β-Copper(II) Ketones. Generation, Coupling, and Highly Stereoselective Trapping by Electron-Deficient Acetylenes

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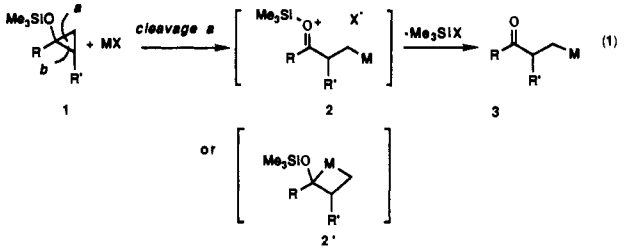
Abstract: The generation and the reaction of β-copper(II) ketones via electrophilic ring opening of siloxycyclopropanes with copper(II) tetrafluoroborate ($Cu(BF_4)_2$) were studied. Treatment of siloxycyclopropane with $Cu(BF_4)_2$ resulted in desilylative dimerization to give a 1,6-diketone in good yield. The ring opening took place regioselectively across the bond between the methylene and siloxy carbons. The reaction is reasonably interpreted by assuming the electrophilic ring opening by cupric ion to form β-copper(II) ketone and trimethylsilylfluoride, followed by dimerization. With dimethyl acetylene dicarboxylate (DMAD) and water, β-(acyl)alkyls were captured to give dimethyl 2-(3-oxoalkyl)-maleate with high degree of stereoselectivity. The stereoselective transfer of β-(acyl)alkyl arises from syn addition across the triple bond followed by in situ protonation of the resulting vinylcopper species with retention of configuration. The stereoselective transfer of β-(acyl)alkyls to acetylenic sulfones, which gives β-(acyl)alkylated vinylic sulfones, was also successful.

Since their first appearance in the early 1970s,[1] siloxycyclopropanes **1** have been widely investigated, and a variety of synthetically useful transformations have been developed.[2] Some of the remarkable aspects of siloxycyclopropane chemistry are based on the metal-induced ring-opening reactions (eq 1), which give stable or intermediary β-metal-substituted ketones **3**, organometallics having considerable synthetic potential.[3] The reaction results in the loss of the trialkylsilyl moiety as a cationic leaving group and site-selective ring cleavage of bond *a* is observed in the case of 1-siloxybicyclo[*n*.1.0]alkanes. This regioselectivity may be explained by attack of a metal ion at the least hindered site or by the formation of a metalacycle. Nakamura, Kuwajima, and co-workers have reported some impressive achievements in the ring-opening reaction of 1-alkoxy-1-siloxycyclopropanes with metal salts to give β-metallo *esters*.[3b-d] Some of these function as versatile *β-carbanion of esters*.[4] Due to the electron donation by the extra alkoxy group, a large number of metal salts are able to cleave the cyclopropane ring, compared to simple siloxycyclopropane **1**. However, it should be noted that the reactivities of siloxycyclopropanes and 1-alkoxy-1-siloxycyclopropanes with the same metal salt are not uniformly equivalent.[5]



(1)

Isolated examples of β-metallo ketones **3** by the siloxycyclopropane route include those of Hg(II),[6a] Sn(IV),[6b] Te(IV),[6c] Au(I),[6d] and Pt(II).[6e] In spite of the difficulty of their isolation, some unstable β-metallo ketones **3** undergo useful synthetic transformations. For example, silver tetrafluoroborate reacts with 1-siloxybicyclo[4.1.0]heptane **1g** at −20 to 15 °C to give the symmetrical 1,6-diketone **4g**, with regioselective cleavage of bond *a*, and metallic silver.[7] The formation of the 1,6-diketone can be explained by the dimerization of a β-silver(I) ketone formed by the ionic mechanism as outlined in eq 2. The reaction of siloxycyclopropane with copper(II) tetrafluoroborate proceeds efficiently at room temperature to give the same 1,6-diketone and reduced copper(0). We have proposed a similar mechanism involving the formation of intermediary β-copper ketone and subsequent dimerization (eq 3). This desilylative dimerization system should include a copper induced *oxidation* (from Cu(II) to Cu(0) (or Cu(I))). We believed that in a rationally designed system the interception of the intermediate would be achieved.

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(1) (a) Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354. (b) Rubottom, G. M.; Lopez, M. I. *J. Org. Chem.* **1973**, *38*, 2097. (c) Le Goaller, R.; Pierre, J. L. *Bull. Soc. Chim. Fr.* **1973**, 1531. (d) Girard, C.; Conia, J. M. *Tetrahedron Lett.* **1973**, 2767.

(2) For reviews, see: (a) Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121. (b) Salaün, J. *Chem. Rev.* **1983**, *83*, 619. (c) Ryu, I.; Murai, S. In *Methoden der Organischen Chemie (Houben-Weyl)*; de Meijere, A., Ed.; Georg Thieme; New York, Vol E17, in press.

(3) For reviews, see: (a) Ryu, I.; Sonoda, N. *J. Syn. Org. Chem. Jpn.* **1985**, *43*, 112. (b) Nakamura, E. *Ibid.* **1989**, *47*, 931. (c) Kuwajima, I.; Nakamura, E. *Top. Curr. Chem.* **1990**, *133*, 1. (d) Kuwajima, I.; Nakamura, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol 2, pp 441–454. (e) Reference 2c.

(4) The phrase "metal homoenolate", as a general term for β-metal substituted carbonyl compounds, is in current use. We would like to point out some ambiguities in this wording: (i) the majority of β-metal substituted carbonyl compounds would never operate as *β-acylcarbanions*; (ii) the wording has often been used without specifying the carbonyl character; (iii) the "homoenolate" function is difficult to visualize; and (iv) the ambident character of β-lithio ketones has yet to be established, see: Shiner, C. S.; Berks, A. H.; Fisher, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 957.

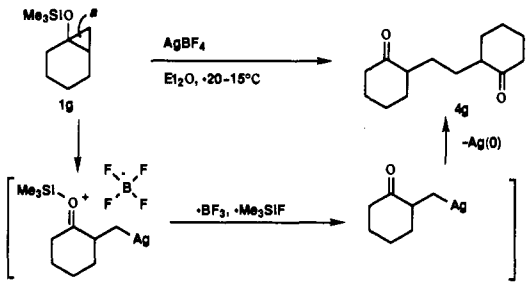
(5) For example, while the reaction of 1-siloxybicyclo[*n*.1.0]alkanes with zinc iodide results in the isomerization to allyl silyl ethers (see ref 5a), the ring opening of 1-alkoxy-1-siloxycyclopropane by zinc halides gives β-zinc esters and trimethylchlorosilane (see ref 5b). (a) Ryu, I.; Aya, T.; Otani, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279. (b) Nakamura, E.; Aoki, S.; Sekiya, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056.

(6) (a) Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283. (b) Nakahira, H.; Ryu, I.; Ikebe, M.; Oku, Y.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 17. (c) Nakahira, H.; Ryu, I.; Han, L.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1991**, *32*, 229. (d) Ito, Y.; Inouye, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.* **1988**, *342*, C41. (e) Ikura, K.; Ryu, I.; Sonoda, N.; Harada, S.; Kasai, N. *Organometallics* **1991**, *10*, 528.

(7) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192.

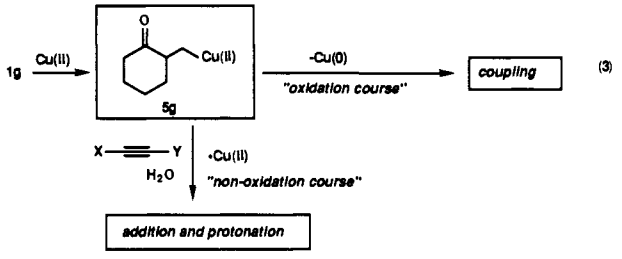
0002-7863/93/1515-12330$04.00/0

If the organocopper intermediate could be intercepted and then quenched by a proton, the aforementioned oxidation process might be shifted to a *nonoxidation* pathway, where no change in the valency of the copper ions occurs throughout the reaction. From a synthetic point of view, the interception of a β-(acyl)alkylcopper intermediate by electrophiles is significant, since the overall process represents a straightforward polarity inversion β to a ketone carbonyl.



(2)

In this paper we describe the full details of the reaction of siloxycyclopropanes with copper tetrafluoroborate ($Cu(BF_4)_2$). In an attempt to trap the intermediary β-copper(II) ketones with carbon electrophiles, we have uncovered a highly stereoselective β-(acyl)alkyl transfer to electron-deficient acetylenes (e.g., dimethyl acetylene dicarboxylate (DMAD), acetylenic phenyl-sulfones, etc.), which gives β-(acyl)alkylated alkenes in good yields. The nonoxidative C–C bond forming reaction realized from this reaction system lends a strong support for the intermediacy of β-copper(II) ketones rather than the intervention of β-(acyl)-alkyl radicals. A recent report by Snider and co-workers examined the reaction of copper fluoroborate with siloxycyclopropanes possessing an internal alkenyl group. They obtained modest amounts of cyclization product and favored the intermediacy of cation radicals rather than organocopper species. However, a radical addition mechanism appears inconsistent with the highly stereoselective addition observed in the present study.[8]

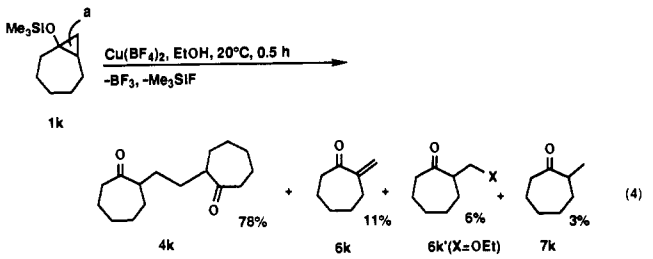


(3)

Results and Discussion

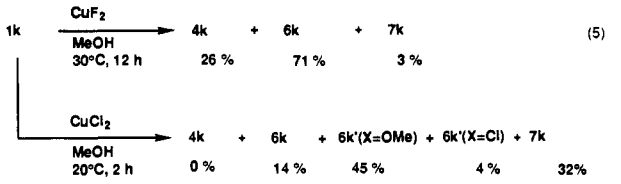
Desilylative Coupling of Siloxycyclopropanes 1 with $Cu(BF_4)_2$. As reported in our preliminary communication,[7] desilylative dimerization of siloxycyclopropanes with copper(II) fluoroborate gave 1,6-diketones in good yields. For example, the reaction of 1-(trimethylsiloxy)bicyclo[5.1.0]octane (**1k**) with $Cu(BF_4)_2$ in EtOH at 20 °C was complete within 0.5 h with deposition of copper(0). 1,6-Diketone **4k** was formed in 78% yield, and no products from central bond fission were observed. Analysis of the crude reaction mixture indicated the existence of three byproducts, which included 2-methylenecycloheptanone (**6k**) (11%), 2-(ethoxymethyl)cycloheptanone (**6k'**) (6%), and 2-methylcycloheptanone (**7k**) (3%). 2-Methyl ketone **7k** was formed presumably by acidic hydrolysis of **1k**. Trimethylsilylfluoride was also detected (^1H NMR, δ 0.21 (d, J_{H-F} = 7 Hz)).

(8) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1992**, *57*, 2399.



