COPPER-ION CATALYSED DECOMPOSITION OF BIS-5-(1-CYCLOHEXENYL)PENTANOYL PEROXIDE¹ D.L. Struble,² A.L.J. Beckwith and G.E. Gream Organic Chemistry Department, The University of Adelaide, Adelaide, South Australia

(Received in UK 10 October 1970; accepted for publication 28 October 1970)

4-(1-Cyclohexenyl)butyl radical (II) generated from the appropriate bromide, or by thermolysis of the peroxide (I), has been shown³ to undergo intramolecular homolytic addition with formation of the 9-decalyl (IV) and 6-spiro-4,5-decyl (V) radicals. The ratio of rate constants k_2 and k_3 for the 1,6- and 1,5-modes of cyclization respectively, is $k_2/k_3 = 0.85$. Since cationic cyclization, as exemplified by solvolysis of suitable derivatives,⁴ affords exclusively six-membered ring products,⁴ the 4-(cyclohexenyl)butyl system provides an excellent substrate for experiments designed to identify the reactive intermediates in transformations of uncertain mechanism. One such reaction is the formation of alkenes by cupric-ion oxidation of alkyl radicals.⁵

The nature and yields of products obtained when the peroxide (I) and cupric octanoate were heated in benzene or acetic acid at 80° are summarised in Table I. The more significant features of the reactions in benzene are: (i) the total yield of monomeric products is enhanced by the presence of the cupric salt, (ii) the yield of the diene (III) increases with increase in Cu^{II} concentration, and (iii) the yields of octalins (VI, VII) and the spirene (VIII) decrease with increase in Cu^{II} concentration. In view of the known ready propensity of the 4-(cyclohexenyl)butyl system to undergo both homolytic³ and cationic⁴ cyclization, it is clear that reaction of the radical (II) with Cu^{II} is very rapid and probably proceeds to diene (III) without intervention of the related carbonium ion.

The results are consistent with the proposed reaction scheme. Since reaction of the radical (II) with Cu^{II} competes directly with cyclization processes having known rate constants⁶ it is possible to deduce k_1 . The value obtained, $k_1 = 5 \times 10^7 \text{ M}^{-1} \text{sec}^{-1}$, is of the same order of magnitude as those determined by completely different methods for Cu^{II} oxidation of primary alkyl radicals.⁷

Solvent	Benzene	Benzene	Benzene	Benzene	Acetic Acid
[(RC0 ₂) ₂]	1.4 x 10 ⁻² M	1.25 x 10 ⁻² M	1.36 x 10 ⁻² M	$1.31 \times 10^{-2} M$	2.5 x 10 ⁻² M
[CuOc]	0	3.1 x 10 ⁻⁴ M	$3.6 \times 10^{-4} M$	$1.64 \times 10^{-3} M$	$6.6 \times 10^{-4} M$
total yield ^a	34	85	67	59	66
()) ^b	40	1.9	2.2	0.5	1.6
Û)₽	c	21	33	56	17.9
$\bigcirc \bigcirc ^{\tt b}$	25	0	0	0	5.1
	0	21	17	5.9	2.2
<u>cis</u> -decalin ^b	2.5	0	0	0	c
trans-decalin ^b	10	0	0	0	4.1
1,9-octalin ^b	13	46	41	33	11.1
9,10-octalin ^b	3.7	9.4	6.8	4.9	58
rco ₂ h ^a	c	77	87	92	c
cyclized products b	54	77	65	43	80

 TABLE I.
 Products from Cupric Octanoate (CuOc) Catalysed Decomposition of Bis-5-(1-cyclohexenyl)pentanoyl Peroxide (RCO2)

a Z of theoretical based on peroxide

c not accurately determined

b moles per 100 moles of total products

The spirodecene (VIII) undoubtedly arises by Cu^{II} oxidation of spirodecyl radicals (V). The reaction probably proceeds predominately, but not exclusively, without concomitant rearrangement. When (V) was generated directly by lead tetra-acetate oxidation of the spiro-acid (IX) in the presence of Cu^{II} the products were VIII (88%), VI (6%) and VII (6%). Since the corresponding cation (X) yields mainly octalins and other rearrangement products^{8,9} it cannot play an important role in the Cu^{II} oxidation process.





We believe that the octalins obtained arise mainly *via* Cu^{II} oxidation of decalyl radicals (IV), although simultaneous oxidation-rearrangement of (V) and oxidation-cyclization of (II) probably contribute to the total yield. There is also some indication, unconfirmed as yet, of a direct route from the peroxide (I) to octalins.

The low yields of saturated compounds from the reaction in acetic acid indicate that radicals (II), (IV) and (V) are efficiently trapped by Cu^{II} but the oxidation step is different from that in benzene in that it proceeds mainly *via* rearrangement or 1,6-cyclization. In this respect the reaction resembles solvolyses in these systems.^{4,8,9}



We suggest that all of these results are best rationalised in terms of the formation of organo-copper intermediates by reaction of radicals with Cu^{II} carboxylate. In benzene, such compounds decompose preferentially by concerted elimination leading directly to olefin (e.g. XI \rightarrow XII), but in solvents of greater ionizing power, such as acetic acid, suitable systems (e.g. XIII) may undergo heterolysis with participation leading, eventually, through a carbonium ion (e.g. XIV) to rearranged products.

Kinetic evidence in support of this hypothesis will be reported later.

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