TABLE I

THE SYNTHESIS OF α-DISULFONES BY COBALT(III) OXIDATION OF SULFINIC ACIDS

α-Disulfone	Mp, °C	Lit. mp, °C	Yield, %	% S Found	% S Calcd	Infrared,[a] μ [b]	[c]	[b]	[d]	Ultraviolet, mμ λ_{max}	Log ε
$[n\text{-}C_8H_{17}SO_2]_2$	89.0–89.5	89.2–89.8[e]	43[f,g]			7.48			9.04		
$[n\text{-}C_8H_{17}SO_2]_2$	88.0–89.0	89.2–89.8[e]	23[f,h]			7.49			9.04		
$[n\text{-}C_{12}H_{25}SO_2]_2$	100.0–101.0	101.7–102.5[e]	40[f,g]			7.49			9.04		
$[n\text{-}C_{14}H_{29}SO_2]_2$	106.0–106.5	105.3–106.2[e]	35[f,g]			7.48			9.04		
$[C_6H_5SO_2]_2$	196.0–196.5	193–194[i]	65[f,j]			7.49	7.70	8.80	9.42	237	4.30
$[p\text{-}CH_3C_6H_4SO_2]_2$	222	218–220[k]	54[f,j]			7.42	7.70	8.78	9.38	250	4.36
$[m\text{-}NO_2C_6H_4SO_2]_2$	198		43[j]	17.45	17.22	7.50	7.80	8.75	9.42		
$[p\text{-}NO_2C_6H_4SO_2]_2$	246		48[j]	17.11	17.22	7.52	7.78	8.72	9.43		
$[m\text{-}HOOCC_6H_4SO_2]_2$	190		65[j]	17.42	17.25	7.42	7.78	8.71	9.40		
$[p\text{-}HOOCC_6H_4SO_2]_2$	265		65[j]	17.33	17.25	7.42	7.82	8.87	9.42	270	3.73
$[p\text{-}CH_3OC_6H_4SO_2]_2$	232		65[j]			7.52	7.92	8.90	9.42	277	4.45
$[m\text{-}BrC_6H_4SO_2]_2$	190		43[j]	14.46	14.54	7.50	7.78	8.80	9.42	235	4.18
$[p\text{-}BrC_6H_4SO_2]_2$	205		52[j]	14.24	14.54	7.52	7.80	8.88	9.42	262	4.29

[a] KBr pellet. [b] Strong. [c] Weak. [d] Medium. [e] Reference 5. [f] Mixture melting points with authentic sample of the α-disulfone and comparison infrared spectra were satisfactory. [g] The free sulfinic acid was used after liberation from the magnesium salt with 10 N H_2SO_4 plus ether, extraction of the aqueous layer with CH_2Cl_2, drying with $MgSO_4$, and solvent removal in the cold to prevent decomposition of the free acid. [h] RSO_2Mg was used directly. [i] Reference 7. [j] RSO_2Na was used directly. [k] Reference 6.

contrast, the Co^{III} method yields an easily purified product in relatively high yield. The principal by-product is RSO_3H. A possible reaction mechanism is one-electron abstraction to yield a free radical ($RSO_2\cdot$) followed by radical pairing to yield the disulfone (RSO_2-SO_2R). Another mechanism involving preliminary coordination of two molecules of RSO_2^- with one Co^{+3} ion can not be excluded *a priori*. Reduction to Co^I

$$2RSO_2^- + Co^{+3} \longrightarrow (RSO_2)_2Co^+$$

$$(RSO_2)_2Co^+ \longrightarrow RSO_2SO_2R + Co^+$$

$$Co^+ + Co^{+3} \longrightarrow 2Co^{+2} \qquad \text{(fast)}$$

followed by rapid oxidation to Co^{II} has some parallel to known chromic acid and permanganate pathways where apparent one-electron changes are in fact two-electron changes followed by rapid oxidation.[3]

Experimental Section

Preparation of Cobaltic Sulfate.[4]—$Co_2(SO_4)_3$ was prepared by electrolysis of a saturated $CoSO_4$ solution in 10 N H_2SO_4 at 0° using a platinum anode and copper cathode. The platinum anode had an area of 42 cm² and satisfactorily granular product was obtained with a current of 4.5 amp. The light blue solid $Co_2(SO_4)_3$ collected in the porous cup (Coors No. 700) surrounding the anode and could be isolated by decanting the solvent and stored at 0° as a moist solid. A saturated solution of $Co_2(SO_4)_3$ was used in the oxidation studies.

