these two isomers was made by trapping out the separate compounds at the exit port of the instrument. The methyl ester of smaller retention time was a liquid which, after saponification in alcoholic potassium hydroxide and acidification of the potassium salt, yielded pure white 1-methoxy-2-naphthoic acid, mp 126–127° (lit.[3] mp 126–127°).

The methyl ester with a longer retention time was collected as a solid, mp 46–48° (lit.[15] for methyl 8-methoxynaphthoate, mp 51–52°). Saponification of this ester with alcoholic potassium hydroxide and isolation of the free acid gave 8-methoxy-1-naphthoic acid which melted at 159–160° after recrystallization from benzene (lit.[15] mp 162–163°).

There were some additional minor peaks which followed these two major products on the chromatograph and probably represented trace quantities of other isomers. The results are shown in Table I. The relative amounts of the isomers are given as "percentage yield" of each isomer, with the total amount of monocarboxylic acids from a metalation run representing 100%. The data were derived from relative peak areas from the chromatograms and assume equal instrumental response from equal numbers of molecules of each isomer. It should be noted that an appreciable quantity of other isomers was formed in the run containing added lithium ethoxide, and this may be another case of apparent alteration of metalation rates at different ring positions due to the presence of alkoxides.[9,16] If the other isomers are neglected in expt 4, the ratio of metalation in the 2 position to the 8 position is 87:13, not significantly different from the other runs.

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Tracer Studies of Acid-Catalyzed Reactions.
III. Preparation of Perdeuterio Olefins and Cyclopropane by Reaction with Deuterium over Alumina

J. G. LARSON, JOE W. HIGHTOWER, AND W. KEITH HALL

Mellon Institute, Pittsburgh, Pennsylvania

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Very pure alumina, prepared from either redistilled aluminum isopropoxide or from a commercially available β-alumina trihydrate, is an excellent catalyst for exchanging the hydrogen atoms in olefins or cyclopropane without causing extensive saturation or skeletal isomerization. This method has been used successfully to prepare ethylene-d_4, propylene-d_6, the three n-butenes-d_8, the three n-pentenes-d_{10}, and cyclopropane-d_6.

Alumina has long been known to be a catalyst for H_2–D_2 exchange,[1–3] for double-bond, *cis–trans*,[4–7] and skeletal isomerizations[8] in olefins, for saturating olefins,[9] for isomerizing cyclic paraffins,[10–12] for cracking hydrocarbons,[13] and for dehydrating alcohols.[14] This communication reports other useful reactions for which alumina is a catalyst, *i.e.*, for replacing hydrogen atoms in olefins and cyclopropane with deuterium without saturating the olefins or opening the cyclopropane ring. By repeated equilibration of the hydrocarbon with fresh deuterium, it is possible to prepare the perdeuterio compounds with isotopic purities greater than 98%. A detailed study of this reaction may lead to a better understanding of hydrocarbon interactions with these and other heterogeneous oxide catalysts.

Results and Discussion

The nine unsaturated perdeuterio compounds which we have prepared are listed in Table I. Column 3 shows the initial pressure of the hydrocarbon admitted to the circulation system, but up to 50% was lost through a constant capillary bleed into the mass spectrometer during the deuterium treatments; this could have been avoided. Column 4 shows the average pressure of deuterium used in each of the doses numbered in column 5. The per cent isotopic purity is simply the ratio $100D/(D + H)$ in the final hydrocarbon.

No detectable polymerization or skeletal isomerization occurred, and the only other products formed from the olefins were small amounts (last column) of normal paraffins. For cyclopropane the number in column 9 includes 0.2% propane and 22.9% propylene. In all cases the "yield" of perdeuterio material was greater than 75%, and this could probably be improved by lowering the temperature. This improvement would depend on the assumption that the energy of activation for exchange is lower than that for saturation. For this assumption, we have some evidence.

Both the butenes and pentenes underwent rapid *cis–trans* and double-bond isomerization, for after the first D_2 treatment the three n-olefins were in thermodynamic equilibrium. It is not known whether the exchange reaction is associated with the isomerization of the butenes and pentenes.

Alumina, prepared from the commercial β-alumina trihydrate, was also shown to catalyze the exchange of propylene and n-butenes without causing saturation of the olefins. Other less pure aluminas were tried and found unsuitable. Small amounts of transition

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TABLE I

EXPERIMENTAL CONDITIONS FOR PREPARATION OF PERDEUTERIO COMPOUNDS BY EXCHANGE OF HYDROCARBONS WITH DEUTERIUM OVER ALUMINA

Perdeuterio compound prepared	Starting material	Initial hydrocarbon pressure, mm	Av D_2 pressure, mm	Doses of D_2	Catalyst temp, °C	Catalyst size, g	Product isotopic purity, 100D/(D + H), %	Other compd formed,[a] %
Ethylene-d_4	Ethylene	14	50	6	210	1.6	98.5	3.6
Propylene-d_6	Propylene	19	50	8	210	1.6	99.0	3.9
n-Butenes-d_8	Butene-1	25	100	10	170	1.1	98.5	1.0
n-Pentenes-d_{10}	Pentene-1	25	100	12	180	1.1	92.0	15.0
Cyclopropane-d_6	Cyclopropane	68	87	8	103	1.6	98.0	23.1

