Supplementary Material Available. Table II (26 pages). Ordering information is given on any current masthead page.

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(35) The choice of ligands O(1), O(2) of catechol A as the pair, and of ligand O(3) plus ligands O(4), O(5) of catechol C as the trio, provides an alternate and nearly equivalent TR mechanism for compound **9**. To visualize this alternative rotate formula a, Figure 4, 180° about bond P–O(3), and carry out a set of motions analogous to those depicted in Figure 4, using the appropriate ligands. The TR mechanisms of **9** using O(1), O(2) or O(4), O(5) as the pair generate configurations which are indistinguishable within the uncertainty in the data of Tables III–VII.
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(38) NOTE ADDED IN PROOF. The term "static TR configuration" is a convenient designation for those phosphoranes which clearly do not resemble a TBP about the phosphorus atom. As originally conceived (ref 13), "TR configuration" had the dynamic connotation defined in Figure 4; however, this concept now seems more general and capable of providing an adequate description of the molecular geometry of certain complex phosphoranes. X-Ray analyses carried out since the submisssion of this paper have uncovered other examples of 5,5-spirobicyclic homophosphoranes (five oxygen ligands), and 5-monocyclic heterophosphoranes (two oxygen and three carbon ligands) whose geometry conform to the definition of static TR configuration.

Structural Effects on Excited State Production by Dioxetanes. 3,4-Dimethyl-3,4-diphenyldioxetane and 3-Methyl-3-phenyldioxetane

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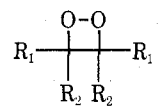
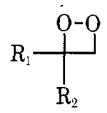
The preparation of 3,4-dimethyl-3,4-diphenyldioxetane (**1c**) is reported. Its activation energy for decomposition is 25 ± 1 kcal/mol, and its activation entropy is −3 ± 3 eu. The efficiency of excited triplet ketone production of **1c** is equal to that of tetramethyldioxetane (**1a**) as determined by direct comparison of dioxetane-induced dibromoanthracene emission. The efficiency of 3-methyl-3-phenyldioxetane (**2c**), determined by the same method, is less than one-third that of **1a**.

Excited triplet carbonyl products are efficiently generated in the thermal cleavage of 1,2-dioxetanes in apparent violation of spin-conservation rules.[1,2] Large differences have been observed in the yields of triplet products (in effect, the percentage of carbonyl products formed in the triplet state) from various dioxetanes,[1,3] although no explanations for this have been advanced. The efficiencies range from 30–50% for tetramethyldioxetane (**1a**) (100% corresponds to one triplet carbonyl per dioxetane[4])[1b] to 2–4% for 3,4-dimethyl-3,4-di-*n*-butyldioxetane (**1b**)[3a,5] and 3,3-dibenzyl- and 3,3-diphenyldioxetanes (**2a**[3b] and **2b**).[3c] In an effort to identify some of the basic structural factors affecting the efficiency of triplet production, we wish to report the efficiences of excited state formation of the dioxetanes **1c** and **2c** relative to **1a**.



1a, $R_1 = R_2 = Me$
b, $R_1 = Me$; $R_2 = n\text{-}Bu$
c, $R_1 = Me$; $R_2 = Ph$
d, $R_1 = H$; $R_2 = OEt$



2a, $R_1 = R_2 = CH_2Ph$
b, $R_1 = R_2 = Ph$
c, $R_1 = Me$; $R_2 = Ph$

We have prepared the new dioxetane, 3,4-dimethyl-3,4-diphenyldioxetane (**1c**), via the bromohydroperoxide, by a

Table I
Triplet Yields of 1c and 2c Relative to 1a[a]

