Tetrahedron Letters No.22, pp. 2487-2490, 1966. Pergamon Press Ltd.
Printed in Great Britain.

NOVEL CYCLOÖXIDATION OF BIALLYL

Iwao Tabushi and Ryohei Oda

Department of Synthetic Chemistry, Kyoto Univ.,
Kyoto, Japan

(Received 28 March 1966)

Some unconjugated dienes give cyclic compounds by the attack of free radical species. Thus polymers of alicyclic chain were obtained from diallylether, diallyl ketone or other unconjugated dienes[1].

And, in the presence of a sufficient amount of a chain-transfer reagent such as trichlorobromomethane, 1 : 1 cyclic adduct was obtained[2].

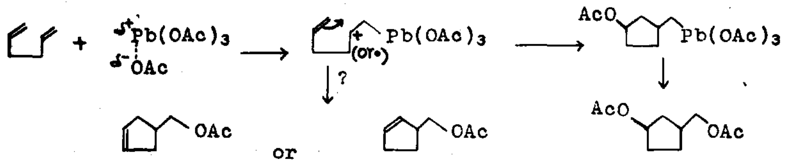
This preliminary report concerns with oxidative addition cyclization of unconjugated diene, 1,5-hexadiene, by means of lead tetraacetate oxidation in acetic acid.

8.2g of biallyl (0.1 mole) was heated at ca. 70° with 25g of lead tetraacetate in acetic acid for 24 hrs. After working up, ca. 3.0g of a mixture of products was obtained, but a distillation (7 fractions over the temperature range 70-145° at 7 mmHg) was ineffective to separate the 2 major and several minor products (by VPC). A preparative VPC gave these products in isolated states and investigation of nmr, IR of them and/or VPC identification of these with authentic samples showed the presence of following compounds.

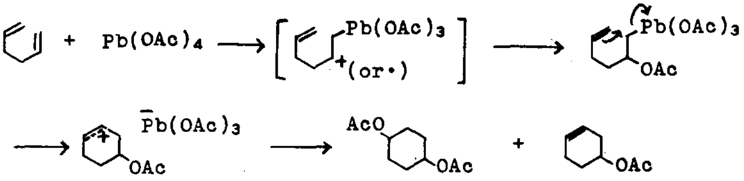
1,4-diacetoxycyclohexane (major), 1,4-dihydroxycyclohexane (in a very small amount), 4-acetoxycyclohexene (in a very small amount) and 1-acetoxymethyl-3-acetoxycyclopentane (major).

Dihydroxycyclohexane may be derived from a lead complex (or adduct) of the diene, since no appreciable hydrolyzed product was obtained from 1,4-diacetoxycyclohexane in the working up condition. When the reaction was continued for 72 hrs at 90°, no diol was obtained at all and the yield of acetoxycyclohexene increased.

Formation of cyclohexane derivatives together with cyclopentylmethyl derivatives seems quite interesting, since a simple free-radical or cationic methanism[3] requires the formation of stabler secondary radical or cation, leading exclusively to cyclopentylmethyl derivatives as follows :



Thus, the reaction also involves the two step addition-cyclization, i.e., an addition of lead tetraacetate on one of the double bonds and a successive cyclization of the lead compound as shown by the following scheme.



Diacetoxycyclohexane was stable enough at the reaction- and working up conditions, so that cyclohexenyl acetate may be formed from an intermediary carbonium ion.

This type of cycloöxidation has never been reported.

Investigation of "cycloöxidation" of various unconjugated dienes with various oxidants is now under way on the bases of preparative and mechanistic point of views.

Acknowledgement :

The author wishes to express his appreciation to Prof. Paul D. Bartlett for giving him opportunity to attend the seminar on "double bond participation in solvolysis."

REFERENCES

(1) There are many examples especially presented by Matsoyan and Marvel, eg., S. G. Matsoyan et al, Vysokomol. Soed., 4, 882(1962), B. Reichel and C. S. Marvel J. Polymer Sci., A1, 2945(1936)

(2) W. F. Friedlander, G. D. Tiers, *German Patent*, *Chem. Abstr.*, **56**, 5810(1962), but Aso claims that the ring must be 5-membered, *J. Chem. Soc. Japan*, *Industrial Section*, **68**, 1970(1965)

(3) Bartlett presented many examples of double bond participation with carbonium ions, eg., P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297(1965)