resulting yellow solution and the residue purified by medium-pressure chromatography to give the quinonemethide **2** as a yellow solid (0.13 g, 81%, mp 72–73 °C).[16] Suitable conditions for medium-pressure chromatographic purification involved the use of Fluka silica gel 60, eluted with petroleum ether (bp 40–60 °C)/dichloromethane (4:1 v/v).

Controlled Potential Electrolyses. Conventional glass cells were used with the anode and cathode compartments separated either by medium-porosity sintered glass or, better, by Celgard 2500 microporous polypropylene film. Solutions were degassed and an inert atmosphere was maintained in the cells by bubbling of dry nitrogen. Where DMF/TBAP was used, the electrolyte was preelectrolyzed at −1.7 V until the background current reached a low steady value (ca. 1 mA).

The following description is typical of the electrolysis procedures and methods for workup and isolation of products.

2,6-Di-*tert*-butyl-4-(diphenylmethylene)-2,5-cyclohexadien-1-one (3) (0.111 g, 0.3 mmol), dissolved in 55 mL of DMF/TBAP (0.1 M), was electrolyzed at an Hg pool cathode (7.0 cm^2) held at −1.70 V (Ag/AgI). A deep green color developed in the catholyte which decreased in intensity as reaction proceeded. Reaction was judged completed when the cell current had fallen to the background level (0.6 mA) after the passage of 1.02 F mol^{-1}. The light yellow catholyte was isolated, water added (25 mL), and the solution extracted with successive portions of ether. The combined extracts were washed (water) and dried ($MgSO_4$). Removal of solvent gave a yellow residue; medium-pressure chromatography (Fluka silica gel 60, petroleum ether (bp 60–80 °C)/dichloromethane (1:1) yielded **13** (0.077 g, 69%), recovered **3** (0.012 g, 0.033 mmol), and **11** (0.015 g, 13%).

The procedure was only slightly modified for electrolyses involving added methyl iodide. The methyl iodide could be added prior to electrolysis or following exhaustive electrolysis. As before, aqueous workup was followed by ether extraction and medium-pressure chromatography. In some cases it was advantageous to wash the ether extracts with saturated aqueous sodium chloride. Several difficult separations required repeated preparative-scale TLC. Plates used were coated (1 mm) with Merck silica gel 60 HF_{254}; for separation of **13** plus **14** from **3**, **11**, and **12**, CH_2Cl_2/Et_2O (1:1 v/v) was used with subsequently petroleum ether (bp 40–60 °C)/EtOAc (5%) to effect separations of **13** from **14**. The separation of **19** from **21** was also difficult; petroleum ether (bp 40–60 °C)/CH_2Cl_2 (95:5 v/v) proved to be a good solvent, yet three successive elutions were necessary.

A complete collection of ^1H NMR spectroscopic data of new compounds involved in this work is available (supplementary material). Table IV correspondingly lists physical, IR spectroscopic, mass spectrometric, and, where the amount of material was sufficient, microanalytical data. Where small amounts were obtained, the purity of samples was confirmed by TLC analysis in at least two solvent systems; in these cases, high-resolution mass spectrometry was used to confirm molecular formulas. For compounds **7** and **8**, the diastereoisomeric ratios were determined from the ^1H NMR spectra of the crude products; the benzylic protons are clearly resolved at high field. Benzylic proton signals for the meso isomers are upfield of those for the (±) isomers.[17]

Acknowledgment. We are grateful to the University of London Central Research Fund for an equipment grant and to the CNPq (Brazil) and the Federal University of Alagoas (Maceio, Brazil) for, respectively, a Fellowship and leave of absence to M.O.F.G.

Registry No. **1**, 2607-52-5; **2**, 7078-98-0; **3**, 13131-76-5; **4**, 809-73-4; **5**, 57196-35-7; **6**, 57196-25-5; **8**, 113894-03-4; **10**, 113894-04-5; **11**, 13145-53-4; **12**, 113894-05-6; **13**, 13145-54-5; **14**, 113894-06-7; **15**, 113924-39-3; **16**, 57196-50-6; **17**, 57196-34-6; **18**, 113894-07-8; **19**, 113894-08-9; **20**, 113894-09-0; **21**, 113894-10-3; **22**, 113894-11-4; **23**, 80826-88-6; **24**, 113894-12-5; **25**, 2950-01-8; **26**, 113894-13-6; **27**, 1516-94-5; DMF, 68-12-2; TBAP, 1923-70-2; CH_2Cl_2, 75-09-2; $LiClO_4$, 7791-03-9; CH_3I, 74-88-4; benzophenone, 119-61-9.

Supplementary Material Available: Cyclic voltammograms for fuchsone **3** in neutral and basic conditions; full ^1H NMR data for compounds **8**, **10**, **12**, **14**, **15**, **18–24** (3 pages). Ordering information is given on any current masthead page.

(16) Koutek, B.; Pavlickova, L.; Soucek, M. *Synth. Commun.* **1976**, *6*, 305.

(17) Schmid, G. H. *Can. J. Chem.* **1968**, *46*, 3415.

Oxidative [3 + 2] Cycloaddition of 1,3-Diketone and Olefin Using Electroorganic Chemistry

Jun-ichi Yoshida,* Kazuhiko Sakaguchi, and Sachihiko Isoe*

Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

Received August 14, 1987

The electrochemical oxidation of 1,3-diketones and 2-substituted 1,3-diketones in the presence of olefin gave the [3 + 2] cycloadducts, dihydrofuran and tetrahydrofuran derivatives, respectively. A mechanism involving electrooxidative formation of the radical intermediate from the diketone followed by addition to the olefin has been proposed.

Introduction

With increasing interest in synthetic application of radical reactions, a number of free radical mediated carbon–carbon bond-forming reactions have been reported recently.[1] The majority of such free radical reactions have been performed under reductive conditions. Oxidative radical reactions, however, seem to be advantageous from a synthetic point of view, because the radical is usually terminated by oxidation to the cation followed by the reaction with a nucleophile rather than by simple hydrogen abstraction. Although there have been reported several oxidative radical reactions mediated by metal salts such as Mn(III),[2,3] we have been interested in the generation

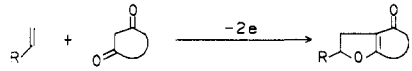
(1) (1) For example: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pegamon: Oxford, 1986. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (c) Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883.

(2) For example: (a) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456. (b) Ito, N.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3527. (c) Corey, E. J.; Kang, M.-C. *J. Am. Chem. Soc.* **1984**, *106*, 5384. (d) Snider, B. B.; Mohan, R.; Kates, S. A. *J. Org. Chem.* **1985**, *50*, 3661. (e) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10. (f) Corey, E. J.; Ghosh, A. K. *Chem. Lett.* **1987**, 223 and references cited therein.

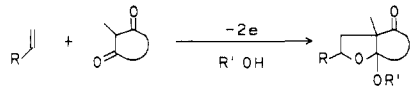
(3) Oxidative radical C–C bond formation promoted by other metal salts such as cobalt has been reported. For example: (a) Bhandal, H.; Pattenden, G.; Russell, J. J. *Tetrahedron Lett.* **1986**, *27*, 2299. (b) Patel, V. F.; Pattenden, G.; Russell, J. J. *Tetrahedron Lett.* **1986**, *27*, 2303.

0022-3263/88/1953-2525$01.50/0

of a radical species by electrochemical methods. Pioneering works of Schaefer and others[4] revealed that anodic oxidation of anions of 1,3-diketones and related comounds generates the corresponding radical species and that thus produced radicals add to the olefin to form the second radical intermediate. Unfortunately there are several possible fates of such radical species, for example, dimerization and oxidation to the cation and so on. Therefore several products are usually formed under the electrochemical conditions. We have been interested in electrochemical oxidation of the neutral form of 1,3-diketones[5] because Mn(III)-promoted oxidations were carried out with the neutral form rather than the anionic form. The preliminary report from our laboratory pointed out that the neutral form of 1,3-diketones can be oxidized electrochemically in the presence of olefin to give the formal [3 + 2] cycloadducts as essentially the sole product (eq 1 and 2).[6,7] We report herein the full details of this study.



(1)

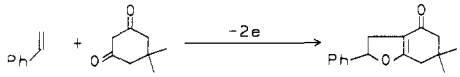


(2)

Results and Discussion

A. Voltammetric Study. The initial work on this project was directed to examination of anodic behavior of the neutral form of 1,3-diketones by using cyclic voltammetric techniques. 5,5-Dimethyl-1,3-cyclohexanedione (dimedone) showed the anodic peak at 1.47 V vs Ag/AgCl in acetonitrile. Although this oxidation potential was more anodic than those of the anion of 1,3-diketones reported so far,[8] the present data indicated that even the neutral form of 1,3-diketones can be oxidized at a reasonable anodic potential. Oxidation potential of styrene was also measured under similar conditions. Styrene exhibited an oxidation wave at more anodic potential than that of dimedone (1.80 V vs Ag/AgCl). These observations suggest that 1,3-diketones can be oxidized electrochemically without oxidizing the olefin.

B. Oxidative [3 + 2] Cycloaddition of 1,3-Diketone and Olefin. Reaction Conditions. The next stage of the project was finding the best set of conditions for preparative electrolysis of 1,3-diketones in the presence of olefins to obtain the cycloadduct. Thus 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and styrene were chosen as the representative 1,3-diketone and olefin, respectively (eq 3).



