Ring Size Effects in the Neophyl Rearrangement. VIII. The Synthesis and Solvolysis of 1-Methyl-2,3-benzocycloalkenylcarbinyl Tosylates[1,2]

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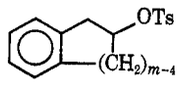
1-Methyl-2,3-benzocycloalkenylcarbinyl tosylates **5** were synthesized and their solvolytic reactivity was determined. Neither in acetolysis nor in hydrolysis in 60% acetone was a ring size effect of any significance evidenced. The reactivities mirrored those of the unmethylated analogs **3**. Products from **5** were totally rearranged *via* aryl ring migration indicating that aryl participation was essentially the only solvolysis pathway. The opposing factors in **3** of strain in the phenonium ion intermediate *vs.* conformational effects are discussed together with a reactant strain effect in **5**. The conclusion is drawn that the three effects are balanced to produce the similarity in behavior between the two sets of tosylates.

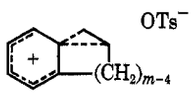
Some years ago Huisgen and coworkers[4] observed that the formolysis of tosylates **1** exhibited a ring size effect, as indicated in **1**. Inspection of molecular



1

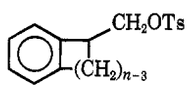
m (ring size)	6	7	8	9	(1)
$10^5 k_1$ (35°, sec^{-1})	27.3	152	2250	741	

models suggested that this rate effect was caused by strain energy differences existing in the phenonium ion intermediates **2** produced in the reaction, with maximum stability being accorded **2**, $m = 8$. The



2

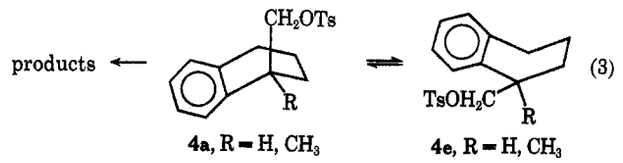
formolysis of tosylates **3**, which utilize the same phenonium ion intermediates, failed to exhibit as pronounced an effect, however (2), with the tetralyl analog (**3**,



3

n (ring size)	5	6	7	8	(2)
$10^5 k_1$ (35°, sec^{-1})	2.51	6.80	1.80	0.180	

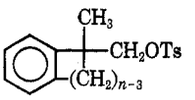
$n = 6$) exhibiting a weakly maximum reactivity.[5] To account for this decreased spread in reactivity, Huisgen and coworkers proposed that two counteracting effects were operative with **3**, the *strain effect* in **2** which increased reactivity with increasing ring size (at least to a point) and a *conformational effect* which decreased reactivity similarly. For example, with **3**, $n = 6$, only axial conformer **4a** (R = H) in eq 3 is sterically able to form **2** ($m = 7$) *via* phenyl participation. From relative rate comparisons, a "conformational hindrance effect" was calculated for **3**, with decelerating rate factors of 0, 2, 115, and 380 fold for $n = 5$, 6, 7, and 8,



4a, R = H, CH_3 **4e**, R = H, CH_3 (3)

respectively. These factors measured the decreased ability to achieve the proper axial conformation for formolysis with phenyl participation as the ring size increased. The two effects mentioned apparently were in best balance for reactivity for the tetralyl compound. The effects understandably became less important in acetolysis and ethanolysis where phenyl participation is not so strongly evident.

Because of our interest in conformational effects in the neophyl rearrangement[6] we decided to study the related neophyllike tosylates **5**. Both a poorly ion-

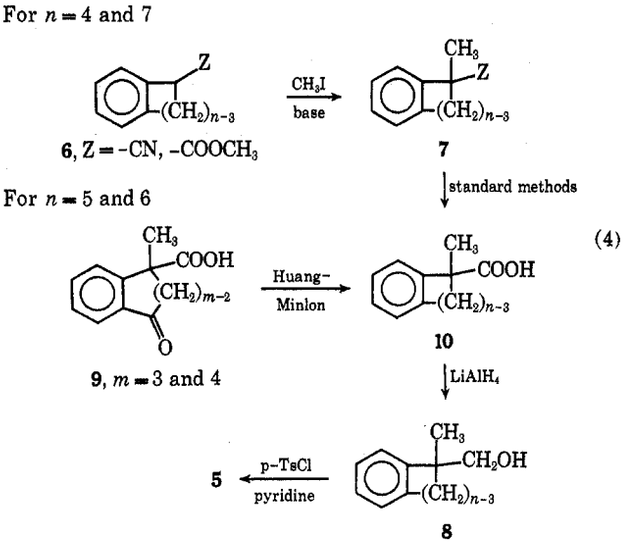


5

$n = 4, 5, 6, 7$

izing medium, acetic acid ($Y^7 = -1.65$), and a better one, 60% acetone–40% water ($Y^7 = +0.796$), were chosen as solvents for the study.

The tosylate syntheses were straightforward and warrant little discussion. Two general routes (4) were



6, Z = -CN, $-COOCH_3$ **7** **9**, $m = 3$ and 4 **10** **8** (4)

(1) Paper VII: J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

(2) Taken from portions of the dissertation of W. W. P., Jr., Loyola University of Chicago, 1970, and the M.S. thesis of J. J. W., Loyola University of Chicago, 1966.

(3) National Science Foundation Trainee, 1968–1969.

(4) R. Huisgen, E. Rauenbusch, G. Seidl, and I. Wimmer, *Justus Liebigs Ann. Chem.*, **671**, 41 (1954). See also R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2730 (1963).

(5) R. Huisgen, G. Seidl, and I. Wimmer, *Tetrahedron*, **20**, 623 (1964).

(6) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3434 (1962).