	Temp,[b] °C	10^4 k, sec^{-1} [c]	k(1a)/k[d]	I/I(1a)[e]	$^3\Phi/^3\Phi$ (1a)[f]
1c[g]	71	1.76 ± 0.10	2.6 ± 0.2	0.34 ± 0.02	0.98 ± 0.10
	55	0.30 ± 0.04	2.6 ± 0.4	0.32 ± 0.02	0.92 ± 0.15
2c[h]	48.5	4.49 ± 0.10	0.080 ± 0.009	4.8 ± 0.3	0.29 ± 0.04
	37	1.22 ± 0.05	0.070 ± 0.013	5.1 ± 0.3	0.27 ± 0.06

[a] Solvent, xylenes. [b] Corrected internal temperature, ±0.5°. [c] Calculated from the Arrhenius equation, using E_a = 25 ± 1 kcal/mol for 1c and 22.6 ± 0.3 kcal/mol for 2c. Errors show range. [d] Using k(1a) calculated from the Arrhenius equation, E_a = 25 ± 1 kcal/mol. Errors propagated as variance, treating ranges as standard deviations. [e] Errors estimated graphically. [f] Errors propagated as variance. [g] c(1c) 2.9 × 10^{-3} M, c(1a) 3.2 × 10^{-3} M, c(DBA) 2 × 10^{-3} to 2 × 10^{-2} M. [h] c(2c) 5.4 ± 0.3 × 10^{-3} M, c(1a) 4.1 × 10^{-3} M, c(DBA) 1.5 × 10^{-3} to 1.5 × 10^{-2} M.

modification of the procedure developed by Kopecky et al.[6] Both geometric isomers of the dioxetane were observed in solution by NMR, but only the major isomer was obtained crystalline, and was the material studied.[7] Thermolysis of **1c** produced only acetophenone by NMR and ir analysis. Its decomposition in toluene or xylenes, followed by the fluorescence decay of added dibromoanthracene (DBA), was first order, with E_a = 25 ± 1 kcal/mol and $\Delta S^\ddagger$ = −3 ± 3 eu. (For **1a** we observed E_a = 25 ± 1 kcal/mol and $\Delta S^\ddagger$ = −1 ± 3 eu; lit.[6a] E_a = 25.8 ± 0.5 kcal/mol, $\Delta S^\ddagger$ = −2 ± 2 eu.) Dioxetane **2c** was prepared according to literature procedures,[1a,8] and was not isolated from solution. Its decomposition in xylenes was first order, with E_a = 22.6 ± 0.3 kcal/mol and $\Delta S^\ddagger$ = −3.4 ± 1 eu (lit.[8] E_a = 22.9 kcal/mol, $\Delta s^\ddagger$ = −5.3 ± 0.9 eu).

The efficiency of triplet production by **1c** and **2c** relative to **1a** was obtained by comparing the emission intensity from solutions of the dioxetane and DBA.[9] It has been shown that the fluorescence of DBA in the presence of decomposing dioxetanes is due essentially only to energy transfer from triplet carbonyl species.[9] The intensity is thus described by eq 1

$$I = k[\text{dioxetane}]\,{}^3\Phi\,\Phi_{ET}\,\Phi_F \qquad (1)$$

where k is the rate constant for dioxetane decomposition, $^3\Phi$ is the efficiency of triplet formation, Φ_{ET} is the efficiency of triplet–singlet energy transfer from the excited carbonyl to DBA, and Φ_F is the fluorescence quantum yield of DBA. At sufficiently high DBA concentrations, Φ_{ET} reaches a limiting value of 0.25, which is determined by the competition between triplet–triplet and triplet–singlet energy transfer to DBA, and is assumed to be general for carbonyl compounds.[9] The ratio of intensities from two dioxetane solutions, when extrapolated to infinitely high DBA concentration, is expressed in eq 2.

$$\frac{I_A}{I_B} = \frac{{}^3\Phi_A\, k_A\, [A]}{{}^3\Phi_B\, k_B\, [B]} \qquad (2)$$

