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SELECTIVITY IN RETRO-ENE vs. CYCLOPENTENE REARRANGEMENTS OF A CIS-METHYLVINYLCYCLOPROPANE

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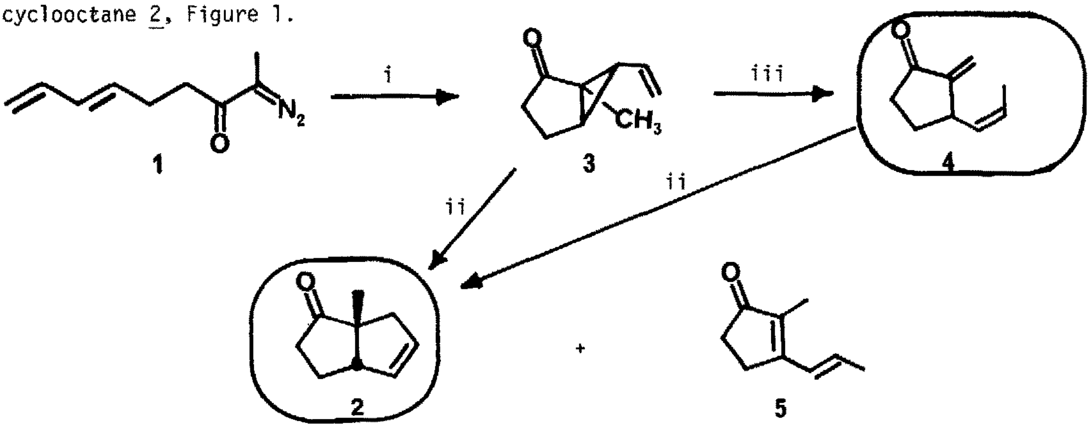
Abstract: The thermolytic behavior of 6β-ethenyl-1β-methyl-bicyclo [3.1.0] hexane-2-one was examined at a wide range of temperatures and with diverse catalytic surfaces. Conditions are reported to effect selectivity between the retro-ene and the cyclopentene modes of rearrangement. The synthetic scope of these transformations is indicated.

Recently we have demonstrated the availability of bicyclooctanes and bicyclononanes in useful yields[1] via the intramolecular cyclopropanation-rearrangement sequence of the corresponding dienic diazoketones[2]. An extension of this methodology to diazoethylketones such as 1 would provide rapid access to angularly methylated bicyclic ketone 2, which constitutes a structural subunit of such terpenes as hirsutene[3], isocomene[4] and retigeranic acid[5]. Our interest in the development of new synthetic routes to these terpenes has prompted us to initially investigate the thermolysis of vinylcyclopropane 3 as a source of bicyclooctane 2, Figure 1.



i. Cu(acac)$_2$/benzene; ii. 600°C; iii. 400°C

Figure 1

A review of literature suggested several avenues available to systems such as 3 on pyrolysis. A few reviews describing the thermal unimolecular decomposition of diversely functionalized cyclopropanes have appeared[6]. The conversions of cis-substituted carboxy-, carbalkoxy-, and vinyl- methylcyclopropanes into γ,δ-unsaturated ketones[7], esters[8] and into 1,4-dienes[9] have been exploited from both the mechanistic[6,10] and the synthetic stands. However, we have not found any examples of preparatively useful cyclopentene rearrangements of cis-methylvinylcyclopropane[11] although the corresponding process involving otherwise substituted vinylcyclopropanes has been featured in several annulation procedures[1,12].

Of the above processes only the formation of 1,4-diene and of cyclopentene applies to the cyclopropane 3. We now wish to report the selective conditions to achieve either the formation of 1,4-diene or of cyclopentene.

Diazoketone 1, prepared in quantitative yield by the action of etheral diazoethane[13] on 4,6-heptadienoyl chloride[2], furnished vinylcyclopropane 3 (94%, b.p. 54°C/0.3mm), stereospecifically[14], in refluxing benzene containing 20 mole percent of Cu(acac)$_2$. In a typical pyrolysis experiment, a 100 mg sample of 3 was evaporated at 0.01 mm/Hg through a properly conditioned, horizontally situated, hot tube. The collected material (~95% recovery) was analyzed by gas chromatography and the components of the crude mixtures were isolated and characterized[14].

The results of our experiments are summarized in Table 1. Thus bicyclooctane 2[14] was obtained in 70% isolated yield (600°C, vycor, PbCO$_3$), which result compared favorable with our previous experience concerning the unmethylated cases[1].

Similarly, enone 4[14] was prepared from 3 (pyrex, 400°C) in 85% isolated yield. The complete stereoselectivity observed in the formation of enone 4, as well as the relatively low temperature required to bring about this conversion, are in line with a concerted retro-ene reaction[6,10,15] operating on cyclopropane 3. The transformation of the retro-ene product 4 into bicyclooctane 2 and dienone 5 necessitates the reformation of cyclopropane 3 which then undergoes fast, radical, dissociation affording 2 and 5. No vinylcyclopropane 3 was detected in the control pyrolyses of enone 4 suggesting undetectable concentrations of 3 at equilibrium, should such thermal equilibrium between 3 and 4 exist at 600°C. Finally, the cis-trans isomerization of cyclopropane 3 has not been detected.[14]

Higher temperatures may favor biradical intermediates which lead to 2 and 5, the expected competing products of a "normal" vinylcyclopropane rearrangement. That dienone 5 originates in cyclopropane 3 is supported by the inertness of bicyclooctane 2 at 600°C[16]. In view of the marked differences in the results obtained on plain vs. PbCO$_3$-treated columns a speculation lends itself concerning lead-stabilized radicals as possible intermediates. Silylated or carbonate (K$_2$CO$_3$) treated glass gave results identical to those obtained with untreated columns.

