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Isotopic Exchange of Some Bicyclic Hydrocarbons with Deuterium Catalyzed by Palladium on Silica

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ISOTOPIC EXCHANGE OF SOME BICYCLIC
HYDROCARBONS WITH DEUTERIUM CATALYZED BY
PALLADIUM ON SILICA

by

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B. S., Northern Michigan University

A Thesis

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Arts in Chemistry

School of Graduate Studies

Northern Michigan University

Marquette, Michigan

December 1972

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Abstract

The isotopic exchange of cis- and trans-bicyclo[4.4.0]-
decane, cis- and trans-bicyclo[4.3.0]nonane, cis-bicyclo-
[3.3.0]octane, 1-methyl-cis-bicyclo[4.4.0]decane, and 1-methyl-
cis-bicyclo[4.3.0]nonane has been investigated on a silica
supported palladium catalyst.

The process which leads to multiple exchange is discussed
in terms of the "π-allyl" and "roll-over" mechanisms. The
results show the process is more complicated than previously
thought. The competition between five and six membered rings
is discussed in terms of the fused ring systems, along with
the possibility of more than one process occurring to lead
to the observed distributions. An end adsorbed π bonded
intermediate is shown not to be involved in the exchange mechan-
ism.

Acknowledgments

The author wishes to express his sincere appreciation to Dr. Jerome A. Roth for his guidance and encouragement throughout this research.

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Introduction

In the deuteration of olefins over transition metal catalysts it has been observed by mass spectrometry that, besides addition of deuterium to the double bond, a number of hydrogens already present in the molecule are "exchanged" for deuterium (1). This isotopic exchange reaction has been useful in determining what interaction is occurring on the metal surface with an organic molecule.

During the past decade investigations of isotopic exchange between deuterium and cyclic hydrocarbons have been carried out in order to elucidate the mechanistic intermediates which lead to the observed products. The exchange itself is much more evident on Palladium catalysts than other heterogeneous hydrogenation catalysts (1). Therefore, it was chosen for this study. The interest in cyclic hydrocarbons arose from the fact that they exchange the hydrogens on both sides of the ring during one surface residence. This is illustrated with cyclopentane (2) where maxima for exchange are observed at d(5) and d(10), corresponding to two sets of hydrogens, a set of G hydrogens on one side of the ring and a H set on the other side, Fig. I.

FIGURE I
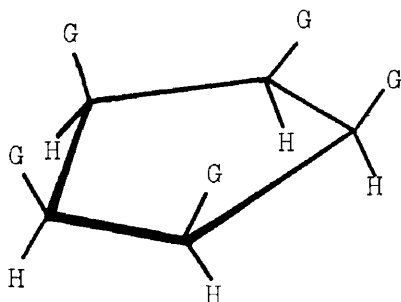
The reason for interest in this fact is that if the molecule can only approach the metal from one side, it is difficult to explain how the G set of hydrogens can be exchanged by intermediates bound to the metal on the opposite side of the ring as in Figure II (where the * represents active sites on the metal surface to which the molecule and Deuterium are "bound").

FIGURE II
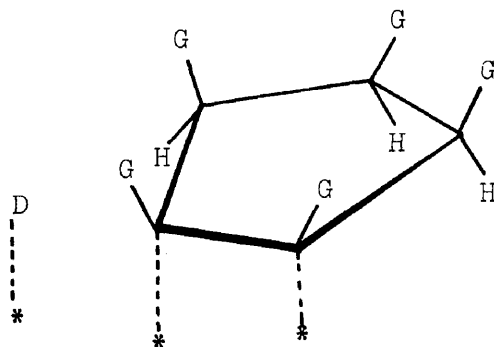
In order to accommodate this observation two mechanisms have been proposed: the "π-allyl" (3) (Figure III) and the "roll over" mechanism (4) (Figure IV).

Both the mechanisms explain the observed products in the exchange of cyclic hydrocarbons such as cyclopentane, cyclohexane, cycloheptane, and cyclooctane (3), along with racemization of optically active hydrocarbons and epimerization of molecules such as dimethyl cyclopentanes (3,4,6).

Some authors (4), however, argue against the "π allylic" intermediate on the basis that the ratio of d(6) to d(12)

FIGURE III

"π allyl" mechanism
(all reactions are reversible)
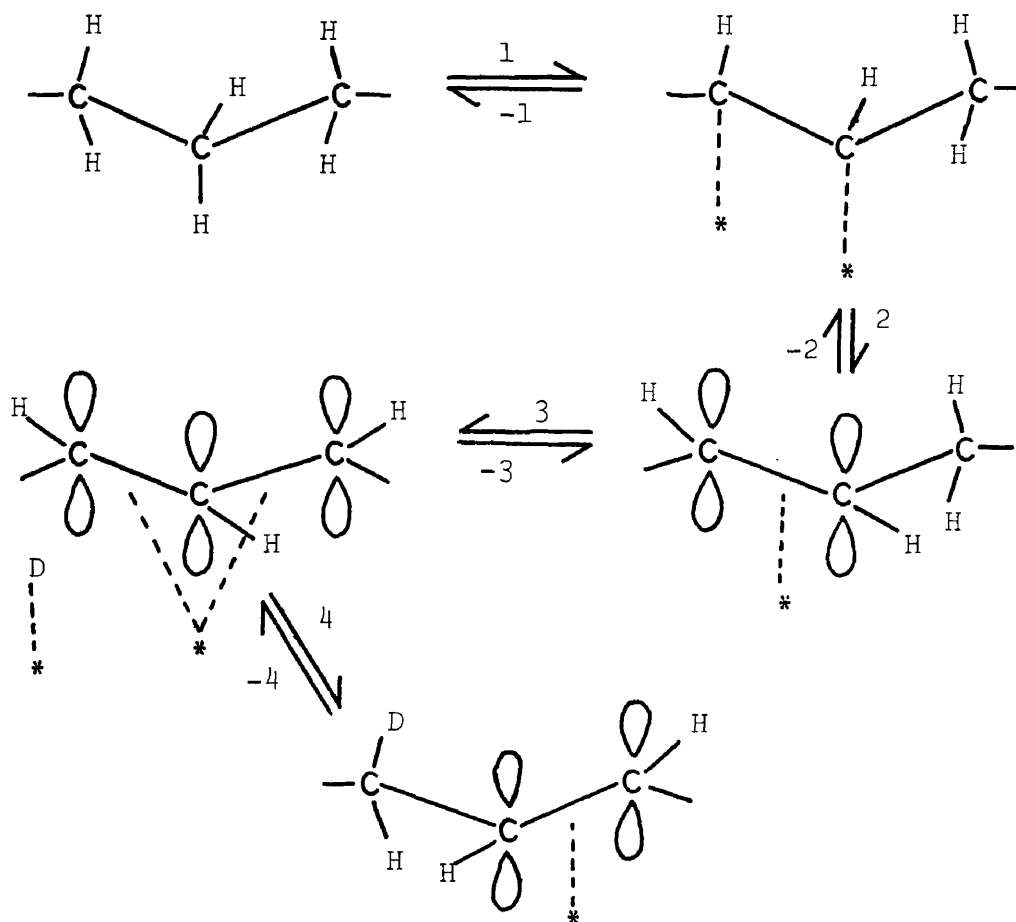
FIGURE IV

