[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. V. Stereochemistry

BY MARTIN CARDEW AND ROBERT L. BURWELL, JR.

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The addition of deuterium to *cis*- and *trans*-2-butene catalyzed by chromium oxide gel at about 0° proceeds by *cis*-addition and leads to the formation of *meso*- and *dl*-butane-2,3-d_2, respectively. The intrusion of any trans-addition process does not exceed 10%. The hydrogenation of 1,2-dimethylcyclohexene at 100° is less stereoselective; *cis*- and *trans*-dimethylcyclohexane are formed in a ratio of about one. The lowered stereoselectivity probably results from isomerization of 1,2- to 2,3-dimethylcyclohexene or to methyl methylenecyclohexane before hydrogenation. The latter two compounds could hydrogenate to either *cis*- or *trans*-dimethylcyclohexane by *cis*-addition. (+)3-Methylhexane undergoes isotopic exchange with deuterium accompanied by a small amount of racemization. The racemization probably results from that process which leads to the formation of extensively multiply exchanged species in isotopic exchange.

This paper reports certain aspects of the stereochemistry of the interaction of hydrocarbons and deuterium or hydrogen on chromium oxide gel. We have studied addition of deuterium to *cis*- and *trans*-2-butene, addition of hydrogen to 1,2-dimethylcyclohexene and isotopic exchange between (+)3-methylhexane and deuterium.

Experimental

Materials.—1,2-Dimethylcyclohexene was prepared following Chiurdoglu[53] by the addition of methylmagnesium iodide to 2-methylcyclohexanone followed by iodine catalyzed dehydration of the resulting carbinol at reflux. The olefinic product, as analyzed by gas chromatography (tricresyl phosphate), consisted of 73% 1,2-dimethylcyclohexene, 24% 2,3-dimethylcyclohexene and 3% methylenemethylcyclohexane. Fractional distillation afforded fractions which were nearly pure 1,2-dimethylcyclohexene (~98%), b.p. 136°, and fractions rich in the 2,3-isomer. The preparation of (+)3-methylhexane has been described (paper I, ref. 40). The butenes were Phillips Petroleum Company Pure Grade.

Technique.—Procedures have been described in the previous papers of this series. However, where feeds of mixtures of hydrocarbons in deuterium were desired, they were prepared by use of a motor-driven hypodermic syringe injector. Catalyst samples amounted to about 1.5 g. Hydrogen flow rates are given in cc. (STP) per gram of catalyst per min.

Results

A. Deuterogenation of 2-Butenes.—Simple addition of deuterium to 2-butene would form butane-2,3-d_2 which could exist in two stereoisomeric forms, *meso*- and *dl*-. Table I presents results of two such runs. All olefin was consumed. A number of other runs gave results consistent with these. In particular, runs at 0 and 30° gave products the infrared spectra of which were nearly indistinguishable from that of the run with *trans*-2-butene in Table I.

TABLE I

DEUTEROGENATION OF 2-BUTENES

Run	A *cis*-2-Butene	B *trans*-2-Butene
D_2, cc./min.[a]	2.6	2.7
Butene, cc./min.[a]	1.1	0.7
Temp., °C.	0	−19
D_1, % in product	2.1	nil
D_2, %	92.5	91.0
D_3, %	5.2	8.5
D_4, %	0.3	0.5

[a] Per gram of catalyst.

Meso- and L-butane-2,3-d_2 have been prepared by Helmkamp[54] by stereospecific syntheses. Dr. Helmkamp kindly furnished us with the infrared spectra which were the basis of our analyses. In addition, comparisons were run between two of our products and Helmkamp's samples on the Perkin–Elmer double beam spectrometer at his laboratory. The product of the addition of deuterium to *cis*-butene was *meso*-butane-d_2 and to *trans*-butene, *dl*-butane-d_2. We could detect no evidence for any product of *trans*-addition. However, our products contained several % of butane-d_3 while Helmkamp's contained several % of butane-d_1. We believe that we may reasonably conclude that the dideuterobutanes in our products are the results of *cis*-addition to the degree of 90% or better.

These results imply that, at temperatures of about 0°, the rate of addition of deuterium is much greater than that of *cis–trans* isomerization. Results with catalysts whose activity was not quite adequate for complete deuterogenation support this. In a run at 0° with 16% of *cis*-2-butene unreacted, there was 2% of *trans*-2-butene. In a run at 30° with 8% of *trans*-2-butene unreacted, there was less than 1% of *cis*-2-butene.

