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(6) While a detailed analysis of the data is deferred to the full paper, several correlations emerge even from a cursory comparison with analogous nonchlorinated dienes. Thus, in both systems (a) increased size of the alkyl group enhances their endo selectivity;[5g] (b) increased steric bulk destabilizes both the endo and exo transition states;[1,5g] (c) repulsive nonbonding interactions between the diene and a bulky substituent seem to be the major cause for their endo selectivity;[1,5c,g] size and its unfavorable geometry for secondary overlap are probably responsible for the low endo selectivity of the nitrile group.[5g]
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(8) J. Sauer, Habilitationsschrift, University of Munich, 1963, p 113.
(9) The assignment of the downfield doublet to the endo proton in **6A** is supported also by its line widths, which are somewhat broader than those upfield, thus suggesting a ^4J W-coupling with the methyl protons and, hence, a trans relationship. In epimer **6B** it is again the downfield doublet, assigned now to the exo proton that is broader in accordance with the proposed structure.
(10) The reaction of **1** and **5-*d*** is often quoted[11] in support of the concerted nature of the Diels–Alder reaction, which, although heavily weighted in favor of a biradical pathway, still yielded, reportedly, one cis/trans stereospecific adduct.[7] Although our finding that **6A** has the stereochemistry opposite to that proposed[12] does not invalidate the conclusion that the stereochemical integrity of the deuterium-labeled olefin was maintained in the adduct, the formation in significant proportion of **6B** weakens the validity of the argument in support of the mechanism of the Diels–Alder reaction until the cis–trans stereospecificity of **6B** is determined. Should, however, subsequent experiments establish, *e.g., via* similar deuterium labeling, the conservation of the steric integrity of the olefin in **6B** as well, the finding would reinforce the argument in favor of the one-step mechanism, since it would clearly underline the relevance of molecular alignment in the preadduction state.
(11) *Cf., inter alia,* (a) T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry," Cambridge University Press, London, 1972, p 97; (b) S. Seltzer in "Advances in Alicyclic Chemistry," H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., 1968, p 43; (c) J. Sauer, *Angew. Chem. Int. Ed. Engl.*, **6**, 16 (1967); (d) B. Capon, M. J. Perkins and C. W. Rees, "Organic Reaction Mechanisms," Interscience, New York, N.Y., 1965, p 123.
(12) The reversal of assignment in the stereochemistry of **6A** was not unanticipated.[7] While recognizing that it violated the endo rule, and done only reluctantly, the placement of the phenyl group in the exo position was necessary based on the then available chemical shift data, which indicated that, without exception, the endo methylene protons in adducts of **1** resonate at higher field.[7,13]
(13) Other examples where the endo methylene proton is not upfield from the exo include the adduct of **1** with 2-chloropropene (in the *exo*-methyl epimer), with *ar*-pentachloro- and *ar*-pentabromostyrene, and with α-methylacrylonitrile (where they are adventitiously equivalent in the exo methyl epimer in $CDCl_3$, but not in C_6D_6 solution).
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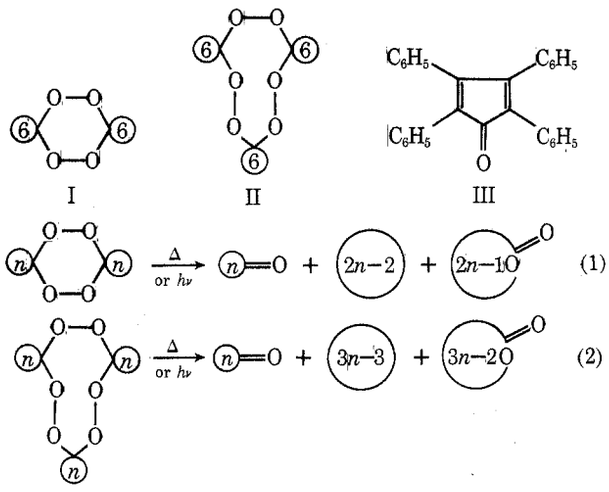
Singlet Oxygen Scavenger Method for the Determination of Ketone Peroxide Kinetics

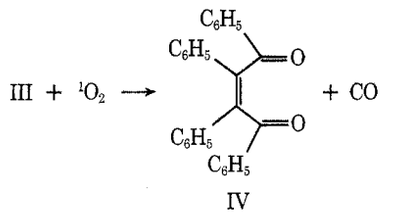
Summary: The rate of decomposition of dicyclohexylidene diperoxide (I) has been monitored spectrophotometrically by use of the colored singlet oxygen scavenger "tetracyclone" (III) (tetraphenylcyclopentadienone). The rate constants determined for I are in good agreement with those determined iodometrically.

