in Ethanol and Pyridine. 2-Phenoxycyclohexanone (*Z*)- [and (*E*)-] Oxime (5).[2]—A mixture of 2-phenoxycyclohexanone[2] (10, g, 0.0525 mol), hydroxylamine hydrochloride (10 g, 0.144 mol), 10 ml of pyridine, and 80 ml of ethanol was refluxed for 17 hr and worked up as usual.[3] The crude product (10.43 g) showed a ratio of *ca.* 25% (*Z*)-oxime and 75% (*E*)-oxime **5** based on the -OCH- positions at δ 5.70 and 4.82, respectively. No vinyl hydrogen was detectable by nmr. The mass spectrum showed a molecular ion at *m/e* 205 and a peak at 203 (*ca.* 2%) which can be due either to M − 2 ion, or less likely, to a dehydro compound. The above oxime mixture showed the same nmr and mass spectra after distillation at 0.05 mm (bp 145-155°).

Registry No.—**1**, 27920-40-7; (*Z*)-**2**, 36540-08-6; (*E*)-**2**, 36540-09-7; **3**, 36540-10-0; (*Z*)-**5**, 36540-11-1; (*E*)-**5**, 36540-12-2.

The Reactivity of Diazo Ketones. II.[1] Reaction of α-Diazo Ketones with Sulfur Dioxide

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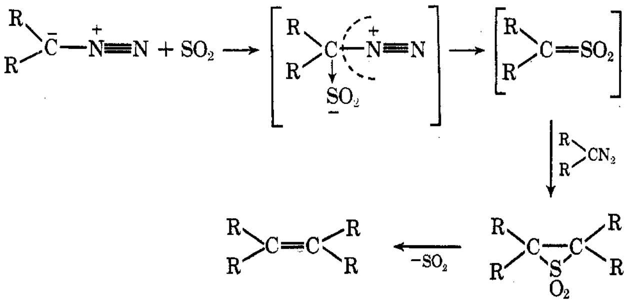
Received March 10, 1972

Reactions of some α-diazo ketones with sulfur dioxide were carried out by means of pyrolysis or photolysis. The reactions appeared to proceed *via* a free ketocarbene and a remarkable substituent effect was observed. Diazo ketones of the type $PhCN_2COR$ (R = Ph, Me) gave six-membered cyclic sulfones and sultones, while diazo ketones of the type RCN_2COPh (R = H, Me) gave products resulting from a 1,2-hydrogen shift or a 1,3-dipolar addition reaction of the ketocarbene intermediate. The mechanism of these reactions and the radical reactivity of the PhCCOR type ketocarbenes are discussed in this report.

A number of reactions of sulfur dioxide with diazo alkanes have been reported.[2,3] These reactions proceed readily at low temperature to form either stable or transient episulfones, followed by evolution of sulfur dioxide to give olefins. The proposed mechanism is as follows (Scheme I).

SCHEME I

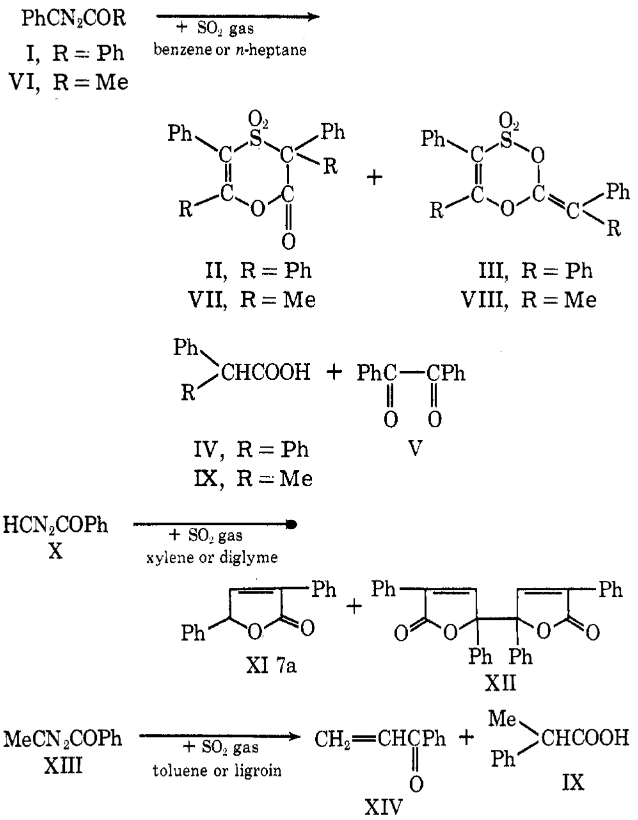
REACTION OF DIAZO ALKANE WITH SO_2



In a preceding communication,[1] we reported that the reaction of azibenzil (I) with sulfur dioxide did not proceed at room temperature, but proceeded at elevated temperature or by means of photolysis to give the cyclic sulfone II and sultone III,[4] instead of the expected episulfone or olefin (Scheme II). In order to obtain further information on the scope and mechanism of this reaction, the reactions of several α-diazo ketones with sulfur dioxide were investigated.

