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(12) 6-Methoxyphthaldehydic acid was prepared from ethyl 2-methyl-6-methoxybenzoate by dibrominating the 2-methyl group followed by hydrolysis in acetic acid–hydrochloric acid medium. This conversion of an aromatic methyl group to an aldehyde follows a procedure described by E. L. Eliel, D. E. Rivard, and A. W. Burgstahler, *J. Org. Chem.*, **18**, 1679 (1953).
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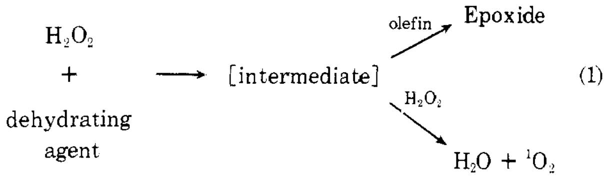
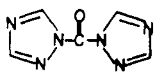
Singlet Oxygen and Epoxidation from the Dehydration of Hydrogen Peroxide

Summary: New epoxidizing reagents and chemical sources of singlet oxygen result from the action of dehydrating agents on hydrogen peroxide.

Sir: We have recently reported that the action of dehydrating agents I or II on H_2O_2 produces intermediates capable of olefin epoxidation.[1] Here we relate that a variety of dehydrating agents behave similarly (eq 1) and that the intermediates involved also lead to the production of singlet molecular oxygen.





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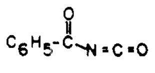

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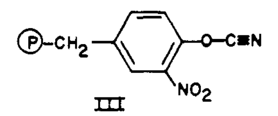


III

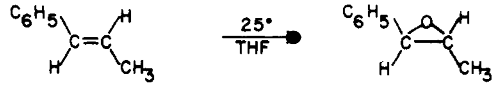
When compounds I or II are added to THF solutions of H_2O_2, CO_2 and oxygen are rapidly evolved. That the oxygen is generated in its singlet (${}^1O_2$) state can be demonstrated by its trapping with 9,10-diphenylanthracene (DPA).[2a] Table I shows the yields of ${}^1O_2$ as indicated by the formation of the endoperoxide of DPA and the β value (rate ratio of ${}^1O_2$ decay to trapping) determined for DPA in THF.[2b] The polymer-bound cyanate III[3] is also an efficient ${}^1O_2$ source. The reduced yield of ${}^1O_2$, probably due to quenching and diffusion effects of the polystyrene matrix, is offset by thee ase of handling and recyclability of this insoluble reagent.[2d] Compounds IV,[4] V,[5] and VI[6] also produce ${}^1O_2$ slowly under these conditions, but with much reduced efficiency.[2c]

Table I

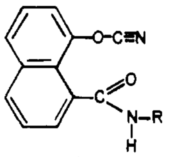
$$\text{agent} + H_2O_2\ (4\ \text{M}) \xrightarrow[25\ °C]{\text{THF}} {}^1O_2$$

	I	II	III
Yield of ${}^1O_2$, %	94	98	61
Half-life, min	<10	<10	30

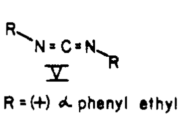
Table II



Compound	IV	VII[12]	VIII[13]	V
Asymmetric induction, %	7.5	7.1	5.2	2.0

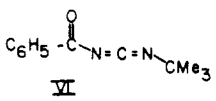


IV



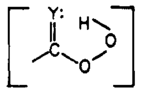
V

R = (+) α-phenyl ethyl



VI

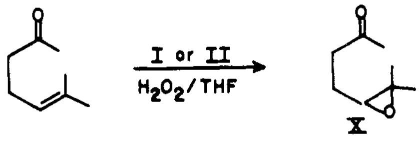
The intermediates produced in these systems can be intercepted by olefins and epoxidation occurs at the expense of ${}^1O_2$ generation. Both products are formed in the presence of monoalkylethylenes, but di- and higher alkyl-substituted olefins divert the intermediates to the epoxidation pathway exclusively. Competition studies with a wide variety of olefins revealed that the behavior of these intermediates in epoxidation reactions resembles that of peracids. Epoxidation rates as a function of olefin substituents,[7] selectivities toward cis vs. trans olefins[8] or cyclohexene vs. norbornene,[9] and Baeyer–Villiger oxidations of 2-allylcyclohexanone[10] are, with minor variations, those found for typical peracids. Therefore, while the structures of the actual epoxidizing agents are unknown, intermediates such as IX are not unlikely. Indeed such structures, incorporating the peculiar intramolecular hydrogen bond of peracids, have provided the model for our selection of dehydrating agents.



Y = N,O

IX

For preparative epoxidations, reagents I and II were consistently the most effective, e.g., either of these reagents permitted the isolation of the labile epoxide X in >90% yield.



X

Further, a recent report[11] of the successful isolation of an arene oxide from an H_2O_2–carbodiimide epoxidation should encourage the increased use of such systems, since these reagents lead to products of low acidity. Somewhat less encouraging is the stereospecificity of the optically active reagents tested (Table II) for epoxidations of *trans*-β-methylstyrene. Compared to monoperoxycamphoric acid (4.1%)[15] these reagents offer only modest advantages at best.[14] The design of more effective systems is one of our present goals.

