A Convenient Route to 2-Lithio-1,3-butadiene from Chloroprene *via* 2-Stannyl-1,3-butadiene

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A convenient route to 2-lithio-1,3-butadiene from chloroprene *via* a 2-stannyl-1,3-butadiene is presented, and the regioselective additions to a variety of carbonyl groups are demonstrated.

Introduction of a 1,3-butadienyl unit to a molecule is important in organic synthesis as the diene moiety can be used usefully to construct a stereochemically defined six-membered ring. One of the most useful reagents along this purpose is 1-methylene-2-propenylmagnesium chloride which is easily accessible in a large quantity from an industrial material, chloroprene.[1] However, a serious disadvantage is a poor regioselectivity in the additions to carbonyl groups. In most reported cases, it reacts at both the α- and γ-positions and major products are usually the γ-adducts,[2] while its cross coupling reactions with alkyl halides[3] and the Michael reactions take place in a highly regioselective manner at the α-position.[4]

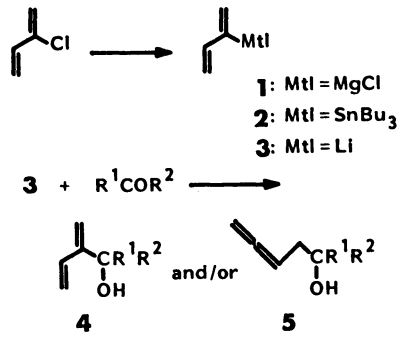
Recently it has been reported that 2-lithio-1,3-butadiene reacts with several aldehydes mainly at the α-position.[5] However, this reagent was prepared only in a fair yield from the Shapiro reaction of trisylhydrazone (2,4,6-triisopropylphenylsulfonylhydrazone) of methyl vinyl ketone, its use in organic synthesis having been quite limited.

The present work aims at opening a more convenient and efficient route to 2-lithio-1,3-butadiene from chloroprene, and also knowing the degree of α-regioselectivity of this reagent in the reactions with some other types of carbonyl compounds.

Results and Discussion

The Grignard reagent **1**, prepared from chloroprene and metal magnesium in the presence of zinc chloride in dry tetrahydrofuran (THF) was transmetalated with chlorotributyltin affording an excellent yield of 2-(tributylstannyl)-1,3-butadiene **2**, which had been previously synthesized from the Grignard reagent of 4-chloro-1,2-butadiene with the stannyl reagent.[6] The tin-lithium exchange reaction was examined in dry THF at −78 °C using butyllithium, and 2-lithio-1,3-butadiene **3** generated was allowed to react with a variety of carbonyl compounds as shown in Scheme 1.

Treatment of **2** with an equivalent of butyllithium in dry THF, at −78 °C for 0.5 h, provided a deep red-colored solution of **3** to which was then



Scheme 1.

added an equivalent of benzaldehyde in THF. The mixture was quenched, after 0.5 h at the same temperature, with an ice-cold ammonium chloride solution. The crude product which was obtained in 80% yield by the filtration through a short column over silica gel was found to be a mixture of two isomeric alcohols, the 2-methylene-3-buten-1-ol **4a** as an α-adduct and the 3,4-pentadien-1-ol **5a** as a γ-adduct, in 9:1 ratio.

Table 1 summarizes the results obtained from the reactions of **3** with other carbonyl compounds under similar conditions. Aliphatic aldehydes, whichever with a straight alkyl chain or a bulky substituent, α,β-unsaturated aldehydes carrying a variety of substituents at the β-position, and acetophenones all smoothly reacted with **3** providing the corresponding alcohols **4b**—**4i** and/or **5b**—**5i** in satisfied yields. The α-selectivity was found excellent in all cases, no γ-adducts being even detected by GLC or ^{1}H-NMR analyses in some cases (the reactions leading to exclusive formation of **4b**, **4c**, **4e**, and **4g**). To be noteworthy is the high α-selectivity toward acetophenones because the Grignard reaction of **1** has shown a very poor afinity at the α-position to this aromatic ketone (**4h**:**5h**=12~19:88~81). Even benzophenone which is known to afford only the γ-adduct **5j** in the Grignard reaction produced a mixture of comparable amounts of **4j** and **5j**, while their separation was unsuccessful.

