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Direct Cyclopropanation of α -Cyano β -Aryl Alkanes by Light Mediated Single Electron Transfer between Donor-Acceptor Pairs

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Abstract: Cyclopropanes are traditionally prepared by the formal [2+1] addition of carbene or radical based C1 units to alkenes. In contrast, the one pot intermolecular cyclopropanation of alkanes by redox active C1 units has remained unrealised. Herein, we achieved this process simply by exposing β -aryl propionitriles and C1 radical precursors (*N*-oxy esters) to base and blue light. The overall process is redox-neutral and a photocatalyst, whether metal- or organic-based, is not required. Our findings support that single electron transfer (SET) from the α -cyano carbanion of the propionitrile to the *N*-oxy ester is facilitated by blue-light via their electron donor-acceptor (EDA) complex. The α -cyano carbon radical thus formed can then lose a β -proton to form a π -resonance stabilised radical anion that preferentially couples at the benzylic β -position with a decarboxylated C1 radical unit. This new transition metal-free chemistry tolerates both electron rich and electron deficient (hetero)aryl systems, even sulfide or alkene functionality, to afford a range of *cis*-aryl/cyano cyclopropanes bearing congested tetrasubstituted quaternary carbons.

redox neutral manner without transition metal catalysts. Moreover, it is a significant challenge to prepare sterically congested cyclopropanes flanked by contiguous quaternary stereocenters.^[8b] In this context, we disclose a direct method to access *cis*-aryl/cyano cyclopropanes from readily available alkanes with redox active esters as C1 components (Figure 1b).

(a) Traditional cyclopropanation of alkenes

(b) Redox-neutral cyclopropanation of alkanes – this study

Figure 1. (a) Cyclopropanation of alkene feedstocks; (b) Cyclopropanation of alkane feedstocks. EWG = electron withdrawing group. Lg = leaving group.

Cycloalkanes feature in a wide variety of bioactive compounds^[1] and natural products,^[2] and are regarded as highly versatile intermediates in synthesis.^[3] Indeed, the development of new methods to access 3-membered cyclopropyl rings continues to test organic chemists on the bench today.^[4] The most traditional and robust methods to prepare cyclopropanes involve reacting alkenes with free carbenes or carbenoids (C1 components) in a formal [2+1] cycloaddition (Figure 1a, left). Representative examples include the generation of carbenoids from diethylzinc and halomethanes (the Simmons–Smith reaction)^[5] or by using transition metals with diazo compounds,^[6] hyperiodo ylides^[7] and so forth.^[8] Other reliable approaches for the cyclopropanation of aryl and electron-deficient alkenes adopt addition-elimination processes (Figure 1a, right).^[8,9] A representative example is the reaction of sulfur ylides with enones (the Corey–Chaykovsky reaction).^[8] Recently, the addition of radicals to alkenes followed by intramolecular polar displacement, as catalysed by photoredox additives, provides a new entry for the preparation of cyclopropanes.^[9] To date, however, direct intermolecular cyclopropanation methods rely heavily on alkenes as the starting materials (Figure 1a) or resort to the intramolecular transition metal mediated C–H activation of alkanes.^[10] To the best of our knowledge, there are no reports for the direct intermolecular cyclopropanation of alkanes with C1 components in an overall

This investigation was inspired by our recent oxidative studies of α -substituted malononitriles using O_2 and neutral nucleophiles (Figure 2a).^[11] Detailed mechanistic studies demonstrated that a single electron transfer (SET) process occurs between α -anionic malononitriles and molecular oxygen to produce α -carbon radicals *en route* to the formation of acyl cyanides.^[11a] The acyl cyanide can then react with different nucleophiles such as amines, alcohols and thiols.^[11b] Given a suitable electron acceptor, under the right conditions, we reasoned that the α -anion of benzyl malononitrile **1a** would undergo a SET event to afford the corresponding carbon-centred radical **1a'** (Figure 2b). As a

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suitable partner for this SET event, we selected the *N*-phthalimido-*N*-oxy ester **2a** as the electron acceptor. Here, the radical anion of **2a** would undergo an entropy favoured decarboxylative expulsion of an *N*-phthalimide anion to release the *O*-stabilised radical **2a'**.^[12] The complementary radicals **1a'** and **2a'** were then expected to couple homogenically at the α -position to afford the sterically congested adduct **3**. In practice, however, treatment of benzyl malononitrile **1a** and the *N*-oxy ester **2a** with KO^tBu in DMSO gave no desired adduct **3** or reaction. Given recent observations that visual light can facilitate SET processes for electron donor-acceptor (EDA) charge-transfer complexes,^[13] **1a** and **2a** were exposed to blue light in the presence of KO^tBu. Although no trace of adduct **3** was observed, the cyclopropane **4a** was isolated in moderate yield. This discovery revealed, for the first time, an unprecedented transition metal-free procedure to form cyclopropanes in one-pot by the redox coupling of matched cyanoalkane donors and C1 acceptors.