(7) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

TABLE I

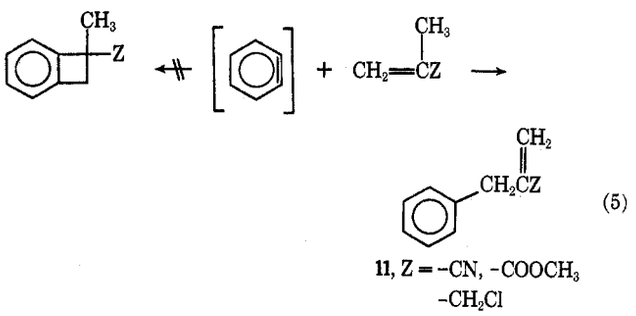
TITRIMETRIC RATE DATA

Tosylate 5, n	Temp, °C	$10^5 k_1$, sec^{-1} (HOAc[a])	$10^5 k_1$, sec^{-1} (Me_2CO–H_2O[b])
4	(25.0)	(0.128)[c]	(0.390)
	44.9	1.64 ± 0.01[d]	4.06 ± 0.08
	44.9	1.34 ± 0.06[e]	
	55.0		10.2 ± 0.31
	64.7	13.7 ± 0.20	26.0 ± 0.20
	76.8	50.1 ± 0.9	99.8 ± 0.30
	81.8	89.1 ± 0.9	
5	(25.0)	(0.034)	(0.128)
	44.9	0.601 ± 0.06	1.58 ± 0.11
	44.9	0.509 ± 0.02[e]	
	56.5		5.11 ± 0.32
	64.7	6.93 ± 0.14	12.10 ± 0.12
	76.8	24.6 ± 0.20	43.1 ± 0.60
	81.8	44.5 ± 0.30	
6	(25.0)	(0.059)	(0.157)
	44.9	0.873 ± 0.02	2.04 ± 0.02
	44.9	0.678 ± 0.02[e]	
	55.1		5.25 ± 0.12
	64.7	9.40 ± 0.32	15.6 ± 0.50
	76.8	25.7 ± 0.80	53.8 ± 0.70
	81.8	58.7 ± 0.24	
7	(25.0)	(0.036)	(0.999)
	56.5		4.63 ± 0.09
	64.7	6.47 ± 0.10	10.63 ± 0.26
	76.8	23.1 ± 0.40	35.5 ± 0.70
	81.8	40.7 ± 0.50	

[a] Redistilled glacial acid, containing 0.3% acetic acid anhydride and sodium acetate (0.050 *M* for 0.025 *M* tosylate). [b] Acetone distilled from potassium permanganate and distilled water (60:40, v/v) with 2,6-lutidine present (0.035 *M* for 0.030 *M* tosylate). [c] All values in parenthesis were extrapolated from data at other temperatures. [d] Errors are average deviations from the mean rate constant. [e] Initial rate constants when sodium acetate was absent.

used and the details may be found in the Experimental Section.

As a note of passing interest, attempts to obtain **5**, $n = 4$, *via* cycloaddition instead gave "ene" products at the initial stage (eq 5).



11, Z = –CN, –$COOCH_3$, –CH_2Cl (5)

Table I contains the titrimetric rate data obtained for these tosylates and Table II lists the activation parameters.

Determination of products indicated complete ring expansion by aromatic ring migration in every case. The products are summarized in Table III.

The quantitative formation of ring-expanded products in both solvents indicates that very likely $k_\Delta \gg k_s$ in these systems. Such was not the case for **3** in 70% dioxane–water (Y[7] = +0.013). Huisgen and Seidl reported[8] considerable nucleophilic solvolysis to unrearranged product (11–26%), increasing as base was

(8) R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2740 (1963).

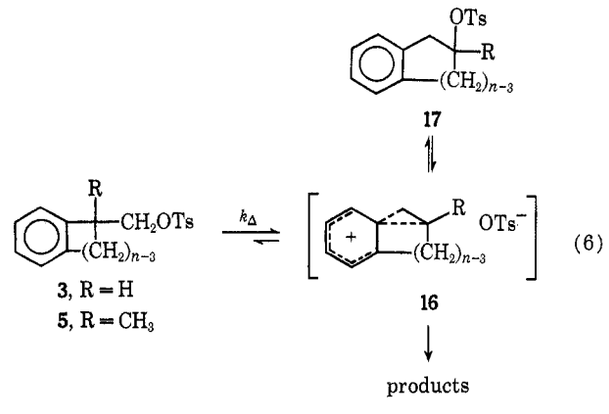
TABLE II

ACTIVATION PARAMETERS[a]

Tosylate 5, n	ΔH^*, kcal mol^{-1}	ΔS^*, eu
	Acetolysis	
4	23.5 ± 0.1	−6.6 ± 0.3
5	25.0 ± 0.1	−3.9 ± 0.4
6	24.8 ± 0.3	−3.7 ± 0.9
7	25.4 ± 0.3	−2.8 ± 0.8
	Hydrolysis	
4	21.4 ± 0.2	−11.6 ± 0.7
5	22.8 ± 0.2	−8.9 ± 0.5
6	22.7 ± 0.3	−8.8 ± 0.7
7	22.9 ± 0.3	−9.0 ± 0.9

[a] Calculated from an Eyring equation plot of $\log k_1/T$ *vs.* $1/T$.

added to the solvent. Moreover, acetolyses of the tosylates **5** showed good first-order kinetics throughout, unlike **3** (n = 5, 6)[5] which showed initial nonlinear kinetic behavior due to ion pair return with rearrangement. It is likely in our cases that the sequence shown in eq 6 (R = CH_3) occurs. From steric and reactivity



3, R = H
5, R = CH_3

12 from capture by solvent

13–15 from proton elimination

considerations, ion pair return from **16** (R = CH_3) either back to inital reactant **5** or to rearranged **17** would be less probable than such return from **16** (R = H). Because ion pair return (mostly to **17**, R = H) complicated Huisgen's acetolysis data,[5] it is unwise for us to compare the ratio of acetolysis rates of **3** and **5** for each value of n. Succinctly, our rates for **5** are very probably determined by k_Δ alone,[9] whereas Huisgen's rates for **3** reflect k_Δ very likely complicated by rates of rearrangement to **17**, R = H instead. Nonetheless, the *relative* rates in each series may be more meaningful because differences in k_Δ are undoubtedly involved in the trends observed.

