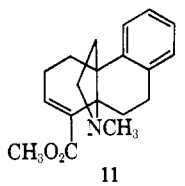
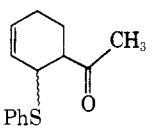
formed the β-resorcyclic acid salt, mp 180–181°.[6] The evidence that **8b** is a single isomer rather than an epimeric alcohol mixture was derived from its behavior on tlc, its cleanly resolved nmr spectrum, and the sharp melting range of the amine salt. The structure of **8b** followed unambiguously from the nmr (60 MHz, $CDCl_3$) which clearly revealed all ring-C protons. The C_8–C_9 vinyl hydrogens appeared as an AB quartet (5.74 ppm, J = 9 Hz) coupled allylically (J = 2.5 Hz) to the C_7 H. The C_7 H appeared as a broadened triplet (3.75 ppm, J = 7 Hz) coupled with the magnetically equivalent protons at C_6 (doublet, 2.2 ppm, J = 7 Hz).[9]

The syn relationship between hydroxyl and nitrogen functions follows from the observance of intramolecular hydrogen bonding in the ir spectrum (CCl_4 at 0.006 M), 3611 (free OH) and 3323 cm^{-1} (bonded OH). Other examples of intramolecular hydrogen bonding from a similar configuration have also been reported.[10] Thus, from the known stereochemical relationships in **8b**, the syn relation between sulfoxide and amine functions in **7** may be inferred. This is the geometry that would be predicted from the preferred endo orientation of **5** and **6** during the cycloaddition step.[11]



11

In a parallel experiment designed to compare the relative reactivity of sulfoxide **5** with more commonly used electron-deficient dienes, enamine **6** was also found to add to methyl pentadienoate[12] (**12**) (CH_3CN, 24 hr, 40°) affording the nicely crystalline tetracyclic ester **11**, mp 96–98°, in 50% yield.[6] Qualitatively, it appears that the sulfoxide-substituted diene **5** is slightly less reactive than **12**, an observation in agreement with the expected activating abilities of ester and sulfoxide functions in nucleophilic addition reactions with substituted ethylene derivatives.[13]



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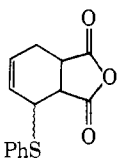

14

In order to extend this annelation sequence to include both electron-deficient as well as electron-rich dienophiles one may simply change the oxidation state of the sulfur-substituted diene. We have found that dienyl sulfide **10** reacts quite cleanly with both methyl vinyl ketone (neat, 125°, 11.5 hr) and maleic anhydride (reflux, benzene, 25 hr) affording adducts **13** and **14** in 67 and 84% yields, respectively.[6,14]

These results indicate that both dienyl sulfoxide **5** and sulfide **10** appear to be effective dienes in Diels–Alder reactions with electron-rich and electron-deficient dienophiles, respectively. As a result of the fact that such sulfoxides can be efficiently transformed into alcohols with allylic rearrangement, this synthetic sequence should extend the utility of the Diels–Alder reaction.

Acknowledgment. This investigation was supported by the National Institutes of Health, the National Science Foundation, and funds provided by Eli Lilly.

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(15) Camille and Henry Dreyfus Teacher-Scholar recipient, 1971–1976.

D. A. Evans,*[15] C. A. Bryan, C. L. Sims
Contribution No. 2902, Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024
Received December 8, 1971

Nucleophilic Participation by Remote Cyclopropane in an Intramolecular Analog to the SN2′ Reaction

Sir:

Previous work in this laboratory[1] has provided nonenzymic precedent for the previously suggested[2] possibility that the squalene oxide cyclization involves a transition state incorporating concerted, multiple, remote double bond π–σ participation. Our interest in nucleophilic participation by remote cyclopropane,[3] the increasing awareness that cyclopropane compounds with widely diverse structures are to be found across the spectrum of natural products,[4] and the emergence of an apparent cyclopropylcarbinyl biosynthetic intermediate[5] prompted us to explore the possibility that a cyclopropane ring might be capable of mimicking the role of one of the internal double bonds in the squalene oxide polycyclization.