SCHEME II

THERMAL REACTIONS OF α-DIAZO KETONES WITH SO_2



These reactions proceeded only under conditions of pyrolysis or irradiation, and gave products which were different from those expected by analogy to the reaction of diazo alkanes with sulfur dioxide. Moreover, a significant substituent effect was observed; diazo ketones of structure A gave six-membered cyclic sulfones and sultones, while those of structure B gave no such sulfones or sultones, but rather products in which sulfur dioxide was not incorporated.

$C_6H_5CN_2COR$
A, $R = C_6H_5, CH_3$

$RCN_2COC_6H_5$
B, $R = H, CH_3$

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[1] T. Nagai, M. Tanaka, and N. Tokura, *Tetrahedron Lett.*, 6293 (1968).

[2] (a) H. Staudinger and F. Pfenninger, *Chem. Ber.*, **49**, 1941 (1916); (b) H. Kloosterziel and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **71**, 1235 (1952); (c) G. Hesse and E. Reichold, *Ber.*, **90**, 2106 (1957); (d) G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965).

[3] (a) L. V. Vargha and E. Kovacs, *Chem. Ber.*, **75**, 794 (1942); (b) G. Hesse, E. Reichold, and S. Majmudar, *ibid.*, **90**, 2106 (1957); (c) G. Hesse and S. Majmudar, *ibid.*, **93**, 1129 (1960).

[4] In the previous communication,[1] four-membered cyclic structures were postulated for the cyclic sulfone and sultone. Storthers, Danks, and King have proposed six-membered ring sulfone and sultone from the analysis of ^{13}C nmr spectra of the two compounds [*Tetrahedron Lett.*, 2551 (1971)]. Recently, the X-ray analyses of these compounds made by the present authors have also supported the six-membered sulfone. The details of the result are to be published shortly [N. Yasuoka, N. Kasai, M. Tanaka, T. Nagai, and N. Tokura, *Acta Crystallogr.*, No. 12 (1972)].

Results and Discussion

As described above, the reactions of α-diazo ketones ($R_1CN_2COR_2$) with sulfur dioxide did not proceed at room temperature, but the reaction could be made to occur at elevated temperature or by means of irradiation. Results of the thermal reactions are shown in Scheme II and Table I. The identification of these sulfones (II, VII) and sultones (III, VIII) was based on the ir, uv, nmr, and mass spectra and elementary analysis as described in the Experimental Section. Moreover, X-ray analysis[4] of the sulfone II indicated the presence of a six-membered ring.

TABLE I

THERMAL REACTION[a] OF $R_1CN_2COR_2$ WITH SO_2

R_1	R_2	Solvent	Temp, °C	Products (yield, mol %)[b]
Ph	Ph	Benzene	70	II (44), III (7), IV (23), V (23)
		n-Heptane	80	II (42.8), III (6.1), IV (20)
H	Ph	Xylene	130	XI (8.5), XII (72)
		Diglyme	140	XI (8), XII (76)
Me	Ph	Toluene	110	XIV (60), IX (trace)
		Ligroin	115	XIV (57), IX (trace)
Ph	Me	Benzene	60	VII (49), VIII (5), IX (17)
		n-Heptane	70	VII (47), VIII (6), IX (15)

[a] Reaction time 4.5 hr. [b] The yields are in mole per cent based on unrecovered starting material for IV, V, IX, and XIV, based on 0.5 mol of unrecovered starting material for II, III, VII, VIII, and XI, and based on 0.25 mol of unrecovered starting material for XII.

These sulfones (II, VII) and sultones (III, VIII) have the structure expected from a [4 + 2][5a] cycloaddition of a keto sulfene with a ketene. Attempts to isolate cycloadducts of sulfenes and ketenes have not yet been successful.[5b] The present result might be the first observation[1,4] of the cycloaddition of sulfene to ketene.

The neat decomposition of II at 280° afforded tetraphenylethylene (XV) with evolution of sulfur dioxide gas. Basic hydrolysis of II and VII yielded quantitatively the related sulfones (XVI, XVII) and carboxylic acids (XIX, XX) (Scheme III).

