Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 4627–4630

Tetrahedron Letters

Quinone imine dye formation via photocycloaddition between isocyanates and chloranil

Kan Wakamatsu*

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005, Japan

Received 12 March 2004; revised 17 April 2004; accepted 21 April 2004

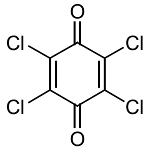
Abstract—Photochemical [2+2]cycloaddition between electron-donating aryl isocyanates and chloranil was observed in acetonitrile or benzene, and the following elimination of carbon dioxide resulted in the formation of the corresponding quinone imine dyes. This new route for synthesis of quinone imine was investigated by product analyses, laser flash photolyses, and molecular orbital calculation.

Photochemical [2+2]cycloaddition between a C═C double bond and a carbonyl group, that is, the Paternò-Büchi reaction, is a well-known photochemical reaction.[1] It has been mentioned that this reaction takes place by way of a charge-transfer (CT) exciplex as well as a preoxetane biradical when an electron-rich olefin and an electron-deficient carbonyl compound such as quinone are used.[2] A C═C double bond of diphenylketene can also form the corresponding four-membered ring with an excited quinone, and the resulting β-lactone may decompose to the quinone methide and carbon dioxide.[3] Similarly, some ketenimines can afford the corresponding iminooxetanes.[4] In an analogous way, isocyanates and their thio-derivatives are expected to undergo the photochemical cycloaddition with quinones, finally affording the quinone imine dyes, which would be useful for imaging systems,[5] after evolving carbon dioxide or carbon thiooxide. However, little is known about the cycloaddition between C═O and C═N. In this paper the photoreaction of chloranil (**CA**) with iso(thio)cyanates is reported.

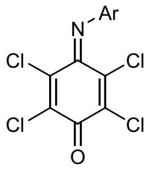
$\mathrm{Ar{-}N{=}C{=}X}$

1

a (X = O, Ar = C_6H_5)
b (X = O, Ar = 1-naphthyl)
c (X = S, Ar = C_6H_5)
d (X = S, Ar = 4-$CH_3C_6H_4$)
e (X = S, Ar = 3,4-$(CH_3)_2C_6H_3$)
f (X = S, Ar = 4-$CH_3OC_6H_4$)



CA



2

In Table 1, the quenching rate constants (k_q) for the excited triplet of chloranil (^{3}**CA***) by the iso(thio)cyanate (**1**) are summarized. As seen from Table 1, k_q is

Table 1. Oxidation potentials (E_{ox}), free energy changes in electron transfer (ΔG_{et}), and quenching rate constants (k_q) for the excited triplet of **CA**

	E_{ox} (V)[a]	ΔG_{et} (kJ mol^{-1})[b]	$10^{-8}k_q$ (mol^{-1} dm^3 s^{-1})	
	In CH_3CN	In CH_3CN	In CH_3CN	In C_6H_6
1a	+1.85	−6.2	0.74	0.055
1b	+1.34	−56	120	33
1c	+1.77	−14	2.2	0.19
1d	+1.59	−31	69	1.3
1e	+1.55	−35	74	1.1
1f	+1.32	−57	91	45

[a] From cyclic voltammograms referred to Ag/Ag$^+$ (irreversible).

[b] Calculated by using Rehm–Weller equation:[6] $\Delta G_{et} = E_{ox}(\mathbf{1}) - E_{red}(\mathbf{CA}) - E_T(\mathbf{CA}) - e^2/\varepsilon d$; the reduction potential of **CA** (E_{red} vs Ag/Ag$^+$): −0.27 V; the excited triplet energy of **CA** (E_T): 205 kJ mol^{-1}; the Coulomb term ($e^2/\varepsilon d$): 0.06 eV.

Keywords: Photocycloaddition; Exciplex; Electron transfer; Quinone imine; Isocyanate.

