15).[6] The fact that azines are the principal side product produced in the oxidation of unsubstituted hydrazones to diazoalkanes by such agents as mercury(II),[7] silver(I),[8] or manganese(IV) oxide[9] prompted us to briefly examine the reaction of several diazoalkanes with superoxide. Diphenyldiazomethane was recovered unchanged after treatment with superoxide. By comparison, the reaction of superoxide with diazofluorene produces fluorenone in high yield. The reason for this difference in reactivity is not obvious.

Our understanding of the detailed course of these reactions is still incomplete; however, several observations concerning the reaction of monosubstituted aryl hydrazines permit a description of the general features of its reaction with superoxide. First, oxidation of phenylhydrazine in benzene-d_6 produced biphenyl-d_5 (16%), and no observable biphenyl-d_0 or -d_{10} equivalent; benzene isolated from the oxidation of phenylhydrazine in toluene-d_8 showed no deuterium incorporation. Second, oxidation of a 1:1 mixture of 4-methylphenyl- and 4-chlorophenylhydrazine in benzene yielded only two coupling products: 4-methylbiphenyl (10%) and 4-chlorobiphenyl (12%). No other biphenyls were observed. Third, the reaction of 4-chlorophenylhydrazine with potassium superoxide in chlorobenzene produced the following mixture of coupling products: 2,4′-dichlorobiphenyl (8%), 3,4′-dichlorobiphenyl (4%), and 4,4′-dichlorobiphenyl (trace). Finally, the analogous oxidation of 4-methylphenylhydrazine in chlorobenzene yielded 2-chloro-4′-methylbiphenyl (9%), 3-chloro-4′-methylbiphenyl (4%), and 4-chloro-4′-methylbiphenyl (0.5%). Again, no other biphenyls were observed. These results are consistent with the intermediacy of free phenyl radicals in the oxidation of phenyl hydrazines by superoxide. Specifically, (i) the observed coupling products are all solvent derived and (ii) the relative biphenyl isomer distributions produced in chlorobenzene parallel those observed in established phenylation reactions.[10] In light of these arguments, a reasonable mechanism for the reaction of *aryl*hydrazines with superoxide would seem to involve its initial oxidation by superoxide to an aryldiazene (diimide) by an as yet undetermined pathway (eq 1).[11] Autoxidation of diazenes is rapid.[2,12] The subsequent oxidation of this intermediate by a radical chain reaction, in which the initial generation of a phenyl radical by a process whose precise nature need not be specified in detail (eq 2), would be followed by a hydrogen atom transfer from diazene followed by the unimolecular decomposition of the resulting arylazo radical (eq 3–4) to aryl radical and nitrogen. Attack of the aryl radical on the aromatic solvent (eq 5) leads to the observed coupling products.

$$\mathrm{ArNHNH_2} \xrightarrow{\mathrm{O_2^-}} \mathrm{ArN{=}NH} \tag{1}$$

$$\mathrm{ArN{=}NH} \rightarrow \mathrm{Ar}\cdot \tag{2}$$

$$\mathrm{Ar}\cdot + \mathrm{ArN{=}NH} \rightarrow \mathrm{ArH} + \mathrm{ArN{=}N}\cdot \tag{3}$$

$$\mathrm{ArN{=}N}\cdot \rightarrow \mathrm{Ar}\cdot + \mathrm{N_2} \tag{4}$$

$$\mathrm{Ar}\cdot + \mathrm{Ar'H} \rightarrow [\mathrm{Ar{-}Ar'H}]\cdot \xrightarrow{\mathrm{S}\cdot} \mathrm{Ar{-}Ar'} + \mathrm{SH} \tag{5}$$

The significance of the observations described here is twofold. First, accepting the limitations on the generality of the reaction, the oxidation of arylhydrazines by superoxide provides a convenient nonphotochemical method for generating free aryl radicals at low temperatures under mild condition. As such, the reaction merits further development as a probe for the study of radical reactions. Second, hydrazo and related azo and azoxy compounds are concerned with a number of important biological reactions[4] including, for example, carcinogenesis[13] and monoamine oxidase inhibitation.[14] In view of the ubiquitous nature of superoxide in aerobic organisms, the results presented here may also provide some insight into the possible metabolic reactions of hydrazo compounds.