The ratio of intensities from dilute xylene solutions of **1c** or **2c** to **1a** were obtained, under identical conditions, over a tenfold range of DBA concentrations and extrapolated graphically to infinite acceptor concentration (intercept of the plot of the intensity ratio vs. the reciprocal of the DBA concentration). Rate constants at the temperatures of the intensity measurements were calculated from the Arrhenius equation, using conveniently measured rate constants and the average E_a determined for each dioxetane. Values of E_a obtained by rapid temperature change experiments[1c,10] agreed with the Arrhenius values within our experimental error, indicating the absence of significant dark decomposition pathways.[11]

The results, which are summarized in Table I, show that **1c** was as efficient in triplet formation as **1a** [$^3\Phi$(**1c**)/$^3\Phi$(**1a**) = 0.98 ± 0.1], while **2c** was significantly less efficient [$^3\Phi$(**2c**)/$^3\Phi$(**1a**) = 0.29 ± 0.04].[12] The reproducibility of the ratios at different temperatures is consistent with the finding that $^3\Phi$ (for **1a**) is temperature independent.[10]

The cleavage products from these dioxetanes, acetone, acetophenone, and formaldehyde, all have lowest energy triplet n,π^* states.[13] In aromatic ketones such as acetophenone, however, a small degree of mixing of this state with a higher energy triplet π,π^* state is believed to occur.[14] The equality of triplet yields from **1c** and **1a** shows that such perturbations caused by a neighboring phenyl ring do not affect the energy surface crossing in dioxetane decompositions. The greatly reduced efficiency of **2c**, which produces acetophenone and formaldehyde, suggests that the large dissymmetry in the dioxetane structure significantly affects excited state production.[15] Consistent with this possibility are the low triplet yields of the geminally disubstituted dioxetanes **2a** and **2b**.[3b,c] The symmetrical disubstituted *cis*-diethoxydioxetane **1d**, in contrast, is almost as efficient as **1a** in excited triplet production.[16] Evidently, other factors are also involved in determining the yield of excited states. The symmetrical **1b**, for example, is relatively inefficient in triplet formation,[3a] while trimethyldioxetane is as efficient as **1a**.[9] Clearly, more experimental studies are needed for a full understanding of this unique reaction.

Experimental Section

Caution! Hydroperoxides and dioxetanes are potentially explosive.[6]

Melting points are uncorrected. NMR spectra were recorded on a Varian A-60 or on a JEOL MH-100 spectrometer, with Me_4Si as the internal standard. Reactions in tetrahydrofuran were conducted under nitrogen and the solvent was freshly distilled from sodium benzophenone ketyl. All water which came into contact with dioxetane solutions had stood for several hours over Na_2EDTA. Anhydrous H_2O_2 solutions were prepared by slowly pouring 84% H_2O_2 (FMC Corp.) into ice-cold anhydrous ether or glyme and stirring with $MgSO_4$ at 0° for 8–10 hr.[17] Molarity was determined by iodometric titration. Authentic samples of *dl*- and *meso*-2,3-dibromo-2,3-diphenylbutane[18] and 3,3-diphenyl-2-butanone[19] were prepared by established routes for spectral comparison with side products formed in the reactions leading to **1c**.