(3)

Since most of the anodic oxidations of the anion of 1,3-diketones reported so far were carried out only in alcoholic solvent, we first examined the effect of solvents on the yield of the cycloadduct. Table I summarizes the results. In methanol the cycloadduct was obtained only in 6% yield. Switching to acetonitrile, however, resulted in a dramatic increase in the yield. The reaction also proceeded in dimethylformamide but the yield was lower. Supporting electrolytes also have a marked effect on this reaction. Tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) was the best electrolyte among those examined. The use of other supporting electrolytes resulted in a significant decrease in the yield of the cycloadduct.

Table I. Electrochemical [3 + 2] Cycloaddition of 5,5-Dimethyl-1,3-cyclohexanedione and Styrene[a]

supporting electrolyte[b]	solvent	yield of 2,[c] %
Et_4NOTs	MeCN	97
Et_4NOTs	DMF	60
Et_4NOTs	MeOH	6
Bu_4NBF_4	MeCN	60
Bu_4NClO_4	MeCN	6
$LiClO_4$[d]	MeCN	46

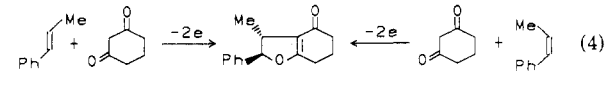
[a] Reactions were carried out with 1.0 mmol of 5,5-dimethyl-1,3-cyclohexanedione and 2.0 mmol of styrene in 13 mL of the solvent. Passed electricity was 3.0 F/mol based upon the 1,3-diketone. [b] 0.20 mol/L. [c] Isolated yields. [d] 0.10 mol/L.

Scope and Limitations. The scope of this new electrochemical [3 + 2] cycloaddition of 1,3-diketones and olefins was then examined with a variety of 1,3-diketones and olefins. As shown in Table II various olefins reacted with 1,3-diketones to give the corresponding cycloadducts. Styrene derivatives, enol ethers, enol esters, allyltrimethylsilane, and 1,3-dienes were effective as olefins, but the reactivity of alkyl-substituted olefins and electron-deficient olefins was low.

The reaction exhibits high regioselectivity as far as the orientation of the olefin is concerned. The oxygen atom of the 1,3-diketone added exclusively onto the more substituted end of the terminal olefin. In the case of 1,3-dienes, the reaction also proceeded regioselectivity to give a single 1,2-addition product. Other regioisomers and 1,4-adducts were not detected under the conditions.

Cyclic 1,3-diketones such as dimedone, 1,3-cyclohexanedione, and 1,3-cyclopentanedione reacted smoothly to give the corresponding dihydrofuran derivatives. Especially, efficient formation of the highly strained bicyclo[3.3.0]octyl system by the reaction of 1,3-cyclopentanedione and styrene seems to be remarkable.[9] However, acyclic 1,3-diketones such as 1,3-pentanedione did not afford the cycloadducts under similar conditions. In the case of unsymmetrical cyclic 1,3-diketones, no regioselectivity was observed with respect to the orientation of the diketone. For example, the reaction of 4-methyl-1,3-cyclohexanedione with styrene gave an essentially equimolar mixture of the two possible regioisomers which were constituted of two stereoisomers.

Reaction of (*E*)- and (*Z*)-β-methylstyrenes with 1,3-cyclohexanedione was carried out in order to examine the stereospecificity of the present reaction. From both olefins were obtained *trans*-3-methyl-4-oxo-2-phenyl-2,3,4,5,6,7-hexahydrobenzofuran (**13**) exclusively (eq 4). The stereochemistry of the product was clearly assigned as trans on



(4)

(4) (a) Schaefer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 911 and references 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.

(5) Electrochemical reduction of the 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. Eds.; Marcell Dekker: New York, 1978; Vol. 12, Chapter 12-1.

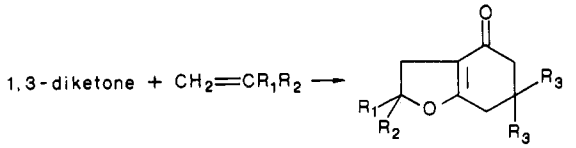
(6) Yoshida, J.; Sakaguchi, K.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 6075.

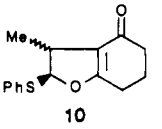
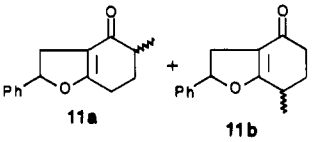
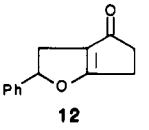
(7) Electrochemical reductive [3 + 2] cycloaddition of 2,2-dibromo 1,3-diketones with olefins has been reported: Yoshida, J.; Yamamoto, M.; Kawabata, N. *Tetrahedron Lett.* **1985**, *26*, 6217.

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

(9) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

Table II. Electrochemical [3 + 2] Cycloaddition of 1,3-Diketones and Olefin[a]



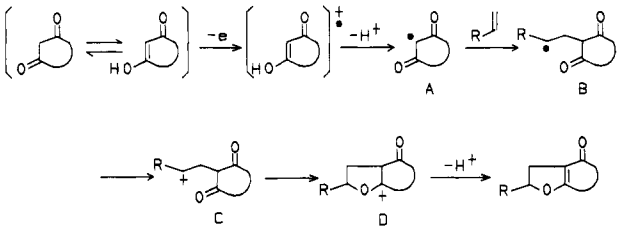
1,3-diketone	olefin R_1	olefin R_2	mmol	product	% yield[b]
5,5-dimethyl-1,3-cyclohexanedione	H	Ph	2.0	1[h]	97
	H	CH_2SiMe_3	5.0	2[h]	45
	H	C_8H_{17}	2.0		0[c]
	Me	OMe	5.0	3[h]	53[d]
	Me	OAc	5.0	4[h]	44[d]
	H	CN	2.0		0[c]
	H	CO_2Et	10	5[h]	17
	H	$COCH_3$	10		0[c]
	e	*e*	2.0		0[c]
1,3-cyclohexanedione	H	Ph	20	6[i]	85
	H	$C(CH_3)=CH_2$	20	7[i]	62
	H	$CH=CHCH_3$	5.0	8[i]	50
	H	OEt	10.5	9[i]	57
	Me	SPh	1.5	 10	48[f]
4-methyl-1,3-cyclohexanedione	H	Ph	1.5	 11a + 11b	56[g]
1,3-cyclopentanedione	H	Ph	20	 12	54
2,4-pentanedione	H	Ph	24		0[c]

[a] Reactions were normally carried out with 1,3-diketone (1.0 mmol) and olefin (1.5–20 mmol) in 13 mL of Et_4NOTs/MeCN (0.20 mol/L). Passed electricity was 3.0 F/mol based upon the 1,3-diketone. [b] Isolated yields. [c] Many unidentified products were observed by VPC or TLC. [d] The reaction was carried out in the presence of a small amount of K_2CO_3 (18–20 mg). [e] Reactant is phenylacetylene. [f] trans/cis = 78/22. [g] Four isomers were obtained in a ratio of 29:24:24:23. [h] $R_3 = CH_3$. [i] $R_3 = H$.

the basis of ^1H NMR data.[10] Since isomerization of the β-methylstyrene and the cycloadduct seems to be less likely under the electrochemical conditions, this observation indicates that the present reaction proceeded in a nonstereospecific way. Therefore a stepwise mechanism involving a freely rotating intermediate is more likely than a concerted cycloaddition mechanism.

Reaction Mechanism. Since the oxidation potentials of 1,3-diketones are less anodic than that of the olefin, the present reaction is considered to proceed by the initial oxidation of 1,3-diketone or its enol form at the anode. Thus the cation radical produced may lose a proton spontaneously to produce the corresponding radical intermediate A (Scheme I). The ambident radical A acts as a carbon-centered radical and adds to the olefin to produce radical B,[11] which is oxidized at the anode to form the corresponding cation C. The carbonyl oxygen then attacks this cation to give the intermediate D, which loses the β-proton to yield the dihydrofuran derivative. Stereochemical results are consistent with this mechanism, since the stereochemistry of the olefin is lost at the stage of radical intermediate B.

Scheme I

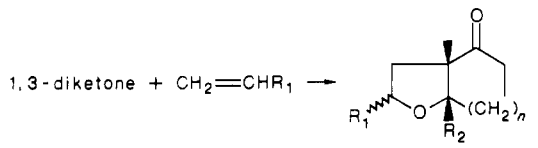


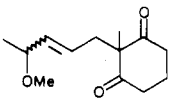
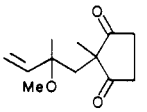
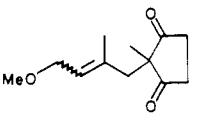
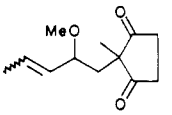
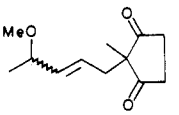
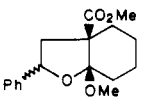
The radical mechanism also receives support from the fact that the reactivity of conjugated olefins such as styrene derivatives and 1,3-dienes is much higher than that of non-conjugated olefins such as 1-decene. The higher reactivity of electron-rich olefins than that of electron-deficient olefins can be explained as follows. The carbon-centered radical A is a very electron-deficient radical, since it is flanked by two carbonyl groups. Therefore the addition of A to an electron-rich olefin is favorable whereas its addition to an electron-deficient olefin is less favorable.

