ORGANIC CHEMISTRY

CATALYTIC REACTIONS OF C_3-CYCLIC OLEFINS IN THE PRESENCE OF METAL COMPLEXES.

4. Ni COMPLEXES AS CATALYSTS FOR THE [2 + 2]-CYCLODIMERIZATION OF SPIRO[2,3]HEX-1-ENE*

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Ni(0), Ni(I), and Ni(II) complexes, differing in the ligand environment of the central atom, bring about di-, tri-, and oligomerization of spiro[2,3]-hex-1-ene (SH). The most efficient catalyst for the [2 + 2]-cyclodimerization of SH is $NiBr(PPh_3)_3$, which gives virtually a single product, the SH cyclo dimer. It has been found that high conversion and selectivity in the [2 + 2]-cyclodimerization of SH is achieved by using organoaluminum compounds as catalysts.

The use of catalysts facilitates the [2 + 2]-cyclodimerization of alkylcyclopropenes [2]. Using metal complexes which differ in the metal and the ligand environment, it is possible to control the course of the reaction to give preferentially either cyclodimers or oligomers.

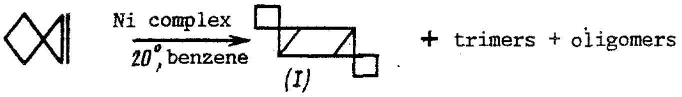
The catalytic [2 + 2]-cycloaddition of spiro[2,3]hex-1-ene (SH) to norbornene and norbornadiene in the presence of $(PhO)_3P \cdot CuCl$ and $Ph_3P \cdot CuCl$ has been reported [3]. Under the conditions used (−20°C, CH_2Cl_2), in addition to the cross-cycloaddition and isomerization products, there was formed up to 25% of cyclobutanespiro-3-tricyclo[3.1.0.0^{2,4}]hexane-6-spirocyclobutane (I). No information on the controlled selective di- and trimerization of SH was given.

We have now examined the influence of nickel complexes on the [2 + 2]-cyclodimerization of SH in order to establish the effect of the valence of the metal and the ligand environment of the central atom on the selectivity of the reaction and the activity of the catalyst.

SH differs from its analog, 3,3-dimethylcyclopropene (DMCP) in being more strained. According to Plemenkov et al. [4], knowledge of the ionization potentials enables conclusions to be drawn concerning the destabilization of the π-ethylene orbitals as a result of interaction with the orbital σ-symmetry of the cyclobutane ring. It is clear that the structure of SH has a considerable effect on its reactivity. For example, unlike DMCP [5, 6], SH undergoes thermal [2 + 2]-cyclodimerization even at 20°C.

Separate experiments showed that in dilute solution (≤1 mole/liter), SH remains largely unchanged for ≥1 month at 20°C. In this way, conditions were found for examining the catalytic reactions of SH.

The catalytic reactions of SH in the presence of nickel complexes (Table 1 and Fig. 1) gave rise to di-, tri-, and oligomers (according to GLC).



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*For previous communication, see [1].

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TABLE 1. Dimerization of Spiro[2,3]hex-1-ene in the Presence of Ni Complexes (benzene, 20°C, $[SH]_0$ = 0.3 moles/liter, $[Ni]_0$ = 3.0 mmoles/liter)

Catalyst	Time, h	Conversion, %	Selectivity in dimer, %
$Ni(COD)_2$	2	70	90*
$Ni(COD)_2$+Dipy	66	14	13
$Ni(COD)_2$+PPh_3 (1 : 1,1)	2	70	55
$Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$	2	68	65
$Ni(PPh_3)_2(CO)_2$	2	56	96
$NiBr(PPh_3)_3$	0,17	70	100
$NiCl(H)(PCy_3)_2$	24	31	40
$Ni(PPh_3)_n$ (n=3, 4)	2	52	74
Dimerization of 3,3-DMCP†			
$Ni(PPh_3)_n$ (n=3, 4)	3	35	99.4

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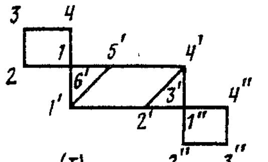
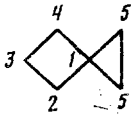
*Remainder, di- and oligomers.

†$[DMCP]_0$ = 1.55, $[Ni]_0$ = 1.8 mmoles/liter.

The ^{1}H NMR spectra (a singlet at 1.21 ppm, and a multiplet at 1.8-2.3 ppm) were almost identical with those reported [3] for (I).



