room temperature. The resulting precipitate was filtered off and after THF was evaporated under reduced pressure, the organic layer was extracted with ether. The extract was dried with Na_2SO_4 and concentrated. Separation by silica gel column chromatography from impurities gives IIIc, homogeneous by tlc and having ir and pmr spectra and elemental analysis in accord with the assigned structure [pmr τ 2.49–3.03 (m, 15 H), 7.28 (m, 2 H), 7.66 (m, 2 H), 8.06 (s, 3 H)].

The generality of the reaction between copper reagents of thioacetal (I) and conjugated enone is apparent from the results summarized in Scheme I and Table I.

Scheme I

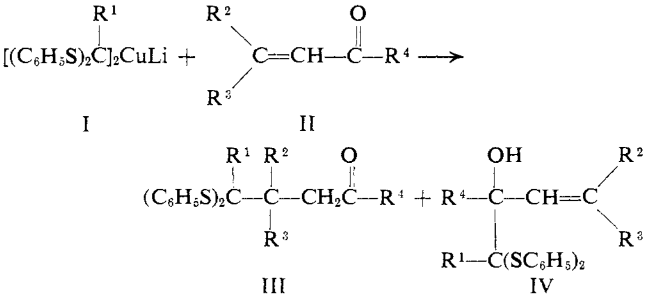
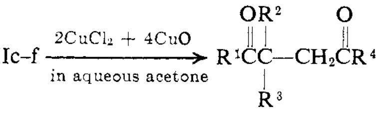


Table I

	I	II			Yield, %	
	R^1	R^2	R^3	R^4	III	IV
a	H	H	H	CH_3	50	23
b	C_6H_5S	H	H	CH_3	70	
c	C_6H_5	H	H	CH_3	94	
d	C_6H_5	CH_3	CH_3	CH_3	82	
e	C_6H_5	C_6H_5	H	CH_3	94	
f	C_6H_5	C_6H_5	H	C_6H_5	94	
g	CH_3	H	H	CH_3	73	4
h	n-C_5H_{11}	H	H	CH_3	73	

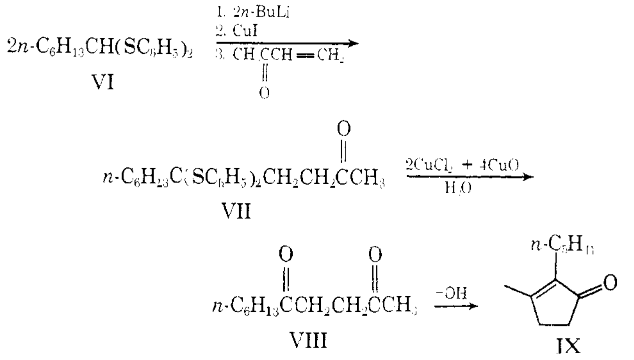
In order to obtain 1,4-diketone from γ-ketothioketal (III), there is a necessity to establish a convenient method for hydrolysis of thioacetal which is carried out under mild conditions, because 1,4-diketone is easily converted to furan or cyclopentenone by the treatment under acidic or basic condition or on heating. Previously, it was found in our laboratory that $CuCl_2$ is effective for the activation of the carbon–sulfur bond.[4] Therefore, we investigated the hydrolysis of γ-ketothioketal using $CuCl_2$ and CuO. 1-Phenyl-1-bis(phenylthio)pentan-4-one (IIIc) was treated with 2 equiv of $CuCl_2$ and 4 equiv of CuO in aqueous 99% acetone at room temperature for 1 hr. After purification by silica gel column chromatography and distillation, 1-phenylpentane-1,4-dione (Vc) was obtained in 91% yield [bp 127° (2 mm); pmr τ 2.03–2.83 (m, 5H), 6.90 (m, 2 H), 7.33 (m, 2 H), 8.95 (s, 3 H)]. Similarly, the other γ-ketothioketals (IIId–f) were converted into the corresponding 1,4-diketones (Vd–f) in more than 90% yields.



$$\text{IIIc–f} \xrightarrow[\text{in aqueous acetone}]{2CuCl_2 + 4CuO} R^1\overset{O}{\overset{\|}{C}}\underset{R^3}{\overset{R^2}{C}}\text{—}CH_2\overset{O}{\overset{\|}{C}}R^4$$

