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Formation of Unsaturated Esters in the Single Electron Transfer Reaction of Cyclopropanone Acetals with Quinones under Non-irradiated Conditions

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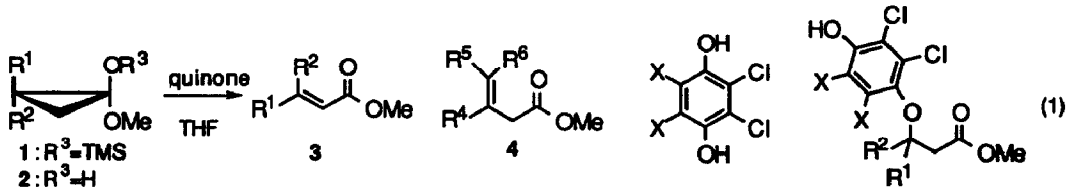
Abstract: Unsaturated esters were formed from cyclopropanone acetals in the reaction with DDQ or chloranil, where ring-opened C-C and C-O bonded adducts were the intermediates formed via a SET mechanism resulting in the ester formation.

While a number of cyclopropane derivatives, which have been regarded to have higher oxidation potentials than alkane homologues, have been investigated in search of their electron transfer profile,[1-5] the reactions were examined mainly under photolysis conditions. Among them, scarcely investigated cyclopropanone acetals **1** and hemiacetals **2** [6] seem to us as promising donors in combination with appropriate acceptors at their ground states because of two oxygenic substituents.[7] In this respect, we report here the intervention of a single electron transfer (SET) reaction mechanism in the non-irradiated reactions of acetals **1** and **2** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) or 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil), where the intervention of C-O and C-C bonded adducts were clearly demonstrated. Also found was that structural variations in both donor and acceptor determine the overall reaction pathway.



(1)

1: R^3=TMS
2: R^3=H

a: R^1=Ph, R^2=H
b: R^1=Ph, R^2=CH_3
c: R^1=Ph, R^2=C_2H_5
d: R^1=Ph, R^2=^iPr
e: R^1=$^nC_5$, R^2=H

3

4

b: R^4=Ph, R^5=R^6=H
c: R^4=Ph, R^5=CH_3, R^6=H
d: R^4=Ph, R^5=R^6=CH_3
e: R^4=H, R^5=$^nC_4$, R^6=H

5 (X=Cl)
6 (X=CN)

7 (X=Cl)
8 (X=CN)

The reactions of **1** or **2** with one equivalent of DDQ or chloranil[8] in refluxing solvent without photo-irradiation were found to give unsaturated ester **3** or its mixture with **4** in moderate yields together with hydroquinone **5** or **6** (eq 1 and Table 1).[9]

A SET process (Scheme 1) is occurring exclusively as verified by trapping the intervening radical ion species with oxygen[10] in the reaction of **1b** or **1c** with chloranil: peroxypropiolactone (50-70%) was formed predominantly but not in the absence of the quinone.

Table 1. Reaction of Cyclopropanone Acetals **1** and **2** with Quinones.

