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Electrocyclic Effects in Solvolysis. I.[1] Aryl Participation and Cyclopropyl Ring Opening in the Solvolysis of *exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]oct-8-yl Tosylates[2]

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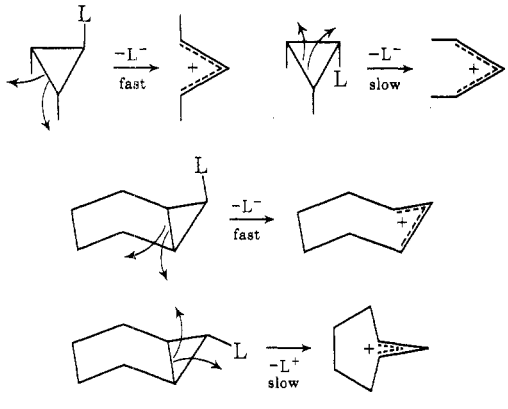
To seek a unique combination of anchimeric participation and electrocyclic ring opening in solvolysis reactions, a number of tosylates of the title were prepared and characterized. The anti-8 tosylates indeed do undergo hydrolysis and acetolysis with concomitant 1,4-aryl migration by the Ar_1-5 route and cyclopropyl ring opening to afford novel 3,*syn*-8-diarylbicyclo[3.2.1]oct-3-en-2-ols. The structures of these products were established by various means, among them ozonation to *cis*-2-arylcyclopentane-*cis*-1,3-dicarboxylic acids (*cis*-2-arylnorcamphoric acids). Although ~ 7000-fold as fast in solvolysis as their nonphenyl analogs (evidence for anchimeric participation), the anti-8 tosylates exhibit a low ρ value (−1.68 for hydrolysis and −1.3 for acetolysis) among themselves. This fact, together with the slight rate retardation caused by the introduction of a C-6,7 double bond, indicates considerable concertedness in the aryl migration and cyclopropyl ring opening processes. An example of a syn-8 tosylate of the title was found to rearrange differently, following a combination of paths most closely related to that reported for *syn*-7-norbornenyl tosylate. Because this path does not involve aryl participation in the slow step, this syn-8 tosylate was essentially equal in rate to its nonphenyl analog.

Electrocyclic ring opening in cyclopropyl substrates can lead to rapid solvolysis when the leaving group is suitably positioned. Literature support abounds for disrotatory opening of the ring and a faster solvolysis rate for trans leaving groups in monocyclic cases and for endo leaving groups in bicyclic cases (eq 1).[4] Similarly, suitably positioned aryl groups can accelerate solvolysis *via* anchimeric participation, a phenomenon of long-standing interest (eq 2).[5] It was our aim to seek examples wherein these two accelerative effects might be combined. Such a combination could afford novel rearrangements and shed further light on the nature of the two effects mentioned.



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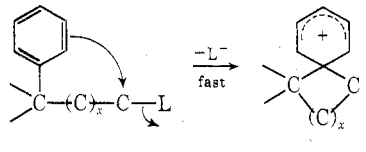

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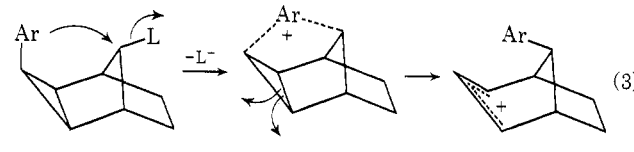
The *exo*-tricyclo[3.2.1.$0^{2,4}$]octane system seemed ideal for the purpose desired. With an aryl group at C-3 and an anti leaving group at C-8 it seemed possible that aryl participation during solvolysis would be sterically propitious. The disrotatory opening of the cyclopropyl portion of the tricycle would also be favorable because the migrating aryl group is properly placed for displacement. Moreover, the bicyclic ion finally formed would be allylic in nature and presumably less strained than the parent species (eq 3).



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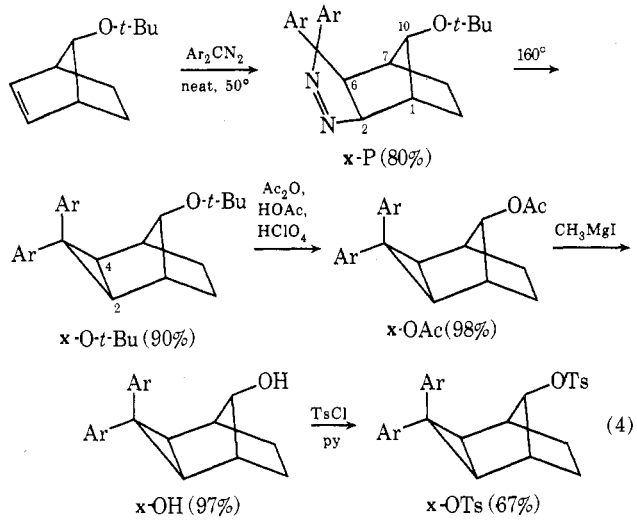
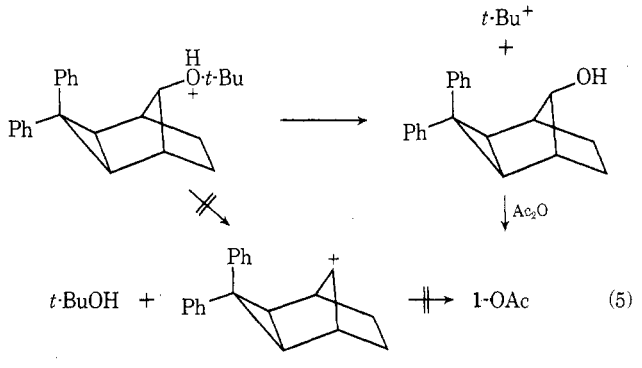
Results

Preparations. The compound initially chosen to exemplify eq 3 was *exo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-*anti*-8-yl tosylate (**1**-OTs). Its synthesis, together with those of related compounds, is given in eq 4. The 1,3-dipolar cycloaddition of diphenyldiazomethane to *anti*-7-*tert*-butoxynorbornene proceeded best in excess olefin as solvent, although dioxane was occasionally used. With some diaryldiazomethanes, however, dioxane seemed to retard the cycloaddition. The cycloaddition proceeded totally exo to produce pyrazoline **1**-P.[6] The methine proton H-2 adjacent to the azo function was a doublet in the nmr spec-



Ar = Ph, x = 1
Ar = *p*-anisyl, x = 2
Ar = *p*-tolyl, x = 3
Ar = *p*-chlorophenyl, x = 4

trum, giving evidence for coupling to H-6 but not to H-1. This would be expected from the dihedral angles of these various H–H interactions in an exo adduct. Heating **1-P** at 160° until the evolution of nitrogen ceased led in high yield to one product, the tricyclic ether **1-O-*t*-Bu**. The orientation of the cyclopropyl moiety was clearly still exo because the identical hydrogens H-2,4 were a singlet ($W_{1/2}$ = 2 Hz) in the nmr spectrum. Again, the unfavorable angle relationship between these hydrogens and those at the bridgehead precluded coupling.[9] In contrast, in those isomers where the cyclopropyl moiety is endo, a favorable angle relationship exists with the bridgehead hydrogens, and H-2,4 appear as a triplet.[8,11] The subsequent conversions to ester **1-OAc**, alcohol **1-OH**, and tosylate **1-OTs** were standard procedures and details are relegated to the Experimental Section. The cleavage of **1-O-*t*-Bu** to **1-OAc** must involve oxygen–*tert*-butyl bond cleavage and not oxygen–C-8 bond cleavage (eq 5), because the spectral

