Tetrahedron Letters No.11, pp. 829-832, 1970. Pergamon Press. Printed in Great Britain.

A CONVENIENT PREPARATION OF PERDEUTERATED CYCLOOCTENE: EFFECT OF INHIBITORS ON CATALYTIC EXCHANGE

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(Received in USA 29 December 1969; received in UK for publication 2 February 1970)

Perdeuterocyclooctene is a very useful intermediate for the synthesis of deuterium labelled cyclooctanes and substituted cyclooctanes needed for certain conformational[1] and mechanistic[2] studies. We reported recently a preparation of perdeuterocyclooctene by repeated palladium-catalyzed exchanges of cyclooctene with deuterium oxide at elevated temperatures in a pressure vessel.[1] However, the method is somewhat laborious and not always reproducible. We have now developed a convenient exchange procedure which avoids the use of pressure vessels, and which gives reproducible results. The success of the method depends on preventing the formation and accumulation of even small concentrations of 1,3-cyclooctadiene in the cyclooctene. We have found that this diene as well as some other dienes and polyenes are powerful inhibitors of the exchange reaction.

In a typical procedure a mixture of 5 g of cyclooctene and 5 ml (or more) of deuterium oxide, 50 mg of magnesium turnings, and 500 mg of sodium chloride is boiled in a 25 ml 3-necked flask to which is attached a jacketed glass column containing 3 g of alumina (Matheson Coleman and Bell, 8-14 mesh) on which has been deposited about 0.6 g of palladium metal. The vapors of cyclooctene and deuterium oxide pass through the column, and, after condensation in a reflux condenser, are returned to the 3-necked flask through a glass tube. The catalyst is heated to about 160° by passing the vapors of boiling diglyme through the jacket around the column. The jacket and other hot parts of the apparatus are insulated with glass wool. Exchange of cyclooctene for about 4 hr yields a product which is 40-50% deuterated as shown by infrared spectroscopy. Further exchanges can be accomplished by removal of the deuterium oxide layer with a pipette and introduction of fresh deuterium oxide. After three or four exchanges the cyclooctene is better than 97% deuterated and contains less than 15% of partially deuterated cyclooctane as an impurity. The cyclooctene-d_{14} could be separated by preparative vpc or by fractional distillation, but purification is unnecessary when the cyclooctene-d_{14} is used as a precursor in a synthetic scheme. The procedure should be also useful on a larger scale.

If the magnesium and sodium chloride are omitted from the procedure described above, the first exchange takes place satisfactorily, but further attempted exchanges with fresh deuterium oxide do not give any additional deuterium incorporation beyond the 40-50% of the first exchange. Vpc analysis of this partially exchanged cyclooctene shows the presence of up to 5% of 1,3-cyclooctadiene. Separate experiments indicate that as little as 1% of 1,3-cyclooctadiene added to cyclooctene effectively suppresses the exchange reaction. Reaction of magnesium with deuterium oxide produces enough deuterium gas to reduce the diene which has accumulated in partially exchanged samples and to prevent the formation of diene in fresh samples of cyclooctene. The boiling point difference (<2°) between cyclooctene and 1,3-cyclooctadiene makes a separation of these compounds by distillation impractical.

We have performed several experiments to see if the exchange of cyclooctene is also affected by the addition of 2-3% of other cyclic olefins and diolefins. The results in Table I indicate that a variety of non-aromatic cyclic polyolefins prevent both exchange of cyclooctene and formation of 1,3-cyclooctadiene while aromatics have little effect on either reaction. Cyclohexadiene, though a cyclic diene, fails to have a noticeable

Table I

Effect of Added Compounds on the Exchange of Cyclooctene

Compound	Exchange[a]	Cyclooctadiene Formed
Cyclooctatetraene	No	No
Cycloheptatriene	No	No
Norbornadiene	No	No
Benzene	Yes	Yes
Naphthalene	Yes	Yes
1,3-Cyclohexadiene	Yes	Yes
Norbornene	Small	Large Amount
Limonene	Yes	Small
α-Pinene	Yes	Yes
1,5-Cyclooctadiene	Very small[b]	-----
1,3-Cyclooctadiene	No	-----

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[a] as measured by the appearance of C-D stretching bands in the ir of the hydrocarbon phase. [b] see text

effect but is rapidly converted to benzene on the catalyst. The results for α-pinene and limonene are of doubtful significance since vpc indicates that these olefins react to form unknown products on the catalyst. Cyclooctene seems to undergo some exchange in the presence of 1,5-cyclooctadiene. However, the 1,5-cyclooctadiene is rapidly isomerized to 1,3-cyclooctadiene, and the apparent exchange could be due to incorporation of deuterium into the diene during isomerization. Finally, norbornene shows an unusual effect in that very little exchange is observed, but more 1,3-cyclooctadiene is formed than is produced in the absence of any added compound. Norbornene is a very strained olefin, though, and should be reduced with cyclooctene as a hydrogen donor to produce cyclooctadiene.

In exchange experiments where a reducing agent is not used, 1,3-cyclooctadiene accumulates in the reaction vessel, but the compound absorbed on the catalyst and responsible for the inhibition of exchange may actually be the 1,5-isomer. 1,5-Cyclooctadiene is a powerful chelating olefin for compounds of palladium and related elements, and in at least one case it is observed that the complexed cyclooctadiene is the 1,5-isomer although the uncomplexed diene in the same reaction mixture is the 1,3-isomer.[3]

Inhibitor effects resulting from reversible competition for catalytic sites (e.g. 2-butyne and cis-2-butene) have been observed during hydrogenations[4], but, to our knowledge, competition between different olefins has not been reported for heterogeneous catalytic exchange reactions of olefins with deuterium oxide.

References

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