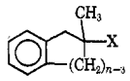
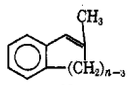
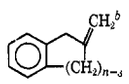
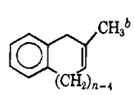
A comparison of relative formolysis rates for **3** and relative hydrolysis rates for **5** would seem even less faulty. Formolysis of **3** was smoothly first order and essentially totally limiting in nature,[5] and ring-expanded products formed over 90% of the products.[8] Such also was found in this study for the hydrolysis of **5**. The solvents each possess a $+Y$ value, though no claim is made for any other similarity. Nevertheless,

(9) Product formation *via* total rearrangement by aromatic ring migration, the lack of nonlinear kinetic behavior,[5] and analogy to neophyl tosylate itself (which is governed totally by k_Δ in solvolysis[10]) all point to the equality of the titrimetric rate constant k_1 with k_Δ in **5**.

(10) *Cf.* A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968).

TABLE III

PRODUCTS OF SOLVOLYSIS[a]

Tosylate 5, n	 12	 13	 14	 15
		Acetolysis		
4	15 (X = OAc)	74	11	
5	9	52	6	33
6	32	26	21	21
7	92	Trace	Trace	Trace
		Hydrolysis		
4	26 (X = OH)	61	13	
5	89	———	11[c] ———	
6	85	10	2	3
7	96	Trace	Trace	Trace

[a] The yields of products were essentially quantitative. [b] From nmr and glpc analyses only. Hydrogenation of the total olefins led to 2-methylbenzocyclenes only. [c] Obtained as 2-methylnaphthalene, presumably *via* air oxidation of the hydroaromatic olefinic products.

TABLE IV

RELATIVE RATES

Tosylate	Solvent	Temp, °C	k_{rel}, ring size 4	5	6	7
1[a]	HCOOH	35			1.0	5.6
3	HCOOH[b]	35[c]		1.0	2.7	0.7
		70		1.0	3.4	1.1
	70% Dioxane[b]	70			3.0	1.0
	60% Acetone[d,e]	82	1.4	1.0	2.9	0.67
	HOAc	70[b]		1.0	2.4	0.95
		82[d,e]	0.9	1.0	1.7	1.1
5	60% Acetone[d]	35[f]	2.6	1.0	1.2	0.81
		70[f]	2.0	1.0	1.2	0.82
		77	2.3	1.0	1.3	0.82
	HOAc[d]	35[f]	3.0	1.0	1.5	0.90
		70[f]	2.3	1.0	1.5	0.97
		82	2.0	1.0	1.3	0.91

[a] Reference 4. For ring size 8 and 9, k_{rel} = 82 and 27, respectively. [b] Reference 5. [c] For ring size 8, k_{rel} = 0.07. [d] This work. [e] The preparation of these tosylates was achieved as reported for n = 5–7[8] and n = 4 [M. R. Cava and M. J. Mitchell, *J. Org. Chem.*, **27**, 631 (1962); J. A. Skorcz and J. E. Robertson, *J. Med. Chem.*, **8**, 255 (1965)]. The details of these solvolyses may be found in the dissertation of W. W. P., Jr. [f] Calculated from data in Table II.

in such solvents the process in question should be essentially determined by k_Δ and one could examine the rates to look for "conformational hindrance effects" on k_Δ. These rate comparisons made from literature data and the results of the present study are collected in Table IV.

One sees immediately that the reduced spread in reactivity with the partial rate order of ring size = 6 > 7 was maintained in **5** comparably to **3**, regardless of the variety of solvents and temperatures listed. This is unexpected because the 1-methyl substituent should render axial and equatorial conformers in the six- and seven-membered ring cases more equivalent, *e.g.*, **4a** and **4e** (R = CH_3) in 3, and essentially cancel Huisgen and coworkers' conformational effect,[5] allowing a relative rate series more like that of **1** where the strain effect predominates, *i.e.*, a partial rate order of ring size 6 < 7.

We conclude that another factor, reactant internal energy, becomes important with tosylates **5**. The 1-methyl substituent would not in all likelihood add to the strain in **16** (R ≈ CH_3) very much, but the quaternary carbon at C-1 in **5** would undoubtedly increase the torsional strain due to bond eclipsing and thus raise the internal energy of the tosylates in the order n = 4 > 5 > 6 > 7, *i.e.*, an effect that would decrease with ring size. Thus, for either **3** or **5**, n = 4, the strain in **16** would be considerable but so would be the reactant internal energy in **5**, n = 4, and the balance of these factors could be such as to give this ring size the modest maximum in reactivity noted in Table IV. For the other ring sizes these effects could be in balance such that the low spread in reactivity again occurs, even without the missing conformational hindrance effect of Huisgen.

In summary, the solvolytic reactivity of the neophyl-like tosylates **5** shows essentially no real change from the nonquaternary analogs **3**. The neophyl rearrangement therefore fails to demonstrate a noteworthy ring size effect in these instances.

Experimental Section

Melting points (Fisher-John block) and boiling points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by the analytical department of G. D. Searle and Co., Skokie, Ill. Infrared data (λ in microns) were obtained on Beckman IR-5A and Perkin-Elmer Model 21 instruments. Only partial spectral assignments are given. Nuclear magnetic resonance spectra (δ) in parts per million were determined on a Varian A-60A spectrometer using TMS as an internal standard. Peak integrals were in agreement with the assignments given. The usual splitting abbreviations are used. Centers of complex multiplets are given unless a range is specified. AB patterns, however, have been assigned true chemical shifts.