Vc–f

As an example of a synthetic utility of this method, we carried out a simple synthesis of dihydrojasmone according to the following procedure. Heptanal diphenylthioacetal (VI) was treated with 1 equiv of n-BuLi in THF at −40 to − 30° for 1 hr under an argon atmosphere and 0.5 equiv of CuI was added at once at −78°. After being stirred for 1 hr, a THF solution of MVK was added dropwise to the reaction mixture and stirred for 2 hr at −78°. The corresponding γ-ketothioketal (VII) was isolated in 80% yield [pmr τ 2.25–2.86 (m, 10 H), 7.04–7.45 (m, 2 H), 7.97 (s, 3 H), 8.00–9.33 (m, 15 H). *Anal.* Calcd for $C_{23}H_{30}OS_2$: C, 71.48; H, 7.82; S, 16.56. Found: C, 71.75; H, 7.66; S, 16.40]. The treatment of VII with 2 equiv of $CuCl_2$ and 4 equiv of CuO in aqueous 99% acetone gave corresponding 1,4-diketone VIII in 90% yield [bp 93–94° (0.5 mm); lit.[5] bp 141° (14 mm); pmr τ 7.45 (s, 4 H), 7.66 (t, 2 H), 7.96 (s, 3 H), 8.33–9.33 (m, 11 H)]. According to Hunsdiecker's method,[6] VIII was converted into dihydrojasmone (IX) in 94% yield by refluxing for 6 hr with 2% aqueous NaOH and ethanol [bp 129–131° (19 mm); lit.[6] bp 122–124° (12 mm); homogeneous by tlc and vpc and having pmr and ir spectra and elemental analysis in accord with IX].



Acknowledgment. Financial assistance by the Mitsubishi Foundation is gratefully acknowledged. We wish to thank Mr. Tsutomu Shinoda for experimental assistance.

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[4] T. Mukaiyama, K. Narasaka, and H. Hokonoki, *J. Amer. Chem. Soc.*, **91**, 4315 (1969); T. Mukaiyama, K. Maekawa, and K. Narasaka, *Tetrahedron Lett.*, 4669 (1970); T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, *Bull. Chem. Soc. Jap.*, **44**, 2285 (1971).

(5) H. Hunsdiecker, *Chem. Ber.*, 75, 447 (1942).

(6) H. Hunsdiecker, *ibid.*, 75, 455 (1942).

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Reaction of Sulfur Dioxide with Enol Ethers

Sir:

Sulfur dioxide readily undergoes 1,4-cycloaddition reactions with a variety of conjugated dienes to give the corresponding 2,5-dihydrothiophene 1,1-dioxides.[1] On the other hand, while sulfur dioxide reacts with

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(1) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 13.

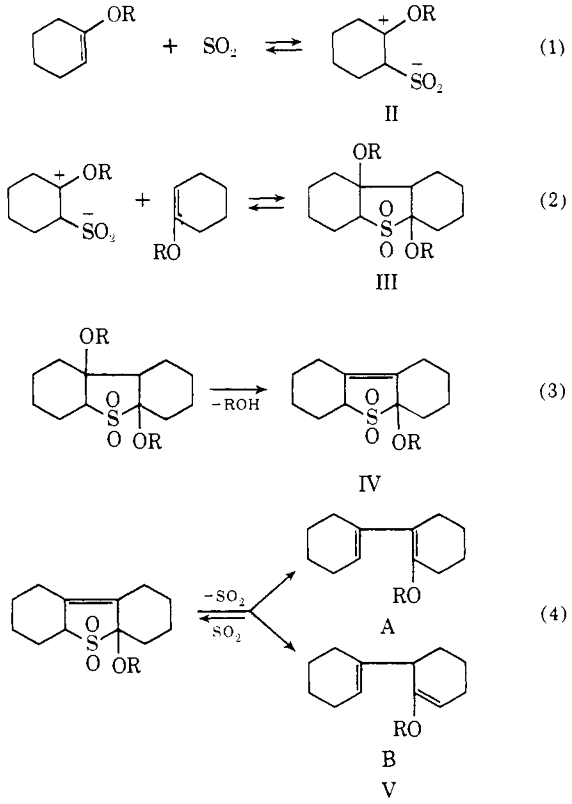
various olefinic compounds in the presence of radical initiators to give polysulfones,[2] to our knowledge no ionic reaction of sulfur dioxide with isolated double bonds has been reported. We wish to report what we believe is the first example of such a reaction.