Further observations relevant to the mechanisms of these reactions will be reported in later papers.

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(6) A substantial fraction (>90%) of this substrate and potassium superoxide were recovered unreacted after several days of mixing. The failure to observe an appreciable reaction between 1,2-di-*n*-butylhydrazine or cyclohexylhydrazone and superoxide may reflect the fact that the pK_a of alkylhydrazines and -hydrazones is significantly higher than that of arylhydrazines and -hydrazones (cf. P. A. S. Smith, "Open-Chain Nitrogen Compounds", Vol. II, W. A. Benjamin, New York, N.Y., 1966, pp 150, 151). If, as this observation suggests, the ability of O_2^- to effect the oxidation of these substrates is related to their acidity, it follows that proton abstraction is a necessary step in the oxidation of these substances by superoxide.

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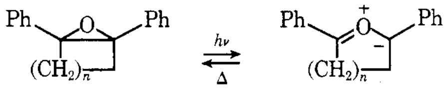
New Photochromic Oxiranes. A Potential Precursor for 2,3-Diphenyloxirene

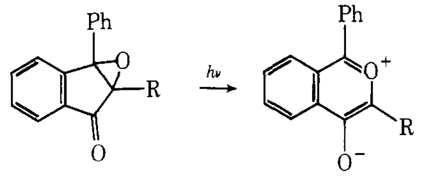
Summary. A pair of heterobicyclic oxides has been synthesized which undergoes photolysis to give stable cyclic carbonyl ylides; these ylides are highly colored, stable in the solid state as well as in fluid solution at low temperature, and bleach upon exposure to visible light; the photochemistry of epoxydiphenylmaleic anhydride in solution is described.

Sir: The thermal[1] and photoinduced[2] interconversion of three-membered heterocycles into singlet and triplet heterotrimethylene systems or ylides has evoked widespread theoretical[3] and synthetic interest.[1c–e,2] It has been established that stabilization of carbonyl ylides may be achieved by incorporation of this moiety into a cyclic structure such as **2a–2c**, where ground-state recyclization of these 4n systems is constrained to occur in a disrotatory ("thermally forbidden") manner.[2a,b,g,4] Stable ylides including **4a** and **4b** also have been generated from substrates incorporating aryl-substituted cyclopentadienone or indenone oxide entities such as those present in **3a** and **3b**, respectively.[5]



1a, $n = 1$
b, $n = 2$
c, $n = 3$

2

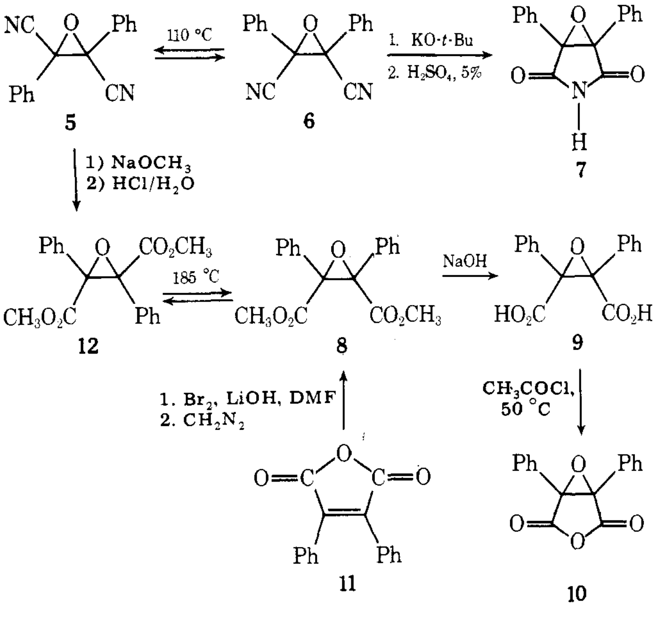


3a, R = Ph
b, R = CH_3

4

We wish to report at this time the results of a recent study in which a new class of stable cyclic carbonyl ylides has been synthesized (Scheme I) and the chemistry investigated. *cis*-2,3-Dicyanostilbene oxide (**6**, mp 146–147 °C) was prepared by thermal equilibration of the trans isomer **5** (toluene, 110 °C),[1c] obtained in turn by reductive condensation of benzoyl cyanide in accordance with the procedure of Mukaiyama and co-workers.[6] The pure cis isomer **6**, separated from its epimer **5** by fractional crystallization, was then treated with potassium *tert*-butoxide in *tert*-butyl alcohol at room temperature (3 h) and quenched with 5% sulfuric acid to give epoxydiphenylsuccinimide (**7**, 74%, mp 157–158 °C).