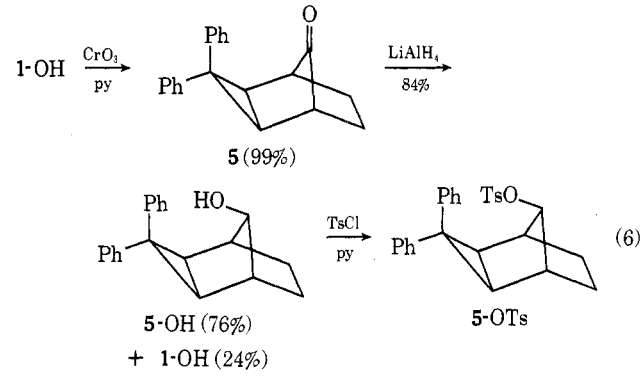


(would rearrange as in eq 3)

characteristics of **1-OAc** were clearly related to those of **1-O-*t*-Bu**. From data presented later, formation of a cationic center at C-8 in this cleavage would have led to skeletal rearrangement as in eq 3.[12]

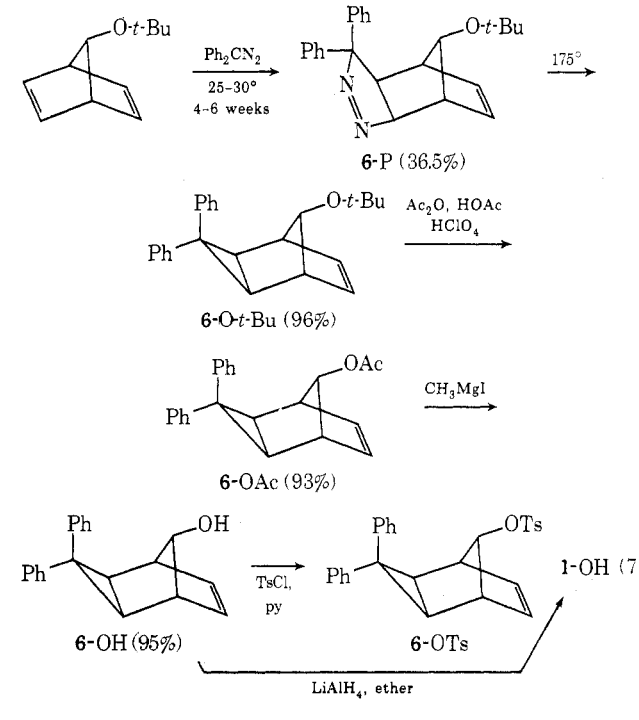
Exactly analogous characterizations applied to the preparation of the related tosylates **2-OTs**, **3-OTs**, and **4-OTs** by the same sequence, which differed only in the use of the appropriate diaryldiazomethane. With **2-P** and **3-P** the use of dioxane solvent in the cycloaddition was deleterious. Yields of adduct were *ca.* 20% in its presence but *ca.* 80% without it.

Oxidation of **1-OH** with chromium trioxide in pyridine gave the corresponding ketone **5**, from which the syn alcohol **5-OH** and tosylate **5-OTs** were easily prepared (eq 6). Ketone **5** was characterized by its carbonyl stretch in the



infrared spectrum at 1769 cm^{-1} (2% in CCl_4) and its H-2,4 (cyclopropane) singlet resonance at δ 1.95 in the nmr spectrum. Reduction of **5** with lithium aluminum hydride yielded a mixture of **5-OH** and **1-OH** (76:24, respectively). Attack by hydride from the less hindered side of the carbonyl was anticipated, and recrystallization allowed the ready isolation of the very sterically crowded **5-OH**.[13] The syn assignment to **5-OH** was made on the basis of its –CHOH– resonances. The methine proton was a broad multiplet centered at δ 3.50 while the hydroxyl proton was a broad singlet at δ 0.47, a large upfield shift ascribable to the shielding influence of the proximate π face of the phenyl group at C-3. In **1-OH** the corresponding chemical shifts were δ 3.37 for the methine proton and δ 1.23 for the hydroxyl proton. The difference in chemical shift for these methine protons ($\Delta\delta$ = 0.13) was doubled in their respective tosylates: **1-OTs**, H-8, δ 3.95; **5-OTs**, H-8, δ 4.20 ($\Delta\delta$ = 0.25). These differences can be understood in terms of a shielding effect caused by the nearby phenyl group and/or the well-known distinction of axial *vs.* equatorial protons. In **1-OH** (OTs) H-8 is axial in the boat cyclohexane portion of the tricycle. In **5-OH** (OTs) it is equatorial.

Addition of diphenyldiazomethane to 7-*tert*-butoxynorbornadiene led to all possible monoadducts, of which **6-P** is relevant to the present study (eq 7).[8,11] The addition was best performed in diene solvent (dioxane was poor) at

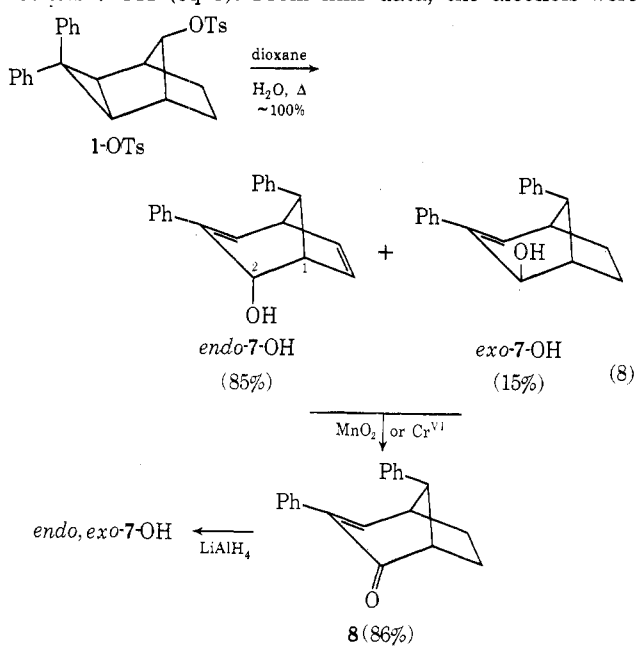


25° over a 4-week time period. Conversion of 6-P *via* the same sequence used for 1-P led to the unsaturated analog 6-OTs. The evidence for the correspondence of the two sequences rested upon the reduction of 6-OH to 1-OH by means of lithium aluminum hydride.[15] Detailed description of the spectral evidence for the intermediate products in eq 7 will be reserved for the more germane paper.

Kinetic Studies. Solvolyses of 1-OTs–4-OTs were performed both in dioxane–water (80:20 v/v) and in dry acetic acid. Tosylate 5-OTs was studied only in aqueous dioxane. The dioxane solvent contained 2,6-lutidine and the acetic acid contained sodium acetate. Good first-order kinetics by titrimetry were observed for all cases. A least-squares computer program[16] was used to calculate the rate constants and activation parameters. The values obtained are collected in Tables I and II.

From the data in Table I a Hammett–Brown $\rho\sigma^+$ correlation was obtained. Each $r = 0.99$. In 80% dioxane at 112°, $\rho = -1.68 \pm 0.03$. In acetic acid at 110.5°, $\rho = -1.30 \pm 0.03$. In addition, the syn/anti rate ratio k(5-OTs)/k(1-OTs) is 1.35 at 112° in aqueous dioxane. The influence of the double bond in 6-OTs on the reaction can also be determined; k(6-OTs)/k(1-OTs) = 0.92 at 112° in aqueous dioxane and 0.27 at 110.5° in acetic acid.