(4)

The reactions of **1k** with several other copper salts, such as CuF_2, $CuCl_2$, and $CuBr_2$, were also examined for comparison. The reaction of **1k** with CuF_2 was considerably slower than the reaction with $Cu(BF_4)_2$, probably due to low solubility of CuF_2. This reaction afforded lower yields of the coupled product **4k** and increased amounts of 2-methylenecycloheptanone (**6k**) (eq 5). The absence of the 2-alkoxymethyl ketone **6k'** (X = OMe) in this case suggests that the formation of **6k'** in eq 4 is due to the BF_3-promoted addition of the solvent to **6k**. Although the reaction of siloxycyclopropane **1k** with 1.5 equiv of $CuCl_2$ in MeOH did not give the 1,6-diketone **4k**, the ring opening was again site-selective at *a* (eq 5). A similar reaction pattern was also observed in the reaction of **1k** with $CuBr_2$. The fact that the ring opening was uniformly site-selective at the peripheral methylene carbon of the cyclopropane ring suggests a common or similar reaction pathway irrespective of the copper salts and argues against an oxy radical induced ring-opening mechanism proposed in Fe(III) systems, which should lead to a ring expansion.[9]



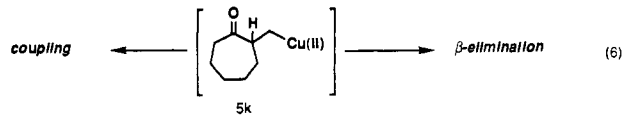
(5)

The reaction leading to **4k** appears to be consistent with a bimolecular coupling of β-copper(II) ketone **5k** as a key intermediate, which results from the electrophilic attack of *Cu^{2+} ion* at the least substituted cyclopropane carbon to cause ring opening followed by desilylation.[10] The formation of 2-methylene ketone **6k** could be explained by competing β-elimination from the common intermediate **5k** (eq 6). The seemingly marked difference in product selectivity for **4k** and **6k** observed between $Cu(BF_4)_2$ and CuF_2 may suggest the importance of the smooth generation of *naked Cu^{2+}* for the coupling reaction. This would allow for the rapid accumulation of **5k**, and the bimolecular coupling would then be the predominant reaction course. In spite of the absence of **4k** in the products, the results of $CuCl_2$ were also indicative of the key role of the corresponding β-copper(II) ketone as the first intermediate, which would undergo β-elimination to give **6k**. The validity of the employment of fluoroborate as the anionic counterpart to cause effective siloxycyclopropane cleavage has also been shown by the recent study of Nakamura, Kuwajima, and co-workers which deals with the ring-opening of **1** by ArPdOTf and $ArPdBF_4$.[11]

(9) (a) Ito, Y.; Saegusa, T. *J. Org. Chem.* **1977**, *42*, 2326. For the case of 1-methoxycyclopropanol, see: (b) Schaafsma, S. E.; Jorritsma, R.; Steinberg, H.; de Boer, T. J. *Tetrahedron Lett.* **1973**, 827. Also see some recent applications based on the cyclopropoxy radical rearrangements: (c) Booker-Milburn, K. I. *Synlett* **1992**, 809. (d) Iwasawa, N.; Hayakawa, S.; Funahashi, M.; Isobe, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 819.

(10) For the formation of **5**, a mechanism involving one-electron transfer from a siloxycyclopropane to cupric ion to give a cation radical and cuprous ion[8] and their subsequent rapid combination[16] may provide an alternative explanation. As for the bimolecular coupling of **5**, we have not ruled out a possibility of a mechanism that involves a rapid trap of a radical from **5** by another molecule of **5** to form unstable $R_3Cu(III)X$ that would rapidly reductively eliminate **4** generating CuX. We thank one referee for calling our attention to these mechanistic possibilities as well as to the paper in ref 16.

(11) Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988**, *110*, 3296.



(6)

For the coupling reaction of siloxycyclopropanes **1**, $Cu(BF_4)_2$ was found to be the reagent of choice. Thus, we examined the reaction of siloxycyclopropane **1g** with $Cu(BF_4)_2$ in detail. The results are summarized in Table I. The 1,6-diketone **4g** was obtained in good yields in both protic and aprotic solvents, but some polar solvents such as DMF and acetonitrile were unsuitable. *Notably, when a half molar equiv of $Cu(BF_4)_2$ was employed, **4g** was obtained without a decrease in the yield (run 2).* A similar stoichiometry was observed when $^1/_4$ mol equiv of $Cu(BF_4)_2$ was used (run 1). In these cases, a clean copper mirror appeared on the surface of the reaction flask.

The observed efficient consumption of Cu(II) to Cu(0) through the overall process might be accounted for by assuming the rapid disproportionation of transiently formed $Cu(I)BF_4$, which is expected to be very unstable,[12] to a more stable $Cu(BF_4)_2$ and Cu(0) (Scheme I). The pathway involving organocopper(I) **5g'** seems less likely since it requires the central role of *unstable* Cu^IBF_4 throughout the reaction.[13] On the other hand, some previous work suggested the formation of free radicals from divalent copper species such as $RCu^{II}X$ (X = Cl, Br, OAc, etc.) and their role as key intermediates for bimolecular coupling.[14,15] In our system, however, we have been unable to detect the intermediacy of β-(keto)alkyl radicals, which would be formed by the decomposition of β-copper(II) ketones. The attempted trapping of radicals with styrene, 2,3-dimethylbutadiene, *p*-cymene, and carbon monoxide was unsuccessful. Thus, we are intrigued by a possible rationale based on the anionic counterpart. That is, Cl^-, Br^-, and OAc^- could give stable monovalent copper salts and the corresponding carbon radical, but F^- and BF_4^- would prevent this (Scheme II).[16]

Table II lists the results of the synthesis of a variety of symmetrical 1,6-diketones **4** via the $Cu(BF_4)_2$-induced desilylative coupling of siloxycyclopropanes **1**. Some of these are not readily available by existing methods.[17] This method for the preparation of **4** involves mild reaction conditions and a simple procedure (admixing of **1** with $Cu(BF_4)_2$ at ambient temperature for 0.5–1 h). The products were purified by either recrystallization or chromatographic separation on silica gel. A recent report that uses **4f** as a ligand precursor shows that the yield is reproducible on scales of up to 50 mmol of siloxycyclopropane.[18]

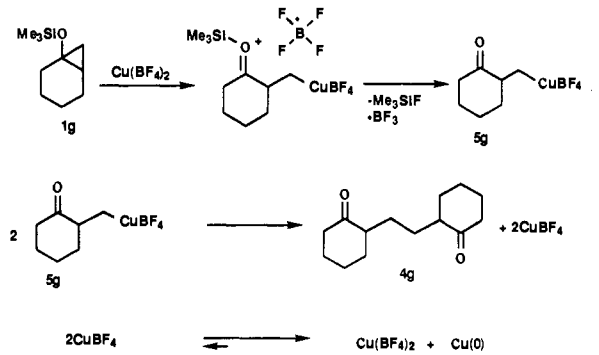
In contrast to the above reaction, attempted extension of the reaction to yield dialdehydes from siloxycyclopropane **1m** resulted in only desilylation to give cyclopropanol **8m**. Perhaps this reaction

Table I. Reaction of Siloxycyclopropane **1g** with $Cu(BF_4)_2$ Leading to 1,6-Diketone **4**[a]

run	**1g** (mmol)	$Cu(BF_4)_2$ (mmol)	solvent	yield of **4g**[b] (%)
1	1	0.25	Et_2O	42
2	1	0.5	Et_2O	83
3	1	1	Et_2O	87
4	1	2	Et_2O	83
5	1	1	EtOH[c]	86
6	1	1	*i*-PrOH[c]	82
7	1	1	*t*-BuOH	89
8	1	1	AcOEt	81
9	1	1	C_6H_6	28
10	1	1	CH_3CN	trace[d]
11	1	1	DMF[c]	5

[a] Reactions were conducted on a 1 mmol scale at 15 °C for 0.5 h in a concentration of [**1g**] = 1 M. [b] GC yield based on **1g**. [c] Homogeneous. [d] White predicitates were formed.

Scheme I



Scheme II

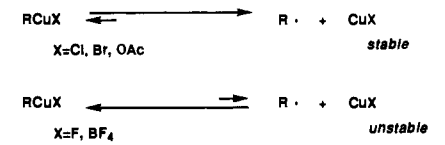
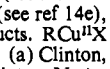


Table II. Cu(II)-Induced Desilylative Coupling of Siloxycyclopropanes Leading to 1,6-Diketones[a]

run	R	R′	R″	substrate no.	product no.	yield[b] (%)
1	*t*-Bu	H	H	**1a**	**4a**	80
2	Ph	H	H	**1b**	**4b**	78
3	2-furanyl	H	H	**1c**	**4c**	(65)
4	2-thiofuranyl	H	H	**1d**	**4d**	81
5	*o*-MeOPh	H	H	**1e**	**4e**	(40)
6	$-(CH_2)_3-$		H	**1f**	**4f**	77
7	$-(CH_2)_4-$		H	**1g**	**4g**	(80)
8	$-(CH_2)_4-$		CH_3	**1i**	**4i**	69
9			H	**1j**	**4j**	(74)
10	$-(CH_2)_5-$		H	**1k**	**4k**	(70)
11	$-(CH_2)_6-$		H	**1l**	**4l**	63

[a] Reactions were performed on 1–5 mmol scale according to the procedure described in the text using Et_2O as the solvent. 1,6-Diketones from bicyclic siloxycyclopropanes were obtained as a mixture of meso and racemic isomers. [b] GC (isolated) yields.

(12) (a) Sharp, D. W. A.; Sharpe, A. G. *J. Chem. Soc.* **1956**, 1858. To the best of our knowledge, isolable Cu^IBF_4 has not been known except for as a complexed form with solvents. For stable $Cu^IBF_4(MeCN)_4$ complex, see: (b) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215.

(13) For coupling of organocopper(I) species induced by oxidizing reagents, see: (R_2CuLi) (a) Whitesides, G. M.; San Filippo, J., Jr.; Casey, C. P.; Paneky, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302. (RCu^I) (b) Ku, R. V.; San Filippo, J., Jr. *Organometallics* **1983**, *2*, 1360. (c) Tamura, M.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *42*, 205.

(14) It is known that the reactions of organometallics (R_4Pb (see refs 14a and 14b), RMgX (see ref 14c), R_2Hg (see ref 14d) and R_2Zn (see ref 14e), with copper(II) chloride, bromide, and acetate, give coupling products. $RCu^{II}X$ were postulated as the first intermediates of these reactions, see: (a) Clinton, N. A.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *42*, 241. (b) Clinton, N. A.; Kochi, J. K. *J. Organomet. Chem.* **1973**, *56*, 243. (c) Tamura, M.; Kochi, J. K. *J. Organomet. Chem.* **1972**, *42*, 205. (d) Beletskaya, I. P.; Artamkina, Y. A.; Reutov, O. A. *J. Organomet. Chem.* **1975**, *99*, 343. (e) Thiele, K.-H.; Köhler, J. *J. Organomet. Chem.* **1968**, *12*, 225. Also see a review: (f) Kochi, J. K. *Acc. Chem. Res.* **1974**, 351.

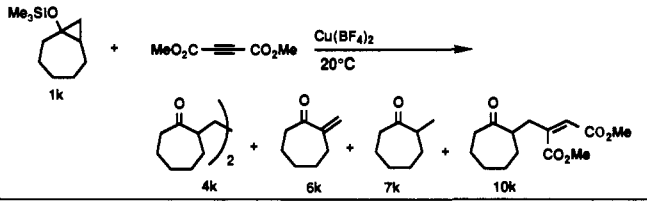
(15) Dimerization of alkenylcopper species (from $RLi/CuCl_2$ (see ref 15a) or $RSnR'_3/Cu(NO_3)_2$ (see ref 15b) to give bisalkenes has been known to proceed with retention of configuration at the vinylic carbons, which appears inconsistent with a free-radical mechanism. See: (a) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379. (b) Ghosal, S.; Luke, G. P.; Kyler, K. S. *J. Org. Chem.* **1987**, *52*, 4296.

