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PHOTOCHEMISTRY OF α,α-DISUBSTITUTED BICYCLIC CYCLOBUTANONES - A POTENTIAL THERMAL-PHOTOCHEMICAL METATHESIS REACTION

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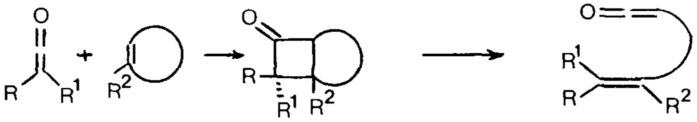
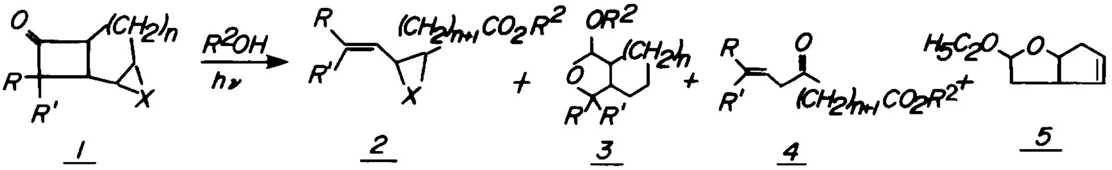
ABSTRACT: Under certain conditions the photolysis of α,α-disubstituted cyclobutanones give terminal olefinic esters. A two-stage thermal photochemical metathesis is described.

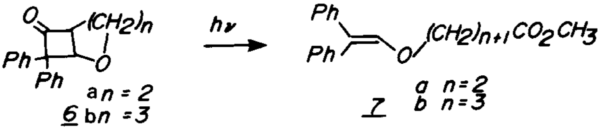
The metal catalyzed metathesis reaction has found limited use in organic synthesis[1]. Such processes are often complicated by non-regio and non-stereoselectivity and often accompanied by polymerizations. Recently[2] a number of two-step metathesis equivalent reactions have been reported which involve four membered rings as intermediates and which occur in a regio and stereoselective manner. We wish to report an example of such reactions using cyclobutanones as intermediates. Cycloadditions of ketenes with olefins proceed both regio and stereospecifically giving stereospecifically substituted cyclobutanones[3]. The photocycloelimination process has also been shown to occur in a stereospecific manner[4]. The combination of the two processes could be used in principle as a two-step metathesis reaction leading to stereospecifically functionalized olefins (e.g. scheme 1). The photochemistry of cyclobutanones is however complicated by two other competing processes: decarbonylation and ring-expansion with formation of acetals in alcoholic medium. Decarbonylation can be minimized by the choice of appropriate substituents on the ring[5] and we report here that the extent to which ring expansion occurs can be controlled by varying the alcohol concentration. Cyclobutanones 1 a-i, n-p, 6 a,b and 8 were prepared by standard literature methods[6] involving cycloadditions of the appropriate ketene with cycloalkene or 1,3-cycloalkadiene. The tricyclic ketones 1 j-m were readily available from epoxidation with MCPBA or dichlorocarbene addition with $CHC\ell_3$ on the bicyclic ketones 1 c and d. Irradiation[7] of 1 b in methanol/ether led to formation of acetal 3 b and ester 2[8] b in 70 and 30% yields respectively. Irradiation of 1 b in benzene containing trace amounts of CH_3OH led to production of ester 2 b as the only product. With larger concentrations of CH_3OH in benzene the acetal 3 b to ester 2 b distribution was found to be a function of methanol concentration