B. Hydrogenation of 1,2-Dimethylcyclohexene.—Investigation of the stereochemistry of hydrogenation of 1,2-disubstituted ethylenes requires the use of deuterium but with tetrasubstituted ethylenes one may employ conventional hydrogenation.[22] We have studied the hydrogenation of 1,2-dimethylcyclohexene, *cis*-addition to which would give *cis*-1,2-dimethylcyclohexane. Unfortunately, because of the necessarily rather high boiling point of any suitably tetrasubstituted ethylene, one cannot study the vapor phase hydrogenation at temperatures much below 100° at hydrogen–hydrocarbon ratios similar to those which we have usually employed.

Several hydrogenations of 1,2-dimethylcyclohexene at 100° with hydrogen flow rates of about 3 cc. per g. of catalyst per min. and with hydrogen–hydrocarbon ratios of about 6 gave 52 ± 2% *cis*-dimethylcyclohexane, the remainder being *trans*.

The much lower degree of stereospecificity in this hydrogenation as compared with that in the addition of deuterium to the 2-butenes may be somewhat unexpected but we believe that it is under-

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(53) G. Chiurdoglu, *Bull. soc. chim. Belges*, **47**, 241 (1938).

(54) G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957).

standable. Since tetrasubstituted olefin would be expected to hydrogenate more slowly than simpler olefins, the rate of double bond isomerization might be much larger relative to that of hydrogenation than in the case of the butenes. Further, the higher temperature of hydrogenation of dimethylcyclohexene (100° *vs.* −19 to 30°) favors greater intrusion of isomerization. Hydrogenation of either 2,3-dimethylcyclohexene or methylenemethylcyclohexane would give a mixture of *cis* and *trans*. The following considerations support this explanation of the diminished stereospecificity but they cannot be said to establish it rigorously.

Similar hydrogenation at 100° of a mixture rich in the 2,3-isomer (74% 2,3-; 18% 1,2-dimethylcyclohexene and 8% methylenemethylcyclohexane) gave nearly the same product as that from the pure 1,2-isomer. We attempted hydrogenation of the 1,2-olefin at 45° with a hydrogen flow rate of 6 cc. per g. per min. and a hydrogen–hydrocarbon ratio set by saturation of the hydrogen with hydrocarbon at 40° (the ratio is about 40). Hydrogenation occurred but the activity of the catalyst steadily declined perhaps owing to capillary condensation of the olefin. However, during the first 3 hr., the product of which was about half-hydrogenated, the fraction *cis* in the dimethylcyclohexane was 63%.

For our explanation of the lowered stereospecificity of hydrogenation of 1,2-dimethylcyclohexene to be correct, the equilibrium concentration of the 2,3- or of the methylene isomer would need to be adequate. We roughly measured the equilibrium at 40° using an acidic silica–alumina (Houdry cracking catalyst, S-45) as a catalyst and approaching the equilibrium from both the 1,2- and the 2,3- sides. It corresponds to 84 ± 4% of the 1,2-isomer, the remainder being the 2,3-.[55]

For our explanation to be correct, the rate of hydrogenation of 2,3-dimethylcyclohexene or of the methylene isomer must be substantially greater than that of 1,2-dimethylcyclohexene. We attempted to get somewhat more direct evidence with regard to this than that mentioned above. Cyclohexene was found to hydrogenate 4.4 times as fast as methylcyclohexene.[56] In a similar experiment we found 1-methylcyclohexene to react 1.6 times as fast as 1,2-dimethylcyclohexene, but this figure is subject to some uncertainty since the chromatographic resolution was not as good as one would like and since the assumed isomerization would mean that one was in part measuring the rate of hydrogenation of the 2,3- and of the methylene isomers. However, it does appear that the rate of hydrogenation falls with increasing substitution at the double bond.

