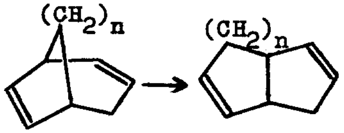
Tetrahedron Letters No. 12, pp 1029 - 1030, 1975. Pergamon Press. Printed in Great Britain.

THE THERMOLYSIS OF 3-METHYLENEBICYCLO[3.2.1]OCT-6-ENE AND OF 3-OXOBICYCLO[3.2.1]OCT-6-ENE

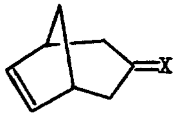
J. Japenga, M. Kool, and G.W. Klumpp*
Scheikundig Laboratorium der Vrije Universiteit,
De Lairessestraat 174, Amsterdam-Z, The Netherlands

(Received in UK 17 January 1975; accepted for publication 12 February 1975)

In connection with our work on the thermal 1.3-carbon shifts of bicyclo[3.2.n]-alka-2,6-dienes (n = 1,2; cf. I→II)[1] we have also examined the thermal behaviour of 3-methylenebicyclo[3.2.1]oct-6-ene (IIIa)[2] and of 3-oxobicyclo[3.2.1]-oct-6-ene (IIIb)[3], which contain a double bond at C-3 in the exocyclic position. The study of these compounds is also of interest with regard to recent work on the structurally related 1.5-hexadiene derivatives IV - VI.[4,5]

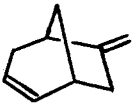


I II

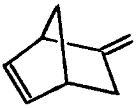


III

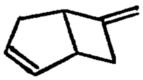
a: X = CH_2
b: X = O



IV

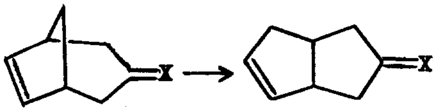


V

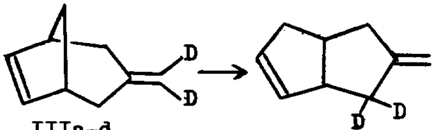


VI

In a flow-system at 450 - 500°, 1 Torr, and a reaction time of about 2 seconds IIIa is transformed cleanly into 7-methylenebicyclo[3.3.0]oct-2-ene (VIIa):



III VII a: X = CH_2 b: X = O

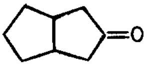


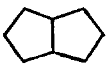
IIIa-d_2 VIIa-d_2

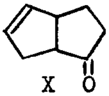
Cope rearrangement, [1,3]-sigmatropic shift of C-2, formation and reclosure of a bisallylic diradical or a mixture of these mechanisms can account for this result. The same mechanistic possibilities can also be invoked to explain the thermal rearrangements observed with IV - VI, however, a clear choice has not yet been possible with these compounds.[4,5] In our case use of 3-(methylene-d_2)-bicyclo[3.2.1]oct-6-ene (IIIa-d_2) identified the reorganization - which, significantly, occurred at lower temperature than the 1.3-carbon shifts I→II - as a Cope rearrangement. Reasons for this preference of the Cope rearrangement may be the higher degree of coplanarity that can be achieved by the C-1-C-2 bond and the $2p_z$ orbital on C-3 and the shorter distance between the termini of the 1.5-hexadiene system in III. According to models this distance increases from about 4 Å in IIIa to about 4.4 Å in VI.

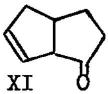
Thermolysis of IIIb occurred at 700° (1 Torr, 2 sec) and yielded 7-oxobicyclo[3.3.0]oct-2-ene (VIIb).[6,7] The high temperature needed to induce rearrangement seems to indicate a nonconcerted proces and little stabilization energy of oxaallyl radicals.[8]

VIIb was converted into VIIa by a Wittig reaction. Catalytic hydrogenation of VIIb yielded a ketone, whose IR-spectrum appears identical with the published spectrum of VIII.[6] Huang-Minlon reduction of this ketone yielded IX. VIIb is also distinguished from its isomers X and XI by a LIS-experiment and by a deuterium exchange experiment.[7] On addition of increasing amounts of $Eu(fod)_3$ the highest slope was exhibited by a group of four protons. Mass-spectrometry of VIIb recovered from the deuterium exchange experiment showed that partial tetradeuteriation had taken place. In earlier work material for which the NMR-characteristics of VIIb were reported, was assigned structure X.[7] The present results require revision of this assignment.


VIII


IX


X


XI

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8) The reaction conditions resemble those required for the transformation of bicyclo[3.2.1]oct-6-ene into bicyclo[3.3.0]oct-2-ene (J.Japenga, unpubl.).