this indicated a total recovery of 39%, based on initial moles of cyclohexene. The distillation was not carried to completion, however, since the presence of the peroxide was anticipated.

Small-scale experiments (2 mmol) carried out in the above manner with or without 0.1 mmol of hydroquinone showed, by GLC analysis (10% UCW-98 on 80-100-mesh Gas Chrom Q), that hydroquinone completely suppressed the formation of 5c, but that the amount of 5b was unchanged.

Oxidation of Cyclooctene (6). Cyclooctene (20 mmol) was reacted with 10 mmol of SeO₂ and 40 mmol of tert-butyl hydroperoxide in 40 mL of CH_2Cl_2 at 25 °C for 48 h. The aqueous Na_2CO_3 quench to remove SeO_2 was followed by reduction of the excess hydroperoxide with Na₂SO₃.¹⁷ Standard workup and chromatography on silica gel (5% ethyl acetate in hexanes) gave 2-cycloocten-1-ol 6a, identified by spectral comparison to authentic material,¹⁸ and a mixture of the ether 6b and peroxide 6c. A LiAlH₄ reduction of this mixture afforded, after hydrolysis, a mixture of 6a and 3-tert-butoxy-1-cyclooctene (6b) from which the latter was obtained pure by chromatography: NMR (CCl₄) δ 5.5 (m, 2, olefinic H), 4.4 (br m, 1, CHOR), 1.15 (s, 9, tert-butyl); IR (CCl₄) 3020 (w, olefinic CH), 1200 (s) cm⁻¹. Medium-pressure chromatography (Merck LiChroprep Si-60) on the mixture of the nonpolar products afforded a sample of pure 3-(tert-butylperoxy)-1-cyclooctene (6c): NMR (CCl₄) δ 5.6 (m, 2, olefinic H), 4.85 (br m, CHOR), 1.25 (s, 9, tert-butyl).

Oxidation of Cyclododecene (7). Cyclododecene (16 mmol) was oxidized with 8 mmol of SeO₂ and 32 mmol of tert-butyl hydroperoxide under the same conditions described above for cyclooctene. Chromatography of the crude oil afforded pure 2-cyclododecen-1-ol (7a), identical with an authentic sample¹⁸ by NMR and IR, 2-cyclododecen-1-one, identified by spectral comparison to a sample prepared by MnO₂ oxidation of 7a, and a mixture of 7b and 7c. The latter compounds were obtained in pure form by the methods described above for cyclooctene. 3tert-butoxy-1-cyclododecene (7b): NMR (CCl₄) δ 5.45 (m, 2, olefinic H), 3.40 (br m, 1, CHOR), 1.18 (s, 9, tert-butyl); IR (CCl₄) 3020 (olefinic CH), 1200 (s) cm⁻¹. 3-tert-(Butylperoxy)-1-cyclododecene (7c): NMR (CCl₄) δ 5.45 (m, 2, olefinic H), 4.25 (br m, 1, CHOR), 1.22 (s, 9, tert-butyl). Conversion of the alcohol 7a to the acetate with acetic anhydride in pyridine at 25 °C and analysis by GLC on an OV-101 capillary column revealed the E/Zratio to be 77:23 when starting from (E)-cyclododecene and 80:20 when starting from (Z)-cyclododecene.

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Dye-Sensitized Photooxidation of Silyl Diazo Compounds. Intramolecular **Oxygen Transfer of Carbonyl Oxides**

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The dye-sensitized photooxidation of silyl diazo compounds produced the corresponding silyl ketones and silyl esters, and the latter may be formed by the rearrangement of silyl-substituted carbonyl oxides. The reactions of a carbonyl oxide with various silyl ketones were also studied. The dye-sensitized photooxidation of diphenyldiazomethane in the presence of silyl ketones gave silyl esters together with benzophenone by reactions of a carbonyl oxide with the silyl ketones accompanying 1,2-anionic rearrangement of the silyl group.

