9 °C; ^{1}H NMR δ 2.21 (s, 6H), 2.31 (s, 3H), 3.84 (s, 3H), 5.78 (s, 1H), 6.17 (s, 1H), 6.86 (s, 2H), 6.93 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H); ^{13}C NMR δ 19.1, 21.0, 55.2, 113.6, 128.2, 128.4, 129.0, 29.7, 134.2, 137.2, 138.3, 148.6, 159.7, 201.7. Anal. Calcd for $C_{19}H_{20}O$: C, 81.40; H, 7.19. Found: C, 81.56; H, 7.45.

Procedure for the Preparation of 2-(4-Chlorophenyl)-1-phenylprop-2-en-1-one (7): Benzotriazole (0.325 g, 2.72 mmol) and 4-chlorobenzyl chloride (0.337 g, 2.10 mmol) in dry toluene (3.5 mL) were stirred under reflux for 2 days. The cooled mixture was sequentially washed with aqueous sodium carbonate solution (10%, 2 × 10 mL) and aqueous hydrogen chloride solution (1 N, 2 × 10 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford a white solid (0.500 g, 2.05 mmol). The solid was dissolved in THF (20 mL), and the mixture was cooled to −78 °C. *n*-BuLi in hexanes (1.55 M, 1.26 mL, 1.95 mmol) was added, and after the mixture was stirred for 30 min (chloromethyl)trimethylsilane (0.272 mL, 1.95 mmol) was added; the reaction mixture was allowed to reach room temperature in 16 h. The mixture was cooled to −78 °C, and *n*-BuLi in hexanes (1.55 M, 1.33 mL, 2.05 mmol) was added. After 30 min benzoyl chloride (0.238 mL, 2.05 mmol) was added, and the mixture was allowed to reach room temperature in 9 h. The solution was washed with saturated aqueous ammonium chloride solution (50 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford a pale yellow solid. This solid was dissolved in dry methylene chloride (8 mL), and trifluoroacetic acid (0.316 mL, 4.11 mmol) was added dropwise under stirring. The resulting mixture was allowed to react overnight. The reaction mixture was washed with aqueous sodium hydroxide solution (5%, 2 × 20 mL), was extracted with methylene chloride, and was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography on silica gel to afford **7** as light yellow prisms (0.244 g, 48%): mp 181.4−183.4 °C; ^{1}H NMR δ 5.67 (s, 1H), 6.07 (s, 1H), 7.31 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.44 (t, J = 7.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.88 (d, J = 7.3 Hz, 2H); ^{13}C NMR δ 121.8, 128.4, 128.8, 129.9, 133.2, 134.4, 135.4, 136.9, 147.1, 201.21. Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.22; H, 4.58. Found: C, 74.23; H, 4.71.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **3f**−**h**, and **4e,g** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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