under vacuum and connected through grease traps to 14/35 joints, which could then be connected to a vacuum manifold through a cow. Reaction mixtures, containing a known amount of purified dodecane, were added to the sample tube *via* a calibrated syringe, and the samples were subjected to five freeze–thaw outgassing cycles on the vacuum manifold at an ultimate pressure of about 10^{-4} mm. After sealoff, the tubes were irradiated for the desired period of time in a "merry-go-round" rotating sample stage apparatus, with a Hanovia 450-W medium-pressure mercury lamp whose output was filtered (Corning C.S. Number 7-83) to pass only the 3660-Å region.

Actinometry was carried out with potassium ferrioxalate in the standard manner.[20] Reproducibility of quadruplicate (or more) samples throughout the period of a run was $\pm 2\%$ in general and often $\pm 0.5\%$.

Yields of **2** and **3** measured gas chromatographically relative to dodecane were corrected for differences in detector response. Analyses were performed on 0.25 in. × 6 ft Carbowax 20M columns, 5–10% on either Chromosorb P or Chromosorb W. It was shown that both isomers were stable to the analysis conditions and that **1** did not give **2** and **3** by pyrolysis during analysis.

Registry No.—**1**, 7698-06-8; **2**, 19191-10-7; **3**, 19191-11-8.

Acknowledgment.—I wish to thank Research Corporation for funds used for the purchase of a gas chromatograph, the Petroleum Research Fund for support of this work through Grants 519-G-1 and 3031-A-4, Mr. G. W. Sovocool for assistance with actinometry, and Dr. Stephen Shrader for mass spectrometric analyses and helpful discussions.

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Homogeneous Catalytic Deuteration of Olefinic Double Bonds[1]

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Received September 10, 1968

The specific deuteration of olefins using tris(triphenylphosphine)rhodium(I) chloride (A) as a homogeneous catalyst has been investigated. Seventeen *n*-monoolefins were deuterated and the distribution and the vicinal positions of the deuterium atoms were located by mass spectrometry. Deuterium adds specifically across the double bonds in *n*-monoolefins and the reaction proceeds to completion in a reasonable time. The mass spectral fragmentation patterns for the deuterioalkanes formed by this specific labeling technique can be used to locate the deuterium atoms and thus to determine the position of the double bond in the original olefin.

For some time, we have been interested in the location of double bonds in olefins for characterization of olefin fractions of shale-oil distillates. About one-third of Green River shale-oil middle distillate (C_{12}–C_{20}) consists of olefins. Knowledge about the type of olefins and the positions of the double bonds in the olefins would be an aid in their utilization.

Young and coworkers[2a] have demonstrated the connection between the formation of a hydride intermediate and homogeneous hydrogenation by using a new compound, tris(triphenylphosphine)rhodium(I) chloride (A). They state that the compound can be used as a catalyst for the reduction of compounds containing double or triple bonds. In a later article, Osborn and coworkers[2b] studied the properties and reactions of A and proposed a mechanism for the hydrogenation of olefins and acetylenes. Birch and Walker[3,4] used A as a homogeneous catalyst for hydrogenation and deuteration. They found that cyclohexene, methyl oleate, methyl linoleate, and ergosterol were deuterated without introduction of additional deuterium. Djerassi[5] and Bielmann[6] have used A as a homogeneous catalyst for the deuteration of steroids, and Zeeh[7] used this homogeneous catalyst to deuterate hydrindanones.

This homogeneous catalytic research is of interest because the heterogeneous, catalytic deuteration of straight-chain olefins is an unsatisfactory method for the selective introduction of deuterium.[8] Heterogeneous catalysts cause double-bond migration and/or exchange reactions between the chemisorbed olefin and the adsorbed deuterium resulting in unspecific labeling.[9,10] For example, Nguyen and Ryhage[11] reported the deuteration of methyl oleate using Adam's platinum catalyst. Their mass spectral results showed a series of molecular ion peaks whose intensities decrease with increasing mass number, due to unspecific labeling.

This paper reports the specific deuteration of 17 *n*-monoolefins using deuterium and A as a homogeneous catalyst. Mass spectrometry was used to determine the location of the deuterium in the alkanes formed.

Monoolefins are readily deuterated using deuterium and A as a homogeneous catalyst to give the corresponding dideuterioalkanes. For example, 1-tridecene was deuterated without difficulty in less than 2 hr at room temperature and slightly above atmospheric pressure. Examination of the mass spectra of the deuterated tridecane showed the addition of two deuteriums to the monoolefin with little evidence of unspecific labeling.