A carbonyl oxide is a well-known Criegee-type intermediate in ozonolysis of alkenes or alkynes,¹ and recently its important role in biological systems has been recog-The most clean formation of carbonyl oxides nized.² involves the reaction of singlet oxygen with diazo compounds³ or the direct carbene reaction with ground-state molecular oxygen.⁴ Carbonyl oxides react intermolecularly with several substrates such as alkanes,⁵ alkenes,⁶ sulfides,⁷

sulfoxides,^{7,8} and aromatic compounds⁹ and can transfer an oxygen atom to their substrates. Although many types of intermolecular reactions of carbonyl oxides have been reported, intramolecular ones seem to be less investigated so far.¹⁰ Here, we report the detailed study on the dyesensitized photooxidation of silyl diazo compounds and suggest the formation of silyl-substituted carbonyl oxides

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Table I. Dve-Sensitized Photooxidation of 1^a

solvent	sensi- tizer	additive	product yield, %	
			2	3
Me ₂ CO	TPP		58	27
Et ₀	TPP		57	32
Et_2O^b	TPP		68	26
CĆl₄	TPP		60	38
C, H,	TPP		48	40
C H	TPP	PhCHO	48	30
CHCl,	TPP		57	38
CHCl	TPP	Ph_2S	60	24
CHCI	MB^{c}	2	55	36
CH ₂ Cl ₂	TPP		53	41
CH ₂ Cl ₂ ^b	TPP		54	43
CH,Cl,	MB ^c		45	43

^a The reactions were carried out under bubbling oxygen for 10 min at room temperature. ^b Reaction at -78 °C. ^c Methylene blue.

and their rearrangement to silyl esters via intramolecular reactions.¹¹

Results and Discussion

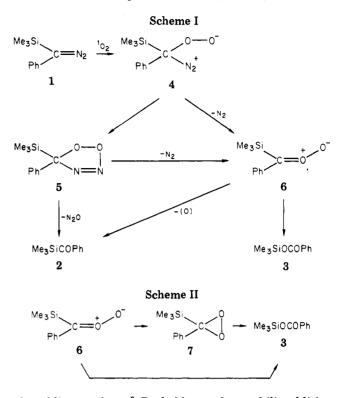
The generation of carbonyl oxides by the ozonolysis of alkenes and alkynes is well-known, but these systems are not appropriate for the study of a carbonyl oxide because of the involvement of some other peroxidic species.¹ The most suitable method for carbonyl oxide formation is the dye-sensitized photooxidation of diazo compounds.³ Silyl-substituted diazo compounds may be specially suitable targets for the investigation of the intramolecular reaction of carbonyl oxides since silicon has a strong affinity for oxygen. We have therefore studied the dye-sensitized photooxidation of (trimethylsilyl)phenyldiazomethane and ethyl (trimethylsilyl)diazoacetate.

Photooxidation of (Trimethylsilyl)phenyldiazomethane. A mixture of (trimethylsilyl)phenyldiazomethane (1, 0.704 mmol) in 10 mL of carbon tetrachloride containing TPP (*meso*-tetraphenylporphine) as a sensitizer was photolyzed in a water-cooled Pyrex tube with a 300-W halogen lamp under bubbling oxygen. The strong infrared absorption of the diazo group disappeared within 10 min. Analysis of the reaction mixture by GLC showed the formation of two products, trimethylsilyl phenyl ketone (2) and trimethylsilyl benzoate (3), in 60% and 38% yields,

$$\begin{array}{c} \text{Me}_{3}\text{SiC}(\text{N}_{2})\text{Ph} \xrightarrow{h\nu/\text{O}_{2}/\text{sens}} \text{Me}_{3}\text{SiCOPh} + \text{Me}_{3}\text{SiOCOPh} \\ 1 & 2 & 3 \end{array}$$
(1)

respectively. The structures of the silyl ketone 2 and the silyl benzoate 3 were confirmed by comparison of their NMR and IR spectra with those of authentic samples. Similar results were obtained when the reaction was carried out in acetone, ether, benzene, chloroform, and dichloromethane. Significant differences in the product yields were not observed. Reaction temperatures and sensitizers also did not affect their yields. These results are summarized in Table I.

