

TABLE I
EFFECT OF PRESSURE^a ON THE SOLVOLYSIS RATE CONSTANTS^b OF SEVERAL NOSYLATES
IN AQUEOUS ACETONE AT 25°

I		II		III		IV		V	
p	10 ⁴ k ₁	p	10 ⁴ k ₁	p	10 ⁴ k ₁	p	10 ⁴ k ₁	p	10 ⁴ k ₁
0.001	5.60	0.001	2.39	0.001	12.30	0.001	0.367	0.001	2.22
0.072	6.19	0.155	2.74	0.076	13.33	0.100	0.397	0.083	2.40
0.151	6.52	0.244	2.99	0.236	15.14	0.193	0.431	0.178	2.55
0.211	6.82	0.325	3.07	0.402	16.97	0.350	0.478	0.215	2.62
0.311	7.30	0.481	3.50	0.563	18.89	0.517	0.514	0.390	2.93
0.381	7.76	0.640	3.93	0.636	19.98	0.668	0.551	0.455	3.06
0.448	8.04	0.763	4.28	0.721	21.21	0.777	0.588	0.541	3.14
0.555	8.54	0.881	4.66	0.849	22.60			0.599	3.29
0.692	9.34							0.801	3.50
0.857	10.17								
ΔV ₀ ^{‡c} = -20.0		-20.5		-21.6		-20.6		-21.0	

^a In kbar. ^b In sec⁻¹. ^c In cm³/mol.

than those of III-V, the differences are very small and almost certainly within the limit of error, estimated to be ±0.3 cm³/mol. We conclude that the difference between the ΔV[‡] values of V and its epimer^{2,3} is not due to steric hindrance. Such effects might be demonstrated in more severely hindered solvolyses, but many such reactions are characterized by extensive concomitant rearrangement, so that participation and charge delocalization begin to cloud the picture, and in others the steric rate retardation is so great that the accurate conductance measurements employed here can no longer be used, at least not under the same conditions.

Experimental Section

The nosylate esters used were prepared by adding about 0.1 mol of *p*-nitrobenzenesulfonyl chloride to an equimolar amount of the alcohol at -10°, stirring for 0.5 hr, and adding a cold solution of 100 ml of concentrated hydrochloric acid and 500 ml of water. The mixture was extracted several times with ether and the combined extracts were dried with anhydrous magnesium sulfate and evaporated to small volume. The residue was decolorized and crystallized from ether; the yields were in the 50-70% range. The structures were verified by nmr; the analytical data are shown in Table II.

TABLE II
ANALYTICAL DATA OF THE NOSYLATE ESTERS

Alkyl group	Mp, °C	Calcd, %		Found, %	
		C	H	C	H
Cyclohexyl (I)	77.0-77.2	50.51	5.29	50.33	5.32
<i>trans</i> -4- <i>tert</i> -Butyl- cyclohexyl (II)	101.0-101.4	56.29	6.79	56.57	6.91
<i>cis</i> -4- <i>tert</i> -Butyl- cyclohexyl (III)	95.2-97.8	56.29	6.79	56.28	6.79
2-Adamantyl (IV)	137-139	56.96	5.67	56.89	5.88
2- <i>endo</i> -Norbornyl (V)	102.3-103.3	52.52	5.095	2.36	5.06

The conductance cell was similar to that used by Whalley.⁹ Platinum tubing¹⁰ (0.5 mm diameter) was used for the leads going through the Pyrex walls to avoid the problem¹¹ of frequent breakage due to the compressibility difference between Pyrex and platinum; in hundreds of pressure applications we did not experience a single breakage. The cells were conditioned with dilute solutions of *p*-nitrobenzenesulfonic acid in aqueous acetone and stored in the same solution when not in use. A mercury pool in the bottom of the cell provided the means for separating the solution from the pressure transmission fluid. The electrodes were about 1 cm apart and 4 mm in diameter; they were welded to the leads and platinized by the procedure of Jones and Bolin-