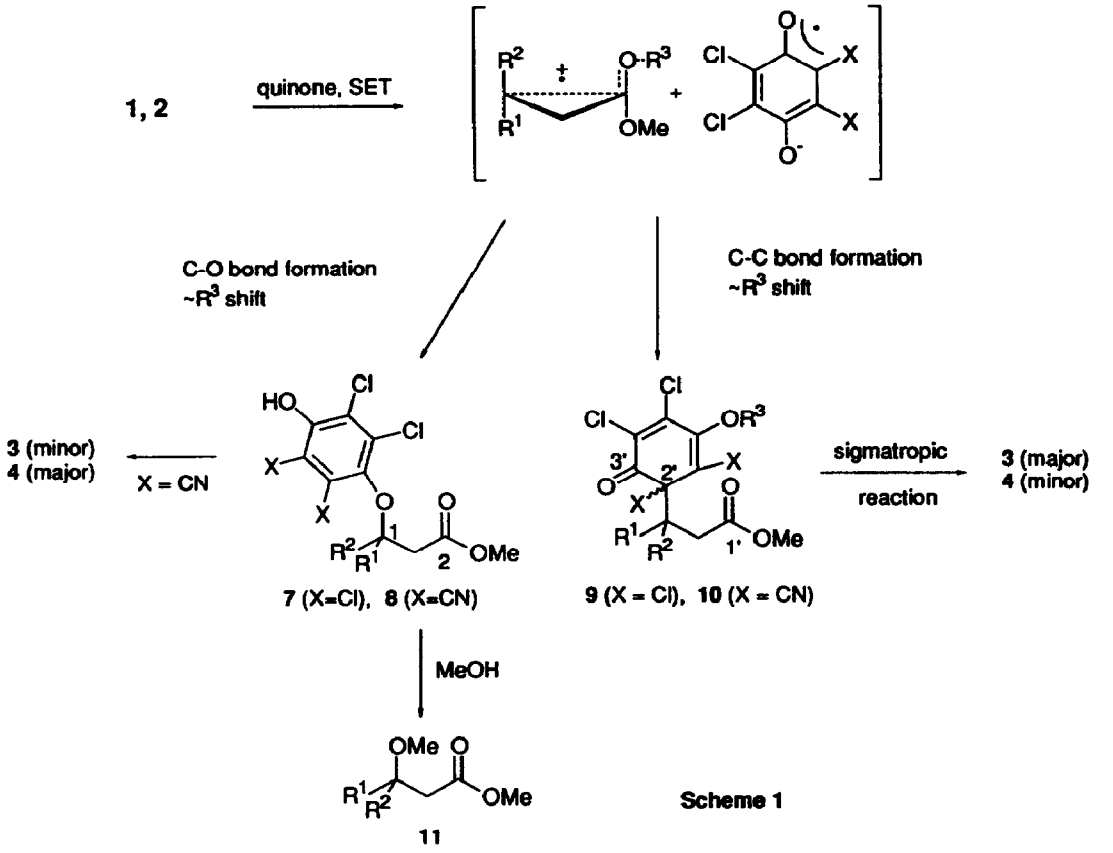
entry	quinone[a]	cyclopropanone acetal	R^1	R^2	R^3	time / h	product and yield / %[b]			
1	D	**1a**	Ph	H	TMS	0.2	**3a**(74)[d]			**6**(65)
2	D	**1b**	Ph	CH_3	TMS	2.0	**3b**(23)[e]	**4b**(41)		**6**(56)
3	D	**1c**	Ph	C_2H_5	TMS	6.0	**3c**(34)[f]	**4c**(48)[h]		**6**(82)
4	D	**1d**	Ph	^iPr	TMS	15.0	**3d**(62)[g]	**4d**(14)		**6**(77)
5	D	**1e**	$^nC_5$	H	TMS	20.0	**3e**(27)[d]	**4e**(3)[i]		**6**(28)
6[c]	D	**1e**	$^nC_5$	H	TMS	20.0	**3e**(76)[d]	**4e**(15)[i]		**6**(86)
7	D	**2a**	Ph	H	H	0.2	**3a**(61)[d]			**6**(55)
8	C	**1a**	Ph	H	TMS	1.0	**3a**(84)[d]		**7a**(4)	**5**(81)
9	C	**1b**	Ph	CH_3	TMS	30.0	**3d**(43)[d]	**4d**(16)	**7b**(28)	**5**(58)
10	C	**1c**	Ph	C_2H_5	TMS	89.0	**3e**(26)[j]	**4e**(8)[h]	**7c**(16)	**5**(33)
11	C	**1d**	Ph	^iPr	TMS	120.0	-[k]			
12	C	**2a**	Ph	H	H	1.0	**3a**(72)[d]			**5**(68)

[a] D: DDQ, C: chloranil. [b] Isolated Yield. [c] The reaction was performed in dry CH_3CN at 60 °C. [d] Only *E* isomer was formed. [e] *E* / *Z* = 8 / 1. [f] *E* / *Z* = 3 / 1. [g] *E* / *Z* = 1 / 4. [h] *E*, *Z* mixture. [i] *E* / *Z* = 2.5 / 1. [j] *E* / *Z* = 5 / 1. [k] 89% of **1d** was recovered.

First observation of note is that while C-O bonded chloranil-adduct **7** was formed and remained intact under the reaction conditions, similar adduct **8** with DDQ was formed only as a transient intermediate, together with **3** and **4**, within minutes at 21 °C (identified by the time-split ^1H and ^{13}C NMR in the reaction of **1b** or **1c** with DDQ in CD_3CN) [11]. On heating to 60 °C, **8** completely transformed to a mixture of **3** and **4**. Thus, C-O bonded DDQ-adduct **8**, being formed after a SET reaction, undergoes elimination reaction leading to the unsaturated esters,[12] whereas **7** does not. The clear difference in reactivity between **7** and **8** bases on the difference of the hydroquinone part, its elimination being easier in **8** than **7**.