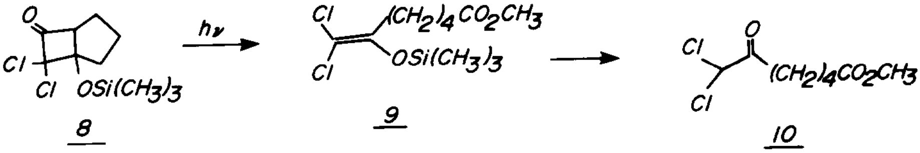
Scheme 1



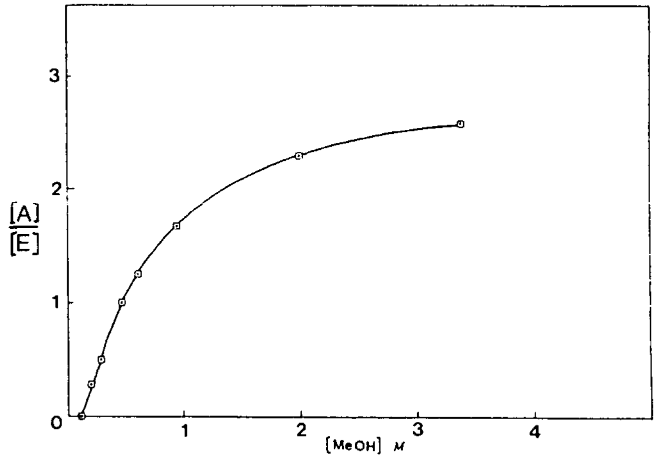


a:	$R=R^1=C_6H_5$	$X=H_2$	n=1		i:	$R=C_6H_5$	$R^1=C\ell$	X=bond	n=1
b:	$R=R^1=C_6H_5$	$X=H_2$	n=2		j:	$R=R^1=C_6H_5$		X=O	n=1
c:	$R=R^1=C_6H_5$	X=bond	n=1		k:	$R=R^1=C_6H_5$		X=O	n=2
d:	$R=R^1=C_6H_5$	X=bond	n=2		l:	$R=R^1=C_6H_5$		$X=CC\ell_2$	n=1
e:	$R=R^1=H$	X=bond	n=1		m:	$R=R^1=C_6H_5$		$X=CC\ell_2$	n=2
f:	$R=R^1=C\ell$	X=bond	n=1		n:	R=α-naphthyl	$R^1=H$	X=bond	n=1
g:	$R=R^1=C\ell$	$X=H_2$	n=1		o:	R=α-naphthyl	$R^1=H$	X=bond	n=2
h:	$R=R^1=C\ell$	X=bond	n=2		p:	$R=C_6H_5$	$R^1=H$	X=bond	n=1





and varied according to the expression $\frac{[MeOH]}{[MeOH]+C}$ (graph 1).[11] Similar behaviour was observed for ketones 1 a,c and d. Thus in order to maximize the cycloelimination products 2 irradiations had to be carried out under minimal concentration of alcohol. Photolysis of ketones 1 a-p, 6 a,b and 8 in benzene containing 0.2M or less of CH_3OH or C_2H_5OH resulted in the formation of the cycloelimination products 2 a-p, 7 a,b and 10 as major products (see Table 1). For the epoxyke-



Graph 1 -Acetal(A)to Ester(E)distribution as a function of methanol concentration.

tones 1 j and k transient photoproducts 2 j and k were observed by proton nmr spectroscopy. These underwent secondary photolysis to give enone esters 4 j and k. The production of ketones 4 from vinylepoxides 2 can be rationalized in terms of a hydrogen shift of the 1,3-diradical 11 (Scheme 2). Similar photorearrangements have been reported for arene oxides[9]. In the case of the dichlorosiloxyketone 8, the photoproduct 9 was labile to aqueous work-up and under these conditions was cleanly transformed to the α,α-dichloroketoester 10. For the photoproducts 2 c, n-p secondary photoisomerization took place as was evident from the multiplicity of the proton nmr signals associated with the ester alkyl group. Hydrogenation of the isomeric mixture led to a single tetrahydrogenated product in all cases.

Scheme 2

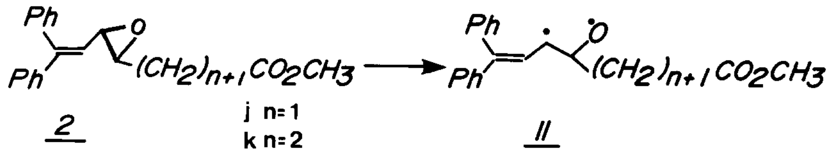


Table 1 - Yields of Photoproducts[a]

