

hand, is +1.00 ppm. We shall discuss the solvents giving rise to S values outside the range from 1,5-cyclooctadiene ($S = -0.01$) to piperylene ($S = +0.12$). The numbers in parentheses are S values in parts per million, plus signs denoting upfield shifts.

1,3,5-Cycloheptatriene (Tropilidene) ($S = +0.33$). It appears reasonable to ascribe the solvent effect to the presence of a homoaromatic ring current, in accord with the diamagnetic exaltation observed by Dauben.⁶ As expected, the S value of 1,3,5-cyclooctatriene ($S = +0.04$) is much smaller than that of tropilidene.

Cyclopentadiene ($S = +0.39$). A diamagnetic ring current due to hyperconjugation has been considered by Dauben.⁶ The susceptibility exaltation method, however, was considered too inaccurate to permit definitive conclusions. The high S value is in accord with Flygare's very recent microwave data⁷ which indicate a magnetic anisotropy of almost 60% of the benzene value. Note that the S value of 1,4-cyclohexadiene ($S = +0.01$) is very small.

Cyclooctatetraene (COT) ($S = -0.16$). As a $[4n]$ -annulene COT should show a strong paramagnetic ring current if it were planar.⁸ Being far from planar, however, it is expected to show only weak ring current effects. Considering 1,3-cyclooctadiene ($S = +0.02$), 1,5-cyclooctadiene ($S = -0.01$), and 1,3,5-cyclooctatriene ($S = +0.04$) as model compounds, it seems likely that the downfield shift is at least partly due to a paramagnetic ring current. Previous workers⁶ have concluded that COT has no ring current. However, the exaltation method is limited by the reliability of the Pascal-type increments used and an exaltation of less than 20% of the benzene value might easily go undetected.

Norbornadiene ($S = +0.16$). The strong shielding experienced in norbornadiene is surprising in view of the low S value of 1,4-cyclohexadiene ($S = +0.01$). These compounds are of interest because of their potential bishomocyclobutadiene character. However, data on related compounds are needed before any conclusions can be drawn.

Solids may be studied in 1,5-cyclooctadiene (1,5-COD) solution.⁹ The S value of a mixture of 1,5-COD and the compound under investigation may then be compared with the S value of a corresponding mixture (same concentrations) of 1,5-COD and some suitable reference compound. Thus we find the ratio of S values (biphenylene-1,5-COD:naphthalene-1,5-COD) to be 1:3,¹⁰ further strong evidence for a considerable antiaromatic contribution to the total anisotropy of biphenylene.¹¹

(4) Cyclohexane, 1.4% by volume (1.3 M); acetonitrile, 1.4% by volume (2.67 M); temperature, $33 \pm 1.5^\circ$. S_x values should be extrapolated to infinite dilution of acetonitrile for the evaluation of subtle differences.

(5) Presumably the small shielding effect of normal double bonds is largely cancelled by a slight deshielding contribution due to association.

(6) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).

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(9) 1,5-COD is a better solvent for olefins than cyclohexane, has a low anisotropy, and has no nmr absorptions close to acetonitrile or cyclohexane.

(10) Molar ratio of solute:1,5-COD = 1:12.4.

(11) H. P. Figeys, *Angew. Chem., Int. Ed., Engl.*, **7**, 642 (1968).

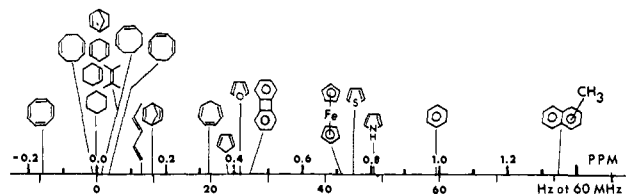


Figure 1. Acetonitrile solvent shifts.

