Experimental Section

Alkylation with Lower Aliphatic and Alicyclic Alcohols (Procedure A) (Table I, Experiment 1–8).—A mixture of 0.1 mol of **2** and 0.3 mol of alcohol was heated with stirring in an autoclave at 210–220° for 1 hr. Water was added to the content of the autoclave, the resulting suspension was stirred, and the upper clear layer was removed by decantation from the precipitated sodium acetate hydrate. Removal of excess alcohol and ether by distillation gave light brown residual oil which was dissolved in ether. The ethereal solution was washed with several portions of water until the solution became clear, and the ethereal layer was dried (K_2CO_3), concentrated, and distilled, giving α-alkyl phenylacetonitrile.

Akylation with Higher Aliphatic Alcohols (Procedure B), (Table II, Experiment 9–16).—A mixed slurry of 0.05 mol of **2** and 0.075 mol of alcohol was heated at 210° for a few minutes when a vigorous reaction started. This was heated at 210–220° for 30 min. After cooling, water was added to the brownish-yellow cake, the resulting oily layer was extracted with ether, and the ethereal layer was washed with water, dried (K_2CO_3), concentrated, and distilled, giving α-alkylphenylacetonitrile.

Alkylation with Aralkyl Alcohols (Procedure B) (Table II, Experiment 17–23).—A mixed slurry of 0.05 mol of **2** and 0.075 mol of aralkyl alcohol was heated at 200–210° for 20 min. After cooling, water was added to the brownish-yellow cake. The resulting oily layer was extracted with ether, and the ethereal layer was washed with water, dried (K_2CO_3), concentrated, and distilled, giving α-aralkylphenylacetonitrile. The product, which solidified on cooling, was recrystallized from methanol or ethanol. In two cases, expt 20 and 21, crude products were directly obtained as crystals when water was added to the mixture after the reaction was complete.

Registry No.—**2**, 32970-68-6.

Proton Magnetic Resonance and Chemical Evidence for Stereospecificity in the Reaction of *cis*- and *trans*-1-Phenyl-4-*tert*-butylcyclohexanol with HCl. Proton Magnetic Resonance Analysis of the Reaction of Several Substituted 1-Arylcyclohexyl Systems with HCl and FSO_3H–SbF_5–SO_2

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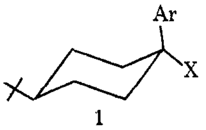
The isolation of stereoisomers from the addition of HX to cyclohexenes[1] or other cycloalkenes[2] has been reported only rarely. To our knowledge, the identification and isolation of similar stereoisomers from substituted cyclohexanols has not been recorded. We selected alcohols *cis*-**1a**, *cis*-**1b**, *trans*-**2a**, and *trans*-**2b** for the study with HCl since the stereomeric chlorides *cis*-**1c** and *trans*-**2c** have been characterized.[1]



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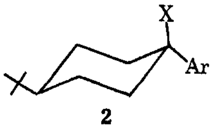

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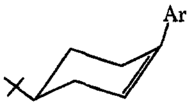

3

	X	Ar
a	OH	C_6H_5
b	OH	p-$CH_3OC_6H_4$
c	Cl	C_6H_5
d	Cl	p-$CH_3OC_6H_4$

a, Ar = C_6H_5
b, Ar = p-$CH_3OC_6H_4$

We have now found that alcohols *cis*-**1a** and *trans*-**2a**[3] react in a stereospecific fashion with HCl(g). Suspended in anhydrous pentane at −30° under N_2, *cis*-**1a** was treated with anhydrous HCl(g) and gave (after 45 min) a ratio of 3.67:1 for the chlorides *cis*-**1c**:*trans*-**2c** as measured from peak areas for the corresponding *tert*-butyl protons (δ 0.74 and 0.92, respectively) in the pmr spectrum of the reaction mixture. These peaks are clearly separated in $DCCl_3$ at 50-Hz sweep width. The complete disappearance of a signal for the proton on oxygen suggested a nearly quantitative conversion of alcohol *cis*-**1a**.

$$cis\text{-}\mathbf{1a} + \mathrm{HCl} \xrightarrow[-30^\circ]{\text{pentane}} \underset{(78.6\%)}{cis\text{-}\mathbf{1c}} + \underset{(21.4\%)}{trans\text{-}\mathbf{2c}}$$

$$trans\text{-}\mathbf{2a} + \mathrm{HCl} \xrightarrow[-30^\circ]{\text{pentane}} \underset{(19.4\%)}{cis\text{-}\mathbf{1c}} + \underset{(80.6\%)}{trans\text{-}\mathbf{2c}}$$