The present method offers an alternative for the preparation of **3** and seems more convenient and effi-

Table 1. Reactions of 2-lithio-1,3-butadiene **3** with carbonyl compounds[a)]

Carbonyl compounds	Products			Yield/%[b)]		Products from **1**	
	4, 5	R^1	R^2	**4+5**	**4 : 5**	Yield/%	**4 : 5**
PhCHO	**a**	H	Ph	80	91 : 9 (46%, 93 : 7)[c)]	73[d)] 68[e)]	39 : 61[d)] 30 : 70[e)]
$Me(CH_2)_5CHO$	**b**	H	$Me(CH_2)_5$	61	Only **4b**		
Me_3CCHO	**c**	H	Me_3C	61	Only **4c**		
CH_2=CHCHO	**d**	H	CH_2=CH	59	96 : 4		
MeCH=CHCHO (t)	**e**	H	MeCH=CH (t)	80	Only **4e**		
PhCH=CHCHO (t)	**f**	H	PhCH=CH (t)	76	19 : 1 (32%, 81 : 19)[c)]	84[f)]	7 : 9[f)]
Me_2C=CHCHO	**g**	H	Me_2C=CH	45	Only **4g**		
PhCOMe	**h**	Me	Ph	70	9 : 1	63[d)] 45[e)]	19 : 81[d)] 12 : 88[e)]
p-$MeOC_6H_4COMe$	**i**	Me	*p*-$MeOC_6H_4$	78	95 : 5		
PhCOPh	**j**	Ph	Ph	73	1 : 1	92[d)]	Only **5j**[d)]

a) Conditions: **2** : *n*-BuLi : R^1COR^2 = 1 : 1 : 1 in dry THF at −78 °C. b) Isolated yields. The isomer ratio was determined by GPLC or ^{1}H-NMR. c) Ref. 2a. d) Ref. 1. f) Our unpublished results.

cient than the Shapiro procedure. It is certain that this method stimulates the wide applications of the industrial material, chloroprene, in organic synthesis. We have recently developed a new [6.6] annelation method by the diene-transmissive Diels-Alder reaction equivalent of 2-methylene-3-buten-1-ols which were prepared by the Grignard reactions of chloroprene.[2b)] These carbinols are now being employed in a research directed toward the [6.5] annelation processes by the sequence of Diels-Alder reaction and Nazarov cyclization or Diels-Alder cycloaddition and electrocyclic reaction.

Experimental

General. IR spectra were recorded on a JASCO IRA-1 or a JASCO A-102 IR spectrometer. ^{1}H-NMR spectra were taken with a Hitachi R-40 (90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C-NMR spectra on a JEOL FX-100 spectrometer at 25.04 MHz. Chemical shifts are expressed in part per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL JMS-01SG-2 mass spectrometer at 70 or 40 eV of ionization energy. Elemental analyses were obtained with a Hitachi 026 CHN micro analyzer. GPLC analysis was performed on a Yanagimoto gas chromatograph YANACO G-2800 model equipped with a hydrogen flame ionization detector (column: SE 30, 3 mm×2 m). Micro vacuum distillation was carried out with a Shibata GTO-250R Kugelrohr distilling apparatus, and boiling points are all uncorrected. For preparative column chromatography, either of Wakogel C 300 or Silicagel 60 (Merck, 70—230 mesh) was used. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type V at 0 °C to room temperature unless otherwise stated.

Materials. Tetrahydrofuran as a reaction solvent was distilled over lithium aluminum hydride prior to its use. Chloroprene was purified by distillation under nitrogen stream from the xylene solution also immediately before it was used. Anhydrous zinc chloride was obtained by the crystallization of commercial material from dioxane containing a small amount of zinc powder. Metal magnesium (turning), chlorotributyltin, and butyllitium (15% in hexane) are commercially available and were used without further purification. The carbonyl compounds which are also all commercially available were purified by distillation or crystallization.

2-(Tributylstannyl)-1,3-butadiene **2**. To a solution of **1**, prepared from chloroprene (21 g, 0.187 mol), magnesium (5 g, 0.206 g atom), anhydrous zinc chloride (1.2 g) in dry tetrahydrofuran (80 ml) according to the reported method,[1)] was added dropwise a solution of chlorotributyltin (55.3 g, 0.17 mol) in tetrahydrofuran (80 ml) at −12 to −10 °C. After heated under reflux for 0.5 h, the mixture was treated with aqueous solution of ammonium chloride at 0 °C. The tetrahydrofuran was condensed *in vacuo*, the residue extracted with ether, the ether dried over anhydrous magnesium sulfate, and finally evaporated *in vacuo*. The liquid obtained was distilled under vacuum giving 51.6 g (89%) of pure **2** as a colorless liquid: bp 92—95 °C (93 Pa) (lit,[6)] bp 80—90 °C (53 Pa)).