Finally, the method may be extended to compounds other than hydrocarbons, such as heteroaromatics and organometallics. For ferrocene, $S \approx +0.72$ ppm is obtained,¹² in qualitative agreement with the results of Mulay's^{13a} and Fox's^{13b} single-crystal studies ($\Delta\chi = 0.83$ and $\Delta\chi = 0.94$, respectively).¹⁴ For pyrrole S is slightly higher ($S = +0.82$, $\Delta\chi = 0.71$),^{14,15} and for furan S is lower ($S = +0.42$, $\Delta\chi = 0.65$)^{14,15} than expected on the basis of Flygare's microwave data, reflecting the high π basicity of pyrrole and the concomitant increase of the association constant, and in furan presumably the involvement of association at the periphery resulting in a deshielding contribution.

Acknowledgments. G. E. Schenck thanks the University of California for a Regents' Graduate Intern Fellowship. This work was supported by National Science Foundation Grant No. GP-10571.

(12) In 1,5-COD, referred to benzene in 1,5-COD.

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Cyclic Peroxides. V.¹ An α -Lactone Intermediate via Photodecarboxylation of a Monomeric Malonyl Peroxide

Sir:

Among the small ring heterocycles, the α -lactones are experimentally as well as theoretically intriguing and challenging molecules. Their isoelectronic relationship to cyclopropanones at least in part accounts for their elusive nature.² The first mention of α -lactone intermediates in the chemical literature was made by Cowdrey, Hughes, and Ingold³ in their classical work on the hydrolysis of optically active α -bromopropionic acid. Since then α -lactones have been sporadically invoked as reactive intermediates in nucleophilic substitution reactions,⁴⁻⁶ in free-radical substitution reactions,⁷⁻⁹ in the thermolysis of cyclic anhydrosulfites¹⁰

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(2) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

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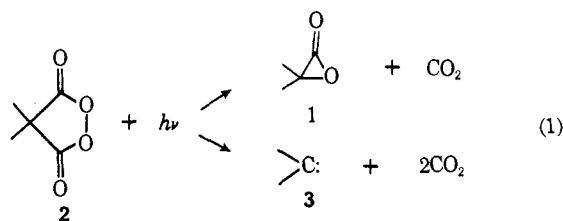
(6) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2956 (1970).

(7) C. Walling and E. S. Savas, *J. Amer. Chem. Soc.*, **82**, 1738 (1960).

(8) (a) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963); (b) N. A. Milas and A. Golubovic, *ibid.*, **80**, 5994 (1958).

and anhydrocarbonates,¹¹ and most recently in the ozonolysis of ketenes.¹²

Recent work from this laboratory has demonstrated that photodecarboxylation of β -peroxylactones affords epoxides as major products.¹³ Therefore, at least in principle, it is conceivable to generate α -lactones **1** by photodecarboxylation of suitable cyclic peroxides such as the monomeric malonyl peroxides **2** (eq 1). Of



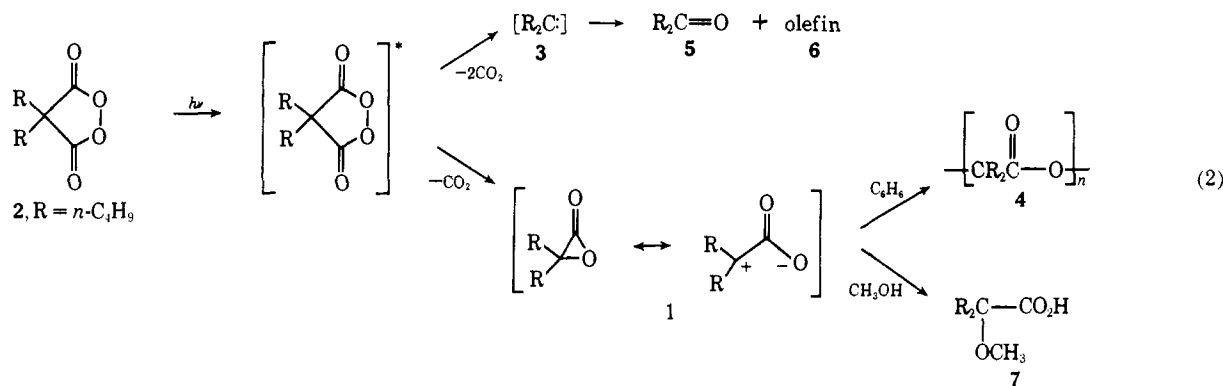
course, carbene formation **3** is anticipated as a worrisome side reaction. In this communication we report on the synthesis and photolysis of 4,4-di-*n*-butyl-1,2-dioxolane-3,5-dione (**2**), the first member of the general class of monomeric, cyclic malonyl peroxide.