Sir: In 1967 Story and coworkers[1] found that the thermal and photochemical decomposition of cyclic ketone peroxides such as I and II produced macrocyclic hydrocarbons and lactones (eq 1 and 2). About 5–10% ketone was also produced. Story suggested that the ketone was produced with the evolution of singlet oxygen.

The detection of singlet oxygen in liquid phases is restricted almost entirely to chemical methods which might be misleading (but several methods are available).[2–4] In order to determine the singlet oxygen in a liquid phase, one may decompose the precursor in the presence of an appropriate singlet oxygen acceptor.[5]



For example, Murray and coworkers used tetracyclone to measure the per cent of singlet oxygen evolved from ozone adducts of isopropyl alcohol and isopropyl ether (eq 3).[6] In our laboratory Brennan used tetracyclone to scavenge singlet oxygen from phosphorus ozone adducts.[7]



It occurred to us that this highly colored compound might be used (if thermally stable) to measure the singlet oxygen evolved from peroxide precursors. The extinction coefficient of this compound is high [$\epsilon \simeq 1250$ l./(mol cm)], thus allowing the singlet oxygen yields to be determined on dilute peroxide solutions with the aid of a spectrophotometer.

The stable free radical technique for the determination of free radical initiator kinetics had been so successful for the determination of the kinetics and free radical efficiencies of diacyl peroxides that we decided to apply the same technique to peroxides which might give singlet oxygen on decomposition.[8]

The advantages are (a) the solution of peroxide is dilute enough so that induced decomposition is negligible; (b) the rate constant and the efficiency of singlet oxygen production (the fraction of singlet oxygen per mole of peroxide which reacts with the scavenger) may be determined in a single experiment.

The rate data for the decomposition of cyclohexanone diperoxide obtained by monitoring the disappearance of the colored band at 510 mμ in tetracyclone were calculated from eq 4 and are presented in Table I (see ref 8 for derivation of a similar equation). The rate data are in good agreement with that obtained by following the rate iodometrically in all solvents except cyclohexane.[9] The reason for this discrepancy has not been completely resolved.

$$\ln (A - A_\infty) = -kt + \ln \varepsilon P_o e_s \quad (4)^{10}$$

The values of e_s for I range from 0.05 to 0.02 in the solvents studied, and it appears that the peroxide is not an efficient source of singlet oxygen. The yield of cyclohexanone varies from 0.10 to 0.20 mol/mol of peroxide; so the maximum available singlet oxygen is 5 to 10% (0.05 to 0.10 for e_s). Furthermore, it is likely that the values of e_s recorded in Table I are too high since it is possible for the fading of

Table I
Kinetics and Singlet Oxygen Efficiencies for Dicyclohexylidene Diperoxide in Some Solvents[a]

Solvent	$10^3 P_0$, mol/l.[b]	T^*, C	$10^5 k$ (± std dev), sec^{-1}	$t_{1/2}$, min	$t_{1/2}$, min[c]	e_s
Toluene	10.0	170.1	96.3 (±4.6)	12.0	13.2	0.038
	10.6	170.1	99.1 (±4.0)	11.6		0.035
	5.00	170.1	84.0 (±6.2)	13.7		0.039
	8.46	160.1	27.9 (±1.3)	41.4	39.6	0.048
	10.0	160.1	31.2 (±1.2)	37.0		0.035
	10.0	160.1	25.8 (±0.7)	44.7		0.044
	10.1	160.1	29.3 (±4.0)	39.4		0.035
Cyclohexane	10.0	160.1	23.5 (±1.3)	30.0	41.6	0.038
	10.0	155.1	14.6 (±0.7)	61.4	86.8	0.043
Chlorobenzene	10.0	155.1	27.4 (±2.8)	42.1	45.0	0.050
Bromobenzene	13.5	160.1	45.5 (±0.4)	25.4	26.2	0.046
	13.5	155.1	27.0 (±0.8)	42.8	45.0	0.049
o-Dichlorobenzene	10.0	160.1	36.0 (±1.9)	32.0		0.022
	10.0	155.1	27.3 (±1.4)	42.3		0.026
	10.0	150.0	18.0 (±2.0)	64.3		0.019
Acetophenone	10.0	155.1	27.8 (±0.6)	41.6	37.3	0.043

[a] The initial scavenger concentration (S_0) was 8.00×10^{-4} *M*. [b] Initial peroxide concentration in moles per liter. [c] The half-life in this column came from iodometric rate studies ($P_0 \cong 0.02$ mol/l.).

the tetracyclone to be caused by addition of radicals to the double bonds (eq 5).

