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A VINYL CATION INTERMEDIATE IN THE ELECTROOXIDATION OF CIS-1-(4-MORPHOLINO)-1,2-DIPHENYLETHENE

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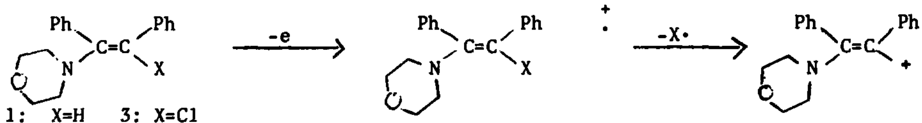
We reported earlier that upon electron impact, cis-1-(4-morpholino)-1,2-diphenylethene (1) and its halo-derivatives (2) and (3) give the 2-(4-morpholino)-1,2-diphenylethenyl cation (5) via the fragmentation of the cation-radical (6).[1] We also reported the formation of 5 by the solvolysis of 2 and 3. We now report the formation of 5 by the electrooxidation of 1 and a deuterated derivative (4).



1: X=H 3: X=Cl

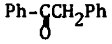
2: X=Br 4: X=D

6

5

(1)

The electrooxidation of 1 proceeded smoothly in t-butanol-water with lithium perchlorate as supporting electrolyte.[2] The polarograph showed a half-wave potential of 0.72V.[3] The products of the reaction were desoxybenzoin (7a), benzoin (8), benzil (9), and morpholine hydroperchlorate (10). The electrooxidation of the deuterated enamine, 4,[4] under the same condition gave a mixture of α-d-desoxybenzoin (7b) and α,α-d_2-desoxybenzoin (7c) together with 8, 9, and 10. The yields of these products are listed in Table I. These results suggest that the reaction might proceed as shown in eq. 2-8.

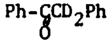


$\mathrm{Ph\text{-}\underset{O}{C}CH_2Ph}$

7a

$\mathrm{Ph\underset{O}{C}CDHPh}$

7b

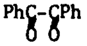


$\mathrm{Ph\text{-}\underset{O}{C}CD_2Ph}$

7c

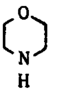
$\mathrm{Ph\underset{O}{C}\underset{OH}{C}HPh}$

8



$\mathrm{Ph\underset{O}{C}\text{-}\underset{O}{C}Ph}$

9



$\cdot HClO_4$

10

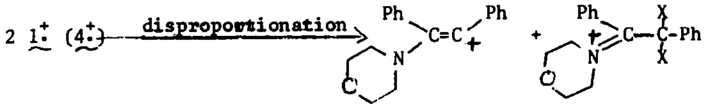
Table I. Products of Electrooxidation of 1 and 4

	% Yield			
	7		8	9
1 in two-compartment oxidation	26.4	7a	19.8	12.5
1 in one-compartment oxidation	31.3	7a	34.3	16.2
4 in two-compartment oxidation	25.3	7b*	19.3	12.2
	6.3	7c*		

* Analyzed by IR, NMR, and Mass Spectrometry.

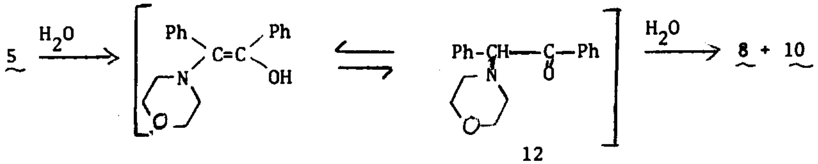
$1\ (4) \xrightarrow{H_2O,\ HClO_4} 7a\ (7b) + 10$ (2)

$1\ (4) \xrightarrow{-e,\ \text{electrooxidation}} 1^{\dot{+}}\ (4^{\dot{+}})$ (3)



(4)

5 11 : X=H(D)



12

(5)

$11 \xrightarrow{H_2O} 7a\ (7c) + 10$ (6)

$8 \xrightarrow{\text{electrooxidation}} 9$ (7)

$12 \xrightarrow{[O],\ \text{work up}} 9$ (8)

As reported earlier benzoin, 8 and the morpholine salt (10) are the solvolytic products for the vinyl cation 5.[1] Separately run control reactions confirmed the following: (a) enamines 1 and 4 were partially hydrolyzed to desoxybenzoin (7a) and α-d-desoxybenzoin (7b) respectively in the same solvent system used for the electrooxidation but α,α-d_2-desoxybenzoin (7c) was definitely a product from the electrooxidation of 4; (b) under the same electrooxidation conditions, benzoin (8) was partially converted to benzil (9); (c) the morpholinoketone (12)[5] did not undergo electrooxidation under the conditions employed but was hydrolyzed to benzoin (8) and oxidized to benzil (9) after chromatography on silica gel. This was the procedure used for the separation of products from the electrooxidation; (d) desoxybenzoin (7a) did not undergo electrooxidation under the conditions employed.

The presence of α,α-d_2-desoxybenzoin (7c) among the products of the electrooxidation of 4 strongly suggests the formation of the vinyl cation, 5, by disproportionation of cation-radicals, eq. 4. Such disproportionation of cation-radicals has been suggested by Cauguis, Fauvelot, and Rigaudy in the electrooxidation of 2,4,6-tri-t-butylaniline.[6,7] However, the possibility that some of the vinyl cation 5 might have derived from further oxidation of $\overset{+}{1\cdot}$ or $\overset{+}{4\cdot}$, eq. 9, can not be completely ruled out since Weinberg and coworkers have reported stepwise two-electron oxidation of amines to give cations.[7-9]

$$\overset{+}{1\cdot}\ (\overset{+}{4\cdot}) \xrightarrow{-e,\ -H^+(-D^+)} 5 \qquad (9)$$

It is interesting to compare the fates of cation-radicals generated in gas phase by electron impact with that of cation-radicals generated in solution by electrooxidation. The former fragment to give one type of cations, eq. 1, whereas the later disproportionate to give two types of cations, eq. 4, because of relative high concentration of cation-radicals near the electrode. It is also interesting to compare our finding with that of Fritsch and coworkers on the electrooxidation of 1-dimethylaminostyrene.[3] The sterically unhindered 1-dimethylaminostyrenyl cation-radical undergoes coupling reaction while the sterically hindered cation-radicals $\overset{+}{1\cdot}$ and $\overset{+}{4\cdot}$ undergo disproportionation reaction.

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