Simple and Efficient Synthesis of α-Allenic Alcohols and Their Novel Conversion into 1-Aryl-3-formyloxy-1,3-butadienes

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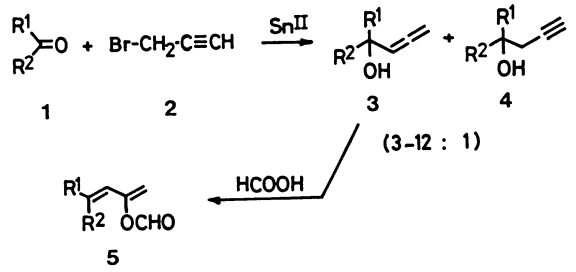
Synopsis. Reactions of carbonyl compounds with 3-bromo-1-propyne in the presence of $SnCl_2 \cdot 2H_2O$ and $LiI \cdot 3H_2O$ gave α-allenic alcohols in moderate yields together with small amounts of β-acetylenic alcohols. The α-allenic alcohols can be converted into 1-aryl-3-formyloxy-1,3-butadienes, novel 1,3-butadiene derivatives.

In connection with our interest in the synthetic utility of cumulenic compounds,[1] we required a simple method for the preparation of α-allenic alcohols **3**.[2] Although the reactions of carbonyl compounds with 3-halo-1-propynes are known to give α-allenic alcohols **3**,[3,4] the yields were usually low and large amounts of β-acetylenic alcohols **4** were obtained as a major product of these reactions. We report here a very convenient solution of this problem and the synthesis of 1-aryl-3-formyloxy-1,3-butadienes **5** from the α-allenic alcohols **3**.



1 2 3 4 5

Scheme 1.

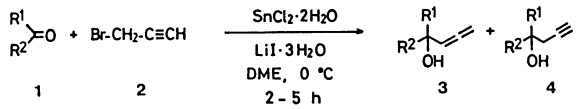
The reactions of **1** with 3-iodo-1-propyne in the presence of anhydrous $SnCl_2$ were reported to give α-allenic alcohols **3**, but considerable amounts of β-acetylenic alcohols **4** were also formed [e.g., the reaction of benzaldehyde with 3-iodo-1-propyne in the presence of $SnCl_2$ gave **3** and **4** in the ratio of 48 : 52 in 98% yield].[3a]

As shown in Table 1, the reaction of carbonyl compounds **1** with 3-bromo-1-propyne (**2**) proceeds smoothly under mild conditions to give α-allenic alcohols **3** as a major product. The hydrates of both $SnCl_2$ and LiI are employed for the reaction without removing water. Thus, benzaldehyde and its derivatives (**1a—h**: R^1=aryl and R^2=H) react with **2** in the presence of $SnCl_2 \cdot 2H_2O$ to give α-allenic alcohols **3a—h** in relatively good yields (Entries 1—9). In the case of 4-methoxybenzaldehyde (**1i**), the yield of a mixture of **3i** and **4i** obtained in the reaction reduced to 40%, owing to the instability of the α-allenic alcohol (**3i**) under the reaction conditions. The reactions of phenylacetaldehyde (**1j**) and butyraldehyde (**1k**) with **2** under similar conditions afforded the corresponding α-allenic alcohols **3j** and **3k** also as a major product (Entries 9 and 10). Furthermore, similar treatment of cyclohexanone (**1l**) with **2** gave the α-allenic alcohol **3l** selectively (Entry 11). Therefore, our method provides a simple and convenient way for the preparation of **3**.

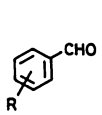
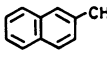
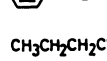
Synthesis of 2-formyloxy-1,3-butadiene (**5**: R^1=R^2=H) was reported five decades ago,[5] and Diels-Alder reaction of this compound was discussed experimentally and theoretically as a typical diene.[6] However, the synthetic methodology for access to 2-formyloxy-1,3-butadiene derivatives is still very limited.

