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), $n^{24}\text{D}$ 1.4757 [lit.[17] bp 62–64° (3 mm), $n^{24}\text{D}$ 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), $n^{25}\text{D}$ 1.4689 [lit.[18] bp 84-87° (15 mm), $n^{20}\text{D}$ 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), $n^{25}\text{D}$ 1.4555 (lit. bp 154.7-157.7°, $n^{20}\text{D}$ 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, $n^{25}\text{D}$ 1.4346 (lit. $n^{20}\text{D}$ 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), $n^{25}\text{D}$ 1.4700 [lit.[19,20] bp 166.5° (746 mm), $n^{25}\text{D}$ 1.4700, $n^{20}\text{D}$ 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.

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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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or nitromethane and $H_2{}^{18}O$ after treatment (heterogeneous system) at 150° for 16 hr in 0.5 *N* hydrochloric acid or sodium hydroxide.

Since electron-withdrawing or -donating substituents often cause considerable variations in exchange rate,[3,4] it was decided to investigate the exchange behavior of *p*-methoxy-, *p*-methyl-, *p*-chloro-, and *p*-dinitrobenzene.

The conditions used were (1) dilute acid, 0.1 *M* RNO_2, 0.12 *M* $HClO_4$, 80% dioxane–20% $H_2{}^{18}O$ (1.66 atom %), 100°, 24 hr; (2) strong acid, 0.1 *M* RNO_2, 7.75 *M* $HClO_4$, 0.83 atom % $H_2{}^{18}O$ (homogeneous solution without added dioxane), 100°, 48 hr; (3) dilute base (using *p*-methoxy- and *p*-chloronitrobenzene only), 0.1 *M* RNO_2, 0.62 *M* NaOH, 50% dioxane–50% $H_2{}^{18}O$ (1.66 atom %), 100°, 16 hr. (Under more drastic basic conditions, the nitro compounds could not be recovered from the solutions.) At the end of the reaction period, the nitro compounds were recovered, recrystallized, and analyzed for oxygen-18. No excess oxygen-18 was found in any of the nitro compounds under any of the reaction conditions.

This lack of exchange makes it very clear that the nitro group is far less susceptible than the carboxyl group to acid- or base-catalyzed nucleophilic attack.

Experimental Section

Acidic Exchange Experiments.—Approximately 0.24-g samples (0.1 *M* solutions) of *p*-methoxy-, *p*-methyl-, *p*-chloro-, and *p*-dinitrobenzene were refluxed for 24 hr in 15 ml of 80% dioxane–20% $H_2{}^{18}O$ (1.66 atom % oxygen-18) 0.12 *M* in perchloric acid. The solutions were poured onto ice, and the precipitated nitro compounds were filtered, dried, recrystallized from heptane, and analyzed for oxygen-18. No excess was found. The chance that exchange might be very rapid and hence that the nitro compounds might be undergoing complete back exchange during the work-up procedure was considered. That this was not the case was shown by the fact that *p*-dinitrobenzene showed no exchange when recovery was effected by rapid cooling (Dry Ice bath) without the addition of ice or water.

In the strong acid experiments approximately 0.24-g samples of the nitro compounds were dissolved in 15 ml of 7.75 *M* perchloric acid in which the water was enriched in oxygen-18 to the extent of 0.83 atom %. The samples were heated in sealed tubes in a steam bath for 48 hr, and then cooled in a Dry Ice bath. The precipitated nitro compounds were filtered, recrystallized from heptane, and analyzed for oxygen-18. No excess was found.

Basic Exchange Experiments.—Approximately 0.24-g samples of *p*-methoxy- and *p*-chloronitrobenzene were refluxed for 16 hr in 20 ml of 50% dioxane–50% $H_2{}^{18}O$ (1.66 atom % oxygen-18) 0.62 *M* in sodium hydroxide. The solutions were poured onto ice, and the precipitated nitro compounds were worked up and analyzed as before. No excess oxygen-18 was found. Several sets of more drastic basic conditions were tried, but none gave positive results. Without an added organic solvent, two-phase systems were obtained at all temperatures. When sufficient dioxane was added to dissolve the nitro compounds, the sodium hydroxide was relatively insoluble. Using alkaline aqueous alcohol solutions, the nitro compounds could not be recovered; after a relatively short time only a thick, brown paste was obtained.

Isotopic Analyses.—The oxygen-18 in the nitro compounds was converted to carbon dioxide by pyrolysis at 500° for 5 hr with 1:1 mixture of mercuric chloride and mercuric cyanide.[7] (The fact that carbon dioxide was obtained in all cases shows that the lack of exchange is not due to failure of the nitro oxygens to be converted to an analyzable form.) The *m/e* 46/44 ion current ratio was determined in an isotope ratio mass spectrometer, and these results were converted to atom per cent oxygen-18. In all cases, within the experimental measurement errors, the samples contained the natural abundance of oxygen-18.

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Ionization Constants of 3- and 4-Substituted *cis*- and *trans*-Cinnamic Acids in 50% Ethanol

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The ionization constants of a series of *meta*-substituted *trans*-cinnamic acids and a series of *meta*- and *para*-substituted *cis*-cinnamic acids have been measured in 50% ethanol at 25°. For the *trans* series ρ is +0.68, and $-\log K_0 = 5.68$. In the *cis* series the *meta* and *para* compounds describe two separate lines, corresponding with ρ values of +0.63 ($-\log K_0 = 5.22$) and +0.77 ($-\log K_0 = 5.17$), respectively.

The question of the relative abilities of *cis*- and *trans*-ethylenic groups to transmit electronic effects has been of interest for some time. Data related to this question are the rates of alkaline hydrolysis of a series of *cis*- and *trans*-ethyl cinnamates.[2] The somewhat larger Hammett ρ value of 1.31 for the *trans* series (compared with 1.12 for the *cis*) appeared consistent with the longer wavelength of *trans* absorption[2,3] in suggesting a superior π-bond interaction across the ethylenic system in *trans* isomers. However, the limited data on the ionization of the *cis*-cinnamic acids in water[4] suggested a larger substituent effect on acidity than in the *trans* acids.[5] We have, therefore, reexamined these series, in 50% ethanol as the solvent, using a larger number (eight) of *cis* acids. The ionization constants of *trans*-cinnamic acids in this solvent have not previously been reported, and are of interest for comparison with the phenylpropiolic acids and other series. Only *trans*-cinnamic acids with *meta* substituents having relatively invariant σ values have been examined. (A number of *para*-substituted acids are of insufficient solubility for convenient potentiometric measurement). Both *meta*- and *para*-substituted *cis*-cinnamic acids have been included in this study. The results are shown in Table I.

Table I

Apparent pK_a Values for *meta*- and *para*-Substituted *cis*- and *trans*-Cinnamic Acids in 50% Ethanol at 25.0°

	cis		
Substituent	*meta*	*para*	*trans, meta*
OCH_3		5.38	5.62
CH_3		5.30	5.72
H	5.22		5.68
F		5.11_5	5.44
Cl	4.99	5.02	5.42_5
Br			5.42
NO_2	4.77	4.58	5.19_5

ρ for the *trans* series is +0.68 (average deviation ±0.008 σ unit). The data for the *cis* compounds are scattered, and fit a single line with an average devia-

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