(I)



(II)

Conformational analysis using the Stuart—Briegleb models shows that trans-(I) is highly strained, and no cis conformation for (I) could be obtained.

Assignment of the signals in the ^{13}C NMR spectrum of the dimer (I) was made using the ^{13}C spectral data for the model compound (II) (δ, ppm, J, Hz): C^1 (19.8); C^2, C^4 30.7 (135); C^3 16.9 (135), C^5 120 (160) ppm. The high resolution ^{13}C NMR spectrum of the dimer (I) (δ, ppm from TMS; $^1J_{^{13}C\text{-}H}$, Hz) contained three signals for nonequivalent groups $CH_2C^3(C^{3''})$, 16.62 (133), $C^{2''}(C^4)$ 25.18 (130), $C^2(C^{4''})$ 27.41 (133) of relative intensities 1:1:1, a signal for four equivalent CH groups $C^{2'}$, $C^{4'}$, $C^{1'}$, and $C^{5'}$ at 26.36 (155), and a signal for two equivalent quaternary carbons $C^1(C^{1''})$ at 41.82. The observed nonequivalence of the carbons $C^{2''}(C^4)$ and $C^2(C^{4''})$ is due to the different orientation of these atoms and the central four-membered ring relative to the plane of the three-membered ring in the cis and trans positions, respectively. The $^1J_{C\text{-}H}$ value for $C^{1'}$ ($C^{2'}$, $C^{4'}$, $C^{5'}$) (155 Hz) apparently arose as a result of these carbons forming part of the four-membered and three-membered rings simultaneously ($^1J_{C\text{-}H}$ for cyclobutane is 135 Hz, and for cyclopropane 164 Hz).

The ligand environment of the metal has a considerable effect on the rate and selectivity of conversion of SH to [I]. This is shown quite clearly in the case of the Ni(0) complex (Table 1). For example, in the presence of $Ni(COD)_2$, the selectivity of formation of [I] from SH is 90%. Introduction of Dipy as a modifier reduces the yield of dimer to 1 mole per mole of Ni. It appears that Ni(Dipy)(COD) is formed, and this then reacts with SH stoichimetrically, as described for DMCP [7, 8].

Triphenylphosphine complexes of Ni(0), whether previously prepared or obtained in situ from $Ni(COD)_2$ and PPh_3, are less selective in the dimerization of SH (55-65%) than $Ni(COD)_2$ (90%). The reaction proceeds differently in the presence of $Ni(PPh_3)_2(CO)_2$, selectivity of formation of (I) reaching 96%. A distinguishing feature of the dimerization of SH in the presence of this complex is the occurrence of an induction period (Fig. 1). The cyclodimerization of DMCP proceeds similarly in the presence of $Ni(PPh_3)_2(CO)_2$ bound to an Al_2O_3 surface [9], the induction period in this case being due to the slow formation of the reactive intermediates. It is most likely that in the initial stages of the catalytic [2 + 2]-cycloaddition the $Ni(PPh_3)_2(CO)_2$ complex reacts with SH to give first a π-complex with one, and then with two molecules of the olefin. The subsequent reaction could be oxidative addition

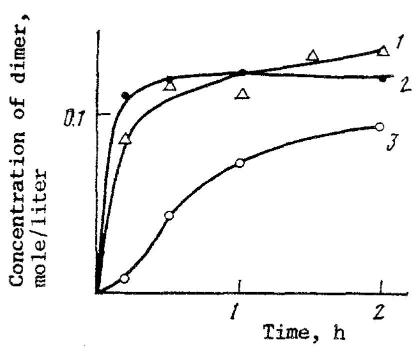
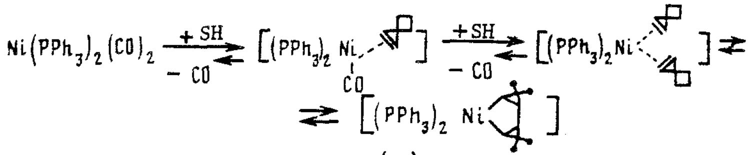


Fig. 1. Kinetic plots of the formation of the dimer (I) in the presence of the nickel complexes: 1) $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$, 2) $NiBr(PPh_3)_3$; 3) $Ni\cdot(PPh_3)_2(CO)_2$ (20°C, benzene, $[SH]_0 = 0.30$, $[Ni] = 3.0\cdot10^{-3}$ mole/liter).

of an SH molecule to Ni(0), followed by reductive elimination of (I), as proposed for DMCP [10].