The reaction did not proceed in the absence of the sensitizer, and ca. 86% of 1 was recovered after 10 min of irradiation. The silyl ketone 2 was stable under the photooxidation conditions and did not give the silyl benzoate 3. Singlet oxygen may be the reactive species as reported by Murray in the dye-sensitized photooxidation of di-



phenyldiazomethane.³ Probably, an electrophilic addition of singlet oxygen to the carbanion center of the diazo compound 1 gives zwitterion 4 which cyclizes to peroxide 5 (Scheme I). Elimination of nitrous oxide or nitrogen from 4 or 5 gives the silvl ketone 2 or the silvl carbonyl oxide 6. Gas analysis of the reaction mixture by GLC showed the formation of nitrogen and nitrous oxide. The retention times of these gases were identical with those of authentic samples, and their mass spectra showed the strong molecular ion peaks at m/e 28 and 44, respectively. Although carbonyl oxides are known to be trapped by aldehydes,³ the reaction of 1 in the presence of excess benzaldehyde did not affect the product yields. Similarly, the reaction of 1 in the presence of diphenyl sulfide as an oxygen-accepting reagent did not give any diphenyl sulfoxide. These results strongly suggest that the silvl benzoate 3 is produced by the intramolecular reaction of the silyl carbonyl oxide 6.

The possibility of the reaction of the silyl carbonyl oxide 6 with the silyl ketone 2 was eliminated since the reaction of 1 in the presence of dimethylphenylsilyl phenyl ketone did not give any dimethylphenylsilyl benzoate, and the silyl benzoate 3 was formed (eq 2). Furthermore, the reaction

$$\begin{array}{c} \text{Me}_{3}\text{SiC}(\text{N}_{2})\text{Ph} + \text{PhMe}_{2}\text{SiCOPh} & \xrightarrow{h\nu/\text{O}_{2}/\text{TPP}} \\ \hline \text{Me}_{3}\text{SiCOPh} + \text{Me}_{3}\text{SiOCOPh} + \text{PhMe}_{2}\text{SiCOPh} + \\ 2 (55\%) & 3 (36\%) & \text{recovered} \\ & \text{PhMe}_{2}\text{SiOCOPh} (2) \\ & 0\% \end{array}$$

of (dimethylphenylsilyl)phenyldiazomethane in the presence of 2 produced dimethylphenylsilyl benzoate and dimethylphenylsilyl phenyl ketone in 30% and 65% yields, respectively (eq 3), and no trimethylsilyl benzoate was observed.

PhMe₂SiC(N₂)Ph + Me₃SiCOPh
$$\xrightarrow{h\nu/O_2/\text{TPP}}$$

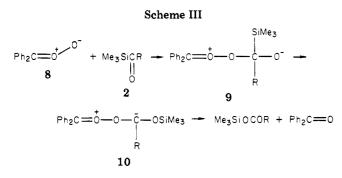
PhMe₂SiCOPh + PhMe₂SiOCOPh + Me₃SiCOPh + 65% 30% recovered
Me₃SiOCOPh (3) 0%

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Table II. Dye-Sensitized Photooxidation of Diphenyldiazomethane in the Presence of Silyl Ketones a

			product yield	, %
solvent	irr time, min	silyl ketone	silyl ester ^b	benzo- phenone ^c
Et,O	30	Me ₃ SiCOPh	64 (Me ₃ SiOCOPh)	67
C ₆ Ĥ ₆	10	Me SiCOPh	67 (Me ₃ SiOCOPh)	67
CCl₄	10	Me _s SiCOPh	42 (Me SiOCOPh)	74
CHCl ₃	20	Me ₃ SiCOPh	38 (Me SiOCOPh)	72
CH_2CI_2	30	Me ₃ SiCOPh	33 (Me ₃ SiOCOPh)	70
$\operatorname{Et}_2 \operatorname{O}^{d^2}$	40	Me ₃ SiCOPh	49 (Me ₃ SiOCOPh)	64
$C\dot{H}_2 Cl_2 d$	30	Me ₃ SiCOPh	trace (Me ₃ SiOCOPh)	67
$C_6 \tilde{H_6}$	20	Et, SiCOPh	47 (Et SiOCOPh)	65
$\mathbf{C}_{6}^{r}\mathbf{H}_{6}^{r}$	10	PhMe,SiCOPh	48 (PhMe,SiOCOPh)	74
$\mathbf{C}_{6}^{\circ}\mathbf{H}_{6}^{\circ}$	10	Me₃SiCO- <i>i</i> -Pr	21 (Me ₃ SiOCO- <i>i</i> -Pr)	72

^a 0.5 equiv of silyl ketone for each 1 equiv of diphenyldiazomethane was used. The reaction was carried out until the diazo compound was completely decomposed with TPP as the sensitizer under bubbling oxygen at room temperature. ^b Yields based on the silyl ketone. ^c Yields based on diphenyldiazomethane. ^d Reaction at -78 °C.