(a) Generation of α -centered malononitrile radicals – previous work^[10]

(b) Discovery of the direct cyclopropanation of benzyl malononitrile

Figure 2. (a) Oxidative amidation/esterification using O₂; (b) Unexpected cyclopropanation. NPhth = *N*-phthalimide. DMSO = dimethyl sulfoxide.

To capitalise on this discovery in a more general context, we selected α -benzylmalononitrile **1a** as the model substrate to optimise the formation of cyclopropane **4a** (Table 1). We found that the reaction depended strongly on the type of leaving group (Lg) on compounds **2**. Whereas no product was observed with **2b** (Lg = OCOCF₃) and **2d** (Lg = Br), **2c** (Lg = OBz) provided the desired product **4a** in a lower yield than **2a** (Lg = OAc) (cf. entry 1 and 3). We thus decided to employ **1a** and **2a** for further optimisation studies. When the reaction was carried out in the dark (entry 5) or in the absence of a base (entry 6), no desired product **4a** was observed. Next, we turned our attention to screening the bases and solvents. Several bases such as NaO^tBu and K₂CO₃ gave lower yields relative to KO^tBu (entry 7 and 8). Solvents such as DMF, CH₃CN and THF resulted in low efficiency in this system (entry 9–11). Finally, the yield of the desired product **4a** was improved to 73% when the amount of KO^tBu and **2a** was increased to 1.2 and 1.5 equivalents, respectively (entry 12).

With an optimal method in hand, we investigated the scope of this new cyclopropanation method. As shown in Figure 3a, the redox-active ester **2a** can react with both α -benzyl malononitrile

and α -benzyl cyanoethanoate to afford the desired cyclopropanes **4a** and **4d** in good yields, respectively. In addition, this process exhibited excellent chemoselectivity for electron rich (NHAc, **4e**;

Table 1. Optimisation of the reaction conditions^[a]

entry	2	base	Solvents	Yield (%) ^b
1	2a	KO ^t Bu	DMSO	61
2	2b	KO ^t Bu	DMSO	<5
3	2c	KO ^t Bu	DMSO	51
4	2d	KO ^t Bu	DMSO	<5
5 ^c	2a	KO ^t Bu	DMSO	<5
6	2a	no base	DMSO	<5
7	2a	NaO ^t Bu	DMSO	57
8	2a	K ₂ CO ₃	DMSO	55
9	2a	KO ^t Bu	DMF	54
10	2a	KO ^t Bu	CH ₃ CN	10
11	2a	KO ^t Bu	THF	<5
12 ^d	2a	KO ^t Bu	DMSO	73

[a] Reaction was carried out with **1a** (0.2 mmol), **2a–d** (1.3 equiv.), base (1.1 equiv.) in DMSO (2 mL) at 35 °C for 20 h. [b] Isolated yields. [c] Reaction was carried in the dark. [d] **2a** (1.5 equiv.) and KO^tBu (1.2 equiv.) were used.

–OMe, **4f**) and electron poor (–CF₃, **4g**; –CN, **4h**) para-substituted phenyl groups, providing cyclopropane products in good yields (60–89%) as single geometric isomers.^[8b] Aryl halogens (F, Cl, Br; **4i–4k**) also displayed excellent tolerance to these reaction conditions. Similar functional group compatibilities were exhibited among aromatic substrates with substituents at the *meta*- and *ortho*-positions (**4l**, **4m**). Fused aromatics (**4n**), pyridine (**4o**) and thiophene (**4p**) moieties were tolerated by this method in good yield. Besides aromatic *N*- and *S*-functionality, this cyclopropanation method was also found compatible with non-activated alkenes as demonstrated with the *O*-allylic ester (**4r**).

While arylmethyl malononitriles successfully gave cyclopropanes, presumably due to aryl stabilisation of intermediates, alkyl malononitriles lacking β -aryl groups gave no reaction and unsubstituted or α -monosubstituted derivatives of **2** resulted in low product yields, due to competing coupling between the liberated C1 radicals and the liberated *N*-phthalimide byproduct (see supporting information for details). Nevertheless, expansion of this method to α,α -disubstituted redox-active esters **2** was found to be possible (Figure 3b). Cyclic systems performed particularly well and afforded a range of spirocyclopropanes in excellent yields (**5a–5d**). The spirocyclopropane product **5e** is notable because competing reactions involving sulfur were not observed under the transition metal-free conditions, which prevails in metal carbenoid chemistry.^[14] In addition, the α -allylic redox ester (**2**) bearing a competing alkene functionality gave the

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Figure 3. Scope of the photoinduced decarboxylative cyclopropanation of alkanes. For **5g–i**, dr ratios were determined by ^1H NMR analysis of crude material.

cyclopropane **5g** in moderate yield. Overall, excellent chemoselectivity and functional group tolerance were observed, although difficult-to-remove minor amounts of unreactive alkene side-products occurred in some instances, giving trace impurities in the spectroscopic data (see Supporting Information).