General Procedure for the Preparation of 2-Lithio-1,3-butadiene **3** *and its Reactions with Carbonyl Compounds.* To a solution of **2** (1.25 g, 3.64 mmol) in dry tetrahydrofuran (9 ml), was added butyllithium (2.25 ml, 3.6 mmol) at −78 °C under nitrogen and then the mixture was stirred for 0.5 h during which time the color of solution gradually turned deep red. When carbonyl compounds (3.6 mmol) in tetrahydrofuran (2 ml) was added by the use of a syringe, the red color immediately faded away. The mixture was stirred for 0.5 h at the same temperature and treated with ice-cold ammonium chloride solution. Organic products were extracted with ether (20 ml×2), the ether dried over magnesium sulfate, and then evaporated *in vacuo*. The residue was chromatographed through a short column packed with silica gel. The first fraction containing tetrabutyltin as an undesired product was eluted with hexane and disregarded. After all the tin compound was removed out, the second fraction was collected using hexane–ether (3:1) for the low-boiling products or hexane-

ethyl acetate (9:1) for the nonvolatile products. At this moment, the isomer ratios between **4** and **5** were determined by GPLC and/or ^{1}H-NMR analyses. The combined yields as well as the isomer ratios for **4** and **5** are given in Table 1.

Although the 2-methylene-3-buten-1-ols **4a** to **4i** could be separated and purified through repeated chromatographic operations over silica gel in a long column (15 mm×400 mm) using hexane–ether (20:1) or hexane–ethyl acetate (9:1) as an eluent, no authentic samples of allenic alcohols **5** were obtained because of the too poor formation and the contamination by the major products **5**. The formation of **5** was, however, confirmed on the basis of the analysis of ^{1}H-NMR spectra for the crude reaction mixtures. The separation of either **4j** or **5j** which was yielded from benzophenone was unsuccessful.

The spectral data and elemental analyses for the products are given below. Some of the products were transformed to their derivatives which were then submitted for elemental analyses.

2-Methylene-1-phenyl-3-buten-1-ol ***4a***: Colorless viscous oil; IR (neat) 3350 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=2.82 (1H, br. s, OH), 4.97 (1H, d, $J_{4-3\,(cis)}$=11.2 Hz, one of 4-H), 5.11 (1H, d, $J_{4-3\,(trans)}$=17.8 Hz, the other of 4-H), 5.22 (1H, s, 1-H), 5.30 (2H, s, 2-(CH_2=)), 6.23 (1H, dd, J_{3-4}=17.8 and 11.2 Hz, 3-H), and 7.23 ppm (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=73.78 (d, 1-C), 115.25, 115.49 (each t, 4-C and 2-($\underline{C}H_2$=)), 126.89, 127.62, 128.31 (each d, *o*-, *m*-, and *p*-C of Ph), 135.81 (d, 3-C), 142.00 (s, 1-C of Ph), and 147.56 ppm (s, 2-C); MS *m/z* (rel. intensity, %) 160 (M^+, 33), 142 (16), 129 (10), 115 (11), 107 (83), 105 (28), 91 (18), 79 (base peak), 78 (18), and 77 (64).

Found: *m/z* 160.0880. Calcd for $C_{11}H_{12}O$: M, 160.0888. ^{1}H-NMR ($CDCl_3$) of the isomeric alcohol **5a**: δ=2.36 (m, CH_2) and 4.60 ppm (m, =CH_2). The ratio of **4a**:**5a**=9:1.

3-Methylene-1-decen-4-ol ***4b***: Colorless oil; IR (neat) 3330 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=0.87 (3H, t, Me), 1.05—1.80 (10H, m, CH_2), 2.47 (1H, br. s, OH), 4.37 (1H, t, J_{4-5}=5.7 Hz, 4-H), 5.04 (1H, d, $J_{1-2\,(cis)}$=11.0 Hz, one of 1-H), 5.10, 5.18 (each 1H, s, 3-(CH_2=)), 5.29 (1H, d, $J_{1-2\,(trans)}$=17.9 Hz, the other of 1-H), and 6.31 ppm (1H, dd, J_{2-1}=17.9 and 11.0 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ=14.13 (q, 10-C), 22.71, 25.88, 29.34, 31.92, 36.50 (each t, 5-, 6-, 7-, 8-, and 9-C), 71.63 (d, 4-C), 113.78 (t, 3-($\underline{C}H_2$=)), 114.08 (t, 1-C), 136.30 (d, 2-C), and 149.40 ppm (s, 3-C); MS *m/z* (rel. intensity, %) 168 (M^+, 5), 151 (9), 97 (29), 84 (98), and 83 (base peak).