Second of note is that, in the reaction of **1c** ($R^2 = C_2H_5$) with DDQ, the product ratio **3**/**4** was 1.5 at the initial stage of the reaction (25 °C, mol ratio of (**3**+**4**)/**8** = 1 / 3.9, determined by ^1H NMR) but it changed to 0.77 at the final stage (60 °C, **8** disappeared). We had a time before we have identified C-C bonded adduct **10e** by ^1H and ^{13}C NMR as a transient intermediate leading to **3** and **4** in the reaction of **1e** ($R^1 = C_5H_{11}$) with DDQ.[13] Since C-O adducts **7** are not the precursors of unsaturated esters, how are the esters formed in the reactions with chloranil ? The following observations deserve attention: (1) Reversal of product ratios **3**/**4** between the reactions of two quinones was observed (compare entries 2 and 3 with 9 and 10 in Table 1).[14] (2) When **3** and **4** were formed, C-O adduct **7** was always found whereas C-C bonded chloranil-adduct **9** was not detected by ^1H NMR. These support the intervention of **9** as the only, but labile precursor of unsaturated esters, undergoing a rapid sigmatropic reaction (Scheme 1).

To summarize, in the SET reaction with chloranil under non-irradiated conditions, unsaturated esters are exclusively formed from C-C adduct **9**, but not C-O adduct **7**, yielding preferably **3** to **4**. With DDQ, in concurrence with a fast sigmatropic pathway via C-C adduct **10** where formation of **3** predominates over **4**, a relatively slower elimination reaction of C-O adduct **8** takes place yielding preferably **4** to **3**. In addition, key intermediate C-O adducts **7**, **8** as well as C-C adduct **10** were detected and characterized. Detailed mechanistic account of the present reaction will be reported shortly.



Scheme 1

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2. Miyashi, T.; Takahashi, Y.; Ohaku, H.; Ikeda, H.; and Moroshima, S. *Pure & Appl. Chem.*, **1991**, *63 (2)*, 223.
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4 Nishida, S.; Murakami, M.; Mizuno, T.; and Tsuji, T. *J. Org. Chem.*, **1989**, *54*, 3868.

5. Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. *J. Am. Chem. Soc.*, **1986**, *108*, 6828.
6. **1** and **2** were prepared by Rousseau's method. Rousseau, G.; Slougui, N. *Tetrahedron Lett.*, **1983**, *24*, 1251.
7. The reason why cyclopropanone acetals **1** and **2** were selected as the donor is that their HOMOs' energies are increased by replacing two ring-hydrogen atoms with two oxygen substituents. Kuwajima and coworkers calculated that the HOMO's energy of 1,1-dihydroxycyclopropane is 1.6 eV or 0.4 eV higher than that of cyclopropane or ethylene, respectively. Aoki, S.; Fujima, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.*, **1981**, *103*, 7675.
8. $E_{1/2}$(DDQ) = 0.51 V vs SCE, $E_{1/2}$(chloranil) = 0.01 V vs SCE; see Meites, L.; Zuman, P. *Electrochemical Data Part 1, vol. A*; John Wiley and Sons, New York, 1974.
9. Dimethyl acetal (R^1 = Ph, R^2 = CH_3, R^3 = CH_3 in **2**), in the reaction with DDQ, smoothly underwent an analogous SET reaction to give unsaturated esters **3b** (53%), **4b** (14%), together with **6** (63%). Thus, observation of analogous reactions over three R^3 groups (TMS, CH_3, H), which have different redox property, indicates that the essential structural unit of the donor required for the SET process is an oxy-substituted cyclopropane and the variation in R^3 substituent does not influence the net reaction profile.
10. For O_2-trappings as the probe of SET mechanism in cyclopropane systems, see (a) Ichinose, N.; Mizuno, K.; Tamai, T.; Y. Otsuji, Y. *J. Org. Chem.*, **1990**, *55*, 4079. (b) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.*, **1987**, *109*, 2780.
11. The key ^{13}C NMR chemical shifts of **8b** are C-1 (89.83) and C-2 (169.47), and those of **8c** are C-1 (94.85) and C-2 (169.45). See structure **8** in Scheme 1.
12. The reaction of **1** with DDQ in the presence of MeOH afforded MeOH-trapping product **11** (11, 20, and 25% from **1b**, **1c**, and **1d**, respectively) in addition to **3** and **4**. The same product was also formed when MeOH was added after the consumption of **1** (10, 18, and 22%, respectively).
13. Analogous C-C adduct was hypothetically proposed for a different reaction system. See Bhattacharya, A.; DiMichele, L. M.; Dolling, Ulf-H.; Grabowski, E. J. J.; Grenda, V. J. *J. Org. Chem.*, **1989**, *54*, 6118. The key ^{13}C NMR chemical shifts of **10e** are C-1'(171.44, 171.60), C-2'(54.68, 56.27), and C-3'(181.41, 181.62). See structure **10** in Scheme 1.
14. In entries 9 and 10, **3** and **4** were undoubtedly formed via C-C adduct **9**.

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