Enantioselective Protonation of Radical Anion Intermediates in Photoallylation and Photoreduction Reactions of 3,3-Diaryl-1,1-dicyano-2-methylprop-1-ene with Allyltrimethylsilane

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Abstract: Photoreactions of acetonitrile solutions of 3,3-diaryl-1,1-dicyano-2-methylprop-1-enes (1a–c) with allyltrimethylsilane (2) in the presence of phenanthrene as a photoredox catalyst and acetic acid as a proton source formed photoallylation (3) and photoreduction (4) products via photoinduced electron transfer pathways. When (S)-mandelic acid was used as the proton source, the reactions proceeded with 3.4 and 4.8 %ee for formation of 3 and 4, respectively. The results of studies of the effect of aryl ring substituents and several chiral carboxylic acids suggested that the enantioselectivities of the reactions are governed by steric controlled proton transfer in intermediate complexes formed by π-π and OH-π interactions of anion radicals derived from 1a–c and chiral carboxylic acids.

Keywords: photoreaction; photoinduced electron transfer; photoredox catalyst; Felkin-Anh model; radical anion; electron deficient alkene; allylsilane; mandelic acid; enantioselectivity; enantiomer

1. Introduction

Coupling reactions proceeding through photoinduced electron transfer (PET) pathways have been extensively studied from both a synthetic as well as a mechanistic viewpoint [1–14]. Because radical ions that serve as intermediates in these processes are short-lived and highly reactive, control of the stereochemistry of these reactions is often difficult [15–21]. We have previously developed photoallylation and photoreduction reactions of electron deficient alkenes with allyltrimethylsilane that occur via PET pathways [22–24]. In addition, we also demonstrated that diastereoselectivity of this process can be achieved by steric control of allyl radical or proton addition to radical anions that are generated from electron deficient alkenes (Scheme 1) [25–27]. The current study was aimed at the development of enantioselective PET promoted coupling reactions, and specifically, at assessing the effect of chiral carboxylic acids on the stereochemical outcomes of photoallylation and photoreduction reactions of prochiral electron deficient alkenes. The results showed that these processes took place with maximum 3.4–4.8 %ee when (S)-mandelic acid was used as the chiral proton source.
2. Results and Discussion

Irradiation of an acetonitrile solution containing 1,1-dicyano-2-methyl-3,3-diphenylprop-1-ene (1a), 3 equiv of allyltrimethylsilane (2), a catalytic amount of phenanthrene (Phen) as a photoredox catalyst in a Pyrex vessel using a 300 W high-pressure mercury lamp was found to produce reduction product 4a in 53% yield (Scheme 2, Table 1, entry 1, supplementary). Photoreaction of 1a with 2 in the presence of acetic acid produced the allylated product 3a in addition to 4a in 34 and 31% yields, respectively (entry 2). The corresponding products 3b–c and 4b–c were produced in photoreactions of bis(p-methoxyphenyl) (1b) and bis(p-chlorophenyl) (1c) derivatives conducted under the same conditions (entries 3–6). The irradiation times used for these processes are those required for complete consumption of 1a–c. The observed efficiencies of the reactions, based on the required irradiation times, decreased in the order 1c > 1a > 1b.

![Scheme 1. Our previous works.](image)

| Entry | Substrate | Additive | Irradiation Time/h | Yields/% |
|-------|-----------|----------|--------------------|---------|
|       |           |          |                   | 3       | 4       |
| 1     | 1a (Ar = Ph) | none     | 4                  | 0<sup>b</sup> | 53<sup>b</sup> |
| 2     | 1a (Ar = Ph) | acetic acid<sup>c</sup> | 4                  | 34<sup>b</sup> | 31<sup>b</sup> |
| 3     | 1b (Ar = p-MeOC<sub>6</sub>H<sub>4</sub>) | none | 24                 | 0<sup>d</sup>   | 44<sup>d</sup> |
| 4     | 1b (Ar = p-MeOC<sub>6</sub>H<sub>4</sub>) | acetic acid<sup>c</sup> | 24                 | 20<sup>d</sup> | 46<sup>d</sup> |
| 5     | 1c (p-CIC<sub>6</sub>H<sub>4</sub>) | none | 2                  | 0<sup>d</sup>   | 36<sup>d</sup> |
| 6     | 1c (p-CIC<sub>6</sub>H<sub>4</sub>) | acetic acid<sup>c</sup> | 2                  | 33<sup>d</sup> | 47<sup>d</sup> |

<sup>a</sup> Conditions: 1a–c (0.14 mmol), 2 (0.42 mmol), phenanthrene (0.07 mmol), CH<sub>3</sub>CN (8 mL), 300 W high-pressure mercury lamp, Pyrex, r.t.  
<sup>b</sup> Determined by using GC.  
<sup>c</sup> 1 mL.  
<sup>d</sup> Determined by using <sup>1</sup>H-NMR.

