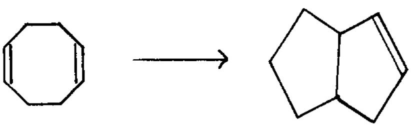
A Nickel(II) Catalyzed Bicyclization Reaction of 1,5-Cyclooctadiene

Several catalytic methods for the synthesis of bicyclo[3.3.0]oct-2-ene (I) from 1,3- or 1,5-cyclooctadiene (COD) have been reported. Acid catalysts (*1–3*) and two examples of transition metal catalysts (*4, 5*) are known to convert 1,5-COD to I. A variety of metal hydrides (*6*) and phenyl potassium (*7*) are useful catalysts in the conversion of 1,3-COD to I. The above catalyst systems all are disadvantageous from the standpoint of one or more of the problems: high temperatures, large ratios of catalyst to olefin, long reaction times, contamination with several by-products, and relatively low yields of I obtained.

We report a new catalyst system composed of a soluble Ni(II) salt and $C_2H_5AlCl_2$, which appears to be the most efficient in the synthesis of I to date, i.e., the conversion:



Methods

Starting Materials. Nickel-2-ethylhexanoate (10% solution in xylene from Mooney Chemical Co.) was diluted with dry benzene to a 0.2 M solution. The 1,5-COD was dried by distillation over Na, and the alkyl aluminum chlorides (Texas Alkyl) were used as 25% (2 M) solutions in toluene.

Identification of Products. The products were identified by gas chromatography, NMR, and ir; corresponding data from these instruments were identical with those of authentic samples of I and 1,3-COD (one of the by-products).

Preparation of Bicyclo[3.3.0]oct-2-ene. In a typical experiment, a mixture of 6 ml of 1,5-COD (49 mmole), 30 ml of benzene, and 2 ml of pentane in a closed 100-ml flask under nitrogen was treated with 0.5 ml (0.1 mmole) of a 0.2 M solution of nickel 2-ethylhexanoate in xylene and 1 ml (2 mmole) of $C_2H_5AlCl_2$, in that order. The reaction mixture was shaken in a constant temperature bath maintained at 25°C or 50°C. The reactions were terminated by treatment with 1 ml of butanol. The products were separated by gas chromatography.

Results and Discussion

The products obtained from the reaction are mainly I, small amounts of an as yet unidentified compound, and 1,3-COD. The table gives the pertinent data.

The preferred cocatalyst is $C_2H_5AlCl_2$ rather than $(C_2H_5)_2AlCl$; use of the latter results in much slower reaction and lower selectivity to I. No reaction is observed with $(C_2H_5)_3Al$ as the cocatalyst. It is necessary that both cocatalysts be present to promote the reaction.

The optimum 1,5-COD/Ni molar ratio appears to be about 500/1, but ratios up to 1000/1 give up to 99% conversion with 94% selectivity to I. Ratios up to 2000/1 give good selectivity to I, but conversion of 1,5-COD is significantly lower (72%).

The reaction as promoted by the catalyst system is not reversible. When experiments were carried out on I, only 1,3-COD was detected in very small amounts. It is possible that 1,3-COD in the conversion of 1,5 COD comes from reaction of I rather than isomerization of 1,5-COD. 1,3-COD is not converted to I by this means, hence, the conversion of 1,5-COD does not proceed through that intermediate.

Finally, Ni(II) may be unique to this

TABLE 1
TIME-TEMPERATURE STUDY

Time (min)	% Conversion		% Selectivity					
			I[a]		Unknown		1,3-COD	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
1	10.5	75.6	88.3	92.8	5.1	5.8	6.2	1.5
5	42.2	99+	89.4	92.6	4.1	5.6	1.5	1.8
15	92.2	100	92.5	92.5	6.3	5.9	1.3	1.7
30	100	100	95.9	93.0	2.2	5.5	1.9	1.5

[a] I, bicyclo[3.3.0]oct-2-ene.

reaction. When the conversion of 1,5-COD was attempted using soluble Co(II) and Fe(II) salts with the Al co-catalyst, no reaction was observed.

ACKNOWLEDGMENT

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On the Question of Hydrogen Spillover in Ethylene Hydrogenation on Supported Platinum

The kinetic evidence of Sinfelt and Lucchesi (*1*) for spillover of hydrogen from platinum in a Pt–SiO_2 catalyst to Al_2O_3 to give enhanced rates of ethylene hydrogenation on the Al_2O_3 has been strongly challenged recently by Schlatter and Boudart (*2*). In a recent letter (*3*) we present evidence which supports the results of Schlatter and Boudart inasmuch as it confirms the importance of achieving clean platinum surfaces through removal of contaminant inherent in the supporting material. By coincidence we have also obtained new information regarding the occurrence or nonoccurrence of hydrogen spillover in the system first described by Sinfelt and Lucchesi, from the deuteration of ethylene on Pt–SiO_2, which we present here.

This investigation arose from a study, as yet incomplete, of the effect of the