(16) The rate constant for the trap of 2-hydroxycyclohexyl free radical with $Cu^I(aq)$ ion to form $RCu^{II}X$ is estimated to be ca. 10^9 M^{-1} s^{-1} (27 °C), which is two orders of magnitude faster than the trap with $Cu^{II}(aq)$ ion. See: Masarwa, M.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1991**, *30*, 1849.

(17) (a) Ghera, E.; Gibson, M.; Sondheimer, F. *J. Am. Chem. Soc.* **1962**, *84*, 2953. (b) Watanabe, S.; Suga, K.; Fujita, T.; Takahashi, Y. *Can. J. Chem.* **1972**, *50*, 2786.

(18) Collins, S.; Hong, Y.; Ramachandran, R.; Traylor, N. J. *Organometallics* **1991**, *10*, 2349.

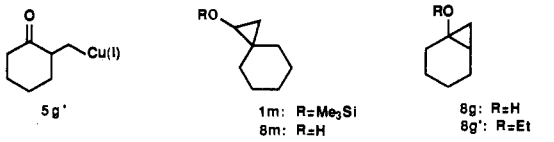
Table III. Reaction of Siloxycyclopropane **1k** with $Cu(BF_4)_2$ in the Presence of DMAD[a]



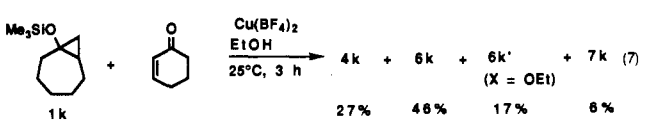
run	**1k** (mmol)	$Cu(BF_4)_2$ (mmol)	DMAD (mmol)	solvent (2 mL)	additive (mL)	yield[b] (%) **4k**	**6k**	**7k**	**10k**
1	1	1	1.2	EtOH		2	39[c]	1	28
2	1	1		EtOH		78	17[c]	3	
3[d]	1	1.1	1.1	Et_2O		3	20[c]	4	15
4[d]	1.2	1.2	1	t-BuOH		1	28[c]	1	23
5	1	1	1	$CHCl_3$			1	21	50
6	1	1	1	CH_2Cl_2			2	35	45
7	1	1		CH_2Cl_2		30	1	52	
8	1	1		CH_2Cl_2	BuOTMS (0.2)	60	4	32	
9	1	1	1	CH_2Cl_2	BuOTMS (0.2)		4	4	65
10	1	1	1.1	CH_2Cl_2	BuOTMS (0.2) + H_2O (0.02)		4	6	73
11[d]	1	1	1	CH_2Cl_2	BuOTMS (0.6)		10	2	35
12	1	1	1	CH_2Cl_2	TMS_2O (0.2)	2	3	22	59

[a] Reactions were conducted on a 1 mmol scale at 20 °C for 2–5 h under N_2. Except for runs 1, 2, and 4, the reactions were heterogeneous. [b] GC yields. [c] Yield including **6k'**. [d] High boiling products were also detected by GC.

failed because the siloxy carbon of **1m** is monosubstituted. Disubstitution with cation-stabilizing alkyl groups appears essential for the electrophilic ring opening to occur.[5a] Alkoxycyclopropane **8g'** also failed to react with $Cu(BF_4)_2$, whereas **8g**, the free alcohol of **1g**, readily reacted to give 1,6-diketone **4g** (64%). The possibility of the participation of desilylated cyclopropanols as substrates in the present system remains uncertain.[19]



Copper(II)-Mediated Highly Stereoselective Transfer of β-(Acyl)alkyls from 1 to Electron-Deficient Acetylenes. If the proposed β-copper(II) ketone **5** is captured by an appropriate carbon electrophile, the net outcome would provide a straightforward method for the transfer of β-(acyl)alkyl anions.[20] From this work we also expected to obtain strong supporting evidence for the intermediacy of this rather exotic organocopper species **5**. Thus, we examined the reaction of **1** with $Cu(BF_4)_2$ in the presence of carbon based electrophiles. Our choice of the carbon electrophiles, which worked well for the trapping of **5**, was at first limited. For example, the attempted capture with cyclohexenone, which is a typical Michael acceptor for RCu^1 or R_2CuLi, was unsuccessful. In this case the 2-methylene ketone **6k** was formed via β-elimination along with the 1,6-diketone **4k** (eq 7),[21] suggesting that the present organocopper species might not be well-known organocopper(I)-like.



After a survey of a variety of carbon electrophiles, we were pleased to find that some electron-deficient acetylenes, such as DMAD (dimethylacetylenedicarboxylate) and acetylenic sulfones efficiently intercepted the generated β-acylalkylcopper species. Surprisingly, the reaction can be conducted in the presence of water without significant decomposition of the generated species. When the reaction of 1-(trimethylsiloxy)bicyclo[5.1.0]octane (**1k**) with $Cu(BF_4)_2$ was carried out in ethanol at 20 °C in the presence of 1.2 equiv of DMAD, the coupling reaction (which would lead to **4k**) was almost completely suppressed, and the 1:1 adduct **10k** was obtained in 28% yield (Table III, run 1). However, in ethanol, β-elimination to give **6k** and its ethanol adduct **6k'** considerably lowered the yield of the desired product **10k**. The use of *t*-BuOH did not improve the yield of **10k** (run 4). Although the reaction of **1k** with $Cu(BF_4)_2$ proceeded at a slower rate in CH_2Cl_2 and $CHCl_3$ due to the very low solubility of the Cu salt, these solvents suppressed the production of β-elimination byproducts (runs 5 and 6). With these solvents, however, 2-methylcycloheptanone (**7k**), from hydrolysis of **1k**, was formed as a significant byproduct. The addition of a *Lewis base* capable of complexing BF_3, which could promote the hydrolysis, solved the problem. Based on some results reported by other groups,[22] we anticipated that trimethylalkoxysilane would react readily with BF_3 with liberation of silylfluoride to form relatively inert alkoxyboranes. The addition of small amounts of trimethylsiloxybutane or hexamethyldisiloxane (10 vol% in CH_2Cl_2) was found to be quite effective (runs 9 and 12).

Although ether was a good solvent for 1,6-diketone synthesis, in this solvent both the yield of **10k** and the total material balance were low in spite of the satisfactory consumption of DMAD (run 3). A similar tendency was observed even in CH_2Cl_2 when larger amounts of butoxysilane (23 vol% in CH_2Cl_2) was added (run 11). Careful GC analysis of the reaction mixture suggested the existence of high boiling byproducts. GC–MS analysis of three high boiling byproducts from **1a** revealed their parent peaks (*m/e*) to be 368, 398, and 510. These mass numbers correspond to those of the combination of β-(acyl)alkyl, DMAD, and hydrogen in the ratio of 2:1:0, 1:2:1, and 2:2:0, respectively. Presumably the two products having peaks at 368 and 510 would be derived from oxidative coupling of vinylcopper intermediates.

In order to obtain better product selectivity of the 1:1 addition/protonation product **10k** over the oxidation products, we con-

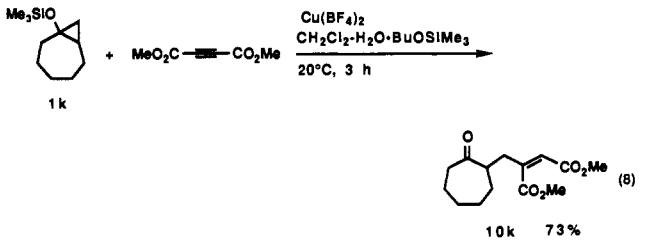
(19) The reaction of 1-(*tert*-butyldimethylsiloxy)-1-isopropylcyclopropane with $Cu(BF_4)_2$ was very sluggish (ether, 20 °C, 3 h), resulting in the only partial consumption of the siloxycyclopropane. This fact may suggest the importance of desilylation in the present reaction system.

(20) For some recent advances on synthetic equivalents of β-lithio carbonyl species, see: (a) Nakahira, H.; Ryu, I.; Ikebe, M.; Kambe, N.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 177. (b) Cherkauskas, J. P. *J. Org. Chem.* **1992**, *57*, 6. (c) Ahlbrecht, H.; Weber, P. *Synthesis* **1992**, 1018. (d) Ibanez, P. L.; Najera, C. H. *Tetrahedron Lett.* **1993**, *34*, 2003.

(21) For example, treatment of siloxycyclopropane **1a** with methyl vinyl ketone in the presence of $Cu(BF_4)_2$ in ethanol at 25 °C for 3 h gave low yield of 2,2-dimethyl-3,8-nonanedione. Attempts to trap **5** with ethyl vinyl ether, vinyl acetate, and allyl acetate were unsuccessful. Cf.: Sakata, H.; Aoki, Y.; Kuwajima, I. *Tetrahedron Lett.* **1990**, *31*, 1161.

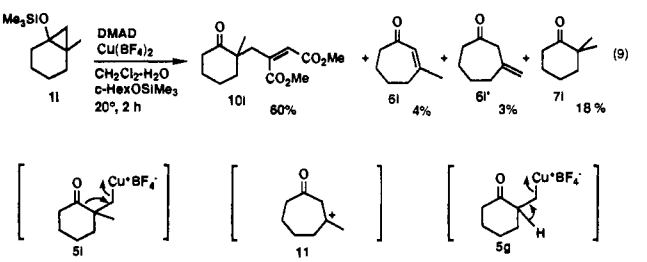
(22) (a) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649. (b) Kelly, D. R.; Roberts, S. M.; Newton, R. F. *Synth. Commun.* **1979**, *9*, 295.

sidered that immediate in situ protonolysis, prior to oxidation via vinylcopper species, should be ensured by adding a proton source to the reaction media beforehand. Indeed, the addition of small amounts of water prior to the reaction proved to be effective for the improvement of the yield of **10k** (run 10, eq 8).



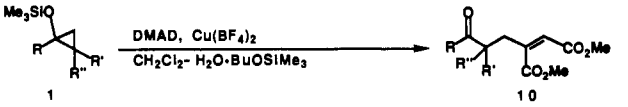
Thus, we employed the experimental procedure of run 10 for other β-(acyl)alkyl transfer reactions from siloxycyclopropanes **1** to DMAD (**1** (1 mmol), $Cu(BF_4)_2$ (1 mmol), DMAD (1 mmol), $BuOSiMe_3$ (0.2 mL), H_2O (0.02 mL), dichloromethane (2 mL), 20 °C, 2–3 h). These results are summarized in Table IV. Thus, a variety of β-(acyl)alkyls can be transferred from siloxycyclopropanes to DMAD. From the structural analyses of the adducts, the mode of ring cleavage was again site-selective at methylene carbons, consistent with the results of the homo-coupling reaction shown in Table II. This is important since this ensures the generation of a single β-(acyl)alkylcopper species from the bicyclic substrates **1**. Noteworthy is the stereoselectivity of this reaction. It has been previously reported that the stereoselectivity in the addition of alkylcopper(I) species to DMAD was highly sensitive to the reaction temperature.[23] Even though our reactions are conducted at ambient temperatures, the transfer occurs in a highly selective syn manner. For example, in the case of **10k**, enlargement of the vinylic region in ^1H NMR spectra of the crude product showed two quite uneven vinyl proton signals which resonate at δ 5.68 and 6.75 ppm in a 93:7 ratio. These two peaks were attributed to the *Z* and *E* isomers of the 1:1 adduct, respectively.[23] Preparative TLC (silica gel) permitted the easy isolation of pure β-(acyl)alkyl-substituted dimethyl maleates **10**.

