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Regioselective photoaddition of alcohols to 1,2,3-butatriene derivatives via photoinduced electron transfer

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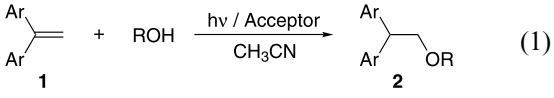
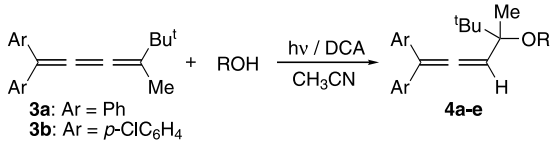
Abstract—Photochemical polar addition of alcohols to 1,1-diaryl-1,2,3-butatriene derivatives in the presence of a catalytic amount of 9,10-dicyanoanthracene regioselectively afforded 1,1-diaryl-4-alkoxy-1,2-butadienes as addition products in good yields via photoinduced electron transfer.

Since Neunteufel and Arnold reported the photochemical polar addition of methanol to 1,1-diphenylethene in the presence of methyl *p*-cyanobenzoate in 1973,[1] photoaddition of alcohols to electron-donating molecules via photoinduced electron transfer has been attracted much attention.[2] Photoaddition of alcohols to arylalkenes such as 1,1-diarylethene **1** or styrene derivatives in the presence of an electron-accepting photosensitizer is a representative example to give the product **2** regioselectively resulting from *anti*-Markovnikov addition (Eq. (1)).[1,3,4] This strategy has been extensively utilized not only to the synthesis of ethers,[3] but also to the trapping experiments of transient radical cations,[5] alcohol/olefin/aromatics coupling reaction so-called photo-NOCAS reaction,[6] and development of photochemical enantiodifferentiation.[7] In addition, the photoaddition of alcohols has been effectively applicable to the trapping of radical cations derived from cyclopropanes[8] and cyclobutanes.[9] The photoaddition of alcohols to aliphatic alkenes[6,10] aliphatic 1,3-dienes,[11] and tetraarylallenes[12] via photoinduced electron-transfer also occurs, but it frequently suffers low chemoselectivity and low efficiency. To the best of our knowledge, the photoaddition of alcohols to more condensed cumulenes has not appeared in literatures. We now report a novel type of regioselective photoaddition of alcohols to 1,1-diaryl-1,2,3-butatriene derivatives.



(1)

Photoirradiation of an acetonitrile/methanol solution (3:1 vol%) containing 1,1-diphenyl-4,5,5-trimethyl-1,2,3-hexatriene (**3a**)[13] in the presence of a catalytic amount of 9,10-dicyanoanthracene (DCA) for 12 h afforded 1,1-diphenyl-4-methoxy-4,5,5-trimethyl-1,2-hexadiene (**4a**) in a 57% isolated yield (Eq. (2), Table 1, entry 1). Similar irradiation of *p*-chloro derivative **3b** gave also the corresponding adduct **4b** in a 60% yield (entry 2). Photoreaction of **3b** in benzene/methanol solution (3:1 vol%) caused the almost recovery of the starting material (entry 3). The yields of adducts decreased with increasing the size of R groups of the alcohols used in the order of Me>Et>*n*-Pr≫*t*-Bu (entries 2, 4–6).



(2)

Structures of **4a–e** were determined by their spectral and analytical data.[14] The allenyl absorption bands of **4a–e** appeared at 1938–1942 cm^{-1} in their IR spectra. ^1H NMR spectra of **4a–e** showed singlet peaks at 5.72–5.81 ppm in $CDCl_3$ assigned to the each allenyl proton. The singlet of allenyl proton of **4b** at 5.74 ppm disappeared when MeOD was used instead of MeOH, which indicates the allenyl proton comes only from alcohol (Eq. (3)). The fluorescence of DCA in acetonitrile was efficiently quenched by **3a–b** at nearly diffusion-controlled rates.

Keywords: photochemical polar addition; 1,2,3-butatriene; alcohol; photoinduced electron transfer; 9,10-dicyanoanthracene.