When a heterogeneous catalyst, such as platinum black, was used for the deuteration of 1-tridecene,

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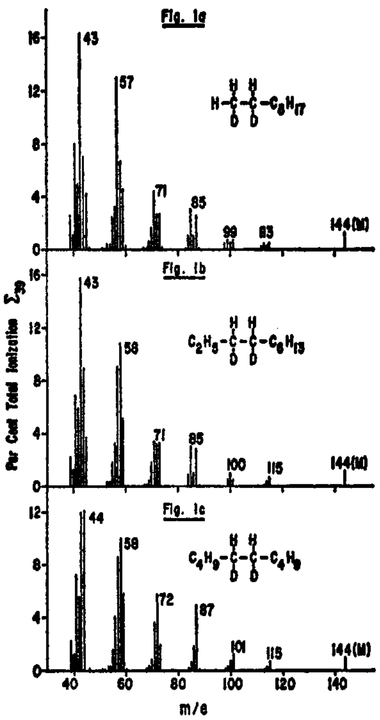

Figure 1.—Mass spectra of vicinal dideuteriodecanes: (a) decane-1,2-d_2, (b) decane-3,4-d_2, and (c) decane-5,6-d_2.

unspecific labeling occurred. Mass spectrometry showed the product to contain from zero to as many as 17 deuterium atoms per molecule.

Some of the olefins deuterated using the tris(triphenylphosphine)rhodium(I) chloride catalyst are as follows: *cis*-2-decene, *trans*-2-decene, *cis*-3-decene, *cis*-4-decene, *cis*-5-decene, *trans*-5-decene, and all the α olefins from decene through eicosene inclusively. In each case, the corresponding dideuterioalkane was the product obtained.

The ability to locate the position of the double bonds in olefins requires that two deuteriums per double bond be added and that the deuterium add specifically to each carbon atom originally joined by the double bond. Mass spectrometry showed that two deuterium atoms per double bond were added when the homogeneous catalyst A was used.

That the deuterium adds specifically to the carbon atoms originally joined by the double bond can be shown by examination of the mass spectra of selected, deuterated decenes. Figure 1 shows the mass spectra of the products from the homogeneous deuteration of 1-decene, *cis*-3-decene, and *cis*-5-decene. If the deuterium adds specifically to the double bond in each of these decenes, these are the spectra of decane-1,2-d_2, decane-3,4-d_2, and decane-5,6-d_2, respectively. This will be demonstrated later.

For correlation of the mass spectra of these vicinal dideuterio-*n*-alkanes with their structure, we will assume that fragment ions are formed by simple carbon–carbon bond cleavage of the parent ion. Using this assumption, the fragmentation peaks expected from the three selected deuterated decanes are as follows: for decane-1,2-d_2 (C_8) 113, 115, (C_7) 99, 101, (C_6) 85, 87, (C_5) 71, 73, (C_4) 57, 59, (C_3) 43, 45; for decane-3,4-d_2 (C_8) 115, (C_7) 100, 101, (C_6) 85, 87, (C_5) 71, 73, (C_4) 57, 59, (C_3) 43, 44; for decane-5,6-d_2 (C_8) 115, (C_7) 101, (C_6) 87, (C_5) 72, (C_4) 57, (C_3) 43.

Comparison of the peaks shown in Figure 1 with the expected peaks listed above shows the assumptions to be correct for some regions of the mass spectra. For example, in the spectra of the deuterated products, the fragment peaks having six, seven and eight carbon atoms, shown in Figure 1, occur where the above list predicts they should. Also, they occur either singly or in pairs just as the assumption of simple carbon–carbon bond cleavage would predict. Thus the C_6 ions for decane-1,2-d_2 and for decane-3,4-d_2 occur equally at *m/e* 85 and *m/e* 87, whereas the C_6 ions for decane-5,6-d_2 occur only at *m/e* 87. Similar observations and conclusions are possible for the fragments occurring at the C_7 and C_8 regions in these three spectra. Because cleavage should occur from either end of the molecule with equal ease, peaks such as 100 and 101 in Figure 1b should be of equal size. Examination of the Figure 1b shows that this is not the case. The fragment ion peak from the decane-3,4-d_2 having a mass of 101 has as its source the fragment produced by cleavage between the 7 and the 8 carbon atoms. The fragment ion peak of mass 100 has two sources: the fragment produced by cleavage between the 3 and 4 carbon atoms and the fragment produced from the 101 fragment ion by hydrogen loss. Therefore, the peak at *m/e* 100 is larger than the peak at *m/e* 101. The peak at *m/e* 99 is produced by hydrogen loss from the fragment ion of mass 100. Hydrogen loss from the major fragment peaks accounts for peaks such as those at *m/e* 84, 86, 98, 100, 112, and 114 in Figure 1a, and peaks 84, 86, 99, part of 100, and 114 in Figure 1b, etc. Peaks produced by hydrogen loss occur in the mass spectra of alkanes. For example, in the mass spectra of *n*-decane, simple carbon–carbon bond cleavage accounts for the peak at *m/e* 113, 99, etc., but the peaks at *m/e* 112 and 98, etc., are produced from the 113 and 99 fragment ions, respectively, by hydrogen loss. Although, for the fragment ions with five or less carbons, the ratios of fragment ion peaks cannot be predicted by simple carbon–carbon bond cleavage, the fragment ion having more than half the carbon atoms (C_6–C_8 fragment ions) are sufficient to locate the deuterium atoms.

The conclusiveness of the data for locating the deuterium atoms for the other deuterated alkanes prepared is as positive as that shown for the three dideuteriodecanes whose spectra are shown in Figure 1.