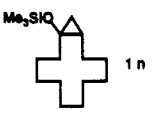
Siloxycyclopropane **1i** having a quaternary carbon at the cyclopropane ring gave the adduct **10i** in 60% yield after isolation by flash chromatography on silica gel (eq 9). Since the proposed intermediate **5i** should have a structure incapable of undergoing β-hydride elimination, we became interested in what the byproducts were formed in this reaction. The byproducts obtained were the seven-membered ring enones, **6i** (4%) and **6i′** (3%), and the hydrolyzed 2,2-dimethylcyclohexanone (**7i**) (18%). A possible mechanism of the formation of the oxidized products **6i** and **6i′** may involve the elimination of copper(0) from **5i** followed by acyl migration to give the tertiary cation **11** accompanied by a ring-enlargement.[24] With regard to a mechanism to give 2-methylene ketone from the β-copper(II) ketone **5g**, the intermediate having a β-hydrogen, an analogous elimination of copper(0) from the intermediate may be operative.[25]



(23) Except for alkylcopper(I)–Lewis acid reagents, the stereoselectivity of the addition of alkylcopper(I) species to DMAD is generally low (for example, the addition of Bu_2CuLi to DMAD at −70 °C gave a 4:6 *E*/*Z* mixture of the adducts). See: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Org. Chem.* **1979**, *44*, 1744. We thank Prof. Yoshinori Yamamoto at Tohoku University for the NMR spectra of the reference compounds.

Table IV. Cu(II)-Induced Desilylative Transfer of Siloxycyclopropanes to DMAD[a]

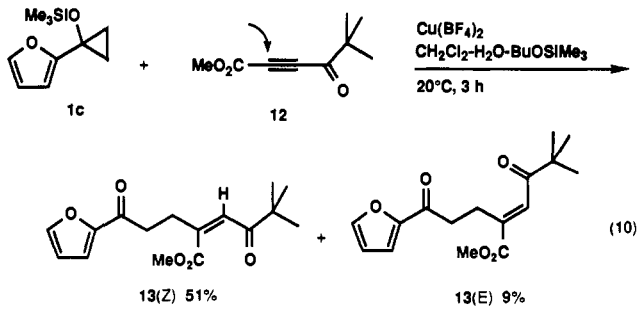


run	substrate 1	product 10	yield[b] (%)
1	1a	10a	80
2	1b	10b	60
3	1e	10e	(45)
4	1f	10f	71
5	1g	10g	(60)
6	1h[c]	10h[d]	67
7[e]	1i	10i	(60)
8[e]	1j	10j	(65)
9	1k	10k	73 (70)
10	1l	10l	68
11	 1n	10n	42

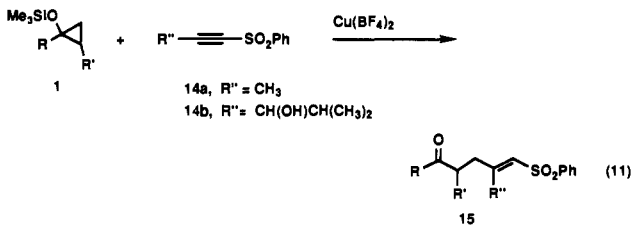
[a] All reactions were carried out in CH_2Cl_2 at 20 °C for 2–3 h: **1**, 1–1.1 mmol; DMAD, 1 mmol; $Cu(BF_4)_2$, 1 mmol; CH_2Cl_2, 2 mL; *n*-$BuOSiMe_3$, 0.2 mL; H_2O, 0.02 mL. [b] GC yields of *Z* products. Isolated yields are in parentheses. [c] A mixture of cis and trans isomers (1:1). [d] A mixture of diastereomers (1:1). [e] *c*-$HexOSiMe_3$ was used in place of *n*-$BuOSiMe_3$.

A regioselective copper(II) mediated β-(acyl)alkyl transfer reaction was observed when an unsymmetrical acetylene having two different carbonyl moieties was used. The reaction of methyl 3-(pivaloyl)propiolate (**12**) with furanyl substituted siloxycyclopropane **1c** proceeded with complete regioselectivity with respect to the triple bond to give the ester-functionalized 1,6-diketone **13** (eq 10). The stereoselectivity of this reaction was rather modest compared with the case of DMAD. Configurational isomerization via a ketone allenolate of the vinylcopper(II), initially formed by the syn addition of β-(acyl)alkylcopper species to the acetylene, might cause the loss in the stereochemistry.

(24) Although it seems less likely, an alternative mechanism involving β-elimination accompanied with carbon–carbon bond breaking, followed by internal acylcupration may also be viable.



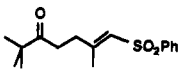
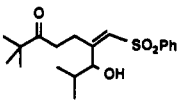
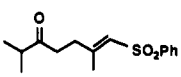
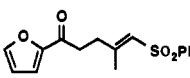
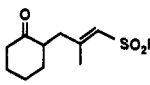
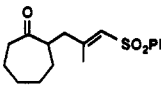
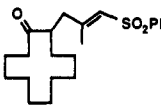
Next we examined sulfur-substituted acetylenes, such as acetylenic sulfides, sulfoxides, and sulfones. Among them, only acetylenic sulfones underwent the β-(acyl)alkyl transfer reaction. Notably, the addition proceeded in a completely regio- and stereoselective manner to give β-(acyl)alkylated vinylic sulfones **15** (eq 11). The results obtained under similar reaction conditions (CH_2Cl_2–H_2O plus $BuOSiMe_3$) as in the DMAD reactions are summarized in Table V. In all cases examined, the vinyl sulfones **15** were obtained as single geometric isomers.[26] The syn addition mechanism of the organocopper species across the triple bond, coupled with the lack of isomerization path, may account for the observed high stereoselectivity. The hydroxyl functionality in **14b** did not interfere with the addition. When the reaction was carried out using excess siloxycyclopropane and $Cu(BF_4)_2$, the yields were improved (runs 6 and 8). Even in such cases, no further transfer of β-(acyl)alkyls to the newly formed vinylic sulfone took place.



Mechanistic Aspects. In contrast to the rich chemistry of RCu^I, the reactivity patterns of RCu^{II} additions to both heteroatom and carbon based electrophiles involving carbon–carbon multiple bonds is still largely unexplored. Let us compare several features of the present organocopper species **5** to the well-known RCu^I species.[27] (1) In the present Cu^{II} systems, both coupling and addition reactions can be conducted in protic media. In other words, protonolysis of the organocopper species generated from **1** and a copper(II) salt is not a serious problem. This stands in sharp contrast to the well-known susceptibility of RCu^I species toward protic sources including alcohols. (2) The coupling reaction leading to a 1,6-diketone seems closely related to the coupling of alkylcopper(I) induced by oxidizing reagents, giving a bisalkane as the major product and an alkene as the byproduct.[13] (3) Only when a proton source is present in the reaction media can the present vinylcopper species be quenched. (4) The stereoselectivity of the addition of RCu^I to acetylenes is generally sensitive to the reaction temperature.[23,26] In contrast, the present β-(acyl)alkyl transfer to acetylenes occurs in highly stereoselective manner at ambient temperatures. (5) The present copper(II) reaction system imposes a larger limitation on acetylenes compared with RCu^I.[28,29] (6) It has been established that the thermal decomposition of alkylcopper(I) results in disproportionation to give a nearly equal amount of alkane and alkene.[30] However, in our case, no meaningful relationship between the formation of 2-methylene ketone and 2-methyl ketone was recognized.

As shown in Scheme I, the intermediacy of β-copper(II) ketones **5** is strongly suggested in the Cu^{II}-induced ring opening and dimerization of siloxycyclopropanes yielding 1,6-diketones. The formation of 2-methylene ketones can also be interpreted by assuming the intermediacy of **5**. Consistent with this proposal,

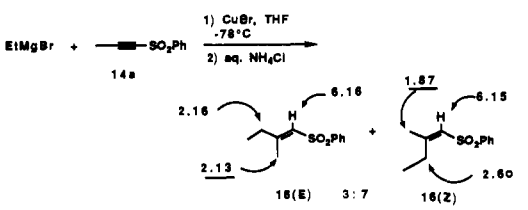
Table V. Cu(II)-Induced Desilylative Transfer of Siloxycyclopropanes to Acetylenic Sulfones[a]

run	substrate 1	acetylene 14	product 15		yield(%)[b]
1	1a	14a		15a	(70)
2	1a	14b		15x	(41)
3	 1o	14a		15o	66(55)
4	1c	14a		15c	45
5 6[c]	1g	14a		15g	76(52) 85
7 8[c]	1k	14a		15k	67 90
9	1n	14a		15n	40

[a] All reactions were carried out in CH_2Cl_2 at 25 °C for 2–3 h: **1**, 1.5 mmol; **14**, 1.8 mmol; $Cu(BF_4)_2$, 1.8 mmol; CH_2Cl_2, 3 mL; $BuOSiMe_3$, 0.2 mL; H_2O, 0.03 mL. In all cases, only *Z* isomers were obtained.[b] GC yields. Isolated yields are in parentheses. [c] 1.5 mol equiv of substrate and copper salt were used.

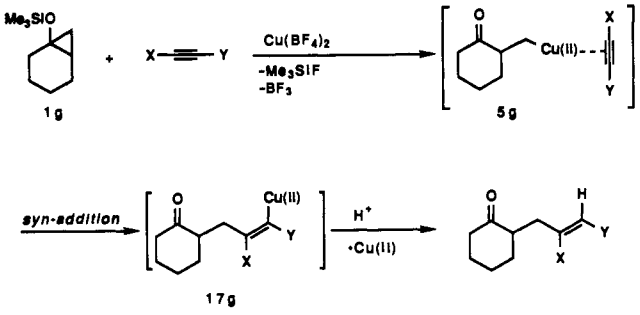
(25) Highly stereoselective syn reduction was observed in the reaction of $HSiEt_2Me/Cu^{II}(BF_4)_2$ with DMAD and acetylenic sulfones, see: (a) Ryu, I.; Kusumoto, N.; Ogawa, A.; Kambe, N.; Sonoda, N. *Organometallics* **1989**, 8, 2279. For the reduction, we proposed a mechanism involving the syn addition of $HCuBF_4$. Unlike the reduction system, we were unable to detect any H_2 in the reaction of **1k** with $Cu(BF_4)_2$. This fact may rule out a simple syn elimination pathway to give $HCuBF_4$. On the other hand, the possibility of the path involving oxidation of **5k** with or without a homolytic cleavage of the C–Cu bond by Cu(II) salts still remains as a possible alternative path. For the related references to this mechanism, see: (b) Kochi, J. K.; Subramanian, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 4855. (c) Groves, J. T. *Tetrahedron Lett.* **1975**, 3113. (d) Schreiber, S. L. *J. Am. Chem. Soc.* **1980**, *102*, 6165.

(26) Grignard cuprate addition to acetylenic sulfones is reported to proceed with low stereoselectivity, see: (a) Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 14. In order to obtain the reference ^1H NMR data for the structural assignment of **15**. We prepared compounds **16**(*E*) and **16**(*Z*) according to this literature method (see ref 26a). The structures of **16**(*E*) and **16**(*Z*) were assigned based on the previous observation that the *cis*-allylic methyl and methylene protons in vinyl sulfones resonate downfield from the corresponding trans isomer (see ref 26b). Chemical shifts of allylic methyls of **15** appeared in the range of 2.05–2.11, which were in good accordance with 2.13, the value of **16**(*E*). Thus, we concluded that adducts **15** have trans configurations. (b) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252.