High regioselectivity exerted by various olefins is also readily rationalized in light of this possible mechanism. 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. Since it has been pointed out that steric factors play the dominant role in regioselectivity of free radical addition

(10) Yoshida, J.; Yano, S.; Ozawa, T.; Kawabata, N. *J. Org. Chem.* **1985**, *50*, 3467 and references cited therein.
(11) Chow, Y. L.; Buono-Core, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 1234.

Table III. Electrochemical [3 + 2] Cycloaddition of 2-Substituted 1,3-Diketone and Olefin[a]



1,3-diketone	R_1	mmol	condition[b]		product R_2	product n	% yield[c]
2-methyl-1,3-cyclohexanedione	Ph	2.0	A	**14**	OMe	2	30
		1.7	B	**15**	OH	2	30
	$CH=CHCH_3$	4.0	A	**16**	OMe	2	54
				 **17**			12
2-methyl-1,3-pentanedione	Ph	2.0	A	**18**	OMe	1	70
	Ph	2.0	B	**19**	OH	1	46
	$C(CH_3)=CH_2$	3.0	A	**20**	OMe	1	23
				 **21**			10
				 **22**			16
	$CH=CHCH_3$	3.7	A	**23**	OMe	1	30
				 **24**			13
				 **25**			36
2-carbomethoxycyclohexanone	Ph	1.7	A	 **26**			12[d]

[a] 1,3-Diketone (1.0 mmol) and olefin (1.7–4.0 mmol). Passed electricity was 2.0 F/mol. [b] A: Et_4NOTs/MeOH (0.2 mol/L, 12 mL). B: Et_4NOTs/MeCN (0.2 mol/L, 12 mL) containing 1.1–11 mmol of water. [c] Isolated yields. [d] The reaction was carried out with 54 mg of NaOMe.

reactions,[12] the regioselectivity observed here seems to be quite reasonable. Frontier electron densities of olefins for radical reactions also rationalizes the present regioselectivity.[13] High regioselectivity observed for the reaction with 1,3-dienes can also be explained in a similar fashion.

It is also interesting to note that the reaction with allyltrimethylsilane resulted in the formation of the silicon-containing product. β-Silyl carbocations are known to undergo a spontaneous elimination reaction to form the corresponding olefins.[14] If the present reaction involves the carbocation intermediate C (R=CH_2SiMe_3) (Scheme I), it might lose silicon to form the corresponding olefin. However, such product was not detected under the present conditions. Presumably cyclization of the cation C is much faster than the elimination of silicon. Another explanation to be considered is that cyclization with carbonyl oxygen may take place at the radical stage (B). The cyclized radical is then electrochemically oxidized to the cation D which loses the proton to give the dihydrofuran derivative. Although it is difficult to distinguish these two mechanism, very fast cyclization with carbonyl oxygen seems to control the fate of the active species and is responsible for high product selectivity of the present reaction.

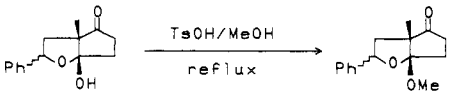
C. Electrochemical [3 + 2] Cycloaddition of 2-Substituted 1,3-Diketone and Olefin. Electrochemical oxidation of 2-substituted 1,3-diketones in the presence of olefin was also examined. For example, when 2-methyl-1,3-cyclopentanedione was electrolyzed in the presence of styrene in methanol, the [3 + 2] cycloadduct containing a methoxy group (**18**) was obtained in 70% yield

(12) Reference 1b.
(13) Hayashi, K.; Yonezawa, T.; Nagata, C.; Okamura, S.; Fukui, K. *J. Polym. Sci.* **1956**, *20*, 537.
(14) For example: Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1, Chapter 6.

(Table III). In the presence of water instead of methanol the corresponding [3 + 2] cycloadduct containing the hydroxyl group (**19**) was obtained. Other examples of the electrochemical oxidation of 2-substituted 1,3-diketones in the presence of olefins are also listed in Table III.

This reaction seemed to proceed by a similar mechanism as described for that with 2-unsubstituted 1,3-diketones (Scheme I). The cyclized cation D was trapped by a nucleophile such as methanol or water to give the tetrahydrofuran derivative.

The stereochemistry of the cycloadduct warrants comment. The tetrahydrofuran derivatives obtained here were mixtures of two isomers and based upon the following arguments they were identified as stereoisomers with respect to the carbon bearing the substituent of the original olefin such as a phenyl group. As far as the cycloadduct containing the free hydroxyl group is concerned, there seems to exist the equilibrium between the bicyclic hemiacetal form and the monocylic keto–alcohol form. Therefore the stereochemistry at the ring junction is controlled by thermodynamic stability of the product. Since the trans-fused bicyclo[3.3.0]octyl system is much more strained than the corresponding cis isomer,[15] the stereochemistry with respect to the ring junction should be cis. In the case of the bicyclo[4.3.0]nonyl system the situation is the same. Although the trans-fused bicyclo[4.3.0]nonyl system is known to be more stable than the cis isomer,[16] introduction of the substituents at the ring junctions reverses the situation.[17] Cis-fused compounds are more stable than the trans isomer. In the case of the cycloadducts containing the methoxy group such equilibrium is unlikely. However, their ^{1}H NMR were quite similar to those of the corresponding hydroxyl compounds. Thus in these cases also the ring junction seemed to be cis and the products were mixtures of the stereoisomers with respect to the carbon bearing the substituent of the original olefin. The stereochemistry of the methoxy compounds were also confirmed by the following acid-catalyzed methoxylation of the hydroxyl compound (eq 5). In the

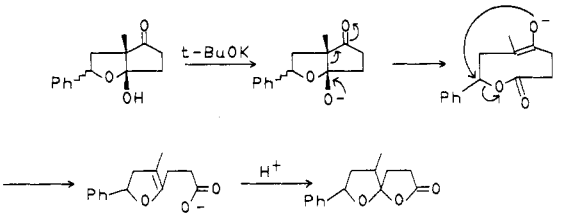


(5)

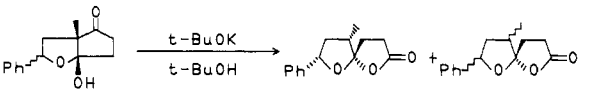
presence of a strong acid such as *p*-toluenesulfonic acid the equilibrium between the bicyclic form and the monocyclic form may exist even in the case of the methoxy compound. Therefore the product of the acid-catalyzed reaction should be the thermodynamically more stable cis compound, and this product exhibited the same ^{1}H NMR spectrum as that obtained by the electrolysis in methanol.

It should be noted that the reaction with 1,3-dienes gave noncyclized products together with the [3 + 2] cycloadducts. Presumably the oxygen nucleophile in the reaction medium trapped the cationic intermediate before cyclization with carbonyl oxygen. In this case the nucleophile attacked either end of the allylic cation intermediate.

Scheme II



Fragmentation Reaction. Since the tetrahydrofuran derivatives thus obtained from the reaction with water have the β-hydroxy ketone unit which is suitable for a retroaldol-type fragmentation reaction, we have examined the base-promoted fragmentation of such compounds. Thus tetrahydrofuran **19** was treated with potassium *tert*-butoxide in refluxing 2-methyl-2-propanol. Acidic workup followed by chromatography yielded two unusual products in 84% total yield. By ^{1}H and ^{13}C NMR analyses they were identified as stereoisomeric spiro compounds as shown in eq 6. Although the stereochemistry of one isomer was clarified by X-ray analysis, it was difficult to reveal the stereochemistry of the other isomer because of its oily nature.



(6)

A possible mechanism for the formation of these unusual products involves the following steps. The initial fragmentation of the β-hydroxy ketone produced the enolate intermediate. The oxygen atom of the enolate attacks the carbon-bearing phenyl group to produce the dihydrofuran derivative. Under the acidic workup the carboxyl group cyclized with this dihydrofuran moiety to yield the spiro compound (Scheme II).

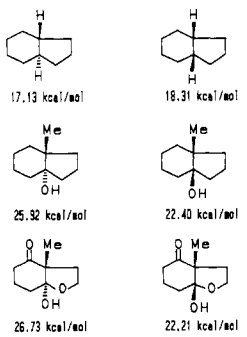
Although the mechanism has not been fully established as yet, this reaction seems to have potential utility for the synthesis of the dioxaspiro functionality which frequently occurs in many natural products.[19]

Concluding Remarks. The present study revealed that the neutral forms of cyclic 1,3-diketones are oxidized electrochemically in the presence of olefins to give the formal [3 + 2] cycloadducts, dihydrofuran or tetrahydrofuran derivatives which can be converted to various furan derivatives.[20] Since great attention has been paid for furan, dihydrofuran, and tetrahydrofuran derivatives because of their utility as synthetic intermediates and their occurrence in natural products, various methods have been developed for their synthesis. The present reaction pro-

(15) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, S. M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.