Gas–liquid partition chromatography (glpc) was performed on a Varian Aerograph A-90P instrument with helium as the carrier gas. Columns and other details are given where appropriate. Peak areas were integrated with a disc integrator. General synthetic procedures are described with specific properties relegated to summaries, unless obviously otherwise.

Methylation Reactions. A. To Form 7 (Z = CN).—A solution of freshly prepared potassium *tert*-butoxide (0.23 mol) in dry *tert*-butyl alcohol was added to dimethyl sulfoxide (30 ml). The appropriate nitrile **6**, $n = 4$[11,12] or **7**,[11,12] Z = CN (0.054 mol), was then added at 50°. After being stirred for 30 min, the solution was cooled and methyl iodide (0.23 mol) was added dropwise over 30 min with additional cooling to moderate the reaction. Reaction was continued for 1 hr. Excess hydrochloric acid was then added cautiously and most of the solvent was removed by vacuum distillation. The residue was taken up in ether and washed with sodium thiosulfate solution and water. The dried (Na_2SO_4) ether solution was then distilled to obtain the product **7**.

1-Methylbenzocyclobutene-1-carbonitrile (**7**, $n = 4$, Z = CN): 67.7%; bp 95–99° (3.5 mm); $n^{26}D$ 1.5256; d^{27}_4 0.970; λ (neat) 4.5 (CN), 7.25 (CH_3); δ ($CDCl_3$) 7.37 m (ArH), 3.80 d, 3.10 d (CH_2, AB, J = 14 Hz), 1.75 s (CH_3).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.33. Found: C, 83.90; H, 6.37.

1-Methylbenzosuberene-1-carbonitrile (**7**, $n = 7$, Z = CN): 71.2%; bp 105–106° (0.25 mm); $n^{26}D$ 1.5428; d^{26}_4 0.992; λ (neat) 4.5 (CN), 7.21 (CH_3); δ ($CDCl_3$) 7.5–7.0 m (ArH), 3.7–2.9 m (4-CH_2), 2.9–1.2 m (other ring H's), 1.80 s (CH_3).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: 84.46; H, 8.20.

B. To Form 7 (Z = $COOCH_3$).—The appropriate methyl ester **6**, $n = 4$[13] or **7**,[14] Z = $COOCH_3$ (0.086 mol) in ether (25 ml) was added to liquid ammonia (300 ml) containing sodium amide (0.09 mol). The solution was stirred at −55° for 1 hr. Methyl iodide (0.18 mol) in ether (25 ml) was then added dropwise over 30 min. The reaction warmed to −37°, at which temperature stirring was continued for 3 hr. Ammonium chloride (0.2 mol) was added and the ammonia was allowed to evaporate as it was replaced by ether. Subsequent operations were the same as described in A.

Methyl 1-methylcyclobutene-1-carboxylate (**7**, $n = 4$, Z = $COOCH_3$): 69%; bp 84° (1.4 mm); $n^{27}D$ 1.5130; λ (neat) 5.80 (CO), 7.28 (1-CH_3); δ ($CDCl_3$) 7.23 m (ArH), 3.73 d, 3.03 d (CH_2, AB, J = 14 Hz), 3.67 s (OCH_3), 1.67 s (CH_3).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.10; H, 6.94.

Methyl 1-methylbenzosuberene-1-carboxylate (**7**, $n = 7$, Z = $COOCH_3$): 19%;[15] bp 134° (1.5 mm); $n^{26}D$ 1.5350; d^{26}_4 1.117; λ(neat) 5.80 (CO), 7.25 (1-CH_3); δ ($CDCl_3$) 7.1 m (ArH), 3.62 s (OCH_3), 2.80–2.52 m (4-CH_2), 2.50–1.2 m (other ring H's), 1.62 s (CH_3).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.21; H, 8.14.

Conversion of 7 to 10.—Saponification of the methyl esters **7** with aqueous sodium hydroxide containing 20% ethanol produced the following compounds.

1-Methylbenzocyclobutene-1-carboxylic acid (**10**, $n = 4$): 84.4%; bp 134° (1.6 mm); $n^{28}D$ 1.5315; λ (neat) 3.0–4.5, 5.9 (COOH); δ ($CDCl_3$) 12.2 s (COOH), 7.23 s (ArH), 3.78 d, 3.02 d (ring CH_2, AB, J = 14 Hz), 1.70 s (CH_3).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.97; H, 6.31.

1-Methylbenzosuberene-1-carboxylic acid (**10**, $n = 7$): 45%; mp 161–162°; λ (KBr) 3.0–4.5, 6.0 (COOH); δ ($CDCl_3$) 10.3 br s (COOH), 7.38 m (ArH), 2.80 m (4-CH_2), 2.6–1.0 m (other ring H's), 1.73 s (CH_3).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.60; H, 7.95.

These acids were also obtained by various hydrolysis methods from the nitriles **7**. The tertiary nature of the latter hindered such hydrolyses, however, and only poor to modest yields could be obtained.[16]

Huang-Minlon Reduction of 9 to 10.—To a solution of potassium hydroxide (1.0 mol) in diethylene glycol (700 ml) was added the appropriate acid **9** (0.25 mol), $m = 3$[17] or 4,[18] together with hydrazine hydrate (90%, 50 ml). The solution was heated to reflux and the distillate was removed until the pot temperature rose to 220°. Heating at this temperature was continued under reflux for 12 hr. The cooled solution was then acidified with hydrochloric acid. Recrystallization of the precipitated material from benzene–hexane gave the following compounds.

