

Catalytic Ability of 9-Cyanophenanthrene in Oxidative Photodimerization of 2,5-Dimethyl-2,4-hexadiene

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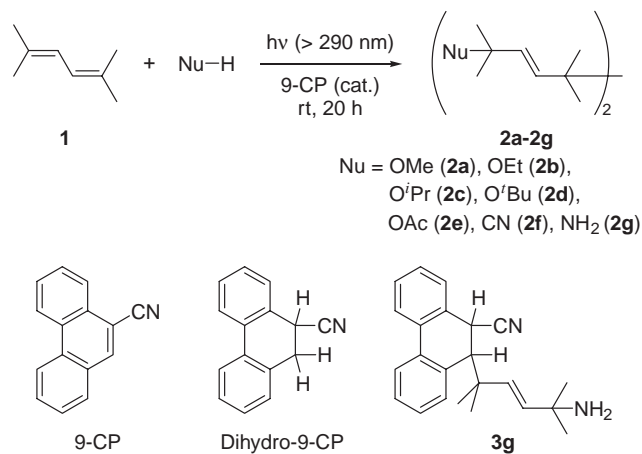
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The oxidative photodimerization reaction of 2,5-dimethyl-2,4-hexadiene (**1**) in the presence of nucleophiles was efficiently catalyzed by 9-cyanophenanthrene (9-CP) to give nucleophile-substituted 3,7-decadienes.

Oxidative and reductive photodimerization reactions have been a subject of diverse studies among organic chemists not only from mechanistic interests but from their potentiality to form complicated skeletons, in particular those of natural compounds, from rather simple moieties. For example, pinacol coupling¹ is one of the most well-known reductive photodimerization reactions. Becker has reported the case of acetophenones, which both oxidative and reductive dimerizations occur concomitantly to produce 1,2-dibenzoyl ethanes and acetophenone pinacols, respectively.² Johnson et al. have revealed oxidative photocoupling of phenols at *ortho*- and *para*-positions.³ In terms of natural compounds, Hino et al. have succeeded in synthesizing folicanthine, chimonanthine, calycanthine, and ditryptophenaline using ring closing photodimerization reaction of indoles for key steps.⁴

Previously, we have reported that photoirradiation of a methanol solution of 2,5-dimethyl-2,4-hexadiene (**1**) in the presence of 9-cyanophenanthrene (9-CP) gave dimethoxy-substituted dimer of **1**, 2,9-dimethoxy-2,5,5,6,6,9-hexamethyl-3,7-decadiene (**2a**), and 9-cyano-9,10-dihydrophenanthrene (dihydro-9-CP).⁵ In this work, we found out that 9-CP performed as a catalyst for the formation of **2** and that various nucleophiles could be introduced to the dimer (Scheme 1).

The dimer **2a** was formed almost quantitatively from **1** upon 20 h irradiation of a methanol solution containing **1** and a catalytic amount of 9-CP under argon atmosphere (Table 1, Entry 1). Various alcohols could be used as nucleophiles for



Scheme 1.

Table 1. Oxidative photodimerization of **1**^a

Entry	Nucleophile and Solvent(s)	Product	Yield ^b /%
1	MeOH	2a	>96 (87 ^c)
2	EtOH	2b	86 (51)
3	<i>i</i> -PrOH	2c	28
4	<i>t</i> -BuOH	2d	9
5	AcOH, ^d MeCN	2e	69 (27)
6 ^e	KCN, MeCN, H ₂ O ^f	2f	23 (11)
7	NH ₃ , ^d MeCN, H ₂ O ^f	{ 2g 3g }	{ 56 34 ^g }

^aConditions: 300-W high-pressure mercury lamp, Pyrex filter, [1] = 15 mM, [9-CP] = 5 mM, under Ar, rt, 20 h. ^bDetermined by ¹H NMR based on **1** used. Isolated yields in parentheses. ^c[1] = 1 M, [9-CP] = 29 mM. ^d[AcOH] = [NH₃] = 500 mM. ^e[1] = 150 mM, [KCN] = 1 M, [*n*-Bu₄NClO₄ (additive)] = 500 mM. ^fMeCN:H₂O = 4:1. ^gBased on 9-CP used.

the reaction, whereas the use of bulky (and less polar) alcohols resulted in lower yields (Entries 2–4).⁶ Acetic acid and potassium cyanide also acted as nucleophiles to yield acetoxy- and cyano-substituted dimers **2e** and **2f**, respectively (Entries 5 and 6).^{7,8} Figure 1 shows an ORTEP drawing of **2f**. When ammonia was used as a nucleophile, three-component adduct **3g** was formed along with 3,7-decadiene **2g** and dihydro-9-CP (Entry 7).^{9,10}

These results indicated that 9-CP acted as a catalyst for the formation of dimer **2**. Turn over number of 9-CP in methanol increased up to 30 in proportion to the initial concentration of **1**, without any considerable side reactions. It is known that 9-CP turns into dihydro-9-CP concurrently with the formation of **2a** in this photoinduced electron-transfer reaction,⁵ so there must be an oxidation pathway to reproduce 9-CP from dihydro-9-CP. In fact, irradiation of isolated dihydro-9-CP resulted in regeneration of 9-CP within 30 min. On the other hand, dihydro-9-CP remained unchanged under dark for a month. The oxidant of this process was affirmed as molecular oxygen by the evidence that

