# Transannular Reactions in, and Rearrangement of, the Cyclodecane System in the Lead Tetra-acetate Oxidation of Cyclodecanol[1]

By M. Lj. Mihailović,*† V. Andrejević, M. Jakovljević, D. Jeremić, and A. Stojiljković

*(Department of Chemistry, Faculty of Sciences, University of Belgrade, and Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia)*

and R. E. Partch

*(Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676)*

*Summary* The reaction of $Pb(OAc)_4$ with cyclodecanol gives a variety of products (Scheme A), most of which are formed by successive transannular hydrogen shifts (Scheme B) and by $\beta$-fragmentation–hydrogen migration–recombination processes (Scheme C).

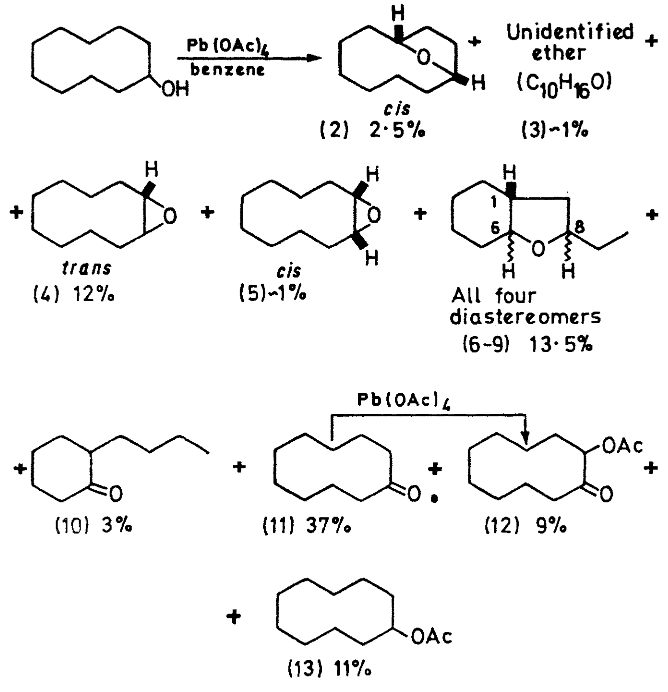
The special geometry of the medium-sized cyclodecane ring is clearly reflected in the unusual behaviour of cyclodecanol (**1**) towards $Pb(OAc)_4$. In refluxing benzene this alcohol (**1**) gives various products shown (with their yields) in Scheme A.‡ As can be seen, intramolecular ether formation (**2**)—(**9**) occurs to a considerable extent (27·5—30%). However the major oxido-products obtained have structures which are unusual for ethers isolated in $Pb(OAc)_4$ oxidations of alcohols, *i.e.* 1,2-epoxycyclodecane [*trans* (**4**), and *cis* (**5**)][2] and the rearranged 8-ethyl-7-oxabicyclo[4,3,0]-nonane [in the form of all four diastereomers (**6**)—(**9**)],

---

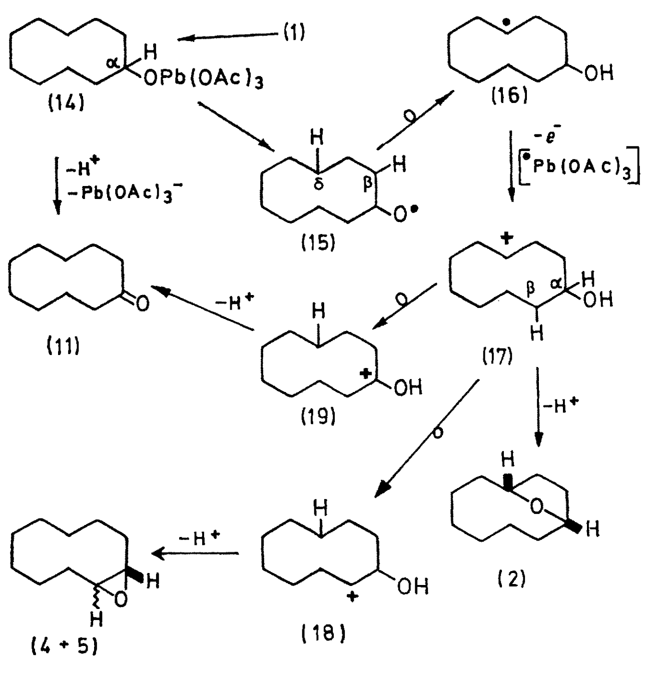
† Correspondence to: Department of Chemistry, Faculty of Sciences, Studentski trg 16, P.O. Box 550, Belgrade, Yugoslavia.