We observed that sulfur dioxide reacts readily with the double bond of an enol ether. Thus, addition of 1-methoxycyclohexene Ia (100 mmol, 11.2 g) to an excess of sulfur dioxide (50 ml) at $-10°$ resulted in the formation of an intense orange color. A 60-MHz nmr spectrum of the reaction mixture taken immediately after the addition showed that the vinylic proton at C_2 was absent. The spectrum showed two different OCH_3 groups at δ 3.35 and 3.08. After stirring for 1 hr at $-10°$, an excess of dry ether was added and the mixture stirred 30 min; both solvents were removed under reduced pressure. The nmr spectrum of the resulting oil in carbon tetrachloride solution was essentially the same as that of the original reaction mixture. After stirring in pentane overnight at 0°, white crystals of IVa, mp 72–73°, separated out (yield 85%). The nmr spectrum of IVa in carbon tetrachloride solution showed only one methoxy group at δ 3.35, indicating that the higher field methoxy group observed earlier was lost as methanol during the work-up. The infrared spectrum of IVa in carbon tetrachloride solution showed strong absorptions at 1305 and 1120 cm^{-1}, as well as several strong absorptions in the region between 1150 and 1050 cm^{-1}, thus suggesting the presence of a sulfone group and carbon–oxygen bonds. The mass spectrum of IVa revealed very intense peaks at *m/e* 192 and 64, evidently due to a $C_{13}H_{20}O$ fragment and sulfur dioxide, the components of thermal decomposition of the parent $C_{13}H_{20}SO_3$ molecule. Elemental analysis confirmed the same molecular formula.

Under similar conditions 1-ethoxycyclohexene reacted with sulfur dioxide to give IVb, mp 63–64°, in 95% yield, the spectral and analytical data being in agreement with the structure. Heating IVb at 60–70° (200–300 mm) produced a yellow liquid which distilled at 89° (3 mm) to give colorless Vb. Elemental analysis and the mass spectrum of Vb established the molecular formula $C_{14}H_{22}O$. Mass spectra of both IVb and Vb were essentially the same, except for the presence of a sulfur dioxide peak in the former, thus establishing that IVb must be an addition compound of Vb and sulfur dioxide. Acid-catalyzed hydrolysis of Vb gave the known 2-cyclohex-1′-enylcyclohexanone[3] VI. This information, together with the fact that a 100-MHz spectrum of Vb in carbon tetrachloride solution showed three vinylic protons of almost equal intensities at δ 5.6, 5.5, and 4.7, indicated that Vb is a 1:1 mixture of isomeric 3-ethoxy-1,3- and -1,4-dienes Vb-A and Vb-B.[4,5]

When the mixture of Vb-A and Vb-B (50 mmol, 10.3 g) was added at $-10°$ to an excess of sulfur dioxide (50 ml), an immediate orange color was formed. The nmr spectrum of the reaction mixture was essentially the same as the spectrum of IVb. Evaporation of sulfur dioxide gave a 95% yield of IVb, mp 63–64°. Similarly, a 1:1 mixture of Va-A and Va-B, obtained by heating IVa, reacted with sulfur dioxide to give back IVa.

Although we have not yet undertaken a detailed study of the mechanism, it is probable that the reaction of sulfur dioxide with 1-alkoxycyclohexenes involves the following steps: (a) reversible formation of a 1:1 adduct represented as a 1,3-dipolar ion II (eq 1); (b) reaction of this dipolar ion with a second molecule of the enol ether as a dipolarophile to give the cyclic product III (eq 2); and (c) the elimination of the alcohol from III to give the final product IV (eq 3). A 60-MHz nmr spectrum of a solution of either a 1:1 mixture of 1-ethoxycyclohexene and ethanol or cyclohexanone diethyl acetal in sulfur dioxide showed the presence of a free hydroxyl proton at δ 2.73 (1 H). At 0° this proton appeared at δ 3.15 and integrated for only 0.4 H. Clearly, sulfur dioxide cleaves ethanol from diethyl acetal (eq 5).[6,7] Since in both cases no



a, R = CH_3
b, R = C_2H_5

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(2) E. S. Dainton and K. J. Ivin, *Proc. Roy. Soc., Ser. A*, **212**, 96, 207 (1952).