This novel cyclic diacyl peroxide was prepared in 78% yield, bp 49–50° (0.05 mm), in 99.5% purity (iodometric titration) by treating di-*n*-butylmalonic acid with 98% hydrogen peroxide in methanesulfonic acid. The structure assignment is based on the molecular weight (osmometry in chloroform) of 213 ± 1 vs. 214.3 calculated for $C_{11}H_{18}O_4$ (*Anal.* Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.59; H, 8.55) and conversion in 94% yield to its malonic acid by treating with an acidic, aqueous acetone solution of sodium iodide. The infrared spectrum in CCl_4 shows a strong $C=O$ fre-

quency at 1783 cm^{-1} with a shoulder at 1820 cm^{-1} , the nmr spectrum CCl_4 exhibits the typical resonances of the *n*-butyl protons at δ (ppm) 0.95, 1.35, 1.85, overlapping multiplets, ratio 3:4:2 (TMS internal standard), while the ultraviolet spectrum exhibits no absorption maximum between 210 and 350 nm; the absorbances at 250 and 350 nm have molar extinction coefficients of 100 and 8.4, respectively. Unusual and surprising is the thermal stability of **2** since heating at 70–80° initiates a smooth decomposition with visible evolution of carbon dioxide. Even at more elevated temperatures only

a vigorous but silent decomposition can be provoked, resulting in a glassy, clear polymer as product.¹⁴ The photolysis of 0.1 *M* solutions of the cyclic peroxide **2** in hydrocarbon solvents at 350 nm for 20 hr at 35–40° in Pyrex test tubes gave a solid residue **4** as major product (82% in hexane, 89% in benzene) and two minor volatile products **5** (8.6% in hexane, 5.9% in benzene) and **6** (7.9% in hexane, 3.5% in benzene), making a total product balance of better than 98.0%.¹⁵ The solid residue **4**, mp 146–146.5° (hexane) and 138.5–140.5° (benzene), was identified as poly-3,3-di-*n*-butyl-oxiran-2-one (polyester) (**4**) on the basis of its elemental analysis (Calcd: C, 70.55; H, 10.65. Found: C, 70.79; H, 10.56) for the α -lactone unit $C_{10}H_{16}O_2$, its molecular weight of 4996 (osmometry in $CHCl_3$) corresponding to 29.2 such α -lactone units, its $C=O$ frequency at 1740 cm^{-1} , and its reduction to 2-*n*-butylhexane-1,2-diol in 72% yield (after distillation). The volatile product **5** was identified as 5-nonanone by comparison of its infrared spectrum, glpc retention time, and semicarbazone derivative with the authentic substance. On the basis of the infrared spectrum of **6** it is most probably 4-nonene.¹⁶ Control experiments show that the polyester **4** is photostable when submitted to the photolysis conditions, indicating that the 5-nonanone and 4-nonene are primary photoproducts.