We have found that α-allenic alcohols **3** yield 3-formyloxy-1,3-butadienes (**5**) readily by dissolving **3** in formic acid. Thus, a solution of **3** in ether is added to formic acid at room temperature and the mixture is

Table 1. Reaction of **1** with **2** in the Presence of $SnCl_2 \cdot 2H_2O$ and $LiI \cdot 3H_2O$

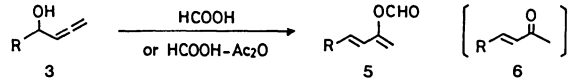


1 2 3 4

Entry	Carbonyl compound 1		R	Yield/% (3/4)	Entry	Carbonyl compound 1		Yield/% (3/4)
1		**1a**	H	92 (3.8/1)[a]	8		**1h**	89 (4.0/1)[a]
2		**1b**	4-Me	88 (3.3/1)[a]				
3		**1c**	4-Cl	84 (3.1/1)[a]	9		**1j**	91 (3.2/1)[a]
4		**1d**	4-Br	86 (3.3/1)[a]				
5		**1e**	3-OMe	96 (3.5/1)[a]	10	$CH_3CH_2CH_2CHO$	**1k**	67 (4.3/1)[b]
6		**1f**	2-Cl	80 (3.3/1)[a]				
7		**1g**	2-NO_2	77 (4.0/1)[a]	11		**1l**	54 (12/1)[b]

a) Reaction time 2 h. b) Reaction time 5 h.

Table 2. Preparation of 1-Aryl-3-formyloxy-1,3-butadiene (**5**)



3 5 6

Entry	Starting material 3	X	Product 5	Method[a]	Yield/%
1	**3a**	H	**5a**	A	42
2	**3a**	H	**5a**	B	69
3	**3c**	4-Cl	**5c**	A	55
4	**3c**	4-Cl	**5c**	B	69
5	**3f**	2-Cl	**5f**	A	66
6	**3f**	2-Cl	**5f**	B	63
7	**3b**	4-Me	**5b**	A	27
8	**3b**	4-Me	**5b**	B	49
9	**3h**		**5h**	A	7
10	**3h**		**5h**	B	35

a) Method A: HCOOH, room temperature, 30 min. Method B: HCOOH, Ac_2O, 0 °C, 1 h.

stirred for 30 min (Method A in Table 2). A side reaction of this conversion is the formation of α,β-unsaturated ketones **6** which may be attributable to the competitive addition of water instead of formic acid to the *sp*-carbon of **3**. Therefore, some modification was carried out for the conversion of **3** into **5**. A solution of **3** in ether is added to a solution of formic acid containing acetic anhydride at 0 °C and the mixture is stirred for 1 h at the same temperature (Method B in Table 2). α-Allenic alcohols **3** having electron-withdrawing groups as substituents of aryl rings gave **5** in satisfactory yields by either Method A or B (Entries 1—6). In the case of *p*-tolyl derivative, however, **5b** was obtained in 27% yield by Method A and the yield was improved to 49% by Method B (Entries 7 and 8). A marked difference in yields of **5** was observed for the case involving 2-naphthyl substituent. Thus, the 2-naphthyl-substituted α-allenic alcohol **3h** was converted into the corresponding butadiene **5h** only in 7% yield using Method A, but this conversion was achieved in 35% yield by Method B (Entries 9 and 10).

In conclusion, the 2- or 3-formyloxy-1,3-butadiene derivatives **5** are now readily available through the acid-catalyzed rearrangement of α-allenic alcohols **3**.

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-100 or JEOL JNM-PMX60Si and JNM-FX90Q instruments, and are reported in δ from tetramethylsilane. IR spectra were observed on a Hitachi EPI-G3 spectrometer. Mass spectral analysis (MS) were performed on a JEOL JMS-O1SG-2 instrument. Melting points were determined on a Mettler FP-2 apparatus and are uncorrected. Column chromatography was carried out with use of Merck silica gel 60, 70—230 mesh, art 7734, or Merck neutral alumina activity II—III, 70—230 mesh.

General Procedure for Table 1. The Reaction of Carbonyl Compound 1 with 3-Bromo-1-propyne (2). To a solution of $SnCl_2{\cdot}2H_2O$ (677 mg, 3 mmol) and $LiI{\cdot}3H_2O$ (752 mg, 4 mmol) in 1,2-dimethoxyethane (DME) (10 ml) were added successively 3-bromo-1-propyne (**2**) (476 mg, 4 mmol) and a solution of carbonyl compound **1** (2 mmol) in DME (5 ml) at 0 °C under argon atmosphere. After the reaction mixture had been stirred at 0 °C for 2—5 h, water (10 ml) was added. Benzene (30 ml) was then added, and the organic layer separated. The aqueous layer was extracted with ether. The combined organic layers were washed successively with aqueous 5% $Na_2S_2O_3$ and saturated NaCl, and dried over $MgSO_4$. After removal of $MgSO_4$, the solution was filtered through a short column of alumina (ca. 20 g) in order to avoid isomerization of **3** to **6**. The filtrate was evaporated and the residue was chromatographed on silica gel with benzene-ether as eluent to give a mixture of α-allenic alcohol **3** and β-acetylenic alcohol **4**. Separation of **3** and **4** can be carried out by column chromatography on silica gel with hexane-ethyl acetate as eluent. α-Allenic alcohols **3** decompose gradually on standing at room temperature, but can be stored at 0 °C in solution using hexane, benzene or carbon tetrachloride as solvent.