(16) *cis*-[4.3.0]Nonane is about 1 kcal/mol more strained than the trans isomer (ref 15).

(17) The following data were obtained by molecular mechanics.[18]



(18) Allinger's MM2 program (QCMP 004) modified by E. Osawa was used for the calculation. Although care was used in the search for initial conformations, we cannot be sure that other low energy conformers were not overlooked in some instances.

(19) For example: (a) Kurth, M. J.; Brown, E. G.; Hendra, E.; Hope, H. *J. Org. Chem.* **1985**, *50*, 1115. (b) Iwata, C.; Hattori, K.; Uchida, S.; Imanishi, T. *Tetrahedron Lett.* **1984**, *25*, 2995 and references cited therein.

(20) For example, ref 2f and 7 and references cited therein.

vides a useful alternative access to such compounds because of mild and neutral conditions and avoidance of toxic metal oxidizing agents such as Mn(III).

Experimental Section

General Comments. Glass-support precoated (Merk Silica gel 60 F_{254}, 0.25 mm) plates were employed for analytical TLC. Vapor-phase chromatography (VPC) was performed on a Shimadzu gas chromatography equipped with 1 m × 3 mm column packed with Silicone OV-1 (2%) on Chromosorb WAW DMCS. Proton NMR spectra were determined on a JEOL PMX-60 spectrometer (60 MHz), Hitachi R-90H spectrometer (90 MHz), or JEOL JNM-GX-400 spectrometer (400 MHz). Carbon NMR spectra were determined on a JEOL JNM-GX-400 spectrometer. The sign (+) indicates the positive signal and (−) indicates the negative signal obtained in the INEPT method. Infrared (IR) spectra were determined on a JASCO A-102 diffraction grating spectrophotometer. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer. Ionization potential was 70 eV. Cyclic voltammetry was performed on a Hokuto Potetiastat/Garvanostat HA-301 connected to a function generator HB-104 and Graphtec WX1000 X-Y plotter. Constant current electrolyses were performed by using Kikusui Model PAB-32-0.5 and PAB-32-1.2A regulated DC power supplies.

Tetraethylammonium *p*-toluenesulfonate (Et_4NOTS) was prepared according to the literature,[21] and its solution in acetonitrile was dried over 4A molecular sieves at least overnight before use. Styrene was washed with aqueous NaOH, dried over Na_2SO_4, and distilled under reduced pressure before use.

General Procedure for Electrochemical [3 + 2] Cycloaddition of 1,3-Diketone and Olefin. A solution of 1,3-diketone (1.0 mmol) and olefin (1.5–20 mmol) in 0.2 M Et_4NOTs/CH_3CN (13 mL) was placed in an undivided cell equipped with carbon rod anode (i.d. 6 mm × 30 mm) and platinum plate cathode (20 mm × 30 mm). Constant current (10 mA) was passed and the reaction was monitored by TLC or VPC. After 3.0 F/mol of electricity was passed, the reaction mixture was poured into brine (20 mL) and the organic materials were extracted with ether and dried over Na_2SO_4. After removal of the solvent under vacuum, the crude product was purified by flash chromatography on silica gel.

Dihydrofurans 1 and 6 were identified by comparison of their spectral data with those of authentic samples.[10]

6,6-Dimethyl-2-[(trimethylsilyl)methyl]-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran (2): TLC R_f 0.44 (hexane/ethyl acetate 3:1); VPC t_R 4.0 min (OV-1 2% 1 m, 170 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 0.04 (s, 9 H), 1.06 (s, 6 H), 1.17 (d, J = 5.49 Hz, 2 H), 2.18 (s, 2 H), 2.22 (d, J = 1.54 Hz, 2 H), 2.30–2.46 (m, 1 H), 2.76–3.08 (m, 1 H), 4.74–5.10 (m, 1 H); IR (neat) 3480 (w), 2960 (s), 2900 (m), 1715 (w), 1630 (s), 1470 (m), 1400 (s), 1370 (m), 1350 (m), 1250 (s), 1220 (s), 1180 (m), 1165 (m), 1140 (m), 1120 (m), 1100 (m), 1040 (m), 920 (m), 855 (s), 840 (s), 760 (m), 690 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 253 (M + 1, 4), 252 (M, 18), 239 (6), 238 (21), 237 (100), 219 (2), 209 (2), 181 (11), 168 (5), 152 (9), 145 (5), 73 (98); high resolution MS calcd for $C_{14}H_{24}O_2Si$ 252.1544, found 252.1526.

2-Methoxy-2,6,6-trimethyl-2,3,4,5,6,7-hexahydrobenzofuran (3): TLC R_f 0.55 (hexane/ethyl acetate 1:1); VPC t_R 2.1 min (OV-1 2% 1 m, 160 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.11 (s, 6 H), 1.61 (s, 3 H), 2.23 (s, 2 H), 2.25–2.35 (m, 2 H), 2.65–2.83 (m, 2 H), 3.28 (s, 3 H); IR (neat) 2930 (s), 1630 (s), 1450 (w), 1400 (s), 1380 (s), 1350 (m), 1280 (s), 1235 (s), 1160 (m), 1140 (m), 1120 (m), 1100 (m), 1050 (m), 1015 (m), 1005 (m), 910 (w), 835 (m), 735 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 211 (M + 1, 12), 210 (M, 81), 195 (22), 180 (22), 179 (79), 178 (59), 164 (23), 155 (22), 140 (26), 122 (100), 111 (17), 94 (62), 83 (41); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1255, found 210.1260.

2-Acetoxy-2,6,6-trimethyl-2,3,4,5,6,7-hexahydrobenzofuran (4): TLC R_f 0.60 (hexane/ethyl acetate 1:1); VPC t_R 5.2 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.11 (s), 1.14 (s) (total 6 H), 1.78 (s, 3 H), 2.05 (s, 3 H), 2.13–2.33 (m, 4 H), 2.35–3.25 (m, 2 H); IR (neat) 2920 (m), 1740 (s), 1710 (s), 1630 (s), 1400 (s), 1365 (s), 1280 (m), 1240 (m), 1200 (s), 1125 (m), 1080 (m), 1010 (m), 910 (w), 850 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 179 (5), 178 (38), 163 (4), 123 (10), 122 (100), 121 (3), 95 (5), 94 (57), 60 (11); high resolution MS calcd for $C_{11}H_{14}O_2$ (M − HOAc) 178.0995, found 178.1005.

2-Carbethoxy-6,6-dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran (5): TLC R_f 0.42 (hexane/ethyl acetate 1:1); VPC t_R 10 min (OV-1 2% 1 m, 100–230 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.07 (s, 6 H), 1.25 (t, J = 7 Hz, 3 H), 2.18 (s, 2 H), 2.2–2.4 (m, 2 H), 2.5–3.3 (m, 2 H), 4.21 (q, J = 7 Hz, 2 H), 5.12 (dd, J = 7 and 11 Hz, 1 H); IR (neat) 2950 (m), 2875 (vw), 1735 (s), 1640 (s), 1400 (m), 1200 (m), 1035 (m); low resolution MS, m/e (relative intensity) 239 (M + 1, 5), 238 (M, 28), 192 (27), 182 (36), 165 (100), 136 (40); high resolution MS calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1205.

2-Methyl-4-oxo-2-vinyl-2,3,4,5,6,7-hexahydrobenzofuran (7): TLC R_f 0.29 (hexane/ethyl acetate 1:1); VPC t_R 3.1 min (OV-1 2% 1 m, 100–200 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.51 (s, 3 H), 2.04–2.76 (m, 8 H), 5.04–5.33 (m, 2 H), 5.99 (dd, J = 16.83 and 10.55 Hz, 1 H); IR (neat) 2940 (w), 1630 (s), 1400 (m), 1370 (w), 1250 (m), 1180 (m), 1130 (w), 1055 (w), 1000 (m), 925 (w), 900 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 179 (M + 1, 13), 178 (M, 83), 163 (53), 150 (54), 135 (41), 122 (100), 107 (75), 79 (40); high resolution MS calcd for $C_{11}H_{14}O_2$ 178.0992, found 178.0985.

4-Oxo-2-(1-propenyl)-2,3,4,5,6,7-hexahydrobenzofuran (8): TLC R_f 0.38 (hexane/ethyl acetate 1:1); VPC t_R 6.7 min (OV-1 2% 1 m, 140 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.75 (d, J = 5.49 Hz, 3 H), 1.93–3.07 (m, 8 H), 5.02–5.20 (m, 1 H), 5.44–5.96 (m, 2 H); IR ($CHCl_3$) 2950 (w), 1620 (s), 1400 (m), 1375 (m), 1205 (w), 1140 (w), 1100 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 179 (M + 1, 16), 178 (M, 100), 149 (36), 148 (64), 136 (28), 135 (40), 122 (50), 106 (59); high resolution MS calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0969.