Oxidations.—A chilled solution of the oxidizing reagent was run into a solution (or slurry) of the sulfinic acid in 10 N H_2SO_4 (or 50:50 *t*-butyl alcohol–10 N H_2SO_4) until the blue-green color of Co^{III} persisted for 1 min. The mixture was immediately run into water and the insoluble disulfone was isolated and purified. The yields, melting points, spectral data, and sulfur analyses for several α-disulfones prepared by Co^{III} oxidation are reported in Table I. In each case the yield is that after one recrystallization from a suitable solvent, benzene for diaryldisulfones and either hexane or CH_2Cl_2 for dialkyldisulfones. Several of the substituted aromatic disulfones have not been reported before, but the analysis data, spectra, and method of preparation support the disulfone structure.[5-7]

Acknowledgment.—This work was supported in part by a National Institutes of Health Grant No. GM-11317.

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[6] P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1962).

[7] T. P. Hilditch, *J. Chem. Soc.*, **93**, 1526 (1908).

Stereospecific Formation of *cis*-Hydrindan *via* an Organoaluminum Cyclization Reaction[1a]

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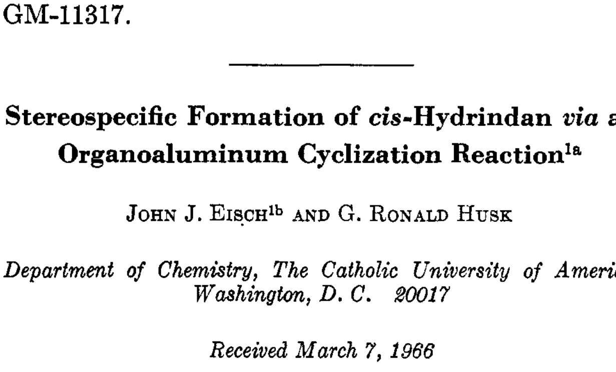
Current interest in the chemical consequences of unsaturation in organoaluminum compounds[2] has suggested a study of the thermal behavior of Δ^4-alkenylaluminum systems (I). From the known behavior of 1,4-alkadienes[3,4] or of 1,5-alkadienes[4,5] toward dialkylaluminum hydrides, structure I might be expected to undergo carbocyclization (II), or aluminum heterocycle formation *via* olefin displacement (III, eq 1). In order to observe the stereochemistry of any possible carbocyclization, the Δ^4-alkenylaluminum system



(1)

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[1] (a) Part VII of the series, "Organometallic Compounds of Group III." Previous paper: J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, in press. (b) To whom inquiries should be addressed.

[2] J. J. Eisch, *Trans. N. Y. Acad. Sci.*, **27**, 450 (1965).

[3] R. Polster, *Ann. Chem.*, **654**, 20 (1962).

[4] G. Hata and A. Miyake, *J. Org. Chem.*, **28**, 3237 (1963).

[5] K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 234.