1-Phenyl-2,3-butadien-1-ol (3a),[3a—c] 1,2-heptadien-4-ol (3K),[7] and 1-(1,2-propadienyl)cyclohexan-1-ol (3l)[8] were characterized by comparison of the ^1H NMR, IR, and mass spectra with those of literatures.

1-(*p*-Tolyl)-2,3-butadien-1-ol (3b): Colorless oil, IR (neat) 3365 and 1960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (br. s, 1H), 2.34 (s, 3H), 4.92 (m, 2H), 5.24 (m, 1H), 5.45 (m, 1H), 7.16 (d, J=7.5 Hz, 2H), and 7.31 (d, J=7.5, 2H); MS *m/z* 160 (M^+).

1-(4-Chlorophenyl)-2,3-butadien-1-ol (3c): Colorless oil, IR (neat) 3370 and 1955 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.77 (br. s, 1H), 4.88 (m, 2H), 5.20 (m, 1H), 5.38 (m, 1H), and 7.28 (s, 4H); MS *m/z* 182 and 180 (M^+).

1-(4-Bromophenyl)-2,3-butadien-1-ol (3d): Colorless oil, IR (neat) 3340 and 1952 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (br. s, 1H), 4.90 (m, 2H), 5.21 (m, 1H), 5.40 (m, 1H), 7.24 (d, J=8.5, 2H), and 7.41 (d, J=8.5, 2H); MS *m/z* 226 and 224 (M^+).

1-(3-Methoxyphenyl)-2,3-butadien-1-ol (3e): Colorless oil, IR (neat) 3375 and 1957 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.19 (br. s, 1H), 3.80 (s, 3H), 4.93 (m, 2H), 5.25 (m, 1H), 5.45 (m, 1H), 6.76—7.05 (m, 3H), and 7.28 (t, J=8.0, 1H); MS *m/z* 176 (M^+).

1-(2-Chlorophenyl)-2,3-butadien-1-ol (3f): Colorless oil, IR (neat) 3325 and 1958 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.39 (br. s, 1H), 4.91 (m, 2H), 5.46 (m, 1H), 5.65 (m, 1H), 7.10—7.45 (m, 3H), and 7.58 (m, 1H); MS *m/z* 182 and 180 (M^+).

1-(2-Nitrophenyl)-2,3-butadien-1-ol (3g): Colorless oil, IR (neat) 3370 and 1952 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.67 (br. s, 1H), 4.89 (m, 2H), 5.56 (m, 1H), 5.86 (m, 1H), and 7.35—7.97 (m, 4H); MS *m/z* 191 (M^+).

1-(2-Naphthyl)-2,3-butadien-1-ol (3h): Colorless crystals, mp 47.5—48.0 °C, IR (KBr) 3230 and 1955 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.35 (br. s, 1H), 4.92 (m, 2H), 5.35—5.62 (m, 2H), 7.39—7.58 (m, 3H), 7.77 (s, 1H), and 7.73—7.93 (m, 3H); MS *m/z* 196 (M^+); Found: C, 85.48; H, 6.14%. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16%.

1-Phenyl-3,4-pentadien-2-ol (3j): Colorless oil, IR (neat) 3350 and 1957 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.97 (br. s, 1H), 2.85 (d, *J*=6.0, 2H), 4.39 (m, 1H), 4.81 (m, 2H), 5.28 (m, 1H), and 7.11—7.42 (m, 5H); MS *m/z* 160 (M^+).

3b—g and **3j** were not satisfied with their elemental analyses because of their instabity.

General Procedure for the Synthesis of 5 (Table 2). Method A. To 99% formic acid (5 ml) was added a solution of **3** (1 mmol) in ether (2 ml) at room temperature. After stirring at room temperature for 30 min, benzene was added and the resulting solution was evaporated in vacuo (the bath temperature was kept below 30 °C). 1-Aryl-3-formyloxy-1,3-butadienes (**5a—c**, **5f**, and **5h**) were obtained after passing a short column of silica gel (20 g, activity V) at 0 °C using benzene-hexane as eluents. 1-Aryl-3-formyloxy-1,3-butadienes thus obtained are rather unstable and decomposes gradually on standing at room temperature.