1-Methylindan-1-carboxylic acid (**10**, $n = 5$): 94%; mp 71.5–72.5° (occasionally samples had mp 57–59°); λ (KBr) 3.0–4.5, 6.05 (COOH), 7.21 (CH_3); δ ($CDCl_3$) 10.49 br s (COOH), 7.20 m (ArH), 3.15 m and 1.63 m (centers of ABX_2 pattern for ring CH_2's), 1.55 s (CH_3).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.13; H, 7.05.

1-Methyltetralin-1-carboxylic acid (**10**, $n = 6$): 94%; mp 118–119° (lit.[20] mp 81°); λ (KBr) 3.0–4.5, 6.0 (COOH), 7.29 (CH_3); δ ($CDCl_3$) 11.25 br s (COOH), 7.00–7.34 (ArH), 2.79, 2.24, 1.83 all m (4-, 5-, 6-CH_2, respectively), 1.57 s (CH_3).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.39.

Reduction of 7 and 10 to the Carbinols 8.—Reduction of the methyl esters (see B above) or the carboxylic acids **10** was achieved with lithium aluminum hydride in ether in standard fashion.[16]

1-Methylbenzocyclobutenyl-1-carbinol (**8**, $n = 4$): 95%; bp 78° (0.3 mm); $n^{26}D$ 1.5366; λ (neat) 3.0 (OH), 7.3 (CH_3), 9.7 (1° CO); δ ($CDCl_3$) 7.20 m (ArH), 3.67 br s (-CH_2OH, probably center of AB pattern), 3.08 d, 2.82 d (ring CH_2, AB, J = 14 Hz), 2.8 br s (OH), 1.40 s (CH_3).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.34; H, 8.07.

1-Methylindanyl-1-carbinol (**8**, $n = 5$): 92%; bp 90° (1.0 mm); $n^{26}D$ 1.5392; λ 3.03 (OH), 7.30 (CH_3), 9.7 (1° CO); δ ($CDCl_3$) 7.20 s (ArH), 3.50 s (CH_2OH), 2.90 m (4-CH_2), 2.4–1.6 sharp series of peaks (5-CH_2, probably AB portion of ABX_2 pattern, and OH), 1.23 s (CH_3).

Anal. Calcd for $C_{11}H_{14}O$: C, 80.99; H, 8.65. Found: C, 81.12; H, 8.88.

1-Methyltetralyl-1-carbinol (**8**, $n = 6$): 82%; bp 112° (1.25 mm); $n^{26}D$ 1.5530; λ (neat) 3.05 (OH), 7.3 (CH_3), 9.75 (1° CO); δ ($CDCl_3$) 7.18 m (ArH), 3.77 d, 3.51 d (CH_2OH, AB because of adjacent asymmetry,[21] J = 11 Hz), 2.80 m (4-CH_2), 2.2–1.4 m (other ring H's), 1.90 s (OH), 1.25 s (CH_3).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.24.

1-Methylbenzosuberenyl-1-carbinol (**8**, $n = 7$): 100%; bp 105° (0.1 mm); $n^{26}D$ 1.5560; d^{26}_4 1.120; λ (neat) 3.05 (OH), 7.25 (CH_3), 9.8 (1° CO); δ ($CDCl_3$) 7.4–7.0 m (ArH), 3.72 sharp m (-CH_2OH, probably close AB pattern), 2.86 broad envelope (4-CH_2), 2.1–1.3 m (other ring H's), 1.55 s (OH), 1.32 s (CH_3).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.12; H, 9.38.

Preparation of Tosylates 5.—All tosylates were prepared from the alcohol in pyridine using *p*-toluenesulfonyl chloride in customary fashion.[22]

1-Methylbenzocyclobutenyl-1-carbinyl tosylate (**5**, $n = 4$): 89%; mp 55–56°; consonant spectra.

(11) J. F. Bunnett and J. A. Skorcz, *J. Org. Chem.*, **27**, 3836 (1962).

(12) We thank Dr. Skorcz for detailed information on the preparation of these nitriles.

(13) L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(14) Prepared from the acid[11] and diazomethane, 86%, bp 118° (0.5 mm). *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.31; H, 7.88.

(15) The principal product was unchanged starting ester. Various other methylation procedures gave no better results.

(16) Details of these and related experimental procedures are omitted for reasons of space. Full descriptions may be found elsewhere.[2]

(17) G. F. Woods, T. L. Heying, L. H. Schwartzman, S. M. Grenell, W. F. Gasser, E. W. Rowe, and N. C. Bolgiano, *J. Org. Chem.*, **19**, 1290 (1954).

(18) Prepared by ring closure of α-methyl-α-phenylglutaric acid[19] (0.1 mol) in concentrated sulfuric acid (150 g) at 100° for 1 hr. The hot mixture was poured over cracked ice (300 g) and the precipitated acid was collected and recrystallized from benzene–hexane, 66%, mp 128–129°, spectra consonant with structure. *Anal.* Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.84.

(19) F. S. Legagneur and C. Neveu, *Bull. Soc. Chim. Fr.*, 70 (1953).

(20) M. Protiva, J. O. Jílek, Z. J. Vejdělek, and P. Finglová, *Chem. Listy* **47**, 584 (1953), report mp 81°. We have no explanation for the discrepancy, although it would be unusual to have such a quaternary acid with the same melting point as the parent (unmethylated) acid (81°).

(21) The expected AB character for the methylene protons in the -CH_2OH group of the alcohols **8** was clear only in this case.

(22) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 5.99. Found: C, 67.59; H, 6.00.

1-Methylindanyl-1-carbinyl tosylate (**5**, n = 5): 53%; mp 38–39°; consonant spectra.

Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.32; H, 6.37. Found: C, 68.71; H, 6.28.

1-Methyltetralyl-1-carbinyl tosylate (**5**, n = 6): 83%; mp 53–53.5°; consonant spectra.

Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 68.95; H, 6.76.