Solvolysis Products. Reaction of 1-OTs in aqueous dioxane led quantitatively to only two products, which subsequent investigation showed to be a mixture of epimeric alcohols 7-OH (eq 8). From nmr data, the alcohols were



present in a ratio of 85:15. The major component was assigned the endo configuration both from the nmr data (see below) and from chemical findings. When the alcohol mixture was oxidized with activated manganese dioxide or Sarett's reagent a single ketone 8 was obtained. Reduction of 8 with lithium aluminum hydride produced 7-OH once more, but with an epimeric ratio of 61.5:38.5. Such reduction in bicyclo[3.2.1]oct-3-en-2-one gave 90% endo alcohol (exo attack by hydride),[17] so the major product from this reduction in the present case is very probably *endo*-7-OH also. The major reduction product correlated spectrally with the major solvolysis product. Hence the endo assignment was given to it as well. The nmr evidence for assignment is somewhat ambiguous. Exo protons in nmr spectra of such bicyclic systems are known to resonate downfield relative to endo protons.[18] In the major solvolysis product the -CHOH- methine proton showed δ 4.25, whereas in the minor product this proton was at δ 4.60. On this basis,

Table I
Titrimetric Rate Constants for Solvolysis of *exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]oct-8-yl Tosylates

Tosylate	Solvent	Temp, °C[a]	10^5k, sec^{-1}
1-OTs	Dioxane–water[b]	112.0	1.55 ± 0.04
		120.0	3.09 ± 0.03
		130.0	9.61 ± 0.08
2-OTs	Dioxane–water	87.0	2.72 ± 0.03
		100.0	9.64 ± 0.13
		110.0	25.0 ± 1.2
3-OTs	Dioxane–water	100.0	1.69 ± 0.06
		112.0	5.36 ± 0.16
		120.0	11.3 ± 0.50
4-OTs	Dioxane–water	112.0	0.961 ± 0.01
		120.5	2.26 ± 0.05
		130.0	4.66 ± 0.11
5-OTs	Dioxane–water	112.0	2.09 ± 0.03
		122.5	5.57 ± 0.10
		133.0	15.2 ± 0.05
6-OTs	Dioxane–water	112.0	1.43 ± 0.02
1-OTs	Acetic acid[c]	110.5	7.31 ± 0.07
2-OTs	Acetic acid	110.5	78.2 ± 0.50
3-OTs	Acetic acid	110.0	6.50 ± 0.06
		110.5	19.9 ± 0.70
		122.0	67.4 ± 0.90
4-OTs	Acetic acid	110.5	5.57 ± 0.12
6-OTs	Acetic acid	100.0	0.725 ± 0.04
		110.5	1.97 ± 0.03[d]
		112.0	2.43 ± 0.01
		122.0	7.31 ± 0.07

[a] ±0.2°. [b] Dioxane–water (80:20 v/v). The solutions were 0.03 *M* in tosylate and 0.04 *M* in 2,6-lutidine. [c] Purified, anhydrous acetic acid. The solutions were 0.03 *M* in tosylate and 0.04 *M* in sodium acetate. [d] Calculated by computer from activation parameter values by means of the Eyring equation.

Table II
Activation Parameters for Solvolysis of *exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]oct-8-yl Tosylates

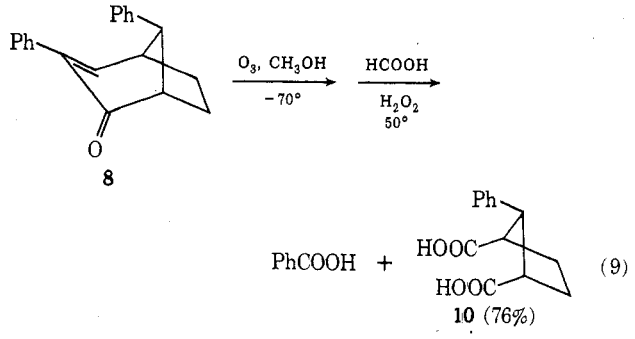
Tosylate	Solvent	ΔH^*, kcal mol^{-1}	ΔS^*, eu
1-OTs	Dioxane–water	26.5 ± 0.3	−12.3 ± 0.7
2-OTs	Dioxane–water	25.6 ± 0.3	−8.6 ± 0.8
3-OTs	Dioxane–water	26.2 ± 0.4	−10.6 ± 1.1
4-OTs	Dioxane–water	26.9 ± 0.2	−12.3 ± 0.4
5-OTs	Dioxane–water	28.7 ± 1.0	−6.0 ± 2.5
3-OTs	Acetic acid	30.3 ± 0.4	3.3 ± 1.3
6-OTs	Acetic acid	30.6 ± 0.8	−0.5 ± 2.1

the major product should be *exo*-7-OH. However, the coupling constant J of this proton with the bridgehead proton ($J_{1,2}$) was ~5 Hz in the minor product and ~10 Hz in the major. These values are in better keeping with *endo*-7-OH as the major product because the dihedral angle relationship is more favorable in this case.[20] The anomalous chemical shift for the methine proton in *endo*-7-OH can, in fact, be rationalized in terms of shielding by the overhanging phenyl group at C-8.

The allylic alcohol nature of 7-OH was attested by its ready oxidation to 8 with manganese dioxide, a reagent generally recognized as specific for such alcohols. Ketone 8 was clearly an α,β-unsaturated ketone from its spectra, λ 6.03 μ (carbonyl stretch) and λ_{max} (ethanol) 265 nm (ϵ 4460). A parent peak, m/e 274, was observed in its mass spectrum. Mass spectral fragments from 1-OTs included the *geminal* diphenyl moieties Ph_2C^+-C≡CH and Ph_2C^+-CH=CH· at m/e 191 and 192, respectively. Alcohol 7-OH, conversely, gave the *separated* phenyl moieties $PhCH{=}CHCH_2^+$ and $CH_2{=}CHC^+(OH)C(Ph){=}CH_2$ at m/e 117 and 159 (base peak), respectively. Such data prompted the structures given in eq 8.

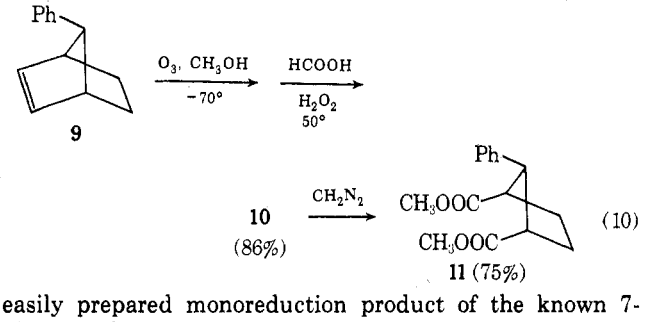
Because an alternative synthesis of 7-OH was not accomplished, its degradation was carried out instead. Oxi-

dation of 7-OH or ketone 8 with potassium permanganate, osmium tetroxide–sodium periodate, potassium permanganate–sodium periodate, or nitric acid either gave benzoic acid (overoxidation) or returned the reactant (underoxidation). Action of ozone on ketone 8, followed by performic acid,[21] was successful, however, and both benzoic acid and *cis*-2-phenylcyclopentane-*cis*-1,3-dicarboxylic acid (*cis*-2-phenylnorcamphoric acid, 10) were isolated (eq 9). The acids formed upon ozonation were converted to



(9)

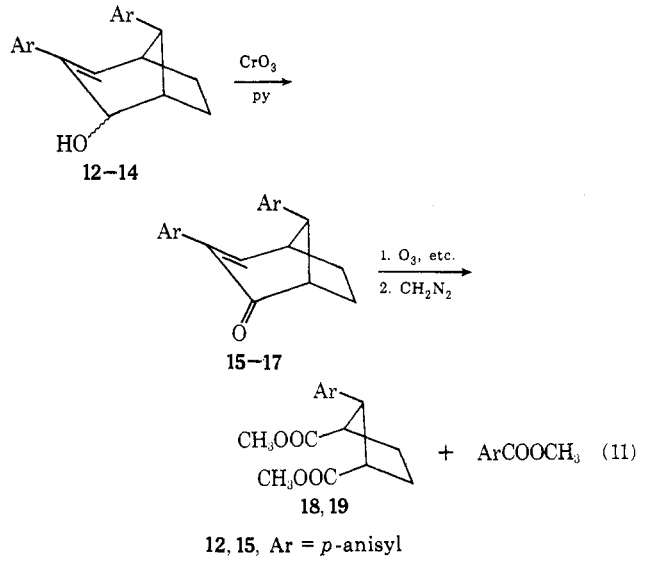
their methyl esters with diazomethane. The methyl benzoate was identical with a known sample. Dimethyl *cis*-2-phenylnorcamphorate (11) was identical with a sample prepared by analogous ozonation of alkene 9 (eq 10), an



(10)

easily prepared monoreduction product of the known 7-phenylnorbornadiene. Ester 11 showed in its nmr spectrum a sharp singlet at δ 3.27 for the *equivalent* methyl protons and a triplet (J = 7 Hz) at δ 3.90 for the benzylic proton. Both these spectral features and the mode of synthesis from 9 indicated an all-cis nature for 11 (and 10). On the basis of its allylic nature, separated phenyl groups, and degradation products, the structure of 7-OH shown throughout the foregoing is considered to be established.