Method B. To a solution of acetic anhydride (1 ml) in formic acid (5 ml) was added a solution of **3** (1 mmol) in ether (2 ml) at 0 °C. The solution was stirred at the same temperature for 1 h, and benzene was added. The resulting mixture was evaporated in vacuo below 30 °C, and the evaporations with benzene were repeated until most formic acid and acetic anhydride were removed. After passing through a short column of silica gel (20 g, activity V, 0 °C) with benzene-hexane **5** was obtained in yields summarized in Table 2.

1-Phenyl-3-formyloxy-1,3-butadiene (5a): Colorless oil, decomposed by distillation, IR (neat) 1745, 1645, and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.98 (d, *J*=2.0, 1H), 5.12 (d, *J*=2.0, 1H), 6.60 (d, *J*=17.0, 1H), 6.80 (d, *J*=17.0, 1H), 7.26—7.45 (m, 5H), and 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=105.1 t, 121.8 d, 127.0 d, 128.6 d, 128.7 d, 131.2 d, 135.7 s, 151.8 s, and 159.0 d; MS *m/z* 174 (M^+).

1-(*p*-Tolyl)-3-formyloxy-1,3-butadiene (5b): Colorless oil, IR (neat) 1742, 1642, and 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.35 (s, 3H), 4.96 (d, *J*=2.0, 1H), 5.09 (d, *J*=2.0, 1H), 6.56 (d, *J*=17.5, 1H), 6.78 (d, *J*=17.5, 1H), 7.15 (d, *J*=8.5, 2H), 7.32 (d, *J*=8.5, 2H), 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=21.2 q, 104.4 t, 120.8 d, 126.9 d, 129.4 d, 131.1 d, 132.9 s, 138.6 s, 152.0 s, and 159.3 d; MS *m/z* 188 (M^+).

1-(4-Chlorophenyl)-3-formyloxy-1,3-butadiene (5c): Colorless needles, mp 35.5—36.5 °C, IR (KBr) 1725, 1640, and 1608 cm^{-1}; ^1H NMR (acetone-d_6) δ=5.08 (d, *J*=2.0, 1H), 5.25 (d, *J*=2.0, 1H), 6.77 (d, *J*=16.0, 1H), 6.98 (d, *J*=16.0, 1H), 7.38 (d, *J*=8.0, 2H), 7.57 (d, *J*=8.0, 2H), and 8.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=105.5 t, 122.4 d, 128.1 d, 128.9 d, 129.3 s, 129.6 d, 134.2 s, 151.5 s, and 158.8 d; MS *m/z* 210 and 208 (M^+).

1-(2-Chlorophenyl)-3-formyloxy-1,3-butadiene (5f): Colorless oil, IR (neat) 1745, 1641, and 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.05 (d, *J*=2.0, 1H), 5.17 (d, *J*=2.0, 1H), 6.61 (d, *J*=15.0, 1H), 7.14 (d, *J*=15.0, 1H), 7.16—7.60 (m, 4H), and 8.27 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=106.2 t, 124.3 d, 126.7 d, 126.8 d, 127.0 d, 129.3 d, 129.9 s, 133.8 s, 151.4 s, and 158.9 d; MS *m/z* 210 and 208 (M^+).

1-(2-Naphthyl)-3-formyloxy-1,3-butadiene (5h): Colorless plates, mp 57—58 °C, IR (KBr) 1740, 1643, and 1610 cm^{-1}; ^1H NMR (acetone-d_6) δ=5.08 (d, *J*=2.0, 1H), 5.27 (d, *J*=2.0, 1H), 6.92 (d, *J*=16.0, 1H), 7.10 (d, *J*=16.0, 1H), 7.43—7.97 (m, 7H), and 8.44 (s, 1H); ^{13}C NMR (acetone-d_6) δ=106.3 t, 124.1 d, 124.8 d, 127.7 d, 127.8 d, 128.9 d, 129.0 d, 129.4 d, 129.7 d, 131.9 d, 134.7 s, 134.9 s, 135.0 s, 153.6 s, and 160.8 d; MS *m/z* 224 (M^+).

Elemental analyses of **5a—c**, **5f**, and **5h** were not satisfactory because of their instability.

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