The overall phenomenon is surprising in view of the predominance of the chloride *cis*-**2c** at short reaction times (*ca.* 15 min) when **3a** was treated with HCl at −70°.[1] A check on the reaction of *cis*-**1a** at −70° after 45 min did *not* reveal a significant change in the ratio of products (Table I). In contrast, if **3a** was allowed to react with HCl for 45 min, no starting material could be detected in the mixture by pmr, and *cis*-**1c**:*trans*-**2c** was 1.0:2.06. Since the ratio *cis*-**1a**:**3a** in the two separate experiments was only 1.3:1, these above data can be compared, all other reaction conditions being identical. It should be noted (Table I), of course, that there is a dependence of [*cis*-**1c**]:[*trans*-**2c**] upon the initial concentration of **3a** as expected for the same period of time. A similar dependence upon rate of addition of HCl to **3a** was reported.[1]

Table I

Compd	Temp, °C	*cis*-**1c**, %	*trans*-**2c**, %	Time, min
cis-**1a** (alcohol)	−30	78.6	21.4	45
(0.0017 mol)[a]	−70	78.6	21.4	45
trans-**2a** (alcohol)	−30	19.4	80.6	45
(0.0022 mol)[a]	−70	28.2	71.8	45
3a (alkene)	−70	48.6	20.5	15[b]
(0.0013 mol)[a]	−70	32.3	67.7	45
3a (alkene)	−70	79.1	20.9	15
(0.0037 mol)[a]	−70	71.8	28.2	45

[a] Per 100 ml of *n*-pentane. [b] Unreacted **3a** detected was 30.9%.

It appears that no common intermediate is formed from the reaction of HCl with either **3a** *or* **1a** (*or* **2a**) *in pentane at* −70°. Therefore the mechanisms differ. To our knowledge, this is the first report of the reaction of HCl

$$\begin{tikzcd}
\mathbf{3a} \arrow[dr] & \\
& cis\text{-}\mathbf{1c} + trans\text{-}\mathbf{2c} \\
cis\text{-}\mathbf{1a} \text{ or } trans\text{-}\mathbf{2a} \arrow[ur] &
\end{tikzcd}$$

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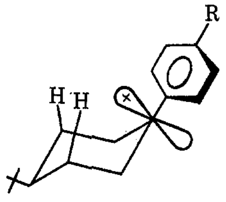
(1) K. D. Berlin, R. O. Lyerla, D. E. Gibbs, and J. P. Devlin, *Chem. Commun.*, 1246 (1970).

(2) P. K. Freeman, F. A. Raymond, and M. F. Raymond, *J. Org. Chem.*, **32**, 24 (1967).

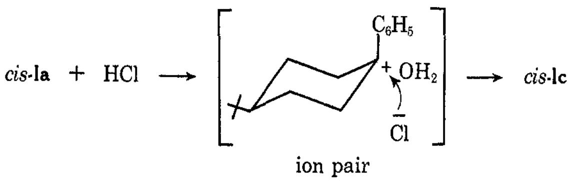
(3) The alcohols were of purity greater than 99.5% by glc analysis. Although the preparation [E. W. Garbisch, Jr., and D. B. Patterson, *J. Amer. Chem. Soc.*, **85**, 3228 (1963)] and purification technique [G. D. Meakins, R. K. Percy, E. E. Richards, and R. N. Young, *J. Chem. Soc. C*, 1106 (1968)] are reported, modification of procedures afforded more pure products in a simpler process; see R. O. Lyerla, Ph.D. Dissertation, Oklahoma State University, 1970.

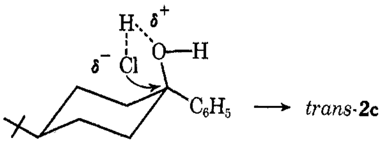
with epimeric cyclohexanols to give the corresponding epimeric chlorocyclohexanes predominantly with retention of configuration. It is interesting to note that reduction of either *cis*-**1a** or *trans*-**2a** with several silanes has been observed to give the same *cis*:*trans* ratio of hydrocarbons regardless of alcohol used.[4] A common carbonium ion intermediate **4a** was postulated.[4]



4a, R = H
b, R = OCH_3

In our work this conclusion is untenable in view of the data cited. Interestingly, we *do not* obtain the cis chloride **1c** as the major product from trans alcohol **2a** under conditions comparable (Table I) to the identical reaction of cis alcohol **1a** with HCl. Consequently, a reasonable explanation for retention of configuration may involve ion pairs as shown with *cis*-**1a** → *cis*-**1c** or *via* a type of S_Ni mechanism as illustrated.