* Tel.: +81-86-256-9663; fax: +81-86-254-2891; e-mail: waka@chem.ous.ac.jp

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.04.107

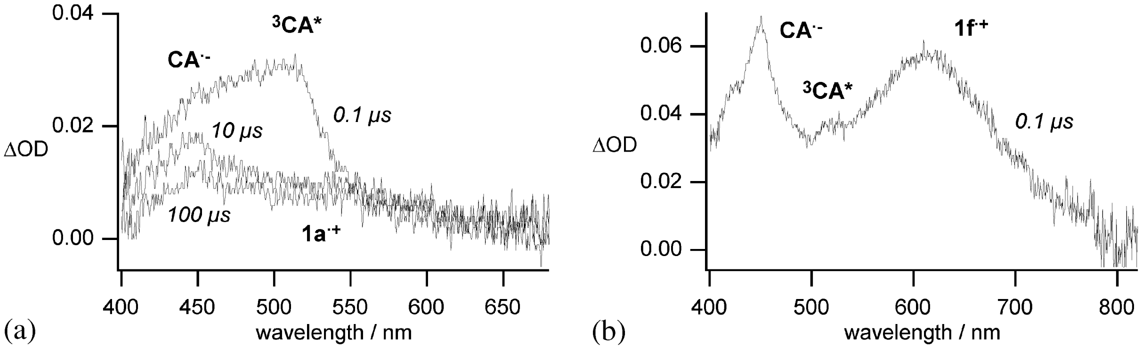


Figure 1. Transient absorption in acetonitrile containing (a) **1a** or (b) **1f** after excitation by a 355-nm laser pulse ([**1a**] = 0.04 mol dm^{-3}, [**1f**] = 0.0007 mol dm^{-3}, [**CA**] = 0.004 mol dm^{-3}).

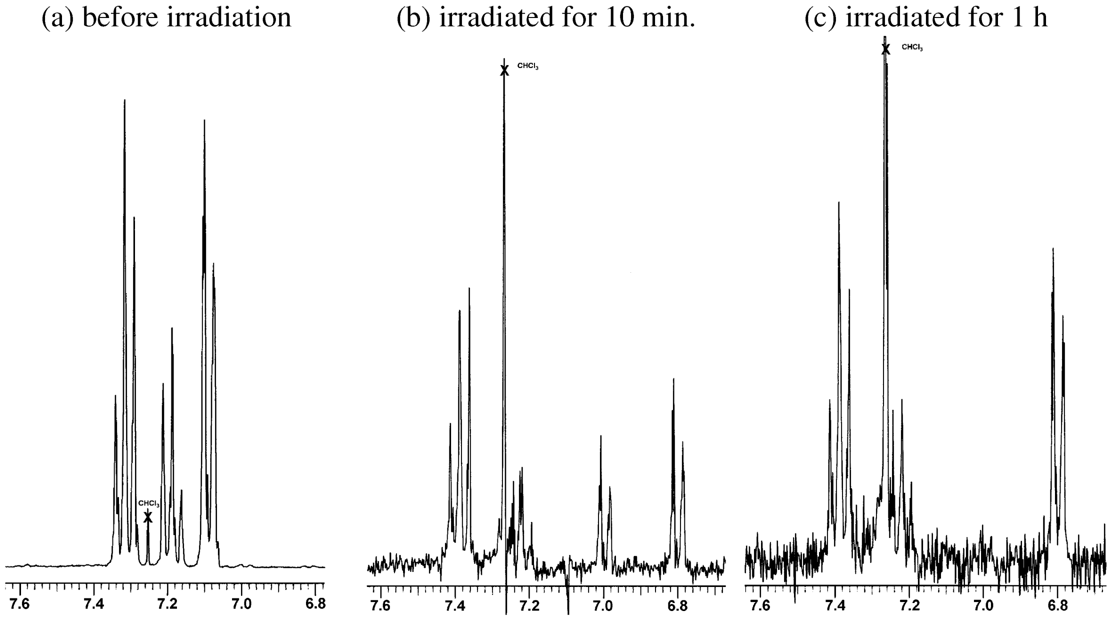

(a) before irradiation (b) irradiated for 10 min. (c) irradiated for 1 h

Figure 2. The time course of ^{1}H NMR spectrum change for photoreaction of **1a** and **CA**.

correlated to the free energy changes in electron transfer (ΔG_{et}), so that the quenching should be due to electron transfer or exciplex formation between **1** and ^{3}**CA***. When an acetonitrile solution containing **1** and **CA** was irradiated by a 355-nm laser pulse (Nd-YAG), transient absorption bands assigned to the radical cation of **1** and the radical anion of **CA** appeared after the quenching of ^{3}**CA*** (Fig. 1). The transient absorptions of the radical ions were more rapidly appeared in the case of the more electron-donating compound (**1f**).

