Tetrahedron Letters No. 8, pp 563 - 564, 1975. Pergamon Press. Printed in Great Britain.

ESR - EVIDENCE FOR A RADICAL 1,5-HYDROGEN SHIFT FROM OXYGEN TO CARBON

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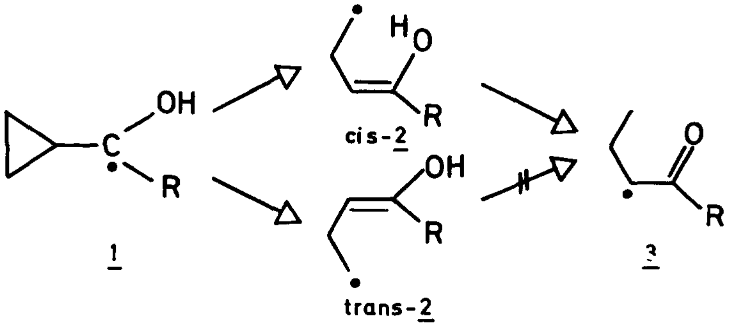
(Received in UK 9 October 1974; accepted for publication 16 January 1975)

Intramolecular 1,5-hydrogen shifts from carbon atoms to oxygen radical-centers are well known[1]), the Barton-reaction[2]) being one of the examples. We wish to report the observation of an unusual intramolecular 1,5-hydrogen shift in the reverse direction, i.e. from oxygen to a carbon radical-center. The previously reported[3]) reaction of tert.-butoxy radicals with substituted 1-cyclopropyl-carbinols was reinvestigated by ESR-spectroscopy . The primary substituted 1-cyclopropyl-1-hydroxy-carbinyl radicals 1 undergo the cyclopropyl-homoallyl-rearrangement[4]) to the two isomers of substituted 3-buten-4-ol radicals cis-2 and trans-2 which are observable by ESR[3]). For temperatures $T \geq -50°C$ we also detect α-keto-radicals 3. They are formed by an intramolecular rearrangement of cis-2 involving the 1,5-hydrogen shift. This rearrangement was not observed for trans-2 and was not found reversible.



R = -H, $-CH_3$, -cyclopropyl, -phenyl

Solutions of di-tert.-butylperoxide and 1-cyclopropyl-carbinols (R = -H, $-CH_3$, -cyclopropyl, -phenyl) in n-hexane or 1,1,2-trichloro-trifluoroethane (10% by volume in peroxide and carbinol) were photolysed in the cavity of an ESR-spectrometer using a slow-flow technique[5]). Fig.1 shows ESR-spectra obtained at different temperatures for R = CH_3. Radical 1 was not observed in the temperature range covered ($-130°C \leq T \leq +60°C$). For $T \leq -60°C$ the ESR-spectrum shows the lines of cis-2 (Fig. 1a) [a_α^H = 2.214 mT; a_β^H = 3.076 mT; a_γ^H = 0.064 mT for T = -60°C, g = 2.00269]. At higher temperatures the spectrum is a superposition of lines belonging to cis-2, 3 and the 2-cyclopropyl-2-hydroxyethyl radical $\triangleright$-CH(OH)$\dot{C}H_2$, 4 (Fig. 1b). For $T \geq +30°C$, 3[a_α^H = 1.884 mT; a_β^H = 2.055 mT; a_γ^H ($-COCH_3$) = 0.103 mT; a_γ^H ($-CH_3$) ≈ 0.012 mT for T = -33°C; g = 2.0042[5])] and 4 are the only observable radicals (Fig. 1c).

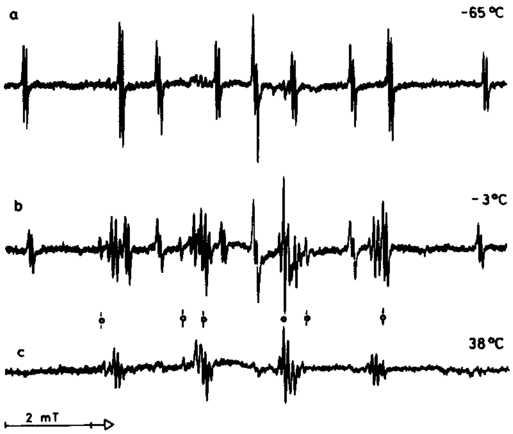


Fig.1 1,5-hydrogen shift for R = CH_3; ESR-spectra (circles denote lines of radical 4)

Analysis of the relative radical concentrations of cis-2 and 3 by a steady-state kinetic treatment$^{6)}$ of the scheme leads to the activation energy for the rearrangement of (20 ± 4)kJ·Mol^{-1} and an estimated frequency factor of 10^8 sec^{-1}. If the OH-hydrogen of 1 is replaced by deuterium the same rearrangement takes place as evident from ESR-spectra. However, for T = -3°C the concentration ratio of cis-2 to 3 differ from those indicated by Fig. 1b. Thus the rearrangement shows a deuterium isotope effect.

For R = H both cis-2 and trans-2 are observed$^{3b)}$ if $T \leq +30°C$. For $T \geq -50°C$ 3 can also be detected. Analysis of the temperature dependence of the concentrations of cis-2, trans-2 and 3 allows the conclusion that trans-2 does not rearrange to 3. For R = cyclopropyl the same behaviour is found as for R = CH_3, whereas for R = phenyl$^{3a)}$ radical 1 can be observed in the entire temperature range.

The occurence of the unusual 1,5-hydrogen shift can be explained by the formation of a six-membered ring-transition state and a resonance-stabilised radical in the reaction cis-2 → 3.

Support by the Swiss National Foundation for Scientific Research is greatfully acknowledged.

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