The question to be posed, then, is: can a cyclopropane ring function as a remote, nucleophilic neighboring group by attacking a carbon–carbon double bond which is itself a source of electronic stabilization for a developing cationic center? We chose to examine this question by probing for participation by a structurally remote cyclopropane ring functioning as an internal analog to the nucleophile in an SN2′ reaction. We are now pleased to report not only that a cyclopropane ring can prove to be *more* efficient in a reaction of this type than an identically situated carbon–carbon double bond, but also to describe a striking example of sterically hindered, stereospecific, leaving group return to a

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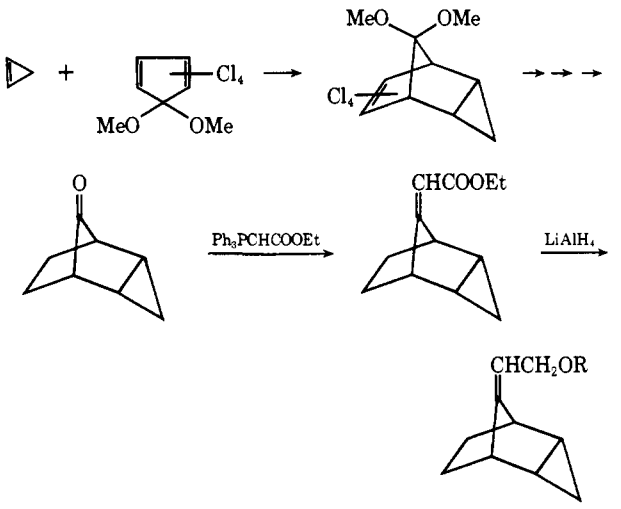
carbon *four* bonds removed from the site of initial ionization.

The synthesis of the substrate **1** selected for investigation is outlined in Chart I. The synthesis of the tri-

Chart I



1a, R = H
b, R = 3,5-dinitrobenzoyl

cyclic ketone and its subsequent conversion to the unsaturated ester were developed independently, but by parallel procedures described elsewhere.[6,7] Alcohol **1a** (bp 80° (1 mm)) and its dinitrobenzoate (mp 45–46°) were characterized by microanalysis and infrared and nmr spectroscopy, the results of which are in full accord with the structures assigned.

The solvolysis of **1b** in 70% aqueous acetone containing a twofold excess of urea, a nonnucleophilic base added to sequester 3,5-dinitrobenzoic acid as it is formed, was followed titrimetrically using the standard ampoule technique. The results of the kinetic analysis are presented in Table I along with those for other

Table I. Rates and Activation Parameters for Solvolysis of Dinitrobenzoates in 70% Aqueous Acetone at 100°

Dinitrobenzoate	**1b**	CHCH$_2$ODNB (3)	CHCH$_2$ODNB (4)
$k \times 10^5$, sec^{-1}	210	8.90[a]	0.337[b]
$\Delta H^{\ddagger}$, kcal/mol	23.6	25.3	27.2
$\Delta S^{\ddagger}$, eu	−7.7	−9.8	−11.0
k_{rel}	622	26.2	(1.0)

[a] Reference 1. [b] G. D. Sargent and M. J. Harrison, *Tetrahedron Lett.*, 3699 (1970); see also ref 1.