Elemental analysis was carried out with an authentic sample of the *p*-nitrobenzoate of **4b** (pale yellow oil).

Found: C, 67.98; H, 7.35; N, 4.57%. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.31; N, 4.41%.

2,2-Dimethyl-4-methylene-5-hexen-3-ol ***4c***: Colorless viscous oil; IR (neat) 3450 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=0.90 (9H, s, *t*-Bu), 2.10 (1H, br. s, OH), 4.10 (1H, s, 3-H), 4.99 (1H, dd, $J_{6-5\,(cis)}$=11.2 and J_{gem}=1.2 Hz, one of 6-H), 5.10, 5.27 (each 1H, br. s, 4-(CH_2=)), 5.34 (1H, dd, $J_{6-5\,(trans)}$=17.6 and J_{gem}=1.2 Hz, the other of 6-H), and 6.34 ppm (1H, br. dd, J_{5-6}=17.6 and 11.2 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ=26.46 (q, Me of *t*-Bu), 35.50 (s, 2-C), 78.86 (d, 3-C), 113.82 (t, 4-($\underline{C}H_2$=)), 115.67 (t, 6-C), 138.28 (d, 5-C), and 148.58 ppm (s, 4-C).

Elementary analysis was performed with an authentic sample of the *p*-nitrobenzoate of **4c** (pale yellow prisms from hexane, mp 46—47 °C).

Found: C, 66.64; H, 6.66; N, 4.90%. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84%.

4-Methylene-1,5-hexadien-3-ol ***4d***: Colorless viscous oil; bp 75 °C (439 Pa); IR (neat) 3500 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=2.48 (1H, br. s, OH), 4.86 (1H, d, J_{3-2}=5.5 Hz, 3-H), 4.96—5.50 (6H, m, 1-H (2H), 6-H (2H), and 4-(CH_2=) (2H)), 5.93 (1H, ddd, J_{2-1}=17.5 and 10.0 and J_{2-3}=5.5 Hz, 2-H), and 6.32 ppm (1H, dd, $J_{5-6\,(trans)}$=17.5 and $J_{5-6\,(cis)}$=11.0 Hz, 5-H); ^{13}C-NMR ($CDCl_3$) δ=72.32 (d, 3-C), 114.91 (t, 4-($\underline{C}H_2$=)), 115.10, 115.64 (each t, 1- and 6-C), 135.86 (d, 5-C), 139.03 (d, 2-C), and 147.21 ppm (s, 4-C).

This compound **4d** polymerized in the oven of mass spectrometer, showing some higher fragment peaks than that for the parent ion.

The elemental analysis was carried out with an authentic sample of the *p*-nitrobenzoate of **4d** (pale yellow viscous oil).

Found: C, 64.88; H, 5.15; N, 5.59%. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40%.

^{1}H-NMR ($CDCl_3$) of the isomeric alcohol **5d**: δ=2.23 (m, CH_2) and 4.64 ppm (m, =CH_2).

(E)-3-Methylene-1,5-heptadien-4-ol ***4e***: Colorless viscous oil; bp 100 °C (399 Pa); IR (neat) 3350 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.70 (3H, dd, J_{7-6}=5.0 and J_{7-5}=0.5 Hz, Me), 2.46 (1H,br. s, OH), 4.80 (1H, d, J_{4-5}=5.5 Hz, 4-H), 5.00—5.92 (6H, m, 1-H (2H), 3-(CH_2=) (2H), 5-H, and 6-H), and 6.30 ppm (1H, $J_{2-1\,(trans)}$=17.5 and $J_{2-1\,(cis)}$=10.0 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ=17.67 (q, 7-C), 72.17 (d, 4-C), 114.12 (t, 3-($\underline{C}H_2$=)), 114.71 (t, 1-C), 127.81 (d, 5-C), 132.25 (d, 6-C), 136.06 (d, 2-C), and 147.84 ppm (s, 3-C); MS *m/z* (rel. intensity, %) 124 (M^+, 5), 110 (18), 106 (11), 95 (36), 91 (13), 81 (15), 80 (17), 79 (13), and 71 (base peak).