Additional evidence for the specificity of the deuteration reaction when using the homogeneous catalyst A can be obtained from the nmr spectra of the deuterated alkanes. Calculations made from the nmr spectra of the decane-1,2-d_2 showed the presence of only five methyl hydrogens indicating that one of the deuteriums was located on one of the terminal carbon atoms. Similar calculations made on the spectra of decane-2,3-d_2, decane-3,4-d_2, and decane-4,5-d_2 showed the presence of six methyl hydrogens indicating no deuteriums present on the terminal carbon atoms.

Examination of the relative rates of the reaction of the *cis* and the *trans* olefins should suggest a possible mechanism for homogeneous catalytic reduction. That a faster reaction rate was observed for the *cis* olefin suggests that the rate-determining step may be the formation of the olefin complex as suggested by Osborn.[2b] He proposed that the initial step is the formation of $RhCl(PPh_3)_2H_2$ (solvent), displacement of the solvent by the olefin, and stereospecific *cis* transfer of the bound hydrogen to the olefin in an actual intermediate or in an activated complex.[12] He postulated that the rate-determining step in the reaction is the displacement of the solvent from the complex and the complexing of the olefin. If the olefin in the complex occupies a position *cis* to both rhodium–hydrogen bonds as Osborn suggests we suggest that the *trans*-olefins probably do not form the complex as readily as the *cis* isomers. We suggest that the formation of the complex with the *trans* olefins is slower because of the orientation of the bulky groups of the *trans* isomers and possibly a suitable alignment of these groups with respect to the double bond may be necessary to form the complex.

The specific labeling of the double-bonded carbons of olefins is a potentially useful device in an analytical scheme for characterizing mixtures of olefins. Present indications are that mass spectra of the alkane-d_2 compounds reflect the location of the deuterium atoms so that characterization of single compounds or simple mixtures is possible. Work is proceeding on the development of a method for the analysis of olefins using homogeneous deuteration and mass spectrometry.

Experimental Section

The deuteration equipment was similar to the hydrogenation apparatus described by Joshel.[13] A Teflon-coated[14] magnet driven by an external motor was used as a stirrer. The reaction flask was equipped with a side arm that was fitted with a silicone-rubber plug which enabled the withdrawal of samples with a syringe during deuteration.

Gas chromatographic separations were performed on an Aerograph Autoprep Model A-700 instrument using a 0.25 in. × 30 ft column of 15% Tween 20 on Chromosorb P. All mass spectra of the deuterioalkanes were obtained on a Consolidated Electrodynamics Model 21-103 mass spectrometer at an ionization voltage of 70 eV. Nuclear magnetic resonance spectra on selected deuterioalkanes were obtained on a Varian HA-100.

The homogeneous catalyst tris(triphenylphosphine)rhodium(I) chloride was prepared from rhodium chloride trihydrate and triphenylphosphine as described by Young.[2a] The deuterium used at first was 98 mol %, but later deuterations were performed using 99.5 mol % deuterium. The olefins were of 98% or better purity as determined by gas–liquid partition chromatography.

The heterogeneous catalysts such as platinum black and palladium were prepared from chloroplatinic acid and palladium chloride, respectively, by reduction with sodium borohydride in the reaction flask just prior to use.

About 0.40 g of the olefin was weighed into the reaction flask and diluted with 20 ml of benzene. Catalyst A was added in the amount of 15 wt % of the olefin to be reduced. The deuteration apparatus was connected to a manifold and the system was alternately evacuated and filled four times with deuterium gas, at which time the magnetic stirrer was turned on. Pressure was maintained at slightly above atmospheric pressure (positive pressure of about 10 mm).[15] The deuteration was monitored periodically by withdrawing a small sample of the solution with a syringe and analyzing the solution by gas–liquid partition chromatography. The heterogeneous catalytic deuteration was performed using similar conditions as the homogeneous catalytic deuteration.

Registry No.—Decane-1,2-d_2, 19165-56-1; decane-3,4-d_2, 19165-57-2; decane-5,6-d_2, 19165-58-3; tris(triphenylphosphine)rhodium(I) chloride, 14694-95-2.

Acknowledgment.—The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U. S. Department of the Interior, and the University of Wyoming.

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[15] Atmospheric pressure at this altitude is approximately 585 mm.

Ozonolysis. Steric Effects in the Aldehyde

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Received August 26, 1968

The ozonolysis of 1-olefins results in little or no cross-ozonide formation. Ozonolysis of 3,3-dimethylbutene-1 in the presence of added aldehydes with varying substituent size indicates that both aldehyde substituent size and concentration have a pronounced effect on the ozonide *cis–trans* ratio in the new ozonide produced. Larger substituent size and lower aldehyde concentration lead to a higher percentage *cis*-ozonide. The effect of substituent size on the ozonide *cis–trans* ratio is essentially the same whether the substituent is located in the olefin or the aldehyde.

A number of experimental facts which suggest that some modification to the Criegee[2] mechanism of ozonolysis should be considered have now been reported. Perhaps the most striking of these observations is the dependence of cross-ozonide *cis–trans* ratios on olefin stereochemistry.[3–6] These observations have stimulated several new suggestions regarding the mechanism. One, in the form of a working hypothesis, has as its

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