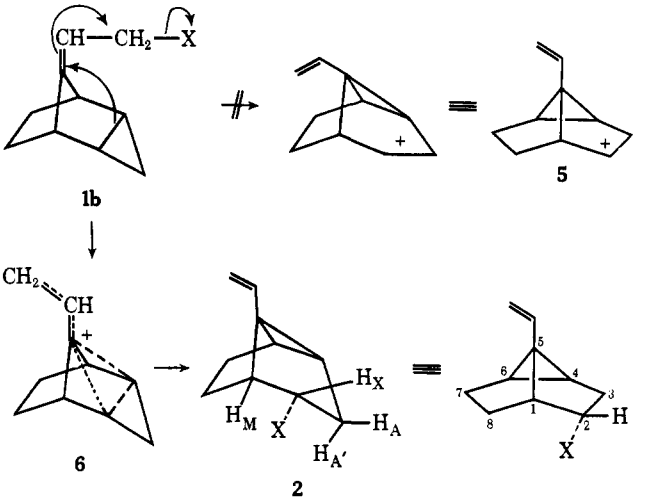
relevant model systems. Although the solvolysis of **1b** demonstrated good first-order behavior through at least 3 half-lives, the infinity titer proved to be only 60% of theoretical. This result is readily explained by the observation that *ca.* 40% (nmr) of the solvolysis product mixture consists of a rearranged dinitrobenzoate which remains inert under conditions sufficient to solvolyze completely dinitrobenzoate **1b**. Other than rearranged dinitrobenzoate, the solvolysis product consists of a single (>99.5%) alcohol. This alcohol was demonstrated not to be alcohol **1a** or either of its epimeric tertiary allylic isomers, all of which were shown to be sufficiently stable under the solvolysis conditions to permit their detection.

The structure of the product alcohol is revealed by its nmr spectrum (CCl_4): τ 9.1–7.3 (envelope of complex multiplets, rel area, 9.3), 6.7 (singlet, 1.0), 5.80 (doublet, J = 6.2 Hz, of triplets, J = 9.1 Hz, 1.0), 4.06–5.45 (characteristic pattern of an isolated vinyl (−CH=CH$_2$) group, 3.0). Washing the product alcohol with D_2O led to the disappearance of the singlet at τ 6.7 and a slight sharpening of the 5.80 multiplet. This multiplet can readily be interpreted as arising from the X proton of an AA′MX system ($J_{AX} = J_{A'X}$ = 9.1 Hz; J_{MX} = 6.2 Hz). The spectrum is thus wholly consistent with that to be expected for the primary product of ionization assisted by cyclopropane participation, alcohol **2**. The magnitude of the observed coupling constants requires that H_X have the exo configuration and that the −OH function *perforce* be assigned the endo configuration.[6]

Saponification (KOH–ethanol) of the rearranged dinitrobenzoate gave, with the exception of trace impurities with relatively very short glc retention times, a single alcohol which was shown to be identical with that generated by solvolysis of **1b**.

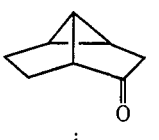
Reference to Table I demonstrates that solvolysis of allylic dinitrobenzoate **1b** is markedly accelerated (k_{1b}/k_4 = 622) over that of a model allylic ester lacking a remote intramolecular nucleophile. Indeed, in this system participation by cyclopropane at the γ position of the allylic ester is seen to be significantly more effective than participation by an identically situated carbon–carbon double bond (k_{1b}/k_3 = 23.6).

Even more striking is the stereospecificity which attends the collapse of the intermediate cation generated during solvolysis of **1b**. Both solvent and dinitro-



benzoate anion attack solely from the more sterically hindered direction,[8] a carbon atom four bonds and

(8) Reduction of tricyclo[3.3.0.0^{4,6}]octan-2-one (i) with LiAlH$_4$



i

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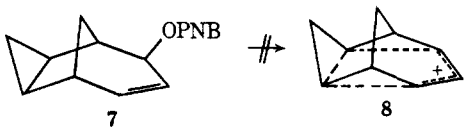
(7) R. Muneyuki, T. Yano, and H. Tanida, *ibid.*, **91**, 2408 (1969).

more than 4 Å removed from the site of initial ionization. The remarkable longevity of this cation, which permits the weakly nucleophilic leaving group to compete with water in the product-forming step, suggests a greater stability than one would attribute to an isolated secondary cation, **5**. In addition, such a cation could not reasonably be expected to yield **2a** or **2b** with the high stereospecificity observed; in fact, one would expect capture of this cation to lead to a predominance of product epimeric with **2**. In light of these considerations, the $\sigma-\pi$ delocalized structure **6** presents an attractive alternative.