The thermal reactions shown in Scheme II were carried out around the corresponding decomposition points of the diazo ketones. Benzene, toluene, or xylene were used as solvents. Also, the reactions were carried out in *n*-heptane, diglyme, or ligroin, but no appreciable solvent effect was observed (Table I). On the other hand, the substituent attached to the diazo carbon atom exerted a significant influence on the course of these reactions. In this case, however, it was not clear whether the substituent or the difference in the reaction temperature was responsible for the difference in the course of these reactions. In order to make this point clear, the photolysis of these diazo ketones was carried out under as similar conditions as possible, *i.e.*, in liquid sulfur dioxide at a low temperature (0–10°). The results are shown in Table II.

SCHEME III

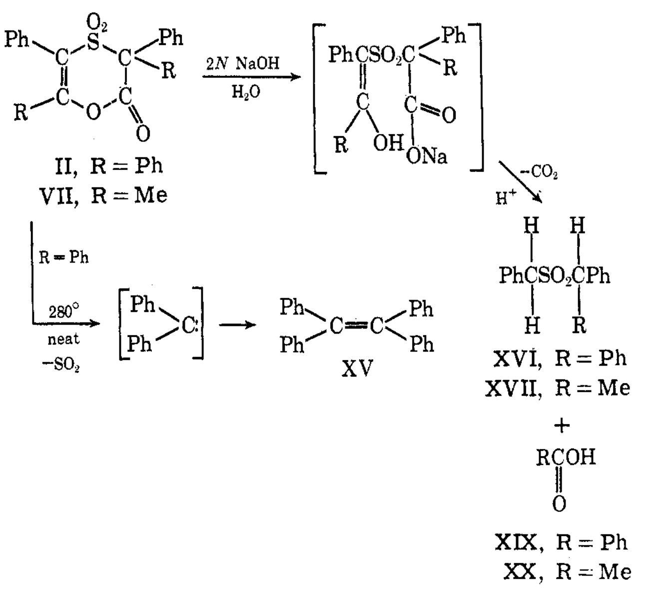


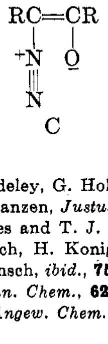
TABLE II

PHOTOLYSIS[a] OF $R_1CN_2COR_2$ IN LIQUID SO_2

R_1	R_2	Time, hr	Products (yield, mol %)[b]
Ph	Ph	6	II (35), III (17), IV (14)
H	Ph	8	XII (82), XI (trace)
Me	Ph	9	XIV (60), IX (trace)
Ph	Me	4	VII (54), VIII (11), IX (5)

[a] The irradiation was undertaken by using a 300-W high-pressure mercury lamp in a Pyrex tube at 0–10°. [b] See Table I, footnote *b*.

The results of photolysis closely resembled those of the thermal reactions, revealing an interesting substituent effect; namely, $PhCN_2COR$ (R = Ph, Me) type diazo ketones gave six-membered cyclic sulfones (II, VII) and sultones (III, VIII), possibly *via* a free ketocarbene. By contrast, RCN_2COPh (R = H, Me) type diazo ketones yielded no sulfone or sultone, but gave products resulting from a 1,2-hydrogen shift[6] or a 1,3-dipolar cycloaddition[7] of the ketocarbene intermediates (Scheme II). It has been proposed[8] that the reactions of diazo alkanes with sulfur dioxide proceed by an electrophilic attack of sulfur dioxide on the diazo carbon atom, the evolution of N_2 occurring concertedly. In these reactions, such a substituent effect as observed here has not been found. Thus, both diazoethane and diphenyldiazomethane give similar products. It seems that with α-diazo ketones such a reaction as observed in diazo alkanes does not occur, since the electron density on the diazo carbon atom is too small for electrophilic attack by sulfur dioxide, owing to the conjugation with the carbonyl group (structure C).[7d]



$$\begin{matrix} RC{=}CR \\ {}^{+}N\quad O^{-} \\ \| \\ N \end{matrix}$$

major contribution

C

---

[5] (a) Fusco and coworkers have reported a [4 + 2] cycloaddition dimer of ketosulfene: *Gazz. Chim. Ital.*, **95**, 774 (1965). (b) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Amer. Chem. Soc.*, **84**, 3030 (1962).