(3) E. Wenkert, S. K. Bhattacharya, and E. M. Wilson, *J. Chem. Soc.*, 5617 (1964).

(4) Glpc analysis on a 6-ft 10% SE-30 on Chromosorb W column showed the presence of two partially resolved peaks of approximately equal intensities.

(5) The same mixture of 3-alkoxy-1,3- and -1,4-dienes 3A and 3B was obtained by slow distillation of the required amount of alcohol from the corresponding 1-alkoxycyclohexene in the presence of a catalytic amount of *p*-toluenesulfonic acid, followed by neutralization and distillation.

(6) The reactions of sulfur dioxide with acetals, ortho esters, etc., which appear to be of a fairly general nature, will be described shortly.

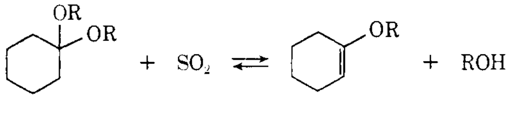
(7) The nmr spectrum of ethanol in sulfur dioxide showed the hydroxyl proton at δ 2.7, approximately the same chemical shift as that of the hydroxyl proton appearing in the sulfur dioxide solution of cyclohexanone diethyl acetal. It is known that sulfur dioxide enters the equilibrium i with alcohols, which can be shifted entirely to the right, for example, by reaction with diazomethane ii[8]

$$ROH + SO_2 \rightleftharpoons ROSO_2H \qquad (i)$$

$$ROSO_2H + CH_2N_2 \longrightarrow ROSO_2CH_3 \qquad (ii)$$

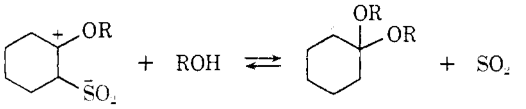
Consequently, it is conceivable that the ethanol cleaved from the acetal also enters a similar equilibrium with sulfur dioxide.

(8) G. Hesse and S. Majmudar, *Chem. Ber.*, **93**, 1129 (1960).



(5)

signal for the vinyl proton was observed, it would appear that the enol ether reacts with sulfur dioxide to form the 1,3-dipolar ion II (eq 1),[9] which is thus in equilibrium with the acetal (eq 6).



(6)

Because the charges in the 1,3-dipolar ion II are separated by an sp^3 hybridized carbon atom, their internal stabilization is not possible.[10] Nevertheless, the necessary stabilization may effectively be achieved through appropriate delocalization of charges over the oxygen atoms attached to positively charged carbon and negative sulfur. Contrary to a generally recognized contention that it is meaningless to assign an electrophilic and nucleophilic end to an internally stabilized 1,3 dipole,[11] such a dipolar ion as II does possess nucleophilic and electrophilic ends, and consequently it should react with appropriate dipolarophiles with predictable orientation. While the cycloadditions of internally stabilized 1,3-dipolar ions are symmetry allowed, concerted, suprafacial processes $({}_{\pi}4_s + {}_{\pi}2_s)$,[12] the cycloaddition of II to 1-alkoxycyclohexene (eq 2) obviously cannot proceed through the same process. Clearly, the flow of four π electrons between the charges which is possible in "regular" 1,3 dipoles of heteroallyl type[10] is not possible in II.

Both isomeric 3-alkoxy-1,3- and -1,4-dienes VA and VB react with sulfur dioxide to give the same product IV (eq 4). This sugests that the 1,4 isomer under reaction conditions isomerizes to the 3-alkoxy-1,3-diene (probably through the intermediate formation of the corresponding 1,3-dipolar ion), which then apparently reacts with sulfur dioxide in the usual manner[1] to give IV. Since it has been shown that sulfur dioxide–1,3-diene adducts lose sulfur dioxide in the concerted suprafacial mode,[13] it seems logical to assume that the cycloaddition reaction itself is also a concerted suprafacial process. On this basis one would assume that in IV, which was formed in a cycloaddition reaction of sulfur dioxide and VA, the hydrogen and alkoxy group α to the sulfone group are cis with respect to each other. Since the same product is also obtained by reaction of sulfur dioxide with 1-alkoxycyclohexene (eq 1–3), formation of III, albeit as a relatively unstable product, must also be a highly stereospecific reaction. However, the exclusive formation of a single product in this reaction should not be taken as evidence for concerted formation of the two new σ bonds in a $({}_{\pi}4_s + {}_{\pi}2_s)$ process. Observed stereospecificity may simply reflect the favored stereochemical arrangement in the transition state leading to III.