1-Methylbenzosuberenyl-1-carbinyl tosylate (**5**, n = 7): 87%; mp 65–66°; consonant spectra.

Anal. Calcd for $C_{20}H_{24}O_3S$: C, 69.73; H, 7.02. Found: C, 69.68; H, 7.03.

"Ene" Reactions to Form 11.—*o*-Benzenediazonium carboxylate was prepared as follows.[23] *Caution must be exercised. Use of a safety shield is advised. The eompound when dry is treacherously explosive.* Anthranilic acid (15 g, 0.11 mol) and a catalytic amount of trifluoroacetic acid (*ca.* 0.1–0.2 g) were dissolved in dry tetrahydrofuran (250 ml). Isoamyl nitrite (25 g, 0.21 mol) was added dropwise to the solution as it was stirred in a cooling bath at 20°. The initial red precipitate slowly became cream-colored. After 30 min the solid was collected on a *plastic* funnel using a *rubber* spatula for transfer. The clinging tetrahydrofuran was washed away with 1,2-dichloroethane. *The solid must be kept moist with solvent.* The moist solid was washed into a large flask with more 1,2-dichloroethane (total volume ~500 ml) and the appropriate olefin (see below, 0.45–0.50 mol) was added to the suspension. Under efficient reflux condensers, the material was warmed to ~83°, whereupon a rapid evolution of nitrogen occurred with considerable foaming. After this brisk reaction was completed, the solvent and excess olefin were removed by rotary evaporation. The residual oil was then distilled and refractionated to give the products listed.[24]

From methacrylonitrile resulted **α-benzylacrylonitrile** (**11**, Z = -CN): 41%; bp 85–89° (1.5 mm); n^{26}D 1.5210; λ (neat) 4.58 (CN), 10.65 (=CH_2 conjugated with -CN); δ (CCl_4) 7.23 m (ArH), 5.75 slightly broadened s (terminal methylene H cis to CN), 5.57 t (terminal methylene H trans to CN, J = 1.5 Hz), 3.45 d (benzylic CH_2, J = 1.5 Hz).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.33. Found: C, 83.72; H, 6.54.

From methyl methacrylate resulted **methyl α-benzylacrylate**[25] (**11**, Z = -$COOCH_3$): 48%; bp 73° (0.6 mm); n^{28}D 1.5063; λ (neat) 5.81 (CO), 10.5 (=CH_2 conjugated with -$COOCH_3$); the nmr spectra corresponded to that reported.[25]

From methallyl chloride resulted two "ene" chlorides in 51% yield, bp 74–75° (5 mm), roughly corresponding to statistical attack by benzyne at the methyl and chloromethyl groups. **α-Benzylallyl chloride** (**11**, Z = CH_2Cl), 65% upon separation on an Reoplex 400 column at 150° and by nmr analysis: n^{24}D 1.5316; λ (neat) 10.95 (=CH_2); δ ($CDCl_3$) 7.45 s (ArH), 5.33 m and 5.08 m (=CH_2), 4.08 sharp m (-CH_2Cl) and 3.63 m (benzylic CH_2). **1-Chloro-2-benzylpropene**, a 78:22 mixture of stereoisomers by nmr analysis, probably richer in the trans-CH_3, Cl isomer: n^{24}D 1.5330; λ (neat) 7.23 (CH_3); δ ($CDCl_3$) 7.40 s (ArH), 6.05 m (=CH), 3.65 s (benzylic CH_2 in principal isomer), 3.42 m (benzylic CH_2 in minor isomer), 1.70 m (CH_3).

Anal. (of mixture). Calcd for $C_{10}H_{11}Cl$: C, 72.06; H, 6.67. Found: C, 71.75; H, 6.72.

The nitrile **11** and the ester **11** above could be hydrolyzed in refluxing ethyl Cellosolve or 20% aqueous alcohol, respectively, using potassium hydroxide for *ca.* 2 hr. Acidification and recrystallization from hexane gave **α-benzylacrylic acid**: 100%; mp 66–67°; λ (KBr) 3.0–4.5, 6.0 (-COOH), 6.2, 10.9 (=CH_2); δ ($CDCl_3$) 11.3 br s (COOH), 7.30 s (ArH), 6.43 s (terminal methylene H cis to -COOH), 5.60 narrow t (terminal methylene H trans to -COOH), 3.67 s (benzylic CH_3).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.19; H, 6.26.

Syntheses of Reference Compounds. 2-Methylbenzocyclen-2-ols.[26a]—Under nitrogen, the appropriate ketone (see below, 0.32 mol) was added to methylmagnesium iodide (0.32 mol) in ether (200 ml) at a rate sufficient to maintain reflux. After 8 hr reaction under reflux, cold aqueous ammonium chloride (200 ml of 0.3 *M* solution) was added to the cooled reaction material. The ether layer was separated, washed and dried. Distillation then gave the alcohols listed.

From 2-indanone[26b] was obtained **2-methyl-2-indanol** (**12**, n = 4, X = OH): 80%; mp 49–50°; bp 91° (1.75 mm); λ (neat melt) 3.03 (OH), 8.9 (3° CO); δ ($CDCl_3$) 7.23 s (ArH), 3.0 s (CH_2's), 2.30 s (OH), 1.47 s (CH_3).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.44; H, 7.95.

From 2-tetralone[27] was formed **2-methyl-2-tetralol** (**12**, n = 5, X = OH): 74%; bp 99° (1 mm); n^{28}D 1.5442; λ (neat) 3.03 (OH), 9.04 (3° CO); δ ($CDCl_3$) 7.22 s (ArH), 2.92 m (1- and 4-CH_2), 2.0–1.5 m (OH and 3-CH_2), 1.32 s (CH_3).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.35; H, 8.55.