The minor products **5** and **6** probably arise from a carbene precursor **3** produced by photoexpulsion¹⁷ of 2 mol of carbon dioxide from the malonyl peroxide (eq 2). The most efficient way to account for the formation of the polyester **4** as the major product is to suppose that an α -lactone intermediate **1** intervenes which subsequently polymerizes.^{18,19} In the hope to trap the α -



quency at 1783 cm^{-1} with a shoulder at 1820 cm^{-1} , the nmr spectrum CCl_4 exhibits the typical resonances of the *n*-butyl protons at δ (ppm) 0.95, 1.35, 1.85, overlapping multiplets, ratio 3:4:2 (TMS internal standard), while the ultraviolet spectrum exhibits no absorption maximum between 210 and 350 nm; the absorbances at 250 and 350 nm have molar extinction coefficients of 100 and 8.4, respectively. Unusual and surprising is the thermal stability of **2** since heating at 70–80° initiates a smooth decomposition with visible evolution of carbon dioxide. Even at more elevated temperatures only

(14) The thermal decomposition of dialkylmalonyl peroxides is the subject of a separate study which shall be reported at the Regional Meeting of the New York–New Jersey–Puerto Rico Sections, Metrochem 71, to be held in San Juan, P. R., April 1971.

(15) Irradiation at 310 and 254 nm under the same conditions gave similar results except that the photolysis was completed within 1–2 hr.

(16) The infrared spectrum shows that the olefin is predominantly the trans isomer, but quantitative work is in progress to assess the cis-trans ratio.

(17) Experiments are under way to test this hypothesis.

(18) The possibility that the polyester arises from the photolysis of 5,5-di-*n*-butyl-1,3-dioxolane-2,4-dione (the carboxy inversion product of **2**) was excluded because the dimethyl derivative was shown to be photostable when irradiated under the photolysis conditions of the cyclic peroxide. However, using a full mercury arc (Hanovia, 450 W), a quartz vessel, and acetonitrile as the solvent, the 3,3-dimethyl-1,3-dioxolane-2,4-dione was converted into acetone and about 10% tarry residue.

(19) Photolysis of the cyclic peroxide **2** at –78° in hexane at 254 nm gives the same product composition as observed at room temperature, indicating that the 3,3-di-*n*-butyl-oxiran-2-one (α -lactone) is an extremely reactive species. This is to be contrasted with the di-*tert*-butyl derivative¹² which is sufficiently stable below –60° to allow posterior chemical trapping.

(9) J. E. Leffler and R. G. Zepp, *J. Amer. Chem. Soc.*, **92**, 3713 (1970).

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(12) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6057 (1970).

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lactone **1** chemically, the photolysis was carried out in methanol. Irradiation of 0.1 *M* methanolic solutions of the cyclic peroxide at 350 nm and 35–40° in Pyrex test tubes afforded 2-*n*-butyl-2-methoxycaproic acid (**7**) as major product (88% yield as its methyl ester²⁰), besides 5-nonanone (5.3%), di-*n*-butylmalonic acid (3.7% yield as its dimethyl ester²⁰), and 2-*n*-butylhex-2-enoic acid (3% as its methyl ester²⁰), giving a quantitative product balance. The α -methoxy acid **7** was identified by its physical constants and spectral data with an authentic sample, prepared by addition of *n*-butyl bromide and dimethyl oxalate to a magnesium and ether suspension in order to obtain methyl 2-*n*-butyl-2-hydroxycaproate,²¹ methylation of the latter with sodium hydride and methyl iodide,²² and finally saponification of the α -methoxy ester to give **7**. Control experiments demonstrated that the polyester **4** is not solvolyzed with methanol to give significant amounts of the α -methoxy acid **7** in the dark or under irradiation. There is, however, a dark reaction between the cyclic peroxide and methanol to give a complex product mixture,²³ but kinetic experiments show that during the time interval of the photolysis, at the very most 3–5% of solvolysis has taken place.

In summary, the mechanism of the photolysis (eq 2) of di-*n*-butylmalonyl peroxide (**2**) is proposed to involve photodecarboxylation to produce an α -lactone intermediate **1**. In hydrocarbon solvents such as hexane and benzene the dipolar α -lactone intermediate polymerizes into the polyester **4**; however, in a hydroxylic solvent such as methanol²⁴ this intermediate is trapped as α -methoxy acid (**7**). As a minor route, probably a carbene intermediate **3** is formed which is converted to 5-nonanone (**5**) and 4-nonene (**6**).²⁵ It is imperative that steric and/or electronic stabilization must be introduced in the α -lactone **1**, in order to enhance its lifetime.