Dimethylstilbene (2,3-Diphenyl-2-butene). Dimethylstilbene was prepared by reductive coupling of acetophenone using either a reduced tungsten[20] or a reduced titanium reagent.[21] To 300 ml of THF cooled to −70° was added 45.4 g (0.114 mol) of WCl_6 (Pressure Chemical Co.), followed by 116 ml (0.232 mol) of 1.97 M *n*-BuLi (Alfa). The vigorously stirred mixture was allowed to reach room temperature and 9 g (0.075 mol) of acetophenone (Amend, distilled) was added. The reaction mixture was stirred at reflux for 4 days, then cooled and poured into an aqueous alkaline tartrate solution and extracted with hexanes. The dried ($MgSO_4$) organic phase was concentrated and the oily product chromatographed on silica gel to give 6 g (78%) of a mixture of roughly equal amounts of *cis*- and *trans*-dimethylstilbene. Fractional recrystallization from methanol gave samples of, first, *trans*-dimethylstilbene, white needles or prisms, mp 94–100° (lit.[22] 105°), NMR (CCl_4) δ 1.88 (s, 6 H), 7.22 (s, 10 H), and then of *cis*-dimethylstilbene, white granular crystals, mp 53–63° (lit.[22] 66°), NMR (CCl_4) δ 2.16 (s, 6 H), 6.96 (m, 9.4 H). Alternatively, to 200 ml of THF at −70° was added 20 g (0.13 mol) of $TiCl_3$ (Alfa) and 2.6 g (0.068 mol) of $LiAlH_4$ (Alfa). The stirred mixture was allowed to warm to room temperature, and 7.4 g (0.062 mol) of acetophenone was added. The reaction mixture was stirred at reflux for 5.5 hr, and then at ambient temperature for ≈12 hr. Work-up as above gave 7 g of products, which was found by NMR to consist of 45% dimethylstilbene diol (CCl_4 δ

1.42, CH_3), 20% *trans*-, and 35% *cis*-dimethylstilbene. The olefins were separated from the diol by recrystallization from methanol.

3-Bromo-2,3-diphenyl-2-butyl Hydroperoxide. Modifications of solvent, reaction time at low temperature, and H_2O_2 concentration were introduced into the literature procedure for bromohydroperoxidation.[6b] A mixture of dimethylstilbene isomers (1.08 g, 5.2 mmol; cis:trans ≈ 3:1) was dissolved in 12 ml of THF under nitrogen. The solution was cooled to −40° and 7 ml of a 7.8 *M* solution of H_2O_2 in anhydrous glyme (55 mmol) was added by pipet. While the solution was stirred at −40°, 0.8 g (2.8 mmol) of 1,3-dibromo-5,5-dimethylhydantoin (Matheson Coleman and Bell) was added in small portions over 1.5–2 hr. The solution, now pale yellow, was allowed to reach −20°, and stirred at that temperature for 5 hr. The reaction flask was stoppered and placed in a freezer (−20°) for ≈12 hr. The mixture was poured into 50 ml of ice-cold water and extracted with ether. The aqueous phase was extracted again with ether, and the combined organic phases were washed with two 50-ml portions of cold water, followed by cold saturated brine, and dried over Na_2SO_4. An NMR of the reaction mixture in benzene showed the isomeric bromohydroperoxides[23] (δ 1.81, 2.11, threo, 44%; 1.88, 2.05, erythro, 6%), the isomeric dibromides (δ 2.45, *dl*, 22%; δ 2.29, meso, 2%), a product believed to be the allylic bromide (δ 1.79, 4.03, 13%), and *trans*-dimethylstilbene (δ 1.92, 14%). The concentrated reaction mixture was applied to a 2.5 × 10 cm silica gel column prepared in hexanes (room temperature). Elution with hexanes removed the unreacted olefin. Ten percent ether in hexanes eluted the bromohydroperoxides, NMR (benzene) δ 1.82 (s), 2.12 (s), threo, 79%; 1.86 (s), 2.05 (s), erythro, 10%. Small amounts of acetophenone (δ 2.1) and of 3,3-diphenyl-2-butanone (δ 1.71, 1.82) were present. A similar product mixture resulted when pure *cis*-dimethylstilbene was used, including the formation of *trans*-dimethylstilbene. Pure *trans*-dimethylstilbene gave analogous yields, but the erythro bromohydroperoxide predominated over the threo 4:1.