[a] Compounds other than those indicated in the first column; these are paraffins and, with cyclopropane, propylene and propane.

metals present in most commercial aluminas are sufficient to catalyze saturation and, therefore, care should be taken in choosing an alumina as free as possible of metallic impurities. The presence of small amounts of alkali metals may also inhibit the exchange reaction. This is in accordance with the much different behavior of the "pure" aluminas reported by Pines and coworkers.[8,14,15]

The fact that alumina will catalyze exchange of hydrogen atoms in *n*-olefins has significance in at least two areas. First, by this method it has been shown that simple perdeuterio olefins, some of which (*e.g.*, butenes and pentenes) are not readily available from commercial sources, can be prepared fairly easily. We have separated the equilibrated *n*-butenes-d_8 by gas chromatography using a 2:1 dimethylsulfolane–hexamethylphosphoramide on firebrick column at 0°. Any undesired isomers (*e.g.*, *trans*-butene-2) could then be reequilibrated over the catalyst and the resulting butene-1 and *cis*-butene-2 again could be separated gas chromatographically and recovered. A microcatalytic apparatus[16] is ideal for this purpose. Presumably perdeuterioisobutene and -isopentene could be prepared by similar techniques.

Secondly, discovery of the ability of alumina to catalyze the exchange of olefins with D_2 without saturation provides another tool by which the catalytic chemist can investigate surface–olefin interactions on oxide catalysts.

It is of considerable interest that the hydrogen of hydrocarbons can be exchanged with D_2 (or H_2 with D_2) over "acidic" alumina at temperatures much below those where skeletal isomerization (or opening the cyclopropane ring) occurs at an appreciable rate; this may be contrasted with the behavior of silica–alumina. Also, the fact that exchange is much more rapid than hydrogenation of olefins is important in a consideration of possible structures of surface complexes. Not much is known about the activation of hydrogen by oxides, but the present data together with some related work[17] suggest that H_2 is cleaved heterolytically on the strong dual acid–base sites of alumina. In this way H_2 can exchange with a very small portion of the catalyst hydroxyl groups. Possibly, the olefin may be adsorbed on the electrophilic Lewis acid part of these sites and undergo exchange with the few adjacent OH (or OD) groups. Further work may better define the nature of the exchange mechanism.

Experimental Section

Catalysts.—The alumina[18] used in all cases described in Table I was prepared from the neutral hydrolysis of very pure aluminum isopropoxide. Its total metallic impurity level was less than 50 ppm, and its surface area was 158 m²/g. X-Ray measurements, made as the catalyst was dehydrated during the final stages of preparation, revealed that it was probably a mixture of η- and γ-alumina. Pretreatment included heating in a stream of dried oxygen at 530° for 2 hr, followed by overnight evacuation at the same temperature.

A second catalyst was prepared by overnight evacuation at 530° of β-alumina trihydrate furnished by the W. R. Grace and Co. The alumina formed under these conditions probably was in the η form,[19] and its hydroxyl groups are known to undergo exchange with D_2 slowly at 180°.[20]

Reactants.—The olefins were Phillips research grade found by gas chromatographic analysis to be better than 99.5% pure. Cyclopropane was obtained from the Ohio Chemical Co. All hydrocarbons were dried by distillation from −78 to −195° and freed from fixed gases by several freeze–pump–thaw cycles before use. The deuterium, obtained from Liquid Carbonic Division, General Dynamics Corp., had an isotopic purity of 99.5% and was dried by passage through a −195° trap before use.

Equipment.—The reactor consisted of a 360-cc circulation system containing a vertical catalyst tube surrounded by a furnace whose temperature could be controlled to ±1°, a mixing chamber large enough to hold about 80% of the gas in the system, a small-volume trap filled with glass beads, an all-glass circulation pump, and a continuous bleed[21] through a 10-in.-long glass capillary into a CEC Type 21-611 mass spectrometer.

The reactor was connected through appropriate stopcocks, lubricated with Dow-Corning high-vacuum silicone grease, to a conventional high-vacuum system containing a mercury diffusion pump, McLeod gauge, and gas storage bulbs. No attempt was made to protect the catalysts from mercury vapor.

Since good resolution of the hydrocarbon peaks could not be attained on the small Consolidated mass spectrometer, final determination of the isotopic purity was made on a Nuclide instrument using 11-15-ev electrons. With these low ionization voltages, fragmentation could be kept to less than 20%. The sensitivity was sufficiently high to permit analysis of the parent peaks to within ±0.5% and the results were corrected both for C^{13} isotopes and for fragmentation.

Procedure.—After the catalyst had been evacuated at 530° to a "sticking" vacuum denoted by a McLeod gauge, it was cooled to reaction temperature and contacted with the first D_2-hydrocarbon mixture, which was allowed to circulate over the catalyst until it was nearly equilibrated. Usually this took about an hour. The hydrocarbon was then frozen at −195° in the trap, the H_2–HD–D_2 mixture was evacuated, and a fresh dose of pure D_2 was admitted. After the trap containing the hydrocarbon had been warmed to room temperature, this mixture was again allowed to circulate for 1 hr before the hydrogen mixture was replaced by a similar procedure with fresh D_2. The process

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was repeated until hydrocarbons of the desired isotopic purity had been reached.