Solvolysis products from tosylates 2-OTs, 3-OTs, and 4-OTs were analogous alcohols 12, 13, and 14. The spectra



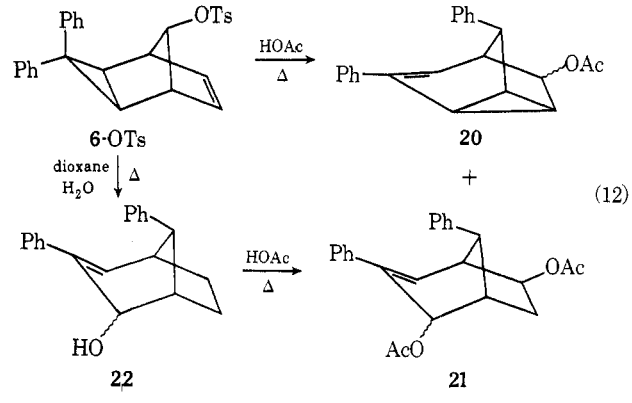
(11)

12, 15, Ar = *p*-anisyl
13, 16, 18, Ar = *p*-tolyl
14, 17, 19, Ar = *p*-chlorophenyl

of these products were similar to those of 7-OH. Again an endo:exo ratio of 80:20 was uniformly found. Oxidation of the alcohols led to ketones 15–17, the last two of which were successfully ozonized to aromatic and *cis*-2-arylnorcamphoric acids. The acids were identified as before as the methyl esters 18 and 19 (eq 11). Esters 18 and 19 showed a clear para pattern in the aromatic region of the nmr spectrum, indicating that the rearranged aryl group maintained its initial para substituent. Ketone 15 yielded methyl *p*-anisate upon ozonation, but the norcamphoric acid product was apparently further oxidized[22] because no other aromatic product was detected.

Acetolysis products were obtained only from 3-OTs as a check on the course of this process. The product was an epimeric mixture of acetates 13-OAc (*ca.* 70% endo, 30% exo), which gave alcohol 13 upon hydrolysis. Clearly, acetolysis and hydrolysis in aqueous dioxane follow the same path.

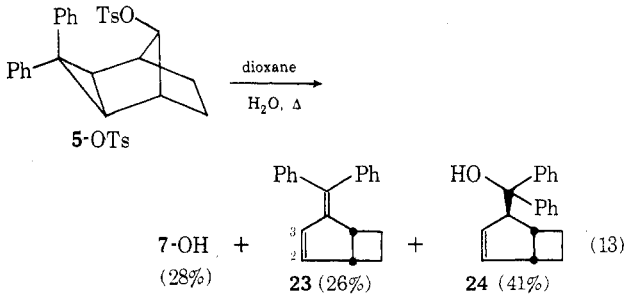
Several products resulted from the solvolysis of the unsaturated tosylate 6-OTs.[8] The characterization of these products will be given in a later paper. Their structures are given in eq 12 to show that the same path is also fol-



(12)

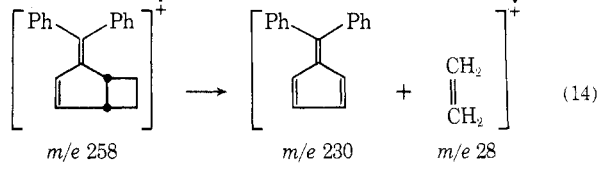
lowed by this tosylate. The acetolysis and hydrolysis studies of 6-OTs were connected *via* the conversion of the epimeric alcohols 22, obtained upon hydrolysis, to the acetates 21, which were among the acetolysis products.

The syn tosylate 5-OTs underwent solvolysis in aqueous dioxane to produce alcohol 7-OH (as did 1-OTs) and two structurally different substances, a hydrocarbon 23 and a related alcohol 24 (eq 13). The alcohol 7-OH was 88%



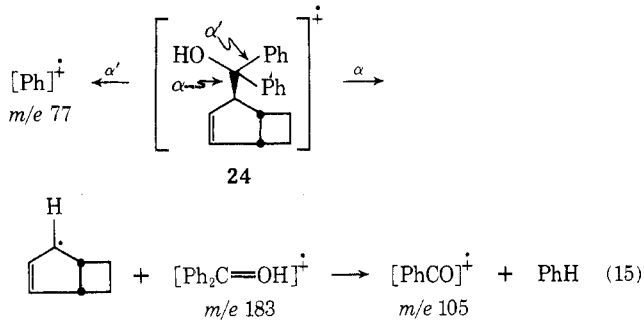
(13)

endo and 12% exo. Ketone 8 was formed upon oxidation. Thus this product was identical with the 7-OH obtained from 1-OTs (see earlier). Hydrocarbon 23 was assigned its structure upon spectral and chemical evidence. Its mass spectrum was exceptionally simple, with fragments at m/e 258 (parent), 230, and 28. The last two fragments are



(14)

probably diphenylfulvene and ethylene obtained by a cycloreversion process (eq 14). The uv spectrum of **23** showed λ_{max} (ethanol) at 242 (ϵ 9650) and 294 nm (ϵ 21,800), which is similar to that reported[23] for 1,1-diphenyl-1,3-butadiene, λ_{max} (cyclohexane) 236 (ϵ 15,800) and 287 nm (ϵ 23,400). Two vinyl protons at δ 6.38 and 6.06 were observed in the nmr spectrum. The downfield proton (H-3) was a doublet, split by its neighbor H-2. This latter proton was a multiplet, split both by H-3 and the bridgehead H-1. The multiplet sharpened to a doublet upon decoupling H-1 from H-2. Ozonation of **23** produced benzhydryl ether,[24] indicating that the phenyl groups were still geminal in **23**. Alcohol **24** showed strong tertiary alcohol absorptions at 2.83 and 8.6 μ. Its nmr spectrum was complex, but vinyl protons were evident at δ 6.08 and 5.50. The hydroxyl proton was a clear singlet at δ 1.90. The mass spectrum showed no parent peak (usually not found for tertiary alcohols[25]) but rather gave fragments at *m/e* 183, 105, 91, and 77. Most of these fragments may be rationalized as shown in eq 15. Attempted dehydration of **24**