Structures of photoproduts 3a–c and 4a–c were determined by using spectroscopic methods. In <sup>1</sup>H-NMR spectra of CDCl<sub>3</sub> solutions of 3a and 4a (Figure 1), the chemical shifts of resonances for protons that are bonded to the asymmetric carbons, i.e., H<sub>b</sub> in 3a and H<sub>b</sub> in 4a, were 2.97 (qd) and 3.02 (qt) ppm, respectively. Authentic samples of the photoproducts were prepared by hydrogenation of 1a using Pd/C to form 4a and ensuing allylation of 4a using allyl chloride to form 3a (Scheme 3). The spectral data for the synthesized compounds were identical to those of photoproduced 3a and 4a.
In order to explore the enantioselectivities of these photoreactions, samples of 3a and 4a were subjected to HPLC using a chiral stationary phase with the effluents being monitored by using UV and CD detectors (Figure 2a–d). The results showed that two peaks in the HPLC trace for the enantiomers of 3a were completely resolved. Unfortunately, HPLC conditions could not be found for resolution of the enantiomers of 4a. Moreover, the enantiomers of 3c and 4c can be separated by using GC with a chiral capillary column (Figure 2e).

**Figure 1.** 300 MHz $^1$H-NMR spectra of 3a and 4a in CDCl$_3$.

**Scheme 3.** Synthesis of authentic samples of 3a and 4a.

**Figure 2.** Resolution of the enantiomers of (a,b) 3a by using chiral HPLC with UV and CD detectors both at 270 nm, (c,d) 4a by chiral HPLC with UV and CD detectors both at 270 nm, and (e) 3c and 4c by chiral GC with a MS detector.
In order to prove that these separation techniques led to the individual enantiomers, the effluents of peaks A–D in Figure 2a–d were collected, concentrated in vacuo and the residues in ethanol were subjected to UV-vis absorption and CD spectroscopic analysis (Figures 3 and 4). The UV-vis absorption spectra of substances in effluents corresponding to peaks A and C were identical to those from peaks B and D, respectively. In addition, $^1$H-NMR and mass spectra of the respective substances in peaks A and C were also identical to those in peaks B and D, respectively. Moreover, CD spectral traces of substances comprising peaks A and B, and peaks C and D, respectively, were mirror images relative to the horizontal baseline. The combined results indicated that the enantiomers of these substances can be resolved by using chromatographic methods.

![Figure 3. UV-vis absorption spectra of ethanol solutions of substances from (a) peak A, (b) peak B, (c) peak C, and (d) peak D.](image)

![Figure 4. Circular dichromism (CD) spectra of ethanol solutions of substances from (a) peaks A and B, (b) peaks C and D.](image)

To assess the potential of introducing enantioselectivity into the photoreactions described above, irradiations were carried out on solutions of 1a–c and allyltrimethylsilane (2) containing chiral carboxylic acids. The yields and percent enantiomeric excesses (%ee) of products formed in these processes are listed in Table 2. The %ee in each case was calculated using the ratio of areas under the chiral HPLC or GC peaks corresponding to the enantiomers as %ee when acetic acid was used becoming zero. A positive %ee value corresponds to a situation in which the major isomer is the second peak, while a negative value shows that the major isomer is the first peak. The absolute structures could not be decided. The data arising from photoreactions in the absence or presence of achiral acetic acid are also included in Table 2 for comparison purposes.