When an acetonitrile solution containing phenyl isocyanate (**1a**) and **CA** was irradiated under nitrogen atmosphere using a 500-W super-high-pressure mercury lamp with an appropriate cut-off filter (λ >390 nm), the color of the solution immediately changed from light-yellow to red-purple, and **1a** completely disappeared after 1 h. The resulting colored material was assigned to the quinone imine (**2a**) by NMR and MS analyses, and no other products were detected.[7,8] The formation of **2a** would be reasonably explained by the photochemical [2+2]cycloaddition and the following release of carbon dioxide. The intermediacy of the [2+2]cycloadduct was confirmed by the time course of the NMR spectrum change (Fig. 2). The *ortho*-protons of the phenyl group of **2a** (6.8 ppm, Fig. 2c) were observed at higher magnetic field than those of **1a** (7.1 ppm, Fig. 2a) owing to magnetic shielding by the quinone imine moiety. When the irradiation was stopped after 10 min, new *ortho*-protons were observed at the middle position (7.0 ppm, Fig. 2b) between **1a** and **2a**. Taking into account the degree of magnetic shielding, these would be assigned to the protons of the [2+2]cycloadduct (**3a**). Since the adduct **3a** almost completely survived for one day in the chloroform solution, the reaction of **3a** producing **2a** might be triggered by a secondary photochemical electron transfer with the excited **CA**.[†]

[†] The calculated activation energy of **3a** → **2a** + CO$_2$ by PM3 is 41 kcal mol^{-1}. Therefore, it is hard to regard the present reaction as thermal decomposition of **3a**.

Table 2. Relative reactivity for the photoreaction of **1** and **CA**, and calculated atomic charges in the radical cation of **1**

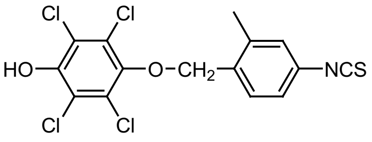
	Relative reactivity[a] (product)		Atomic charge in the radical cation[b]		
	In CH_3CN	In C_6H_6	N	C	X
1a	110 (**2a**)	9 (**2a**)	−0.452	0.724	−0.244
1b	11 (**2b**)	280 (**2b**)	−0.500	0.681	−0.284
1c	0	0	−0.364	0.202	0.271
1d	0	0	−0.378	0.204	0.241
1e	[c]	[c]	−0.386	0.204	0.225
1f	0	7 (**2f**)	−0.400	0.206	0.200

[a] Determined by UV–vis absorption maximum of **2**. The value means the initial increasing rate of the concentration of **2** ($\times 10^{-7}\,mol\,dm^{-3}\,s^{-1}$).

[b] Determined by B3LYP/6-31G* calculation using Gaussian 98 program package.[11]

[c] Hydrogen abstraction yielding the compound **4** occurred instead of photocycloaddition.[10]

Similar irradiation (λ >350 nm) on an acetonitrile solution of **1a** and a weaker electron acceptor, *p*-benzoquinone, resulted in no chemical reaction ($\Delta G_{et} = 30\,kJ\,mol^{-1}$). Therefore, the efficiency of the reaction would depend on the degree of electron transfer interaction between **1a** and the excited quinone. Since nonaromatic isocyanate (propyl isocyanate) did not react with the excited **CA**, an electron-donating nature would be also required for iso(thio)cyanate. Results of the photoreaction of other iso(thio)cyanates are summarized in Table 2.[9,10]



4

Isothiocyanates are less reactive than isocyanates, even if they efficiently quench the excited state of **CA**. This would be attributed to less electrophilicity of the NCS carbon in their radical cations. Calculated[11] atomic charges on the NCX carbon are listed in Table 2, and it is found the carbon in the isocyanate (**1a**,**b**) radical cations has a more positive charge than that in the isothiocyanate (**1c**–**f**) radical cations. The spin densities on the NCX carbon would be less important for the initial stage of the reaction, since their absolute values are rather small (0.006–0.096).

Table 3. Absorption maxima of the quinone imine (**2**)

	λ (nm) (ε, $cm^{-1}\,dm^3\,mol^{-1}$)	
	In CH_3CN	In C_6H_6
2a	524 (1450)	537 (1510)
2b	599 (3100)	619 (3500)
2f	582 (2870)	587 (3340)