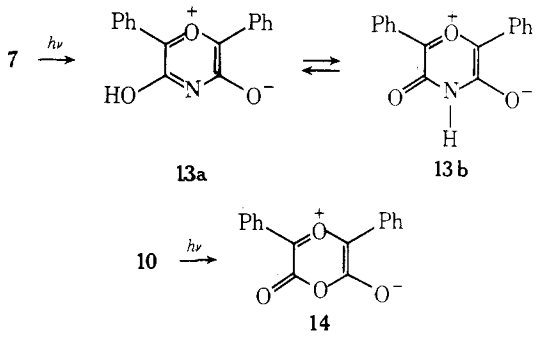
Scheme I



Synthesis of the corresponding anhydride **10** was achieved from *cis*-2,3-dicarbomethoxystilbene oxide (**8**, mp 126–127 °C) which in turn was prepared directly according to the procedure recently developed in these laboratories, which consists of treating methyl phenylglyoxylate with hexamethylphosphorus triamide at room temperature.[8] Hydrolysis of **8** to the dibasic acid **9** (mp 125–126 °C; softens at 98 °C) was accomplished in high yield (97%) by treatment of the diester with aqueous methanolic sodium hydroxide and subsequent acidification with hydrochloric acid (1 N). Dehydration of **9** to diphenylepoxymaleic anhydride (**10**, mp 146–147 °C) occurs smoothly at 50 °C upon treatment with acetyl chloride (>85%).[9] An alternate route for the synthesis of **10** from **5** is depicted in Scheme I, but the overall conversion level is substantially lower. The synthetic details for this process as well as alternate routes to N-substituted analogues of **7** from **10** will be presented in a subsequent full paper on the subject.

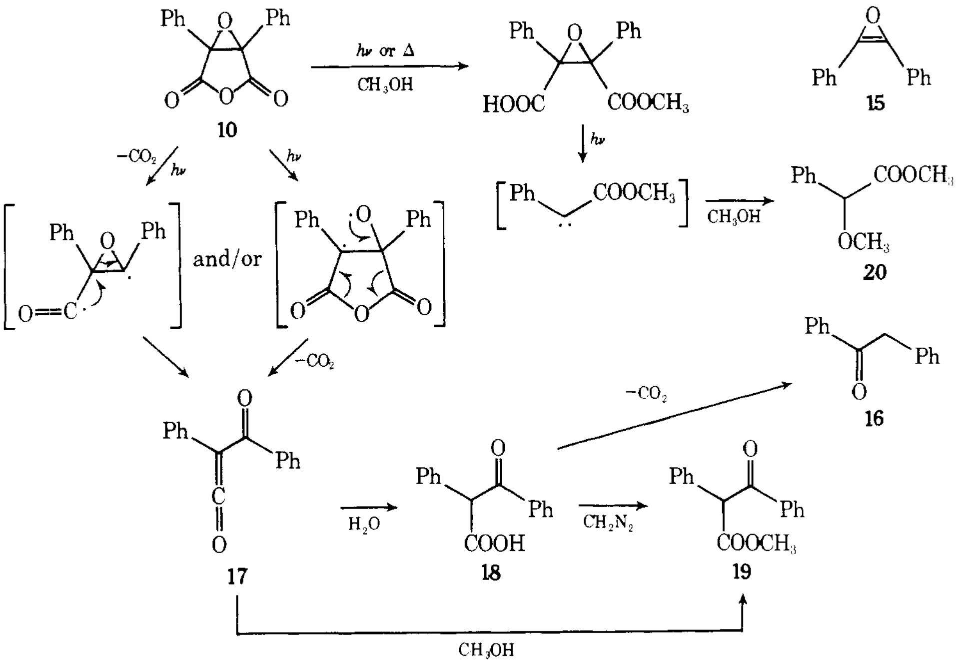
The dilithio salt derived in situ from diphenylmaleic anhydride (**11**) was also found to be a convenient precursor for **8** as well as the dibasic acid **9** and epoxy anhydride **10**. To a solution composed of diphenylmaleic anhydride (**11**) dissolved in dimethylformamide, containing lithium hydroxide (10 equiv) and a limited amount of water (10%), was added liquid bromine until an excess was assured. The resulting reaction mixture was stirred for 6 h at room temperature and then quenched with hydrochloric acid (1 N) and ether added. The crude diacid obtained after removal of solvent from the organic layer was heated with pregenerated diazomethane in ether which gave the more tractable diester **8** (41%). The oxide formation is stereoselective if not stereospecific and the trans diester **12** is not formed at least within limits detectable by conventional NMR techniques.

