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OXIDATIVE [3+2] CYCLOADDITION OF 1,3-DIKETONE AND OLEFIN USING ELECTROORGANIC CHEMISTRY

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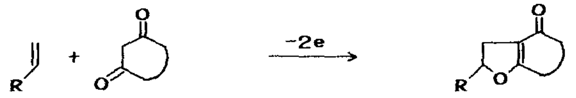
Summary: Electrochemical oxidation of 1,3-diketones in the presence of olefins afforded the formal [3+2] cycloaddition products, dihydrofuran derivatives or tetrahydrofuran derivatives. *A mechanism involving attack of a radical intermediate to an olefin has been proposed.*

It is well known that anodic oxidation of carbanions of 1,3-diketones and related compounds generates the corresponding radical species, which undergoes subsequent reactions such as dimerization or addition to an olefin to give various types of products.[1] However, electrochemical oxidation of neutral form of 1,3-diketones has been little known.[2] In this letter we wish to report that electrochemical oxidation of 1,3-diketones takes place under neutral conditions in the presence of olefins to yield the formal [3+2] cycloaddition products (eqs 1 and 2).[3,4]



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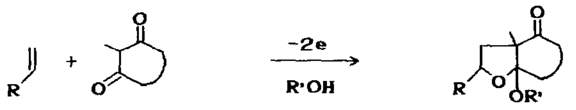
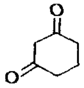
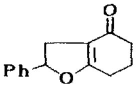
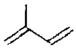
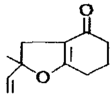
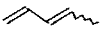
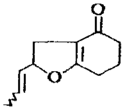
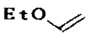
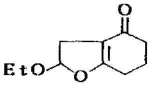
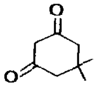
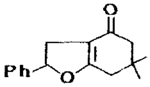
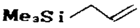
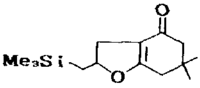
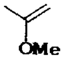
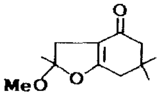


(2)

The reaction was simple to perform as shown in the following typical example. In an undivided cell equipped with a carbon rod anode (ϕ 6 × 20 mm) and a platinum foil cathode (30 × 20 mm) were placed 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol) and styrene (2.0 mmol) dissolved in 0.2 M solution of tetraethylammonium tosylate (Et_4NOTs) in acetonitrile (13 ml). Constant current (10 mA) was passed under an atmosphere of nitrogen at room temperature. After 3 F/mol of electricity were passed, aqueous work-up followed by flash chromatography gave 2-phenyl-4-oxo-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzofuran in 97% yield.

As shown in Table I various olefins reacted with 1,3-diketones in a similar fashion. Styrene derivatives, enol ethers, and 1,3-dienes were effective as olefin but alkyl substituted olefins such as 1-decene were inactive. Although cyclic 1,3-diketones such as 1,3-cyclohexanedione and 1,3-cyclopentanedione reacted smoothly to give the corresponding dihydrofuran derivatives, acyclic 1,3-diketones such as 1,3-pentanedione did not afford the dihydrofurans. The reason is not clear at present.

Table I. Oxidative [3+2] Cycloadditon of 1,3-Diketones and Olefins [a]

1,3-diketone	olefin	(equiv)	product	% yield [b]
	PhCH=CH_2	20		85
		20		62
		5		50
		10		57
	PhCH=CH_2	2		97
		5		45
		5		53
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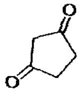
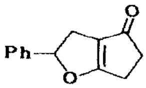
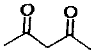
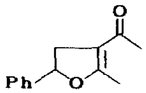
	PhCH=CH_2	20		54
	PhCH=CH_2	2		trace

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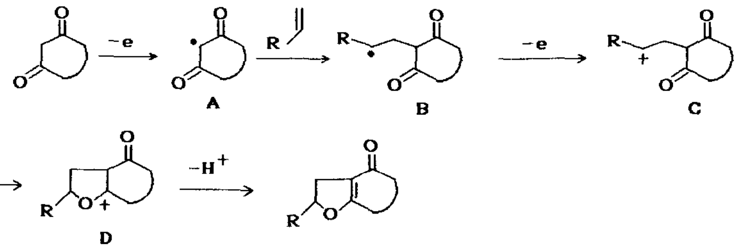
[a] The reactions were normally carried out with 1.0 mmol of 1,3-diketone, and 2-10 mmol of olefin in 0.2 M Et_4NOTs/CH_3CN. Passed electricity was 3.0 F/mol.

[b] Isolated yields.

Cyclic voltammetry of 1,3-cyclohexanedione showed an anodic peak at 1.47 V vs. Ag/AgCl *in acetonitrile.*[5] *Since oxidation potential of styrene under the same conditions* (1.80 V vs. Ag/AgCl) is more anodic than that of the 1,3-diketones, the present reaction is considered to proceed by the oxidation of the 1,3-diketone at the anode to produce the corresponding radical intermediate **A** (Scheme I). This ambient radical acts as a carbon centered radical[6] and adds olefin to produce radical **B**, which is oxidized at the anode to form the corresponding cation **C**.[7] The carbonyl oxygen then attacks this cation to give the intermediate **D**, which loses the ß-proton to yield the dihydrofuran derivative.