Use of 1 equiv of (R)-mandelic acid in photoreaction of 1a with 2 led to formation of 3a and 4a with respective +1.5 and +4.1 %ee values (entry 3). A reversal in major enantiomers of the products arose from the reaction of 1a with 2 conducted in the presence of (S)-mandelic acid (entry 4), which supports the reaction proceeding in an enantioselective manner. Also, when l-lactic acid was used in this photoreaction, the major enantiomers were the reverse of those formed in reactions in the presence of (S)-mandelic acid (entry 5). The use of C$_2$ symmetric dibenzoyl l-tartaric acid did not promote an increase of %ee of either product (entry 6). The photoreaction of 1b with 2 also
occurred when (R)- and (S)-mandelic acids were used, however the %ee of either product could not be determined (entries 9 and 10). Like in the case of 1a, photoreaction of 1c produced products 3c and 4c in which the major enantiomers were reversed when (R)- and (S)-mandelic acids were utilized (entries 13 and 14). Moreover, the results showed that the %ee improved up to 3.5 when (S)-2-(6-methoxy-2-naphthyl)propionic acid was used as a chiral acid (entry 15).

| Entry | Substrate | Additive | Irradiation Time/h | Yields/% (ee)/% |
|-------|-----------|----------|--------------------|----------------|
| 1     | 1a (Ar = Ph) | none | 4 | 0 b 53 b |
| 2     | 1a (Ar = Ph) | acetic acid | 4 | 34 b 31 b |
| 3     | 1a (Ar = Ph) | (R)-mandelic acid | 4 | 34 b (+1.5 d,e) 27 b (+4.1 d,e) |
| 4     | 1a (Ar = Ph) | (S)-mandelic acid | 4 | 22 b (-3.4 d,l) 26 b (-4.8 d,l) |
| 5     | 1a (Ar = Ph) | t-lactic acid | 4 | 28 b (+0.6 d,e) 39 b (+3.2 d,e) |
| 6     | 1a (Ar = Ph) | dibenzoyl l-tartaric acid | 4 | 31 b (-2.0 d,l) 16 b (-3.6 d,l) |
| 7     | 1b (Ar = p-MeOC6H4) | none | 24 | 0 i 44 i |
| 8     | 1b (Ar = p-MeOC6H4) | acetic acid | 24 | 20 i 46 i |
| 9     | 1b (Ar = p-MeOC6H4) | (R)-mandelic acid | 24 | 54 i (nd h) 258 (nd h) |
| 10    | 1b (Ar = p-MeOC6H4) | (S)-mandelic acid | 24 | 13 i (nd h) 488 (nd h) |
| 11    | 1c (p-CIC6H4) | none | 2 | 0 i 36 i |
| 12    | 1c (p-CIC6H4) | acetic acid | 2 | 33 i 47 i |
| 13    | 1c (p-CIC6H4) | (R)-mandelic acid | 2 | 27 i (+2.0 i) 55 i (+2.0 i) |
| 14    | 1c (p-CIC6H4) | (S)-mandelic acid | 2 | 24 i (-2.6 i,k) 61 i (-0.6 i,k) |
| 15    | 1c (p-CIC6H4) | (S)-2-(6-methoxy-2-naphthyl)propionic acid | 2 | 0 i 685 (-3.5 i,k) |

*Conditions: 1a–c (0.14 mmol), 2 (0.42 mmol), phenanthrene (0.07 mmol), CH3CN (8 mL), additive (0.14 mmol), 300 W high-pressure mercury lamp, Pyrex, r.t. a Determined by using GC. b Determined by using chiral HPLC. c Major isomer corresponds to the second peak in the HPLC chart. d Major isomer corresponds to the first peak in the HPLC chart. e Determined by using 1H-NMR. f Yields could not be determined. g Determined by using chiral GC. h Major isomer corresponds to the second peak in the GC chart. i Major isomer corresponds to the first peak in the GC chart.

Each photoreaction described above takes place through a process termed photoredox sensitization by phenanthrene (Phen) (Scheme 4) [22–27]. In the pathway, the excited singlet state of Phen, generated by light absorption, transfers one electron (SET [single electron transfer]) to the electron-deficient alkene 1 to form the phenanthrene radical cation (Phen**) and the alkene radical anion 1•–. The subsequent SET from allyltrimethylsilane (2) to Phen** generates recovered Phen and the radical cation 2**, which undergoes nucleophile-assisted Si-C bond cleavage [28–30] to form the allyl radical. Also, radical anion 1•– is protonated by the carboxylic acid to produce radical 5, which upon coupling with the allyl radical generates the allylation product 3. In a competitive pathway, radical 5 undergoes hydrogen abstraction or one-electron reduction followed by protonation or disproportionation to form reduction product 4 [23]. The inefficiency of the photoreaction of the MeO-substituted substrate 1b and high efficiency of the reaction of Cl-substituted reactant 1c are likely consequences of the stabilities of the corresponding radical anions 1b•– and 1c•– which governs their rates of formation by SET from relative to unproductive decay of the excited singlet state of Phen.