As expected on the basis of previous experience,[2a,b,g] colors are generated when the bicyclic oxides **7** and **10**, which incorporate vicinal diaryl oxirane moieties, are irradiated[10] in rigid matrices such as 2-methyltetrahydrofuran at 77 K (λ_{max} 520 and 541 nm, respectively). To our surprise, however, these colors persist after the matrix is warmed, softens, and appears to become fluid (130–140 K). This represents unique behavior in this series, and suggests that the mesoionic ylides **13** and **14**, presumably responsible for the photochromic behavior, are unusually stable relative to their acyclic[2a,b] and monocyclic analogues **2b** and **2c**.[2g,i] As expected, when the matrix contains a dipolarophile such as ethylene (~1:1 by volume), color fading occurs at a significantly faster rate; however, attempts to date to intercept the ylides at ambient temperature with fumaronitrile and 2,3-dimethyl-2-butene proved more complex than observed with **2** and **4** and their acyclic counterparts.[2d,i,j]



That these ylides are stable in the solid state also was readily demonstrated by application of methylene chloride solutions (~0.1 M) of the oxirane **7** (or **10**) to glass slides or paper, evaporation of solvent, and irradiation at 254 nm.[10] Color formation occurs rapidly and, what is more, can be bleached with a 150-W visible flood lamp. In the absence of visible radiation the stability of the colored species may be extended for prolonged periods (2 h), particularly in the case of **7**. Thus it may be concluded that the ylides **13** and **14** are stable in the solid state even at ambient temperature. Unfortunately, color formation is not visually or spectroscopically

Scheme II



detectable upon irradiation of **7** and **10** in fluid solution at ambient temperature in 2-methyltetrahydrofuran.

The anhydride **10** also represents a potential photochemical precursor for 2,3-diphenyloxirene (**15**), a member of an uncharacterized class of compounds.[11,12] Ample precedent exists for the proposed low-temperature photoconversion of **10** to the 4n π-electron system **15**. A variety of cyclobutene-3,4-dicarboxylic acid anhydrides undergo photofragmentation to cyclobutadienes (4n π systems) as well as carbon dioxide and monoxide upon photolysis in rigid matrices at low temperature (77 K).[13]

Preliminary studies of the photochemistry of the anhydride **10** have been conducted in solution at ambient temperature. A major photoproduct detected upon irradiation[10] of **10** in diethyl ether at 40 °C is deoxybenzoin (**16**). Formation of **16** may be rationalized by assuming initial loss of carbon dioxide (Scheme II) to give a diradical (or the cyclic counterpart) in competition with reversible C–C bond cleavage to the ylide followed by electronic reorganization to the ketene **17**. Alternatively, decarboxylation may occur after initial photocleavage of the oxirane C–O bond to give ultimately the same ketene **17**. Hydration of **17** gives the β-keto acid **18**, which is isolable as the methyl ester **19**, and was identified by comparison with an authentic sample. The decarboxylation of **18** provides a rationale for the formation of **16**. The ketene **17** may also be intercepted with methanol to give **19**directly, although competing photocycloelimination of the solvolyzed anhydride to give phenylcarbomethoxycarbene[8] competes effectively. The latter is trapped by methanol to give the methyl ether of methyl mandelate (24%). It is noteworthy that the rearrangement of **9** and/or **10** to **16** in the ground state is catalyzed by trifluoroacetic acid (80 °C) (43 and 27%, respectively).

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