Found: *m/z* 124.0878. Calcd for $C_8H_{12}O$: M, 124.0888.

(E)-4-Methylene-1-phenyl-1,5-hexadien-3-ol ***4f***: Colorless viscous oil; IR (neat) 3330 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=2.82 (1H, br. s, OH), 4.97 (1H, d, J_{3-2}=6.5 Hz, 3-H), 5.00—5.50 (4H, m, 6-H (2H) and 4-(CH_2=) (2H)), 6.20 (1H, dd, J_{2-3}=6.5 and J_{2-1}=16.0 Hz, 2-H), 6.32 (1H, dd, $J_{5-6\,(trans)}$=17.5 and $J_{5-6\,(cis)}$=11.2 Hz, 5-H), 6.58 (1H, dd, J_{1-2}=16.0 Hz, 1-H), and 7.10—7.40 ppm (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=71.97 (d, 3-C), 115.00 (t, 6-C and 4-($\underline{C}H_2$=)), 126.45, 127.58, 128.45 (each d, *o*-, *m*-, and *p*-C of Ph), 130.35, 130.93 (each d, 1- and 2-C), 135.81 (d, 5-C), 136.54 (s, 1-C of Ph), and 147.26 ppm (s, 4-C); MS *m/z* (rel. intensity, %) 186 (M^+, 26), 142 (15), 134 (11), 133 (base peak), 131 (14), 129 (13), 128 (11), 115 (49), 107 (21), 105 (39), 104 (24), 103 (25), 95 (23), and 91 (52).

Found: *m/z* 186.1048. Calcd for $C_{13}H_{14}O$: M, 186.1044.

^{1}H-NMR ($CDCl_3$) of the isomeric alcohol **5f**: δ=4.66 ppm (m, =CH_2). The ratio of **4f**:**5f**=19:1.

6-Methyl-3-methylene-1,5-heptadien-4-ol ***4g***: Colorless viscous oil; IR (neat) 3300 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.72 (6H, s, Me), 2.18 (1H, br. s, OH), 4.90—5.40 (6H, m, 1-H (2H), 3-(CH_2=) (2H), 4-H, and 5-H), and 6.29 ppm (1H, dd, $J_{2-1\,(trans)}$=18.0 and $J_{2-1\,(cis)}$=11.0 Hz, 2-H); ^{13}C-NMR ($CDCl_3$) δ=18.02, 25.58 (each q, Me), 68.26 (d, 4-C), 113.71 (t, 3-($\underline{C}H_2$=)), 114.45 (t, 1-C), 126.80 (d, 5-C), 136.13 (s, 6-C), 136.23 (d, 2-C), and 148.58 ppm (s, 3-C); MS *m/z* (rel. intensity, %) 138 (M+, 4), 123 (8), 120 (5), 105 (15), 95 (30), 91 (17), 85 (base peak), 83 (37), 80 (26), 79 (18), 77 (17), and 67 (20).

Found: *m/z* 138.1043. Calcd for $C_9H_{14}O$: M, 138.1044.

3-Methylene-2-phenyl-4-penten-2-ol ***4h***: Colorless viscous

oil; IR (neat) 3420 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.66 (3H, s, Me), 2.24 (1H, br. s, OH), 4.94 (1H, dd, $J_{5-4\,(cis)}$= 11.0 and J_{gem}=1.2 Hz, one of 5-H), 5.24 (1H, dd, $J_{5-4\,(trans)}$= 17.5 and J_{gem}=1.2 Hz, the other of 5-H), 5.31, 5.34 (each 1H, s, 3-(CH_2=)), 6.09 (1H, dd, J_{4-5}=17.5 and 11.0 Hz, 4-H), and 7.00—7.60 ppm (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=29.53 (q, Me), 76.12 (s, 2-C), 111.93 (t, 3-($\underline{C}H_2$=)), 116.51 (t, 5-C), 125.33, 126.99, 128.20 (each d, *o*-, *m*-, and *p*-C of Ph), 135.56 (d, 4-C), 146.09 (s, C-1 of Ph), and 151.89 ppm (s, 3-C); MS *m/z* (rel. intensity, %) 174 (M^+, 22), 159 (12), 131 (20), 130 (13), 129 (10), 121 (78), 115 (12), 105 (25), 91 (18), 77 (21), and 43 (base peak).