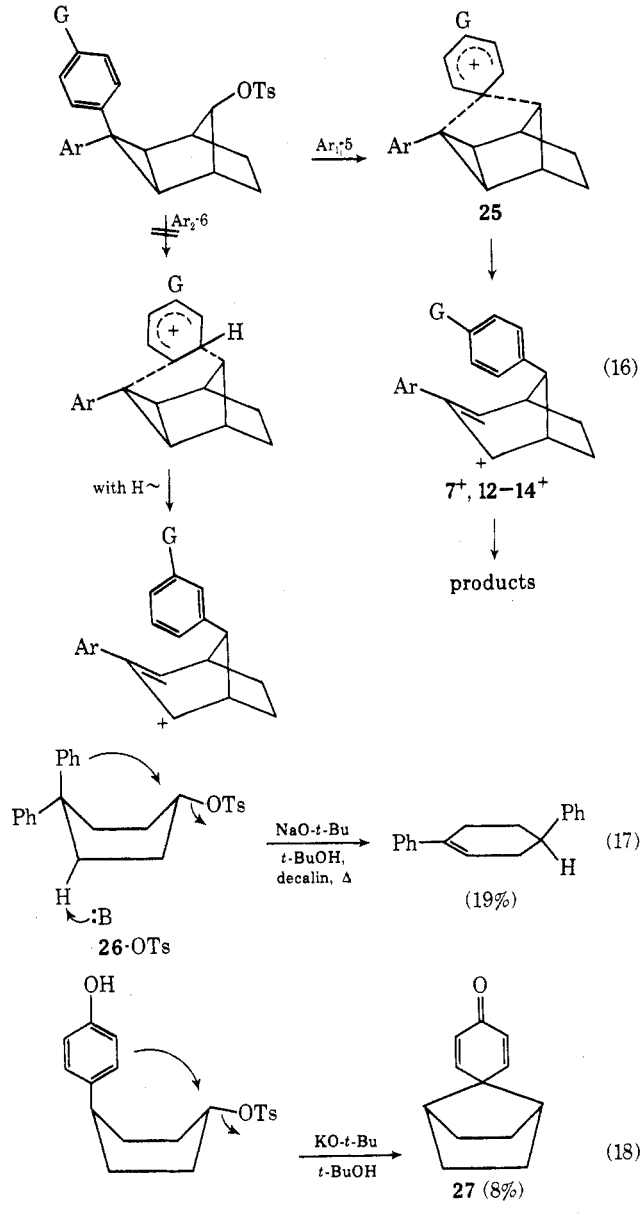
(15)

to **23** either was ineffective (iodine in benzene at reflux) or gave polymer (98% formic acid at 80°). The cis ring juncture in **24** (and **23**) is assumed from the proposed origin of these products (see Discussion).

Discussion

The structure of the solvolysis products from **1**-OTs through **4**-OTs indicates without question that transannular aryl migration and cyclopropyl ring opening have indeed been combined in one process. The site retention of para substituents in the migrated aryl group of **3**-OTs and **4**-OTs (and most probably **2**-OTs as well) further demonstrates that the transannular aryl migration is Ar_1-5 in nature and not Ar_2-6 (eq 16).[26] The allylic ion so formed (**7**$^+$) would then produce the observed epimeric alcohol (or acetate) mixture. Because the syn aryl group at C-8 would sterically hinder solvent capture from the normally favored exo direction, it is not surprising that endo capture is favored instead (*ca.* 80:20).

The transannular aryl shift observed in these reactions (a 1,4 aryl migration) is not common. Two reports indicate that under certain conditions, however, such a 1,4-aryl shift can occur. In the first (eq 17) the phenyl group was induced to migrate by the incipient formation of a double bond.[27] Acetolysis of **26**-OTs or deamination of **26**-NH_2 gave no such rearrangement.[27] In another report, the *p*-hydroxyphenyl group (as the phenoxide) performed a transannular displacement under similar conditions (eq 18).[28] Isolation of a spirodienone such as **27** (and others reported as well[29]) lends support to phenonium ion **25** as an intermediate in the present solvolyses. Furthermore, the tetracyclic parent system in **25**, commonly known as "deltacyclane," has no particular strain disfavorability and considerable investigation of the system has been reported.[30] If ion **25** is involved, the cyclopropyl ring opening must be *subsequent* to the aryl participation.



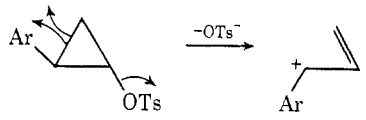
(16)

(17)

(18)

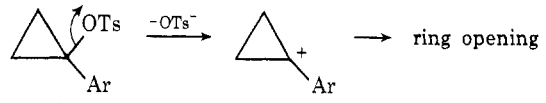
Contrariwise, two experimental facts argue that the cyclopropyl ring opening must be *simultaneous* with the aryl participation. First, the ρ value for the process (−1.68 for hydrolysis and −1.30 for acetolysis) is too small for a process involving phenonium ion intermediacy. Second, an additional double bond, as in **6**-OTs, was mildly rate retarding. Concerning the ρ value, it is informative to note some values associated with the following processes where cationic charge in a transition state is dispersed either into an aromatic ring or into an incipient allyl system.[4] In the cases of **28** and **30**, disrotatory opening of the ring is facile to expel a trans leaving group. The small ρ values indicate that in the transition state little charge is dispersed into the aromatic ring. With **29** and **31**, however, the large ρ values implicate benzylic-type ions in the transition states, and little cyclopropyl ring opening occurs in these transition states.[31]

Also, processes long accepted as involving phenonium ion intermediates have ρ values higher than −1.3 or −1.7. Acetolysis of neophyl substrates, $ArC(CH_3)_2CH_2OBs$, for example, has ρ = −2.96 (75°);[32] that of $ArCH_2CH_2OTs$ has ρ = −2.4 (115°) for the k_Δ portion of the process;[33] and that of **32** has ρ = −3.26 (77.6°).[34] All these reactions involve Ar_1-3 participation, whereas the present rearrangement involves Ar_1-5. Here the situation is less clear. Indeed, smaller ρ values are known for Ar_1-5 participation



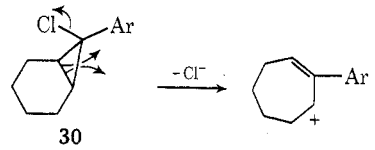
28

$\rho = -1.75$ (108°)



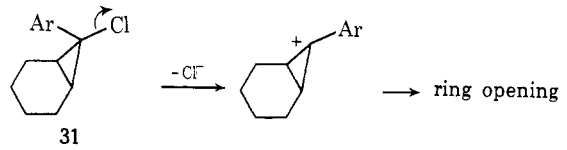
29

$\rho = -4.31$ (108°)



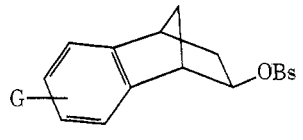
30

$\rho = -2.0$ (100°)



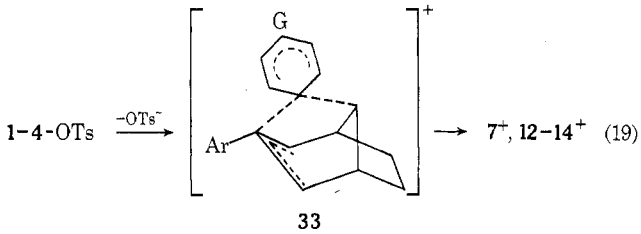
31

$\rho = -4.2$ (100°)



32

in *nonrigid* systems.[35] The tricyclic system used in this present work has, in our opinion, a geometry more akin to the Ar_1-3 cases in that no rotation to a proper conformer must be achieved to allow the participation (and thusly disfavor participation entropically). Rather, the aryl groups in 1-OTs through 4-OTs are always situated properly for participation. From the ρ values it is therefore believed that *ions like* **25** *are not involved in these rearrangements but rather that ions like* **33** *are involved instead* (eq 19). Disrotatory cyclopropyl ring opening accom-

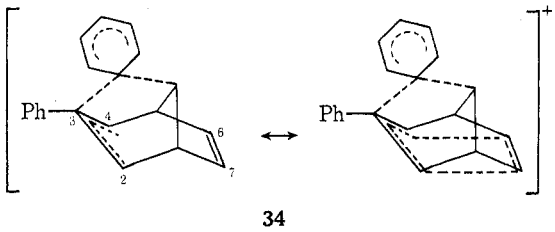


(19)

33

panies the migration of the aryl group as it moves transannularly to displace the anti tosylate function (much as incipient double-bond formation accompanied the aryl migration in 26-OTs[27]). The cationic charge so created is then spread between the half-migrated aromatic ring and the developing allylic system, resulting in low ρ values.