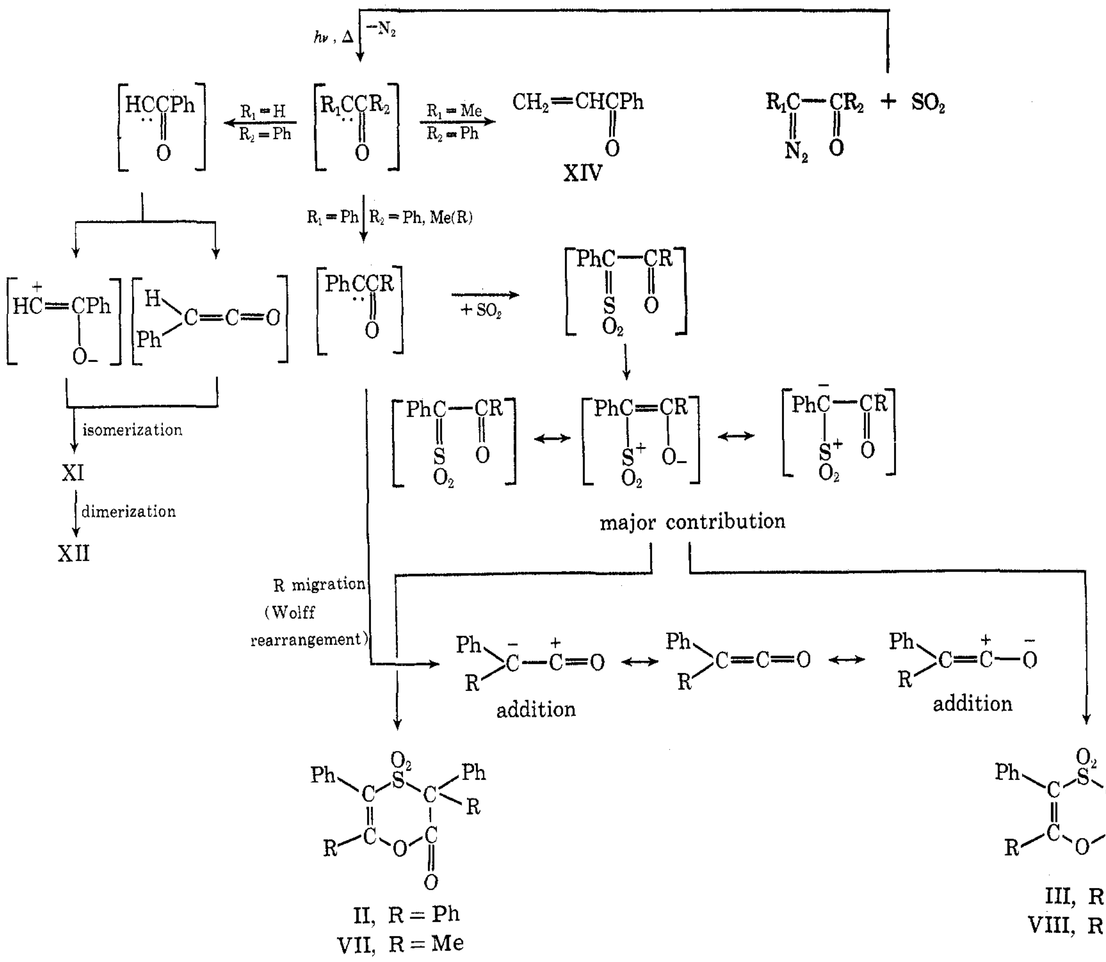
[6] (a) G. Baddeley, G. Holt, and J. Kenner, *Nature (London)*, **163**, 776 (1949); (b) V. Franzen, *Justus Liebigs Ann. Chem.*, **602**, 199 (1957).

[7] (a) D. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961); (b) R. Huisgen, G. Binsch, H. Konig, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961); (c) G. Binsch, *ibid.*, **75**, 634 (1963); (d) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **625**, 34 (1959).

[8] G. Opitz, *Angew. Chem.*, **79**, 161 (1967).

SCHEME IV

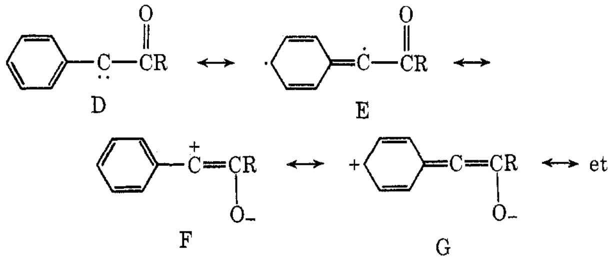
REACTION OF $R_1CN_2COR_2$ WITH SO_2



Since the diazo ketones were stable in liquid sulfur dioxide at 0–10° overnight, but decomposed under irradiation, the evolution of N_2 may occur in the first step to produce the ketocarbene as an intermediate. Thus, a ketocarbene and subsequently a ketosulfene may reasonably be postulated as the intermediate for the formation of the six-membered cyclic sulfones and sultones. The substituent effect may be explained in the following way. Ketocarbenes of the type PhCCOR (R = Ph, Me) (probably the triplet state) react with sulfur dioxide in competition with the Wolff rearrangement,[9] while $R\underset{\cdot\cdot}{C}COPh$ (R = Me, H) type ketocarbenes (probably the singlet state) do not react with sulfur dioxide but undergo intramoleculr reactions such as 1,2-hydrogen shift or 1,3-dipolar reaction (Scheme IV).