| Table 2. | Enantioselective photoallylations and photoreductions of 1a–c a. |
|-----------|---------------------|
| Entry     | Substrate           | Additive          | Irradiation Time/h | Yields/% (ee)/% |
| 1         | 1a (Ar = Ph)        | none               | 4                 | 0 b 53 b |
| 2         | 1a (Ar = Ph)        | acetic acid        | 4                 | 34 b 31 b |
| 3         | 1a (Ar = Ph)        | (R)-mandelic acid  | 4                 | 34 b (+1.5 d,e) 27 b (+4.1 d,e) |
| 4         | 1a (Ar = Ph)        | (S)-mandelic acid  | 4                 | 22 b (-3.4 d,l) 26 b (-4.8 d,l) |
| 5         | 1a (Ar = Ph)        | t-lactic acid      | 4                 | 28 b (+0.6 d,e) 39 b (+3.2 d,e) |
| 6         | 1a (Ar = Ph)        | dibenzoyl l-tartaric acid | 4 | 31 b (-2.0 d,l) 16 b (-3.6 d,l) |
| 7         | 1b (Ar = p-MeOC6H4) | none               | 24                | 0 i 44 i |
| 8         | 1b (Ar = p-MeOC6H4) | acetic acid        | 24                | 20 i 46 i |
| 9         | 1b (Ar = p-MeOC6H4) | (R)-mandelic acid  | 24                | 54 i (nd h) 258 (nd h) |
| 10        | 1b (Ar = p-MeOC6H4) | (S)-mandelic acid  | 24                | 13 i (nd h) 488 (nd h) |
| 11        | 1c (p-CIC6H4)       | none               | 2                 | 0 i 36 i |
| 12        | 1c (p-CIC6H4)       | acetic acid        | 2                 | 33 i 47 i |
| 13        | 1c (p-CIC6H4)       | (R)-mandelic acid  | 2                 | 27 i (+2.0 i) 55 i (+2.0 i) |
| 14        | 1c (p-CIC6H4)       | (S)-mandelic acid  | 2                 | 24 i (-2.6 i,k) 61 i (-0.6 i,k) |
| 15        | 1c (p-CIC6H4)       | (S)-2-(6-methoxy-2-naphthyl)propionic acid | 2 | 0 i 685 (-3.5 i,k) |
Based on the results of molecular orbital calculations with related compounds, it is estimated that the radical contribution to radical anion $1^+$ is large at the dicyano substituted carbon ($\alpha$) and that negative charge density is large at the dialkyl substituted carbon ($\beta$) [23,24,26,27]. In accord with this conclusion, the photoreaction of $1a$ with $2$ using CH$_3$COOD as the additive produced mainly mono-deuteriated forms of $3a$ and $4a$ in which deuterium is present at the stereogenic carbons marked with * in Scheme 4. Therefore, enantioselectivity is governed at the step where protonation of the radical anion takes place.

![Scheme 4](image)

**Scheme 4.** Mechanism for photoallylation and photoreduction of $1$.

The stereochemistry of protonation of the radical anion $1^+$ can be discussed using a Felkin-Anh model (Scheme 5) [31–33]. Specifically, in reaction of $1a$ in the presence of (S)-mandelic acid, proton transfer to the $Re$ face of $1a^+$ should be preferred in a complex in which a $\pi$-$\pi$ stabilizing interaction occurs between the phenyl groups and the OH group of the acid is located in a sterically less hindered position. Proton transfer to the $Re$ face of $1a$ leads to the eventual formation of (S)-$3a$ and (S)-$4a$. On the other hand, in the reaction of $1a$ in the presence of l-lactic acid, an OH-$\pi$ interaction between the OH group of the acid and the phenyl group of $1a^+$ takes place to form a complex in which proton transfer from the carboxylic acid group occurs preferentially to the $Si$ face to minimize steric repulsion of methyl group. This process then gives rise to formation of (R)-$3a$ and (R)-$4a$. In photoreaction of $1c$ in the presence of (S)-2-(6-methoxy-2-naphthyl)propionic acid, the main enantiomers produced were the same as those generated in reaction of $1c$ in the presence of (S)-mandelic acid, and %ee increased. This outcome might be a consequence of a strong $\pi$-$\pi$ interaction between the chlorophenyl and the methoxynaphthyl groups.
3. Experimental Section

3.1. Materials and Equipments

THF was distilled from CaH\textsubscript{2} and then from Na/benzophenone. CH\textsubscript{3}CN was distilled from P\textsubscript{2}O\textsubscript{5} then from Ca(OH)\textsubscript{2}. Hexane and 2-propanol were distilled without using a drying agent. Allyltrimethylsilane (2) was prepared using a reported procedure \[27\]. Activated alumina was dried at 200 °C for 2 h before use. Most other chemical substances were used after purification by distillation or recrystallization.