TABLE I

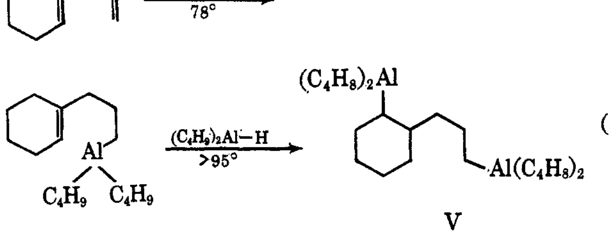
INTERACTION OF 1-ALLYLCYCLOHEXENE WITH DIISOBUTYLALUMINUM HYDRIDE

Expt	Mm of diene	Mm of $(C_4H_9)_2AlH$[a]	Time, hr	Temp, °C	Products, mole % 1-Propyl-cyclohexene	*n*-Propyl cyclohexane	*cis*-Hydrindan	Dehydro-*cis*-hydrindan[b]	Others
1	20	20	24	78	100	...	...	...	...
2	29	58	24	78					
			48	95	85.5	14.5	...	...	...
			43	145	75	25	...	...	...
3	29	29	16	78					
			7	165					
			24	78	40	23	6	27	4[c]
4	29	29	24	140					
			20	160	22.6	15.1	14.3	40.2	8[c]
5	29	29	96	155	13	30	7	45	5[c]
			d	*d*	3	...	5	88	4[e]
6	56	116	100	145	21.1	18.8	16.4	33.9	10[c]
7	57	57	24	78					
			20	145	21.3	14.0	16.7	36.7	11.3[c]
	f	*f*	20	175	13.9	16.4	14.1	47.3	8.3[c]
8	29	2.9	12	140					
			72	165	...	...	...	...	High-boiling products

[a] Calculated as available monomer. This hydride is firmly trimeric in benzene [*cf.* E. G. Hoffmann. *Ann. Chem.*, **629**, 104 (1960)]. [b] So named since this vinylic compound was reducible to *cis*-hydrindan. Conceivably it could be a mixture of cycloolefinic position isomers. [c] These were mixtures of three compounds distinguishable by vpc; probably they were isomeric propylcyclohexenes. [d] Reaction mixture subjected to a reduced pressure of <1 mm. Products in this line isolated by hydrolysis of cold trap condensate. [e] Only one of isomeric propylcyclohexenes was detected in the cold trap condensate. [f] Before heating further at 175°, 25 mg of nickel acetylacetonate was added.

chosen for study was 3-(1-cyclohexenyl)propyldiisobutylaluminum (IV). Carbocyclization to a hydrindan system then could lead to a *cis*-ring fusion, a *trans*-ring fusion, or possibly a mixture of the isomeric hydrindans. This report describes the stereospecific formation of *cis*-hydrindan from the unsaturated aluminum precursor IV and presents evidence favoring the intervention of an aluminacyclohexane intermediate (*cf.* III) in this carbocyclization.

The requisite 3-(1-cyclohexenyl)propylaluminum system (IV) could be obtained most readily by the reaction of 1-allylcyclohexene with 1 equiv of diisobutylaluminum hydride at 78°. The greater reactivity of the terminal C=C linkage over the internal C=C bond[6] was reflected in the exclusive formation of 1-propylcyclohexene upon hydrolysis of the organoaluminum product (Experimental Section). Furthermore, the marked preference for the attachment of $(C_4H_9)_2Al$ to the terminal carbon, as depicted in IV (eq 2), was assured by the extensive studies of Ziegler and co-workers on hydride additions to α-olefins.[7] Further addition of diisobutylaluminum hydride to IV proved to be extremely slow; after 4 days at temperatures >95° only 25% of *n*-propylcyclohexane (from V) was obtained upon hydrolysis (expt 2). However, when compound IV was heated alone above 140°, isobutylene was evolved. Hydrolytic work-up now yielded not only *n*-propylcyclohexene and 1-propylcyclohexane, but also two new hydrocarbons in major amounts and three minor components. One of the principal components proved to be *cis*-hydrindan (VI); the other was an olefinic component (VII) which could be reduced catalytically to *cis*-hydrindan. The minor components seemed to be isomeric propylcyclohexenes, since catalytic hydrogenation of the hydrolysis products resulted in only *n*-propylcyclohexane and *cis*-hydrindan. No *trans*-hydrindan could be detected. Various experimental runs listed in Table I were undertaken, in order to obtain optimum yields of *cis*-hydrindan and its dehydro companion VII. The highest yields of 50–60% of VI + VII were observed when equimolar quantities of 1-allylcyclohexene and the hydride were heated to 145–175° (expt 3–5). The presence of colloidal nickel[8,9] seemed to have a salutary effect on the formation of the dehydrohydrindan VII (compare expt 4 and 7). An attempt to conduct the carbocyclization of 1-allylcyclohexene to VI or VII by means of catalytic amounts of hydride led only to high-boiling residues, presumably olefins dimers[10] (expt 8). However, in several runs it was found possible to separate the VII accumulating in the reaction mixture by volatilizing it under reduced pressure and collecting it in a cold trap (expt 5).