"roll over" mechanism
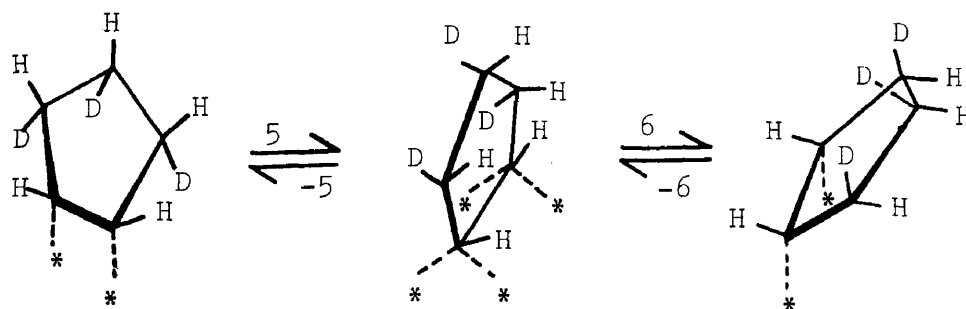
cyclohexane is smaller and more smeared than those of cyclo-
pentane, cycloheptane, and cyclooctane. The basis for this
argument is that the major difference in these molecules is
the ease with which they form eclipsed diadsorbed intermediates.
The "roll over" mechanism, which requires this intermediate,
can better explain this lowering of the multiset exchange (5).

In an effort to test the validity of the "π-allyl"
mechanism it is necessary to exchange molecules which will
give different d(max) for the two mechanisms, thus allowing
determination of which mechanism is operative.

One molecule chosen for this investigation is adamantane.
If it is necessary for a 1,2 diadsorbed molecule to initiate
multiple exchange, then no exchange beyond d(1) should be
found. Indeed this is what has been found (4). If, however,
one of the methylene groups were removed, as in bicyclo[3.3.1]-
nonane, being more flexible, this substance would be capable
of forming a 1,2-diadsorbed specie and undergo multiple exchange
as has been found (4,7). Furthermore, the "π allyl" mechanism
would not exchange past the bridgehead due to the high energy
of formation of this intermediate (4) and would lead only to
a d(3) maximum. On the other hand, the "roll over" mechanism
would predict the observed maxima at d(8), d(10) and d(12)
with d(8) predominating (4,6,7). It is, however, unlikely
that the "π allylic" intermediate can form in the exchange of
a hydrocarbon without initially forming a diadsorbed specie
since a double bond is not present.

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In <u>cis</u>-bicyclo[3.3.0]octane the necessity for multiple exchange via "π-allyl" would require an allylic specie including the tertiary carbon at the bridgehead to explain the observed d(14) maximum (6,7). This allylic specie is disfavored due to the strain imposed at the bridgehead of the ring system (6,7). The maximum at d(10) can be explained by both the "roll over" and the "π-allyl" mechanism. What has not been explained is that there is no maximum observed at d(12) as would be expected for the explanation for bicyclo[3.3.1]nonane where two hydrogens don't exchange (Figure VI).

In order for the d(14) maximum to occur there must be a symmetrical intermediate which involves a double bond between carbon atoms 1 and 5 with end adsorption, followed by roll over and inversion at both carbons (1,6,7) (Figure V).

FIGURE V

This intermediate, however, is planar at the bridgehead as
is the "π allylic", and the very reason a d(14) maximum for
it was considered unlikely.

The authors of the "π allyl" mechanism attempted to
solve this controversy by introducing a methyl group at
the bridgehead and therefore eliminating the possibility of
forming the roll over intermediate in Figure V. There was
found a maximum at d(11); but none at d(13) as would be
expected for the "π allyl" mechanism (6). The d(11) maximum
can be explained by the "roll over" process without exchange
of one of the hydrogens on each of the ring systems. This
is the same process which occurs in bicyclo[3.3.1]nonane
(4,6,7). The process involved is illustrated in Figure
VI where one of the trimethylene bridges is shown. The
starting specie is diadsorbed in the H set and all atoms in
that set have been exchanged by reaction 9 and -9.