2-Ethoxy-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran (9): TLC R_f 0.32 (hexane/ethyl acetate 1:1); VPC t_R 6.8 min (OV-1 2% 1 m, 100–200 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.25 (t, J = 7.03 Hz, 3 H), 1.79–3.09 (m, 8 H), 3.77 (q, J = 7.03 Hz, 2 H), 5.73 (dd, J = 7.03 and 3.73 Hz, 1 H); IR ($CHCl_3$) 2920 (w), 1620 (s), 1400 (m), 1370 (m), 1340 (m), 1200 (m), 1170 (m), 1105 (m), 1055 (w), 710 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 183 (M + 1, 13), 182 (M, 100), 153 (27), 137 (56), 135 (28), 126 (48), 125 (44), 108 (24), 98 (88); high resolution MS calcd for $C_{10}H_{14}O_3$ 182.0942, found 182.0926.

***trans*-3-Methyl-4-oxo-2-(phenylthio)-2,3,4,5,6,7-hexahydrobenzofuran (10a)**: TLC R_f 0.62 (hexane/ethyl acetate 1:1); VPC t_R 3.6 min (OV-1 2% 1 m, 210 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.31 (d, J = 6.81 Hz, 3 H), 1.91–2.51 (m, 6 H), 3.14–3.28 (m, 1 H), 5.53 (d, J = 5.50 Hz, 1 H), 7.21–7.58 (m, 5 H); IR (CCl_4) 2950 (w), 1640 (s), 1440 (w), 1390 (m), 1220 (m), 1180 (m), 1120 (w), 1055 (w), 1000 (w), 980 (w), 900 (m), 875 (w), 840 (w), 730 (m), 690 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 262 (M + 2, 0.3), 261 (M + 1, 1), 260 (M, 3), 232 (2), 217 (3), 203 (5), 151 (100), 150 (38), 122 (42), 111 (42), 94 (38); high resolution MS calcd for $C_{15}H_{16}O_2S$ 260.0869, found 260.0847.

***cis*-3-Methyl-4-oxo-2-(phenylthio)-2,3,4,5,6,7-hexahydrobenzofuran (10b)**: TLC R_f 0.53 (hexane/ethyl acetate 1:1); VPC t_R 2.2 min (OV-1 2% 1 m, 210 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.37 (d, J = 7.03 Hz, 3 H), 1.77–2.55 (m, 6 H), 3.48–3.67 (m, 1 H), 6.08 (d, J = 8.79 Hz, 1 H), 7.21–7.60 (m, 5 H); IR ($CDCl_3$) 2940 (w), 1630 (s), 1395 (m), 1210 (w), 1175 (w); low resolution MS, m/e (relative intenisty) 261 (M + 1, 2), 260 (M, 8), 217 (3), 151 (100); high resolution MS calcd for $C_{15}H_{16}O_2S$ 260.0870, found 260.0862.

5-Methyl-4-oxo-1-phenyl-2,3,4,5,6,7-hexahydrobenzofuran (11a) and 7-Methyl-4-oxo-1-phenyl-2,3,4,5,6,7-hexahydrobenzofuran (11b). Four isomers were obtained in a ratio of 29:24:24:23, but it was difficult to assign their regio- and stereochemistry completely.

Isomer 1: TLC R_f 0.66 (hexane/ethyl acetate 1:1); VPC t_R 7.2 min (OV-1 2% 1 m, 180 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.19 (d, J = 6.81 Hz, 3 H), 1.69–3.40 (m, 7 H), 5.75 (dd, J = 10.44 and 8.02 Hz, 1 H), 7.14–7.61 (m, 5 H); IR (neat) 3000 (w), 2940 (w), 1625 (s), 1450 (w), 1250 (m), 1180 (m), 1190 (m), 1175 (m), 920 (w), 700 (m); low resolution MS, m/e (relative intensity) 229 (M + 1, 19), 228 (M, 100), 227 (12), 211 (5), 199 (8), 185 (42), 171 (32), 158 (14), 144 (27), 129 (9), 115 (21), 104 (12); high resolution MS

(21) Baizer, M. M. *J. Electrochem. Soc.* **1964**, *111*, 215.

calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1151.

Isomer 2: TLC R_f 0.61 (hexane/ethyl acetate 1:1); VPC t_R 7.2 min (OV-1 2% 1 m, 180 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.18 (d, J = 6.81 Hz, 3 H), 1.72–3.40 (m, 7 H), 5.73 (dd, J = 10.11 and 8.35 Hz, 1 H), 7.16–7.37 (m, 5 H); IR (neat) 3000 (w), 2930 (w), 1625 (s), 1450 (w), 1405 (m), 1370 (m), 1200 (m), 1175 (m), 920 (w), 890 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 229 (M + 1, 18), 228 (M, 100), 211 (7), 199 (7), 186 (19), 185 (41), 171 (31), 156 (12), 142 (26), 129 (6), 114 (22); high resolution MS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1152.

Isomer 3: TLC R_f 0.45 (hexane/ethyl acetate 1:1); VPC t_R 7.2 min (OV-1 2% 1 m, 180 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.26 (d, J = 6.81 Hz, 3 H), 1.64–3.40 (m, 7 H), 5.73 (dd, J = 10.44 and 8.24 Hz, 1 H), 7.12–7.36 (m, 5 H); IR (neat) 3000 (w), 2950 (w), 1620 (s), 1450 (w), 1400 (m), 1350 (w), 1200 (m), 1170 (m), 1100 (w), 1010 (w), 895 (w); low resolution MS, m/e (relative intensity) 229 (M + 1, 17), 228 (M, 100), 211 (4), 199 (7), 186 (17), 185 (36), 171 (26), 156 (10), 142 (21), 129 (7), 114 (15); high resolution MS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1159.

Isomer 4: TLC R_f 0.41 (hexane/ethyl acetate 1:1); VPC t_R 7.2 min (OV-1 2% 1 m, 180 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.28 (d, J = 7.03 Hz, 3 H), 1.71–3.40 (m, 7 H), 5.74 (dd, J = 10.55 and 7.91 Hz, 1 H), 7.17–7.42 (m, 5 H); IR (neat) 3000 (w), 2930 (w), 1620 (s), 1450 (w), 1400 (m), 1350 (w), 1200 (m), 1170 (m), 1100 (w), 1010 (w), 920 (w), 895 (w), 700 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 229 (M + 1, 19), 228 (M, 100), 211 (5), 199 (8), 186 (21), 185 (45), 171 (34), 156 (15), 142 (33), 129 (11), 116 (18), 114 (27), 105 (15); high resolution MS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1151.

4-Oxo-2-phenyl-1,2,3,4,5,6-hexahydro-1-oxapentalene (12): TLC R_f 0.26 (hexane/ethyl acetate 1:1); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.69–2.01 (m, 1 H), 2.46–3.34 (m, 5 H), 6.25 (dd, J = 9.89 and 8.13 Hz, 1 H), 7.13–7.49 (m, 5 H); IR (neat) 2990 (w), 2920 (w), 1720 (w), 1675 (m), 1625 (s), 1490 (w), 1440 (w), 1350 (w), 1220 (m), 1070 (w), 915 (w), 880 (w); low resolution MS, m/e (relative intensity) 201 (M + 1, 15), 200 (M, 100), 183 (35), 171 (9), 157 (12), 144 (14), 141 (16), 129 (14), 116 (26), 115 (42), 104 (14), 91 (13); high resolution MS calcd for $C_{13}H_{12}O_2$ 200.0836, found 200.0831.

***trans*-3-Methyl-4-oxo-2-phenyl-2,3,4,5,6,7-hexahydrobenzofuran (13).** The stereochemistry of this compound was clearly assigned as trans on the basis of ^{1}H NMR data by comparison with those of a similar compound.[10] **13**: TLC R_f 0.55 (hexane/ethyl acetate 1:1); VPC t_R 3.9 min (OV-1 2% 1 m, 190 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.38 (d, J = 6.81 Hz, 3 H), 1.65–2.52 (m, 8 H), 3.07–3.30 (m, 1 H), 5.15 (d, J = 7.04 Hz, 1 H), 7.10–7.55 (m, 5 H); IR (neat) 2950 (m), 1630 (s), 1495 (w), 1450 (m), 1395 (s), 1365 (m), 1225 (m), 1175 (s), 1060 (w), 940 (m), 925 (m), 900 (w), 760 (m), 700 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 229 (M + 1, 17), 228 (M, 93), 214 (16), 213 (100), 199 (16), 185 (14), 172 (16), 157 (25), 137 (94); high resolution MS calcd for $C_{15}H_{16}O_2$ 228.1151, found 228.1142.

6-Methoxy-1-methyl-2-oxo-8-phenyl-7-oxabicyclo[4.3.0]nonane (14): TLC R_f 0.80 (hexane/ethyl acetate 1:1); VPC t_R 10.8 min (OV-1 2% 1 m, 100–220 C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.256 (s), 1.264 (s) (total 3 H), 1.58–3.08 (m, 8 H), 3.30 (s), 3.34 (s) (total 3 H), 4.82 (dd, J = 10.4 and 6.5 H), 4.91 (dd, J = 9.8 and 4.9 Hz), (total 1 H), 7.19–7.34 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 211.24, 210.69, 142.06, 141.77, 128.08, 127.26, 127.14, 126.62, 125.92, 108.95, 108.55, 79.93, 76.90, 61.62, 60.92, 48.87, 48.31, 40.21, 40.11, 38.04, 37.99, 27.49, 27.22, 20.32, 19.69, 19.64, 18.78; INEPTR (400 MHz, $CDCl_3$) δ 128.08 (+), 127.26 (+), 127.13 (+), 126.62 (+), 125.90 (+), 79.92 (+), 76.88 (+), 48.85 (+), 48.30 (+), 40.20 (–), 40.10 (–), 38.02 (–), 37.98 (–), 27.47 (–), 27.21 (–), 20.31 (–), 19.68 (+), 19.62 (–), 18.76 (+); IR ($CHCl_3$) 2940 (m), 1705 (s), 1450 (m), 1435 (m), 1075 (s), 985 (m), 925 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 261 (M + 1, 9), 260 (M, 48), 233 (2), 232 (13), 229 (35), 228 (100), 212 (2), 211 (3), 200 (12), 186 (31), 172 (70), 141 (97), 104 (90); high resolution MS calcd for $C_{16}H_{20}O_3$ 260.1413, found 260.1411.