The course of the exchange reaction could be examined continuously by monitoring either the parent peaks of the partially exchanged hydrocarbons or the formation of HD in the mass spectrometer. Since the exchange process was proportional to the distance from equilibrium, the rate became extremely slow as equilibrium was approached. For this reason, the hydrogen mixture was usually removed before complete equilibration in order to minimize the amount of olefin hydrogenation.

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Macro Rings. XXXI. Quinone Derived from [2.2]Paracyclophane, an Intramolecular–Molecular Complex[1]

Donald J. Cram and A. Colin Day

Contribution No. 1814 from the Department of Chemistry, The University of California at Los Angeles, Los Angeles, California 90024

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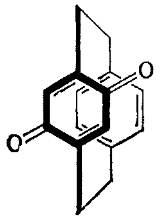
The quinone derived from [2.2]paracyclophane has been synthesized. Its ultraviolet absorption spectrum exhibits a band at 340 mμ (ε 597) not present in model compounds which is probably due to a charge-transfer transition. An aryn was demonstrated to intervene as an intermediate in the conversion of 4-bromo[2.2]paracyclophane to 4-hydroxy[2.2]paracyclophane with potassium *t*-butoxide in dimethyl sulfoxide. In a new reaction, the paracyclophanyl aryn reacted with dimethyl sulfoxide to give 4-hydroxy-5-thiomethoxy[2.2]paracyclophane.

The fixed geometry of [2.2]paracyclophane, known from X-ray diffraction studies,[2] suggests that, with proper structural modification, intramolecular–molecular complexes based on this ring system might be composed. Accordingly, synthetic experiments designed to produce quinones I–III were initiated. The latter two compounds are exotic quinhydrones, which differ from each other in a very interesting way. In II, the proximity of the interannular oxygens would allow maximum interannular hydrogen bonding, a feature absent in III. The synthesis of I has been realized, and progress has been made toward the syntheses of II and III.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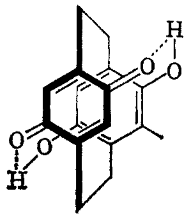
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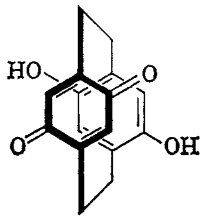
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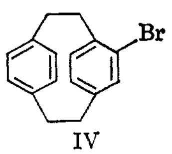
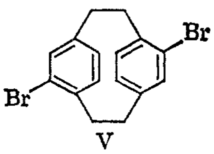
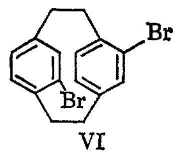
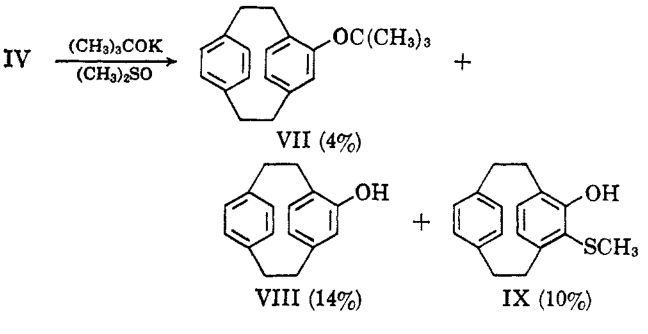
Production and Reaction of Aryns in the [2.2]-Paracyclophane System.—Bromination of [2.2]paracyclophane with 1 equiv of bromine and a trace of ferric bromide gave high yields of the monobromo derivative IV, whereas 2 moles of bromine gave a mixture of at least two dibromo derivatives (V and VI),[3] the structures of which are based on nmr spectra.[3b] The fact that only traces of the dibromides were produced when only 1 equiv of bromine was used provides further evidence that an electron-withdrawing substituent in one ring deactivates both rings toward further electrophilic attack.[4] Treatment of 4-bromo[2.2]paracyclophane (IV) with potassium *t*-butoxide in dimethyl sulfoxide[5] produced a mixture of ether VII, phenol VIII, and the unexpected thioether phenol IX (Scheme I).


IV


V


VI

Scheme I



The last compound probably arose by addition of the elements of dimethyl sulfoxide to an intermediate aryn, followed by demethylation of the sulfonium salt. An attractive mechanism for the direct production of phenol VIII from IV involves addition of *t*-butoxide anion to the aryn intermediate, followed by an intramolecular elimination reaction to give the phenol and isobutylene (Scheme II). Much high molecular weight material also seemed to be produced in this reaction.

The structure assigned to IX was based on the following evidence. The infrared spectrum in carbon tetrachloride of IX gave a band at 3373 cm^{-1} whose extinction coefficient was unaffected by dilution and which appeared to be associated with the presence of an intramolecular hydrogen bond. In contrast, phenol VIII showed hydroxylic absorption at 3571 cm^{-1}.

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