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ARE VINYL CYCLOPROPANES PARTICULARLY ELECTRON RICH?

[THE PHOTOOXYGENATION OF CYCLOPROPYLETHYLENES]

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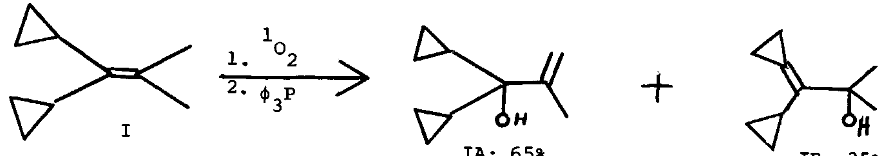
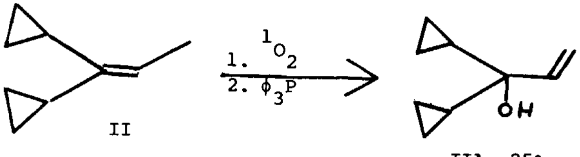
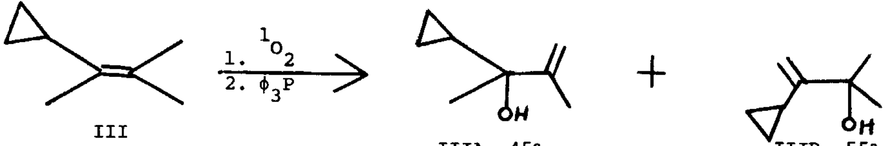
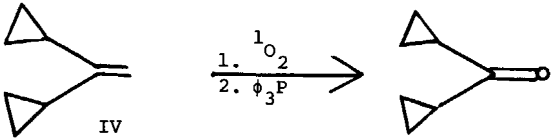
Nishida and coworkers[1] have argued, basing themselves on cycloaddition and ionization potential data, that cyclopropyl olefins are highly electron rich, of the same order as vinylethers. On the other hand, others have demonstrated that cyclopropyl groups are inductively similar to[2] or only somewhat poorer electron donors than alkyl groups.[3] The mode and rate of singlet oxygen ($^1O_2$) attack upon olefins is quite sensitive to the electron density of the double bond.[4] Indeed, the electron rich vinyl ether dihydropyran not only reacts very rapidly to produce, via an "ene" mode, the corresponding allylic hydroperoxide, but cleaves as well, via the intermediacy of a dioxetane, to the corresponding dicarbonyl compound.[5] We were interested therefore in using this sensitivity of $^1O_2$ to test whether the double bond in vinyl cyclopropanes is indeed particularly electron rich.

These olefins are also of interest since abstraction of the allylic cyclopropyl ring hydrogen in an "ene" mode would involve the formation of an alkylidenecyclopropane and the concomitant investment of 11.4 Kcal/Mole of strain energy.[6,7] We were interested therefore in determining the effect this additional strain would have on the product distribution.[8] A recent report of Conia et al.[8e] prompts us to present our results at this time.

For the purpose of this study olefins I-IV were prepared by a Wittig reaction between the appropriate phosphorane and cyclopropylketone.[9] The olefins were photooxygenated[5b] in a variety of solvents,[10] and the resulting mixture was treated with an equivalent of triphenylphosphine. The products were isolated by vapor phase chromatography (VPC) and identified by their spectral data. Relative yields were determined by integration of the VPC peak areas. Relative rates for the reaction of these olefins as compared to tetramethylethylene (TME) were determined in competition studies with 1,2-dimethylcyclohexene (k_{rel} = 0.53;[11] for olefins I and III) or 1-methylcyclohexene (k_{rel} = .0041;[4a] for II) or cyclohexene (k_{rel} = .000048 [4a]; for IV). The results are listed in the table.

Based on the relative rate data, it is clear that the unperturbed vinylcyclopropane double bond is not particularly electron rich and the electronic effect of a cyclopropyl group at least, in $^1O_2$ reactions, is similar to that of a methyl group.[13] It seems then that the well known resonance effect[12] of the cyclopropyl group only comes into play when an electron deficient center is created.