6-Hydroxy-1-methyl-2-oxo-8-phenyl-7-oxabicyclo[4.3.0]nonane (15): TLC R_f 0.68 (hexane/ethyl acetate 1:1); VPC t_R 1.6 min (OV-1 2% 1 m, 190 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 3 H), 1.75 (m, 9 H), 4.84 (dd, J = 10.26 and 6.59 Hz), 5.15–5.20 (m) (total 1 H), 7.17–7.40 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 211.14, 142.41, 128.14, 127.23, 126.05, 106.58, 79.58, 61.08, 40.72, 37.75, 32.92, 20.31, 18.73; INEPTR (400 MHz, $CDCl_3$) δ 128.12 (+), 127.23 (+), 126.05 (+), 106.55 (+), 79.58 (+), 61.07 (+), 40.71 (–), 37.75 (–), 32.90 (–), 20.31 (–), 18.73 (+); IR ($CHCl_3$) 3200–3600 (br), 2925 (w), 1705 (s), 1450 (m), 1350 (w), 1315 (m), 1110 (w), 1060 (m), 1010 (s), 995 (s), 930 (m), cm^{-1}; low resolution MS, m/e (relative intensity) 247 (M + 1, 0.2), 246 (M, 1), 228 (63), 200 (5), 186 (26), 172 (29), 155 (21), 131 (29), 127 (38), 104 (100), 91 (42); high resolution MS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1255. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 72.85; H, 7.35.

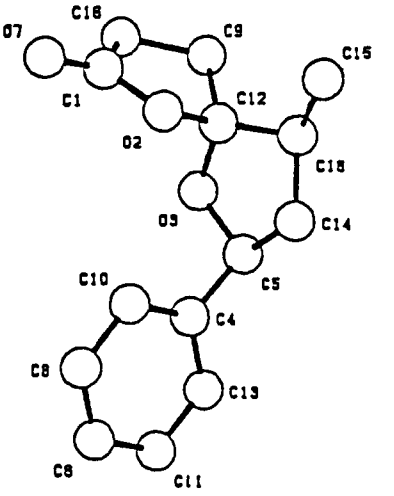


Figure 1. X-ray structure of **27b**.

1-Methyl-6-methoxy-2-oxo-8-(1-propenyl)-7-oxabicyclo[4.3.0]nonane (16): TLC R_f 0.76 (hexane/ethyl acetate 1:1); VPC t_R 6.4 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.188 (s), 1.193 (s), 1.200 (s), 1.203 (s) (total 3 H), 1.64–2.05 (m), 2.34–2.85 (m) (total 11 H), 3.262 (s), 3.263 (s), 3.27 (s), 3.28 (s) (total 3 H), 4.21–4.29 (m), 4.66–4.74 (m) (total 1 H), 5.27–5.66 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 210.92, 210.86, 132.64, 132.19, 131.30, 130.98, 128.27, 127.80, 126.25, 125.83, 108.22, 108.16, 108.13, 108.07, 78.72, 76.83, 72.51, 70.61, 60.67, 60.60, 48.21, 48.15, 38.24, 38.17, 37.78, 37.67, 26.96, 26.74, 20.18, 19.65, 19.07, 18.44, 17.81, 17.74; INEPTR (400 MHz, $CDCl_3$) δ 132.66 (+), 132.21 (+), 131.32 (+), 130.98 (+), 128.27 (+), 127.80 (+), 126.25 (+), 125.83 (+), 108.14 (+), 108.07 (+), 78.74 (+), 76.83 (+), 72.52 (+), 70.61 (+), 48.21 (+), 48.15 (+), 38.26 (–), 38.18 (–), 37.78 (–), 37.69 (–), 26.96 (–), 26.74 (–), 20.18 (–), 19.67 (–), 19.08 (+), 18.44 (+), 17.81 (+), 17.75 (+); IR (neat) 2940 (s), 1705 (s), 1435 (m), 1310 (w), 1170 (m), 1110 (m), 1075 (s), 970 (m), 925 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 225 (M + 1, 2), 224 (M, 8), 209 (2), 193 (12), 192 (23), 141 (100); high resolution MS calcd for $C_{13}H_{20}O_3$ 224.1413, found 224.1421.

2-Methyl-2-(4-methoxy-2-pentenyl)cyclohexane-1,3-dione (17): TLC R_f 0.44 (hexane/ethyl acetate 1:1); VPC t_R 8.1 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.16 (d, J = 6.3 Hz), 1.22 (s, 3 H), 1.74 (m, 2 H), 2.45–2.67 (m, 6 H), 3.16 (s, 3 H), 3.51–3.65 (m, 1 H), 5.28–5.39 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.94, 136.50, 125.51, 77.51, 65.43, 55.97, 39.94, 38.30, 21.62, 19.50, 17.89; IR (neat) 2955 (m), 2925 (m), 1720 (s), 1690 (s), 1445 (w), 1370 (w), 1315 (w), 1190 (w), 1095 (m), 1075 (m), 1020 (w), 970 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 209 (2), 192 (72), 177 (5), 164 (15), 149 (28), 136 (47), 121 (55), 98 (100); high resolution MS calcd for $C_{12}H_{17}O_3$ (M – CH_3) 209.1177, found 209.1172.

1-Methoxy-5-methyl-6-oxo-3-phenyl-2-oxabicyclo[3.3.0]octane (18): TLC R_f 0.68 (hexane/ethyl acetate 2:1); VPC t_R 15.8 min (OV-1 2% 1 m, 40–220 °C, 10 °C/min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s), 1.14 (s) (total 3 H), 1.70–2.75 (m, 6 H), 3.42 (s), 3.47 (s) (total 3 H), 4.85 (dd, J = 9.9 and 6.7 Hz), 5.05 (t, J = 7.7 Hz) (total 1 H), 7.19–7.33 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 218.80, 142.26, 140.79, 128.27, 128.14, 127.54, 127.30, 125.96, 125.87, 114.13, 113.62, 81.25, 78.91, 60.47, 59.77, 49.86, 49.48, 44.53, 43.58, 36.13, 36.02, 27.59, 26.49, 16.47, 15.75; INEPTR (400 MHz, $CDCl_3$) δ 218.85 (+), 128.28 (+), 128.16 (+), 127.55 (+), 127.32 (+), 125.99 (+), 125.89 (+), 81.26 (+), 78.91 (+), 49.87 (+), 49.49 (+), 44.55 (–), 43.58 (–), 36.14 (–), 36.04 (–), 27.59 (–), 26.49 (–),

16.48 (+), 15.77 (+); IR ($CHCl_3$) 2940 (m), 1740 (s), 1490 (w), 1450 (m), 1400 (w), 1370 (w), 1305 (w), 1260 (w), 1130 (m), 1100 (s), 1065 (m), 1045 (m), 990 (m), 910 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 247 (M + 1, 17), 246 (M, 87), 215 (20), 214 (60), 186 (20), 172 (27), 158 (46), 142 (56), 131 (89), 115 (100); high resolution MS calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1251.

1-Hydroxy-5-methyl-6-oxo-3-phenyl-2-oxabicyclo[3.3.0]-octane (19): TLC R_f 0.60 (hexane/ethyl acetate 1:1); VPC t_R 11.2 min and 11.6 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (s), 1.18 (s) (total 3 H), 1.92–3.08 (m, 6 H), 3.26 (br 1 H), 4.83 (dd, J = 10.01 and 6.59 Hz), 5.24 (t, J = 7.69 Hz) (total 1 H), 7.18–7.44 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 219.09, 218.93, 141.82, 140.60, 128.28, 128.22, 127.60, 127.48, 125.79, 125.71, 111.78, 111.31, 80.97, 79.13, 59.71, 59.12, 44.34, 43.52, 36.55, 36.49, 31.68, 30.87, 16.62, 15.96; INEPTR (400 MHz, $CDCl_3$) δ 128.30 (+), 128.24 (+), 127.61 (+), 127.49 (+), 125.80 (+), 125.73 (+), 80.99 (+), 79.15 (+), 44.36 (−), 43.54 (−), 36.56 (−), 36.51 (−), 31.69 (−), 30.89 (−), 16.63 (+), 15.97 (+); IR ($CHCl_3$) 3100–3600 (br), 2900 (w), 1735 (s), 1450 (m), 1305 (w), 1205 (m), 1150 (m), 1050 (s) cm^{-1}; low resolution MS, m/e (relative intensity) 233 (M + 1, 16), 232 (M, 98), 215 (11), 214 (61), 186 (16), 171 (28), 158 (38), 144 (14), 131 (100); high resolution MS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1108. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.62; H, 6.93.