FIGURE VI

Carbon

$$
\begin{array}{c}
2 \\
3 \\
4
\end{array}
\begin{bmatrix}
D-C-h \\
*-C-h' \\
*-C-h
\end{bmatrix}
\equiv
\begin{bmatrix}
Dh \\
*h' \\
*h
\end{bmatrix}
\xrightarrow{10}
\begin{bmatrix}
Dh \\
h'* \\
h*
\end{bmatrix}
$$

$$
\xrightarrow[-9]{9}
\begin{bmatrix}
D* \\
h'* \\
hd
\end{bmatrix}
\xrightarrow{10}
\begin{bmatrix}
*D \\
*h' \\
hd
\end{bmatrix}
\xrightarrow[-9]{9}
\begin{bmatrix}
dD \\
*h' \\
*d
\end{bmatrix}
$$

The fact that small amounts of d(12) and d(13) were observed at higher temperatures (6) does not rule out the "π allyl" mechanisms completely.

In an attempt to determine which, if either, of these possibilities are operating to give multiple exchange two series of compounds have been exchanged over Palladium on silica. Series A, consisting of cis- and trans-bicyclo[4.4.0] decane (I and II), cis- and trans-bicyclo[4.3.0]nonane, (III and IV), and cis-bicyclo[3.3.0]octane (V) (6,7) have been compared to the compound which has been reported (the standard for series A), cis-bicyclo[3.3.0]octane (V). Series B, consisting of 1-methyl-cis-bicyclo[4.4.0]decane, (VI), and 1-methyl-cis-bicyclo[4.3.0]nonane, (VII), have been compared to the standard for series A along with 1-methyl-cis-bicyclo [3.3.0]octane (6).

These compounds should have maxima which can be predicted by the two mechanisms if they are operative. Thus,by predicting the maxima for each mechanism and comparing the predicted maxima with the results,it is possible to determine which, if either, is occurring.

The exchange patterns expected for the two mechanisms are in Table I. The maxima are those which lead to the expected multiple exchange and do not include the lower values except where they are useful in distinguishing between the different mechanisms;that is the case with compound III, IV, and VII where the difference in initial adsorption is important.

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Table I
Expected Maxima

Compound	π allyl	roll over
I	d(10), d(18)	d(10), d(18)
II	d(10), d(18)	d(9), d(18), [d(10)]
III	d(9), d(16)	d(9), d(18)
IV	d(9), d(16)	d(4), d(8), d(16), [d(9)]
V	d(8), d(14)	d(3), d(8), d(14)
VI	d(9), d(17)	d(4), d(9), d(13), d(17)
VII	d(8), d(15)	d(3), d(4), d(8), d(14)

Both mechanisms should give the same exchange patterns for I but for the trans system in II the "π-allyl" process should give a maximum at d(10) whereas the "roll over" process would give a maximum at d(9). This difference is due to the "π allylic" process being able to exchange both the cis and trans hydrogen at the ring juncture through the allylic intermediate, whereas the "roll over" mechanism's being capable of exchanging the hydrogen only on the initial side of adsorption without rolling over and thus exchanging the remaining hydrogens.

The same argument holds for the bicyclo[4.3.0]nonane systems III, and IV with the additional concept that the "roll over" process predicts initial adsorption on the trimethylene bridge. This would lead to a maximum at d(4) for IV. In III this difference should not occur.

A d(10) maximum is possible for II and d(9) for IV via a "roll over" process after exchanging the hydrogens on one side, then rolling over by an unsymmetrical intermediate as in Figure IV. This, however, is questionable since exchanging the bridgehead hydrogen would propagate exchange on the other ring. It this process occurs, the distribution between d(9) and d(10) or d(8) and d(9) for compounds II and IV, respectively, would be smeared in the "roll over" process and sharp in the "π allylic" process.

In the bridgehead methyl systems VI and VII the "π allylic" process should lead to two maxima corresponding to the exchange of all the hydrogens on one side, d(9) for VI and d(8) for VII, plus the exchange of all those on the top side d(17) and d(15) respectively. In the "roll over" process the initial adsorption becomes important as the site of adsorption will affect the observed maxima. The initial adsorption on the side opposite the methyl group cannot exchange past the bridgehead without rolling over to exchange the hydrogen on the bridging carbon. The resulting maxima should be d(4), d(9), d(13), d(17) for VI and d(3), d(4), d(8), and d(14) for VII where d(14) arises from the process where one hydrogen is left on the trimethylene system as in Figure VI. The relative size of the lower (d(3), d(4)) maxima should show the steric effect of bridged methyl group on the molecular interaction with the surface.

Instrumental

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian A-60A high resolution spectrometer. The samples were analyzed as the neat liquid or in solution with chloroform (spectro quality, Matheson Coleman and Bell, East Rutherford, N.J.), carbon tetrachloride (spectro quality, Matheson Coleman and Bell, East Rutherford, N.J.) or deuterochloroform (Diaprep Inc., Atlanta, Ga., isotopic purity 99.8%). Chemical shifts are recorded as ppm (δ) from tetramethylsilane (TMS).

Infrared (IR) spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer using sodium chloride plates. The spectra were recorded as liquid film solutions. The solutions were recorded as neat liquids or as solutions in the solvents listed for NMR spectra.

Gas-liquid chromatography (G.C.) analyses were performed with either a Varian-Aerograph Model 90-75 or a Varian-Aerograph Model A-90-P. Both instruments were of the thermal conductivity detector type; on-column injections and helium carrier gas were used. The flow rate was 40-60 milliliters per minute. Column composition is expressed as a weight/weight percent. The detector amperage was 150 microamps.

Mass spectra were recorded on a Consolidated Electrodynamics Corporation Model 21-104 Mass Spectrometer. Maximum sensitivity was obtained with 200 volts/stage and 12 amps. An ionization voltage of 10 electron volts (e.v.) was used to

minimize fragmentation. However, with compounds I, II, III,
IV and VI the conditions were changed to an ionization
voltage of 30 e.v. 160 volts/stage and 10 amps in order to
get enough sensitivity to observe the exchanged compounds
at a very small amount of exchange. Pump-out time was
determined by scanning the mass region of interest until no
further peaks were recorded.

