

and CCl_4) are 3.40, 5.76, 6.90, 6.95, 7.35, 7.79, 8.03, 8.40, 8.60, 13.0, 13.18, and 13.60 μ . The nmr of **12a** showed absorption at δ 0.4–3.6 (m, ten protons), 7.3, 7.8 (eight protons), and a broad absorption at 9.9 ppm for acid protons (two protons). The nmr of **12a** dimethyl ester (CCl_4) showed absorption at δ 1.4–2.5 (m, ten protons), singlets at 3.40 and 3.53 (six protons), and 7.3 and 7.7 (m, eight protons).

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$: C, 74.1, H, 6.3. Found: C, 74.4, H, 6.4.

Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4$: C, 75.0; H, 6.9; sapon equiv, 176. Found: C, 74.9; H, 7.00; sapon equiv, 176.

9-(Carboxyethyl)-9-(carboxypentyl)fluorene (12b).—A 3-l. stainless steel rocker autoclave was charged with 526 g of methyl 6-(9-fluorenyl)caproate¹³ (1.8 mol), 225 g (3.1 mol) of glacial acrylic acid, and 450 g (6.8 mol) of 85% potassium hydroxide pellets. This mixture was heated to 220° for 20 hr. The product was dissolved in 3 l. of water and filtered, and the filtrate was acidified with concentrated hydrochloric acid liberating a white viscous oil. Upon dissolving this crude oil in 2 l. of methanol approximately 110 g was insoluble. This apparently polymeric material was separated by decantation. To the methanol solution was added 15 g of *p*-toluenesulfonic acid; this mixture was refluxed for 24 hr. After the usual work-up 398 g of the dimethyl ester was isolated by distillation [bp 215–218° (0.3 mm), n_D^{20} 1.5604]. The ir spectrum of the dimethyl ester of **12b** (CS_2 and CCl_4) showed major bands at 3.3 (w), 3.41 (s), 3.50, 5.75, 6.90, 6.95, 7.31, 7.70, 8.05, 8.40, 8.60, 13.0, 13.17, and 13.62 μ . The infrared spectrum of **12b** (KBr pellet) showed major bands at 3.0, 3.32, 3.48, 4.18, 5.88, 6.93, 7.0, 7.65, 8.0, 8.31, 10.7, 12.86, and 13.58 μ .

Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_4$: C, 75.76; H, 7.42; sapon equiv, 190. Found: C, 75.95; H, 7.42; sapon equiv, 202.

Registry No.—**5**, 13099-00-8; **7**, 974-60-7; dimethyl 2-phenylglutarate, 10436-86-9; **12a**, 13098-95-8; **12a** dimethyl ester, 13098-96-9; **12b** dimethyl ester, 13098-99-2; **5** methyl ester, 16423-39-5.

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(13) Prepared by the base-catalyzed reaction of fluorene with ϵ -caprolactone (see ref 3).

The Mills Nixon Effect. II¹

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In an earlier paper¹ we reported a quantitative examination of product distributions in bromination and nitration of *o*-xylene, indan, and tetralin. The results revealed a higher *ar*- β /*ar*- α substitution ratio for indan than for tetralin and it was assumed that this order, which is the reverse of that to be expected on steric grounds, and is also inexplicable on any standard electronic basis, could be explained in terms of the strain developed in the five-membered ring system of indan. We now report work on aromatic hydrogen exchange of the three hydrocarbons in anhydrous trifluoroacetic acid. This system was chosen because it has probably the lowest steric requirement of any electrophilic substitution reaction and any steric masking

of the effect of ring strain should therefore be minimized. The results are shown in Table I.