1-Methoxy-3,5-dimethyl-6-oxo-3-vinyl-2-oxabicyclo-[3.3.0]octane (20): TLC R_f 0.84 (hexane/ethyl acetate 1:1); VPC t_R 5.2 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.01 (s, 3 H), 1.16 (s), 1.37 (s) (total 3 H), 1.59–2.50 (m, 6 H), 3.33 (s), 3.36 (s) (total 3 H), 4.77–5.16 (m, 2 H), 5.69 (dd, J = 17.1 and 9.9 Hz), 5.97 (dd, J = 18.0 and 10.8 Hz) (total 1 H); IR ($CHCl_3$) 2920 (m), 1730 (s), 1445 (m), 1400 (w), 1370 (w), 1305 (m), 1260 (w), 1190 (m), 1125 (s), 1110 (s), 1055 (s), 990 (m), 960 (m), 920 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 211 (M + 1, 2), 210 (M, 14), 195 (34), 178 (16), 163 (27), 142 (31), 123 73), 95 (100); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1264.

2-Methyl-2-(2-methyl-2-methoxy-3-butenyl)cyclopentane-1,3-dione (21): TLC R_f 0.68 (hexane/ethyl acetate 1:1); VPC t_R 6.2 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 0.98 (s, 3 H), 1.17 (s, 3 H), 2.20 (s, 2 H), 2.65 (s, 4 H), 2.92 (s, 3 H), 4.80–5.15 (m, 2 H), 5.45–5.85 (m, 1 H); IR ($CHCl_3$) 2920 (w), 1715 (s), 1450 (w), 1415 (w), 1370 (w), 1155 (w), 1105 (m), 1060 (m), 995 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 210 (M, 1), 195 (1), 178 (4), 163 (1), 98 (10), 85 (100); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1263.

2-Methyl-2-(2-methyl-4-methoxy-2-butenyl)cyclopentane-1,3-dione (22): TLC R_f 0.50 (hexane/ethyl acetate 1:1); VPC, t_R 7.9 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.06 (s), 1.08 (s) (total 3 H), 1.53 (s), 1.72 (s) (total 3 H), 2.36 (s, 2 H), 2.66 (s), 2.68 (s) (total 4 H), 3.20 (s), 3.22 (s) (total 3 H), 3.43 (d, J = 6.3 Hz), 3.79 (d, J = 7.2 Hz) (total 2 H), 5.05–5.30 (m), 6.10–6.35 (m) (total 1 H); IR ($CHCl_3$) 2920 (m), 1715 (s), 1445 (w), 1415 (w), 1370 (w), 1180 (w), 1070 (m), 990 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 210 (0.1), 178 (7), 163 (6), 98 (100); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1256, found, 210.1251.

5-Methyl-1-methoxy-6-oxo-2-(1-propenyl)-2-oxabicyclo-[3.3.0]octane (23): TLC R_f 0.78 (hexane/ethyl acetate 1:1); VPC t_R 5.3 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (400 MHz, $CDCl_3$) δ 1.057 (s), 1.064 (s), 1.08 (s) (total 3 H), 1.10–2.53 (m, 9 H), 3.378 (s), 3.383 (S), 3.340 (s) (total 3 H), 4.26–4.92 (m, 1 H), 5.26–5.72 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 219.24, 219.05, 132.45, 132.18, 130.67, 130.18, 128.73, 128.09, 127.32, 126.15, 113.72, 113.60, 80.20, 78.40, 74.11, 72.48, 59.58, 49.61, 49.55, 49.50, 42.65, 42.04, 41.18, 35.92, 35.86, 35.75, 27.33, 27.20, 26.40, 17.87, 16.31, 16.27, 15.81; INEPTR (400 MHz, $CDCl_3$) δ 132.41 (+), 130.63 (+), 130.13 (+), 128.63 (+), 128.00 (+), 127.25 (+), 80.12 (+), 78.33 (+), 74.07 (+), 72.43 (+), 49.55 (+), 49.51 (+), 49.48 (+), 49.39 (+), 42.61 (−), 41.99 (−), 41.13 (−), 35.86 (−), 35.81 (−), 35.69 (−), 35.64 (−), 27.29 (−), 27.14 (−), 26.33 (−), 17.80 (+), 17.75 (+), 16.34 (+), 16.25 (+), 16.21 (+), 15.75 (+); IR ($CHCl_3$) 2920 (m), 1735 (s), 1450 (w), 1200 (m), 1130 (m), 965 (w), 920 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 211 (M + 1, 10), 210 (M, 64), 195 (5), 179 (17), 178 (75), 163 (20), 142 (35), 126 (40), 115 (100); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1237.

2-Methyl-2-(2-methoxy-3-pentenyl)cyclopentane-1,3-dione (24): TLC R_f 0.64 (hexane/ethyl acetate 1:1); VPC t_R 6.1 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.04 (s, 3 H), 1.55–2.67 (m, 9 H), 2.94 (s), 2.97 (s) (total 3 H), 3.16–3.40 (m, 1 H), 4.94–5.73 (m, 2 H); IR ($CHCl_3$) 2920 (w), 1715 (s), 1445 (w), 1420 (w), 1200 (w), 1095 (m), 970 (w) cm^{-1}; low resolution MS, m/e (relative intensity) 179 (2), 178 (7), 163 (2), 150 (2), 98 (45), 85 (100); high resolution MS calcd for $C_{11}H_{14}O_2$ (M − CH_3OH) 178.0992, found 178.0972.

2-Methyl-2-(4-methoxy-2-pentenyl)cyclopentane-1,3-dione (25): TLC R_f 0.53 (hexane/ethyl acetate 1:1); VPC t_R 6.3 min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) δ 1.10 (s, 3 H), 1.14 (d, J = 5.4 Hz, 3 H), 2.26–2.33 (m, 2 H), 2.67 (s, 4 H), 3.16 (s, 3 H), 3.51–3.65 (m, 1 H), 5.29–5.39 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 215.01, 137.05, 124.49, 77.23, 56.70, 55.91, 38.45, 35.43, 21.52, 18.76; IR (neat) 2975 (m), 2925 (m), 1760 (m), 1720 (s), 1445 (w), 1415 (w), 1365 (w), 1315 (w), 1195 (w), 1110 (m), 1090 (m), 1075 (m), 970 (m) cm^{-1}; low resolution MS, m/e (relative intensity) 196 (1), 195 (4), 178 (10), 163 (10), 150 (2), 135 (10), 99 (44), 98 (100); high resolution MS calcd for $C_{12}H_{18}O_3$ 210.1257, found 210.1265.

1-(Methoxycarbonyl)-6-methoxy-8-phenyl-7-oxabicyclo-[4.3.0]nonane (26): TLC R_f 0.51 (hexane/ethyl acetate 5:1). Two isomers were obtained as a mixture with a small amount of another isomer: VPC t_R 12.7 (A) and 13.0 (B) min (OV-1 2% 1 m, 100–220 °C, 10 °C/min); ^1H NMR (90 MHz, $CDCl_3$) A + B δ 1.20–3.13 (m, 8 H), 3.17 (s), 3.23 (s), 3.26 (s) (total 3 H), 3.45 (s), 3.53 (s), 3.65 (s) (total 3 H), 4.88–5.16 (m, 1 H), 7.20–7.40 (m, 5 H); IR ($CHCl_3$) A + B 2930 (s), 1720 (s), 1495 (w), 1445 (m), 1440 (m), 1355 (w), 1330 (m), 1275 (m), 1205 (s), 1165 (s), 1085 (s), 1025 (m), 970 (m) cm^{-1}; low resolution MS, m/e (relative intensity) A 259 (30), 258 (69), 227 (10), 226 (38), 199 (97), 184 (70), 154 (100); B 291 (M + 1, 4), 290 (M, 20), 259 (73), 258 (40), 227 (20), 226 (65), 200 (40), 199 (100), 181 (60), 170 (45), 154 (87); high resolution MS A, (M − MeO) Calcd for $C_{16}H_{19}O_3$ 259.1333, found 259.1310; B, calcd for $C_{17}H_{22}O_4$ 290.1519, found 290.1488.

Fragmentation Reaction. The adduct **14** (185 mg, 0.79 mmol) was dissolved in 2-methyl-2-propanol. Potassium *tert*-butoxide (88 mg, 0.78 mmol) was added and the mixture was refluxed for 20 min. After being cooled to room temperature, 2 N HCl was added until the pH of the mixture became 1. The mixture was partitioned between brine and ether, and ether layer was separated and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography to obtain two products (**27a**, 73 mg; **27b**, 82 mg; total yield 84%).