Analytical

The percent isomerization of the exchanged compounds were
determined by G.C. (using the triangulation method to measure
the area under the peak) immediately following each pass over
the catalyst.

The total deuterium content was determined by N.M.R. (8)
and mass spectrometry. The mass spectral deuterium content
and distribution of the deuterospecies were calculated on an
IBM 360 Model 40 computer. The method used for the calcula-
tions assumes that a deuteriated compound has a spectrum
identical to that of the undeuteriated (light) compound with
the exception that the peaks are off-set one mass unit for
every deuterium due to the mass ratio of deuterium to the
hydrogen. Therefore, once the spectrum of the light compound
is obtained, the distributions of the deuterium in the sample
can be obtained.

This is done by setting up a system of simultaneous linear
equations where the peak intensity of a given peak is composed
of various component peaks due to molecules of different
deuterium contents, their fragments and their natural isotopic
abundances. These in turn are related to the light compound.
More explicitly the intensity of the peaks (P_j) times the
standardized intensity (S_i) for the light compound for i from
1 to n and j from m = n + 2 to 1. (see below)

Solving this system of equations by matrix inversion
gives the intensity of the parent peak of the various deutero

species containing 0 to n deuterium atoms. This then enables
the total deuterium in the sample to be calculated along with
the percent which is exchanged 1,2,...n deuterium atoms
(the distributions).

$$I_k = \sum_{i=1}^{n} \sum_{j=m}^{1} P(j)S(i)$$

The Catalyst

Palladium on wide pore, 60/80 mesh, silica was used. Catalyst Ia was composed of 2 ml of silica containing 9×10^{-4} moles of Pd. Catalyst Ib was composed of 3 ml of silica containing 1.4×10^{-3} moles of Pd. Catalyst IIa was composed of 2 ml of silica containing 1.4×10^{-3} moles of Pd. The preparation of the catalyst and the support have been described (9). The inertness of the support toward exchange and isomerization has been shown (9).

Exchange Reactions

The apparatus and method have been described previously (9). The flow rate of deuterium was between 16.1 ml/min and 19.2 ml/min for catalysts Ia and Ib, and from 10.7 ml/min to 12.3 ml/min for catalyst IIa. The deuterium to compound ratio in the gas phase was from 12.9/1 to 28.5/1 for runs with catalysts Ia and Ib. The ratio for runs with catalyst IIa was from 7.6/1 to 19.1/1.

Preparations

Cis- and trans- bicyclo[4.4.0]decane, cis- and trans-bicyclo[4.3.0]nonane, and cis-bicyclo[3.3.0]octane were obtained from Chemical Samples Co. in 99% purity. The purity was checked by GC on a 15', 9% Carbowax 20M on 60/80 Firebrick (column at 170°C). The retention times (RT) were 10 minutes, respectively. In all cases the purity was greater than 99%.

1-Morpholino-1-cyclohexene was prepared from 29.4 g of cyclohexanone, 31.4 g of morpholine and 0.30 g of p-toluene sulfonic acid in 100 mls of toluene, following the method described by Monson (10). The product was isolated by distillation. B.P. = 94-98°C/2.4 torr. The yield was 49.1 g or 82.1%.

$\Delta^{1,2}$Bicyclo[4.4.0]decen-3-one was prepared from 49 g of the above enimine with 22 g of methyl vinyl ketone in 300 mls of dry p-dioxane following the procedure of Monson (11). The product was isolated by distillation. B.P. 98-100°C/1.8 torr. The yield was 16.4 g or 44.5%.

1-Methyl-cis-bicyclo[4.4.0]-3-decanone was prepared by a Grignard 1,4-conjugate addition with 16.4 g of the above α,β-unsaturated ketone, 27 g of methyl iodide and 4.8 g of magnesium in 50 mls of dry diethyl ether according to the procedure described by Monson (12). The compound was isolated by distillation B.P. 90-100°C/1.8 torr. The yield was 6.9 g or 37.5%. The fraction contained two products by G.C. (10' 20% QF-1 on 60/80 chromophore W at 190°C, R.T. = 32.5 minutes and 28 minutes). No attempt was made to separate the mixture. The desired product was present in 87% of the mixture (R.T. = 32.5 minutes).

1-Methyl-cis-bicyclo[4.4.0]decane (VI) was prepared from 6.8 g of the above mixture with 8.1 g of potassium hydroxide and 6 mls of 85% hydrazine hydrate in 60 mls of diethylene glycol using the Huang-Minlon modification of the Wolff-Kishner

reduction described by Monson (13). The product was isolated by preparative G.C. (10' 20% QF-1 on Chromosorb W at 140°C, R.T. = 14.2 minutes); the yield was 0.60 g or 9.9%. The NMR analysis indicated a singlet at 55.2 Hz integrating to 3 hydrogens and a multiplet at δ = 1.8 to δ = 0.9 ppm integrating to 17 hydrogens. The values are in agreement with the reported values (14).

1-Pyrolideno-1-cyclopentene was prepared from 37.8 g of cyclopentanone, 38.4 g of pyrolidene and 0.5 g of p-toluene-sulfonic acid in 150 mls of toluene. The same procedure was followed as used for 1-morpholino-1-cyclohexene. The product was isolated by distillation (B.P. 62-66°C/2.4 torr). The yield was 20.6 g or 30.8%.

Methyl vinyl ketone was prepared from 1520 mls of acetone, 12 mls of 1N sodium hydroxide and 430 mls of 35-40% formaldehyde. The procedure has been described (15). The compound was isolated by distillation (BP 33-34°C/130 torr). The product was collected until 14 g was obtained.