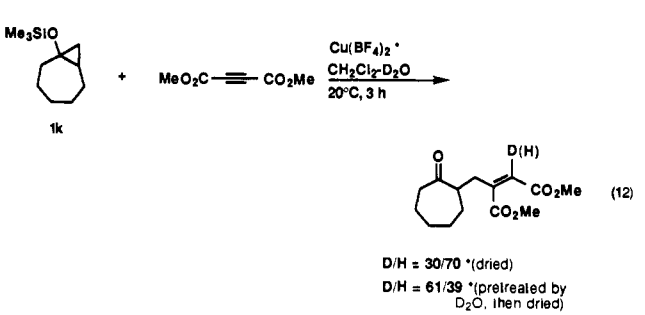
(27) For leading reviews on organocopper chemistry, see: (a) Lipshutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135. (b) Lipshutz, B. H. *Synthesis* **1987**, 325. (c) Posner, G. H. *Org. React.* **1975**, *22*, 253. (d) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley; New York, 1980. (e) Normant, J. F. *Pure Appl. Chem.* **1978**, *50*, 709. (f) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (g) Taylor, R. J. K. *Synthesis* **1985**, 364. (h) Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947.

Scheme III

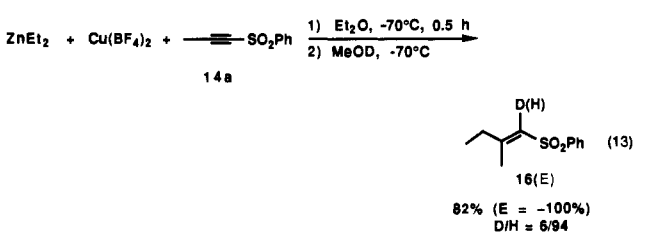


the rationale for the copper(II) mediated β-(acyl)alkyl transfer to acetylenes may also be explained by the syn addition of β-copper(II) ketone **5g** to acetylenes, leading to vinylic copper(II) **17g** (Scheme III). Subsequent in situ protonation of **17g** would afford 1:1 adducts with retention of configuration.[31] The negligible formation of 1,6-diketones in every case suggests that the β-(acyl)alkylcopper addition to acetylenes may be fast. The coordination of acetylenes to Cu^{II} salts may occur at an early stage. The overall transformation, which proceeds with a high degree of stereoselectivity, requires vinylcopper species as the precursors of the 1:1 adducts and this highly syn selective addition, together with the termination by protonation, fully precludes the free radical addition mechanism.

In order to gain further insight into the addition reaction to electron-deficient acetylenes, two additional experiments were carried out. The first is to verify the origin of vinylic proton, and the second is to verify whether similar addition behavior is observed for alkyl copper(II) generated by the reaction of $Cu(BF_4)_2$ with some organometals. Thus, the reaction of **1k** with $Cu(BF_4)_2$/DMAD in the presence of D_2O was carried out. Although we expected predominant deuteration at the vinylic position, the estimated value of deuterium incorporation by both mass and NMR spectra was unexpectedly low (30%) (eq 12). On the other hand, no deuterium incorporation was observed in the experiment using CD_2Cl_2 as the solvent. In an experiment using $Cu(BF_4)_2$ which had been dissolved in D_2O and further dried, we found that the deuterium incorporation doubled. Accordingly, it was concluded that for reactions conducted in CH_2Cl_2, the vinylic proton came not only from the water added to the reaction system but also from $Cu(BF_4)_2$.[32]



Next we examined the reaction of the organocopper species, generated in situ from $ZnEt_2$ and $Cu(BF_4)_2$, with acetylene sulfone **14a**, in the hope that a similar 1,2-addition would take place with high stereoselectivity. When an equimolar amount of $ZnEt_2$ was added dropwise to a mixture consisting of $Cu(BF_4)_2$, **14a**, and ether at −70 °C, the initial blue color of the suspension changed to orange. After the reaction mixture was stirred for 30 min, quenching with methanol at −70 °C gave ethyl substituted vinyl sulfone **16**(*E*) in 82% (eq 13). This result is noteworthy since the corresponding Grignard cuprate reaction exhibited only low *E*/*Z* selectivity.[26a] Notably, quenching the mixture with MeOD at −70 °C resulted in only 6% deuterio incorporation at the vinylic position. It seems likely that most of the quenching at the vinylic position was complete by water of hydration before MeOD addition. Detailed study on the addition of organocopper species, derived from organometallics and copper(II) salts, to carbon–carbon multiple bonds will soon be published.



Conclusions

For the generation of organocopper species, conventional transmetalation techniques using organometallic species and copper salts has generally been employed. Because of the electrophilic nature of the internal carbonyl, however, this conventional route is not applicable to organocopper species having an unmasked ketone functionality. In this paper, we have shown that the novel organocopper species having a β-(acyl)alkyl moiety can be generated from siloxycyclopropanes and copper(II) fluoroborate. Through the organocopper intermediates, two types of synthetically useful transformations have been developed: (i) the oxidative coupling β to a carbonyl to give symmetric 1,6-diketones and (ii) the stereoselective transfer of β-(acyl)alkyls to electron-deficient acetylenes to give alkenes containing ketone functionality. The former reaction proceeds in an oxidative manner, whereas the latter reaction proceeds in a nonoxidative manner. The procedures for both transformations are simple to perform. The latter procedure is unique, since water is added to ensure proton quenching in situ. The mode of siloxycyclopropane ring cleavage is highly regioselective at the least substituted carbons, which is in good accordance with the cases of isolated β-metallo ketones, prepared in a similar way.[6] All of these observations lead us to propose the intermediacy of the rather unfamiliar divalent β-copper ketone species. It should be noted that the recent accomplishment of the enantioselective synthesis

(28) For examples of the addition of organocopper(I) species to acetylenes, see: (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Org. Chem.* **1979**, *44*, 1744. (b) Alexakis, A.; Commercon, A.; Coulentianos, C.; Normant, J. F. *Tetrahedron* **1984**, *40*, 715. (c) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 905. (d) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 1363. (e) Crimmins, M. T.; Mascarella, S. W.; DeLoach, J. A. *J. Org. Chem.* **1984**, *49*, 3033. (f) Rahman, M. T.; Saha, S. L.; Hansson, A.-T. *J. Organomet. Chem.* **1980**, *199*, 9. (g) Linderman, R. J.; Lonikar, M. S. *J. Org. Chem.* **1988**, *53*, 6013. (h) Vermeer, P.; Meijer, J.; Eylander, Mrs. C. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 240. (i) Vermeer, P.; Graaf, C. de.; Meijer, I. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 24. (j) Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 14. (k) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252. (l) Westmijze, H.; Kleijn, H.; Vermeer, P. *Synthesis* **1978**, 454. (m) Lewis, D. E.; Rigby, H. L. *Tetrahedron Lett.* **1985**, *26*, 3437.

(29) For example, treatment of **1k** with methyl propiolate in the presence of $Cu(BF_4)_2$ salt in ethanol immediately gave a yellow precipitate, hardly soluble in ether, without giving any addition product. Other acetylenes, which can undergo organocopper(I) additions,[28] such as 3-hexyne, phenylacetylene, 3-methylphenylthioacetylene, and methylacetylenic sulfoxide, were unsuccessful. Cf.: There have been some reports on the synthetic use of β-copper(I) ester species, generated from β-zinc esters and Cu(I)X, which work as usual copper(I) reagents for Michael addition, allylation, etc., see: (a) Reference 5b. (b) Ochiai, H.; Tamaru, Y.; Tsubaki, K.; Yoshida, Z. *J. Org. Chem.* **1987**, *52*, 4418. (c) Tamaru, Y.; Tanigawa, H.; Yamamoto, T.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 351.

(30) (a) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1426. (b) Wada, K.; Kochi, J. *J. Am. Chem. Soc.* **1970**, *92*, 6656.

(31) The reaction pathway leading to higher boiling byproducts (2:1 and 2:2 adducts) would be also explained in terms of the oxidative coupling pathway from **5** and **17**.

(32) Further study is necessary to determine the exact amount of water included in *dried* $Cu(BF_4)_2$. It has been reported that dehydration from a hexahydrate of $Cu(BF_4)_2$ to give a tetrahydrate takes place easily at reduced pressure at room temperature, while at 60 °C some decomposition competes with dehydration. See: El'kenbard, A. G. *Sbornik Statei po Obschei Khim.* **1953**, *2*, 1239. We thank Dr. Vladimir Grushin at the University of Ottawa for his kind help in translating this paper.

of cyclopropanol by Tai and Sugimura[33] will enhance the potential synthetic utility of the present β-(acyl)alkyl transfer reactions. From the viewpoint of organocopper chemistry, the present work represents a novel reaction of organocopper(II) species, an alkyne insertion into carbon–copper(II) bond, while such a transformation has been well recognized in the isolable methylplatinum(II) chemistry.[34]

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen in oven-dried glassware. Flash chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Preparative TLC was carried out using Merck Kieselgel 60. Copper tetrafluoroborate ($Cu(BF_4)_2$) was obtained from Alfa Inc. and prior to use it was dried over P_2O_5 under reduced pressure with heat (50 °C, 1 mmHg, overnight). Other copper salts and DMAD were obtained from Nacalai Tesque Inc. Methyl 3-pivaloylacetylene carboxylate was prepared by dehydrobromination of methyl 2,2-dibromo-3-pivaloylpropionate,[35] by triethylamine in refluxing benzene. Methylacetylenic sulfone **14a** was prepared according to the method of Truce.[36] Acetylenic sulfone **14b** was prepared by the condensation of lithium salt of phenylthioacetylene[37] with isopropyl aldehyde followed by MCPBA oxidation. Dichloromethane was distilled from calcium hydride. *n*-Butyl trimethylsilyl ether was prepared from *n*-butanol by silylation with $Me_3SiCl/NEt_3/C_6H_6$ under reflux. Siloxycyclopropanes **1** were prepared by the reaction of enol silyl ethers and either of the zinc carbenoid reagents ($CH_2I_2/Zn(Cu)$ or $CH_2I_2/ZnEt_2$) according to our previously published method.[5a] ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer at 100 and 25 MHz, respectively, or on a Model JNM-GX67S spectrometer at 270 and 68 MHz, respectively, and were referenced to tetramethylsilane as the internal standard. IR spectra were recorded on a Shimadzu IR-400 spectrometer or on a Perkin-Elmer 1610 FTIR spectrometer. The mass spectra were obtained on a Hitachi mass spectrometer Model RMU-6E. Elemental analyses were performed by the Analytical Center, Faculty of Engineering, Osaka University. GC data were obtained with a Shimadzu GC-3BF equipped with a flame ionizing detector. Unless otherwise indicated, a stainless steel column (3 m × 3.8 mm or 1.5 m × 3.8 mm) was used, packed with 5% OV-1 on Uniport KS, 10% SE-30 on Chromosorb W, or 15% DEGS on Chromosorb W.