To determine if the stereospecificity of the reactions was preferred under classical ionic conditions, alcohol *trans*-**2a** in hexane was shaken with concentrated HCl at 25° for 5 min. The mixture, *via* pmr analysis, showed *trans*-**2c** (67%) and *cis*-**1c** (33%). However, *cis*-**1a** under identical conditions gave *cis*-**1c** (45%) and *trans*-**2c** (55%). If these reactions are initially stereospecific, isomerization of the chloride *cis*-**1c** to *trans*-**2c** occurs rapidly at 25°. This is in agreement with previous findings[1] that chloride *trans*-**2c** is the thermodynamically more stable isomer. Most interesting was the observation that no alkene **3a** could be detected in either reaction mixture from alcohols *cis*-**1a** or *trans*-**2a**. Under the same conditions at 25°, 1-phenylcyclohexanol gave only 1-phenylcyclohexene. However, it was found that at −10 to 0°, 1-phenylcyclohexanol was converted to 1-chloro-1-phenylcyclohexane (**5**) in a yield of 93% (estimated by pmr). These very fast reactions apparently do not differ in rate strictly because of stability differences in the products, since 1-chloro-1-phenylcyclohexane is unchanged under these conditions at 25°. Also, alkene **3a** and 1-phenylcyclohexene are *not* precursors since they are recovered quantitatively when subjected to the described conditions at 25°. At first glance these results might suggest that the *tert*-butyl group influences the stability of the intermediate formed in conversion of the alcohols *cis*-**1a** and *trans*-**2a** to the respective chlorides under classical ionic conditions at 25°. Differences in partitioning of the individual alcohols between the two phases could explain the results. However, a check of the solubility of the alcohols in water indicates that both are very poorly soluble (estimated <1% at room temperature). Also, since alkenes are not precursors in these reactions, a reasonable interpretation is that ion pairs are involved or an S_Ni mechanism is operative.

On the assumption that a powerful electron-donating group on the arene might lead to increased stability of the intermediate **4b**, *cis*- (**1b**) and *trans*-1-(*p*-methoxyphenyl)-4-*tert*-butylcyclohexanol (**2b**) were prepared and characterized. Alkene **3b** was obtained *via* dehydration of a mixture of *cis*-**1b** and *trans*-**2b**. At −70° in pentane, **3b** or *cis*-**1b** or *trans*-**2b** and HCl(g) (after 45 min) gave the same ratio of **3b**:*cis*-**1d**:*trans*-**2d**[5] which averaged 5.6:1:7.5. In fact, this apparent equilibrium mixture was observed after 15 min. A small increase in *trans*-**2b**:**3b** was noted as the flow rate of HCl increased. Possibly a common intermediate is formed but this cannot be substantiated in view of the rapid formation of the equilibrium mixture.

When alcohol *cis*-**1a** was added to a mixture of FSO_3H–SbF_5–SO_2 (Olah's solvent) and cooled to −70°, a red solution resulted. Pmr analysis showed a strong singlet at δ 0.67 for *tert*-butyl protons plus the other absorptions already described for this system. Similarly, alcohol *trans*-**2a** gave an almost identical spectrum except for signals at δ 0.70 (*tert*-butyl protons) and at δ 0.95 at −70°. The signal at δ 0.95 disappeared rather quickly while the spectrum was recorded at −60° with no other apparent change in signal shapes or positions. Conceivably, the alcohol *trans*-**2a** was not completely ionized (signal for *tert*-butyl protons in $DCCl_3$ is at δ 0.90 and may be shifted to δ 0.95 in Olah's solvent) or a cation is formed initially which rearranges to a cation with a signal at δ 0.70 for the *tert*-butyl protons. This latter cation from *trans*-**2a** essentially gives the same spectrum as was obtained from the alcohol *cis*-**2a** when dissolved in Olah's solvent and is probably **4a**. Although the extrapolation of these data to that from the addition of HCl to the alcohols is not justified, it is interesting that identical spectra from **1a** and **2a** are not immediately obtained in Olah's solvent. Solvation effects could be operative on the ease of protonation of either alcohol, solvation of the protonated form, or rate of loss of water. In any event, a conformational effect perhaps on some intermediate, such as the immediate cation precursor of **4b**, seems reasonable to explain the data in Olah's solvent.