Column chromatography was conducted by using Wakogel C-70~230 (Fujifilm Wako Pure Chemical Corporation, Osaka, Japan). Thin-layer chromatography was performed by using Merck Kiesel gel 60 F\textsubscript{254} plates (Merck KGaA, Darmstadt, Germany). HPLC separations (achiral) were performed on a recycling preparative HPLC equipped with Jasco PU-987 pump, UV-970 UV detector, and a Chemcosorb I-5Si column (Chemco Plus Scientific Co., Ltd., Osaka, Japan) using hexane-AcOEt or hexane-2-propanol as an eluent, or a recycling preparative HPLC equipped with Jasco PU-2086 pump, RI-2031 differential refractometer (Jasco Corporation, Tokyo, Japan), and Megapak GEL 201F columns (GPC) using CHCl\textsubscript{3} as an eluent (Jasco Corporation, Tokyo, Japan).

\textsuperscript{1}H and \textsuperscript{13}C-NMR spectra were recorded using a Varian MERCURY-300 (300 MHz and 75 MHz, respectively, (Varian Inc., Palo Alto, CA, USA) spectrometer with Me\textsubscript{4}Si as an internal standard. Mass spectra (EI, achiral) were recorded on a SHIMADZU GCMS-QP5050 (Shimadzu Corporation, Kyoto, Japan) operating in the electron impact mode (70 eV) equipped with GC-17A and DB-5MS column (J&W Scientific Inc., Serial: 8696181, Folsom, CA, USA). UV-vis spectra were recorded using a Jasco V-530 spectrophotometer (Jasco Corporation, Tokyo, Japan).

3.2. Preparation of 1a

A mixture of 1,1-diphenylacetone (1.051 g, 5.0 mmol), malononitrile (0.330 g, 5.0 mmol) and activated alumina (1.5 g) was stirred at 60 °C for 1 h \[34\]. The solids were removed by filtration. Concentration of the filtrate gave a residue that was subjected to silica gel column chromatography followed by recrystallization from hexane to give 2-(1,1-diphenylpropan-2-ylidene)malononitrile (1a, white solid, 0.531 g, 2.06 mmol, 41% yield). Lit \[35\].

Scheme 5. Plausible explanation for the enantioselectivity.
3.3. Preparation of 1b

A THF (50 mL) solution of 4-bromoanisole (17.53 mL, 140.0 mmol) was added dropwise to stirred Mg turnings (3.889 g, 160.0 mmol). A small amount of I$_2$ was added to facilitate the reaction. A THF (20 mL) solution of ethyl l-lactate (4.587 mL, 40.0 mmol) was added dropwise to the solution, and the resulting mixture was stirred at reflux, cooled, and extracted with Et$_2$O and NH$_4$Cl aq [36]. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography to give 1,1-bis(4-methoxyphenyl)propane-1,2-diol (5.76 g, 20.0 mmol, 50% yield, including impurity).

25% H$_2$SO$_4$ aq (15 mL) was added to stirred 1,1-bis(4-methoxyphenyl)propane-1,2-diol (5.76 g, 20.0 mmol, including impurity), and the resulting solution was stirred at reflux for 3.5 h, cooled, neutralized with Na$_2$CO$_3$ and extracted with Et$_2$O [36]. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography to give 1,1-bis(4-methoxyphenyl)propan-2-one (1.047 g, 3.87 mmol, 19% yield).

A mixture of 1,1-bis(4-methoxyphenyl)propan-2-one (1.047 g, 3.87 mmol), malononitrile (0.384 g, 5.82 mmol) and activated alumina (3.0 g) was stirred at 90$^\circ$C for 1.5 h [34]. The solids were removed by filtration. Concentration of the filtrate gave a residue that was subjected to HPLC to give 2-[1,1-bis(4-methoxyphenyl)propan-2-ylidene]malononitrile (1b, 0.728 g, 2.29 mmol, 59% yield).

