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EVIDENCE FOR AN INTRAMOLECULAR [1,5]SHIFT OF A FORMYL GROUP IN THE THERMOLYSIS OF METHYL-[3,2,0]BICYCLOHEPT-2-EN-7-ONES

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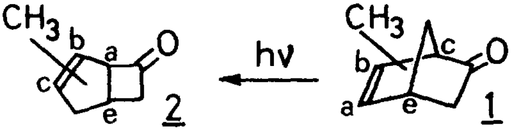
We have prepared the four methyl-[3,2,0]bicyclohept-2-en-7-ones 2a, 2b, 2c and 2e through irradiation [1)] of the appropriate methyl-[2,2,1]bicyclohept-5-en-2-ones 1a, 1b, 1c and 1e [2)] in ether (table I). Vapour phase pyrolysis of compounds 2a - 2e in a flow system (11 torr, 1 s contact time) leads to a mixture of dihydrotolualdehydes 3 and 4 and their aromatization product 5. In addition a small amount of the respective methyl-[2,2,1]bicyclohept-5-en-2-ones 1 is formed (table II). No fragmentation to ketene and methylcyclopentadiene is observed [3)].

Table I

Methyl-[3,2,0]bicyclohept-2-en-7-ones 2

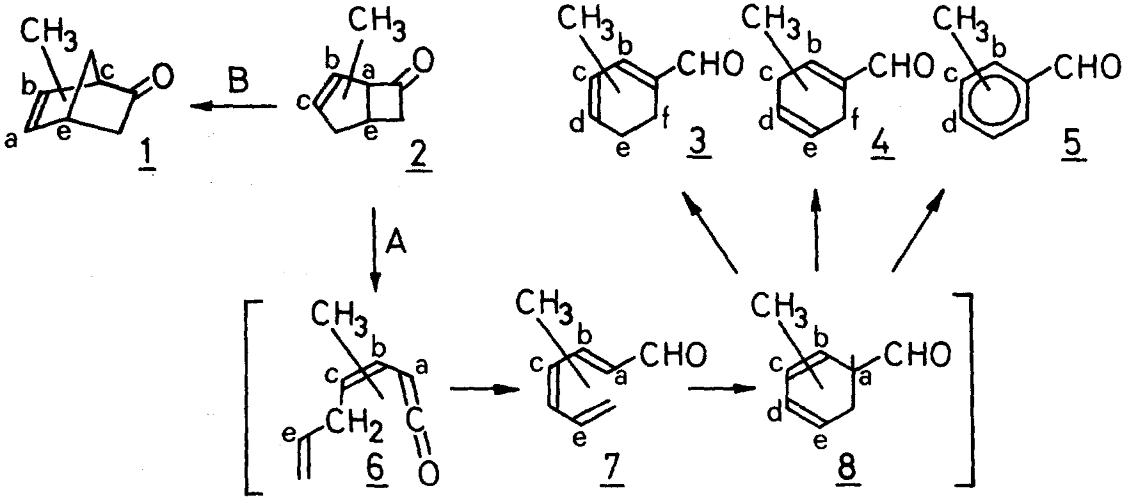


	2a	2b	2c	2e a)
UV (C_2H_5OH): λ_{max} (nm, ε)	302 (290)	302 (310)	301 (340)	-
IR (film): $\nu_{C=O}$ (cm^{-1})	1777	1777	1780	1780
NMR (CCl_4): δ methyl-H	1,23 s	1,75 d/1,5	1,81 d/1,5	1,40 s
bridgehead-H	-	3,98 s br	4,14 s br	3,70 m
vinyl-H	5,45 m 5,76 m	5,40 s br	5,22 s br	5,45 m 5,60 m

a) isolated only as a mixture with 1c and 1e

As with the unsubstituted [3,2,0]bicyclohept-2-en-7-one (2, H instead of CH_3) the conversion of 2 to 3, 4 and 5 is proposed as proceeding through intermediates 6, 7 and 8 (rf. chart I) [3)]. The formation of 8 involves in sequence a [2+2]cycloreversion (step A), an intramolecular [1,5]H-shift and an electrocyclic ring closure. Unconjugated aldehydes of structure 8 which were never isolated from the pyrolysis mixtures, should lead readily to 3, 4 and 5 through [1,5]H-shift, enolization [4)] and aromatization respectively. The formation of 1 is thought to

CHART I



involve a competing primary step of 2 (step B in chart I) proceeding through a biradical intermediate. With the exception of enolization and possibly aromatization all reaction steps discussed are presumed to be uncatalysed thermal processes [5].