Found: *m/z* 174.1032. Calcd for $C_{12}H_{14}O$: M, 174.1044.

^{1}H-NMR ($CDCl_3$) of the isomeric alcohol **5h**: δ=1.53 (s, Me), 2.50 (m, CH_2), and 4.60 ppm (m, =CH_2). The ratio of **4h**:**5h**=9:1.

3-Methylene-2-(p-methoxyphenyl)-4-penten-2-ol ***4i***: Colorless viscous oil; IR (neat) 3450 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.67 (3H, s, Me), 2.31 (1H, br. s, OH), 3.76 (3H, s, *p*-MeO), 4.93 (1H, dd, $J_{5-4\,(cis)}$=11.0 and J_{gem}=1.8 Hz, one of 5-H), 5.24 (1H, dd, $J_{5-4\,(trans)}$=17.5 and J_{gem}=1.8 Hz, the other of 5-H), 5.32 (2H, br. s, 3-(CH_2=)), 6.09 (1H, dd, J_{4-5}=17.5 and 11.0 Hz, 4-H), 6.78, and 7.29 ppm (each 2H, m, Ar); ^{13}C-NMR ($CDCl_3$) δ=29.29 (q, Me), 55.11 (q, *p*-MeO), 75.68 (s, 2-C), 111.35 (t, 3-($\underline{C}H_2$=)), 113.49 (d, 3-C of Ar), 116.12 (t, 5-C), 126.60 (d, 2-C of Ar), 135.61 (d, 4-C), 138.20 (s, 1-C of Ar), 152.13 (s, 3-C), and 158.47 ppm (s, 4-C of Ar); MS *m/z* (rel. intensity, %) 204 (M^+, 7), 152 (99), 135 (17), 108 (55), 77 (12), and 43 (base peak).

Found: C, 75.89; H, 7.95%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

Found: *m/z* 204.1191. Calcd for $C_{13}H_{16}O_2$: M, 204.1149. ^{1}H-NMR ($CDCl_3$) of the isomeric alcohol **5i**: δ=1.53 (s, Me), 2.50 (m, CH_2), and 4.61 ppm (m, =CH_2). The ratio of **4i**:**5i**=20:1.

2-Methylene-1,1-diphenyl-3-buten-1-ol ***4j*** *and 1,1-Diphenyl-3,4-pentadien-1-ol* ***5j***: These alcohols were obtained as the 1:1 mixture whose separation was unsuccessful. The ^{1}H- and ^{13}C-NMR spectra of the mixture were analyzed by the comparison with the spectra of the authentic sample of **5j** which was prepared from the reaction of **1** with benzophenone.[1] **4j**: ^{1}H-NMR ($CDCl_3$) δ=2.88 (1H, s, OH), 4.68 (1H, s, one of 2-(CH_2=)), 4.98 (1H, dd, $J_{4-3\,(cis)}$=11.0 and J_{gem}=1.7 Hz, one of 4-H), 5.30 (1H, dd, $J_{4-3\,(trans)}$=17.7 and J_{gem}=1.7 Hz, the other of 4-H), 5.41 (1H, s, the other of 2-(CH_2=)), 6.22 (1H, dd, J_{3-4}=17.7 and 11.0 Hz, 3-H), and 7.00—7.50 ppm (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ= 83.02 (s, 1-C), 117.89 (t, 2-($\underline{C}H_2$=)), 118.13 (t, 4-C), 128.40, 128.87, 129.05 (each d, *o*-, *m*-, and *p*-C of Ph), 137.15 (d, 3-C), 147.42 (s, 1-C of Ph), and 152.53 ppm (s, 2-C). **5j**: ^{1}H-NMR ($CDCl_3$) δ=2.70 (1H, s, OH), 2.97 (2H, dt, J_{2-3}= 7.4 and J_{2-5}=2.8 Hz, 2-H), 4.57 (2H, br. dt, J_{5-3}=6.2 and J_{5-2}=2.8 Hz, 5-H), 4.93 (1H, dt, J_{3-2}=7.4 and J_{3-5}=6.2 Hz, 3-H), and 7.00—7.50 ppm (10H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=41.80 (t, 2-C), 74.50 (t, 5-C), 77.55 (s, 1-C), 84.83 (d, 3-C), 125.99, 126.81, 128.05 (each d, *o*-, *m*-, and *p*-C of Ph), 146.13 (s, 1-C of Ph), and 210.30 ppm (s, 4-C).

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