Experimental Section

Pmr spectra were recorded on a Varian A-60 unit and checked on an HA-100 unit. Chemical shifts are relative to internal TMS. Infrared spectra were recorded on a Beckman IR-5A. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Alcohols **1a** and **2a** were prepared by the literature procedure and purified by chromatography over neutral alumina by the method of Meakins and coworkers.[3] Technical FSO_3H was from City Chemical Corp., New York, N. Y.,

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[4] F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **90**, 2578 (1968).

[5] All attempts to obtain pure compounds **1d** and **2d** resulted in extensive elimination of HCl. Alkene **3b** was always present in samples as detected by pmr.

and anhydrous SbF_5 was from Research Organic/Inorganic Chemical Co., Sun Valley, Calif. [bp 149.5° (760 mm)]. Reagent grade pentane was dried over a molecular sieve before use. 4-*tert*-Butylcyclohexanone (mp 48–49°) was from International Flavors and Fragrances, Inc. 1-Phenylcyclohexanol[6] and 1-phenylcyclohexene[7] are known compounds.

Preparation of *cis*- (1b) and *trans*-4-*tert*-Butyl-1-(*p*-methoxyphenyl)cyclohexanol (2b).—The Grignard reagent of *p*-bromoanisole (10.0 g, 0.05 mol) was prepared in ether (2 ml) with 1.3 g (0.05 g-atom) of magnesium. 4-*tert*-Butylcyclohexanone (8.24 g, 0.05 mol) was added in ether (*ca.* 20 ml). After 2 hr at reflux, the mixture was decomposed with water (pH 7) to avoid dehydration which occurred at acid pH values. Ether–benzene extracts gave a solution of **1b** and **2b** in the ratio of 36.5:63.5 *via* pmr analysis of the signals for the *tert*-butyl protons. Removal of solvent gave a solid which was treated with *n*-pentane at −70° (two times). The solid, dried at 50° *in vacuo*, melted at 126–127°: yield 1.5 g (10.7%); ir (KBr) 3225 cm^{-1} (OH), 892 (para substitution); pmr ($DCCl_3$) δ 0.77 [s, $(CH_3)_3C$], 1.75 (s, OH), 2.50 (d, 2,6-equatorial ring H), 3.79 (s, CH_3O), and 7.13 (q, ArH). The other ring protons were in a broad signal at *ca.* δ 0.85–1.9.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.80; H, 9.99. Found: C, 77.82; H, 9.99.

The mother liquors from the recrystallizations with *n*-pentane were evaporated to a yellow solid. Dissolving it in low-boiling petroleum ether (bp 30–60°) gave a solution which was chromatographed (neutral alumina) with ether–petroleum ether. The trans alcohol **2b** was eluted with a solvent ratio of 1:19 of ether–petroleum ether (a small amount of cis alcohol **1b** was eluted when the ratio of solvents was 9:1). Purification of **2b** was by the same technique as for **1b**; yield of **2b** was 0.9 g (6.43%) mp 105–107°; ir (KBr) 3333 cm^{-1} (OH), 892 (para substitution); pmr ($DCCl_3$) δ 0.90 [s, $(CH_3)_3C$], 1.60 (s, OH), 3.78 (s, CH_3O), and 7.13 (q, ArH). Again the other ring protons were visible as a broad signal at δ 1.5–2.05, the 2,6-diequatorial protons not being separated in trans alcohol **2b** as in the spectrum of cis alcohol **1b**. Both **1b** and **2b** are hygroscopic but tend to form alkene when left in the atmosphere. An analytical sample of **2b** was obtained only if extreme care was exercised to avoid moisture.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.80; H, 9.99. Found: C, 78.18; H, 9.74.

4-*tert*-Butyl-1-(*p*-methoxyphenyl)cyclohexene (3b).—An equimolar mixture of alcohols **1b** and **2b** (5.0 g, 0.019 mol) was dehydrated with a freshly prepared mixture of 5 ml of concentrated H_2SO_4 and 20 ml of glacial CH_3CO_2H (the solution was magnetically stirred for 30 min).[8] A dark red, viscous solution resulted and was added to a mixture of ether–H_2O (100:200 ml). The organic layer was washed (H_2O followed by 10% K_2CO_3) and dried ($MgSO_4$). Removal of the solvent gave a solid which was extracted with *n*-pentane and purified (*n*-hexane): yield 3.8 g (82.6%); mp 77.5–78°; pmr ($DCCl_3$) δ 0.89 [s, $(CH_3)_3C$], 3.74 (s, CH_3), 6.00 (br s, C=CH), and 7.02 (q, ArH). Ring protons were visible in a broad signal at δ 1.2–2.5 for **3b**.