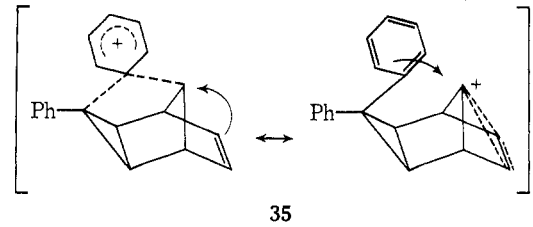
The effect of the additional double bond in 6-OTs on the rearrangement if species **33** indeed be involved should be somewhat rate retarding. This follows because the process would now involve **34** and thereby incur some of the dis-



34

advantage associated with antiaromaticity.[36] The bicyclo[3.2.1]octadienyl cation has been classified as a bishomocyclopentadienyl cation and as such it should be destabilized by conjugation.[37] Because ion **34** is clearly related to the parent [3.2.1] ion, some of this destabilization should be present in **34** as well. The effect should be small, nonetheless, because the cant of the C-2,3,4 portion of **34** would decrease the possibility for effective overlap with the π system at C-6,7. Such seems to be the case, with the ratios for solvolysis rate constants k(6-OTs)/k(1-OTs) = 0.92 (112°, hydrolysis) and 0.27 (110.5°, acetolysis).

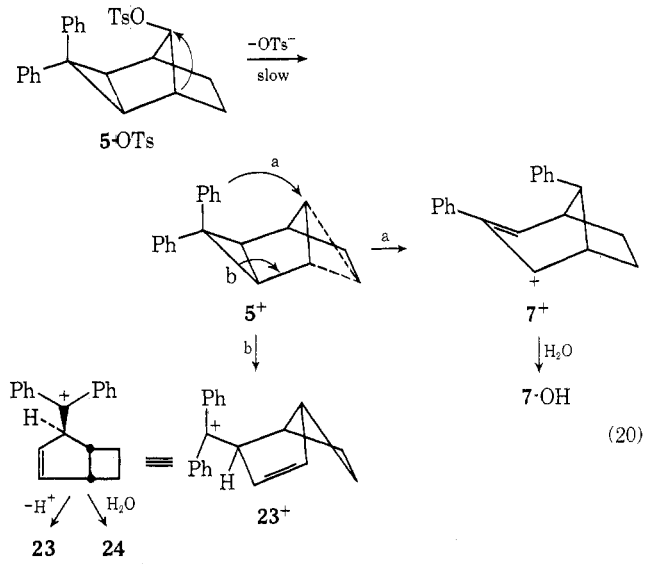
Conversely, if phenonium ions like **25** were involved in these reactions, some acceleration in rate could be expected because additional stabilization as in **35** is possible.



35

Normally, an additional double bond speeds solvolysis in 7-norbornenyl substrates by factors of 100–1000.[38] Although the relationship of such compounds to 6-OTs may not be exact, the slight deceleration in the rate of 6-OTs is in better keeping with an intermediate like **34** rather than **35**.

The products formed from the solvolysis of the syn tosylate 5-OTs can be accommodated by eq 20. This equa-

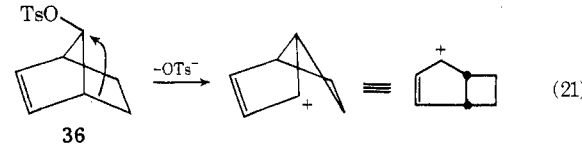


(20)

5-OTs

23 24

tion is based upon the similar behavior of *syn*-7-norbornenyl tosylate (**36**), reported some years ago (eq 21).[39]



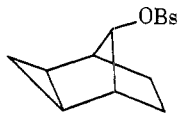
(21)

36

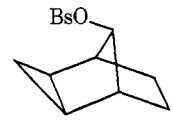
Whereas **36** can form an allylic ion directly upon the displacement of the tosylate leaving group by the σ bond as illustrated, 5-OTs cannot. As a consequence, ion 5^+ (shown in eq 20 as a delocalized ion for convenience) can be partitioned along two paths, each of which is roughly comparable in ease. Path a involves a reoccurrence of the transannular phenyl migration and produces ion 7^+ on the way to the alcohol product 7-OH.[40] Path b involves a cyclopropylcarbinyl–allylcarbinyl rearrangement and more

resembles the behavior shown by **36**. The ring bond in the cyclopropyl portion of 5^+ has considerable p character and its realignment to form ion 23^+ is a plausible occurrence. Once ion 23^+ results, deprotonation to hydrocarbon **23** and solvent capture to alcohol **24** are understandable. This view necessitates the role of intermediate, not just transition state, for 5^+.

The reactivities of **1**-OTs and **5**-OTs can be compared to those of nonphenyl analogs **37** and **38**, studied earlier by

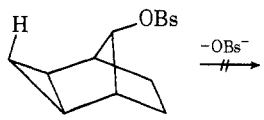


37

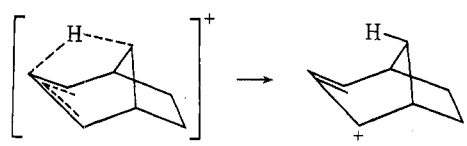


38

Haywood-Farmer and Pincock.[14] Some pertinent data are collected in Table III. Although uncertainties exist in the use of extrapolated rate constants, it is nevertheless clear that the presence of phenyl groups in **1**-OTs greatly increased its solvolytic reactivity (7000-fold) relative to the nonphenyl analog **37**. Such was not the case with **5**-OTs *vis-à-vis* **38** (no change). This great difference can be understood in terms of the pathways given earlier. In **1**-OTs aryl participation coupled with cyclopropyl ring opening caused the increased rate. Apparently a hydride shift in **37** akin to the aryl shift in **1**-OTs, shown in eq 22, does

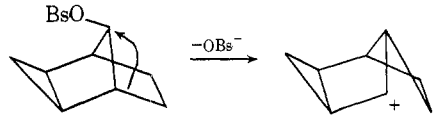


37



(22)

not occur.[41] In **38** a solvolytic pathway suggested by the earlier workers[14] was a σ shift (eq 23), although a steric



(23)

38

acceleration caused by the 3-CH_2 group was an alternative suggestion. Because no products from either **37** or **38** were identified,[14] it is difficult to compare the course of their solvolysis with those of **1**-OTs and **5**-OTs. However, at least with **5**-OTs the pathway shown in eq 20 does mirror that suggested for **38** in eq 23. Moreover, phenyl groups at C-3 should not influence this process greatly because the σ shifts in these equations do not involve them.

Lastly, the carbonyl stretching frequency of ketone **5** (1769 cm^{-1}, 2% in CCl_4) may be used to estimate an acetolysis rate constant for **1**-OTs (or **5**-OTs), provided no anchimeric assistance is involved. Use of Foote's correlation[42] gave for these cases log k_{rel} = −6.3, a value that is comparable to that of 7-norbornyl tosylate itself (log k_{rel} = −7.0) and much slower than that of cyclohexyl tosylate (log k_{rel} = 0.0). On this basis, both **1**-OTs and **5**-OTs are clearly assisted in their solvolysis, because each is much faster than is 7-norbornyl tosylate. In fact, the only unassisted case seems to be **37**.