$\Delta^{1,7}$-Bicyclo[4.3.0]nonen-6-one was prepared by a Michael addition. The condensation and ring closure were done as in $\Delta^{1,2}$-bicyclo[4.4.0]decen-3-one with 20.6 g of the enimine and 12.2 g of methyl vinyl ketone. (BP 87°C/2.2 torr). The yield was 3.2 g or 17.6%. NMR analysis indicated the product was 40% pure by integration relative to the vinyl proton.

1-Methylbicyclo[4.3.0]nonan-7-one was prepared by a Grignard 1,4-conjugate addition following the procedure used for

1-methyl-bicyclo[4.4.0]decan-3-one with the exception that cuprous chloride was used in place of cuprous bromide. No attempt was made to isolate the product from the crude reaction products.

Cis-1-Methylbicyclo[4.3.0]nonane (VII) was prepared from the above ketone by the Wolff-Kishner method described for 1-methylbicyclo[4.3.0]decane. Approximately 3 g of the above ketone with 5 g of potassium hydroxide and 5 mls of 85% hydrazinehydrate in 25 mls of diethylene glycol were used. The product was isolated by preparative GC (RT = 9.5 minutes, 12' 60% [9% Carbowax 20m on 60/80 Firebrick] 40% [9% Carbowax 20m on 60/80 Chromosorb P], column 190°C, injector 200°C, detector 210°C). NMR analysis indicated a cis ring fusion with a multiplet at δ = 1.8 to 0.90 ppm integrating to 15 hydrogens and a singlet at δ = 0.95 ppm (56 Hz). The yield was approximately 0.05 g.

General Procedure for Diels-Alder Cyclizations

The reactions were done in 500 ml Parr Pressure Bottles using a Parr Pressure Apparatus. Butadiene (purity >99.8%) was introduced as a liquid into the reaction vessel which was prechilled in a dry ice-acetone bath to avoid vaporization of the butadiene. At the time of introduction of the diene, the dienophile (with solvent, if used) was frozen in the reaction vessel. The reaction vessel was then immediately flushed with N_2 and transferred to the Parr

Pressure Apparatus where it was sealed and clamped to the
shaker and covered by an explosion shield. The mixture
was allowed to come to room temperature so that its volume
could be measured to ensure that the expanded volume did
not exceed one-half the volume of the reaction vessel.

The reaction mixture was then heated with pressure
monitoring. Heating was continued until the pressure reached
85-90 lbs/in^2 and then kept at constant temperature with
occasional shaking. The reaction was followed by the decrease
in pressure and was terminated when the pressure failed to
decrease any further.

Hydroquinone was introduced as a free radical scavenger
in cases where polymerization was possible.

The Diels-Alder Adduct with 3-methyl-2-cyclopentenone
(Cliff-Dow Charcoal Co.) was prepared by the general procedure
above with 20 mls of butadiene, 15 g of 3-methyl-2-cyclopentenone
and 0.1 g of hydroquinone. The temperature was kept at
60°C and the pressure at 88 lbs/in^2 for 87 hours. No decrease
in pressure was observed. The reaction was repeated with
45 mls of butadiene, 30 g of 3-methyl-2-cyclopentenone and
100 mls of diethyl ether with 0.5 g of hydroquinone at 100°C
and 71.5 lbs/in^2 for 23 hours. No reaction occurred at this
temperature either.

1-Cyano-1-Cyclohexene was prepared by a procedure described
previously (16).

The Diels-Alder Adduct of 1-cyano-1-cyclohexene was
prepared following the general procedure above with 18 mls of

butadiene, 16 g of 1-cyano-1-cyclohexene and 0.5 g of hydro-
quinone. The reaction temperature was 88°C and the reaction
was terminated after 181 hours when the pressure fell to
40 lbs/in^2. The mixture was treated with Norite (Activated
Charcoal) and filtered through celite (filtering aid), flash
evaporated and distilled. (BP 105-108°C/40 torr) The NMR
analysis was identical to that of 1-cyano-1-cyclohexene.

The Diels-Alder Adduct of p-Benzoquinone was prepared
by following the above general procedure with literature
modification (17). The reaction was performed with 30 g of
benzoquinone, 25 mls of butadiene in 175 mls of benzene. The
mixture was kept at room temperature for 3 weeks. The yield
was 15 g or 33.4%.

The preparation of cis-Δ^6-Octalin-1,4-dione has been
described previously (18). The yield was 9.4 g or 66%.

Cis-Bicyclo[4.4.0]-2-decene was prepared from the above
dione via a tosylhydrazone reduction with sodium borohydride
in methanol and also with sodium borohydride in N,N-dimethyl
formamide (DMF) and sulfolane. In each case no product was
isolated, due, apparently, to the extreme insolubility of
the di-tosylhydrazone.

The Stobbe Adduct of Diethyl Succinate and Cyclohexanone
was prepared as described previously (18) with 28 g of potassium,
60 g of cyclohexanone, and 150.5 g of diethyl succinate in
500 mls of tert-butyl alcohol. The yield was 101 g or 74.5%.

The preparation of $\Delta^{1,5}$-Bicyclo[4.3.0]nonen-2-one has
been described previously (19) via a polyphosphoric acid

acylation of the above acid and an acetic acid decarboxylation
on the reaction mixture. The yield was 10.4 g or 24%.