Reaction of 1-(Trimethylsiloxy)bicyclo[5.1.0]octane (1k) with CuF_2 in MeOH. Into a flame-dried flask were placed CuF_2 (0.406 g, 4 mmol), MeOH (5 mL), and internal standard (*n*-tetradecane and *n*-dodecosane). After warming to 30 °C, siloxycyclopropane **1k** (0.396 g, 2 mmol) was added in one portion, and the reaction mixture was stirred for 12 h at 30 °C. The dark brown reaction mixture was diluted with ether and then treated with aqueous saturated NH_4Cl. The organic layer was analyzed by GC (DEGS, 1.5 m, 90 °C, 3.17 (n-$C_{14}H_{30}$), 5.17, and 8.10 min) (10% SE-30 on Chromosorb W, 1.5 m, 190 °C, 14.17 and 18.7 min (n-$C_{22}H_{46}$)). The two peaks with the retention time of 5.17 and 8.10 min were identified as 2-methylenecycloheptanone (**6k**)[6b] and 2-methylcycloheptanone (**7k**), whose yields were estimated to be 71% and 3%, respectively. The peak with the retention time of 14.17 was identified with 1,6-diketone **4k**, whose yield was estimated to be 26%. The reaction of **1k** with $Cu(BF_4)_2$ in EtOH and $CuCl_2$ in MeOH were similarly carried out and analyzed.

Reaction of 1-(Trimethylsiloxy)bicyclo[4.1.0]heptane (1g) with $Cu(BF_4)_2$ under Several Reaction Conditions (Table I). Into a flame-dried flask was placed $Cu(BF_4)_2$ (0.238 g, 1 mmol or indicated amounts in Table I), solvent (1 mL), and internal standard (*n*-eicosane). At 15 °C, siloxycyclopropane **1g** (0.184 g, 1 mmol) was added in one portion. After stirring for 0.5 h at 15 °C, the reaction mixture was diluted with ether and then treated with aqueous saturated NH_4Cl. The organic layer was analyzed by GC and the yield of 1,6-diketone **4g** was estimated in each run (10% SE-30 on Chromosorb W, 1.5 m, 190 °C, 12.7 (**4g**) and 18.7 min (n-$C_{22}H_{46}$)).

1,2-Dicycloheptan-2-one-1-ylethane (4k). To the stirred suspension of $Cu(BF_4)_2$ (1.19 g, 5 mmol) and anhydrous ether (10 mL), siloxycyclopropane **1k** (0.99 g, 5 mmol) was added in one portion at 15 °C. The initial blue color of the copper salt gradually turned green and finally dark brown. After 30 min, the reaction mixture was treated with aqueous saturated NH_4Cl (50 mL) and extracted with ether (40 mL, then 2 × 10 mL). The combined extracts were washed with aqueous saturated $NaHCO_3$ (20 mL) and then with water (20 mL). The organic extracts were dried over anhydrous $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography (silica gel, C_5H_{12}/Et_2O, 70:30) to give 1,6-diketone **4k** (0.438 g, 70%), which was obtained as a mixture of meso and racemic isomers: mp 45.5–49.0 °C (49.0–51.5 °C after recrystallization from EtOH); IR (Nujol) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–2.16 (m, 20H), 2.26–2.96 (m, prominent peak at 2.42, 6H); ^{13}C NMR ($CDCl_3$) δ 216.15, 52.22 (d, α-C of major isomer), 52.04 (d, α-C of minor isomer), 42.84 (major), 42.67 (minor), 31.40 (major), 31.00 (minor), 29.99 (major), 29.49 (minor), 29.41 (minor), 29.20 (major), 28.48 (major), 24.35 (minor), 24.17 (major); MS *m/e* (rel intensity) 250 (3 M^+), 232 (2), 168 (20), 153 (19), 125 (29), 118 (24), 93 (41), 79 (31), 67 (21), 55 (100), 41 (36). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.54; H, 10.52.

General Procedure For Preparation of 1,6-Diketones 4a–l. The 1,6-diketones **4a–l** were prepared in a similar fashion as in **4k**, from the corresponding siloxycyclopropanes **1a–l**.

1,6-Di-*tert*-butyl-1,6-hexadione (4a): mp 52.5–53.5 °C; IR (Nujol) 1702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 18H), 1.40–1.60 (m, prominent peak at 1.51, 4H), 2.36–2.60 (m, prominent peak at 2.48, 4H); ^{13}C NMR ($CDCl_3$) δ 215.73, 44.03, 36.34, 26.37, 23.55; MS *m/e* (rel intensity) 226 (5, M^+), 169 (28), 151 (9), 123 (100), 113 (8), 109 (16), 85 (21), 81 (8), 57 (96), 43 (29), 41 (31), 29 (24); HRMS (*m/e*) calcd for $C_{14}H_{26}O_2$: 226.1934, found 226.1918.

1,6-Diphenyl-1,6-hexadione (4b): mp 105–107.5 °C (lit.[17b] 105 °C); IR (Nujol) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64–2.20 (m, prominent peak at 1.84, 4H), 2.86–3.20 (m, prominent peak at 3.05, 4H), 7.05–7.60 (m, 6H), 7.75–8.15 (m, 4H); MS *m/e* (rel intensity) 260 (2, M^+), 248 (2), 238 (3), 147 (13), 146 (86), 145 (10), 133 (6), 120 (31), 106 (14), 105 (100), 78 (6), 77 (72), 51 (14).

1,6-Di-2-furanyl-1,6-hexadione (4c): mp 128–129.5 °C (after recrystallized from $CHCl_3$); IR (Nujol) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.10 (m, prominent peak at 1.80, 4H), 2.70–3.05 (m, prominent peak at 2.87, 4H), 6.56 (dd, J = 5, 2 Hz, 2H), 7.20 (d, J = 5 Hz, 2H), 7.60 (d, J = 2 Hz, 2H); MS *m/e* (rel intensity) 246 (4, M^+), 218 (4), 136 (38), 110 (85), 95 (100). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.91; H, 5.34.

1,6-Di-2-thiofuranyl-1,6-hexadione (4d): mp 125–126 °C (after recrystallized from $Et_2O/CHCl_3$); IR (Nujol) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–2.10 (m, prominent peak at 1.83, 4H), 2.70–3.20 (m, prominent peak at 2.95, 4H), 7.11 (dd, J = 5, 4 Hz, 2H), 7.48–7.75 (m, 4H); MS *m/e* (rel intensity) 278 (5, M^+), 250 (3), 152 (46), 16 (69), 111 (100); HRMS (*m/e*) calcd for $C_{14}H_{14}O_2S_2$: 278.0435, found 278.0449.

1,6-Di-*o*-anisyl-1,6-hexadione (4e): mp 103–104.5 °C (after recrystallized from MeOH); IR (Nujol) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46–2.00 (m, prominent peak at 1.74, 4H), 2.83–3.28 (m, prominent peak at 3.01, 4H), 3.92 (s, 6H), 6.79–7.19 (m, 4H), 7.19–7.84 (m, 4H); MS *m/e* (rel intensity) 326 (1, M^+), 277 (4), 176 (31), 163 (4), 150 (13), 136 (8), 135 (100), 98 (6), 77 (16). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.21; H, 6.78.

1,2-Dicyclopentan-2-one-1-ylethane (4f). Obtained as a mixture of diastereomeric isomers: mp 76–79.5 °C (84.5–86.0 °C after recrystallized from EtOH); IR (Nujol) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.50 (m); ^{13}C NMR ($CDCl_3$) δ 220.75 (s), 49.16 (d, α-C of a major isomer), 48.64 (d, α-C of a minor isomer), 38.11 (t, α′-carbon of a major isomer), 37.78 (t, α′-carbon of a minor isomer), 29.34, 29.08, 27.71, 27.13, 20.44 (t); MS *m/e* (rel intensity) 194 (7, M^+), 176 (3), 110 (87), 98 (30), 97 (7), 95 (16), 84 (100), 83 (43), 55 (23), 41 (26). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.93; H, 9.48.

1,2-Dicyclohexan-2-one-1-ylethane (4g).[17a] Obtained as a mixture of diastereomeric isomers: mp 77.5–80 °C; IR (Nujol) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98–2.60 (m); ^{13}C NMR ($CDCl_3$) δ 213.08 (s), 50.91 (d, α-C of a major isomer), 50.58, 41.81 (t, α′-carbon of a major isomer), 33.89, 33.43, 32.23, 31.25, 27.84, 27.13, 26.54, 24.66; MS *m/e* (rel intensity) 222 (19, M^+), 204 (7), 147 (11), 134 (13), 112 (26), 111 (15), 98 (100), 97 (15), 83 (15), 70 (12), 67 (14), 55 (20), 41 (20).

1,2-Di-1-methylcyclohexan-2-one-1-ylethane (4i). Obtained as a mixture of diastereomeric isomers: bp 128–133 °C (0.42 Torr); IR (Nujol) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (s, 6H), 1.08–2.08 (m, 16H), 2.08–2.56 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 214.77 (s), 47.66 (d, α-C), 39.02, 38.69, 38.24 (t), 30.90, 26.87, 22.19, 21.74, 20.44; MS *m/e* (rel intensity) 250 (2, M^+), 232 (trace), 139 (3), 138 (3), 125 (2), 113 (10), 97 (8), 83

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(5), 81 (4), 69 (5), 67 (6), 55 (14), 41 (11). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.46; H, 10.62.

1,2-Di-3,4-benzocyclohexan-2-one-1-ylethane (4j). Obtained as a mixture of diastereomeric isomers: mp 116–117.5 °C; IR (Nujol) 1683, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40–2.68 (m, 10H), 2.88–3.20 (m, 4H), 7.14–7.58 (m, 6H), 7.94–8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 199.89 (s), 143.82 (s), 132.97 (s), 132.32, 128.49, 127.19, 126.34, 47.73 (d, α-C of a major isomer), 47.34, 27.91, 27.06, 26.35; MS *m/e* (rel intensity) 318 (3, M$^+$), 300 (4), 173 (12), 172 (37), 160 (10), 159 (12), 147 (13), 146 (100), 145 (19), 131 (34). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.95; H, 6.96.

1,2-Dicyclooctan-2-one-1-ylethane (4l). Obtained as a mixture of diastereomeric isomers: mp 48–55.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.65–2.15 (m, 24H), 2.15–2.67 (m, two prominent peaks at 2.27 and 2.32, 6H); ^{13}C NMR ($CDCl_3$) δ 219.26 (s), 219.06 (s), 50.19 (d, α-C of one isomer), 50.00 (d, α-C of the other isomer), 42.20 (t, α'-carbon of one isomer), 41.29 (t, α'-carbon of the other isomer), 32.72, 31.87, 30.05, 29.60, 27.06, 26.80, 25.24, 25.11, 24.66, 24.34; IR (Nujol) 1700 cm^{-1}; MS *m/e* (rel intensity) 278 (25, M$^+$), 260 (8), 152 (70), 139 (16), 126 (91), 98 (100), 84 (42), 69 (39), 67 (40), 55 (88), 41 (79). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.26; H, 10.98.

Reaction of 1-(Trimethylsiloxy)bicyclo[5.1.0]octane (1k) with $Cu(BF_4)_2$ in the Presence of DMAD under Several Reaction Conditions (Table III). Into a flame-dried flask were placed $Cu(BF_4)_2$ (1–1.2 mmol), DMAD (1–1.2 mmol (0 mmol for runs 2, 7, and 8)), anhydrous solvent (2 mL), and the internal standard (*n*-tetradecane and *n*-dodecosane) under atmosphere of nitrogen. In runs 8–12, additives and/or water were added prior to the reaction, whose amounts were specified in Table III. To this stirred mixture 0.198 g (1 mmol) of siloxycyclopropane **1k** was added in one portion at 20 °C. After being stirred for 2–5 h the reaction mixture was partitioned between ether and saturated aqueous ammonium chloride solution. The ether layer was analyzed by GC (DEGS, 1.5 m, 90 °C, 3.17 (*n*-$C_{14}H_{30}$), 5.17, and 8.10 min) (10% SE-30 on Chromosorb W, 1.5 m, 190 °C, 14.17 and 18.7 min (*n*-$C_{22}H_{46}$)). The peaks with the retention time of 5.17, 8.10, and 25.2 min were identified as 2-methylenecycloheptanone (**6k**), 2-methylcycloheptanone (**7k**), and 2-(ethoxymethyl)-cycloheptanone (**6k'** (X = OEt)), respectively. The peaks with the retention time of 7.04 and 14.17 were identified to be dimethyl 2-(2'-ketocycloheptyl)methylmaleate (**7k**) and 1,6-diketone **4k**, respectively.