Experimental Section[43]

Synthesis of Reactants. ***anti*-10-*tert*-Butoxy-*exo*-5,5-diaryl-3,4-diazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes (Diaryldiazomethane-*anti*-7-*tert*-Butoxynorbornene Adducts 1-P–4-P).** The appropriate diaryldiazomethane[44] (73 mmol) was added in small portions to a stirred excess of *anti*-7-*tert*-butoxynorbornene[15] (63.8 g, 0.39 mol) at 25°. The reaction material was heated at 50° for 18 hr and then briefly at 80°. The mixture was then cooled and the vessel was scratched to precipitate the adduct as a white solid (80–85% yield). Analytical samples were recrystallized several times from methanol.[45] The melting points follow: **1**-P, 167.5–169° dec; **2**-P, 168–169° dec; **3**-P, 141–142° dec; and **4**-P, 143–144° dec.

The yellow filtrate from these reactions contained some dissolved adduct and colored by-products. No attempt was made to separate these components. Rather, the filtrate was recycled for further preparations. After four or five cycles the norbornene was recovered by vacuum distillation for reuse.

***anti*-8-*tert*-Butoxy-*exo*-3,3-diaryltricyclo[3.2.1.$0^{2,4}$]octanes (1-O-*t*-Bu–4-O-*t*-Bu).** The selected adduct above (29.3 mmol) was heated without solvent in a wax bath at 160°. Evolution of nitrogen was essentially quantitative after 30 min. The cooled product (87–93% yield) was purified by recrystallization from methanol.[45] The melting points follow: **1**-O-*t*-Bu, 119.5–121°; **2**-O-*t*-Bu, 131–132°; **3**-O-*t*-Bu, 133–134°; **4**-O-*t*-Bu, 98–99°.

***anti*-8-Acetoxy-*exo*-3,3-diaryltricyclo[3.2.1.$0^{2,4}$]octanes (1-OAc–4-OAc).** The proper ether above (18.2 mmol) was dissolved in glacial acetic acid (18 ml) containing acetic anhydride (3.5 ml). To this solution in an ice bath *at 0°* was added perchloric acid (70%, 0.85 ml) with rapid swirling of the material. *Caution: locally high concentration of the perchloric acid should be avoided by rapid swirling. Vigorous exotherms can result otherwise.* The colored solution was swirled in the ice bath for an additional 1 min after the addition and then poured onto crushed ice (500 g). The solid so formed was collected and dried (80–87% yield). The compound was recrystallized from methanol.[45] The melting points follow: **1**-OAc, 153–155°; **2**-OAc, 136–136.5°; **3**-OAc, 94–95°; **4**-OAc, 157–158°.

***exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-ols (1-OH–4-OH).** The appropriate acetate above (7.2 mmol) in ether (100 ml) was added to methylmagnesium iodide (30 mmol) in ether (50 ml). After reaction at 25° for 4 hr, the mixture was hydrolyzed with water (12 ml) and the ether phase was separated. Upon removal of the ether, the residual alcohol (87–91% yield) was purified by recrystallization from hexane.[45] The melting points follow: **1**-OH, 154.5–155°; **2**-OH, 108–109.5°; **3**-OH, 109–110°; **4**-OH, 179–180°.

Tosylates of these alcohols (and others in this study) were prepared in the usual way using *p*-toluenesulfonyl chloride in pyridine[46] (63–67% yield). Analytical samples were prepared by recrystallization from benzene–hexane mixtures.[45] The melting points follow: **1**-OTs, 140–141°; **2**-OTs, 147–148°; **3**-OTs, 126–127°; **4**-OTs, 129–130°; **5**-OTs, 186–188°; **6**-OTs, 156–157° dec.

***exo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-8-one (5).** Alcohol **1**-OH (1.64 g, 5.93 mmol) in pyridine (15 ml) was added to a solution of chromium trioxide (5.73 g) in pyridine (57 ml) at 25° with stirring. After 12 hr the solution was treated with water and extracted with ether. The dried ether extracts were evaporated to afford crude **5** as a yellow solid (1.63 g, 99%), which was purified by recrystallization from cyclohexane. The pure ketone was colorless: mp 152–154°; λ (KBr) 5.70, 6.70, 6.92, 8.83, 12.45, 13.10–13.31, 14.21–14.30 μ; nmr δ 7.42 (m, ArH), 2.30 (broad m, H-1,5), 1.95 (s, H-2,4), 1.70 (broad s, H-6,7).

Table III
Comparison Data for Selected Tricyclooctyl Arenesulfonates

Sulfonate	k, sec^{-1} (°C)	k_{rel}
37	8.4×10^{-9} (100)[a]	
37-OTs	1.1×10^{-3} (110.5)[b]	1
1-OTs	7.31×10^{-6} (110.5)[c]	7000
38	7.0×10^{-5} (100)[a]	
38-OTs	2.0×10^{-5} (112)[d]	1
5-OTs	2.09×10^{-5} (112)[c]	1

[a] Reference 14. The rate constants were determined in 0.1 *N* NaOAc–HOAc solvent. [b] Extrapolated value corrected for the temperature difference and the OBs/OTs rate ratio of 3, using the values ΔH^* = 29.4 kcal mol^{-1} and ΔS^* = −17.1 eu.[14] [c] This work, Table I. [d] Extrapolated value corrected for the temperature difference, the OBs/OTs rate ratio of 3, and the change in solvent from NaOAc–HOAc to aqueous dioxane (from Table I a factor of 0.25 was chosen). The activation values used for **38** were ΔH^* = 27.1 kcal mol^{-1} and ΔS^* = −5.4 eu.[14]

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.54; H, 6.77.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]octan-*syn*-8-ol (5-OH).** Ketone **5** (1.60 g, 5.84 mmol) was reduced with lithium aluminum hydride (3.5 g) in ether (50 ml) in the standard fashion. Upon processing the reaction, a white solid, 1.35 g (84%), mp 101–130°, was obtained. Spectral analysis indicated that this product was a mixture of syn and anti alcohols. After five recrystallizations from hexane the syn alcohol **5**-OH was obtained pure: mp 132.5–134°; λ (KBr) 2.82, 3.40, 8.60, 9.27, 13.05, 13.29, 14.10, 14.33 μ; nmr δ 7.12–7.80 (m, ArH), 3.48 (broad s, H-8), 2.53 (broad s, H-1,5), 1.73 (s, H-2,4), 1.62 (dd, exo H-6,7), 1.25 (dd, endo H-6,7), 0.47 (broad s, OH).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.87; H, 7.42.

The tosylate was prepared as mentioned above.[45]

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-en-*anti*-8-yl tosylate (6-OTs)** was prepared from the alcohol (mp 126.5–127°)[8] as mentioned above.[45]

Reduction of this alcohol with lithium aluminum hydride in ether at 25° for 6 hr gave alcohol **1**-OH in quantitative yield, as established by identical spectra and mixture melting point.

Solvolysis Studies. Kinetics. Dioxane[47] and acetic acid[48] were purified as reported. Solutions were made 0.03 *M* in tosylate, either in aqueous dioxane (80:20 v/v dioxane–water) or in anhydrous acetic acid. The former solutions contained 0.04 *M* redistilled 2,6-lutidine and the latter solutions contained 0.04 *M* sodium acetate. Ampoules sealed under nitrogen were employed and the reactions were followed as described previously for aqueous dioxane studies.[1b] Acetolysis was followed by back-titration of unreacted sodium acetate with standardized *p*-toluenesulfonic acid in anhydrous acetic acid. Crystal violet was the indicator. Infinity titers were within 2% of the theoretical values. Good first-order kinetics were observed with rate constants obtained by a least-squares WAT IV computer program. Activation parameters were similarly calculated from the Eyring equation. See Table I for values.