3,4-Dimethyl-3,4-diphenyldioxetane (1c). A solution of approximately 0.8 mmol of 3-bromo-2,3-diphenyl-2-butyl hydroperoxide (erythro:threo 4:1) in 6 ml of benzene was cooled to 7°. To the stirred solution was added 35 mg (0.21 mmol) of silver acetate (J. T. Baker, purified powder). After 6 min the suspension was filtered. The orange filtrate was washed with ice-cold water, extracted with ether, and dried (Na_2SO_4). The NMR spectrum (CCl_4) showed 3,3-diphenyl-2-butanone (δ 1.79, 2.02, 7.25, 60%), **1c** (δ 1.98, 7.06, 16%), acetophenone (δ 2.50, 7.4, 7.9, 13%), and six signals due to minor impurities (10%). The reaction mixture in a small volume of benzene was applied to a silica gel column (12 g of Grace silica gel mixed with 200 mg of Na_2EDTA) made up in hexanes and chilled to 5° with an ice–water jacket. Rapid elution with 10% CH_2Cl_2 in hexanes recovered the dioxetane in the second 100 ml of eluent, NMR (CCl_4) δ 1.99 (s, 6.0 H), 7.07 (broad s, 9.5 H), major isomer, 84%; 1.45 (s, 6.0 H), 7.42 (broad s, 10.0 H), minor isomer, 16%. The estimated total yield of pure dioxetanes, based on the NMR signal intensity, was 10%. Starting with a solution of 8:1 threo:erythro bromohydroperoxide resulted in analogous yields, except that the dioxetane isomer ratio was 2:1, with the same isomer predominating. Crystallization from 2–3 ml of cold pentane in either case gave tiny off-white needles of the isomer, mp 85–91° (oil bath preheated to 70°), NMR (CCl_4) δ 1.99 (s, 6 H), 7.06 (s, 10 H). No other signals were present in the NMR spectrum. Refluxing either this isomer or the isomer mixture in CCl_4 for several hours produced only acetophenone by NMR and ir analysis.

1-Bromo-2-phenyl-2-propyl Hydroperoxide.[1a,8] To 2.4 g (20 mmol) of α-methylstyrene (City Chemical Corp.) in 40 ml of anhydrous ether, chilled to −40°, was added 20 ml (130 mmol) of a solution of 6.5 *M* H_2O_2 in anhydrous ether, followed by 3.0 g (10 mmol) of 1,3-dibromo-5,5-dimethylhydantoin (added slowly over 1 hr). The stirred solution was allowed to warm to room temperature over 1 hr, and then was poured into 75 ml of cold saturated $NaHCO_3$ solution. The ether phase was washed with three more portions of cold water and dried over Na_2SO_4 in a freezer. The NMR spectrum (CCl_4) showed 65% of the desired product, and at least 15% of unreacted olefin. The reaction mixture was chromatographed, at room temperature, on a silica gel column prepared in cyclohexane. Cyclohexane elution removed the olefin, and 1:1 ether–cyclohexane recovered the bromohydroperoxide, NMR (CCl_4) δ 1.6 (s, 3.1 H), 3.7 (s, 1.9 H), 7.24 (m, 5.0 H), 7.6 (s, 1.0 H, –OOH) [lit.[1a] δ 1.64 (s, 3 H), 3.76 (s, 2 H), 7.35 (m, 5 H)].

3-Methyl-3-phenyldioxetane (2c).[1a,8] To 10 ml of a methanol solution containing 1 g of NaOH and 20 mg of Na_2EDTA and cooled to −20° was added, dropwise, a methanol–ether suspension of 1-bromo-2-phenyl-2-propyl hydroperoxide (≈3 mmol). The mixture was stirred at −20 to −10° for 50 min, and then poured into 50 ml of cold water and extracted with 50 ml of CCl_4 in several portions. The combined organic phases were washed with several portions of cold water and dried over Na_2SO_4 in a freezer. The NMR (CCl_4) showed 65–70% of **2c,** δ 1.96 (s, 3 H), 5.1 (s, 2 H), 7.3 (m, 5 H) [lit.[8] δ 1.83 (s, 3.0 H), 5.00 (s, 2.0 H), external Me_4Si]. The mixture also contained acetophenone (14%) and unreacted bromohydroperoxide (20%). Efforts to purify the dioxetane by chromatography on silica gel at room temperature resulted in almost complete decomposition. The impure solution of **2c** was used in the studies described, and its concentration was determined by adding toluene as an internal standard and averaging the relative NMR integrations.