C. Isotopic Exchange of (+)3-Methylhexane.—The isotopic exchange of (+)3-methylhexane with deuterium on metallic catalysts is accompanied by extensive racemization and it appears that exchange at the tertiary position entails racemization (paper I, ref. 35). At 200° on chromium oxide, isotopic exchange occurs mainly at the methyl groups and but a single hydrogen atom is exchanged per adsorption step (paper II). If the hydrogen atom at the tertiary position is but rarely disturbed, extensive racemization is unlikely to accompany isotopic exchange. Results of isotopic exchange runs with (+)3-methylhexane are shown in Table II.

TABLE II

ISOTOPIC EXCHANGE OF (+)3-METHYLHEXANE

Run	C	D	E	E[c]	E[d]	F
Temp., °C.	200[b]	263	299			345
D_2 flow[a]	1.5	3.2	2.6			4.4
D_2/hydrocarbon	1.8	1.8	1.8			2.0
$\Delta\alpha/\alpha_0$	0.018	0.032	0.103			0.108
D_0[e]	55.5	48.7	31.7	31.1	32.0	40.9
D_1	31.9	34.6	34.2	35.0	34.1	29.7
D_2	9.9	11.1	17.5	17.5	17.0	10.9
D_3	1.9	2.3	6.1	5.1	5.3	3.6
D_4	0.5	0.55	2.2	1.0	1.2	2.2
D_5	.....	.25	1.4	0.1	0.2	1.45
D_6		.25	1.2	..	..	1.45
D_7		.25	1.2			1.45
D_8		.33	1.2			1.45
D_9		.33	1.1			1.45
D_{10}		.33	0.9			1.45
D_{11}		.33	.7			1.1
D_{12}		.33	.3			1.1
D_{13}		.15	.1			0.7
D_{14}		.15	.....			.7
D_{15}		.....				.4

[a] Deuterium flow rate in cc. per min. (STP) per g. of catalyst. [b] This sample was passed over the catalyst a total of three times. [c] A random distribution assuming that only the 9 primary hydrogen atoms are exchangeable. [d] A random distribution assuming 16 exchangeable hydrogen atoms. The average deuterium content is taken as 1.00 atoms of deuterium per molecule of alkane. This value is taken to exclude contributions from the extensive multiple exchange process. [e] D_0–D_{15} given as per cent. of total product.

The isotopic distributions can be characterized as the superposition of two separate processes: (a) a process leading to a random distribution and in which but one deuterium atom is introduced per adsorption step (see paper II, section A), (b) a process leading to a wide, rather flat distribution. The two columns following run E give random distribution patterns for nine and sixteen exchangeable hydrogen atoms, respectively. These are nearly the same at these rather low levels of exchange. The computation assumes that processes a and b are independent and that the probability of process b is unaffected by previous isotopic exchange. The difference between the observed values and the computed ones leads to a reasonable isotopic distribution for process b. If one assumes that process b must introduce at least two deute-

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(55) Dehydration of 1,2-dimethylcyclohexanol at 150° under acidic conditions gives 73% of the 1,2 isomer; 24% of the 2,3- and 3% of the methylene. This may correspond to equilibrium among the three cyclohexenes particularly because an attempted chromatography of the carbinol resulted in dehydration in the inlet system (about 160°) and gave a mixture of olefins of the same composition.

(56) This figure derives from an experiment in which a mixture of 1-methylcyclohexene, 53.2%; and cyclohexene, 46.8%; and hydrogen was passed over the catalyst at 100°. The product was methylcyclohexene, 40.2%; cyclohexene, 12.8%; methylcyclohexane, 13.0%; cyclohexane, 34.0%. This analysis was confirmed by comparison of the infrared spectra of the sample and of a synthetic mixture of that composition. We assume that

$$\frac{-\mathrm{d}C_1}{-\mathrm{d}C_2} = \frac{k_1C_1}{k_2C_2}$$

The reactivity ratio involves adsorption coefficients as well as reaction rate constants and one would not necessarily find the same ratio in comparing the rates of hydrogenation of the pure compounds. However, the ratio from competitive measurement seems the one appropriate to the present purpose.

rium atoms and if one assumes that D_2 and D_3 amount to a total of 2%, then a total of 11% of the molecules have undergone process b. This value is very close to the percentage racemization, 10.3. One could assume, then, that process b inherently causes racemization.