As for the formation of ketosulfene from the reaction of the ketocarbene with sulfur dioxide, either a radical or a nucleophilic reaction is conceivable, although the ketocarbene may also be electrophilic because of the electron-withdrawing carbonyl group.[10]

It has been reported that carbenes can be stabilized by resonance with the phenyl ring[11] (eq 1).



(1)

At the present stage of our research, it seems plausible that the resonance form D or E of the $Ph\underset{\cdot\cdot}{C}COR$ type ketocarbene as shown in eq 1 above reacts with sulfur dioxide, for sulfur dioxide is known to react electrophilically and radically, but not nucleophilically.

Experimental Section

Materials.—Azibenzil (I), mp 78° (lit.[12] mp 78°), and phenylacetyldiazomethane (VI), mp 59–60° (lit.[12] mp 59–60°), were prepared by diazo transfer reactions from the related ketones.

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[9] (a) L. Wolff, *Justus Liebigs Ann. Chem.*, **325**, 129 (1902); (b) L. Wolff, *ibid.*, **394**, 23 (1912); (c) G. Schroeter, *Ber. Deut. Chem. Ges.*, **42**, 3356 (1909).

[10] When the carbenes have such electron-withdrawing groups as carbonyl, sulfonyl, and ester groups, they are known to be strongly electrophilic. (a) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); (b) J. Diekmann, *J. Org. Chem.*, **30**, 2272 (1965).

[11] The resonance of divalent carbon with the phenyl ring was proposed; see (a) W. Krimse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 214; (b) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

[12] M. Regitz, *Chem. Ber.*, **98**, 1210 (1965).

Diazoacetophenone (X), mp 48–50° (lit.[13] mp 49–50°), and methylbenzoyldiazomethane (XIII),[13] which is the liquid diazo compound recrystallized[14] from ether at −70°, were obtained by the reaction of benzoyl chloride with related diazo alkanes.

Thermal Reactions of α-Diazo Ketones with Sulfur Dioxide. A. The Reaction of Azibenzil (I) with Sulfur Dioxide Gas.—Sulfur dioxide gas (200 g) was introduced into a benzene solution (85 ml of benzene) of azibenzil (8.5 g, 0.038 mol) for 4.5 hr at refluxing temperature (78°). The products were separated by chromatography using silica gel as the adsorbent. Elution with petroleum ether (bp 40–60°), benzene, chloroform, and ether gave the products, benzil (V), 3,3,5,6-tetraphenyl-2,3-dihydro-1,4-oxathiin-2-one 4,4-dioxide (II), 2-diphenylmethylene-5,6-diphenyl-1,3,4-dioxathiin 4,4-dioxide (III), and diphenylacetic acid (IV), successively.

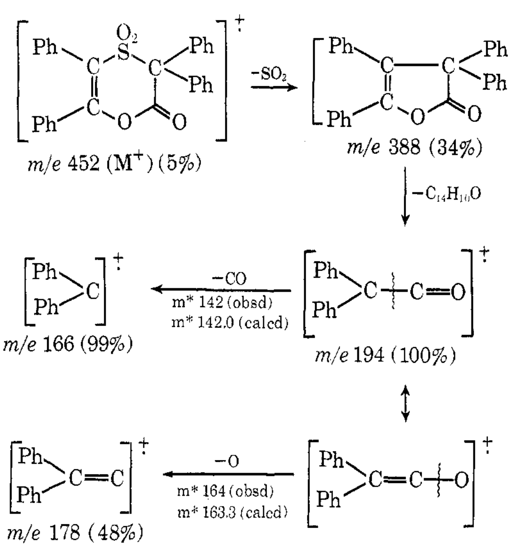
The yield was shown in Table I. Compounds IV and V were identified by infrared spectral comparison and mixture melting point, 148° and 95°, respectively, with the samples (lit. mp of IV, 148°;[15a] mp of V, 95°[15b]).

3,3,5,6-Tetraphenyl-2,3-dihydro-1,4-oxathiin-2-one 4,4-dioxide (II) was recrystallized from benzene: mp 232–233° dec; ir C=O stretching bands at 1785 ($\nu_{C=O}$ of ester group) and 1605 ($\nu_{C=C}$) and sulfone stretching bands at 1350 (ν as SO_2) and 1140 cm^{-1} (ν s SO_2); nmr ($CDCl_3$) τ 2.5–3.0 ppm (m, Ph).