(III)

A complex similar to (III) has been reported with DMCP [5]. The similarity of the catalytic reactions of SH and DMCP in the presence of Ni(0) complexes is also seen when $Ni(PPh_3)_n$ is used as catalyst, the synthesis and identification of which have been reported [1]. These differences in reaction rates and selectivity of formation of (I) (Table 1) are due to the differing reactivities of these cyclopropenes.

The divalent nickel complex containing an Ni—H bond shows poor activity and selectivity (Fig. 1, Table 1). Of the nickel complexes of differing valence examined, the most efficient is $NiBr(PPh_3)_3$, virtually quantitative formation of (I) being obtained at high conversion rates (70%).

It has been found that, like DMCP [11], SH undergoes [2 + 2]-cyclodimerization in the presence of organoaluminium compounds ($AlEt_3$, $Et_3Al_2Cl_3$, Et_2AlCl, $EtAlCl_2$). The reaction is rapid and selective. For example, in the presence of $Et_3Al_2Cl_3$ for 0.1 h, 100% conversion of SH into (I) is obtained with a selectivity of 87%.

It has thus been shown that SH and DMCP in the presence of the same catalysts undergo reactions of the same type, the predominant one being [2 + 2]-cyclodimerization, enabling a single mechanism for the dimerization of these olefins to be put forward.

EXPERIMENTAL

High resolution ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer, operating frequency 62.89 MHz. The chemical shifts (±0.03 ppm) were measured relative to TMS, solvent $CDCl_3$. The $^1J_{^{13}C\text{-}H}$ values were determined to within ±0.9 Hz.

PMR spectra were obtained on the same apparatus as 5-10% solutions in $CDCl_3$.

The required spiro[2,3]hex-1-ene was obtained as described in [11], and the complexes $Ni(PPh_3)_n$, $Ni(COD)_2$, $Ni(PPh_3)_2(\eta^2\text{-}C_2H_4)$, $Ni(PPh_3)_2(CO)_2$, $NiBr(PPh_3)_3$, $NiCl(H)(PCy_3)_2$ as in [12-17]. The catalytic reactions of SH in the presence of nickel complexes, ethereal solutions, and organoaluminium compounds, and the progress of the reactions, were followed as described in [5, 18]. All operations involving the use of nickel complexes or organoaluminium compounds were carried out under argon.

Cyclobutane-1-spiro-3'-tricyclo[3.1.0.$0^{2,4}$]hexane-6'-spiro-1''-cyclobutane (I) was isolated from the reaction mixture, recrystallized from methanol, and purified by sublimation at 1 torr; mp 27.8°C.

PMR spectrum of (I) ($CDCl_3$, ppm): 1.21 s (4H, CH) and 1.8-2.3 m (12H, CH_2).

The ^{13}C NMR spectra have been reported in the discussion of results.

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ISOMERIZATION OF $C_{12}H_{20}$ TRICYCLANES INTO DIMETHYL- AND ETHYLADAMANTANES BY THE ACTION OF COMPLEXES OF ACETYL BROMIDE WITH ALUMINUM BROMIDE

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It has been shown that $AcBr \cdot mAlBr_3$ complexes (m = 1.8-2.0) effectively initiate the isomerization of $C_{12}H_{20}$ tricyclanes into a mixture of dimethyl- and ethyladamantanes. A quantitative conversion of the starting material is achieved in 3-5 min at room temperature, the overall yield of alkyladamantanes AdC_2 amounting to 71-76%.

In connection with the sustained interest in adamantane (AdH) and its derivatives [1-3] a most pressing problem is the development of convenient methods for their synthesis from accessible compounds. Traditional starting materials for the synthesis of hydrocarbons of the AdH series with general formula C_nH_{2n-4} ($n \geq 10$) are the tricyclanes which are isomeric with them, for example, perhydroacenaphthene. Isomerization of perhydroacenaphthene $C_{12}H_{20}$ in the presence of catalysts based on AlX_3 (X = Cl, Br) leads to dimethyl- and ethyladamantanes (AdC_2) and finally to 1,3-dimethyladamantane and generally proceeds more readily [4-6] than the isomerization of trimethylenenorbornane $C_{10}H_{16}$ to adamantane [4]. However, there is

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