

acrylate moiety. This increases that carbon's attraction for the more electron rich carbon atom (C-1) in the isoprene molecule and leads to the higher ratio of the "para" adduct.

In N-vinylphthalimide delocalization of the unshared electron pair on the nitrogen atom should make the β -carbon atom of the vinyl group negative, but this effect would be counteracted by delocalization involving the carbonyl groups as well as by the inductive effects of the oxygen atoms. These effects do not lead to a clear cut prediction of the major adduct to be expected with 9-methoxyanthracene, although with isoprene one would expect an adduct corresponding to **4** as the major product since no dienophile has yet given a major adduct corresponding to **5**.

The Diels-Alder reaction of 1- and 9-methoxyanthracene went readily at 200° and only one adduct was isolated. Its pmr spectrum revealed a doublet for the bridgehead proton which showed it was the nonvicinal adduct corresponding to **3**.

Isoprene and **1** gave a crystalline adduct which was dehydrogenated to N-*p*-tolylphthalimide. The adduct was also synthesized from the known methyl acrylate-isoprene adduct.

It appears that 9-substituted anthracenes are more sensitive to steric and electronic effects governing orientation than are 2-substituted butadienes and that **1** behaves like an unconjugated dienophile in its condensation with 9-methoxyanthracene.

Experimental Section

N-(9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11-yl)phthalimide.— **1** (1 g) and 1.3 g of 9-methoxyanthracene⁵ were fused at 200° for 50 hr. The mixture was then dissolved in ethanol, filtered, and then concentration gave 0.43 g of colorless solid, mp 200–203°. The pmr spectrum (CDCl₃) showed a doublet at 4.4 ppm ($J = 2.5$ Hz) for the bridgehead proton.

Anal. Calcd for C₂₅H₁₉NO₃: C, 78.72; H, 5.02. Found: C, 78.57; H, 4.92.

When anthracene and **1** were condensed in a similar fashion a 60% yield of N-(9,10-dihydro-9,10-ethanoanthracen-11-yl)phthalimide, mp 183–185°, was obtained. Recrystallizations from benzene-petroleum ether gave an analytically pure sample, mp 196–197° (lit.⁵ 180–181°).

N-(1-Methyl-4-cyclohexenyl)phthalimide.— **1** (10 g), 4 g of isoprene and 0.1 g of hydroquinone dissolved in 15 ml of acetone were heated in a rocking autoclave at 175–185° for 28 hr. Extraction of the product with 250 ml of hot ethanol left 3.7 g of apparently polymeric material, mp 175–230° dec. From the extract 1.77 g (13%) of white crystals were obtained. Recrystallization gave the analytical sample, mp 141–143°.

Anal. Calcd for C₁₅H₁₇NO₂: C, 74.66; H, 6.27; N, 5.81. Found: C, 74.99; H, 6.21; N, 5.68.

The methyl acrylate adduct of isoprene⁷ on treatment with hydrazine gave a product which by means of a Curtius reaction was converted into an amine which gave a phthalimide, mp 139–140°, that was identical with the adduct of **1** and isoprene.

When 1.2 g of the N-vinylphthalimide-isoprene adduct was heated for 80 min at 297–358° with 0.1 g of 10% palladium on charcoal, hydrogen was evolved. Fractional crystallization from ethanol then gave 0.19 g of white crystals, mp 201–203°. A mixture of this product and N-*p*-tolylphthalimide,¹⁰ mp 202–203°, melted at 202–203° while a mixture of this product and N-*m*-tolylphthalimide,¹⁰ mp 171–173°, melted at 160–185°.

Registry No.—**2** (R = phthalimido), 25577-21-3; **4** (R = phthalimido), 25577-22-4; N-vinylphthalimide, 3485-84-5; isoprene, 78-79-5; 9-methoxyanthracene, 2395-96-2.

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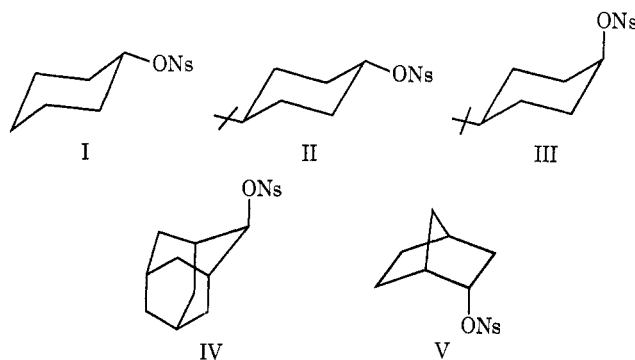
The Effect of Pressure on Some Sterically Hindered Solvolysis Reactions¹

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In several earlier publications^{2–4} we have shown that the activation volume of a solvolysis reaction may depend somewhat on the occurrence of participation. In at least some of the reactions for which participation has been claimed, steric hindrance has been proposed⁵ as an alternative explanation of the rate ratio of epimeric substrates, and since steric hindrance evidently also has small effects on the activation volume, at least in the Menshutkin reaction,^{6,7} we considered it desirable to study the pressure-promoted hydrolysis of the following closely related nosylates.



In these reactions the formation of an ion pair should be unhindered for I and II and hindered for IV and V. In I, the leaving group is expected to depart from an equatorial position. In II, the 4-*tert*-butyl group forces it to leave from that position. In IV, the rigid adamantyl ring system forces it to leave from the axial position; hindrance is then provided by the axial 3- and 5-hydrogen atoms. In V, hindrance has been considered to be exerted by the 6-*endo*-hydrogen atom.⁵ We hoped that a large difference between the pressure coefficients of II and III would furthermore enable us to calculate the effect of pressure on A, a measure of the size of the nosyloxy group.⁸ The results are shown in Table I.

The absolute ΔV^* values are somewhat larger than those observed in earlier studies; the reason for this is that the more precise conductance method employed here allows its determination from observations over a smaller range (1 kbar) and with smaller pressure intervals (see ref 6 for a full discussion of this point).

The observations clearly do not show a correlation between ΔV^* and steric hindrance. While the ΔV^* values for I and II do seem to be slightly less negative

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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 ³ k ₁	p	10 ³ k ₁	p	10 ³ k ₁	p	10 ³ k ₁	p	10 ³ 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%.

Registry No.—I, 788-92-1; II, 25662-47-9; III, 25662-48-0; IV, 25665-65-0; V, 25716-02-3.

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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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