ger.¹² The cell was suspended inside the pressure vessel¹³ from a closure in such a way that the electrodes were connected *via* small cups sealed into a cell and filled with mercury, and prongs protruding from the closure. The prongs were slightly conical and insulated from the closure by means of conical lava sleeves; these sleeves in turn were made leak proof by means of an epoxy resin. The pressure was measured by means of a calibrated Bourdon gauge and could be held constant to about 1 bar more or less indefinitely. The temperature of the pressure vessel was controlled at 25.00 ± 0.02°. The resistances were measured by means of a Leeds and Northrup bridge (1553), Hewlett-Packard wide range oscillator and Model 102B oscilloscope, and a Rhode and Schwartz amplifier (121221-2). A frequency of 1500 Hz proved best for our apparatus. About 3 mg of the ester was employed in each run with 50 ml of solvent; the solvent composition was 55:45 acetone and water by weight. At least 10 pairs of observations were made after 1 hr was allowed for temperature equilibrium. The data were treated by the Guggenheim method to yield the rate constants;¹⁴ the latter were obtained from the data by computer. The correlation coefficient was always larger than 0.999; reproducibility between completely independent runs was usually much better than 1%.

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The Aqueous Dichromate

Oxidation of Primary Alcohols

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The oxidation of primary alcohols to aldehydes is often difficult to accomplish in good yields because the aldehydes are themselves easily converted to carboxylic acids under oxidative conditions. The methods avail-

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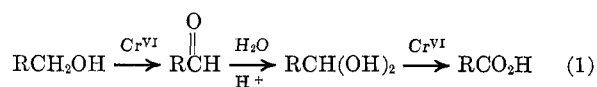
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able to accomplish such transformations have recently been reviewed.¹ Of these methods the most attractive involve either the use of chromium trioxide in pyridine or argentic picolinate in aqueous solutions.^{1,2} However, both of these methods are subject to certain limitations; the CrO₃-pyridine complex is hazardous to prepare and product isolation is sometimes difficult while argentic picolinate is an expensive reagent and time consuming in its preparation.

Sodium dichromate on the other hand is a readily available and inexpensive reagent that is known to have a high oxidation potential under acidic conditions or at elevated temperatures.^{3,4} Under acidic conditions the oxidation of primary alcohols to aldehydes often gives unsatisfactory yields because of the formation of substantial amounts of carboxylic acids or esters^{5,6} unless the aldehyde can be distilled from the reaction mixture as it forms.^{7,8} However, it is known that aldehyde oxidation proceeds *via* the aldehyde hydrate⁹ (eq 1) and,



since the hydration reaction is acid catalyzed, it occurred to us that it might be sufficiently retarded under neutral conditions to make carboxylic acid formation negligibly slow. Consequently, we undertook a study of the oxidation of various types of alcohols by neutral aqueous sodium dichromate at high temperatures. This procedure has previously been used with good success for the oxidation of arene side chains.^{10,11} However, since alcohols are more readily attacked by oxidants than are hydrocarbons, we were able to work under much less vigorous conditions. In fact, although the oxidation of arenes requires the use of a high temperature, high pressure reactor,¹¹ we found that some alcohols could be oxidized in refluxing aqueous dichromate solutions.

As the results presented in Table I indicate, this reaction gives good yields for all benzyl alcohols but much less satisfactory yields for aliphatic alcohols. Hence the value of the reaction lies in its obvious selectivity for α -phenyl alcohols and the ability to use conditions that are completely safe and easy to achieve. Furthermore, product isolation through extraction from the aqueous solution into ether is a relatively simple process.