The uv absorption spectrum of II in a tetrahydrofuran solution has the maximum at 292 nm (ϵ 1.01 × 10^4) indicating the *cis*-stilbene moiety.

Anal. Calcd for $C_{28}H_{20}SO_4$: C, 74.33; H, 4.46; S, 7.07. Found: C, 74.32; H, 4.41; S, 7.07. The mass spectrum of II was explained as shown in Scheme V.

SCHEME V

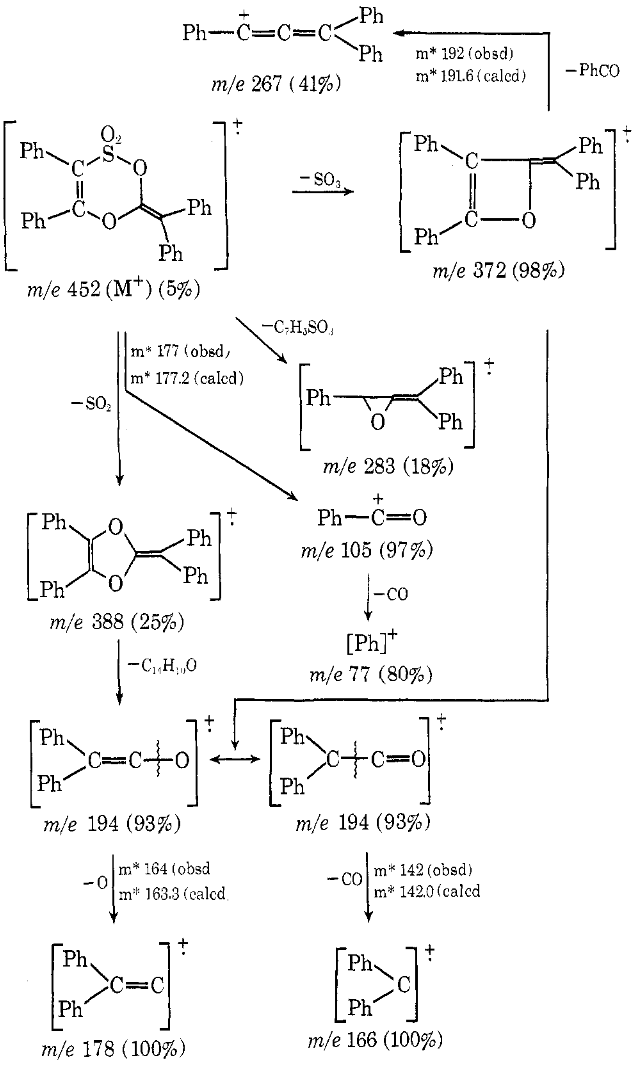


2-Diphenylmethylene-5,6-diphenyl-1,3,4-dioxathiin 4,4-dioxide (III), was recrystallized from ether: mp 173–174° dec; ir 1605 ($\nu_{C=C}$), 1350 (ν as SO_2), and 1130 cm^{-1} (ν s SO_2); nmr ($CDCl_3$) 2.6–3.0 ppm (m, Ph).

Anal. Calcd for $C_{28}H_{20}SO_4$: C, 74.33; H, 4.46. Found: C, 74.11; H, 4.78. The mass spectrum of III is shown in Scheme VI.

The thermal reaction using *n*-heptane instead of benzene as solvent was carried out under the same conditions as described above.

SCHEME VI



B. The Reaction of Diazoacetophenone (X) with Sulfur Dioxide Gas.—Into a xylene solution (73 ml of xylene) of diazoacetophenone (7.3 g, 0.05 mol), sulfur dioxide gas (200 g) was passed for 4.5 hr at 140°. No specific absorption of sulfone was shown in the ir spectrum of the reaction mixture. The products were separated by chromatography on silica gel. Elution with benzene and ether gave successively the corresponding butenolide XI, mp 107–108°, and the dimer XII, mp 288–289°, in the yields which are shown in Table I. These products were identified by infrared spectral comparison and the mixture melting points, 106–108 and 287–289°, respectively, with the authentic samples (lit. mp of XI, 107–108°; XII, 288–289°).[7a]

The reaction also was done in a diglyme solvent under the conditions described above.