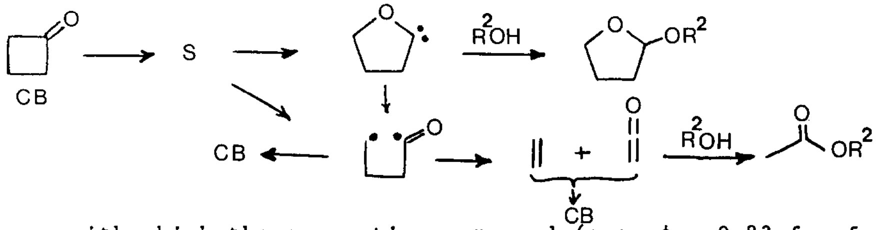
Entry	Conditions	Photoproducts
1 a	C_6H_6/MeOH	2 a (quant)[b,d]
1 b	MeOH/ether	2 b (30)[b] 3 b (70)[b]
1 b	C_6H_6/MeOH	2 b (quant)[b,d]
1 c	C_6H_6/EtOH	2 c (quant)[b,d]
1 d	C_6H_6/EtOH	2 d (quant)[b,d]
1 e	C_6H_6/EtOH	ethyl acetate (40)[c] Ethyl-1,3-heptadienoate (5)[c] 5 (30)[c] dicyclopentadiene (10)[c]
1 f	C_6H_6/EtOH	2 f (90)[d]
1 g	C_6H_6/EtOH	2 g (60)[d]
1 h	C_6H_6/MeOH	2 h (30)[d]
1 i	C_6H_6/MeOH	2 i (30)[d]
1 j	C_6H_6/MeOH	4 j (56)[d]
1 k	C_6H_6/MeOH	3 k (40)[c] 4 k (60)[c]
1 ℓ	C_6H_6/MeOH	2 ℓ (50)[d]
1 m	C_6H_6/MeOH	2 m (40)[d]
1 n	C_6H_6/EtOH	2 n (quant)[b,d]
1 o	C_6H_6/EtOH	2 o (quant)[b,d]
1 p	C_6H_6/EtOH	2 p (quant)[b,d]
6 a	C_6H_6/MeOH	7 a (quant)[b,d]
6 b	C_6H_6/MeOH	7 b (quant)[b,d]
8	C_6H_6/EtOH	10 (58)[d] two unidentified products (18)[d]

[a] Yields in parenthesis. [b] Based on proton nmr integration of relative peak areas. [c] Based on vpc integration of relative peak areas. [d] Isolated yields, (See ref.11).

That unsaturated ketenes (Scheme 1) are involved as direct precursors to the cycloelimination products 2 was shown by irradiating 1 c in dry benzene. The photolysate showed an intense peak at 2070 cm^{-1} in the ir spectrum indicative of ketenes. Reaction of the photolysate with ethanol in the dark led to formation of photoester 2 c. That E/Z photoisomerization occured at the ketene stage was shown by the identical distribution of the E/Z esters 2 c obtained in the dark reaction. That benzene was not involved as a sensitizer in these photoreactions was evident by the similarity in product distribution and efficiency of formation when these were carried out in pentane solution.

The variation of the cycloelimination and oxacarbene derived photoproducts with alcohol concentration (graph 1) suggests a mechanism in which both the diradical and oxacarbene are formed competitively as primary intermediates and that irreversible conversion of the oxacarbene to the diradical occurs under conditions of minimal or no alcohol present (Scheme 3). Such a scheme has been proposed by Quinkert[10] to account for the observed stereospecificity of these photolyses.

Scheme 3



The efficiency with which these reactions proceed (e.g. $\phi = 0.83$ for formation of 2 c) makes this two step sequence a viable route towards the syntheses of terminal functionalized esters. We are currently exploring the possible use of such a route in the preparation of pyrethroid analogues as well as unstable ketenes.

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Footnotes and References

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7. Photolyses were carried out using a Hanovia 450W high-pressure mercury arc lamp in a quartz immersion with a Vycor filter. The 10mm quartz sample tubes were strapped around this well.
8. All new compounds gave satisfactory C,H analyses and/or molecular ion peak in their mass spectra.
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11. Recovery of mixture after evaporation of solvent was consistently greater than 95% in all cases, thus within experimental error the mass balance remains constant throughout all of these runs.

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