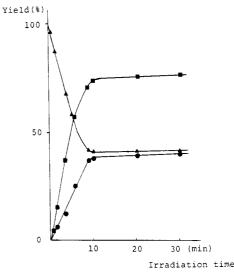


The most probable mechanism for the silyl benzoate 3 involves the formation of three-membered dioxirane 7 (Scheme II) and its rearrangement to the silyl benzoate via 0–0 bond scission.¹² A concerted path from the silyl carbonyl oxide 6 or the dioxirane 7 to the silyl benzoate is also possible. The mechanism involving the dioxirane offers a rationale for the recent results on the ozonolysis of (trimethylsilyl)- and (triethylsilyl)ketenes¹³ and a recent suggestion of Moriarty.¹⁴ Very recently, Adam also presented the similar results in the reaction of silylfuran endoperoxide.¹⁵

Intermolecular oxygen transfer of carbonyl oxide was not observed in the photooxidation of 1 but was observed in the photooxidation of diphenyldiazomethane in the presence of silyl ketones.¹⁶ When a mixture of 2.0 mmol of diphenyldiazomethane and 1.0 mmol of trimethylsilyl phenyl ketone (2) in 10 mL of carbon tetrachloride containing TPP was photolyzed with a 300-W halogen lamp under bubbling oxygen (eq 4), the silyl benzoate 3 was

$$\frac{Ph_2CN_2 + Me_3SiCOPh}{2} \xrightarrow{h\nu/O_2/1PP} CCl_4}{Me_3SiOCOPh + Ph_2CO (4)}$$

obtained in 42% yield (based on the silyl ketone) along with benzophenone (74% yield based on diphenyldiazomethane). Figure 1 shows that the reaction is complete after 10 min of irradiation, and the yields of the silyl benzoate and benzophenone increase with the irradiation time. On the other hand, that of the silyl ketone decreases.



product wold of

Figure 1. Dye-sensitized photooxidation of diphenyldiazomethane in the presence of trimethylsilyl phenyl ketone. The reaction was carried out in carbon tetrachloride by using 2 mmol of diphenyldiazomethane and 1 mmol of 2: \blacktriangle , yield of 2; \bigcirc , yield of 3 based on 2; \blacksquare , yield of benzophenone based on diphenyldiazomethane.

The results under the various conditions are listed in Table II. The corresponding silyl benzoates were obtained by the photooxidation of diphenyldiazomethane in the presence of triethylsilyl phenyl ketone and dimethylphenylsilyl phenyl ketone (Table II). A plausible mechanism for the silyl benzoates involves addition of the carbonyl oxide 8 to the silyl ketone 2 to give the zwitterion 9 (Scheme III). The oxyanion may undergo ring closure or silyl migration. One would expect silicon migration to prevail sufficiently over ring closure to give ozonide, leading to the formation of another zwitterion, 10.

The reaction appears to be closely related to the rearrangement of silylmethanols to the isomeric silyl ethers.¹⁷ Since the yield of the silyl esters from aryl silyl ketones is higher than that of isopropyl trimethylsilyl ketone, migration of the trimethylsilyl group may occur most readily when the aryl group on carbon is able to delocalize a negative charge. Elimination of benzophenone from the zwitterion 10 would result in the formation of the silyl esters.¹⁸ The yields of the silyl esters are relatively lower in halogen-containing solvents than those in solvents of

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Table III. Dye-Sensitized Photooxidation of 11^a

solvent		% yield		
	additive	11	12	13
CCl ₄		5	24	64
CCl	Dabco ^b	100	0	0
C ₆ H ₆		15	21	41

^a The reaction was carried out under bubbling oxygen for 2 h with TPP at room temperature. ^b 1,4-Diazabicyclo[2.2.2]octane.

benzene and ether. Although the reason for these solvent effects is not clear at present, we feel that the carbonyl oxide 8 may oxidize the halogen-containing solvents.