1-Methyl-Cis-Bicyclo[4.3.0]Nonan-2-one was prepared
via a lithium amide condensation of the lithium enolate of
the above α,β-unsaturated ketone with methyl iodide, following
a procedure described previously (20). The procedure was
modified in that 50 mls of liquid ammonia were used instead
of 150 mls. The yield was 4.1 g or 83%. The NMR analysis
indicated two isomers were present: the 1-methyl and the
3-methyl compounds (singlet δ = 0.92 ppm and a doublet
δ = 0.74 ppm). I.R. analysis indicated the presence of an
α,β-unsaturated carbonyl ν = 1690 cm^{-1} along with a tetra
substituted double bond ν = 1620 cm^{-1}. GC analysis indicated
two major products (RT = 25.5 minutes and 27.5 minutes, 9.5'
4% Carbowax 20 M on 60/80 Firebrick, column 190°, injector
200°, det. 205°). The compounds were resolved through
recrystallization of their 2,4-dinitrophenylhydrazones (2,4-
DNP).

1-Methyl-Cis-Bicyclo[4.3.0]Nonane was prepared by a
Wolff-Kishner reduction of the 2,4-DNP above (14). No product
was isolated.

Bicyclo[4.4.0]-2-Decanol (cis and trans) was prepared
by a sodium borohydride reduction (21) of bicyclo[4.4.0]-2-
decanone (cis and trans). The yield was 27.4 g or 75.8%.

1-Carboxyl-Cis-Bicyclo[4.4.0]Decane was prepared by a
Wagner-Meerwein rearrangement of the above alcohol (22). The
yield was 14.1 g or 43.5%

<u>1-Carbinol-Cis-Bicyclo[4.4.0]Decane</u> was prepared by a
lithium aluminium hydride (L.A.H.) reduction of the above
acid (23). The yield was 0.85 g or 49.5%.

<u>1-Carbinol-Cis-Bicyclo[4.4.0]Decane-p-Toluene Sulfonate</u>
was prepared from the above alcohol (24). The yield was 1.3 g
or 90%.

<u>Cis-Bicyclo[3.3.0]-2-Octene</u> was prepared by a potassium
rearrangement of 1,3 cyclooctadiene (6). The yield was 18 g
or 78%.

<u>1-Carboxyl-Cis-Bicyclo[3.3.0]Octane</u> was prepared by a
Wagner-Meerwein rearrangement of the above alkene (6, 22).
The crude yield was 2.5 g or 9.7%.

<u>$\Delta^{1,5}$-Bicyclo[4.3.0]Nonen-7-one</u> was prepared as $\Delta^{1,9}$-<u>cis</u>-
bicyclo[4.3.0]nonen-7-one except that the distillation was
carried out at 34 torr. The yield was 2.4 g or 57%.

<u>Tricyclo[3.3.1.0^{1,5}]Nonan-2-one</u> was prepared by photolytic
rearrangement of the above ketone as described previously
(25, 26). The product was not isolated; however, its possible
presence was detected, indicated by IR absorption at ν = 3160
cm^{-1} and the NMR multiplet at δ = 0.6 ppm. The fraction of
interest was isolated from the residual tar by sublimation at
2.2 torr.

<u>$\Delta^{1,5}$-Bicyclo[4.3.0]Nonene</u> was prepared from 33 g of indan
via a Birch-type reduction with lithium in ethylenediamine
(27). The yield was 19.5 g or 59%.

<u>Tricyclo[4.3.1.0^{1,5}]Decane</u> was prepared by the Simmons-Smith
reaction (28) using the Le Goff modification (29) with the
above alkene. No product was isolated or evident from the G.C.

Results

The extent of exchange for each compound is given as a
percentage of the total deuterium in Table II, along with the
conditions and ratio of deuterium to hydrocarbon in the gas
phase.

The deuterium distributions which are given as d_n and
indicate the amount of deuterium in n positions within a
molecule. These distributions must be considered in terms
of the trends within the distributions produced by each
molecule and not of the specific numbers. This is due to
the small amount of exchange and the resulting accuracy of
measurement of the mass spectral peak intensities.

The distributions shown for compound VI were arrived
at by correcting the standard sample for the P-15 peak and
its resulting isotopic content. This was necessary in order
to obtain distributions which reflect a positive amount of
deuterium. The exchange pattern was not effected by the
correction, but only the specific magnitude of the intensity.

The standard (compound V) exhibits "smearing" in the
region of the d_8 maximum and it does not exhibit the clear
break which has been reported (6, 7). This can be accounted
for by considering that the previous researchers exchanged
the compound at less than 100°C and reported data were
obtained at 144°C. This type of smearing with respect to
temperature has been reported (7).

TABLE II[a]

Compound	I	II	III	IV	V	VI	VII
Flow Rate[b]	11.6	11.7	19.6	11.7	16.5	11.7	17.2
Saturator Temp.	103°C	103°C	67°C	104°C	56°C	104°C	76°C
Furnace Temp.	139°C	134°C	135°C	158°C	144°C	142°C	149°C
D_2/Hydrocarbon[c]	13.3/1	11.8/1	13.3/1	7.6/1	12.9/1	19.1/1	28.5/1
% exchange	1.02%	0.21%	15.1%	0.18%	0.25%	9.5%	12.6%
(d_0	0.00	0.00	0.00	0.00	0.00	0.00	0.00)
d_1	0.0637	0.0001	0.00	0.0024	0.00	0.0382	0.2159
d_2	0.001	0.0001	0.00	0.0003	0.0014	0.0645	0.004C
d_3	0.0109	0.0027	0.0011	0.0052	0.0051	0.1786	0.0316
d_4	0.0066	0.0002	0.0042	0.0057	0.0002	0.1104	0.1364
d_5	0.0054	0.00	0.00	0.00	0.0006	0.0544	0.0486
d_6	0.0069	0.00	0.0621	0.00	0.0013	0.0447	0.0429
d_7	0.0075	0.0002	0.0121	0.0001	0.0010	0.0399	0.0578
d_8	0.0062	0.0003	0.0662	0.0055	0.0012	0.0512	0.0614
d_9	0.0065	0.0005	0.0175	0.0006	0.0012	0.0436	0.0848
d_{10}	0.0082	0.0000	0.1349	0.0000	0.0005	0.0688	0.1066
d_{11}	0.0065	0.0004	0.0105	0.0000	0.0012	0.0545	0.0876
d_{12}	0.0053	0.0000	0.0640	0.0000	0.0015	0.0656	0.1492
d_{13}	0.0060	0.0085	0.0042	0.0145	0.0018	0.0825	0.0727
d_{14}	0.0059	0.0006	2.0857	0.0142	0.0156	0.0656	0.6975
d_{15}	0.0050	0.0011	0.0000	0.0051		0.0742	0.1136
d_{16}	0.0062	0.0003	0.0064	0.0012		0.0692	
d_{17}	0.0066					0.0615	
d_{18}	0.0062						

[a]The values listed are accurate to ±.0003
[b]The flow rate is expressed in ml/min.
[c]The ratio is that of the partial pressures in the gas phase.