IV

V

(2)

Since the mechanism for the formation of *cis*-hydrindan from 1-allylcyclohexene can only be rationalized at the present, certain observations are relevant. First, additions of Al-H and Al-C bonds to cyclo-

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[6] K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann. Chem.*, **589**, 106 (1954).

[7] K. Ziegler, F. Krupp, and K. Zosel, *Angew. Chem.*, **67**, 425 (1955).

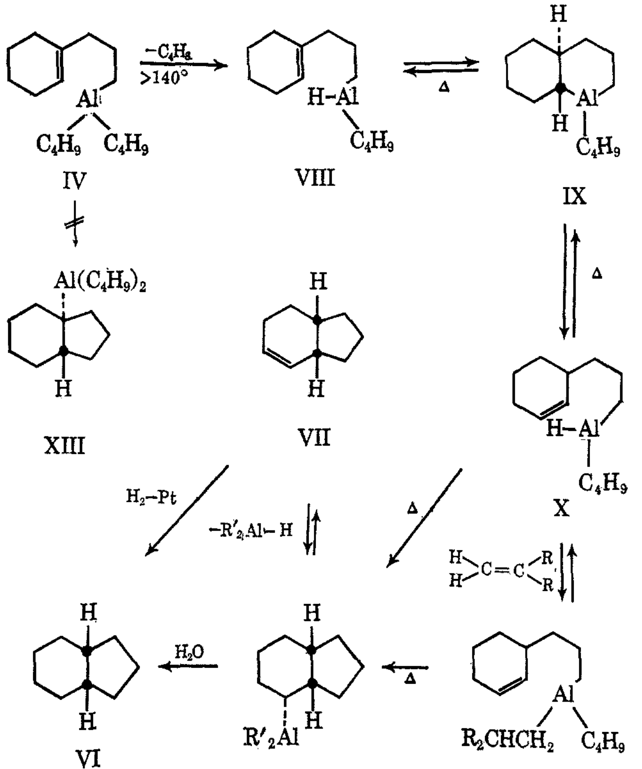
[8] Colloidal nickel is known to promote the displacement reaction between aluminum alkyls and α-olefins: K. Ziegler, H.-G. Gellert, E. Holzkamp, G. Wilke, E. W. Duck, and W.-R. Kroll, *Ann. Chem.*, **629**, 172 (1960).

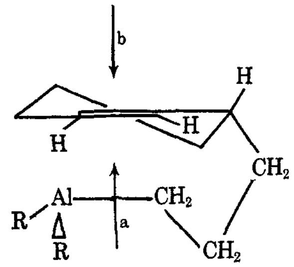
[9] G. Natta, P. Pino, G. Mazzanti, P. Longi, and F. Bernardini, *J. Am. Chem. Soc.*, **81**, 2561 (1959).

[10] *Cf.* K. Ziegler, H.-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll, and W.-R. Kroll [*Ann. Chem.*, **629**, 138 (1960)] for the dimerization of α-olefins by small amounts of aluminum alkyls.

olefins and alkynes generally occur in a *cis* fashion.[11,12] Secondly, aluminum alkyls containing aluminum bonded to a tertiary carbon atom are not known and are presumably too unstable to exist.[13] Thirdly, isobutyl–aluminum bonds tend to dissociate into isobutylene and aluminum–hydrogen bonds at temperatures above 125°. *n*-Alkylaluminum bonds are much more thermally stable.[14] Finally, since the elimination of R_2AlH from R_3Al is just the reverse of the addition reaction, *cis* elimination would be expected. In accord with the foregoing information, a carbocyclization scheme is proposed in Chart I. The possibility of the hydrindan system being formed from the Δ^4-alkenylaluminum system (IV) by an intramolecular addition of R_2AlR' to the double bond (IV → XIII) can be dismissed on two counts. In the first place, *trans*-hydrindan would be the principal hydrolysis product, and, in the second place, a tertiary alkylaluminum intermediate would be involved. In comparison, the proposed pathway, IV → XII, is consonant with the following facts: the optimal yields with a 1:1 stoichiometry of reagents; the evolution of isobutylene above 140°; the formation of aluminacyclohexane products from 1,4-alkadienes and alkyaluminum hydrides;[4] the preferential ring closure to the *cis*-hydrindan system; and the production of a dehydrohydrindan reducible to *cis*-hydrindan. If in this last instance VII were to have its double bond at the bridgehead, hydrogenation would be expected to yield both isomeric hydrindans. Furthermore, the *cis* cyclization of X or XI to yield XII is the only feasible interaction (direction a) between the Δ^5 double bond and the terminal carbon–aluminum bond. Consideration of a Stuart–Briegleb model of XIV convinces one of the impossibility of the *cis* addition of $AlCH_2$ occurring from direction b, leading to the *trans*-hydrindan isomer of XII.