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 2.21 (s, 3H), 3.82 (s, 6H), 5.59 (s, 1H), 6.89 (d, $J = 8.6$ Hz, 4H), 7.05 (d, $J = 8.6$ Hz, 4H) ppm.

3.4. Preparation of 1c

A THF (12 mL) solution of 4-bromochlorobenzene (6.647 g, 34.7 mmol) was added dropwise to stirred Mg turnings (0.729 g, 30.0 mmol). A small amount of I$_2$ was added to facilitate the reaction. A THF (5 mL) solution of ethyl l-lactate (1.247 mL, 10.9 mmol) was added dropwise to the solution, and the resulting solution was stirred at reflux, cooled, and extracted with Et$_2$O and NH$_4$Cl aq [36]. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography to give 1,1-bis(4-chlorophenyl)propane-1,2-diol (4.023 g, including impurity).

To stirred 1,1-bis(4-chlorophenyl)propane-1,2-diol (4.023 g, including impurity) was added 25% H$_2$SO$_4$ aq (12 mL), and the resulting solution was stirred at reflux for 3.5 h, cooled, neutralized with Na$_2$CO$_3$ and extracted with Et$_2$O [36]. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography to give 1,1-bis(4-chlorophenyl)propan-2-one (0.934 g, 3.36 mmol, 31% yield (two steps)).

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 2.24 (s, 3H), 5.05 (s, 1H), 7.11-7.32 (m, 8 H) ppm.

A mixture of 1,1-bis(4-chlorophenyl)propan-2-one (0.934 g, 3.36 mmol), malononitrile (0.444 g, 6.72 mmol) and activated alumina (3.0 g) was stirred at 90$^\circ$C for 1.5 h [34]. The solids were removed by filtration. Concentration of the filtrate gave a residue that was subjected to HPLC to give 2-[1,1-bis(4-chlorophenyl)propan-2-ylidene]malononitrile (1c, 0.602 g, 1.84 mmol, 55% yield).

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 2.21 (s, 3H), 5.62 (s, 1H), 7.05 (d, $J = 8.4$ Hz, 4H), 7.37 (d, $J = 8.4$ Hz, 4H) ppm; $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ 21.33, 55.87, 88.80, 111.37, 111.49, 129.47, 129.94, 134.47, 135.75, 179.56 ppm; MS (EI) m/z (relative intensity, %) = 114 (52), 139 (89), 165 (59), 291 (100), 326 (62, M$^+$).

3.5. General Procedure for Photoreactions

CH$_3$CN (8 mL) solutions of a 3,3-diaryl-1,1-dicyano-2-methylprop-2-ene (1a–c, 0.14 mmol), allyltrimethylsilane (2, 0.42 mmol), phenanthrene (0.07 mmol), and CH$_3$COOH (1 mL) or a chiral carboxylic acid (0.14 mmol) in Pyrex vessels were degassed by argon bubbling for 5 min and then the vessels were sealed. The solutions were irradiated by using a 300 W high pressure mercury lamp (Eikosha, EHB-W-300 or PIH-300) for 2–24 h at room temperature, maintained by using circulated cooling water. The photolysates were extracted with Et$_2$O. The organic layer was washed with H$_2$O,
dried over Na₂SO₄, filtered, and concentrated in vacuo, giving a residue that was subjected to HPLC to give 3a–c and 4a–c.

2- Allyl-2-(1,1-diphenylpropan-2-yl)malononitrile (3a): ^1^H-NMR (300 MHz, CDCl₃) δ 1.20 (d, J = 6.8 Hz, 3H), 2.42–2.59 (m, 2H), 2.91–3.02 (m, 1H), 4.16 (d, J = 9.3 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 9.6 Hz, 1H), 5.76–5.92 (m, 1H), 7.21–7.40 (m, 10H) ppm; MS (EI) m/z = 41, 65, 77, 91, 102, 115, 128, 151, 165, 167, 193, 300 (M^+).

2- Allyl-2-[1,1-bis(4-methoxyphenyl)propan-2-yl]malononitrile (3b): ^1^H-NMR (300 MHz, CDCl₃) δ 1.18 (d, J = 6.7 Hz, 3H), 2.44–2.60 (m, 2H), 2.80–2.91 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 4.08 (d, J = 9.2 Hz, 1H), 5.29 (d, J = 16.9 Hz, 1H), 5.36 (d, J = 10.0 Hz, 1H), 5.77–5.91 (m, 1H), 6.81–6.87 (m, 4H), 7.19–7.26 (m, 4H) ppm.

