while only weakly stabilizing the anionic product,[4c,29] markedly stabilizes the radical[30] produced in the rate-determining step.

A simple application of this technology is illustrated by the two-flask synthesis of brevicomin (**14**), comprising (1) the Diels–Alder addition of commercially available phenyl vinyl sulfide[31] and methyl vinyl ketone (eq 4) and (2) treatment of the adduct (**6**) with LDMAN followed by trapping of the anion (**13**) with propionaldehyde. Acidic workup removes the (dimethylamino)naphthalene and causes the ring closure to an acetal. The product (**14**), a mixture of endo (57%) and exo (43%) isomers, was characterized by the ^{1}H NMR spectrum of the mixture,[32] the relative retention times of the two isomers on a Carbowax 20M GLC column,[33] and the mass spectrum of each isomer[32] obtained by combined gas chromatography–mass spectrometry. Both isomers are exuded by the female Western Pine beetle, the exo isomer being a key component of its aggregation pheromone;[33,34] the endo isomer is a potent inhibitor of the aggregation behavior of the very destructive Southern Pine beetle.[35] The attractive features of the present synthesis compared to other reported syntheses[33,36] include brevity, the use of nonpoisonous and relatively inexpensive reagents, and the probable ease of scale up due to the fact that no chromatographic separations are required; the product is isolated in pure form directly by distillation. No attempt has yet been made to influence the stereoselectivity of the reaction of the anion **13** with propionaldehyde and thus the endo/exo ratio of **14**.

We shall report at a later date on the utility of α-lithiocyclopropyl methyl ethers of the type **15** for the production of cyclobutanones via their aldehyde adducts such as **16**.

α-Lithioethers should be interesting synthetic intermediates not only because of their nucleophilic reactivity as illustrated in this paper but also because of their ability to undergo the Wittig and related rearrangements.[4a] These uses are now under study.

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Aziridine-2,3-diones

Sir:

The study of strained molecules allows chemists to explore the limits of stability in organic chemistry, and permits calibration of theory and experiments in extreme cases.[1] Three-membered rings possessing carbonyl groups are usually unstable and quite reactive because of the large strain energies. α-Lactones have been generated at very low temperatures and observed spectroscopically,[2] and α-lactams are also unstable unless they possess bulky substituents.[3] Introduction of one more carbonyl group to these three-membered rings should further increase the strain energies of the rings. Thus, three-membered rings bearing two carbonyl groups are hitherto unknown. In view of these facts, aziridine-2,3-diones are experimentally as well as theoretically intriguing and challenging molecules. Treatment of oxanilic acid with thionyl chloride does not give *N*-phenylaziridine-2,3-dione but leads instead to a dimeric product, 2,3,5,6-tetraoxo-1,4-diphenylpiperazine.[4] In this communication, we report the formation of these unstable compounds in the low-temperature photolysis of ozonides of diphenylmaleylimides.

An ozonide usually undergoes homolysis of the oxygen–oxygen bond followed by a double β scission on irradiation to give an acid anhydride and a radical pair (or a biradical). Photolysis of ozonides has been utilized for the synthesis of three-membered rings such as cyclopropanes[5] and for the generation of unstable compounds such as cyclobutadienes[6] and Dewar benzenes.[7] Therefore, photolysis of ozonides of maleylimides is a quite promising method for the generation of aziridine-2,3-diones.

Ozonides of diphenylmaleylimides (**1a**–**1d**) were obtained as stable crystalline compounds by ozonolysis of the corresponding imides in acetone at −78 °C. The structures of the ozonides were confirmed by elemental analyses, spectral data,[8] and the fact that reduction of the ozonides with dimethyl sulfide gives the corresponding bis(phenylglyoxalyl)imides quantitatively.

When **1b** in benzene was irradiated with a high-pressure mercury lamp at room temperature, benzoic anhydride and methyl isocyanate were obtained almost quantitatively. The formation of carbon monoxide was also confirmed by both hemoglobin and palladium chloride tests,[9] though the yield was not determined. Photolysis of other ozonides gave similar results. The fact that benzoic anhydride is formed efficiently in the photolysis clearly shows that these ozonides undergo the expected reaction to give 1,3-biradicals (**2**). The isocyanates and carbon monoxide formed in these reaction conditions are presumed to be produced by decomposition of aziridine-2,3-diones (**3**) and/or cleavage of the biradicals (Scheme I).

Next, the low-temperature photolysis of **1** was carried out in order to examine the intermediacy of **3**. The ozonide (**1b**) in a KBr pellet was photolyzed at 77 K for 1 h, and the reaction was

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(8) **1b**: mp 137–138 °C; IR (KBr) 1765 (w), 1705 cm^{-1}; NMR (CDCl$_3$) δ 3.23 (s, 3 H), 7.4–7.8 (m, 10 H). Anal. Calcd for $C_{17}H_{13}O_5N$: C, 65.69; H, 4.20; N, 4.49. Found: C, 65.41; H, 4.08; N, 4.53.