Chart I





XIV

The stereospecific synthesis of 6,5-ring systems by the foregoing method appears to offer some promise. Further work will evaluate the ability of certain transition metals to promote this carbocyclization in both alicyclic and heterocyclic systems. Extension of the reaction to the elaboration of other polycyclic rings is also under active consideration.

Experimental Section

General Technique.—The sensitivity of organoaluminum compounds to oxygen and to protic solvents demanded that all operations be conducted under an atmosphere of dry, oxygen-free nitrogen. The purification of nitrogen, the preparation of reaction vessels, and the transfer of aluminum alkyls have been discussed in a previous article.[15]

Since the hydrolysis of these aluminum alkyls and aluminum hydrides involves the rapid and exothermic generation of gas (isobutane and hydrogen), safety precautions are in order. Accidental hydrolysis of organoaluminum reaction mixtures can be minimized by employing kerosene in external cooling baths and as coolant in reflux condensers. This kerosene can be chilled by permitting it to circulate through a copper coil immersed in ice. In case of rupture of either the reaction flask or the condenser this cooling technique avoids the entry of large amounts of water into a quantity of aluminum alkyl and at the same time reduces its reactivity by dilution with kerosene. The deliberate hydrolysis of small amounts of aluminum alkyls for disposal can be achieved with safety by diluting the sample with hexane and cautiously pouring the solution onto ice.

Nmr spectra were recorded with a Varian A-60 analytical spectrometer. With tetramethylsilane as an internal standard the chemical shifts are reported in ppm on the δ scale. Integration techniques were similar to those of Jungenickel and Forbes and thus will be of comparable precision and accuracy.[16] Viscous liquids were examined in 20–60% solutions in carbon tetrachloride; nonviscous liquids were recorded as neat samples.

Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam spectrophotometer with sodium chloride optics. Samples were recorded as liquid films. Ultraviolet spectra data were obtained with Cary Model 11 spectrophotometer.

A Barber-Colman Model 10 gas chromatograph, which had a strontium-90 ionization source, was used to analyze starting materials and reaction products. Collection of small amounts of pure products was accomplished by passing the effluent gas through a glass U tube situated in a Dry Ice–acetone bath and protected by a drying tube from atmospheric moisture.

Preparation and Purification of Reagents. (a) **Starting Materials.**—Diisobutylaluminum hydride was prepared from triisobutylaluminum according to a published procedure.[15]

1-Allylcyclohexanol.—A solution of 44 g (0.45 mole) of cyclohexanone in 100 ml of anhydrous ether was treated with 0.46 mole of allylmagnesium bromide in 250 ml of ether. After the 1-hr addition period the solution was stirred at room temperature

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[11] G. Wilke and H. Müller, *Ann. Chem.*, **629**, 222 (1960).

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[13] Reference 6, pp 217–218.

[14] K. Ziegler, H. Martin, and F. Krupp, *Ann. Chem.*, **629**, 14 (1960).

[15] Reference 12.