Similar considerations apply to run *D* at 263°. About 3.3% of the molecules underwent process b, the fraction racemized was 3.2%. In run F at 345°, the % of molecules which underwent process b, about 16%, somewhat exceeds the fraction racemized, 10.8%. As will be seen in comparing runs D, E and F, the ratio of the rates of processes b and a increases with temperature. It is even probable that the slight loss in rotation at 200°, run C, is occasioned by process b.[57]

[57] Within the sensitivity limits of this particular mass spectral recording, 0.2% of a species at the parent peak, there were no species more multiply exchanged than those shown in run C, Table II. However, examination of the amyl carbonium ion peaks, which are twentyfold more intense, disclosed the presence of more multiply exchanged species with a distribution rather as in run D. Analysis using these peaks gave values for D_1, D_1 and D_1 reasonably consistent with those obtained using the parent peaks and gave the sum of D_4 to D_{11} as 2.0% which is not far from the degree of racemization, 1.8%.

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The Cadmium–Cadmium Halide Systems[1]

BY L. E. TOPOL AND A. L. LANDIS

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The solubility of cadmium in $CdCl_2$, in $CdBr_2$ and in CdI_2 to about 1000° was determined by thermal analysis and decantation techniques. The monotectics for the systems were found to be 13.7 mole % Cd at 537° in $CdCl_2$, 14.1% at 536° in $CdBr_2$ and 2.5% at 383° in CdI_2. The solubility of the metal was greatest in the bromide, slightly less in the chloride and least in the iodide. The solubilities of the salts in the metal were found to be about 0.05 mole % at 320°. Cryoscopic analyses of the salt-rich liquidus curves yield a cryoscopic number of one and suggest the species, Cd_4X_6 or Cd_3X_4, in the solvents $CdCl_2$ and $CdBr_2$.

Introduction

The solubility of cadmium in cadmium chloride has been studied by many investigators.[2–9] The metal has also been shown to be soluble in its bromide[3] and iodide[3,10] although very few measurements have been made in these systems. In the present work measurements of the Cd–$CdCl_2$ immiscibility curve have been repeated and extended over a larger temperature range. The solubility of the chloride in the metal near its melting point has also been determined. In addition the Cd–$CdBr_2$ and Cd–CdI_2 phase diagrams have been investigated in order to afford a comparison between the systems.

Experimental

Materials.—Reagent grade $CdCl_2$ was dried by heating the salt in an atmosphere of dry HCl; the molten salt was then cooled in argon. The $CdCl_2$ thus treated had a melting point of 569°.

$CdBr_2$ and CdI_2 were synthesized from the elements[10] in a sealed tube. The melting points of the bromide and iodide were 568° and 388°, respectively.

Mallinckrodt's reagent grade cadmium, with an assayed purity of 99.9%, was employed throughout. Before use, the metal was filtered through quartz wool *in vacuo* to remove any oxide present.

Apparatus and Procedure.—In all the measurements Vycor or fused silica tubing was used. The liquidus curves in the $CdBr_2$ and CdI_2 systems were determined by the usual freezing point method.[11] The two-phase liquid regions of these systems were studied by decantation techniques[12] and by differential thermal analysis. In the differential thermal analyses the sample and an aluminum oxide or pure cadmium halide standard were enclosed in a large nickel block; this assembly was heated to a given temperature in a rocking furnace. The furnace was allowed to cool slowly with or without rocking, and the temperature of the sample as well as the difference in temperature between the sample and standard were measured with chromel-alumel thermocouples inserted into wells in the containers. The differential voltage was magnified 200-fold by a Leeds and Northrup stabilized D. C. microvolt amplifier and recorded along with the sample temperature on a Leeds and Northrup Speedomax x-y recorder. The sample temperature could also be read directly and accurately by switching to a Rubicon potentiometer.

Results and Discussion

The solubility of cadmium in its chloride, bromide and iodide is shown in Fig. 1. The results for the Cd–$CdCl_2$ system are in good agreement with those of other investigators,[2–6] especially at temperatures below 700°. For the Cd–$CdBr_2$ system the one solubility reported in the literature,[3] 14.0 mole % Cd at 600°, obtained by quenching, is somewhat less than the 16.2% found in this study. Two studies have yielded widely different values for the solubility of Cd in its iodide; v. Hevesy and Löwenstein[3] reported 6.1 mole % at 600°, whereas Corbett, *et al.*,[10] found 1.5 mole % at the same temperature and 0.6% at 410°.

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