TABLE I
RATE CONSTANTS FOR HYDROGEN EXCHANGE OF TRITIATED HYDROCARBONS IN ANHYDROUS TRIFLUOROACETIC ACID AT 70°

Hydrocarbon	10%, sec ⁻¹	Registry No.
3-[³ H]- <i>o</i> -Xylene	1.10 ± 0.02	16408-68-7
4-[³ H]- <i>o</i> -Xylene	1.55 ± 0.03	16408-69-8
4-[³ H]-Indan	0.82 ± 0.01	16408-70-1
5-[³ H]-Indan	3.34 ± 0.04	16408-71-2
5-[³ H]-Tetralin	3.10 ± 0.02	16408-72-3
6-[³ H]-Tetralin	3.35 ± 0.03	16408-73-4

The rate constants for detritiation of indan confirm that the two aromatic positions have markedly different reactivities. The ratio of the two rate constants *ar*- α /*ar*- β is 0.25, of the same order as the ratios of the percentages of α -bromo and β -bromoindans,¹ which range from 0.19 to 0.28. The two positions in tetralin are almost equally reactive, and again this result is in line with the bromination and nitration studies and with the results for *o*-xylene.² It seems clear, therefore, that indan reflects in its electrophilic substitution reactions the strain imposed on the aromatic ring by the fused, five-membered ring. Tetralin does not show this difference in reactivity, and it is probable that the buckled six-membered ring imposes little strain on the aromatic ring.

One further point should be made. In our previous detailed explanation,¹ we assumed that an increase in the double-bond character of the common bond in indan will result in a less stable system. This is undoubtedly a useful practical assumption but in making it we were directly applying a conclusion drawn by Brown from his results on nonaromatic derivatives of cyclopentane and cyclohexane.³ This we now believe was not justifiable because the kind of interference (involving methylene hydrogens) that allowed Brown to explain his generalization is absent in our compounds. While, therefore, the assumption correlates our results, it does not provide a satisfactory explanation for them.

Experimental Section

Anhydrous trifluoroacetic acid was prepared by fractional distillation of commercial acid from sulfuric acid and then from silver oxide.

Tritiated hydrocarbons were prepared from the corresponding bromo compounds.¹ The bromo compounds were shown to be pure by glpc analysis under conditions known to separate isomeric pairs; the Grignard reagents formed from them were treated with tritiated water (specific activity 10 mCi/ml), and the resulting hydrocarbons were purified by fractional distillation. These showed no impurity on glpc analysis.

Rate Measurements.—These were carried out in anhydrous trifluoroacetic acid solvent at 70° as described previously,⁴ using hydrocarbon concentrations of about 0.05 *M*. First-order rate plots of log count rate vs. time were linear over at least three half-lives in all cases; rate constants calculated from the equation $k = 2.303 \times \text{slope of rate plot}$, were determined at least twice for each substrate and were reproducible to within $\pm 2\%$. The rate constants were not converted into partial rate factors because the rate constant obtained for *p*-[³H]-toluene in this study was 7% lower than that previously reported⁴ and used as standard.

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However, since all runs were carried out in the same trifluoroacetic acid and reproducible rate constants were obtained for all the hydrocarbons, the comparison of rate constants within the series studied is valid.

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Solvolysis of 2-(Δ^2 -Cyclohexenyl)ethyl System

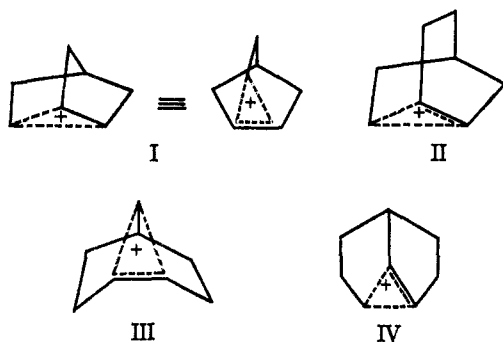
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The field of π -electron participation in solvolytic displacement reactions of unsaturated sulfonate esters has grown rapidly in the last decade and has attracted the interest of many chemists both from the theoretical and synthetic point of view.¹

Recently, it has been commonly accepted that one and the same bridged nonclassical ion can be generated by delocalization of either σ or π electrons. One criterion which has been frequently used to demonstrate the intervention of bridged ions is rate enhancement observed in solvolysis. Examples of this phenomenon include the 2-norbornyl nonclassical ion²⁻⁴ I and the two isomeric nonclassical bicyclo[3.2.1]oct-2-yl cations^{5,6} (II and III)⁷ as well as the nonclassical bicyclo[3.3.0]oct-2-yl cation^{8,9} (IV).