[16] J. L. Jungenickel and J. W. Forbes, *Anal. Chem.*, **35**, 938 (1963).

for 24 hr. The reaction mixture was hydrolyzed and the organic layer was separated. Removal of the solvent and distillation gave essentially a quantitative yield of 1-allylcyclohexanol, bp 54–55° (0.5 mm), $n^{24}\mathrm{D}$ 1.4757 [lit.[17] bp 62–64° (3 mm), $n^{24}\mathrm{D}$ 1.4730]. The infrared spectrum exhibited characteristic bands at 3400 (O–H), 1650 (C=C), 1000 and 910 ($CH{=}CH_2$) cm^{-1}.

1-Allylcyclohexene.—A solution of 58.9 g (0.42 mole) of 1-allylcyclohexanol in 30 ml of benzene was heated at reflux with a few crystals of *p*-toluenesulfonic acid. Over a 60-hr period the theoretical quantity of water was collected in a Dean-Stark trap. The organic layer was washed with aqueous sodium bicarbonate solution and then dried over anhydrous calcium sulfate. Solvent removal and fractional distillation through a 250-cm Vigreux column gave 44 g (85%) of a main fraction, bp 152–157°. Vapor phase chromatography of this fraction on a 10% Ucon-on-firebrick column revealed one principal component and two minor impurities. Careful refractionation through a 200-cm column filled with glass helices yielded the desired 1-allylcyclohexene in 98% purity, bp 154–155°.

The ultraviolet spectrum of the product showed only end absorption and specifically no absorption characteristic of a conjugated double bond (*e.g.*, 1,1-cyclohexylidenebutadiene). The infrared spectrum displayed bands at 800 (out-of-plane deformation of vinyl C–H), 910 and 995 (terminal vinyl) and 1645 cm^{-1} (unconjugated C=C stretch). The nmr spectrum consisted of vinyl multiplets centered at 4.83, 5.09, and 5.44 ppm as well as a complex series of absorptions between 5.58 and 613 ppm (total intensity of 4.0). Saturated C–H signals were centered at 1.60, 1.90, and 2.63 ppm. The last signal was resolved into a sharp doublet (J = 7 cps), attributable to the methylene protons of the allyl group.

(b) **Products. 1-Propylcyclohexene.**—1-Propylcyclohexanol was prepared from cyclohexanone and *n*-propymagnesium bromide according to a published procedure, bp 85–86° (2 mm), $n^{25}\mathrm{D}$ 1.4689 [lit.[18] bp 84-87° (15 mm), $n^{20}\mathrm{D}$ 1.4635]. According to the procedure for the preparation of 1-allylcyclohexene, 19.8 g (0.14 mole) of this carbinol was dehydrated to yield 11.5 g (67%) of 1-propylcyclohexene, bp 35–38° (13 mm), $n^{25}\mathrm{D}$ 1.4555 (lit. bp 154.7-157.7°, $n^{20}\mathrm{D}$ 1.4578). Vapor phase chromatography on 10% Ucon on firebrick indicated only one component.

The nmr spectrum displayed a broadened vinyl absorption at 5.38 ppm (intensity of 1.0), saturated C–H multiplets between 1.1 and 2.1 ppm[12] and a triplet at 0.86 ppm (CH_3, intensity of 3.0).

n-**Propylcyclohexane**, obtained from the Columbia Chemical Co., was found to contain only one component upon various vpc columns, $n^{25}\mathrm{D}$ 1.4346 (lit. $n^{20}\mathrm{D}$ 1.4370).

cis-**Hydrindan.**—Freshly distilled indene (19.7 ml, 0.17 mole), 200 ml of anhydrous methanol, and 1.5 g of platinum oxide were placed under 50 psi of hydrogen in a Parr hydrogenator at 25°. After 48 hr only 0.19 mole of hydrogen had been absorbed. Usual work-up and distillation yielded 14.7 g (75%) of pure indan, bp 51–52° (20 mm), as identified by infrared spectral analysis.

The aforementioned indan was subjected to high-pressure hydrogenation at 50° in an ethanolic suspension of ruthenium oxide. Filtration of the reaction mixture, solvent removal, and fractional distillation yielded 8.0 g (54%) of *cis*-hydrindan, bp 41° (14 mm), $n^{25}\mathrm{D}$ 1.4700 [lit.[19,20] bp 166.5° (746 mm), $n^{25}\mathrm{D}$ 1.4700, $n^{20}\mathrm{D}$ 1.4720]. The infrared and nmr spectra of the product were identical with the published spectra of *cis*-hydrindan. No indication of the presence of the *trans* isomer could be detected.