From benzosuberen-2-one[4] was produced **2-methylbenzosuberen-2-ol** (**12**, n = 6, X = OH): 72%; bp 86–87° (0.25 mm); n^{25}D 1.5460; λ (neat) 2.98 (OH), 8.8–9.06 (3° CO); δ ($CDCl_3$) 7.22 s (ArH), 3.0 s (1-CH_2), 2.82 m (5-CH_2), 2.23 br s (OH), 2.08–1.42 m (3, 4-CH_2's), 1.17 s (CH_3).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.89; H, 9.44.

From benzocyclocten-2-one[28] was made **2-methylbenzocyclooctен-2-ol** (**12**, n = 7, X = OH): 75%; bp 122° (2.25 mm); n^{26}D 1.5497; λ (neat) 3.0 (OH), 9.1 (3° CO); δ ($CDCl_3$) 7.13 s (ArH), 2.82 s (1-CH_2), 2.75 m (6-CH_2), 1.85–1.1 m (other CH_2's), 1.68 s (OH), 1.27 s (CH_3).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found C, 81.51; H, 9.63.

Conversion of these alcohols to their corresponding acetates by a variety of techniques gave varying amounts of olefin by dehydration.[16] Consequently, the acetate products **12**, Z = OAc, formed in the acetolysis study were characterized by saponification to **12**, Z = OH, or by pyrolysis to the following olefins: **2-methylindene**[29] (**13**, n = 4); **2-methyl-3,4-dihydronaphthalene**[30] (**13**, n = 5); **4-methylbenzo[1.2]cyclohepta-1,3-diene**[31] (**13**, n = 6); and **4-methylbenzo[1.2]cyclocta-1,3-diene** (**13**, n = 7). This last olefin was prepared from alcohol **12**, n = 7, X = OH, by dehydration in hot benzene containing a little iodine: 100%; bp 82–83° (1 mm); n^{27}D 1.5594; d^{27}_4 0.946; λ (neat) 7.22 (CH_3); δ ($CDCl_3$) 7.03 s (ArH), 6.23 m (=CH), 2.62 m (benzylic CH_2), 2.2–1.2 m (all other CH_2's), 1.87 d (CH_3, J = 2 Hz).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.71; H, 9.31.

Products **14** and **15** were characterized by instrumental methods only. Hydrogenation of them over Pd/C at 25° gave the following benzocyclenes: **2-methylindan**[32] from **14**, n = 4; **2-methyltetralin**[33] from **14**, n = 5; and **2-methylbenzosuberene**: bp 100° (1 mm); n^{25}D 1.5282; d^{25}_4 0.940; λ (neat) 7.28 (CH_3); δ ($CDCl_3$) 7.05 s (ArH), 2.70 m (benzylic CH_2's), 2.03–1.12 m (all other rings H's), 0.95 distorted d (CH_3, $J \sim 6$ Hz).

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.97; H, 9.94.

The solvolysis products **14** and **15** from tosylate **5**, n = 7, were obtained in too small amounts for even characterization. Their structures are assumed.

In all cases, the 1-methyl analogs of the above alcohols and hydrocarbons were also prepared.[16] They were totally absent in the solvolysis reaction products.

Solvolysis Studies. Kinetic Runs. Acetolysis.—The procedure used was that of Winstein and coworkers.[34] The acetic

(23) We thank Dr. L. Friedman of Case Western Reserve University for this procedure.

(24) All glassware used to prepare the diazonium salt must be quickly rinsed with water and flushed into wide drains. The distillation residue must be taken up in 1,2-dichloroethane to prevent solidification to refractory tars.

(25) I. Tabushi, K. Okazaki, and R. Oda, *Tetrahedron*, **25**, 4401 (1969).

(26) (a) Except for **13**, these reference compounds have been numbered with the benzylic position as 1, according to usual practice, and thence around the alicyclic portion of the molecule *away* from the benzo moiety. (b) J. E. Horan and R. W. Schuessler, *Org. Syn.*, **41**, 53 (1961).

(27) M. D. Soffer, M. D. Bellis, E. Gellerson, and R. A. Stewart, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 902.

(28) W. Rapp, *Justus Liebigs Ann. Chem.*, **586**, 1 (1954).

(29) E. R. Alexander and A. Mudrak, *J. Amer. Chem. Soc.*, **73**, 59 (1951).

(30) W. Hückel, R. Cramer, and S. Laufer, *Justus Liebigs Ann. Chem.*, **630**, 89 (1960).

(31) P. Rona, *J. Chem. Soc.*, 3629 (1962).

(32) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

(33) J. W. Wilt and C. A. Schneider, *ibid.*, **26**, 4196 (1961).

(34) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1113 (1952).

acid was redistilled and contained 0.3% acetic anhydride. Ampoules containing the reactants were sealed under nitrogen. The tables contain further information.

Hydrolysis.—Rate studies in 60% acetone were conducted as earlier described.[35] The acetone was freshly distilled from potassium permanganate. Again, ampoules were sealed under nitrogen. Further details may be found in the tables and ref 2.

Product Runs. Acetolysis.—Tosylate solutions (0.025 *M*) were prepared as for the acetolysis rate studies but in larger volume (50 ml). The solutions were heated under nitrogen in a pressure bottle at 95° for 25 hr. The material was added to water (1 l.) and thoroughly extracted with 1:1 ether–pentane. The organic extracts were washed and dried. Removal of solvent left an oil in each case. This oil was analyzed by spectral methods and by glpc to give the product data in Table III. Most glpc work was done on Flexol 8N8 columns, 6 ft × 0.25 in. at 175°. Acetate esters **12**, X = OAc, were characterized by λ 5.75, δ ≅ 2 s (-OCOCH$_3$). Olefins **13** have been described above. Olefins **14** were signified by λ 11, δ ≅ 5 (=CH$_2$). Olefins **15** were best evidenced by δ 5.5 (=CH), an upfield resonance relative to the vinyl proton in **13** (δ 6.3). Proper composition was better obtained prior to glpc because considerable acetate pyrolysis accompanied elution, enriching the vinyl products and decreasing the acetate esters. The olefin materials eluted at half the time of the esters and were easily distinguished. The olefin mixture could subsequently be simplified in composition by hydrogenation. Spectral and glpc data then indicated only the benzocyclenes mentioned above. Saponification of the crude product gave alcohols **12** (X = OH) which were correlated with the hydrolysis study (see below).