Compound III and IV both have a maximum at d_4 indicating they both easily exchange four hydrogens. Compound III has a maximum at d_6 whereas IV has one at d_7 but none at d_6. There are maxima at d_8 and d_{10} in III whereas compound IV has no other maxima except d_{13} and d_{14}. Compound III also has a distinct peak at d_{14} and indeed is the major component in the distribution. There is also a maximum at d_{12} in III.

In V there is a sharp break after d_3 whereas in III and IV the break occurs after d_4. The middle range value (d_8 for V), which has been interpreted as exchange of all hydrogens on the side bearing the bridgehead hydrogens, is not present in III. Instead, III has a maximum at d_8 as does IV. In the case of IV, however, this also could correspond to the exchange of all hydrogens on one side. The maximum at d_{14} in V indicates the exchange of all the hydrogens but the d_{14} maxima for III and IV are two hydrogens less than sixteen.

In compound I and II there are sharp breaks after d_3 with breaks after d_4 also. The maxima at d_7 and d_{10} in I are not present in II although II has maxima at d_9 and d_{11}. A large maximum at d_{13} is present in II and a small maximum at d_{13} is present for I. In I there is exchange up to d_{18} with a maximum at d_{17} and in II there is no exchange past d_{16} with a d_{15} maximum. In both I and II the maxima are small and not distinct except for the d_{13} maximum in II.

There are d_3 maxima in I, II and V; however the maxima corresponding to d_8 in V is not present in II (d_9) although it

is in I (d_{10}). The large maximum corresponding to total
exchange that is present as d_{14} in V is not present in either
I or II (d_{18}).

In the methyl systems (VI and VII) the first sharp break
occurs at d_4 for VI and VII, but VI also has a large maximum
at d_3. There are maxima at d_{10} in both compounds but in VII
the maximum is more pronounced. The d_8 maximum in VI is not
present in VII; however, there is a substantial amount with
no break following it. There are maxima at d_{12} and d_{13} in
VII and VI, respectively, along with d_{14} in VII and d_{15} in
VI, reflecting some differences in the ring sizes. There is
also a maximum at d_{15} for VII corresponding to the exchange
of all but two hydrogens. In VI there are small amounts at
d_{16} and d_{17} corresponding to the exchange of all but one and
all hydrogens respectively.

In 1-methyl-cis-bicyclo[3.3.0]octane (6) there are maxima
at d_{11} corresponding to the exchange of all but two hydrogens
at 120°C and at d_7 which has been interpreted as the exchange
of the hydrogens on the side bearing the methyl group at 30°.
The corresponding maximum at d_8 for VII is present but not
the d_9 maximum for VI. The maximum at d_{11} for 1-methyl-cis-
bicyclo[3.3.0]octane (6) can be equated with a d_{14} maximum
in VII. However, although present, this is smaller than that
at d_{13}. In VI the expected results would lead to a maximum
at d_{17} but, although present, it is not the major component
at higher exchange. The d_{15} maximum is the major one in VI
for multiple exchange.

There is a maximum at d_{10} in both III and VII but none in IV. The d_8 maximum is present in all three but it is small in VII. The d_{14} maximum is present in III and VII and in small amounts in IV.

With the bicyclo[4.4.0]decane systems, I, II and VI, there is a maximum at d_3 in all compounds. The only major breaks in II are at d_{13} and d_{15}. In I and VI there are small breaks at d_6, d_{10} and d_{13}. Compound I has a maximum at d_7 which VI does not have. The break at d_{15} in VI does not occur in I, but instead a small d_{17} maximum is present. This is also present in I but is small.

Isomerization

Of the compounds exchanged only one isomerized. That was compound I which isomerized to yield 2.8% of II. The mass spectrum was not obtained on the isomerized sample. The others were exchanged at various temperatures and no isomerization was detected. Although IV was expected to isomerize to III, at temperature as high as 161°C on a fresh catalyst no isomerization was detected. The highest temperature for which the isomerization were attempted are: 146°C (for I), 135°C (for III), 161°C (for IV), 149°C (for VI) and 146°C (for VII).

Discussion

Synthetic Problem

Of the synthetic routes available for the synthesis of
the bridgehead methyl compounds, the Michael addition to the
enimine, Grignard conjugate addition and subsequent reduction
is favorable, especially in the case of 1-methyl-cis-bicyclo-
[4.4.0]decane. The favorability is due to the availability
of starting material, the overall number of reactions necessary
and the low yield reactions being at the end of the synthetic
route.

The synthetic route utilizing the Wagner-Meerwein
Rearrangement and subsequent reductions of the carboxylic
acid function suffers from three reactions where the yields
are low. It is, however, still a good route due to the
availability of reagents.