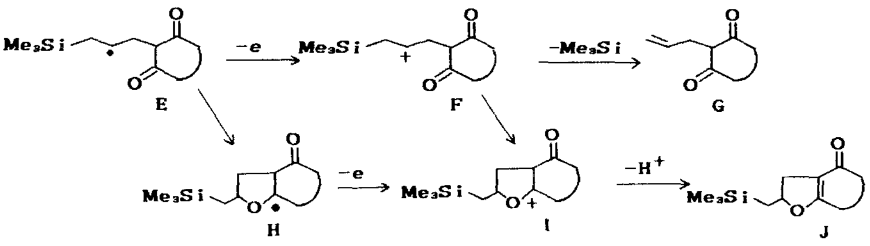
Scheme I.



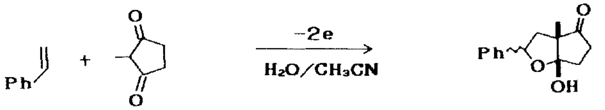
In light of this possible mechanism, high regioselectivity exerted by various olefins is readily rationalized. Radical attack on olefin is the regiochemistry controlling step (**A** → **B**), and regiochemistry of the products suggests that radical **A** attacks the less substituted end of the olefin. *This seems to be quite reasonable since it has been pointed out that* steric factor plays the dominant role in regioselectivity of free radical addition.[8] Frontier electron densities of olefins for radical reactions also rationalizes the present regiochemistry.[9] High regioselectivity observed for the reaction with 1,3-dienes can also be explained in a similar fashion.

The reaction with allyltrimethylsilane resulted in the formation of the silicon containing product. It is well known that ß-silyl carbocation undergoes a spontaneous elimination reaction to form the corresponding unsaturated compounds.[10] If the present reaction involves the carbocation intermediate, **F** (Scheme II), it might spontaneously loose silicon to form the carbon-carbon double bond, **G**. However, this is not the case. Presumably cyclization of the cation **F** is faster than the elimination of silicon. Another explanation to be considered is that cyclization with carbonyl oxygen may take place at the radical stage (**E**), and the resulting radical **H** is then electrochemically oxidized to the cation **I** which looses the proton to give the dihydrofuran **J**. But it seems premature to make a conclusion at present.

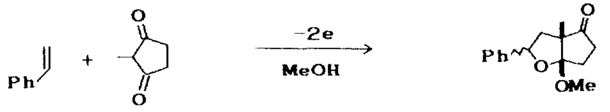
Scheme II



Electrochemical oxidation of 2-substituted 1,3-diketones such as 2-methyl-1,3-cyclopentanedione in the presence of olefin also proceeded smoothly to give the tetrahydrofuran derivatives[11] (eqs 3 and 4). The reaction seemed to proceed in a similar way as described in Scheme I and the cationic intermediate **K** was trapped by an oxygen nucleophile such as water or methanol (Scheme III).

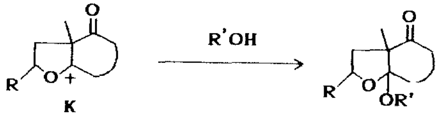


(3) 46%



(4) 70%

Scheme III



Further work is in progress to explore the full scope of this reaction and to gain more insight into mechanistic details.

References and Notes

(1) (a) Schaefer, H. J. Angew. Chem. Int. Ed. Engl. **1981**, 20, 911. and references cited therein. See also (b) VandenBorn, H. W.; Evans, D. H. J. Am. Chem. Soc. **1974**, 96, 4296. (c) Torii, S.; Uneyama, K.; Onishi, T.; Fujita, Y.; Ishiguro, M.; Nishida, T. Chem. Lett. **1980**, 1603.

(2) Electrochemical reduction of neutral form of 1,3-diketones is well known. See Evans, D. H. in "Encyclopedia of Electrochemistry of the Elements", Bard, A. J.; Lund, H. Ed., Marcell Dekker: New York, 1978, Vol 12, Chapt. 12-1.

(3) Manganese(III) promoted oxidative cycloaddition of 1,3-diketones with olefins, see Heiba, E. I.; Dessau, R. M. J. Org. Chem. **1974**, 39, 3456. See also Snider, B. B.; Mohan, R.; Kates, S. A. J. Org. Chem. **1985**, 50, 3659 and references cited therein.

(4) Electrochemical reductive [3+2] cycloaddition of 2,2-dibromo-1,3-diketones with olefins, see Yoshida, J.; Yamamoto, M.; Kawabata, N. Tetrahedron Lett. **1985**, 26, 6217.

(5) It is reported that oxidation potential ($E_{1/2}$) of sodium acetylacetonate in methanol is 0.8 V vs. Ag/AgCl. Schaefer, H.; Alazrak, A. Angew. Chem. **1968**, 80, 485.

(6) Chow, Y. L.; Buono-Core, G. E. J. Am. Chem. Soc. **1986**, 108, 1234.

(7) Benzyl radical is readily oxidized at the potential that 1,3-diketone is oxidized. See Wayner, D. D. M.; Griller, D. J. Am. Chem. Soc. **1985**, 107, 7764. $E_{1/2}$ = 0.40 vs. $Ag/AgNO_3$ in CH_3CN.

(8) Giese, B. Angew. Chem. Int. Ed. Engl. **1983**, 22, 753.

(9) Hayashi, K.; Yonezawa, T.; Nagata, C.; Okamura, S.; Fukui, K. J. Polym. Sci. **1956**, 20, 537.

(10) For example, Negishi, E. "Organometallics in Organic Synthesis", Wiley: New York, 1980, Vol. 1, Chapt. 6.

(11) Although regioselectivity was complete, the products were mixtures of two stereoisomers with respect to the carbon bearing the phenyl substituent.

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