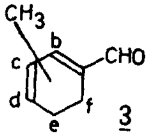
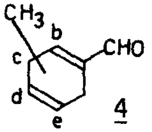
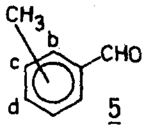
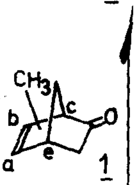
Pyrolysis of 2c and 2e (rf. table II) leads almost exclusively to aldehydes 3, 4 and 5 bearing the methyl group at the position predicted by the proposed reaction course (chart I). A minor amount of additional aldehydes (3e and 4e from 2c; 3c and 4c from 2e) could have been formed through a sequence of [1,5]H-shifts starting from intermediates 3 or 8.

In the product obtained from 2a no unconjugated aldehyde 8a could be detected. Instead a mixture of similar composition was obtained as with 2c and 2e. We therefore have to assume that intermediate 8a reacts through a [1,5]shift of either the methyl group to 3e or the formyl group to 8e (chart II). The aldehydes isolated could result from both 3e or 8e through a combination of [1,5]H-shift, enolization and aromatization processes.

In the mixture from pyrolysis of 2b the expected ortho-aldehydes 3b, 4b and 5b are formed in addition to para-aldehydes 3d, 4d and 5d. The ratio of ortho- to para-products ($N_{ortho/para}$) is found to depend on the pyrolysis temperature: At 375° ortho-aldehydes prevail ($N_{ortho/para} = 4$). At 465° more of the para-aldehydes are formed ($N_{ortho/para} = 0.5$). This temperature dependence of product composition can be interpreted as a result of kinetic vs. thermodynamic control in the product forming steps: At lower temperature labile intermediate 8b leads to ortho-aldehydes mainly through 3b formed by a reversible [1,5]H-shift. At higher temperature 8b reacts through a [1,5]shift of the formyl group leading to 8d and from there to more stable para-products 3d, 4d and 5d (path A in chart III).

Table II

Products from vapour phase pyrolysis of methyl-[3,2,0]bicyclohept-2-en-7-ones 2 a)b)

	Temperature °C	conversion %	 3					 4				 5			 1	other prod. c)
			b	c e)	d	e	f	b	c	d	e	b	c	d	CH_3 at:	
2a d)	450	98	-	8	-	4	-	-	-	-	12	-	56	-	a: 10	8
2b	420	95	11	-	24	-	2	6	-	9	-	17	-	9	b: 7	9
2c	450	97	-	17	-	2	-	-	3	-	2	-	45	-	c: 11	17
2e	420	f)	-	2	-	18	-	-	2	-	30	-	28	-	e: f)	20

a) All compounds in this table have been identified, except where indicated, by comparison with samples prepared independently or by IR-, UV- and NMR-spectra. The structure of aldehydes has been verified by aromatisation with choranil.

b) Percentage of components in recovered pyrolysis product, as determined by capillary vpc, is given (recovery 80 - 90%).

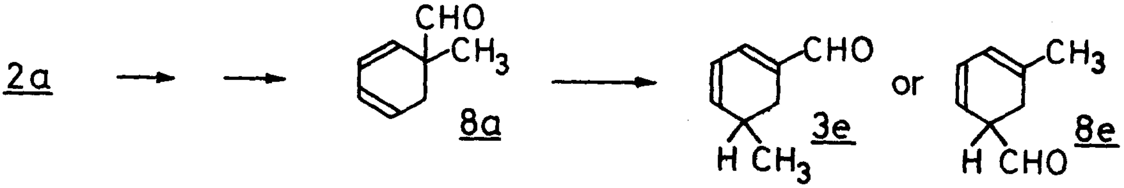
c) Benzaldehyde, toluene and compounds of undetermined structure.

d) At lower temperature up to 5 % of ketone 2c is formed from 2a.

e) Tentative structural assignment.