C. The Reaction of Methylbenzoyldiazomethane (XIII) with Sulfur Dioxide Gas.—Sulfur dioxide gas (200 g) was passed into a toluene solution (64 ml of toluene) of methylbenzoyldiazomethane (6.4 g, 0.04 mol) for 4.5 hr at 110–115°. Absorption of a sulfone group was absent in the ir spectrum of the reaction mixture. The products were separated by chromatography on silica gel. Elution with benzene and ether successively gave vinyl phenyl ketone (XIV), and 2-phenylpropionic acid (IX) was obtained in the yield as shown in Table I. XIV was identified by infrared spectral and boiling point comparison with the authentic sample,[6b] bp 115° (18 mm) [lit. bp 115° (18 mm)]. 2-Phenylpropionic acid, obtained after hydrolysis, was identified by the mixture melting point (264–267°) with the sample[16] (lit. mp 265–268°). The reaction using ligroin instead of toluene as solvent was carried out under the same conditions as described above.

D. The Reaction of Phenylacetyldiazomethane (VI) with Sulfur Dioxide Gas.—To a benzene solution (70 ml of benzene) of phenylacetyldiazomethane (3.2 g, 0.02 mol), sulfur dioxide gas (200 g) was introduced at 70° for 4.5 hr. Separation of the reaction mixture by chromatography on silica gel was carried out. Elution with benzene, chloroform, and ether gave successively 3,6-dimethyl-3,5-diphenyl-2,3-dihydro-1,4-oxathiin-2-one 4,4-dioxide (VII), 6-methyl-5-phenyl-2-(1-phenylethylidene)-1,3,4-dioxathiin 4,4-dioxide (VIII), and 2-phenylpropionic acid (IX),

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(13) F. Arndt and B. Eistert, *Chem. Ber.*, **68**, 200 (1935).

(14) M. Regitz, *Angew. Chem.*, **79**, 733 (1967).

(15) (a) R. Adams and C. S. Marvel, *Org. Syn.*, **1**, 25 (1921); (b) C. S. Marvel, F. D. Hager, and E. C. Caudle, *ibid.*, **3**, 45 (1923).

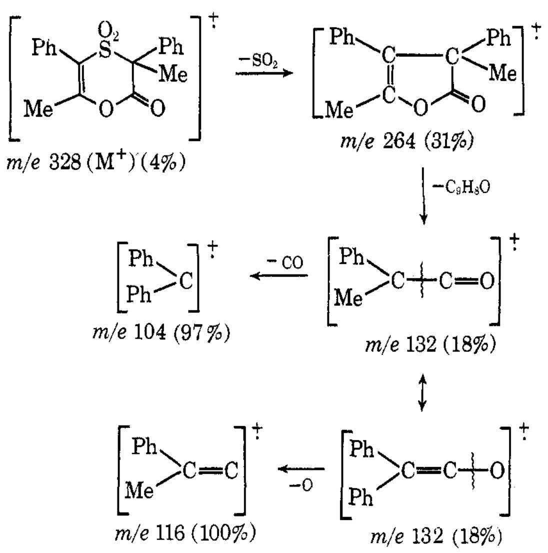
(16) W. Johnson, *J. Amer. Chem. Soc.*, **24**, 686 (1902).

in the yield as shown in Table I. IX was identified by infrared spectral comparison and the mixture melting point (264–267°) with the sample[16] (lit. mp 265–268°).

3,6-Dimethyl-3,5-diphenyl-2,3-dihydro-1,4-oxathiin-2-one 4,4-dioxide (VII) was recrystallized from benzene: mp 117–118° dec; ir 1790 ($\nu_{C=O}$ of ester group), 1650 ($\nu_{C=C}$), and sulfone stretching bands at 1320 (ν as SO_2) and 1140 cm^{-1} (ν s SO_2); nmr ($CDCl_3$) 2.55–3.25 (10 H, m, Ph), 7.95 (3 H, s, CH_3), 8.10 (3 H, s, CH_3).

Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.85; H, 4.88; S, 9.76. Found: C, 65.80; H, 4.82; S, 10.12. The mass spectrum of VII was explained as shown in Scheme VII.

SCHEME VII



6-Methyl-5-phenyl-2-(1-phenylethylene)-1,3,4-dioxathiin 4,4-dioxide (VIII)[17] was recrystallized from ether: mp 129° dec; ir 1650 ($\nu_{C=C}$), 1340 (ν a s, SO_2), and 1160 cm^{-1} (ν s, SO_2); nmr ($CDCl_3$) τ 2.55–2.80 (10 H, m, Ph), 7.85 (3 H, s, CH_3), 8.10 ppm (3 H, s, CH_3).