Photooxidation of Ethyl (Trimethylsilyl)diazoacetate. Silyl oxalate 12 and silyl ketone 13 were obtained by the dye-sensitized photooxidation of ethyl(trimethylsilyl)diazoacetate 11 (eq 5). The oxidation of the diazo

$$\begin{array}{c} \text{Me}_{3}\text{SiC}(\text{N}_{2})\text{CO}_{2}\text{Et} \xrightarrow[\text{TPP}]{}{} \\ 11 \\ \text{Me}_{3}\text{SiOCOCO}_{2}\text{Et} + \text{Me}_{3}\text{SiCOCO}_{2}\text{Et} \ (5) \\ 12 \\ 13 \end{array}$$

ester was very slow as compared with that of 1 since the diazo ester has a strong electron-withdrawing group. Thus, it takes more than 2 h for the complete consumption of the diazo ester 11. Singlet oxygen might be the reactive species for the oxidation of 11 because the reaction is completely inhibited in the presence of 1,4-diazabicyclo-[2.2.2]octane. The results under the various conditions are shown in Table III. Since silyl ketone 13 is stable under the photooxidation conditions, the silyl ester 12 is formed via intramolecular rearrangement of a silyl carbonyl oxide.

In summary, it is now clear that the silyl ester in the photooxidation of silyl diazo compounds arises from the intramolecular rearrangement of the silyl carbonyl oxide. A strong Si-O bond formation prevails sufficiently over the intermolecular reaction of the carbonyl oxide. Direct evidence for the transformation of the silyl carbonyl oxide to the silyl esters was given.

Experimental Section

The NMR and IR spectra were recorded on Varian EM 360A and Hitachi 260-50 spectrometers. UV spectra were obtained on a JASCO UVIDC-1 spectrometer. Gas chromatographic analyses were performed on a Hitachi gas chromatograph with a 4.5 mm \times 3 m glass column of 10% SF-96 on Celite 545 and on an Ohkura gas chromatograph with a 4 mm \times 2 m stainless-steel column of 10% SF-96 on Celite 545. Preparative gas chromatograph with a 6 mm \times 1.5 m stainless-steel column of 10% SF-96 on Celite 545. Gas produced in the dye-sensitized photooxidation of (trimethylsilyl)phenyldiazomethane was analyzed by a 4.5 mm \times 1 m glass column packed with molecular sieves. GC/MS analysis was carried out with a Hitachi RMU-6M spectrometer.

Materials. (Trimethylsilyl)phenyldiazomethane,¹⁹ (dimethylphenylsilyl)phenyldiazomethane,¹⁹ ethyl (trimethylsilyl)diazoacetate,²⁰ and diphenyldiazomethane²¹ were prepared by known procedures as referenced. Trimethylsilyl phenyl ketone, dimethylphenylsilyl phenyl ketone, triethylsilyl phenyl ketone, and trimethylsilyl isopropyl ketone were prepared according to the method of Brook²² or Kuwajima.²³ Authentic silyl esters were prepared by the reaction of sodium salts of the corresponding acids with chlorosilanes in ether. The silyl oxalate 12 was prepared by the reaction of diethyl oxalate with trimethylsilyl iodide.²⁴

Typical Procedure of the Photooxidation of (Trimethylsilyl)phenyldiazomethane. A 10-mL carbon tetrachloride solution of (trimethylsilyl)phenyldiazomethane (0.7 mmol) and 10-30 mg of TPP in a water-cooled Pyrex tube was irradiated with a 300-W halogen lamp with bubbling of oxygen through the mixture for 10 min. Products were separated by preparative GLC and identified by comparison of their NMR and IR spectra with those of authentic samples. Yields were determined by GLC by using an internal standard. The results under the various conditions are given in Table I.

Photooxidation of (Trimethylsilyl)phenyldiazomethane in the Presence of Benzaldehyde. A solution of (trimethylsilyl)phenyldiazomethane (137 mg, 0.719 mmol), benzaldehyde (381 mg, 3.60 mmol), and TPP in benzene (10 mL) was irradiated with bubbling oxygen for 10 min. The results are given in Table I.