Anal. Calcd fo $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.64; H, 9.90.

Attempted Preparation of 1-Chloro-1-phenylcyclohexane (5).—Hydrogen chloride was bubbled into 1-phenylcyclohexene (3.0 g, 0.019 mol) in pentane (50 ml) at −78° for 1 hr. Distillation gave an oil which partially decomposed. Pmr analysis showed multiplets at δ 1.8 and 7.3 in the ratio of 2:1; $n^{27}D$ 1.5524. Attempted elemental analysis gave inferior results, apparently due to loss of HCl.

Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.01; H, 7.77; Cl, 18.22. Found: C, 74.86; H, 7.51; Cl, 17.52.

For pmr analysis, pentane was simply stripped from the oil at 0.1 mm (25°). A small sample was dissolved in CCl_4. The sample of **5** was deemed relatively free of 1-phenylcyclohexene since the latter has a signal at δ 5.95 for a vinyl proton which was absent in the spectrum of **5**.

Addition of HCl(g) to the Alcohols. General Procedure.—The description given is for the addition of HCl(g) to *trans*-**2a** at −30°; this is quite typical of the procedures employed.

Hydrogen chloride (predried through molecular sieve, Linde grade 3A) was bubbled through a suspension of *trans*-**2a** (0.5 g, 0.002 mol) in 100 ml of dried *n*-pentane. A Dry Ice–95% ethanol bath maintained the temperature at −30° throughout the addition. Aliquots were removed for analysis at intervals. After 45 min, HCl addition was stopped, the pentane was removed *in vacuo* (aspirator), and the resulting white solid was dissolved in $DCCl_3$ for nmr analysis. Loss of the signal for OH (of *trans*-**2a**) at δ 1.83 and proper integration of the other proton signals demonstrated the essentially complete conversion of *trans*-**2a**. Authentic samples of *trans*-**2c**[1] and cis-**1c**[1] were used to confirm the identities of the isomers in the $DCCl_3$. The ratio of *trans*-**2c** to *cis*-**1c** was 80.6:19.4 after 45 min as obtained from peak area measurements for the *tert*-butyl protons (δ 0.92 for *trans*-**2c** and 0.74 for *cis*-**1c**).

Reaction of *trans*-4-*tert*-Butyl-1-phenylcyclohexanol (2a) with FSO_3H-SbF_5-SO_2 at −70°.—Samples of FSO_3H (1 g, 0.01 mol) and SbF_5 (2.17 g, 0.01 mol) were mixed in a quartz test tube with vigorous shaking.[9] To a separate quartz test tube was added 0.3 g (0.0013 mol) of **2a**. After cooling (ice), 1.5 ml of liquid SO_2 was pipetted into the tube forming a suspension with **2a**. The tube was then cooled to −70° with stirring.

The total acid solution (2.8 ml) was pipetted into the SO_2-suspended **2a** in three equal portions with vigorous stirring between additions. The dark red solution was added to an nmr tube which was cooled to −70°. Two peaks were discernable in the region for *tert*-butyl protons (δ 0.70 and 0.95) at −70° but one disappeared when the temperature was raised to −60° and did not reappear at the lower temperatures.

A similar experiment with **1a** gave essentially identical results.

Registry No.—*cis*-**1a**, 21024-55-5; *cis*-**1b**, 33066-12-5; *cis*-**1c**, 28140-27-4; *trans*-**2a**, 17807-26-0; *trans*-**2b**, 33066-15-8; *trans*-**2c**, 28140-28-5; **3b**, 33061-20-0; **5**, 29479-98-9; HCl, 7647-01-0; FHO_3S, 7789-21-1; F_5Sb, 7783-70-2; O_2S, 7446-09-5.

Acknowledgment.—We thank the Research Foundation of Oklahoma State University for partial support, Phillips Petroleum Company for a fellowship (R. O. L.), and N. D. E. A. (D. E. G.) for a fellowship.

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(6) T. R. Govindachari, K. Nagarajan, B. R. Pai, and N. Arumugam, *J. Chem. Soc.*, 4280 (1956).

(7) R. C. Carlin and H. P. Landerl, *J. Amer. Chem. Soc.*, **75**, 3969 (1953).

(8) The dehydration procedure is similar to that used for the synthesis of **3a** by Garbisch and Patterson (ref 3).

(9) The general procedure used was very similar to that reported in the literature; see G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2692 (1967).