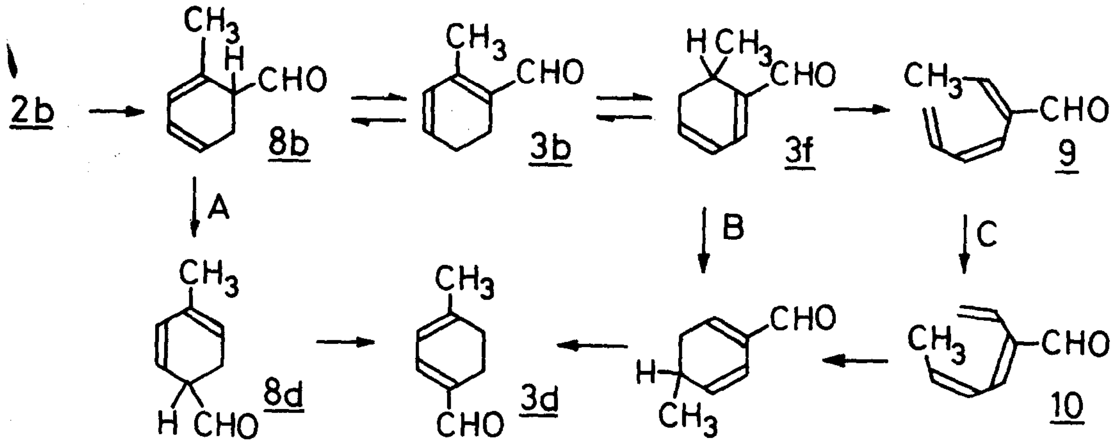
f) Ketone 2e was contaminated with 1e; percentage of products other than 1e and 2e is given for this run.

CHART II



Aldehyde 3f, a minor pyrolysis product of 2b, must have been formed from 3b or 8b through a sequence of thermal [1,5]H-shifts. It is conceivable that ortho-para rearrangement could have occurred from 3f through a [1,5]shift of the methyl group (path B in chart III) or through a series of steps involving a [1,7]H-shift in open chain intermediates 9 and 10 6) (path C in chart III). Indeed it was found that 3f 7) leads to rearranged para-products 3d, 4d and 5d if pyrolyzed above 500°. However, at a temperature of 420°, at which ketone 2b was submitted to pyrolysis, no rearrangement of 3f is observed ! Ortho-para rearrangement therefore must occur

CHART III



from an intermediate which ist formed faster from 2b than from 3f. This intermediate can only have structure 8b ! From this we conclude that the rearrangement of the carbon skeleton observed to occur upon pyrolysis of 2a and 2b as well as of 3f at higher temperature involves an intramolecular [1,5]shift of a formyl group and not a [1,5]methyl shift or a [1,7]H-shift in an open chain intermediate [6]. - Certain reports in the literature [8] can be interpreted as involving similar thermal formyl migrations.

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FOOTNOTES

1) D.I. Schuster, M. Axelrod and J. Auerbach, Tetrahedron Letters 1963, 1911.

2) S.E. Masar and H. Krieger, Suomen Kem. 42, 1 (1969).

3) P.W. Schiess and M. Wisson, Tetrahedron Letters 1971, 2389.

4) This could be a surface catalyzed process (rf. W.E. Erman, R.S. Treptow, P. Bakuzis and E. Wenkert, J. Amer. Chem. Soc. 83, 657 (1971), footnote 29).

5) A kinetic study of the gas phase thermolysis of ketone 2a has been carried out: A.T. Cooks and K.W. Egger, J. Chem. Soc. Perkin II, to be published. Using a pyrex or a teflon coated stainless steel reaction vessel these authors find the same pyrolysis products, except aldehyde 4e, as we do in our flow system. This indicates that the process leading to 4e is subject to surface catalysis.

6) Such a reaction course has been proposed for the thermal rearrangement of 5,5-dimethyl-1,3-cyclohexadiene: H. Pines and R.H. Kozlowski, J. Amer. Chem. Soc. 78, 3776 (1958); H. Pines and C.T. Chen, ibid. 81, 928 (1959).

7) C. Grundmann, Chem. Ber. 81, 513 (1948).

8) J.J. Beereboom, J. Org. Chem. 30, 4230 (1965); P.Y. Blanc, Helv. Chim. Acta 41, 625 (1958).