In the synthesis of 1-methyl-cis-bicyclo[4.3.0]nonane
the route described above utilizing the Grignard conjugate
addition offers less reactions than other routes but suffers
from low yields. The route employing a Stobbe condensation
offers advantages over the former method. These advantages
include the high yield of the Stobbe product along with a
short reaction time (10 minutes) and, if needed, larger quanti-
ties of product. The major problem with the synthesis is the
polyphosphoric acid acylation which under reported conditions
gives a 46% yield (20). However, if scaled up, the temperature
becomes difficult to hold at 100°C and thus reduces the yield.
This problem can be partially counteracted by reducing the

reaction time to 2 hours. The condensation with methyl iodide

yields two products which could be separated after reduction

by preparative G.C. Another possibility is the introduction

of a blocking group prior to the methyl iodide condensation

to prevent the formation of one of the isomers.

The synthesis of these compounds by the Diels-Alder

cyclization with butadiene can be accomplished but the

conditions are so drastic that special apparatus is required

(30).

The synthesis of the tricyclic systems has been accom-

plished for tricyclo[4.4.1.0^{1,6}]undecane (31) and tricyclo-

[4.3.1.0^{1,5}]decane (25, 26, 31, 32). Of the synthetic

methods, the most feasible one seems to be the diazomethane

reaction (32), which only involves two steps. The preparation

of tricyclo[3.3.1.0^{1,5}]nonane, which has not yet been prepared,

should be possible from the diazomethane reaction with

$\Delta^{1,5}$-bicyclo[3.3.0]octane prepared by reduction of the ketone

resulting from the polyphosphoric acid acylation of the Stobbe

adduct derived from cyclopentanone and diethyl succinate.

The interest in cyclopropanated bridgehead compounds

arises from attempting to answer the question of whether

cyclopropanes can _initiate_ catalytic exchange with deuterium

without actually exchanging. They could also be helpful

in determining whether the exchange can occur on both rings

of fused bicyclic hydrocarbons without exchanging the hydrogen

at the bridgehead.

Distributions

Throughout the samples of the bicyclo[4.3.0]nonanes there is a maximum at d_4 and d_8. This indicates a direct competition between a five and a six membered ring in the exchange reaction, the six membered ring exchanges more easily. The increased flexibility of the six membered ring will account for this observation.

By comparing the observed results from Table II to those predicted by the "roll over" and the "π-allyl" mechanism in Table I, it is clear that although there are maxima which agree with the predicted values, there are also deviations from them. These deviations occur where large maxima should be, such as d_{18} in the bicyclo[4.4.0]decanes, I and II, the distinct break at d_{14} in III and the substantial peaks at d_{15} in VI, d_{14} and d_{15} in VII.

From the over-all appearance of the exchanged samples it would appear that the molecules exchange by some mechanism which involves two hydrogens since the trend in the maxima is to occur in sets of two. The best example of this is III which has maxima at d_4, d_6, d_8, d_{10}, d_{12}, and d_{14}. This is true of the other samples also except for breaks in the pattern such as II with maxima at d_9, d_{11}, d_{13} and d_{15}. This break could involve the bridgehead methine hydrogen and result in the distribution maximizing at odd integers instead of even ones.

Compound III has an interesting distribution in light of the "roll over" mechanism with a break at d_{14} as was predicted.

However, there is a substantial amount of d_{15}. According to the "roll over" mechanism as shown in Figure VI the hydrogen on the middle methylene in the trimethylene bridge system should be left (6). Such a large maximum cannot be accounted for by a second residence on the surface.

Compounds VI and VII have distributions which show an influence of the methyl group. The distribution of VI has maxima similar to both I and II with maxima at d_{13} and d_{15} as in II along with d_{10} and some d_{17} as in I. The intensity of the peaks at d_{16} and d_{17} are not as strong as the d_{15}, however. This would indicate that the methyl is influencing the hydrogens next to it, along with the over-all distribution. In comparing the cis-systems VII is more similar to III than VI is to I. This is shown by the d_{10}, d_{12} and d_{14} maxima in VII and III. In VI and I the similar maxima are at d_{13} and d_{10}. The break at d_{14} in VI may indicate that one hydrogen is more difficult to exchange. Initially, it might be thought that the methyl group would hinder the exchange of the adjacent hydrogen on the six membered ring. However, when compared to the d_{11} maximum in 1-methyl-cis-bicyclo[3.3.0]-octane the meaning becomes vague.

The similarities in the distribution patterns of the bicyclodecanes and the bicyclononanes along with the lack of exchange of all the hydrogens indicates that a symmetrical intermediate such as the one proposed for V (7) is not involved in these compounds. This is further demonstrated by the lack of isomerization of IV to III and I to II.

Of the two possible mechanisms the "π-allyl" does not correspond to most of these results. Predictions based upon the "roll over" mechanism correspond to the data better than those of "π-allyl", but do not match well in many respects.

Conclusion

In comparing the mechanisms of interest to the results
for the bicyclononane systems it is clear that the process
which is occurring is more complicated then originally
thought. It appears that two distinct processes could be
occurring in these systems since there appears to be some
difficulty in exchanging the hydrogens on the bridging
(methine) carbons. This process could be explained by a
difference in the mechanism in propagating from one ring to
the other or by the involvement of a "double bond" in changing
from one diadsorbed specie to another, since the double bond
on the bridging carbon is sterically less favorable. A
lot of importance has been placed on the initial formation
of an α,β diadsorbed specie (Figure II) to initiate the
exchange process. Since the cyclopentyl ring is naturally
in a conformation to form this specie, the initial adsorption
should occur on the five membered ring; yet exchange occurs
initially on the six membered ring as shown by d_4 and d_8 maxima.

The process which is occurring with the bicyclodecanes
is difficult to resolve since there are no sharp breaks in
the distributions throughout the series, again indicating
more ready exchange and propagation from one ring to the other.

In comparing the d_3, d_6 (and d_3, d_5) maxima to the d_4, d_8
maxima in III, IV and VII it appears that not only does the
molecule adsorb more easily on the six membered ring but also
exchanges the other side of the ring more easily.

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