27a: TLC R_f 0.70 (hexane/ethyl acetate 1:1); VPC t_R 3.7 min (OV-1 2% 1 m, 180 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, J = 6.35 Hz), 1.32 (d, J = 7.32 Hz) (total 3 H), 2.05–2.90 (m, 7 H), 5.15–5.35 (m, 1 H), 7.25–7.45 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 175.42, 142.25, 128.14, 127.20, 125.07, 116.81, 79.53, 40.45, 39.72, 29.38, 29.00, 12.75; INEPTR (400 MHz, $CDCl_3$) δ 142.23 (+), 128.15 (+), 127.22 (+), 125.07 (+), 116.84 (+), 79.53 (+), 40.43 (+), 39.70 (−), 29.37 (−), 29.02 (−), 12.76 (+); IR ($CHCl_3$) 2910 (m), 2850 (m), 1760 (s), 1445 (m), 1360 (m), 1210 (m), 1150 (s), 1105 (s), 1000 (m), 955 (m), 900 (s) cm^{-1}; low resolution MS, m/e (relative intensity) 232 (M, 20), 214 (2), 203 (1), 188 (19), 177 (3), 173 (4), 159 (3), 132 (14), 131 (18), 126 (100), 117 (46), 112 (28), 111 (57); high resolution MS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1101.

27b: TLC R_f 0.61 (hexane/ethyl acetate 1:1); VPC t_R 3.7 min (OV-1 2% 1 m, 180 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.12 (d, J = 7.8 Hz, 3 H), 1.70–3.05 (m, 7 H), 5.02 (dd, J = 13.3 and 6.7 Hz, 1 H), 7.15–7.45 (m, 5 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 175.31, 141.20, 128.19, 127.57, 126.03, 116.43, 82.18, 43.42, 41.51, 30.10, 29.14, 12.35; INEPTR (400 MHz, $CDCl_3$) δ 128.19 (+), 127.57 (+), 126.03 (+), 82.18 (+), 43.42 (+), 41.51 (−), 30.10 (−), 29.14 (−), 12.35 (+); IR ($CHCl_3$) 2920 (w), 1760 (s), 1445 (w), 1320 (w), 1220 (m), 1190 (m), 1165 (s), 1120 (m), 1000 (m), 980 (m), 955 (m), 895 (s) cm^{-1}; low resolution MS, m/e (relative intensity) 232 (32), 212 (2), 203 (2), 188 (14), 184 (4), 177 (4), 173 (5), 159 (5), 133 (18), 132 (22), 126 (100), 117 (54), 111 (54); high resolution MS calcd for $C_{14}H_{16}O_3$ 232.1100, found 232.1088. The stereochemistry was determined by X-ray analysis (Figure 1).

Acknowledgment. We thank the Ministry of Educa-

tion for the Grant-in-Aid for Scientific Research (No. 60750803) for support of this work. We also thank Dr. K. Hirotsu, Osaka City University for X-ray analysis of the spiro compound.

Registry No. **2**, 109704-12-3; **3**, 109735-36-6; **4**, 113924-34-8; **5**, 108967-79-9; **6**, 92898-23-2; **7**, 91969-81-2; **8**, 109704-11-2; **9**, 76327-74-7; **10a**, 113893-91-7; **10b**, 113893-92-8; **11a**, 113924-35-9; **11b**, 113924-36-0; **14**, 113924-37-1; **15**, 113893-93-9; **16**, 113893-94-0; **17**, 113893-95-1; **18**, 113893-96-2; **19**, 113974-17-7; **20**, 113893-97-3; **21**, 113893-98-4; **22**, 113893-99-5; **23**, 113894-00-1; **24**, 113924-38-2; **25**, 113894-01-2; **26**, 113894-02-3; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = Ph), 100-42-5; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = CH_2SiMe_3), 762-72-1; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = C_8H_{17}), 872-05-9; $CH_2{=}CR_1R_2$ (R_1 = Me, R_2 = OMe), 116-11-0; $CH_2{=}CR_1R_2$ (R_1 = Me, R_2 = OAc), 108-22-5; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = CN), 107-13-1; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = CO_2Et), 140-88-5; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = $COCH_3$), 78-94-4; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = $C(CH_3){=}CH_2$), 78-79-5; $CH_2{=}CR_1R_2$ (R_1 = H, R_2 = OEt), 109-92-2; $CH_2{=}CR_1R_2$ (R_1 = Me, R_2 = SPh), 7594-43-6; MeOH, 67-56-1; MeCN, 75-05-8; DMF, 68-12-2; Bu_4NBF_4, 429-42-5; Bu_4NClO_4, 1923-70-2; $LiClO_4$, 7791-03-9; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 1,3-cyclohexanedione, 504-02-9; 4-methyl-1,3-cyclohexanedione, 14203-46-4; 1,3-cyclopentanedione, 3859-41-4; 2,4-pentanedione, 123-54-6; 2-methyl-1,3-cyclohexanedione, 1193-55-1; 2-methyl-1,3-pentanedione, 14848-68-1; 2-carbomethoxycyclohexanone, 41302-34-5; dihydrofuran, 36312-17-1; tetraethylammonium *p*-toluenesulfonate, 733-44-8.

Free-Radical Additions of Diselenides to Dimethyl Acetylenedicarboxylate, Methyl Propiolate, and Dimethyl Maleate[1]

Thomas G. Back* and M. Vijaya Krishna

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received December 11, 1987

The photolysis of diphenyl or dimesityl diselenide with dimethyl acetylenedicarboxylate or methyl propiolate resulted principally in the formation of the corresponding vicinal bisselenides **1a,b**, **2a,b**, and **6a,b** via a free-radical chain addition mechanism. Dimethyl maleate underwent a selenyl radical mediated isomerization to dimethyl fumarate when similarly photolyzed with diphenyl diselenide.

The 1,2-additions of many kinds of reagents to multiple bonds are known to proceed via free-radical chain mechanisms.[2,3] Despite growing interest in the radical reactions of selenium compounds,[4] only a few types such as selenosulfonates[5] ($ArSO_2SePh$) and selenenyl thiocarboxylates[6] (PhC(=O)SSePh) have been reported to undergo free-radical 1,2-additions to olefins or acetylenes. To our knowledge, similar addition reactions of the more common diselenides have not yet been documented.

The phenylselenyl radical (PhSe•) can be conveniently generated by photolysis of the corresponding diselenide[7] (eq 1). Ito[8] recently reported that this species adds reversibly to olefins containing substituents that stabilize the resulting alkyl radicals (eq 2). Although the latter

$$PhSeSePh \overset{h\nu}{\rightleftharpoons} 2\ PhSe\bullet \qquad (1)$$

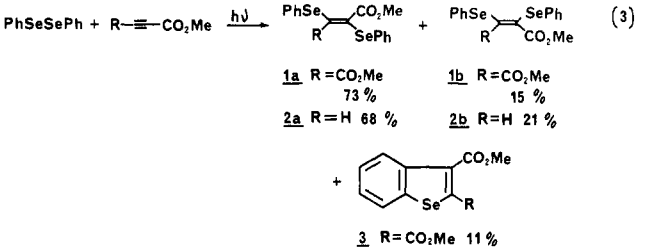
$$PhSe\bullet + RCH{=}CH_2 \rightleftharpoons R\dot{C}HCH_2SePh \qquad (2)$$

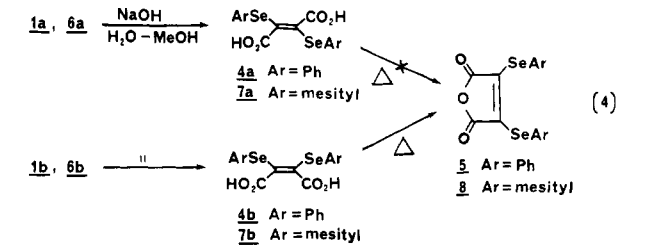
$$R\dot{C}HCH_2SePh + PhSeSePh \rightarrow PhSeCH(R)CH_2SePh + PhSe\bullet$$

intermediates could be trapped with oxygen, they did not undergo chain transfer to a second molecule of the diselenide to afford the corresponding vicinal bisselenides. We are unaware of any comparable studies with activated acetylenes.

We report that the photochemical reaction of diphenyl or dimesityl diselenide with dimethyl acetylenedicarboxylate (DMAD) or methyl propiolate resulted in the first examples of the free-radical addition of a diselenide to an acetylene. We also observed a selenyl radical mediated isomerization of dimethyl maleate to dimethyl fumarate under similar conditions.

When diphenyl diselenide was photolyzed with UV light in the presence of an equimolar amount of DMAD or methyl propiolate in benzene for 24 h, the bisselenides **1** and **2** were produced in high yield as separable mixtures of *E* and *Z* isomers in which the *E* isomers **1a** and **2a** predominated (eq 3). The minor isomer **1b** was assigned the *Z* configuration on the basis of its conversion to the corresponding cyclic anhydride **5** by saponification and dehydration of the diacid **4b** (eq 4). The isomers **2a** and





2b were assigned the *E* and *Z* configurations, respectively, on the basis of the lower field NMR absorption of the

(1) We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

(2) Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, Chapter 13.
(3) Nonhebel, D. C.; Walton, J. C. In *Free-Radical Chemistry*; Cambridge University: Cambridge, 1974; pp 210–238 and 272–292.
(4) For a review of radical reactions of selenium compounds, see: Back, T. G. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 7.
(5) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.
(6) Toru, T.; Seko, T.; Maekawa, E. *Tetrahedron Lett.* **1985**, *26*, 3263.
(7) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405. Franzi, R.; Geoffroy, M. *J. Organomet. Chem.* **1981**, *218*, 321.
(8) Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.

0022-3263/88/1953-2533$01.50/0