Dimethyl 2-(2-Oxocycloheptyl)methylmaleate (10k). To a stirred suspension of $Cu(BF_4)_2$ (0.238 g, 1 mmol), DMAD (0.156 g, 1.1 mmol), *n*-BuOSiMe$_3$ (0.2 mL), and water (0.02 mL) in CH_2Cl_2 (2 mL) was added siloxycyclopropane **1k** (0.198 g, 1 mmol) in one portion at 20 °C. The initial blue color of the heterogeneous solution was gradually changed to green, and insoluble gum-like precipitates were formed in the bottom of the reaction flask. The stirring was continued for 3 h at 20 °C. Then the reaction mixture was diluted with 30 mL of ether and treated with saturated aqueous NH_4Cl. The organic layer was separated and washed with another 20 mL of saturated aqueous NH_4Cl. The combined aqueous layer was extracted with two 20-mL portions of ether. The combined organic layers were washed with 20 mL of saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting oil was purified by PTLC (silica gel, ether/hexane, 80:20) to give **10k** (0.188 g, 70%) as a colorless oil: IR (neat) 1734, 1704, 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15–1.95 (m, 8H), 2.20–2.62 (m, 3H), 2.75–2.93 (m, 2H), 3.71 (s, 3H), 3.82 (s, 3H), 5.83 (s, 1H); MS *m/e* (rel intensity) 268 (M$^+$ 3), 236 (65), 208 (33), 204 (35), 177 (46), 149 (100). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.42; H, 7.56.

General Procedure for Preparation of Dimethyl 2-(2-(Oxoalkyl))-maleates 10a–o. The dimethyl maleates **10a–o** were obtained in a similar fashion as in **10k**, from the corresponding siloxycyclopropanes **1a–o** and DMAD. Unless otherwise noted, *n*-BuOSiMe$_3$ was used as the additive. The products were obtained as colorless oils after purification by PTLC (silica gel, ether/hexane, 80:20).

Dimethyl 2-(2-Pivaloyl)ethylmaleate (10a): IR (neat) 1740, 1731, 1710, 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 9H), 2.61 (t, J = 7 Hz, 2H), 2.73 (t, J = 7 Hz, 2H), 3.72 (s, 3H), 3.82 (s, 3H), 5.88 (s, 1H); MS *m/e* (rel intensity) 256 (M$^+$ 1), 224 (25), 199 (28), 181 (23), 167 (30), 165 (21), 140 (23), 139 (100), 111 (20), 57 (57). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.84; H, 7.88.

Dimethyl 2-(2-Benzoyl)ethylmaleate (10b): IR (neat) 1740, 1738, 1699, 1651, 1600 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.48 (t, J = 6 Hz, 2H), 3.10 (t, J = 6 Hz, 2H), 3.64 (s, 3H), 3.72 (s, 3H), 5.84 (s, 1H), 7.26–7.60 (m, 3H), 7.81–8.00 (m, 2H); MS *m/e* 276 (M$^+$ 2), 244 (31), 185 (24), 157 (20), 105 (100), 77 (25). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84. Found: C, 65.27; H, 5.81.

Dimethyl 2-(*o*-Anisoyl)ethylmaleate (10e): IR (neat) 1740, 1737, 1680, 1655, 1600 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.62 (t, J = 6 Hz, 2H), 3.08 (t, J = 6 Hz, 2H), 3.62 (s, 3H), 3.71 (s, 3H), 3.86 (s, 3H), 5.77 (s, 1H), 6.75–7.08 (m, 2H), 7.30–7.80 (m, 2H); MS *m/e* 306 (M$^+$ 4), 274 (19), 215 (16), 189 (16), 135 (100)). Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.82; H, 5.95.

Dimethyl 2-(2-Oxocyclopentyl)methylmaleate (10f): IR (neat) 1730, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–2.40 (m, 8H), 2.90 (d-like, J = 12 Hz, 1H), 3.73 (s, 3H), 3.82 (s, 3H), 5.86 (s, 1H); MS *m/e* (rel intensity) 240 (M$^+$ 1), 208 (41), 176 (100), 149 (43), 121 (41). Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.22; H, 6.75.

Dimethyl 2-(2-Oxocyclohexyl)methylmaleate (10g): IR (neat) 1740, 1737, 1720, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20–2.48 (m, 9H), 2.48–2.64 (m, 1H), 2.95 (dd, J = 4, 14 Hz, 1H), 3.76 (s, 3H), 3.82 (s, 3H), 5.80 (s, 1H); MS *m/e* (rel intensity) 254 (M$^+$ 3), 222 (65), 190 (93), 163 (75), 135 (100). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.64; H, 7.21.

Dimethyl 2-(3-Methyl-2-oxocyclohexyl)methylmaleate (10h). This compound was prepared from a 1:1 cis and trans mixture of the siloxycyclopropane **1h** and DMAD following the general procedure. The product **10h** was obtained as a 1:1 mixture of two diastereomers: IR (neat) 1740, 1731, 1715, 1654 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (d, J = 7 Hz, 1.5H), 1.15 (d, J = 7 Hz, 1.5H), 1.20–2.80 (m, 9H), 2.88 (dd, J = 6, 14.5 Hz, 0.5H), 2.95 (dd, J = 6, 14.5 Hz, 0.5H), 3.72 (s, 3H), 3.82 (s, 3H), 5.85 (s, 1H); MS *m/e* (rel intensity) 268 (M$^+$ 5), 236 (100), 204 (83), 193 (51), 177 (86), 149 (51). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.81; H, 7.63.

Dimethyl 2-(1-Methyl-2-oxocyclohexyl)methylmaleate (10i). *c*-HexOSiMe$_3$ was used in place of *n*-BuOSiMe$_3$. The product was purified by flash chromatography (silica gel, ether/hexane, 70:30): IR (neat) 1740, 1738, 1715, 1648 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.10 (s, 3H), 1.45–2.00 (c, 6H), 2.15–2.40 (m, 2H), 2.34, 2.75 (ABq, J = 14 Hz, 2H), 3.63 (s, 3H), 3.65 (s, 3H), 5.72 (s, 1H); MS *m/e* (rel intensity) 268 (M$^+$ 21), 236 (51), 133 (71), 126 (91), 55 (100). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.96; H, 7.61.

2,2-Dimethylcyclohexanone (7i)/3-Methyl-2-cycloheptenone (6i)/3-Methylenecycloheptanone (6i'). Compounds **7i**, **6i**, and **6i'** were formed as byproducts of the reaction of siloxycyclopropane **1i** and DMAD which mainly gave **10i** as indicated above. The residue obtained from the less polar fraction from the column was subjected to PTLC separation (silica gel, AcOEt/hexane, 30:70) to give the pure products: ^{1}H NMR of **7i** ($CDCl_3$) δ 1.11 (s, 6H), 1.50–1.94 (m, 6H), 2.31–2.50 (m, 2H); ^{1}H NMR of **6i** ($CDCl_3$) δ 1.70–1.84 (m, 4H), 1.96 (s, 3H), 2.37–2.46 (m, 2H), 2.51–2.62 (m, 2H), 5.93 (s, 1H); ^{1}H NMR of **6i'** ($CDCl_3$) δ 1.58–1.94 (m, 4H), 2.19–2.32 (m, 2H), 2.40–2.50 (m, 2H), 3.19 (s, 2H), 4.88 (s, 1H), 4.94 (s, 1H); MS of **7i** *m/e* 126 (M$^+$), 82, 69; MS of **6i** *m/e* 124 (M$^+$), 109, 95, 72, 67; MS of **6i'** *m/e* 124 (M$^+$), 96, 81.

Dimethyl 2-(2-Oxo-3,4-benzocyclohexyl)methylmaleate (10j). *c*-HexOSiMe$_3$ was used in place of *n*-BuOSiMe$_3$. The product was purified by flash chromatography (silica gel, ether/hexane, 70:30): IR (neat) 1730, 1685, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70–1.95 (c, 1H), 2.25–2.34 (c, 1H), 2.40 (dd, J = 14.3, 8.91 Hz, 1H), 2.65–2.85 (m, 1H), 2.90–3.15 (c, 2H), 3.26 (dd, J = 14.3, 2.8 Hz, 1H), 3.62 (s, 3H), 3.74 (s, 3H), 5.74 (s, 1H), 7.20–7.35 (m, 2H), 7.48 (t, J = 8 Hz, 1H), 8.01 (d, J = 8 Hz, 1H); FABMS *m/e* 303 (M$^+$ + 1). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.70; H, 6.06.

Dimethyl 2-(2-Oxocyclooctyl)methylmaleate (10l): IR (neat) 1740, 1730, 1700, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95–2.15 (m, 10H), 2.20–2.36 (c, 2H), 2.50 (ddd, J = 3, 8, 14 Hz, 1H), 2.79 (dd, J = 8, 14 Hz, 1H), 2.90–3.05 (c, 1H), 3.70 (s, 3H), 3.83 (s, 3H), 5.81 (s, 1H); MS *m/e* (rel intensity) 282 (M$^+$ 5), 250 (100), 218 (47), 191 (54), 163 (60). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 64.09; H, 8.04.

Dimethyl 2-(2-Oxocyclododecyl)methylmaleate (10n): IR (neat) 1743, 1738, 1718, 1655 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.90–3.00 (m, 23H), 3.64 (s, 3H), 3.71 (s, 3H), 5.73 (s, 1H); MS *m/e* (rel intensity) 338 (M$^+$ 21), 308 (100), 274 (41), 126 (47), 55 (88), 41 (92). Anal. Calcd for $C_{19}H_{30}O_5$: C, 67.43; H, 8.94. Found: C, 67.17; H, 9.03.

(*E*)- and (*Z*)-8-(2-Furanyl)-5-(methoxycarbonyl)-2,2-dimethyloct-4-ene-3,8-dione (13). To a stirred suspension of $Cu(BF_4)_2$ (0.60 g, 2.5 mmol), methyl (3-pivaloyl)propiolate (0.39 g, 2.2 mmol), *n*-BuOSiMe$_3$ (0.3 mL), and water (0.04 mL) in 4 mL of CH_2Cl_2 was added the siloxycyclopropane **1c** (0.392 g, 2 mmol) in one portion at 20 °C. The initial blue color of the heterogeneous solution was gradually changed to green, and insoluble gum-like precipitates were formed in the bottom of the reaction flask. The stirring was continued for 3 h at 20 °C. After usual workup, the resulting oil was subjected to flash chromatography (silica gel, ether/hexane, 70:30). The faster fraction contained *E* isomer

of **13** (0.052 g, 9%): IR (neat) 1725, 1680, 1620 cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (s, 9H), 2.80–3.00 (m, 4H), 3.77 (s, 3H), 6.45 (dd, J = 4, 1.2 Hz, 1H), 7.08 (d, J = 4 Hz, 1H), 7.28 (s, vinylic H of C4), 7.48 (br s, 1H). Further elution of the column gave the Z isomer of **13** (0.298 g, 51%): IR (neat) 1725, 1680, 1620 cm^{-1}; ^1H NMR (CCl_4) δ 1.10 (s, 9H), 2.64 (t, J = 7 Hz, 2H), 2.98 (t, J = 7 Hz, 2H), 3.68 (s, 3H), 6.40–6.55 (m, 2H, including vinylic H of C_4), 7.12 (d, J = 4 Hz, 1H), 7.53 (br s, 1H); mass spectrum m/e (rel intensity) 292 (M^+ 1), 260 (21), 236 (31), 276 (47), 275 (50), 110 (40), 95 (80), 57 (100). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.67; H, 7.06. The structure of the adduct **13**(Z) was confirmed by the NOE enhancement of vinylic proton (13%) on irradiation of the *tert*-butyl group. **13**(E) was identified with the product obtained by the acid-promoted isomerization of **13**(Z) by CF_3COOH in CCl_4. The major isomer was determined to be Z on the basis that the vinylic proton resonated at higher field.