Such rate enhancement is not, however, the general rule for all compounds possessing a nonconjugated double bond. Thus Wilcox and Chibber¹⁰ reported the absence of double bond interaction in the solvolysis

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(10) C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

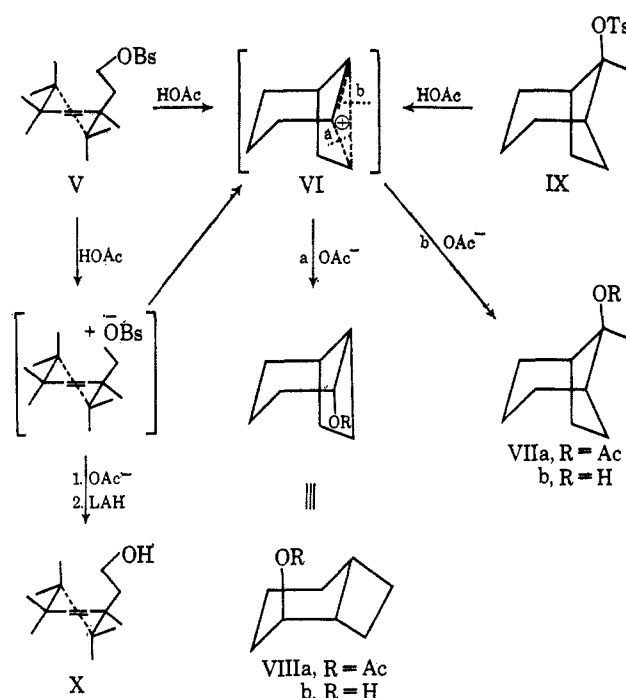


Figure 1.

of Δ^3 -cyclohexenylcarbinyl derivatives. A similar conclusion was reached for 2-(Δ^2 -cyclopentenyl)ethyl-,¹¹ 3-(Δ^1 -cyclopentenyl)propyl-,⁹ and 3-(Δ^3 -cyclopentenyl)propyl brosylates.³

In view of the general interest of double-bond interactions we wish to report the synthesis of 2-(Δ^2 -cyclohexenyl)ethyl brosylate and its acetolysis along with the saturated analog.

Results and Discussion

2-(Δ^2 -Cyclohexenyl)ethyl alcohol and the brosylate ester were prepared as outlined in the Experimental Section. The purity of the ester, which is a liquid at room temperature, was estimated from the infinity titer of kinetic runs to be better than 95–96%. The solvolysis was conducted in anhydrous acetic acid at two temperatures, and the first-order reactions were followed to about 60% reaction. The kinetic data are collected in Table I along with pertinent reference rates.

Product Analysis.—Infrared analysis, vapor phase chromatography, and nuclear magnetic resonance techniques were used to determine product composition. Acetolysis products were reduced by lithium aluminum hydride to the corresponding alcohols and analyzed. Possible bicyclic products, *endo*-bicyclo[3.2.1]octanol-8 (VIIb) and *endo*-bicyclo[4.2.0]octanol-2 (VIIIb), which could have been formed if double-bond participation was significant, were looked for carefully and found to be absent within experimental error. Acetolysis of V gave only compound X (See Figure 1).

The slight decrease in the rate of acetolysis of V compared with the saturated analog is attributed to the double bond which destabilizes the transition state for solvolysis by inductively retarding the departure of the incipient anion. The ratio $k_{\text{satd}}/k_{\text{unsatd}} = 1.73$ agrees with that found by Wilcox¹⁰ for the solvolysis of Δ^3 -

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