2- Allyl-2-[1,1-bis(4-methoxyphenyl)propan-2-yl]malononitrile (3c): ^1^H-NMR (300 MHz, CDCl₃) δ 1.18 (d, J = 6.7 Hz, 3H), 2.52 (dd, J = 13.8, 7.5 Hz, 1H), 2.62 (dd, J = 13.9, 6.7 Hz, 1H), 2.88 (dq, J = 8.9, 6.7 Hz, 1H), 4.15 (d, J = 9.1 Hz, 1H), 5.31 (d, J = 16.9 Hz, 1H), 5.40 (d, J = 10.2 Hz, 1H), 5.76–5.91 (m, 1H), 7.19–7.36 (m, 8H) ppm; ^13^C-NMR (75 MHz, CDCl₃) δ 15.47, 41.40, 42.40, 42.79, 54.31, 114.18, 123.29, 128.44, 129.24, 129.27, 129.67, 129.93, 133.41, 133.76, 139.09, 139.24 ppm.

2-(1,1-DiPhenylpropan-2-yl)malononitrile (4a): ^1^H-NMR (300 MHz, CDCl₃) δ 1.30 (d, J = 6.6 Hz, 3H), 2.95–3.06 (m, 1H), 3.64 (d, J = 3.3 Hz, 1H), 3.80 (d, J = 11.7 Hz, 1H), 7.21–7.36 (m, 10H) ppm; MS (EI) m/z = 51, 63, 77, 83, 102, 128, 151, 165, 167, 193, 300 (M^+).

2- Allyl-2-(1,1-diaryl-1,1-dicyano-2-methylprop-1-enes 1a–c by allyltrimethylsilane, carried in the presence of enantiomerically pure chiral carboxylic acids, generates photoallylation and photoreduction products with low but finite levels of enantioselectivity. The percent enantiomeric excesses in the products of the process was highest (4.8 %ee) when (S)-mandelic acid was used. Enantioselectivities in these reactions are a consequence of sterically governed asymmetric proton transfer in intermediate complexes formed by π-π and OH-π interactions between radical anions of the prochiral alkenes and the chiral carboxylic acids.

3.6. Resolution of Enantiomers

Resolutions of enantiomers of 3a and 4a were performed on a recycling preparative HPLC equipped with Jasco PU-980 pump, Jasco UV-970 and CD-2095 detectors (Jasco Corporation, Tokyo, Japan), Daicel CHIRALCEL OJ (3a) or OJ-H (4a) columns (Daicel Corporation, Osaka, Japan). Eluents were hexane:2-propanol = 7:3 (3a) or 9:1 (4a). [3a] = 0.068 M, [4a] = 0.078 M. Both 3a and 4a were detected by UV and CD detectors at 270 nm.

Resolutions of enantiomers of 3c and 4c were performed by using a SHIMADZU GCMS-QP5050 (Shimadzu Corporation, Kyoto, Japan) operating in the electron impact mode (70 eV) equipped with SUPELCO GAMMA DEXTM 225 column (Sigma-Aldrich Co., LLC, St. Louis, MO, USA). Detector temp = 215 °C, injection temp = 220 °C, inlet pressure = 93.7 kPa, flow rate = 1.0mL/min, linear velocity = 28.1 cm/s, split ratio = 50, carrier gas = N₂.

4. Conclusions

In summary, we found that photo reactions of prochiral 3,3-diaryl-1,1-dicyano-2-methylprop-1-enes 1a–c with allyltrimethylsilane, carried in the presence of enantiomerically pure chiral carboxylic acids, generates photoallylation and photoreduction products with low but finite levels of enantioselectivity. The percent enantiomeric excesses in the products of the process was highest (4.8 %ee) when (S)-mandelic acid was used. Enantioselectivities in these reactions are a consequence of sterically governed asymmetric proton transfer in intermediate complexes formed by π-π and OH-π interactions between radical anions of the prochiral alkenes and the chiral carboxylic acids.

Supplementary Materials: The following are available online: ^1^H-NMR spectra of 1b, 1c, 3a, 3b, 3c, 4a, and 4c, ^13^C-NMR spectra of 1c and 3c.

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