To the best of our knowledge, this represents the first demonstration that a remote cyclopropane ring is capable of nucleophilic attack on a carbon–carbon double bond or that such interaction can lead to an extensively delocalized, stabilized, cationic intermediate. The results reported here lend added credence to the explanation recently offered to explain the failure to observe such participation and stabilization in a closely related system, **7**; namely, that participation in that



7 **8**

PNB = *p*-nitrobenzoyl

case would lead to an antiaromatic delocalized cation **8**.[9]

Acknowledgment. We are pleased to thank the National Science Foundation for financial support.

yields exclusively *endo*-2-tricyclo[3.3.0.0^{4,6}]octanol, *i.e.*, the product of exo attack by hydride.[6] Inspection of a model clearly demonstrates that the presence of the vinyl substituent at C-5 would not significantly shield exo attack at C-2 of cation **5**.

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(10) National Science Foundation Undergraduate Research Participant.

G. Dann Sargent,* Miles A. Herkenham[10]
Department of Chemistry, Amherst College
Amherst, Massachusetts 01002
Received August 5, 1971

An α-Peroxy Lactone. Synthesis and Chemiluminescence[1]

Sir:

The suggestion of α-peroxy lactones as intermediates in bioluminescence and chemiluminescence has been amply documented in recent years.[2,3] Among the extensively studied biological substrates we mention the luminescence observed for the *Cypridina hilgendorfii*,[4a,b] the latia neritoides,[5] and the firefly luciferin.[6a–d] In the latter case, detailed oxygen-18 labeling experiments seriously question the α-peroxy lactone intermediacy, at least in the enzymatic oxidation.[6e,6f] Yet, very convincing arguments have been put forward on the involvement of α-peroxy lactones in the chemiluminescence observed in the reaction of acridinium salts with hydrogen peroxide[7] and in the reaction of ketenes with singlet oxygen.[8] However, to the best of our knowledge the synthesis and characterization of an authentic α-peroxy lactone derivative has not been reported so far. Our success in preparing β-peroxy lactones[9] and γ-peroxy lactones[10] encouraged us to undertake the synthetic challenge inherent with the α-peroxy lactone structure. We now report on the synthesis of 4-*tert*-butyl-1,2-dioxetan-3-one (**4**), the first α-peroxy lactone to be prepared and characterized.

Among the initial, obvious approaches to the preparation of α-peroxy lactones, we attempted the base-catalyzed cyclization of α-haloperoxy acids, but decomposition of the α-halo percarboxylate anion prevailed over the desired intramolecular cyclization.[11] Attempts to add singlet oxygen, chemically as well as photochemically,[12] to bis(trifluoromethyl)ketene and bis(*tert*-butyl)ketene failed; both ketenes were recovered unchanged. The addition of singlet oxygen to ketene dithioketals proceeded smoothly to give the respective 1,2-dioxetanes, but the latter fragmented even at Dry Ice temperatures.[13]

After these numerous failures we decided to mimic the biological systems[2,3] by preparing first an authentic α-hydroperoxy acid and attempting to cyclize it to the α-peroxy lactone, employing one of the various cyclants that have proved useful for the preparation of β-lactones from β-hydroxy acids.[14] Although α-hydroperoxy esters are readily available *via* base-catalyzed autoxidation of the corresponding esters,[15] attempts to hydrolyze these met with failure due to facile decarboxylative fragmentation of the intermediary α-hydroperoxy acids under basic as well as acidic conditions.[16] α-Lactones can be efficiently trapped by methanol in the form of α-methoxy acids.[17] Analogous photodecarboxylation of an ether solution of di-*n*-butylmalonoyl peroxide in the presence of concentrated hydrogen peroxide resulted in the desired α-hydroperoxy acid, but all efforts to obtain a pure sample met with failure. However, photooxidation of the ketene bis(trimethylsilyl)ketal (**1**),

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