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[9] An alternative explanation that thus generated enol ether undergoes proton-catalyzed dimerization to 3-alkoxy-1,3- and -1,4-dienes V,[5] which is then removed from the system through reaction with sulfur dioxide, is inconsistent with the observed spectra. The absence of "free" ethanol in the reaction of the 1-alkoxycyclohexene itself with sulfur dioxide also seems to rule out this possibility.

[10] (a) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); (b) R. Huisgen, *ibid.*, **7**, 321 (1968).

[11] R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

[12] (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192, 2212 (1967).

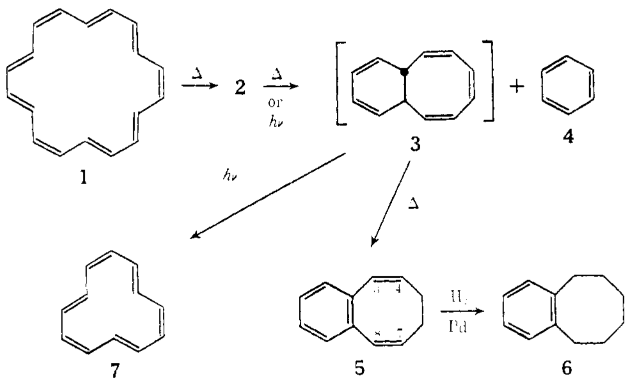
[13] (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

The Thermolysis of [18]Annulene[1]

Sir:

Although the nonaromatic [10]-, [12]-, and [16]-annulenes undergo ready thermal valence isomerization in solution to polycyclic isomers at room temperature or below,[2] it has previously not been possible to bring about similar reactions with the other known annulenes.[3] We now report the results obtained on heating solutions of the aromatic [18]annulene (**1**),[2] which surprisingly caused cleavage of the molecules to benzene (**4**)[4] and 1,2-benzo-1,3,7-cyclooctatriene (**5**). Furthermore, irradiation of an intermediate in this reaction has resulted in a new synthesis of [12]annulene (**7**).

[18]Annulene (**1**) in dry dimethylformamide (bp 163°) was boiled under reflux in nitrogen for 80 min. Chromatography on silica gel gave 63% of **5** as a colorless liquid: *m/e* 156; nmr spectrum (CCl_4, 60 MHz) τ 2.95 (s, 4 H, benzenoid), 3.53 (d, $J = 12$ Hz, 2 H, H^3, H^8), 3.9–4.4 (m, 2 H, H^4, H^7), 7.6–7.8 (m, 4 H, methylene). Structure **5** follows from these spectral data, as well as from the correspondence of the uv and ir spectra with those reported.[6] Further proof of identity was provided by preparation of the silver nitrate complex (mp 164–166° dec; reported mp 163–165° dec[6]) and by catalytic hydrogenation in cyclohexane over 5% Pd/



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[1] Unsaturated Macrocyclic Compounds. XCV. For part XCIV, see P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Lett.*, 3695 (1972).

[2] For references, see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

[3] [24]Annulene appears to be converted into a polycyclic isomer on standing in solution, but this reaction has not been investigated in detail (F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Amer. Chem. Soc.*, **84**, 274 (1962)).

[4] The cleavage of benzene was also observed to occur from 1,2-difluoro- and 1-chloro-2-fluoro[18]annulene,[5] in tetrahydrofuran at 80° and above, in the course of nmr studies (G. Schröder and J. F. M. Oth, unpublished observations).

[5] G. Schröder, R. Neuberg, and J. F. M. Oth, *Angew. Chem.*, **84**, 36 (1972).

[6] G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).