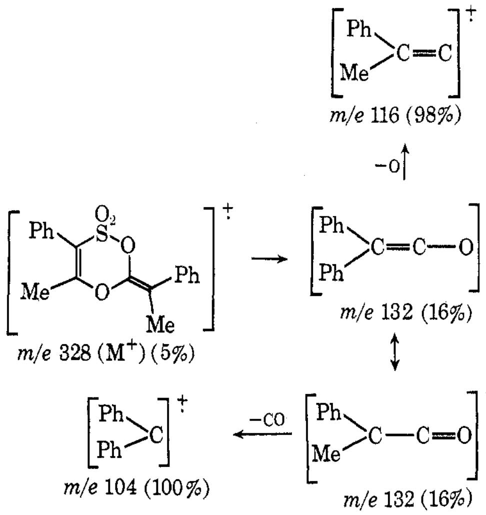
Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.85; H, 4.88; S, 9.76. Found: C, 65.82; H, 4.85; S, 9.95.

The mass spectrum of VIII obtained is explicable as shown in Scheme VIII.

The ^{13}C spectrum of VIII contains no signals around 190–235 ppm (corresponding to carbonyl carbons),[4,18] but three signals at δ 148, 157, and 159 ppm over the range 140–240 ppm from TMS, indicating the six-membered ring of VIII.

E. Derivatives of Cyclic Sulfones II and VII.—Two derivatives of II were obtained by neat thermal decomposition and basic hydrolysis. The neat thermal decomposition of II at 280° for 4 hr gave the tetraphenylethylene XV (yield 35%). XV was identified by infrared spectral comparsion and mixture melting point, 232–233°, with an authentic sample (lit.[19] mp 234°).

SCHEME VIII



The basic hydrolysis of II, under 2 *N* sodium hydroxide in 1:1 water–dioxane for 4 hr at 60°, yielded quantitatively diphenylmethyl benzyl sulfone (XVI), mp 157–158° dec, and benzoic acid (XIX). The identification of the sulfone was made by the following manner: ir 1310 (ν as SO_2) and 1130 cm^{-1} (ν s SO_2); nmr 2.4–2.9 (15 H, m, Ph), 4.85 (1 H, s, CH), and 5.85 ppm (2 H, CH_2). The mass spectrum was also in good agreement with the structure of the sulfone, *m/e* 258 ($M^+ - SO_2$), major peaks at *m/e* 167 [$(C_6H_5)_2CH^+$] and 91 ($C_7H_7^+$).

Anal. Calcd for $C_{20}H_{18}SO_2$: C, 74.53; H, 5.59; S, 9.95; Found: C, 74.52; H, 5.56; S, 10.28.

Benzoic acid (XIX) was identified by mixture melting point with the authentic sample.

The hydrolysis of VII with sodium hydroxide in 1:1 water–dioxane at 60° for 4 hr yields quantitative moles of α-phenethyl benzyl sulfone (XVII), mp 101° dec. This identification was made by the following manner: ir 1310 (ν as SO_2) and 1130 cm^{-1} (ν s SO_2); nmr ($CDCl_3$) τ 2.60–2.75 (10 H, m, Ph), 5.85 (1 H, q, CH), 6.00 (2 H, s, CH_2), 8.25 ppm (3 H, d, CH_3).

Anal. Calcd for $C_{15}H_{16}SO_2$: C, 69.23; H, 6.15; S, 12.29. Found: C, 69.25; H, 6.18; S, 12.32.

Photolysis of α-Diazo Ketones in Liquid Sulfur Dioxide.—Four α-diazo ketones as described in the thermal reaction were used. The α-diazo ketones (0.01 mol) were dissolved in liquid sulfur dioxide (32 g, 0.5 mol) in a Pyrex tube, which was irradiated by a high-pressure mercury lamp at 0–10°. The irradiation was stopped with disappearance of the absorption in the ir caused by the diazo group. The products were separated by silica gel chromatography in yields given in Table II. These products were identified by infrared spectral comparison and mixture melting point with samples previously prepared.

Apparatus.—Ir spectra were taken on a Hitachi EPI-S2 type infrared spectrometer. Nmr spectra were obtained with a JNM3H-60 spectrometer. Mass spectra were run on a Hitachi VD-10001-A spectrometer.

Registry No.—I, 3469-17-8; II, 33250-43-0; III, 33250-42-9; IV, 3893-35-4; VII, 36611-84-4; VIII, 36611-85-5; X, 3282-32-4; XIII, 31164-01-9; XVI, 21711-81-9; XVII, 36611-88-8; sulfur dioxide, 7446-09-5.

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[17] At present, there is no evidence to indicate whether VIII is the cis or trans isomer.

[18] E. W. Randall, *Curr. Awareness*, **26**, 371 (1971).

[19] C. E. Coffey, *J. Amer. Chem. Soc.*, **83**, 1623 (1961).