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PREPARATION OF 2-VINYLCYCLOBUTANONES AND THEIR CONVERSION TO CYCLOPENTENONES

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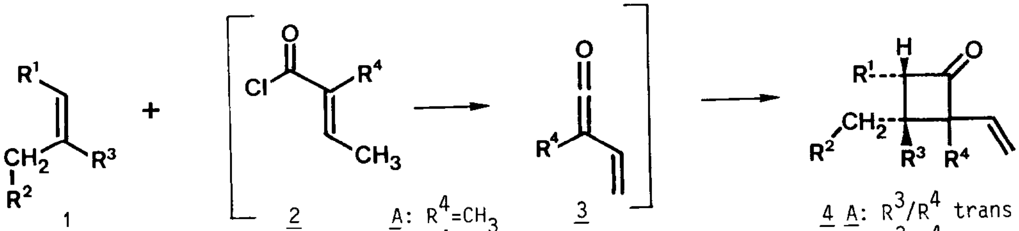
Abstract: Methyl- and ethyl-vinylketene 3 were added to several simple olefins 1 to afford alkylated 2-vinylcyclobutanones 4, which in turn rearranged to cyclopentenones 6 (via dienones 5A,B) or 7 (via 1,2-acyl migration) under acid catalysis. Evidence is presented for a cyclopropyl-carbinyl intermediate 8.

Following our interest[1] (cf. also[2]) in the reactions of vinylketenes, we have found that methyl- (3A) and ethyl-vinylketene (3B),[3] generated in situ from 2-methyl- (2A) and 2-ethylbut-2-enoyl chloride (2B) and triethylamine, can be made to react even with unactivated olefins 1 (cf.[4]) to give alkylated 2-vinylcyclobutanones 4 (Table[5]). The conditions, which at least partially suppressed the known[6] self-condensation of 2 to 2-pyrones, entailed high temperature (ca. 150°, mostly requiring a sealed tube) and a six-fold excess of neat olefin (recoverable). This method to prepare 4 has the advantage (cf. alternative methods[7]) of using readily available starting materials in a one-step procedure; some of the low yields may be improved by using a larger excess of the olefin.

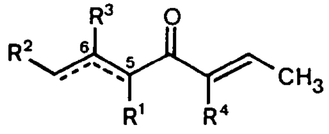


1 2 A: R^4=CH_3 3 4 A: R^3/R^4 trans
B: R^4=C_2H_5 B: R^3/R^4 cis

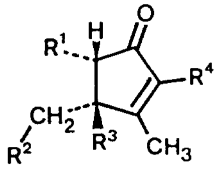
Depending on the substitution pattern (R^1,R^2,R^3) of the olefin 1, the [2+2]-cycloadditions with 3 were found to be highly regioselective (substituent control, leading to 4a-d, g) and stereoselective with respect to the olefin (suprafacial participation, leading to 4e, f, h). The stereoselectivity due to antarafacial participation of the ketene[8], i.e. the preferred appearance of its (bulkier) methyl or ethyl group (R_4) in the more hindered position of 4, was less pronounced, as mixtures of stereoisomers 4A and 4B were formed where possible (products 4a, d-f, h).

Under mild acid catalysis (procedures i and ii, Table) the 3,3-dialkyl-cyclobutanones (4a-c, g) underwent ring opening to substituted allyl-vinyl-ketones (5A) and divinyl-ketones (5B). With higher acid concentration (procedure iii) 4a-c, g were transformed into cyclopentenones (6a-c, g). We assume the 4 → 6 transformations to occur by a Nazarov-type cyclisation[9] of the intermediate dienones (5a-c, g), which was confirmed by the conversion of 5gA into 6g (36%) under procedure iii.

The 3-alkyl- (4d) and 3,4-dialkyl-cyclobutanones (4e, f, h) did not yield dienones 5 or cyclopentenones 6 by procedures i-iii. They were, however, converted to cyclopentenones (7d-f, h) under more vigorous conditions (procedure v) or under stronger acid catalysis (procedure iv). That these latter conversions proceed by a different mechanism, a 1,2-acyl migration (cf.[10]), may be deduced from the transformation of 4h into 7h ($\delta(CH_3)$ = 1.64 ppm) instead of 6h (which should show $\delta(CH_3)$ in the range of 1.90-2.05 ppm).



