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PHOTOCHEMICAL GENERATION OF VINYLKETENES BY ELECTROCYCLIC OPENING OF CYCLOBUTENONES[1]

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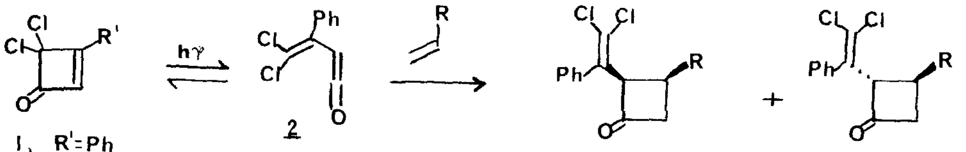
Abstract: 4,4-Dichloro-2-cyclobutenones 1, available by cycloaddition of acetylenes to dichloroketene, can be photolyzed in the presence of olefins or dienes to produce regiospecifically 2-vinylcyclobutanones 3-11. The photochemical reaction succeeds even in some cases where thermolysis fails and was shown to proceed by electrocyclic ring opening to a vinylketene. Stereochemically the results of photolysis of 1 differ from thermolysis with identical olefinic substrates.

Ketenes have long been known as useful reactive intermediates, and the reaction of dichloroketene with olefins has found many synthetic and mechanistic applications.[2] Recently there has been considerable interest in vinylketenes as synthetic intermediates and two pathways to these compounds have been explored.[3] The oldest method is thermolysis of cyclobutenones, usually above 120°C, in the presence of dienes or alcohols as trapping agents.[3] The second pathway involves generation of the vinylketene by HCl elimination from unsaturated acid chlorides.[3c,e,f] Both methods have considerable limitations, e.g. high temperatures, or presence of amine salts that cause polymerization. Inspite of extensive use of thermolysis in the electrocyclic ring opening of cyclubutenones, there has apparently been onlyone report on photolytic ring opening of these compounds, namely in the presence of methanol to produce ring opened esters.[4] We decided to explore the photochemical reaction as a potentially useful and cleaner method of generation of vinylketene intermediates and as a route to 2-vinylcylobutanones.

We report here our preliminary findings that photochemical ring opening of cyclobutenones 1, readily available by cycloaddition of acetylenes to dichloroketene,[3g] proceeds at ambient temperature, in some cases even where thermolysis fails, and the intermediate vinylketenes 2 can be trapped with alkenes, leading to 2-vinylsubstituted cyclobutanones 3-11, or with nucleophiles providing unsaturated acid derivatives. Our investigation was prompted by an unsuccessful attempt (polymerization) to thermolyze 4,4-dichloro-3-phenylcyclobutenone 1 in the presence of isoprene. By contrast photochemical irradiation of the two components in benzene led in good yield to a 5:1 mixture of cis and trans divinylcyclobutenones 5 and 5a, resulting from a regiospecific cycloaddition of the ring opened vinylketene 2 to isoprene.

Reagents that were used to trap the vinylketene 2 include methanol, ethanol, allylamine and a number of monosubstituted, 1,1- and 1,2-disubstituted alkenes, enol ethers and dienes (see Table). The cycloaddition is usually regiospecific as shown in the case of unsymmetrical olefins or dienes, however a mixture of stereoisomers is generally obtained. No [4+2] adducts were observed. A comparison between thermolysis and photolysis of 1 in the presence of cyclohexadiene reveals significant stereochemical differences. Thus photolysis in benzene furnished

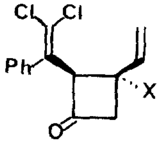


1, R'=Ph
1a, R'=Bu

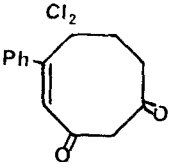
2

3, R-OEt
4, R=Ph

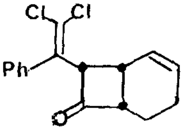
3a, R=OEt
4a, R=Ph



5, X=Me
6, X=OSiMe$_3$



14



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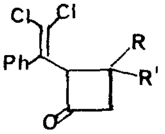
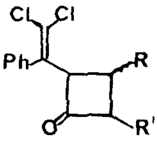
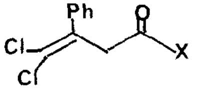