Photooxidation of (Trimethylsilyl)phenyldiazomethane in the Presence of Diphenyl Sulfide. A solution of (trimethylsilyl)phenyldiazomethane (134 mg, 0.705 mmol), diphenyl sulfide (650 mg, 3.49 mmol), and TPP in chloroform (10 mL) was irradiated with bubbling of oxygen through the mixture for 10 min. The results are given in Table I. No diphenyl sulfoxide was found by GLC analysis.

Photooxidation of (Trimethylsilyl)phenyldiazomethane in the Prescence of Dimethylphenylsilyl Phenyl Ketone. A solution of (trimethylsilyl)phenyldiazomethane (190 mg, 1 mmol), dimethylphenylsilyl phenyl ketone (240 mg, 1 mmol), and TPP in benzene (10 mL) was irradiated with bubbling of oxygen through the mixture for 10 min. Trimethylsilyl phenyl ketone and trimethylsilyl benzoate were formed in 55% and 36% yields, respectively. No dimethylphenylsilyl benzoate was found by GLC analysis.

Photooxidation of (Dimethylphenylsilyl)phenyldiazomethane in the Presence of Trimethylsilyl Phenyl Ketone. A solution of (dimethylphenylsilyl)phenyldiazomethane (250 mg, 1 mmol), trimethylsilyl phenyl ketone (180 mg, 1 mmol), and TPP in benzene (10 mL) was irradiated with bubbling of oxygen through the mixture for 10 min. Dimethylphenylsilyl phenyl ketone and dimethylphenylsilyl benzoate were formed in 65% and 30% yields, respectively. No trimethylsilyl benzoate was found by GLC analysis.

Typical Procedure of the Photooxidation of Diphenyldiazomethane in the Presence of Silyl Ketones. A 10-mL carbon tetrachloride solution of diphenyldiazomethane (2 mmol), silyl ketone (1 mmol), and TPP in a water-cooled Pyrex tube was irradiated with a 300-W halogen lamp with bubbling of oxygen through the mixture for 10 min. The results under the various conditions are given in Table II.

Photooxidation of Ethyl (Trimethylsilyl)diazoacetate. A solution of ethyl (trimethylsilyl)diazoacetate (190 mg, 1.02 mmol) and TPP in carbon tetrachloride (10 mL) was irradiated with bubbling of oxygen through the mixture for 2 h. Products were collected by preparative GLC and identified as the silyl oxalate 12 and the silyl ketone 13. The silyl ketone 13 was identified by NMR, IR, and UV spectra and elemental analyses: NMR (CCl₄) δ 0.33 (s, 9 H, SiMe₃), 1.40 (t, 3 H, OCCH₃), 4.27 (q, 2 H, OCH₂); IR (NaCl) 1740 and 1710 (CO₂Et), 1660 cm⁻¹ (SiCO); UV (C₆H₁₂) λ_{max} 455 (ϵ 97), 230 (388). Anal. Calcd for C₇H₁₄O₃Si: C, 48.24; H, 8.09. Found: C, 48.25; H, 8.12.

Photooxidation of Ethyl (Trimethylsilyl)diazoacetate in the Presence of 1,4-Diazabicyclo[2.2.2]octane. A solution of ethyl (trimethylsilyl)diazoacetate (95 mg, 0.511 mmol), Dabco (346 mg, 3.09 mmol), and TPP in carbon tetrachloride (60 mL) was irradiated with bubbling of oxygen through the mixture for 2 h. The silyl diazo ester 11 was completely recovered.

Registry No. 1, 24379-49-5; 2, 5908-41-8; 3, 2078-12-8; 11, 17145-48-1; 12, 72450-53-4; 13, 71419-94-8; PhMe₂SiCOPh, 17909-51-2; PhMe₂SiC(N₂)Ph, 55983-29-4; PhMe₂SiOCOPh, 53358-43-3; Ph₂CN₂, 883-40-9; TPP, 917-23-7; MB, 61-73-4; Me₃SiCO-*i*-Pr, 56583-93-8; Et₃SiCOPh, 63935-93-3; benzaldehyde, 100-52-7; diphenyl sulfide, 139-66-2; 1,4-diazabicyclo[2.2.2.]octane, 280-57-9.

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