Acknowledgments. Financial support by the A. P. Sloan Foundation, National Science Foundation, the Petroleum Research Fund, and the Research Corporation and a Fullbright travel grant to R. R. are gratefully appreciated. We thank Professor P. D. Bartlett (Harvard University) for releasing to us his results on related work¹² prior to publication.

(20) The product mixture was treated with diazomethane and submitted to glpc analysis on a Carbowax 20M column.

(21) H. Hepworth, *J. Chem. Soc. London*, **115**, 1206 (1919).

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(23) The methanolysis of the malonyl peroxide shall be the subject of a separate publication.

(24) Preliminary experiments indicate that ethyl alcohol, isopropyl alcohol, and *tert*-butyl alcohol also serve as trapping agents of the α -lactone intermediate.

(25) Alternatively, the ketone could be formed by photodecarbonylation of the α -lactone.

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Reactions of Sulfur Atoms. XII. Arrhenius Parameters for the Addition to Olefins and Acetylenes

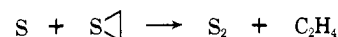
Sir:

The reactions of ground-state S(³P) atoms with olefins proceed *via* a stereospecific path resulting in the forma-

tion of the corresponding episulfide as the only principal product.¹ These reactions provide the only known example of a stereospecific path of a divalent triplet-state reagent. In order to elucidate details of the mechanism we have determined relative Arrhenius parameters for a representative series of olefins and acetylenes.

Ground-state S(³P_{2,1,0}) atoms were generated by the direct photolysis of COS admixed with a large excess of CO₂ or by Hg(³P₁) photosensitization² in the presence of known concentrations of two competing olefins. Relative rates as a function of temperature were obtained from the gas chromatographically determined yields of the two episulfides produced. The results are presented in Table I. Check experiments using direct photolysis or sensitization, varying the olefin concentrations, or using different pairs of olefins, a + b, b + c, or a + c, have led to concordant results. In cases where the primary reaction product was unstable (*e.g.*, acetylenes), rates were obtained from determining the suppressing effect of one of the olefins on the yields of the stable episulfide from the other olefin. A narrow temperature range, from 298°K to the thermal decomposition point, ~450°K, of the less stable product episulfide, was covered.

The trend in activation energies clearly manifests the electrophilic nature of attack by the sulfur atom; increasing the number of alkyl substituents on the doubly bonded carbons decreases E_a , while increasing the number of halogen substituents increases E_a . These variations can be correlated with molecular properties such as ionization potentials, excitation energies, and bond orders in a similar fashion as for O(³P) atoms,³ the CF₃ radical,⁴ and other electrophilic reagents.³ The activation energy for the ethylene reaction is 3.36 kcal larger than for the tetramethylethylene (TME) reaction. If the latter is zero or positive, then $E_a(\text{C}_2\text{H}_4) \geq 3.4$ kcal. The A factor for the ethylene reaction is 8.3-fold lower than that for the abstraction reaction



which in turn cannot be higher than a few tenths of the gas kinetic collision frequency. Thus, the upper limit for $A(\text{C}_2\text{H}_4)$ is $\leq 10^{10}$ l. mol⁻¹ sec⁻¹. Therefore, the upper limit for $k(\text{C}_2\text{H}_4) = 10^{10} e^{-3.360/RT}$. At room temperature this leads to a value of 3.7×10^7 l. mol⁻¹ sec⁻¹, while absolute measurements^{5,6} give $(7-9) \times 10^8$ l. mol⁻¹ sec⁻¹. The discrepancy can be resolved by assuming that the activation energy for the TME reaction has a negative value of 1.9 kcal, as discussed in the accompanying communication,⁶ which results in $E_a(\text{C}_2\text{H}_4) = 1.5$ kcal.

Changes in the A factor require the involvement of at least two opposing effects. Of these, for alkyl substituents, steric repulsion seems to predominate. For

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