(35) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, S. J. Wagner, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

Hydrolysis.—The product runs were performed upon tosylate solutions (0.030 *M*) made as for the hydrolysis rate studies and as described for acetolysis. Alcohols **12** and the olefin products have been described above and the spectral properties there reported were used to establish their presence in the product. Columns of Reoplex 400, Apiezon L and SE-30 at 175° caused extensive dehydration of **12** upon glpc. A column using Flexol 8N8 allowed less such dehydration, but again proper composition data was better obtained prior to glpc. In the instance of tosylate **5**, $n = 5$, the dihydronaphthalene olefin products were adventitiously oxidized to 2-methylnaphthalene. No olefins **13–15** were observed in this case.

Registry No.—**5**, $n = 4$, 33223-64-2; **5**, $n = 5$, 33223-65-3; **5**, $n = 6$, 33223-66-5; **5**, $n = 7$, 33223-67-5; **6**, $n = 7$, Z = COOCH$_3$, 33223-70-0; **7**, $n = 4$, Z = CN, 33223-68-6; **7**, $n = 7$, Z = CN, 33223-69-7; **7**, $n = 4$, Z = COOCH$_3$, 33223-71-1; **7**, $n = 7$, Z = COOCH$_3$, 33223-72-2; **8**, $n = 4$, 33223-73-3; **8**, $n = 5$, 33223-74-4; **8**, $n = 6$, 25634-94-0; **8**, $n = 7$, 33223-76-6; **10**, $n = 4$, 33223-77-7; **10**, $n = 5$, 33223-78-8; **10**, $n = 6$, 26516-28-9; **10**, $n = 7$, 33223-80-2; **11**, Z = CN, 28769-48-4; **11**, Z = COOCH$_3$, 3070-71-1; **11**, Z = CH$_2$Cl, 32223-83-5; **12**, $n = 4$, X = OH, 32223-84-6; **12**, $n = 5$, X = OH, 33223-85-7; **12**, $n = 6$, X = OH, 33223-86-8; **12**, $n = 7$, X = OH, 33223-87-9; **13**, $n = 7$, 33303-93-4; 1-chloro-2-benzylpropene, 33223-88-0; *cis*-α-benzylacrylic acid, 5669-19-2; 2-methylbenzosuberene, 22851-69-0.

Aryl Participation in the Solvolysis of Some *gem*-Dimethyl-Substituted 4-Aryl-1-alkyl *p*-Bromobenzenesulfonates[1]

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A series of 4-phenyl and 4-anisyl-1-butyl *p*-bromobenzenesulfates with 3,3- and 4,4-dimethyl groups was prepared, and acetolysis and formolysis rates were measured. The *gem*-dimethyl group can appreciably increase the tendency for aryl participation to occur in the solvolysis of these derivatives. Participation by both the 1- and 2(6)-carbon atoms of the aromatic ring is observed depending upon the substituents present. The formolysis of 4-(*m*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate produces mainly a mixture of 1,1-dimethyl-7- and 1,1-dimethyl-5-methoxytetralins formed by participation of carbons 2 and 6, respectively, in the solvolysis. With the related *p*-methoxy derivative, formolysis and acetolysis produce an appreciable amount (48% in formolysis) of 1,1-dimethyl-7-methoxytetralin, a rearranged product arising from participation of carbon atom 1 of the *p*-anisyl group producing a spirocationic intermediate which then undergoes a 1:2 shift of the tertiary group in preference to the primary one. In acetolysis, a significant amount (17%) of 1:4 shift of the *p*-anisyl group is also observed. Formolysis rate constants are divided into aryl-assisted and -unassisted fractions and yields of cyclized products were calculated assuming participation resulted in the exclusive formation of cyclized products. Those values were in reasonable agreement with the observed yields.

Participation of remote aryl groups in solvolysis reactions was clearly demonstrated in the previous papers in this series[3,4] with ω-aryl-1-alkyl *p*-bromobenzenesulfonates. Either carbon atom 1 or 2 of the ω-aryl group could assist solvolysis depending upon which was the more susceptible to electrophilic attack and depending upon the distance between the aryl and *p*-bromobenzenesulfonate groups. Participation by either aromatic carbon led exclusively to cyclization. Five- and six-membered rings were preferred. In this paper are reported results on some *gem*-dimethyl substituted aryl-1-alkyl *p*-bromobenzenesulfonates which show the rate-enhancing effect of the *gem*-dimethyl group and the rearrangement of appropriately substituted derivatives during solvolysis.

The compounds prepared and the kinetic data obtained from them are given in Table I. The addition of the 2,2-*gem*-dimethyl group to 2-phenylethyl *p*-bromobenzenesulfonate increases the rate of acetolysis by a factor of about 70,[5] while in the 3-phenyl-1-propyl system the 3,3-*gem*-dimethyl group actually decreases the rate by a factor of 0.7.[3] The *gem*-dimethyl group is apparently sterically inhibiting solvolysis in the last reaction. In the previous study[3,4] addition of methoxyl groups to the aromatic ring enhanced the solvolysis rates when participation was occurring. Since the

(1) Part of the work described in this paper was reported in preliminary form by S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956), and by S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

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(3) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957).

(4) R. Heck and S. Winstein, *ibid.*, **79**, 3114 (1957).

(5) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).