Tetramethyldioxetane (1a). Tetramethyldioxetane was prepared closely following the literature procedure.[6a] The long yellow needles used in these studies were recrystallized twice from pentane and gave only a sharp singlet at δ 1.43 in CCl_4 (lit.[6a] 1.51).

Relative Intensity and Kinetic Measurements. Stock solutions of dioxetanes and of DBA were prepared in xylenes (Baker). For each intensity measurement 0.20 ml of a dioxetane solution and 0.20 ml of a DBA solution were pipetted into a cylindrical glass vial (solutions were not degassed). This was placed in a brass sleeve and attached to an IP-21 photomultiplier photometer. A stirred oil bath (temperature constant within ±0.5°) was raised to a standard level around the brass sleeve. The recorded intensity leveled in 7–10 min. At the higher temperatures the less stable dioxetanes showed a measurable decay; in these cases the decay curve was linearly extrapolated to initial time. Kinetic measurements were made on identically prepared solutions. The externally measured temperature was correlated with the internal temperature of the solution using a copper–constantan thermocouple coiled in a standard vial containing xylenes and mounted on the photometer apparatus. A plot of the internal vs. the oil bath temperature was used to convert the measured temperatures to the actual temperatures of the dioxetane–DBA solutions.

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Registry No.—*cis*-**1c,** 57274-08-5; *trans*-**1c,** 57274-09-6; **2c,** 35322-45-3; acetophenone, 98-86-2; *trans*-dimethylstilbene, 782-06-9; *cis*-dimethylstilbene, 782-05-8; 1,3-dibromo-5,5-dimethylhydantoin, 77-48-5; *threo*-3-bromo-2,3-diphenyl-2-butyl hydroperoxide, 57274-10-9; *erythro*-3-bromo-2,3-diphenyl-2-butyl hydroperoxide, 57288-84-3; 3,3-diphenyl-2-butanone, 2575-20-4; 1-bromo-2-phenyl-2-propyl hydroperoxide, 35295-64-8; α-methylstyrene, 98-83-9.

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(2) (a) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **95,** 264 (1973); (b) N. J. Turro and A. Devaquet, *ibid.*, **97,** 3859 (1975); (c) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **96,** 7525 (1974); (d) M. J. S. Dewar and S. Kirschner, *ibid.*, **96,** 7578 (1974); (e) D. R. Kearns, *ibid.*, **91,** 6554 (1969).

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(7) The major isomer of **1c** exhibited a downfield methyl proton shift and an upfield aryl proton shift relative to the minor isomer in the NMR spectrum (CCl_4). The *cis*-dimethylstilbene epoxide (prepared by the reaction of the olefin with *m*-chloroperbenzoic acid) showed similar shifts relative to the trans epoxide, suggesting that the cis dioxetane was isolated.

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Organic Reactions of Sulfur Dioxide. II. Reaction with Ortho Esters

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Ortho esters react with an excess of sulfur dioxide to produce the corresponding esters and dialkyl sulfites. Thus, triethyl orthoacetate gave ethyl acetate and diethyl sulfite, triethyl orthopropionate, and triethyl orthobenzoate produced ethyl propionate, ethyl benzoate, and diethyl sulfite. On the other hand, triethyl orthoformate was less reactive and in addition to ethyl formate and diethyl sulfite also afforded diethyl carbonate. The reaction evidently involves formation of the corresponding dialkoxy carbonium ions and the alkyl sulfite anions, followed by a nucleophilic attack of the latter at the alkyl group of the dialkoxy carbonium ion to give the ester and the dialkyl sulfite.

