CHEMISTRY LETTERS, pp. 1477-1478, 1988.

Deoxygenation of 1,3-Diene 1,4-Endoperoxides by Tin(II) Chloride

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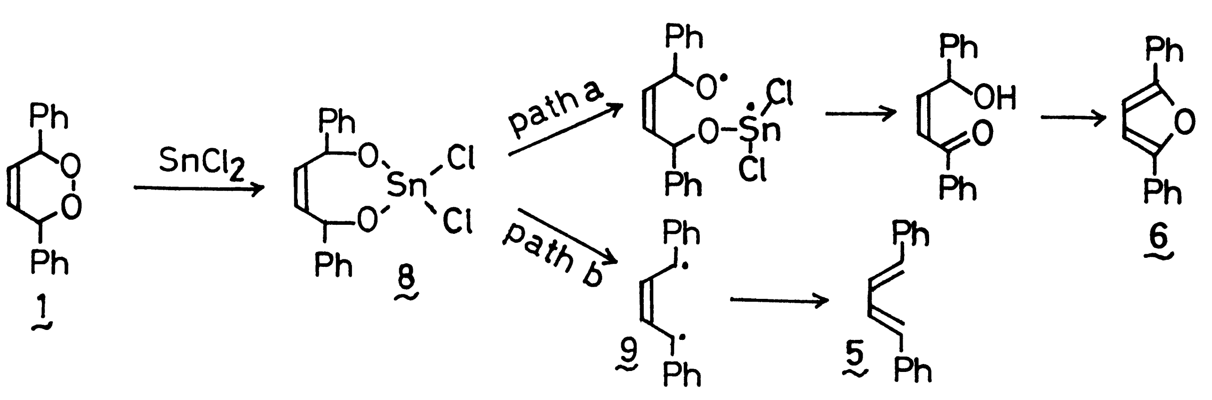
The reaction of bicyclic 1,3-diene 1,4-endoperoxides with $SnCl_2$ re-generated the corresponding dienes in 15—70% yield. The efficiency of the deoxygenation depended on the structure of peroxides. The results were compared with those of Fe(II) as well as Pd(0) assisted reactions.

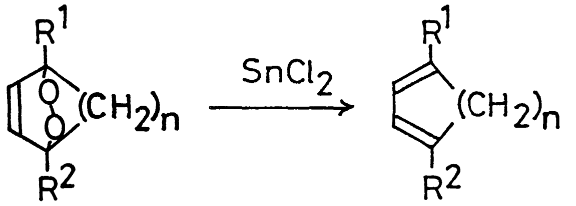
Retro Diels-Alder type reaction of 1,3-diene 1,4-endoperoxides to reproduce 1,3-dienes is quite limited. Thermal decompositions of certain aromatic endoperoxides[1)] and the photolysis of ascaridole with high energy light[2)] are the typical examples. Generally the decomposition is initiated by the breaking of an oxygen-oxygen bond to afford the various products derived by this cleavage.[3)] In this paper, we present the re-generation of 1,3-dienes by $SnCl_2$ in the decomposition of 1,3-diene 1,4-endoperoxides which do not give 1,3-dienes thermally.

The 1,4-endoperoxides are reported to react with $SnCl_2$ giving tin alkoxides, a tetravalent tin intermediate.[4)] Considering the relatively larger tin-oxygen bond energy (95 kcal/mol) than that of a carbon-oxygen bond (85 kcal/mol), we envisioned a change of usual decomposition from an oxygen-oxygen bond to a carbon-oxygen bond. Thus, four endoperoxides, 1,[5)] 2,[6)] 3,[7)] and 4,[8)] were utilized for the present study of decompositions. The Fe(II) and Pd(0) assisted decompositions, whose mechanism was explained by the redox process,[9a,b)] were also carried out.

Decomposition of 1 (2.0 mmol) in CH_2Cl_2 (5 ml) with $SnCl_2$ (3.0 mmol) at room temperature for 21 h afforded the diene (5, 15%) and 1,4-diphenylfuran(6, 33%). The formation of furan was reported to be very characteristic of the decomposition of monocyclic endoperoxides with Fe(II) via redox mechanism.[9a,b)]



The formation of 5 is quite remarkable and to the best of our knowledge, this is the first observation that dienes can be re-generated by metal assistance in the decomposition of 1,4-endoperoxides. Ferrous sulfate assisted decomposition of 1 in THF/H_2O at room temperature gave 6 (54%) as the major product together with diepoxide 7 (6%). The formation of diene can be looked upon a competitive cleavage of this tin-oxygen (path a) and a carbon-oxygen bond (path b) via a tetravalent tin complex.[4)] The concerted process for path b leading to the diene is also plausible. Though a similar cyclic intermediate to 8, via Pd(0)/Pd(II) exchange mechanism was proposed for the Pd(0) catalyzed decomposition,[9b)] 5 was not reported in the $Pd(PPh_3)_4$ catalyzed reaction of 1, instead 1,2-dibenzoylethane was the sole product. Thermolysis of 1 in toluene under reflux gave 6 together with a large amount of unreacted 1.



2 $R^1=R^2=Ph$, n=2 → 10
3 $R^1=R^2=Ph$, n=1 → 11
4 $R^1=Me, R^2={}^iPr$, n=2 → 12

This unique $SnCl_2$ assisted decomposition of 1,4-endoperoxides was further examined with bicyclic 1,4-endoperoxides, 2, 3, and 4. Under similar conditions, the corresponding dienes 10 (48%, conversion yield of 96%), 11 (70%), 12 (25%) were formed respectively. The efficiency of 1,3-diene re-generation seems to be dependent on the substituents which will either stabilize the radical intermediate like 9 (a radical mechanism) or give a stable diene (a concerted mechanism). In this sense, diphenyl derivatives 2 and 3 satisfy both requisites. Again Fe(II) assisted decomposition of 2 and 4[10)] showed a nice contrast to the above results.

The formation of dienes is specific to $SnCl_2$ Deoxygenation of 1,4-endoperoxides, elimination of two oxygen atoms to re-generate 1,3-dienes, is efficiently assisted by $SnCl_2$ in these bicyclic endoperoxides.

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(Received June 15, 1988)