‡ Products were isolated and quantitative data concerning their yields were obtained by g.c. All compounds gave correct elemental analyses. Their constitutions and stereochemistries were deduced from i.r., n.m.r., and mass spectra, and in most cases confirmed by independent syntheses.

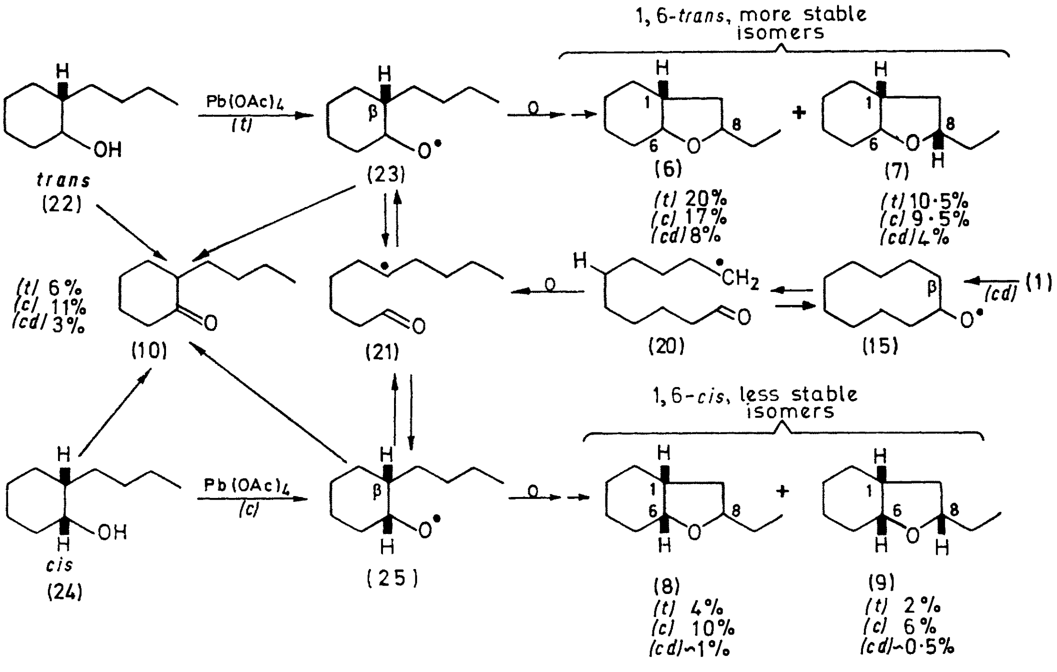
whereas the yield of the "normal" (five-membered) 1,4-epoxycyclodecane (**2**) is unexpectedly low (2·5%). In most $Pb(OAc)_4$ reactions of saturated open-chain[3] and cyclic alcohols,[2,4,5] including the medium-sized cyclo-octanol,[2] unrearranged intramolecular ethers (usually, in major part of the tetrahydrofuran-type) are the only cyclization products. Oxiran ring formation has never been observed before in such oxidations.



SCHEME A



SCHEME B



SCHEME C§

§ The terms (*cd*), (*t*), and (*c*) in Scheme C refer to results (products and yields) obtained in the $Pb(OAc)_4$ oxidation of cyclodecanol (**1**), *trans*-2-butylcyclohexanol (**22**) and *cis*-2-butylcyclohexanol (**24**), respectively.

