

METATHESIS OF (Z,Z)-1,5-CYCLONONADIENE BY A TUNGSTEN HEXACHLORIDE - LITHIUM ALUMINUM HYDRIDE CATALYST

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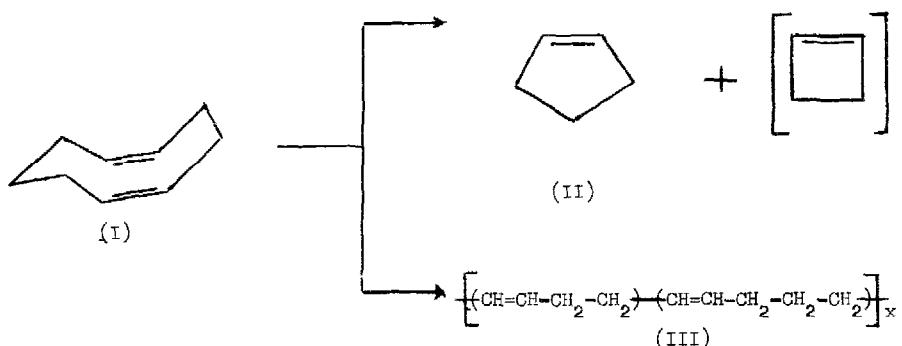
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Current interest in the transition metal catalyzed metathesis of medium ring 1,5- and 1,6-cycloalkadienes¹⁻⁴ prompts us to report the unexpected behaviour of (Z,Z)-1,5-cyclononadiene (I) in this reaction.

On the basis of what it has been reported for $(Z,Z)-1,6$ -cyclodecadiene^{2,3} and $(E,Z)-1,5$ -cyclodecadiene^{3,4} it could be assumed that, in the presence of a metathesis catalyst, (I) could prevalently give rise, in dependence on the reaction temperature, either to cyclopentene (II) and cyclobutene (or low-molecular-weight metathesis products of this cycloalkene), or to a polymer (III) containing 1-butenylene and 1-pentenylene structural units in a 1:1 ratio.



We have examined the metathesis of (I) in the presence of a $WCl_6 \cdot LiAlH_4$ catalyst and describe here some preliminary data that are in disagreement with the expected results.

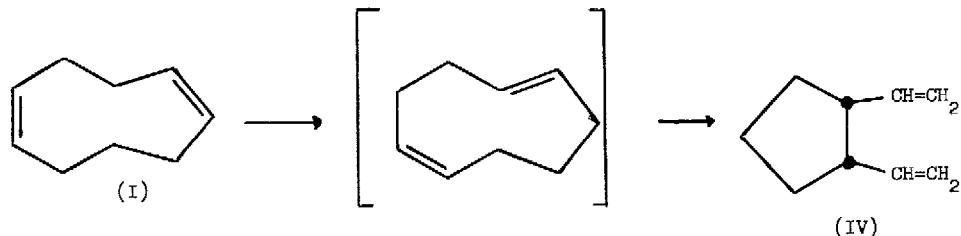
In a typical reaction a solution of WCl_6 (0.18 mmol) in chlorobenzene (8 ml) was added to $LiAlH_4$ (0.70 mmol). The mixture was stirred for 20 min at 25°C, then (I) (18 mmol) was added.⁵ After 12 hr no further conversion was observed. The volatile reaction products were collected at 40°C and 0.02 torr in a cold trap and the non-volatile residue was treated with a large excess of methanol. The precipitated polymer (ca. 75% yield) was purified and analysed. As regards the course of the metathesis reaction it is interesting to note that 1 hr after the addition of (I) to the catalyst system the reaction mixture became very viscose; however, after some hours the viscosity went down.

The isolated solid polymer (M_n 2200) was soluble in aromatic solvents. Its IR spectrum

showed typical bands at 1405, 965 and 725 cm^{-1} . The 60 MHz spectrum (TMS as internal standard) showed three signals at δ 1.40, 2.06 and 5.33 ppm.⁶

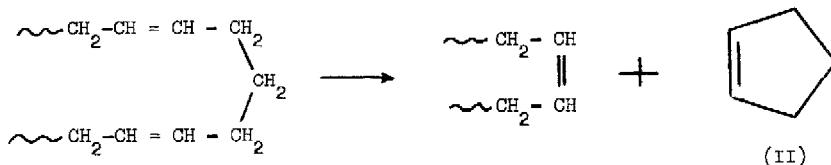
GLC/MS analysis of the volatile reaction products showed the presence of (I), cyclopentene (II) and of an isomer of (I), in a ca. 89:7:4 ratio, respectively. In a metathesis reaction carried out at 50°C these three products were in a ca. 66:23:10 ratio, respectively. Traces (ca. 1%) of a second isomer of (I) were also present.

By comparison with an authentic sample it was possible to assign the structure of *cis*-1,2-di vinylcyclopentane (IV) to the C_9H_{14} compound which constituted 10% of the low-molecular-weight metathesis compounds. (IV) could derive from a Cope reaction of (I). However, taking into account that (I) isomerizes very slowly to (IV) at 220°C and that (E,Z)-1,5-cyclononadiene yields (IV) at a considerably lower temperature⁷, the formation of (IV) can be more reasonably explained supposing that in the course of the metathesis (I) isomerizes in part to its (E,Z)-stereoisomer and that this compound by a Cope reaction gives rise to (IV).⁸



The second isomer of (I) which constituted 1% ca. of the low-molecular-weight metathesis products, may be an isomeric cyclononadiene, probably the (E,Z) stereoisomer of (I).