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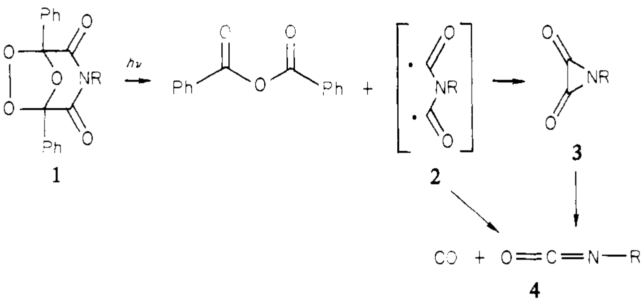
Scheme I



a, R = H
b, R = CH_3
c, R = $CH(CH_3)_2$
d, R = CH_2CH_2Ph

Table I. IR Spectra of Products in the Photolysis of Diphenylmaleylimide Ozonides[a]

reactant	aziridine-2,3-diones	iso-cyanates	carbon monoxide	benzoic anhydride
1a	1954	2260	2130	1785 1720
1b	1940	2270		
	1750	2245		
1c	1930	2260		
	1753			
1d	1933	2265		
	1742			

[a] Units, cm^{-1}; in KBr at 77 K.

followed by IR spectroscopy.[10] The spectrum showed two strong absorptions at 1940 and 1750 cm^{-1}, in addition to the absorptions of methyl isocyanate (2270 and 2245 cm^{-1}), carbon monoxide (2130 cm^{-1}), and benzoic anhydride (1785 and 1720 cm^{-1}). The spectrum did not change when the photolysate in KBr was allowed to stand for 1 h at 77 K after irradiation. However, shortly after liquid nitrogen had been evaporated, the two absorptions rapidly decreased, *with increase of the absorptions of methyl isocyanate and carbon monoxide*, while that of benzoic anhydride remained unchanged. This fact shows that the elusive species decomposes to these two compounds, and strongly indicates that it is *N*-methylaziridine-2,3-dione (**3b**). Thermal decarbonylation of three-membered ring carbonyl compounds is not exceptional. Diaziridinones undergo decarbonylation spontaneously at room temperature.[11]

Imides show two carbonyl absorptions (symmetric and antisymmetric modes).[12] The positions of $\nu_{C=O}$ at 1940 and 1750 cm^{-1} are quite reasonable for the structure of **3b** in comparison with those of other cyclic imides: a *N*-methylmalonimide derivative (1820 and 1710 cm^{-1} in KBr),[13] *N*-methylsuccinimide (1760 and 1690 cm^{-1} in KBr),[14] *N*-methylglutarimide (1718 and 1670 cm^{-1} in KBr).[14] The ring size effects in the carbonyl absorptions of these cyclic imides (3–6-membered rings) are quite analogous to those of other cyclic carbonyl compounds such as lactams and lactones.[2a] The large splitting of the two carbonyl absorptions of **3b** (190 cm^{-1}) is also reasonable for the structure, because the two carbonyls are directly bonded and should be completely coplanar.[12]

The low-temperature photolysis of other ozonides gave similar results (Table I). In the case of **1a**, the absorption of aziridine-2,3-dione was weak, and the lower carbonyl absorption was not clear. It is presumably hidden in the strong absorptions of benzoic anhydride. The isocyanates and carbon monoxide formed in the low-temperature photolysis are presumed to be produced by cleavage of the biradical (**2**) rather than decomposition of **3**, because (a) the absorptions of **3**, **4**, carbon monoxide, and benzoic anhydride increase in parallel during irradiation, and (b) the aziridine-2,3-diones are stable at 77 K. Since the aziridine-2,3-diones (**3a–3d**) were not detected when the ozonides (**1a–1d**) in KBr pellets were photolyzed at −78 °C, they are presumed to decompose rapidly at that temperature. An attempt to trap **3b** with ethanol at low temperature was unsuccessful.[15]

In summary, the ozonides of diphenylmaleylimides (**1a–1d**) are photolyzed according to Scheme I in which oxygen–oxygen bond homolysis is followed by a double β scission, as in the case of most ozonides, to produce benzoic anhydride and the 1,3-biradical (**2**). The IR spectra of the photolysates at 77 K revealed the presence of unstable compounds which decompose to carbon monoxide and the isocyanates. The spectral characteristics of the compounds are in full accord with those expected for three-membered cyclic imides. These results permit the assignment of structure **3**, aziridine-2,3-diones, to the elusive species.

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(10) The apparatus used in the present study consists of a pellet holder, a vacuum shroud, dewar, and two CaF_2 windows. Irradiation and the measurement of IR spectra were carried out through the windows. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. A 300-W high-pressure mercury lamp (Eikosha) was used as an irradiation source.

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Isolation of an Entire Set of the Three Possible Isomers of *trans*-Diammine(triethylenetetraamine)cobalt(III) Ion

Sir:

Triethylenetetraamine ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) is one of the most familiar ligands, and the stereochemistry of its complexes has been studied extensively. In 1967, Buckingham et al.[1] isolated, for the first time, one of the trans catoptromers; i.e., they obtained optically active *trans*-$[CoCl_2(trien)]ClO_4$ by isomerization of Λ,β-*S*,*S*-$[CoCl_2(trien)]ClO_4$. However, no reports have been found on the direct resolution of the racemic isomer of *trans*-$[CoX_2(trien)]^{n+}$. On the other hand, the trans "envelope" (meso) structure, the possible existence of which was also pointed out by Buckingham et al.,[1] has been known only for the trans-dicyano complex.[2] Now we have succeeded in isolating all of the three possible *trans*-$[Co(NH_3)_2(trien)]^{3+}$ isomers, the preliminary study of which will be described.

The trans-diammine complex was prepared by the oxidation of *trans*-$[Co(NCS)_2(trien)]^+$ with KIO_3 according to the method

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