5 A: Δ^6
B: Δ^5



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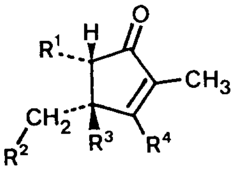

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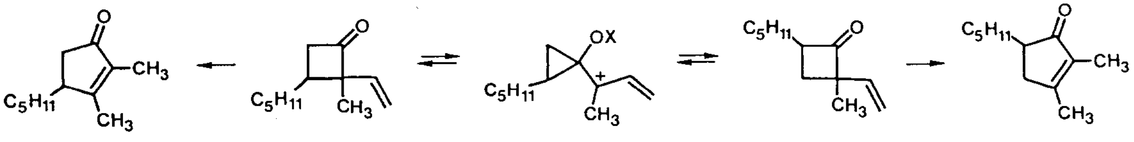
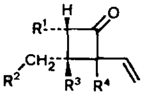
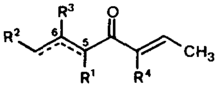
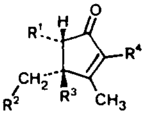
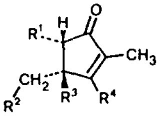
In the rearrangement of the 3-monoalkyl-cyclobutanone 4d (under procedure iv), the 4-alkyl-cyclopentenone 7d (51%) was accompanied by the unexpected 5-alkyl-cyclopentenone 10 (11%). This is explainable by the occurrence of a cyclopropyl-carbinyl intermediate like 8, as has been postulated in similar cases.[11] We have found the 3-alkyl- (4d) and the 4-alkyl-cyclobutanone 9 to be mutually interconvertible (ratio 1:4) under mild conditions (0.3 mol/L in CH_2Cl_2 with 1.1 mol equiv. BF_3-etherate), which supports this hypothesis.



7d 4d 8 9 10

Table. Products of the cycloadditions 1 + 3 and of their acid catalysed rearrangements, with % isolated yields

	substituents				% yield cycloadduct 4 (ratio A : B)	procedure[a]	% yield dienones 5 (ratio A : B)[b]	% yield cyclopentenone[c] 6	7
	R^1	R^2	R^3	R^4					
a	H	$-C_3H_7$	CH_3	CH_3	11 (1:1)	i	80[d]	-	
						ii	73 (5:1)[d]	-	
						iii	11[d]	65	
b	H	$-(CH_2)_3-$		CH_3	79	i	55	-	
						ii	67 (3.7:1)	-	
						iii	8 (0.5:1)	71	
c	H	$-(CH_2)_4-$		CH_3	42	i	75	-	
						ii	89	-	
						iii	4	66	
d	H	$-C_4H_9$	H	CH_3	40 (2.3:1)	iv	-		62[e]
e	$-(CH_2)_2-$		H	CH_3	28 (2.3:1)	v	-		76
						iv	-		46
f	$-(CH_2)_5-$		H	CH_3	60 (3:1)	iv	-		58[f]
g	H	$-(CH_2)_3-$		C_2H_5	67	i	71	-	
						iii	20 (0.5:1)	51	
h	$-(CH_2)_5-$		H	C_2H_5	52 (5.7:1)	iv	-	-	54[f]

[a] Acid catalysed rearrangement: The cyclobutanone 4 was allowed to stand with the acid catalyst until no more 4 remained (procedure i-iv at rt. for 0.25-24 h): i) 0.3-0.6 mol/L in CH_2Cl_2 with 0.2 mol equiv. BF_3-etherate; ii) 0.3-0.6 mol/L in CH_2Cl_2 with 0.2 mol equiv. CH_3SO_3H; iii) 0.3 mol/L in CH_2Cl_2 with 1.0 mol equiv. CH_3SO_3H; iv) ca. 1.0 mol/L in neat CH_3SO_3H; v) 0.7 mol/L in $CDCl_3$ with 1.0 mol equiv. CH_3SO_3H at 60^0 for 12 days.

[b] Where no ratio is given in this column, only dienone A was found.

[c] Cyclopentenones 6 and 7 are identical when $R^4 = CH_3$ (cases a-f).

[d] Mixtures of the (E)- and (Z)-isomers at Δ^6 or at Δ^5.

[e] Including 11% of the cyclopentenone 10, which was separated.

[f] Including some of the trans-ring juncture isomer and some of the $\Delta^{1(8)}$-double bond isomer.

Our method to obtain 5, 6 and 7 uses the same building blocks (unsaturated acid derivatives and olefins) as the Friedel-Crafts approach to make linear dienones[12] and cyclopentenones.[13] Aside from affording vinylcyclobutanones 4 as potentially valuable intermediates, our method has the advantages of a) preventing contact between a strong acid and the starting olefin, thus avoiding double bond migration, and b) permitting in some cases an altogether milder acid catalysis, which could suppress decomposition.

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