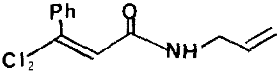
8, R,R'=Me
9, R,R'=(CH$_2$)



10, R,R'=Me
11, R,R'=O(CH$_2$)$_3$



12a, X=NH
b, X=OMe
c, X=OEt
d, X=OH



13a

the all cis adduct 7 in 75% yield, while heating in the same solvent produced a mixture of 7 and its 2,3-trans isomer 7a in 72% yield. Similarly, more cis adduct 3 (cis:trans ratio of 1:2) was formed on photolysis of 1 with ethoxyethylene, while only trans product 3a was obtained on thermolysis at 130°, in the presence of 2,6-di-t-butylphenol. It should be noted that in the absence of the latter free radical inhibitor the thermolysis of 1 in the presence of ethoxyethylene leads only to decomposition products.

Since we were able to show that the trans cycloadduct to vinylketene 2 is usually the more stable isomer, it is possible that the larger proportion of trans isomer resulting from thermolysis is due to thermal isomerization of the cis adduct. Indeed we showed that 2-vinylcyclobutanones readily epimerize. For instance, the photochemical product of styrene addition to 1 is the 2,3-cis adduct 4 which on silica gel chromatography isomerizes to the trans isomer 4a. A similar isomerization occurs with 11. Yet, neither the 2,3-cis nor the trans disubstituted cyclobutanone products interconvert under photolysis conditions.

The stereochemical assignments for the products are based on ir (1770 cm^{-1}), ^{1}H and ^{13}C NMR and mass spectral correlations. For instance, $J_{2,3}$ in 3 (cis) is 7.5 Hz, whereas in 3a (trans) it is 6 Hz and the chemical shift of H-3 in 3 is at δ 4.54 ppm whereas in 3a this proton absorbs at higher field (4.00). The facile Cope rearrangement of 6 to 14 in the presence of F^- is also consistent with a cis-divinyl cyclobutanone structure. The stereochemistry of the products is influenced by solvent polarity as indicated by the reversal of the cis:trans ratio to 10:7 when the photolysis with ethoxyethylene was carried out in acetonitrile instead of in benzene or pentane. In acetone even under scrupulously dry conditions ring opened carboxylic acid 12d was obtained. 12d was also the product in some cases when the olefin reacted very sluggishly which led us to suspect the presence of vinylketene 2 after photochemical irradiation and its conversion to 12a on silica gel. Indeed when 1 was irradiated in benzene for 1.5 hr with or without isoprene and allylamine was added 5 min after irradiation was discontinued the unsaturated amides 12a and 13a were isolated in high yield. No amide was formed from 1 without irradiation. This clearly indicated a photochemical equilibrium in which the vinylketene survives at room temperature to a considerable extent. Earlier studies have indicated a thermal equilibration between cyclobutenones and their electrocyclic ring opened isomers[3a] but the latter ring close fast at elevated temperature so that they are often not trapped by less reactive olefins.

Photochemical electrocyclic ring opening of cyclobutenones should occur in a disrotatory fashion but this is of no concern in the current system. The stereochemistry of the 2-vinyl-3-substituted cyclobutanones should be influenced by the rules guiding thermal [2+2] cycloadditions of ketenes to alkenes[2,3,5] and that explains both the regiospecificity and the cis stereoselectivity observed. The observed solvent effect and the ease of isomerization of the 2-vinylcyclobutanones are unusual and deserve further study.

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TABLE

Products in the Photolysis of 1 + Alkene (or Nucleophile)[a]

Product	cis:trans ratio	isolated yield (%)	Product	isolated yield %
3	1:2 [b]	80	8	40
3 in MeCN	10:7	75	9	50
3 [c] (from 1a)	-	50	10	30
4	cis	90	12a + 13a	90
5	5:1	70	12b	90
6	cis	50	12c	85
7	cis [d]	75		
11	cis	80		

(a) At 300 nm in benzene (unless noted), 20°, 3-24 hr. The products were isolated by chromatography on silica gel (except 4 and 7 which epimerized): All showed consistent ir, NMR and mass spectra.

(b) Thermolysis led to polymerization.

(c) The butyl analog of 3.

(d) Thermolysis led to 7 and its trans isomer.

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