TABLE: PRODUCT DISTRIBUTION AND RELATIVE RATES FOR THE $^1O_2$ REACTION OF CYCLOPROPYL OLEFINS I-IV

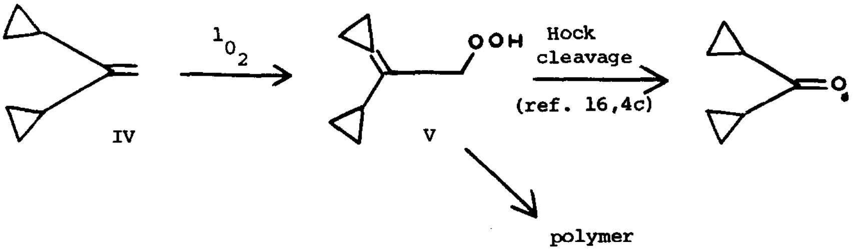
OLEFIN	PRODUCTS	k_{rel}*		
		$\frac{k_{olefin}}{k}$ 	$\frac{k_{olefin}}{k}$ 	$\frac{k_{olefin}}{k}$ 
 I	1. $^1O_2$ 2. ϕ_3P → IA; 65% + IB; 35%	0.33		
 II	1. $^1O_2$ 2. ϕ_3P → IIA; 25% + IIB; 75%	0.041	1	
 III	1. $^1O_2$ 2. ϕ_3P → IIIA; 45% + IIIB; 55%	1.05		
 IV	1. $^1O_2$ 2. ϕ_3P → IVA; 30% + polymer 70%	0.000035		0.43

* k_{rel} : TME = 1.0 [4a] ; *trans*-3-methyl-2-pentene = .04 [4a] ; 2,3-dimethyl-1-butene = .000082 [11]

Noteworthy as well is the formation of alcohols IB and IIB in spite of the additional 11.4 Kcal of strain energy. That cyclopropyl hydrogen abstraction competes favorably with methyl hydrogen removal cannot be a result of the pronounced s-character of the exocyclic cyclopropene C-H bond.[8d] The absence of any analogous product in the photooxidation of III rules this out.

The question of mechanism is a difficult one. The data seems to indicate that we have a two step process. In the initial stage, oxygen "decides" which olefinic carbon to attack and is at this time insensitive to the number and location of the allylic hydrogens and to the strains that may result in the final product. Hence IB and IIB are produced in substantial amounts. However, the absence of any alkylidenecyclopropane product in the photooxidation of III indicates that once this "decision" is made, the product distribution is indeed sensitive to resulting strain factors. Such a duality of sensitivity, does not correspond simply to a concerted "ene" mechanism. Nor does the reaction seem to proceed <u>via</u> a perepoxide intermediate as has been suggested by Conia <u>et al</u>.[8e] In such a situation one would have expected that the strong electron releasing effect of the cyclopropyl groups should stabilize the positive charge α to the rings, thus promoting cyclopropyl hydrogen abstraction.[14] The fact, however, that alcohols IIIA and IIIB are formed in nearly equal amounts puts into question any substantial resonance effect. More importantly, if stabilization of the incipient carbonium ion in the perepoxide intermediate, and hence in the transition state, plays an important role, why does II react with $^1O_2$ 8 times slower than I and 25 times slower than III (where only one cyclopropyl group is present)?[12] Thus, the question of mechanism requires further investigation.

In closing, we would like to comment briefly on the surprising formation of dicyclopropyl ketone in the photooxidation of IV. In light of the results obtained for olefins I-III it is unlikely that the ketone results from a direct 2 + 2 cycloaddition of $^1O_2$ to IV. It is our feeling that the allylic hydroperoxide V is formed initially and in turn cleaves[16,4c] photochemically or thermally (before the addition of ϕ_3P) to ketone or polymerizes. In partial support of this hypothesis, we note that when the photooxygenation reaction mixtures of I-III were injected into the VPC prior to reduction with ϕ_3P, substantial amounts of the corresponding cyclopropyl ketones were formed at the expense of both I-III A and B.



Further studies on the reaction of $^1O_2$ with strained olefins such as methylenecyclopropanes, cyclopropenes and their cyclobutyl analogs are under active investigation and will be reported shortly.

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13. The slight rate lowering for olefin I is probably due to steric considerations; Cf. reference 4c page 142 table II.
14. We note in passing that for a cyclopropyl group to be involved in resonance it must be in a "bisected" conformation[15]. In such a geometry the abstractable hydrogen lies perpendicular to the plane of the p orbitals[15], while the ene reacton requires that it be parallel to this plane[4].
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