We next turned our attention to the reaction mechanism (Figure 4). First, in the absence of blue light (465nm) to activate an EDA complex or a base to form an EDA complex, the decarboxylative cyclopropanation of **1a** and **2a** was completely suppressed (Table

1, cf. entry 5 and 6). Indeed, formation of the possible EDA complex between the active ester **7** and the K^+ salt of **1a** was confirmed in CH_3CN by UV/vis absorption spectroscopy, whereby the dramatic colour change correlated to a large bathochromic shift in the absorption spectrum (Figure 4a; see supporting information for more details).^[13a] Second, when the reaction was carried out at 5 °C instead of 35 °C with the preformed potassium salt of **1a**, the desired cyclopropanation product **4a** was formed in 10% yield together with 41% of the β -alkylated acetate **6a** (Figure

Reaction scheme (3) illustrates the synthesis of 6a and 4a from the K⁺ salt of 1a. The reaction proceeds via two pathways:

(1) Reaction with 2a (AcO-CMe₂-C(=O)-NPhth) under blue LED irradiation in DMSO (0.1 M) at 5 °C for 24 h yields 6a (41%) and 4a (10%).

(2) Reaction with 2a under no light conditions in DMSO (0.1 M) at 35 °C for 24 h yields 4a (83%).

Reaction scheme (4) illustrates the synthesis of 8a from the K⁺ salt of 1a. The reaction proceeds via a single pathway:

(3) Reaction with 7 (Me₂C=C(OMe)-C(=O)-NPhth) under blue LED irradiation in DMSO (0.1 M) at 5 °C for 24 h yields 8a (88%).

Reaction scheme showing the synthesis of **8b** and **8c** from the K⁺ salt of **1a** and compound **9** under blue LED irradiation in DMSO (0.1 M) at 5 °C for 24 h.

The reaction involves the K⁺ salt of **1a** (a 2-cyano-1-phenylethyl anion) reacting with compound **9** (a 2-cyano-1-phenylethyl anion derivative) to yield **8b** (83% yield) and **8c** (< 5% yield).

Structure **10** is shown as a proposed intermediate in a dashed box, which can further react to form **11**.

4, Eq. 1). Third, when acetate **6a** was exposed to KO^tBu without light, the desired cyclopropane **3a** was generated smoothly in excellent yield (Eq. 2). Fourth, reaction of the **1a** salt with the all-carbon α -substituted version **7** of **2a** gave the β -alkylated product **8a** in high yield (Eq. 3). These observations and control reactions strongly indicated the acetate **6a** to be a key intermediate and that both light and base were essential for its generation. Further control reactions were carried out to support the formation of β -

Based on the above control experiments, a plausible mechanism for this new cyclopropanation reaction is proposed in Figure 5. First, the potassium salt of **1** is generated *in-situ* via deprotonation with KO^tBu in DMSO. The generated α -anion of **1** can then react with the *N*-hydroxyphthalimide ester **2** via a photoinduced single electron transfer (SET) event, when paired as its electron-donor/acceptor (EDA) complex.^[13,16] This SET event consequently generates the β -acidic α -radical **1'** and the radical anion of **2**, which fragments to the C1 α -radical **2'** via release of CO₂ and *N*-phthalimide anions.^[12] Loss of the β -proton from the α -radical **1'** then affords the α/β -radical anion of **1'**.^[17,18] Next, intermolecular homogenic coupling between the radical anion **1'** and the O-stabilised radical **2'** forges a new C_{sp3}–C_{sp3} bond at the β -position and the resulting α -anion of **6** cyclises to furnish the corresponding cyclopropane **4** or **5**.

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In summary, we disclose a new photosynthetic method to directly couple cyano alkanes (**1**) with electron accepting C1 carbon units (**2**) to yield functionalised cyclopropanes (**4/5**) in a redox-neutral and highly chemoselective manner. The intermolecular reaction does not necessitate transition metals, photo-catalysts or alkene substrates or intermediates (just exposure to a base and light). Mechanistic evidence supports the reaction to involve a photoinduced single electron transfer (SET) event by virtue of an electron-donor/acceptor (EDA) complex being formed between the anion of the α -substituted malononitrile or cyanoethanoate (**1**) and the redox ester (**2**). This SET event from the α -anion of **1** induces a decarboxylative fragmentation of **2** to form stabilised radical species of **1'** and **2'** en route to β -carbon homogenic coupling and intramolecular S_N2 displacement of the acetate from **6**. In this way, a new intermolecular entry for the preparation of aryl cyclopropanes **4/5** flanked by two adjacent quaternary stereocenters is realised, which circumvented the need for rare transition-metals to β -functionalize carbonyl compounds via C–H bond activation mechanisms.^[19] Given the ubiquity and intermediacy of aryl cyclopropanes in bioactive natural products and drugs,^[1–3] we anticipate this new photo-redox method to be of high interest to the synthesis communities.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Cyclopropanation • Single electron transfer • Decarboxylation • Radical • Alkane

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Light and base are all you need to couple α -acidic cyanoalkanes with C1 units to form cyclopropanes. No photocatalyst, transition metal or alkene is required. Mechanistically, a photoinduced single electron transfer of a transient donor-acceptor complex is proposed to form a reactive β,α -radical anion of the cyanoalkane prior to β -coupling with a decarboxylated C1 radical and α -anionic ring closure.