The above mentioned results and the fact that either cyclobutene or low-molecular-weight metathesis products of such cycloalkene were not present in the reaction mixtures allow to exclude that (II) is formed by an intramolecular metathesis of (I). On the contrary, the formation of (II) may be more reasonably interpreted supposing an intramolecular metathesis of the polymer of (I).⁹

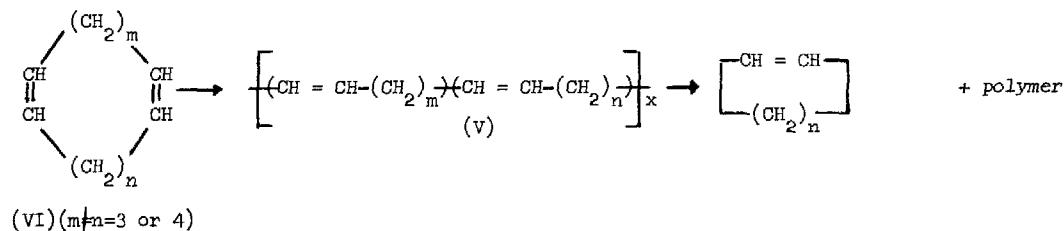


The lack of cyclobutene and of its low-molecular-weight metathesis products in the reaction mixtures would also indicate that the polymers of (I) are not constituted by 1-butenylene and 1-pentenylene structural units in a 1:1 ratio. In particular it might be expected that such polymers, and especially those obtained at temperature higher than 25°C, contain 1-butenylene

units in percentage higher than that of 1-pentenylene units.

The structural analysis of some polymers of (I) carried out either by ozonization and oxidative degradation to succinic and glutaric acid¹⁰, or by ozonization followed by reduction of the obtained ozonides to 1,4-butanediol and 1,5-pentanediol¹² has confirmed, even if qualitatively¹⁴, this hypothesis.

These results suggest that the preparation by metathesis of unsaturated copolymers (V) containing two different alkeneylene structural units in a 1:1 ratio may be difficult when the cycloalkadienes (VI) used as monomers are suitable to yield five or six-membered cycloalkenes. Probably, to obtain such copolymers it is necessary to use a low reaction temperature in order to minimize the polymer intramolecular metathesis.



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References and Notes.

- 1) N. Calderon, J. Macromol. Sci. Revs. Macromol. Chem., 07, 105 (1972) and references cited therein.
- 2) F.W. Klipper, R. Streck, J. Organometal. Chem., 55, 75 (1973).
- 3) F.W. Klipper, R. Streck, Makromol. Chem., 175, 2055 (1974).
- 4) J. Furukawa, Y. Mizoe, J. Polym. Sci., B11, 263 (1973).
- 5) Our results show that the highest selectivity in the metathetical polymerization of cycloalkenes and cycloalkadienes by a $\text{WCl}_6\text{-LiAlH}_4$ catalyst system may be observed employing the following experimental conditions: $\text{LiAlH}_4/\text{WCl}_6$ molar ratio = 4; monomer/ WCl_6 molar ratio $\gg 100$; $\text{C}_6\text{H}_5\text{Cl}$ solvent/monomer volume ratio = 2 : 3; WCl_6 and LiAlH_4 are mixed 20 min before the introduction of the monomer.
- 6) The relative intensity of the signals at δ 1.40, 2.06 and 5.33 ppm (4:8.4:3.5, respectively) was different from that foreseeable for a polymer containing 1-buteneylene and 1-penteneylene structural units into a 1:1 ratio (4:8:2, respectively). Analogous results, observed for many metathetical polymers, have been interpreted supposing that the polymers contained cyclic structural units.
- 7) E. Vogel, W. Grumme, E. Dinné, Angew. Chem., 75, 1103 (1963).

8) It is interesting to note that the products of the metathesis reaction of (Z,Z)-1,6-cyclo decadiene contained also a compound, *cis*-1,2-divinylcyclohexane, that derived from isomerization of the starting diene to (E,Z)-1,5-cyclodecadiene followed by a Cope reaction .

9) A typical example of intramolecular metathesis of a linear unsaturated polymer has been reported for poly(1-pentenylene). [E.A. Ofstead, N. Calderon, Makromol. Chem., 154, 21 (1972)].

10) According to the procedure described by Porri and Pini¹¹ a polymer of (I), obtained in 60% yield by metathesis at 25°C, was oxidatively degraded into a mixture of dicarboxylic acids. GLC analysis of the corresponding dimethyl esters showed the presence of dimethyl glutarate, dimethyl succinate and dimethyl malonate in a 27:67:6 molar ratio, respectively.

11) L. Porri, D. Pini, Chim. Ind. (Milan) "Memorie dedicate al Prof. G. Natta", p. 178 (1973).

12) According to the procedure described by Dall'Asta and Motroni¹³ a polymer of (I) obtained in 75% yield by metathesis at 25°C, was exhaustively ozonized and then converted into a diol diacetates mixture. GLC analysis showed the presence of 1,6-diacetoxyhexane, 1,5-diacetoxypentane, 1,4-diacetoxybutane and 1,3-diacetoxypropane in a ca. 3.5:40:53:3.5 molar ratio, respectively.

13) G. Dall'Asta, G. Motroni, Europ. Polym. J., 7, 707 (1971).

14) The results reported in reference 10 and 12 can be interpreted taking into account that the oxidative degradation of unsaturated polymers gives rise not only to the expected dicarboxylic acids, but also to considerable amounts of acids having one or two less carbon atoms¹⁵. On the other hand, the more selective method which affords glycols, is also associated with side reactions which yield not negligible amounts of diols having one more or one less carbon atoms than those of the expected glycols¹³.
On this basis the relative percentages of the expected dicarboxylic acids or glycols can not represent quantitatively the content of the corresponding alkenamer units.

15) G. Natta, G. Dall'Asta, G. Mazzanti, Angew. Chem. Internat. Ed., 3, 723 (1964).