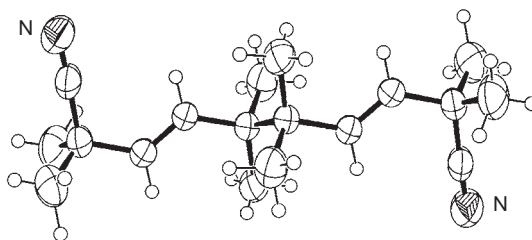
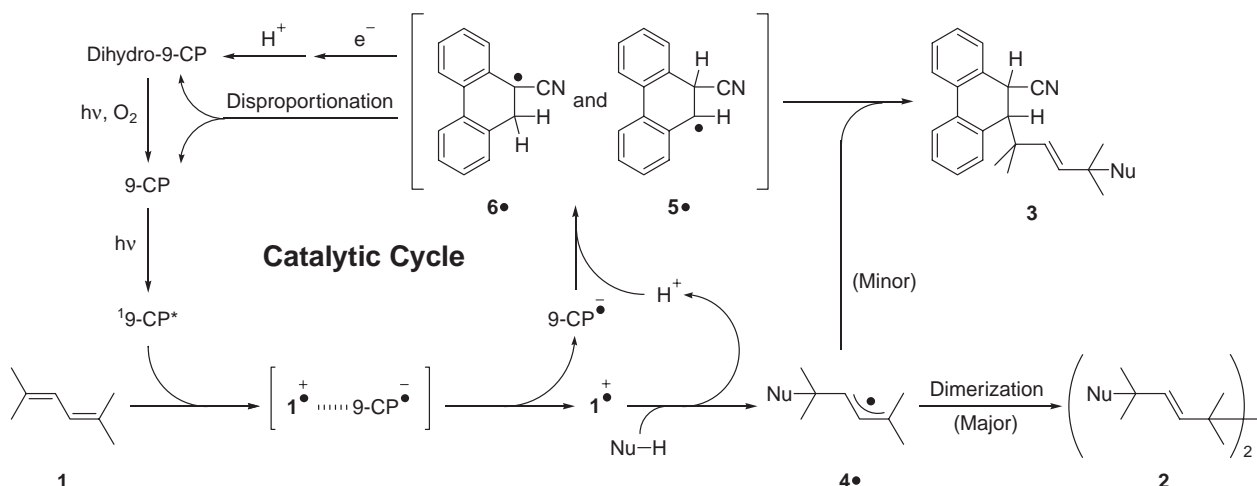


Figure 1. ORTEP drawing of **2f**: monoclinic, *P*2₁/*a* (#14), *Z* = 2, *R* = 0.070, *R*_w = 0.068, *a* = 11.014(9), *b* = 6.651(4), *c* = 12.730(12) Å, β = 97.37(4)°, *V* = 924.8(12) Å³, *D*_{calcd} = 0.978 g/cm³.



Scheme 2. Plausible mechanism for the formation of **2** and the catalysis of 9-CP.

irradiating a sample under identical conditions as Entry 1 of Table 1 after careful degassing by a freeze–pump–thawing method resulted in non-catalytic formation of **2a**. Irradiation under air or oxygen, however, did not produce dimer **2**, possibly owing to the rapid quenching of excited state of 9-CP by molecular oxygen. These results pointed out that irradiation and a small amount of molecular oxygen are essential for the reproduction of 9-CP as a catalyst.

Deuterium was incorporated at 9- and 10-positions of dihydro-9-CP with *d*-contents of 76 and 26%, respectively, when methanol-*O-d* was used instead of methanol.¹¹ This result clearly indicates that protonation of the radical anion of 9-CP occurs predominantly on 9-position rather than on 10-position. It is consistent with the result of molecular orbital calculation using PM3 method: 9-position of radical anion of 9-CP can be thought as a little more basic than its 10-position since partial charges on these positions are -0.194 and -0.176 , respectively.

From these results, we propose the mechanism as follows (Scheme 2). Photoinduced electron transfer from **1** to excited singlet state of 9-CP ($^19\text{-CP}^*$) affords radical ion pairs. The radical cation of **1** reacts with nucleophile and the resulted allylic radical **4**[•] dimerizes to give **2**. The radical anion of 9-CP is protonated on 9- or 10-position, and the resulted radicals (**5**[•] and **6**[•], respectively) undergo disproportionation or further reduction and subsequent protonation to produce dihydro-9-CP. Dihydro-9-CP is stable enough under dark conditions but reacts rapidly under irradiation conditions with a small amount of molecular oxygen remaining in the system to reproduce 9-CP, hence 9-CP has the catalytic ability for the formation of **2**.¹² Three-component adduct **3** can be explained as it derives from the coupling of radicals **4**[•] and **5**[•].¹³

In conclusion, photocatalytic ability of 9-CP for the oxidative dimerization reaction and its mechanism was disclosed. In addition, various nucleophiles were found to be introduced to the dimer. This reaction might be useful for the synthesis of 1,8-disubstituted 2,6-octadiene derivatives.

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- Higher nucleophilicity of ammonia might be responsible for the formation of three-component adduct **3**, observed only in the reaction with ammonia. An alternative pathway might contain that ammonia attacks on radical cation of **1** in the solvent cage of radical ion pair, followed by radical coupling.