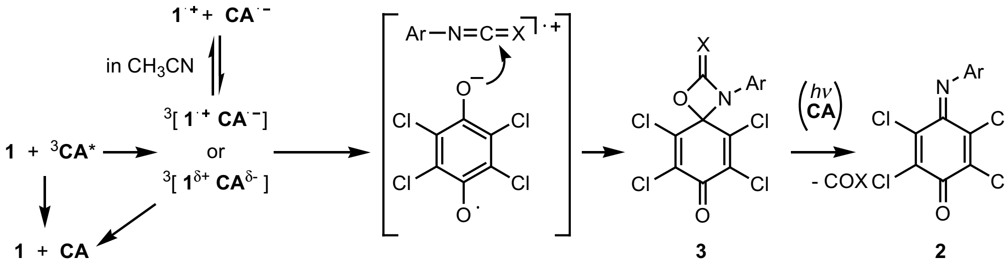
Similar reaction was also observed in benzene. In the case of **1a**, irradiation on the benzene solution afforded less amount of the product than on the acetonitrile solution, while the stronger electron donor, **1b** or **1f**, gave higher yield of the product in benzene. In general, since the quenching efficiency of the excited triplet of **CA** by **1** is lower in benzene than in acetonitrile (Table 1), the radical ion pair (or exciplex) would be generated in higher yield in acetonitrile. However, the radical ion pair in acetonitrile immediately dissociates into free radical ions except in the case that ΔG_{et} is close to zero and the quenching is induced by the exciplex formation.[12] The exciplex would be preferentially formed in a nonpolar solvent such as benzene, so that the cycloaddition occurs more efficiently in benzene if the quenching efficiency is sufficiently high. A possible mechanism is summarized in Scheme 1.

The absorption maxima of the quinone imine **2** are listed in Table 3. The absorption band in the visible region can be assigned to intramolecular CT transition from the aryl group to the quinone imine group.[13]

In summary, photochemical [2+2]cycloaddition between electron-donating aryl isocyanates and chloranil was observed and the following elimination of carbon dioxide resulted in the formation of the corresponding quinone imine dyes.

Acknowledgements

The author is grateful to Professor Tsutomu Miyashi (Tohoku University) and Professor Hideo Tomioka and Professor Yasutake Takahashi (Mie University) for the use of their LFP equipments. The author also thanks Professor Yasumasa Shigetomi (Okayama University of Science) for providing opportunities for this study.



Scheme 1.

References and notes

1. Griesbeck, A. G. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC: Boca Raton, 1995, Chapter 43; and references cited therein.
2. Maruyama, K.; Osuka, A. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: New York, 1988; Vol. 2, Chapter 13.
3. Ogino, K.; Matsumoto, T.; Kozuka, S. *J. Chem. Soc., Chem. Commun.* **1979**, 643.
4. Ogino, K.; Matsumoto, T.; Kawai, T.; Kozuka, S. *J. Org. Chem.* **1979**, *44*, 3352.
5. Nickel, U. *J. Imaging Technol.* **1986**, *12*, 181.
6. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *63*, 4358.
7. A mixture of **1a** (0.1 mmol) and chloranil (0.1 mmol) in acetonitrile (10 dm^3) was irradiated under nitrogen atmosphere. After 1 h the solvent was removed in vacuo, then **2a** was purified by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate, 95/5). Isolated yield: 76%. Compound **2a**: violet crystals; mp 110 °C (lit.[8] 114–115 °C); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.80 (d, 2H, $J = 7.5$ Hz, *ortho*), 7.22 (t, 1H, $J = 7.5$ Hz, *para*), 7.39 (dd, 2H, $J = 7.5$, 7.5 Hz, *meta*); MS (EI, 70 eV) m/z 320 (M$^+$).
8. Boulos, L. S.; Arsanious, M. H. N. *Synth. Commun.* **2002**, *32*, 2779.
9. The isocyanates (**1a**,**b**) and phenyl isothiocyanate (**1c**) can be commercially obtained (>98% pure) and were used without further purification. Chloranil was recrystallized from toluene prior to use. Other isothiocyanates (**1d**–**f**) were synthesized according to the literature method: Hodgkins, J. E.; Reeves, W. P. *J. Org. Chem.* **1964**, *29*, 3098.
10. When the 3,4-dimethyl derivative (**1e**) was used, the compound (**4**) resulting from hydrogen abstraction from the methyl group of **1e** was obtained instead of the quinone imine. The yield of **4** was 8% (in acetonitrile) or 13% (in benzene) after irradiation for 2 h ([**1e**] = [**CA**] = 0.01 mol dm^{-3}). Compound **4**: light yellow crystals; mp 194–198 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.46 (s, 3H, methyl), 4.96 (s, 2H, CH$_2$), 7.11 (d, 1H, $J = 8.8$ Hz, ArH), 7.12 (s, 1H, ArH), 7.50 (d, 1H, $J = 8.8$ Hz, ArH). The hydrogen abstraction from the methyl group of **1e** would occur at the *para*-position rather than the *meta*-position because the resulting radical intermediate would be stabilized by the resonance effect of the isothiocyanato group. Similar reaction also occurred when *p*-xylene or *o*-xylene was used as an electron donor.
11. Gaussian 98 (Revision A.7), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.
12. Kikuchi, K. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 149.
13. Adachi, M.; Murata, Y.; Nakamura, S. *J. Org. Chem.* **1993**, *58*, 5238.