A preliminary kinetic study into the relative rates of oxidation of benzyl alcohol and benzaldehyde was also completed and in agreement with our expectations it

TABLE I
PRODUCTS OBTAINED FROM THE OXIDATION OF
ALCOHOLS WITH AQUEOUS SODIUM DICHROMATE

Alcohol ^a	Product	Con- version, % ^b	Yield, % ^c
Benzyl alcohol ^d	Benzaldehyde	25	66
Benzyl alcohol	Benzaldehyde	70	85
Benzyl alcohol ^e	Benzaldehyde	79	78
	Benzoic Acid	7	7
<i>p</i> -Methoxybenzyl alcohol	<i>p</i> -Methoxybenzaldehyde	70	81
<i>p</i> -Methylbenzyl alcohol	<i>p</i> -Methylbenzaldehyde	48	79
<i>p</i> -Fluorobenzyl alcohol	<i>p</i> -Fluorobenzaldehyde	53	68
<i>p</i> -Chlorobenzyl alcohol	<i>p</i> -Chlorobenzaldehyde	36	85
<i>m</i> -Methoxybenzyl alcohol	<i>m</i> -Methoxybenzaldehyde	51	90
<i>m</i> -Chlorobenzyl alcohol	<i>m</i> -Chlorobenzaldehyde	27	96
<i>p</i> -Nitrobenzyl alcohol	<i>p</i> -Nitrobenzaldehyde	65	76
	<i>p</i> -Nitrobenzoic acid	10	10
<i>o</i> -Nitrobenzyl alcohol	<i>o</i> -Nitrobenzaldehyde	39	86
	<i>o</i> -Nitrobenzoic acid	1	1
β -Naphthylmethanol	β -Naphthaldehyde	65	82
Cinnamic alcohol	Cinnamaldehyde	87	91
α -Phenylethanol ^f	Acetophenone	50	96
α -Phenylethanol ^g	Acetophenone	84	86
β -Phenylethanol		None	None
2-Propanol	Acetone	4	13
Cyclohexanol	Cyclohexanone	2	27
Cyclohexanol ^h	Cyclohexanone	14	58
Cyclohexanol ^b	Cyclohexanone	10	35
1-Heptanol ^b	Heptanal	7	17
Allyl alcohol ⁱ	Acrolein	9	32
2-Methyl-2-propenol ^j	2-Methylpropenal	10	21
1-Hexen-3-ol ^j	1-Hexen-3-one	11	39

^a Unless otherwise indicated a 1:1 mol ratio of Na₂Cr₂O₇ to alcohol (usually 0.10 mol of each component in 100 ml of water) was held at reflux temperature (98°) for 3 hr. ^b Conversion is based on the total amount of material recovered and indicates the extent to which the reaction has proceeded under these conditions. Total recovery varied from 80 to 99%. ^c Yield as based on unrecovered starting material. ^d A molar ratio of Na₂Cr₂O₇ to alcohol of 0.5 was used at 50° for 14 hr. ^e Time increased to 9 hr. ^f Time decreased to 2 hr. ^g Time increased to 6 hr. ^h Time increased to 24 hr. ⁱ 50° for 2 hr. ^j Time decreased to 1.5 hr.

was found that the alcohol was oxidized approximately 18 times as fast as the aldehyde. At the pH of these kinetic experiments (5.6, phosphate buffer) the aldehyde hydrate is probably present in only minute concentrations thus preventing second stage oxidation to benzoic acid.

Experimental Section

Equimolar ratios of sodium dichromate and alcohol (0.1 mol of each) were mixed with 100 ml of water and refluxed in a 250-ml round-bottomed flask equipped with a magnetic stirrer and reflux condenser. Usually the alcohol was not completely soluble in the refluxing mixture and with some alcohols (*e.g.*, *p*-methylbenzyl alcohol), acetone (1–5 ml) was added to prevent sublimation onto the reflux condenser. After 3 hr the mixture was cooled, diluted with 100 ml of water, the pH was adjusted to 9 with 1.0 M NaOH, and the mixture was extracted three times with 100-ml portions of ether. The aqueous portion was then acidified with 3 M H₂SO₄ and again extracted three times with 100-ml portions of ether. The ether extracts were dried over MgSO₄, concentrated, and analyzed by use of gas-liquid chromatography and a Varian A-60A nmr spectrophotometer equipped with a digital voltage monitor to integrate the proton signals.

Registry No.—Sodium dichromate, 10588-01-9.

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