The selectivity achieved in the thermolysis of 3 becomes useful in several ways: firstly it portends well for high yield preparations of angularly methylated bicyclic ketones of value in the above mentioned terpene syntheses. Secondly it poses a possibility of cyclopentene annulation from 1,4-dienes, should such dienes be more accessible than vinylcyclopropanes. The use of 4 as a prostanoid synthon is presently under investigation in our laboratory, in the form of its oxidative conversion into (±)-sarkomycin[17].

TABLE I

Thermolysis of Vinylcyclopropane 3.

Column, Conditions	Temperature	% 2[a]	4	Unreacted 3	5
Pyrex, Plain	360	1	80	19	-
	400	9	91	-	-
	500	37	45	-	18
	600	63	7	-	30
Vycor, plain	250	-	-	100	-
	350	11	78	11	-
	450	15	84	-	-
	600	52	23	-	25
Vycor, Pb(CO_3)	300	0	69	30	-
	400	8	89	3	-
	500	50	36	-	14
	550	63	2	-	35
	600	(80)[c] 68	-	-	(18)[c] 35
Vycor, "aged' [residual $PbCO_3$][b]	300	0.5	69	30	-
	350	5	81	4	1
	400	12	82	3	3
	450	24	63	2	11
	500	63	22	-	15
	550	71	4	-	25
	600	66	0.5	-	34
Control Experiments:					
Pyrolysis of 4: Vycor, $PbCO_3$	600	71	-	-	29
Pyrex	600	70	6	-	25
Vycor	300	-	100	-	-
Pyrolysis of 2: Vycor, $PbCO_3$	600	100	-	-	-

Legend: [a] Product distribution from gas chromatography on Carbowax 1500 (F.I.D.)

[b] After one wash with $PbCO_3$, the column retained its "leaded" character during several uses.

[c] Fresh $PbCO_3$ wash.

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10. See for example: D.S. Glass, R.S. Boikess and S. Winstein, Tetrahedron Lett., 999 (1966); ref. 7,8,9.
11. It should be pointed out that all of the methylvinyl cyclopropanes reported to have been pyrolyzed were exposed to temperature ranges of 200 - 450^{o}C, thus precluding the cyclopentene formation to detectable extents.
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14. All new compounds were analyzed by IR, ^{1}H-NMR, ^{13}C-NMR and high resolution mass spectrometry and gave data consistent with their structures. Spectral data: 1: IR (neat) cm^{-1} 2300, 1640; ^{1}H-NMR (CDCl$_3$) δ 2.0 (s, 3H), 2.4 (br. s, 4H), 5.0-6.4 (m, 5H); ^{13}C-NMR (CDCl$_3$) δ 8.2 (q), 27.5 (t), 37.2 (t), 62.1 (s), 115.6 (t), 132.0, 132.8,136.0 (d), 193.8 (s). 2: IR (neat) cm^{-1} 1738, 1640; ^{1}H-NMR (CDCl$_3$) δ 1.15 (s, 3H), 1.6-2.9 (m, 6H), 3.1 (m, 1H), 5.6 (br. s, 2H); ^{13}C-NMR (CDCl$_3$) δ 20.6 (q), 23.9 (t), 36.2 (t), 45.0 (t), 49.3 (s), 54.6 (d), 130.7 (d), 133.8 (d), 225.3 (s). 3: IR (neat) cm^{-1} 1730, 1640; ^{1}H-NMR (CDCl$_3$) δ 1.2 (s, 3H), 1.9 (m, 2H), 2.1 (m, 4H), 4.9-5.6 (m, 3H); ^{13}C-NMR (CDCl$_3$) δ 9.5 (q), 21.8 (t), 32.2 (t), 33.2 (d), 34.2 (d), 38.6 (s), 116.9 (t), 134.3 (d), 215.0 (s). 4: IR (neat) cm^{-1} 1726, 1640; ^{1}H-NMR (CDCl$_3$) δ 1.6 (d, 3H), 2.3 (m, 4H), 5.1-6.0 (m, 4H); ^{13}C-NMR (CDCl$_3$) δ 12.2 (q), 26.7 (t), 36.6 (t), 39.1 (d), 116.1 (t), 125.2 (d), 130.8 (d), 147.2 (s), 205.0 (s). 5: IR (neat) cm^{-1} 1686, 1640, 1604; ^{1}H-NMR (CDCl$_3$) δ 1.8 (s, 3H), 2 (d, 3H, J=4 Hz), 2.3-2.8 (m, 4H), 6.0-6.9 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 7.9 (q), 19.1 (q), 25.7 (t), 33.6 (t), 126.6 (d), 134.2 (s), 134.9 (d), 164.1 (s), 209.8 (s)
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