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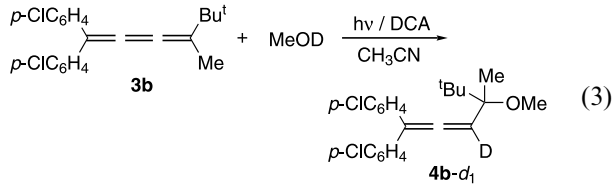
Table 1. Photoaddition of alcohols to 1,2,3-butatriene derivatives[a]

Entry	1,2,3-Butatriene	R	Solvent	Product	Yield[b] (%)
1	**3a**	Me	CH_3CN	**4a**	57
2	**3b**	Me	CH_3CN	**4b**	60
3	**3b**	Me	C_6H_6	**4b**	Trace[c]
4	**3b**	Et	CH_3CN	**4c**	42
5	**3b**	*n*-Pr	CH_3CN	**4d**	26
6	**3b**	*t*-Bu	CH_3CN	**4e**	Trace[c]

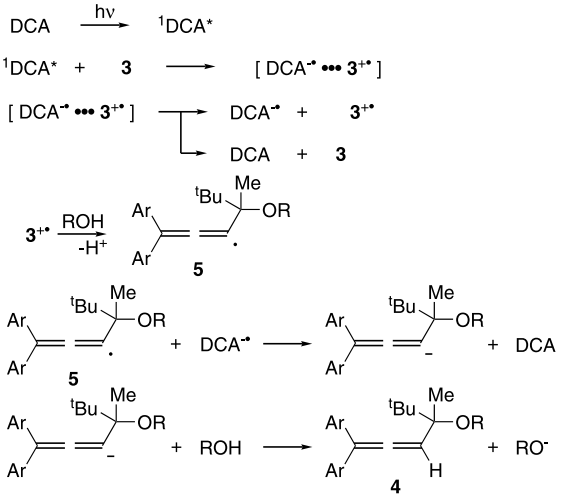
[a] Photoirradiation was carried out by a high-pressure mercury lamp through a Pyrex filter (>280 nm) for 12 h at room temperature. [**3**] = 2.0×10^{-2} M, [DCA] = 1.0×10^{-3} M in solvent:ROH = 3:1 solution.
[b] Isolated yield based on **3** used.
[c] Compound **3b** was almost recovered unchanged.



(3)

From these results, we propose an electron transfer mechanism for the formation of **4** as shown in Scheme 1. The first step is photoinduced electron transfer from **3** to the excited singlet DCA (^{1}DCA*), which produces a radical ion pair [$DCA^{-\bullet}$ ••• $\mathbf{3}^{+\bullet}$]. The radical ion pair dissociates to the free radical ions $DCA^{-\bullet}$ and $\mathbf{3}^{+\bullet}$, or decays by back electron transfer to the ground states of DCA and **3**. Dissociation of the radical ion pair to the free radical ions occurs more efficiently in acetonitrile than in benzene. Then nucleophilic attack of alcohol to $\mathbf{3}^{+\bullet}$ occurred at dialkyl substituted carbon to give allenyl radical **5**. Electron transfer from $DCA^{-\bullet}$ to **5** and the following protonation by alcohol yields the photoadduct **4**.

In conclusion, we have developed a novel regioselective photoaddition of alcohols to 1,1-diaryl-1,2,3-butatriene derivatives via photoinduced electron transfer. Scope and detailed mechanism are now under investigation.



Scheme 1. A possible pathway for the formation of **4**.

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14. Data for **4a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.96 (s, 9H), 1.20 (s, 3H), 3.14 (s, 3H), 5.72 (s, 1H), 7.21–7.32 (m, 10H); IR (neat) 1940 cm^{-1}. Data for **4b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.98 (s, 9H), 1.24 (s, 3H), 3.18 (s, 3H), 5.74 (s, 1H), 7.20–7.33 (m, 8H); IR (neat) 1939 cm^{-1}. Data for **4c**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.10 (t, $J=6.9$ Hz, 3H), 1.24 (s, 3H), 3.35 (q, $J=6.9$ Hz, 2H), 5.76 (s, 1H), 7.20–7.33 (m, 8H); IR (neat) 1939 cm^{-1}. Data for **4d**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, $J=7.3$ Hz, 3H), 1.02 (s, 9H), 1.30 (s, 3H), 1.50–1.61 (m, 2H), 3.28–3.35 (m, 2H), 5.82 (s, 1H), 7.23–7.39 (m, 8H); IR (neat) 1942 cm^{-1}.