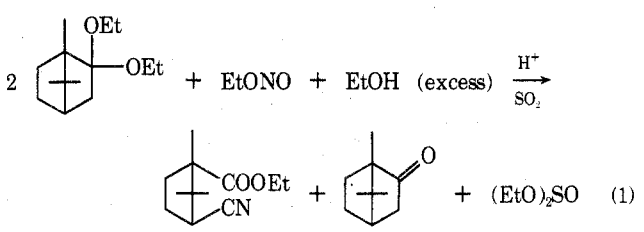
Recently we described the nitrosolysis reaction, a novel single step carbon–carbon bond cleavage of various ketones[1] and ketone acetals[2] effected through nitrosation. In the discussion of the mechanism of the nitrosolysis of cyclohexanone diethyl acetal, it was suggested that the initial cleavage affords the triethyl 6-oximinoorthohexanoate which in the presence of acid underwent dehydration to the ethyl 5-cyanopentanoate. The experimental evidence that this kind of dehydration of aldoximes with ortho esters to the corresponding nitrile is indeed a facile and general reaction was presented earlier.[3]

We wish now to describe a different transformation of an ortho ester intermediate in a particular nitrosolysis reaction, which led to a recognition of a novel and general reaction of ortho esters with sulfur dioxide.

Cyclohexanone enol ethers undergo facile reaction with sulfur dioxide,[4] and there is evidence that sulfur dioxide readily cleaves an alcohol from various ketone acetals.[5] It was recently reported that a reaction of photoexcited sulfur dioxide with trialkyl formates led to the formation of the corresponding "carbenium" ions,[6] but to our knowledge no reaction of ortho esters with unexcited sulfur dioxide was previously described.

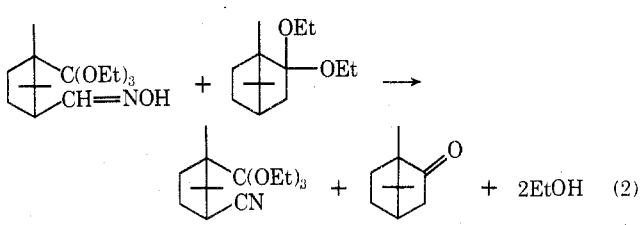
Results and Discussion

A reaction of camphor diethyl acetal with ethyl nitrite in sulfur dioxide solution containing excess ethanol and a catalytic amount of an acid gave about a 50% yield of the expected 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane. A preliminary experiment indicated that the reaction was unusually slow. Consequently, a Fisher pressure bottle, equipped with a pressure gauge and magnetic stirring bar, was charged with sulfur dioxide, camphor diethyl acetal, a solution of ethyl nitrite in ethanol, and ethanol containing a catalytic amount of dry hydrogen chloride. After the dry ice–acetone bath was removed, the reaction mixture was stirred at room temperature overnight. Unexpectedly, a GLC analysis of an aliquot revealed that in addition to approximately 50% of the expected 1-carbethoxy-1,2,2-trimethyl-3-cyanocyclopentane about 50% of camphor and diethyl sulfite were also present (eq 1).



(1)

While camphor diethyl acetal is extremely easily hydrolyzed by water,[7] it was demonstrated that the presence of camphor in the reaction mixture was not a consequence of the hydrolysis of unreacted camphor acetal during the analysis. Neither camphor diethyl acetal–ethanol in sulfur dioxide nor ethyl nitrite–ethanol solution in sulfur dioxide produced any diethyl sulfite. Consequently, it follows that both camphor and diethyl sulfite must be by-products in the nitrosolysis reaction of the camphor acetal itself. Hence, it was postulated that in the nitrosolysis of the acetal, the initially produced ortho ester oxime underwent a fast dehydration reaction with still unreacted camphor diethyl acetal to give the corresponding ortho ester nitrile (eq 2), which in turn reacted with sulfur dioxide to give the



(2)