The pathways by which the ethers [(**2**), (**4**)—(**9**)], cyclodecanone (**11**) and the rearranged 2-butylcyclohexanone (**10**) are produced from cyclodecanol (**1**) have been in part elucidated (Schemes B and C), by using 1-deuteriocyclodecanol and 2,2,10,10-tetradeuteriocyclodecanol as substrates in the oxidation, and by comparing product distribution in all three cases as well as by determining the content and positions of deuterium in the products obtained from the deuteriated cyclodecanols. Thus (Scheme B), the formation of the diastereomeric 1,2-epoxycyclodecanes (**4**) and (**5**) occurs, as the result of proximity effects, by a hydrogen atom shift from a remote carbon ($\gamma$, $\delta$, or $\epsilon$) to oxygen *e.g.* step (**15**) → (**16**),[2–5] followed by a second transannular transfer of hydrogen (as atom or hydride ion) from the $\beta$-carbon to the electron-deficient carbon [*e.g.* step (**17**) → (**18**)], and *not* by direct 1,3-hydrogen migration from the $\beta$-carbon to oxygen in the cyclodecyloxy radical (**15**). Similarly, cyclodecanone (**11**), which is obtained (Scheme A) together with its $\alpha$-acetoxylated derivative (**12**) in an unusually high yield of 46%[2] [for $Pb(OAc)_4$ oxidations of alcohols[2,3,5,6]], was found to arise (Scheme B) not only by the simple direct elimination of the $\alpha$-proton [path (**14**) → (**11**)],[2,3,5,6] but also, and preferentially, by an alternative route consisting of two successive hydrogen transfers, *i.e.* from carbon to oxygen [*e.g.* step (**15**) → (**16**)] and from carbon to carbon [step (**17**) → (**19**)].

The formation (Scheme A) of the rearranged products, *i.e.* the four diastereomeric ethers (**6**)—(**9**) and 2-butylcyclohexanone (**10**) from cyclodecanol (**1**), involves very probably, as shown on Scheme C, two homolytic $\beta$-scission–recombination processes [steps (**15**) ⇋ (**20**), and (**23**) ⇋ (**21**) ⇋ (**25**)], combined with a homolytic 1,5-hydrogen migration from carbon to carbon [step (**20**) → (**21**)]. "Reversible fragmentation" prior to intramolecular ether ring closure in the $Pb(OAc)_4$ oxidation of alcohols has been so far observed only in the case of some steroid alcohols[4,7] and alcohols of the menthol series.[8] It has now been found that cyclodecanol (**1**) and both *trans*-(**22**) and *cis*-2-butylcyclohexanol (**24**) also undergo readily such a process (Scheme C). As can be seen from Scheme C, whichever of these three alcohols (**1**), (**22**), or (**24**) is used as substrate in the $Pb(OAc)_4$ reaction, all four diastereomeric 8-ethyl-7-oxabicyclo[4,3,0]nonanes [(**6**), (**7**), (**8**), and (**9**)] are always formed, in ratios which reflect, in general, the relative stabilities of these products (in their favoured conformations).

We thank the Yugoslav Federal Research Fund and the Serbian Academy of Sciences and Arts for financial support, and Dr. K. Heusler, Ciba A.G., Basel, Switzerland, for most helpful suggestions and stimulating discussions.

(*Received, April 14th,* 1970; *Com.* 533.)

---

[1] For previous publication see: M. Lj. Mihailović, S. Konstantinović, A. Milovanović, J. Janković, Ž. Čeković, and D. Jeremić, *Chem. Comm.*, 1969, 236.

[2] M. Lj. Mihailović, Ž. Čeković, V. Andrejević, R. Matić, and D. Jeremić, *Tetrahedron*, 1968, **24**, 4947.

[3] M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, Lj. Lorenc, and R. I. Mamuzić, *Tetrahedron*, 1965, **21**, 2799.

[4] K. Heusler and J. Kalvoda, *Angew. Chem.*, 1964, **76**, 518; *Angew. Chem. Internat. Edn.*, 1964, **3**, 525, and references therein.

[5] M. Lj. Mihailović and Ž. Čeković, *Synthesis*, 1970, in the press, and references therein.

[6] M. Lj. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, A. Milovanović, and Lj. Lorenc, *Tetrahedron*, 1965, **21**, 1395.

[7] G. Bauslaugh, G. Just, and E. Lee-Ruff, *Canad. J. Chem.*, 1966, **44**, 2837.

[8] G. Ohloff, K. H. Schulte-Elte, and B. Willhalm, *Helv. Chim. Acta*, 1966, **49**, 2135.