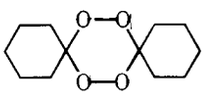
$$R\cdot + \text{III} \longrightarrow R - \text{III}\cdot \longrightarrow \text{colorless products} \quad (5)$$

When III was heated with di-*tert*-butyl peroxide in degassed chlorobenzene solution at 160°, fading occurred. This is presumably due to radical addition to the double bonds of III. No product studies were done however.

Table II shows the yield of *cis*-dibenzoylstilbene determined by vpc analysis. The yield is higher here than the yield determined spectrophotometrically.

It was observed in the vpc trace that there were several unidentified peaks with a retention time higher than those of *cis*-dibenzoylstilbene and tetracyclone. These peaks were shown to be absent when the peroxide was thermolyzed in the absence of tetracyclone. The products which give rise to the unidentified peaks are presumed to be radical addition products of tetracyclone.

It is likely that the oxygen which is generated in the thermal decomposition of ketone peroxides enters into a chain reaction[11] if it does not add to tetracyclone as singlet oxygen. For example, the following free radical chain process is reasonable.



$$\longrightarrow \text{products} + R\cdot + O_2 \quad (6)$$

$$R\cdot + O_2 \longrightarrow R{-}O{-}O\cdot \quad (7)$$

$$R{-}O{-}O\cdot\ (R\cdot) + \text{tetracyclone} \longrightarrow \text{radical adduct} \quad (8)$$

$$R{-}O{-}O\cdot + R{-}O{-}O\cdot \longrightarrow \text{nonradical products} \quad (9)$$

The termination reaction 9 has been shown for the autooxidation of ethylbenzene to give the products in eq 10.[12] This type of termination is well known for secondary peroxy radicals.[12-15]

$$2C_6H_5\overset{CH_3}{\overset{|}{C}}H{-}O{-}O\cdot \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}{-}CH_3 + C_6H_5CH(OH){-}CH_3 + {}^1O_2 \quad (10)$$

The point to be made by eq 6 through 10 is that fading of the tetracyclone may be caused by radical addition (eq 8) or singlet oxygen generated *via* paths such as eq 9.

Table II
Per Cent Yield of *cis*-Dibenzoylstilbene

Solvent	T^*, C	P_0, mol/l.[a]	S_0, mol/l.[b]	e_s[c]	e_s[d]
Cyclohexane	160	0.1	≃0.05	0.053	0.038
	170	0.1	≃0.05	0.078	
n-Decane	150	0.1	≃0.05	0.034	
	160	0.1	≃0.05	0.074	
Toluene	150	0.1	≃0.05	0.058	
	160	0.1	≃0.05	0.078	0.035–0.048
	170	0.1	≃0.05	0.099	0.035–0.039
Chlorobenzene	140	0.1	≃0.05	0.059	
	150	0.1	≃0.05	0.055	0.046
	160	0.1	≃0.05	0.055	
	165	0.1	≃0.05	0.053	

[a] Initial peroxide concentration in moles per liter. [b] Initial scavenger concentration in moles per liter. [c] Yield of *cis*-dibenzoylstilbene determined by vpc analysis. [d] Singlet oxygen efficiency determined by spectrophotometry on dilute solutions ($P_0 = 0.01$, $S_0 = 0.0008$ mol/l.).

Despite the number of interferences, the method presented above appears to be useful for determination of the rate of decomposition of peroxides such as I which are potential singlet oxygen precursors. Indeed, the above is only a fair demonstration of the method. Furthermore, very little was learned about that portion of the decomposition of I which gives cyclohexanone plus oxygen. However, the technique should be very useful for the determination of rates of decomposition and singlet oxygen efficiencies (e_s) in systems which give higher yields of singlet oxygen without the interference encountered in the study of I.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. 34496.