(*E*)-[2-(2-Pivaloyl)ethyl]vinyl Phenyl Sulfone (15a). To a stirred suspension of $Cu(BF_4)_2$ (0.428 g, 1.8 mmol), **14a** (0.324 g, 1.8 mmol), *n*-$BuOSiMe_3$ (0.2 mL), and water (0.03 mL) in CH_2Cl_2 (3 mL) was added siloxycyclopropane **1a** (0.280 g, 1.5 mmol) in one portion at 20 °C. The initial blue color of the heterogeneous solution was gradually changed to green, and insoluble gum-like precipitates were formed in the bottom. The stirring was continued for 3 h at 20 °C. After usual workup, the resulting colorless oil was purified by PTLC (silica gel, CH_2Cl_2/ether/hexane, 35:15:50) to give **15a** (0.308 g, 70%): IR (neat) 1700, 1625, 1300, 1140 cm^{-1}; ^1H NMR (CCl_4) δ 1.06 (s, 9H), 2.11 (s, 3H), 2.36 (t, J = 7 Hz, 2H), 2.61 (t, J = 7 Hz, 2H), 6.20 (s, 1H), 7.40–7.60 (m, 3H), 7.80–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 213.20, 156.53, 142.33, 133.01, 129.11, 127.00, 126.40, 44.00, 34.19, 33.75, 36.28, 17.93; MS m/e (rel intensity) 295 (M^+ trace), 237 (13), 209 (10), 193 (25), 175 (5), 153 (100), 141 (80), 77 (82), 57 (80). Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.28; H, 7.53. Found: C, 65.39; H, 7.55.

General Procedure for Preparation of Dimethyl 2-(2-(Acylalkyl))-vinyl Phenyl Sulfones 15a–x. The vinylic sulfones were obtained in a similar fashion as in **15a**, from the corresponding siloxycyclopropanes and acetylenic sulfones. Except for **15x** and **15n**, the products were obtained as colorless oils.

(*Z*)-2-(2-Pivaloyl)ethyl-2-(1-hydroxy-2-methyl)propylvinyl Phenyl Sulfone (15x): mp 86–88 °C; IR (Nujol) 3460, 1705, 1620, 1280, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (d, J = 6.6 Hz, 3H), 1.06 (br s, 12H), 1.50–2.95 (m, 6H), 4.80–5.11 (m, 1H), 6.07 (s, 1H), 7.40–7.91 (m, 5H); MS m/e (rel intensity) 334 (M^+ 1), 309 (8), 277 (12), 211 (56), 135 (36), 125 (100), 77 (38), 57 (66). Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01. Found: C, 64.54; H, 7.83.

(*E*)-2-(4-Methyl-3-oxopentyl)-1-propenyl Phenyl Sulfone (15o): IR (neat) 1712, 1630, 1305, 1147 cm^{-1}; ^1H NMR (CCl_4) δ 0.97 (d, J = 6 Hz, 6H), 2.08 (s, 3H), 2.17–2.75 (m, 5H), 6.06 (s, 1H), 7.40–7.60 (m, 3H), 7.76–7.90 (m, 2H); MS m/e (rel intensity) 280 (M^+ trace), 237 (3), 209 (8), 139 (100), 77 (70), 43 (68). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.11; H, 7.24.

(*E*)-[3-(2-Furanyl)-3-oxopropyl]-1-propenyl Phenyl Sulfone (15c): IR (neat) 1678, 1630, 1290, 1142 cm^{-1}; ^1H NMR (CCl_4) δ 2.14 (s, 3H), 2.49 (t, J = 8 Hz, 2H), 2.96 (t, J = 8 Hz, 2H), 6.22 (s, 1H), 6.50–6.60 (m, 1H), 7.17 (d, J = 3 Hz, 1H), 7.40–7.68 (m, 4H), 7.80–7.96 (m, 2H); MS m/e (rel intensity) 304 (M^+ trace), 209 (trace), 164 (1), 163 (100), 95 (6), 77 (2). Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30. Found: C, 63.18; H, 5.33.

(*E*)-2-(2-Oxocyclohexyl)methyl-1-propenyl Phenyl Sulfone (15g): IR (neat) 1710, 1625, 1300, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–2.80 (m, 14H, including 2.05 (s, 3H)), 6.16 (s, 1H), 7.40–7.68 (m, 3H), 7.80–7.96 (m, 2H); MS m/e (rel intensity) 292 (M^+ trace), 151 (100), 135 (9), 77 (15). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.81; H, 6.98.

(*E*)-2-(2-Oxocycloheptyl)methyl-1-propenyl Phenyl Sulfone (15k): IR (neat) 1700, 1630, 1305, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.20 (m, 10H), 2.06 (s, 3H), 2.30–2.80 (m, 3H), 6.16 (s, 1H), 7.40–7.65 (m, 3H), 7.80–7.90 (m, 2H); MS m/e (rel intensity) 306 (M^+ trace), 209 (1), 165 (100), 149 (10), 147 (11), 83 (24). Anal. Calcd for $C_{17}H_{22}O_4S$: C, 66.64; H, 7.24. Found: C, 66.38; H, 7.21.

(*E*)-2-(2′-Ketocyclododecyl)methyl-1-propenyl Phenyl Sulfone (15n). This compound was prepared from siloxycyclopropane **1n** and methyl acetylenic sulfone **14a** in a similar procedure as described for **15a**: mp 58–62 °C; IR (neat) 1715, 1630, 1390, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00–1.80 (m, 18H), 2.07 (s, 3H), 2.00–2.90 (m, 5H), 6.17 (s, 1H), 7.40–7.68 (m, 3H), 7.80–7.96 (m, 2H); MS m/e (rel intensity) 376 (M^+ trace), 235 (100), 95 (19), 81 (23), 55 (30). Anal. Calcd for $C_{24}H_{32}O_3S$: C, 70.17; H, 8.57. Found: C, 70.00; H, 8.64.

Dimethyl 1-Deuterio-2-(2-oxocycloheptyl)methylmaleate by Reaction of Siloxycyclopropane 1k with $Cu(BF_4)_2$ in the Presence of DMAD and D_2O. Two experiments with D_2O were carried out on 1 mmol scale by using different samples of $Cu(BF_4)_2$, named A and B; the sample A was the one dried over P_2O_5 (50 °C, 1 mmHg, overnight) and the sample B was the similarly dried one, for which pretreatment with 1 mL of D_2O was made. To a stirred suspension of $Cu(BF_4)_2$ (A or B, 0.238 g, 1 mmol), DMAD (0.156 g, 1.1 mmol), *n*-$BuOSiMe_3$ (0.15 mL), and D_2O (0.04 mL) in CH_2Cl_2 (2 mL) was added siloxycyclopropane **1k** (0.198 g, 1 mmol) in one portion at 20 °C. After stirring for 3 h at 20 °C, the reaction mixture was poured into 30 mL of ether and washed with saturated aqueous NH_4Cl with vigorous shaking. The organic layer was separated and washed with 20 mL of saturated aqueous $NaHCO_3$ and then dried over $MgSO_4$. After evaporation, the resulting colorless oil was separated by PTLC (silica gel, ether/hexane, 80/20) to give **10k**, consisting of a mixture of H and D at vinylic position, whose deuterium contents were determined by both calculation from the comparison of integration of vinyl proton peak to methoxy singlet peak in ^1H NMR and of parent peaks 268 ($C_{14}H_{20}O_5$) and 269 ($C_{14}H_{19}O_5D$) of mass spectra after correction of contamination by isotopes: for the experiment using sample A, D product/H product = 30/70, and for the experiment using sample B, D product/H product = 61/39.

(*E*)- and (*Z*)-1-(2-Methyl)propenyl Phenyl Sulfone (16(*E*) and 16(*Z*)) by Reaction of Ethylmagnesium Bromide and 14a in the Presence of CuBr. For the preparation of a mixture of title compounds previous work was followed.[24a] To a stirred solution of THF solution of EtMgBr (1 mmol, 5 mL) and CuBr (0.086 g, 0.6 mmol) was added over a period of 3 min a solution of the sulfone **14a** (1.80 g, 10 mmol) in 5 mL of THF at −70 °C. After additional stirring for 30 min, the reaction mixture was poured into saturated aqueous NH_4Cl solution and extracted twice with $CHCl_3$. The combined extracts were dried over $MgSO_4$ overnight. After evaporation of solvents, a mixture of **16**(E) and **16**(Z) was obtained as a crude oil in the ratio of 30:70, which was analyzed by ^1H NMR ($CDCl_3$). For **16**(E): δ 1.04 (t, J = 7.4 Hz, 3H), 2.13 (s, 3H), 2.16 (q, J = 7.4 Hz, 2H), 6.17 (s, 1H), 7.50–7.95 (m, 5H). For **16**(Z): δ 1.03 (t, J = 7.5 Hz, 3H), 1.87 (s, 3H), 2.60 (q, J = 7.5 Hz, 2H), 6.15 (s, 1H), 7.50–7.95 (m, 5H).

(*E*)-1-(2-Methyl)propenyl Phenyl Sulfone (16(*E*)) by Reaction of Diethylzinc and 14a in the Presence of $Cu(BF_4)_2$. To a stirred suspension of methylacetylenic sulfone **14a** (0.360 g, 2.0 mmol) and $Cu(BF_4)_2$ (0.524 g, 2.2 mmol) was added dropwise a solution of diethylzinc (0.3 mL, 2.5 mmol) in ether (3 mL) over the period of 5 min at −70 °C. The initial blue color of the reaction mixture immediately changed to orange. After additional stirring for 20 min, the mixture was quenched with 1 mL of MeOH. Then the mixture was poured into 1 N HCl solution and extracted twice with Et_2O. The aqueous layer was extracted with Et_2O, and the combined extracts were washed with aqueous saturated $NaHCO_3$ and dried over $MgSO_4$ overnight. After evaporation of solvents, 0.364 g of a crude oil was obtained. Careful analysis of ^1H NMR of the crude oil indicated the formation of **16**(E) as the sole product. This oil was chromatographed on silica gel using AcOEt/hexane (2:1) as eluent to give **16**(E) (0.345 g, 82%): ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7.4 Hz, 3H), 2.13 (s, 3H), 2.17 (q, J = 7.4 Hz, 2H), 6.17 (s, 1H), 7.50–7.95 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 11.5, 17.9, 33.4, 125.0, 127.1, 129.1, 132.9, 142.4, 159.3; MS m/e (rel intensity) 210 (M^+ 60), 193 (18), 175 (55), 144 (100), 129 (58), 125 (30), 91 (18), 77 (40), 67 (25), 51 (25), 41 (56). The similar reaction was conducted and quenched by MeOD (0.25 mL). Deuterium incorporation at vinylic position was estimated to be ~6% based on the integration of ^1H NMR.

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