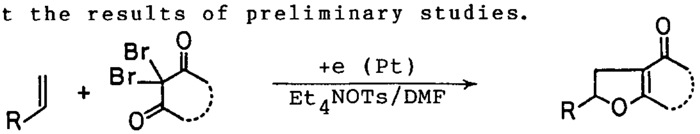
Tetrahedron Letters,Vol.26,No.50,pp 6217-6220,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

ELECTROCHEMICAL REDUCTION OF DIBROMODIKETONES FACILE [3+2] CYCLOADDITION WITH OLEFINS

Jun-ichi Yoshida, Masaaki Yamamoto, Nariyoshi Kawabata*
Department of Chemistry, Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto 606, Japan

ABSTRACT: Electrochemical reduction of 2,2-dibromo-1,3-diketones in the presence of olefins afforded the [3+2] cycloadducts, 2,3-dihydrofuran derivatives, regioselectively.

The importance of [3+2] cycloaddition reactions has emerged as tools for construction of heterocyclic compounds as well as for functionalization of C-C unsaturated bonds.[1] Recently we have reported that reduction of 2,2-dihalo-1,3-diketones with copper powder in the presence of an olefin afforded [3+2] cycloadducts, dihydrofuran derivatives.[2] In exploring other effective reducing agents we envisioned an electrochemical method, i.e. cathodic reduction of dibromodiketones in the presence of an olefin. The reaction does indeed occur as expected (eq. 1), and this reaction seems to provide a new simple and versatile method for the synthesis of dihydrofuran derivatives.[3] Herein we wish to report the results of preliminary studies.



(1)

The reaction is simple to perform. A 2,2-dibromo-1,3-diketone (1.0 mmol) was electrochemically reduced in an H-type divided cell equipped with platinum electrodes in the presence of an olefin (5.0 mmol). After 2.15 F/mol of electricity was passed, aqueous work-up followed by flash chromatography gave the corresponding dihydrofuran derivatives in good yields.

N,N-Dimethylformamide (DMF) and acetonitrile seemed to be the solvent of choice as shown in Table 1. In dimethyl sulfoxide (DMSO) the yields of cycloadducts were low. As a supporting electrolyte tetraethylammonium p-toluenesulfonate (Et_4N OTs) gave the most satisfactory yields among the examined. Use of tetraethylammonium bromide (Et_4N Br) or tetrabutylammonium perchlorate (Bu_4N ClO_4) resulted in lower yields of the dihydrofuran derivative. Current

Table 1. Electrochemical Reduction of Dibromodimedone in the Presence of Styrene [a]

solvent [b]	supporting electrolyte [c]	current density mA/cm^2	% yield of dihydrofuran [d]
DMF	Et_4N OTs	20	46
		10	47
		3.0	67
		0.75	84
		0.50	89
CH_3CN	Et_4N OTs	0.50	97
	Et_4N Br	0.50	55
	Bu_4N ClO_4	0.50	43
DMSO	Et_4N OTs	0.50	34

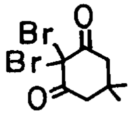
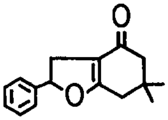
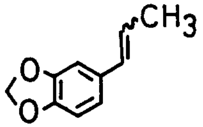
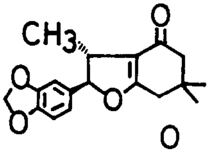
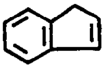
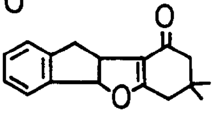
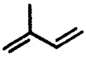
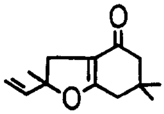
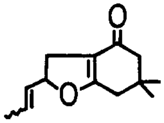
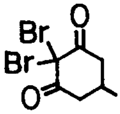
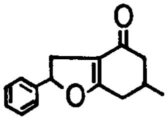
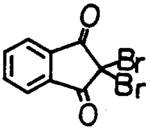
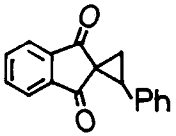
[a] Reactions were normally carried out with 1.0 mmol of dibromodimedone and 5.0 mmol of styrene at room temperature. [b] 2.5 ml. [c] 0.20 mol/l. [d] Yields were determined by GLC.

density has a marked effect on this reaction. The yields increased by reducing the current density, and 0.50 mA/cm^2 seemed to be of choice from a practical point of view.