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(10) Here A is the absorbance at some maximum wavelength. A_∞ is the absorbance at infinity time, ϵ is the molar extinction coefficient, e_s is the singlet oxygen efficiency, and P_0 is the initial peroxide concentration.
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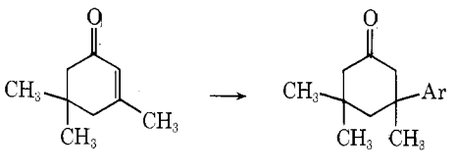
Heteroatom-Directed Photoarylation. A New Method for Introduction of Angular Carbon–Carbon Bonds

Summary: Photocyclization–rearrangement of cyclic 2-thioaryloxyenones to annelated dihydrothiophenes and subsequent desulfurization give 3-arylcycloalkanones in high overall yield.

Sir: Introduction of an aryl substituent at a carbon atom β to a carbonyl group by conjugate addition of organocopper reagents to α,β-unsaturated carbonyl substrates has received considerable attention, *e.g.*, **1** → **2**.[1] Unfortunately, copper catalyzed reactions of arylmagnesium halides with α,β-unsaturated ketones usually give mixtures of 1,2- and 1,4-addition products. Conjugate addition may be more effectively performed by use of stoichiometric organocopper reagents prepared from an aryllithium and cuprous iodide;



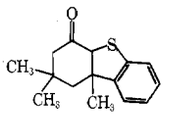
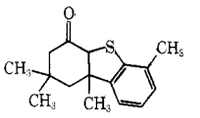
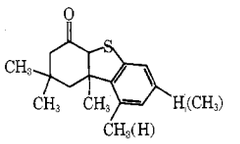
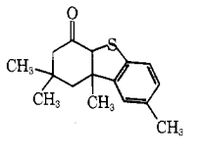
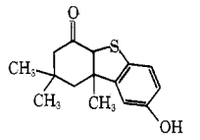
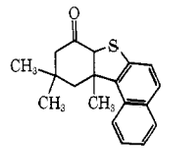
1 **2**

however, the required aryllithium may not always be obtainable. Furthermore, a two- or threefold excess of organocopper reagent is normally required for satisfactory conjugate addition and significant quantities of dimeric by-products may arise from coupling of the organocopper reagent.

In this paper, we report new methodology for the efficient and experimentally simple introduction of an aromatic nucleus β to a carbonyl group. The key step in the process involves the photocyclization–rearrangement of 2-thioaryloxyenones to dihydrothiophenes, *e.g.*, **3** → **5**.

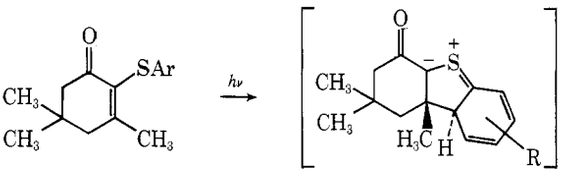
Cyclic 2-thioaryloxyenones **3** were prepared[2] in 92–98% yields by the potassium hydroxide catalyzed reaction of 1 equiv of aryl mercaptan with 2,3-epoxy-3,5,5-trimethylcyclohexanone.[3] Pyrex-filtered irradiation of **3** in benzene–methanol solution (3:1) in a conventional preparative photoreactor gave dihydrothiophenes **5** in excellent yield, Table I. This process presumably occurs by conrotatory photocyclization[4] in the excited state of **3** to give the intermediate thiocarbonyl ylide **4**, which suffers 1,4-hydrogen migration to give dihydrothiophene **5**.[5]

Table I
Photocyclization of 2-Thioaryloxyenones 3 to Dihydrothiophenes 5 and Desulfurization to 3-Arylcyclohexanones 2

2-Thioaryloxyenone	Dihydrothiophene 5 formed	% yield of 5[a]	% yield of 2[a]
3a		91	85
3b		88	87
3c		92[b]	
3d		84	86[c]
3e		83	83
3f		89	50

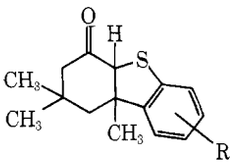
[a] Represents isolated yield of distilled or crystallized product. [b] Ratio of isomers is 70:30. [c] Product identical with that obtained by desulfurization of **5b**.

The conversion **3** → **5** in all cases examined except **3c** is completely regioselective and is applicable to large-scale



3a, Ar = phenyl
b, Ar = *o*-tolyl
c, Ar = *m*-tolyl
d, Ar = *p*-tolyl
e, Ar = *p*-hydroxyphenyl
f, Ar = 2-naphthyl

4



5

synthesis. The following procedure for preparation of **5a** is representative. A solution of **3a** (70.4 g) in benzene (1500 ml) and methanol (500 ml) was placed in a photoreactor fitted with a water-cooled immersion well containing a 450-W high-pressure mercury arc lamp. Dry argon was