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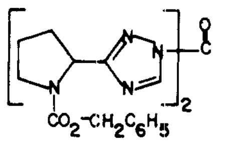
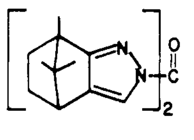


VII



VIII

Acknowledgments. We thank Professor C. S. Foote for his encouragement, advice, and aid in the determination of $^1O_2$. Financial support was provided by the National Science Foundation.

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(13) Camphor was formylated (A. Bishop, L. Claisen, and W. Sinclair, *Justus Liebigs Ann. Chem.*, **281**, 328 (1894) and treated with hydrazine, and the resulting pyrazole was converted to VIII, mp 144–146 °C, IR 1730 cm^{-1}, with 0.25 equiv of phosgene.

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A Convenient Photosynthesis of Aziridinopyrrolo[1,2-*a*]benz[*f*]indoloquinone and Heterocyclic Quinones as Model Compounds of Mitomycins by a One-Pot Reaction

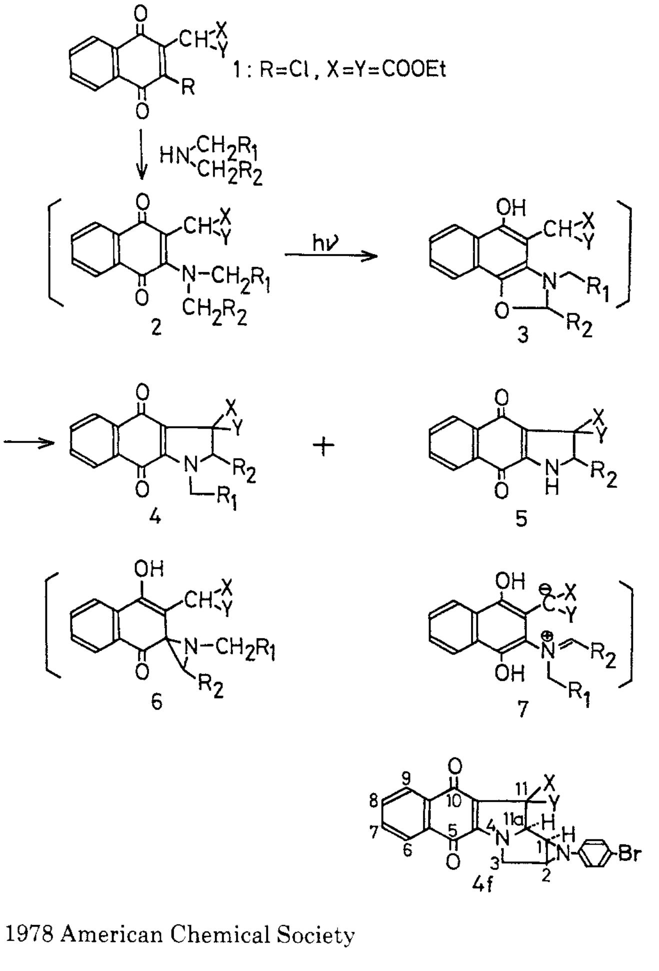
Summary: The photochemical reactions of 3-chloro-2-bis(ethoxycarbonyl)methyl-1,4-naphthoquinone with various secondary amines provide a convenient, one-pot, preparative route to the title compounds (4) in good yields.

Sir: Recently we reported an example of a novel type of photoinduced intramolecular cyclization in various solvents using amino-1,4-naphthoquinones possessing an active methylene group at the 2 position to form indoloquinones.[1] In this communication we wish to describe a novel route to aziridinopyrrolo[1,2-*a*]benz[*f*]indoloquinone, a model compound of mitomycins, and related compounds by a one-pot reaction utilizing this procedure.

A solution of aminoquinones (**2a–e**)[2] prepared from the reaction of 3-chloro-2-bis(ethoxycarbonyl)methyl-1,4-naphthoquinone (**1**)[3] with various amines (pyrrolidine, piperidine, morpholine, hexamethylenimine, and diethylamine) in ethanol was irradiated with a high-pressure mercury arc lamp through Pyrex glass in a stream of nitrogen for 1–2 h (Scheme I). After allowing the irradiated solution of **2a–e** to stand for more than 24 h at room temperature followed by evaporation of the solvent, ring-closed quinones (**4a–e**) were obtained in high yields. In the case of **2e**, **5e**[4] was isolated as a minor product along with **4e**.The results are summarized in Table I. The structural assignments for **4a–f** were based on their analytical and spectral properties, which were in good agreement with their formulations. Their ^1H NMR spectra revealed the presence of a bridgehead methine proton at 4.50–5.00 ppm instead of an active methine.

We have also extended this photocyclization reaction to a simple synthesis of an aziridine-containing pyrroloindoloquinone ring system. A similar photoreaction[5] using 6-(4-bromophenyl)-3,6-diazabicyclo[3.1.0]hexane[6] as an amine gave aziridinopyrrolo[1,2-*a*]benz[*f*]indoloquinone (**4f**) in 63% yield, mp 189–191 °C (from ethanol). The stereochemistry of this compound was determined by ^1H NMR analysis. The

Scheme I



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