Reaction of 1-Allylcyclohexene with Diisobutylaluminum Hydride (Typical Run).—A 100-ml, three-necked flask, equipped with a nitrogen inlet, reflux condenser, and a pressure-equalized addition funnel, alternately was evacuated and filled with nitrogen. By siphoning under a nitrogen atmosphere 4.0 g (5.0 ml, 0.029 mole) of diisobutylaluminum hydride was placed in the flask. The 1-allylcyclohexene (3.4 g, 0.029 mole) was added in one portion, whereupon an exothermic reaction took place. The mixture was stirred magnetically while being heated for the time intervals given in the table. In some runs the volatile organic products (mostly dehydro-*cis*-hydrindan) were removed periodically by reduced pressure distillation.

At the close of the reaction period the system was cooled, diluted with reagent pentane, and treated with water (gas evolution!). The filtered organic layer was dried over anhydrous calcium sulfate; the pentane was removed by fractional distillation. The liquid residue then was analyzed directly with a 6-ft column packed with 10% Ucon oil supported on firebrick. Retention times of a standard mixture of authentic compounds, *n*-propylcyclohexane, 1-propylcyclohexene, 1-allylcyclohexene, and *cis*-hydrindan, were used as identification standards. Furthermore, representative samples of the eluent gas were condensed; their infrared and nmr spectra were compared with those of the authentic compounds. Only three very minor components could not be identified with any assurance. A fourth component, present in major amounts, was shown to be a dehydro-*cis*-hydrindan by the procedure outlined below.

With considerable difficulty the supposed dehydro-*cis*-hydrindan was isolated in *ca.* 88% purity by condensing the eluent gases from the vapor phase chromatograph. The nmr spectrum displayed two rather broad signals at 5.37 and 5.62 ppm. Integration of the latter peaks in comparison to the alkyl absorptions between 1.8 and 2.3 ppm was unreliable due to impurities. However, the separation in the vinyl signals (17 cps) indicates two different vinyl hydrogens, rather than spin–spin splitting.

Hydrogenation of the Hydrolyzed Reaction Mixture.—The mixture of the hydrocarbons obtained above was dissolved in 50 ml of ethyl acetate. Platinum oxide (100 mg) was added and the mixture was treated with hydrogen (50 psi) in a Parr hydrogenator. Filtration and solvent removal gave an organic residue which was shown by vpc to contain only *n*-propylcyclohexane and *cis*-hydrindan. In fact, the increase in the hydrindan in this analysis corresponded to the disappearance in the major unknown component from the foregoing reaction mixture.

Acknowledgment.—The generous support of the donors of the Petroleum Research Fund under PRF Grand 723-A at the University of Michigan is gratefully acknowledged. Certain aspects of this study were conducted under the auspices of Public Health Service Grant GM-12329 at the Catholic University of America.

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[19] N. L. Allinger and J. L. Coke, *ibid.*, **82**, 2553 (1960).

[20] H. Shecter and D. K. Brain, *ibid.*, **85**, 1806 (1963).

An Oxygen-18 Study of the Question of Acid- and Base-Catalyzed Exchange between *para*-Substituted Nitrobenzenes and Water[1]

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Carboxylic acids readily undergo oxygen exchange with water under both acidic[3] and basic[4] conditions. In view of the structural similarity between the carboxyl group and the nitro group, it seemed appropriate to investigate the possibility of similar acid- and base-catalyzed exchange between water and the nitro group.

In the very early days of oxygen exchange work, Roberts[5] reported no exchange when a methanol solution of nitrobenzene was treated with oxygen-18-enriched water 0.03 N in hydrochloric acid or sodium hydroxide for 24 hr at 25°. More recently, Gragerov and Levit reported[6] no exchange between nitrobenzene

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[1] Supported in part by U. S. Atomic Energy Commission Contract AT-(40-1)-3234.

[2] Supported by the National Science Foundation Undergraduate Research Participation Program.

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