Table 2 summarizes the results obtained with several olefins and dibromodiketones. Although the scope of this reaction has not been fully explored, reactivity of cyclic dibromodiketones seems to be much higher than that of acyclic dibromodiketones. Dibromoacetylactone and dibromobenzoylacetophenone did not afford cycloadducts under the conditions. Presumably rigid conformation of cyclic dibromodiketones play a major role. Interestingly, electrochemical reduction of dibromoindandione in the presence of an olefin lead to the formation of a cyclopropane derivative, rather than a dihydrofuran; the reason is not clear at present. Conjugated olefins such as styrene derivatives and 1,3-dienes were quite effective as acceptor, but nonconjugated olefins such as 1-decene failed to react. High regioselectivity of the present reaction should be noted. From styrene derivatives only 2-aryl-substituted dihydrofurans were obtained. 3-Aryl isomers were not detected under the conditions. Reactions with 1,3-dienes also afforded a single regioisomer of the dihydrofuran derivatives.

Baizer et al. reported that gem-polyhalides such as carbon tetrachloride and ethyl trichloroacetate are cathodically reduced to generate carbanion intermediates which attack electron-deficient olefins to produce ultimately cyclopropane derivatives.[4] However, low reactivity of electron-deficient

Table 2. Reduction of Dibromodiketones in the Presence of Olefin [a]

dibromodiketone	olefin	product	% yield [b]
	PhCH=CH$_2$		89
	 [c]	 [d]	53
			58
			70
			94
	C$_8$H$_{17}$CH=CH$_2$	-	0
	PhCH=CH$_2$		37[e]
	PhCH=CH$_2$ [f]		87[e]

[a] Reactions were normally carried out with 1.0 mmol of a dibromodiketone and 5.0 mmol of an olefin in Et$_4$N OTs/DMF at current density of 0.5 mA/cm^2.
[b] Determined by GLC. [c] E/Z = 3.3/1. [d] Only E isomer was obtained. [e] Isolated yield. [f] Carried out in CH$_3$CN.

olefins such as methyl vinyl ketone in the present reaction disfavors this type of mechanism. It has also been reported that electrochemical reduction of carbon tetrachloride leads to the formation of dichlorocarbene which can be trapped by an olefin.[5] Therefore carbene intermediate seems to be a possible candidate of the reactive intermediate.[6] However, loss of stereospecificity observed in the reaction of isosafrole (Table 2) excludes a concerted addition of ketocarbene as a 1,3-dipole,[7] and suggests a stepwise mechanism involving a freely rotating intermediate. Regioselectivity exhibited by styrenes and 1,3-dienes[8] can also be rationalized by considering radical attack to these acceptors.[9] Thus an electro-generated radical seems to be the most likely candidate of the intermediate. Further studies to elucidate a scope of the reaction and a detailed mechanism are currently in progress.

REFERENCES AND NOTES

(1) For example, Desimoni, G,; Tacconi, G.; Barco, A.; Pollini, G. P. "Natural Products Synthesis Through Pericyclic Reaction", American Chemical Society: Washington D. C., 1983.

(2) Yoshida, J.; Yano, S.; Ozawa, T.; Kawabata, N. Tetrahedron Lett. **1984**, 25, 2817.

(3) Synthesis of dihydrofurans: For example, (a) Albin, P.; Blum, J.; Dunkelblum, E.; Sasson, Y. J. Org. Chem. **1975**, 40, 2402. (b) Heiba, E. I.; Dessau, R. M. J. Org. Chem. **1974**, 39, 3456. (c) Uemura, S.; Ichikawa, K. Bull. Chem. Soc. Jpn. **1967**, 40, 1016. (d) Ichikawa, K.; Uemura, S. J. Org. Chem. **1967**, 32, 493. (e) Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. J. Org. Chem. **1980**, 45, 2945. (f) Matsumoto, M.; Watanabe, N. Heterocycles, **1984**, 22, 2313. (g) Torii, S.; Uneyama, K.; Onishi, T.; Fujita, Y.; Ishiguro, M.; Nishida, T. Chem. Lett. **1980**, 1603.

(4) Baizer, M. M.; Chruma, J. L. J. Org. Chem. **1972**, 37, 1951.

(5) Wawzonek, S.; Duty, R. C. J. Electrochem. Soc. **1961**, 108, 1135.

(6) Ketocarbenoid was generated by reductive elimination of dibromodiketones with zinc, see (a) Scott, L. T.; Cotton, W. D. J. Am. Chem. Soc. **1973**, 95, 2708. (b) Scott, L. T.; Cotton, W. D. ibid. **1973**, 95, 5416.

(7) It is known that ketocarbenes generated from diazoketones serve as 1,3-dipoles, see (a) Alonso, M. E.; Morales, A.; Chitty, A. W. J. Org. Chem. **1982**, 47, 3747 and references cited therein. See also (b) Firestone, R. A. Tetrahedron, **1977**, 33, 3009. (c) Huisgen R. J. Org. Chem. **1976**, 41, 403.

(8) Similar regioselectivities were observed in the reaction of dibromodiketones with copper metal in the presence of olefins or dienes. See reference (2).

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

(Received in Japan 28 September 1985)