Solvolysis Studies. Products. Larger scale solvolyses were performed in the same solvents and at the same concentrations as those used above. About 10 mmol of reactant in aqueous dioxane was heated in a pressure bottle under nitrogen at an appropriate temperature for 12 half-lives. The material was poured onto ice and extracted with hexane (ether was used for **4**-OTs). The extracts were dried and evaporated. The white solid (*ca.* 100% yield) was determined to be a mixture of *endo*- and *exo*-**3**-*syn*-**8-diarylbicyclo[3.2.1]oct-3-en-2-ols.** Spectral analysis was used to establish the endo:exo ratio. Analytical samples were obtained by recrystallization from aqueous methanol, although this fractionated the product considerably (by nmr) and gave essentially pure endo alcohols.[45] The melting points follow: **7**-OH, 118.5–119.5°; **12**, 130–132°; **13**, 125–126°; **14**, 136–137°.

The endo–exo mixture (mp 102–109°) obtained from the solvolysis of **1**-OTs was analyzed spectrally using the H-2 resonances in the mixture: δ 4.25 for the endo epimer and δ 4.60 for the exo. Certain differences elsewhere in both the nmr and ir spectra were of course also present.[49]

Acetolysis of **3**-OTs (0.6 g, 1.3 mmol) was performed in dry acetic acid (50 ml), 0.04 *M* in sodium acetate, at 120° for 14 hr. The material was added to ice water and treated with enough sodium carbonate to neutralize most of the acetic acid. Extraction with ether followed. Removal of solvent from the dried, combined extracts afforded the endo and exo acetates **13**-OAc; 0.38 g (92%); mp 130–134°; λ (KBr) 5.80 μ; nmr δ 5.82 (d, H-2 of endo epimer, J = 6 Hz), 5.44 (d, H-2 of exo epimer, J = 3 Hz). The endo:exo ratio was 7:3. Reaction of this material with ethereal methylmagnesium iodide gave alcohol **13** (83%, identical with that obtained by solvolysis in aqueous dioxane).

Solvolysis products from **5**-OTs were isolated by chromatography on alumina (100 g). Elution with 10% benzene–hexane gave **23**, mp 64–64.5°.[45] Use of 1:1 benzene–chloroform gave **24**. Elution with 1:1 ether–chloroform produced **7**-OH. Alcohol **24** was an oil, pure upon elution. Oxidation of the **7**-OH isolated from **5**-OTs with chromium trioxide in pyridine gave ketone **8** just as described later for this oxidation of **7**-OH obtained from **1**-OTs. Treatment of alcohol **24** with a trace of iodine in benzene under reflux produced no change. Reaction of **24** with 98% formic acid at 80° for 3 hr gave a yellow product, mp 197–230°. This material was apparently a polymer but it was not investigated further.

Structural Studies on Solvolysis Products. Oxidation to Ketones. Reaction of the appropriate diarylbicyclooctenol endo–exo mixture (0.73 mmol) with activated manganese dioxide[50] (2.5 g) was carried out at 25° for 12 hr in pentane (50 ml). Removal of the excess oxidant and solvent left a white solid (83–86%), shown to be the corresponding **3**,*syn*-**8-diarylbicyclo[3.2.1]oct-3-en-2-one.** The products from **7**-OH and **13**, ketones **8** and **16**, respectively,[45] had melting points of 107.5–108.5 and 92–93.5°. Larger scale oxidations (*ca.* 2-g scale) were better achieved with chromium trioxide in pyridine. Such oxidation of alcohols **12** and **14** gave the di-*p*-anisyl ketone **15**, mp 135–137°, λ (KBr) 6.01 μ, and the di-*p*-chlorophenyl ketone **17**, mp 138–140.5°, λ (KBr) 5.96 μ, respectively. These two ketones were not purified further, but were used in ozonation studies directly (see later). Treatment of ketone **8** with lithium aluminum hydride in ether in the usual manner produced **7**-OH (72% yield). From its nmr spectrum, the alcohol was still richer in the endo epimer (61.5%).

Ozonation. At −70° the appropriate ketone **8** or **16** (1.8 mmol) in methanol (100 ml) was treated with ozone generated from a Model LOA 2 Corona Generator (Purification Sciences, Inc.), using an oxygen flow rate of 5 ft^3/hr for 12 min. Methanol was removed under reduced pressure at 25°. Formic acid (6 ml) and hydrogen peroxide (30%, 3 ml) were then added to the yellowish-green material. The solution was warmed slowly to 60° on a water bath (Caution: a vigorous reaction may commence).[21] After 30 min the now colorless reaction mixture was poured into cold water and extracted thoroughly with ether. The ether extracts were combined, dried, and treated with excess diazomethane. Upon removal of the remaining diazomethane and ether by rotary evaporation, the residue was chromatographed on alumina (25 g). Elution with either 1:4 benzene–hexane or 1% ether in hexane produced the appropriate aromatic methyl ester. These were identified by comparison with authentic samples. Elution with benzene or 1:4 chloroform–benzene yielded the appropriate dimethyl *cis*-2-arylnorcamphorate (75–80% yield), which was recrystallized from pentane. Esters **11** and **18** had melting points of 66–67.5 and 58–60°,[45] respectively. The aromatic protons in **18** exhibited a singlet resonance in its nmr spectrum. Such is the case for *p*-, but not *m*-, xylene.[51] (see Discussion).

The ozonation of ketone **8** was also processed without the diazomethane. Removal of the ether from the reaction extracts gave an approximately 1:1 mixture of benzoic and *cis*-2-phenylnorcamphoric acids. The former was identical with a known sample and the latter was identical with a sample prepared by ozonation of *syn*-7-phenylnorbornene (see later).

Ozonation of ketones **15** and **17** gave methyl *p*-anisate and methyl *p*-chlorobenzoate, respectively. However, no norcamphorate ester was found among the products from **15**.[22] **Dimethyl *cis*-2-*p*-chlorophenylnorcamphorate (19)** was obtained from ketone **17**, but it was not extensively purified: nmr δ 7.4–7.0 (m, AA′BB′ ArH), 3.98 (t, H-2, J = 8 Hz), 3.40 (s, OMe), 1.8–2.8 (m, all other H's). The aromatic pattern was clearly para (see Discussion).

Ozonation of hydrocarbon **23** (50 mg) was performed as described above, except that methylene chloride was the solvent and the formic acid was omitted. The oily residue from the ether extracts was taken up in ethanol (3 ml) and chilled overnight. A precipate of **benzhydryl ether** (10 mg, mp 107–109°) formed. It was identical with an authentic sample.[52]

***syn*-7-Phenylnorbornene (9).** 7-Phenylnorbornadiene[53] (27.6 g, 0.164 mol) in 95% ethanol (150 ml) containing suspended palladium on charcoal (5%, 0.4 g) was hydrogenated at ambient temperature and 35.5 psig. After 10 min 1 equiv of hydrogen had been taken up. The catalyst was filtered off and the solvent was removed by atmospheric distillation. Vacuum distillation then gave olefin **9** in 88% yield, bp 95–96° (0.75 mm), $n^{25.5}$D 1.5492, δ 5.77 (t, vinyl H's).[45] The product contained about 1% of the anti epimer (δ 6.17, t, vinyl H's) and about 5% of the starting diene. Reaction of the diene with lithium aluminum hydride in ether under reflux for 12 hr gave only 6.7% reduction and the product was a 1:1 mixture of syn and anti epimers. Reduction of the diene with diimide gave a mixture also: 33.8% of syn and anti epimers in the ratio of 82.5:17.5; 39.4% of 7-phenylnorbornane; and 25.8% of recovered diene. This poor result contrasts with other reports.[54] No problem was found using palladium on charcoal for the hydrogenation. It has been reported[55] that such a catalyst is inferior to (more expensive) platinum catalysts in such reductions.

***cis*-2-Phenylnorcamphoric Acid (10).** Olefin **9** (0.5 g, 2.9 mmol) was ozonized as described earlier. After the self-sustaining reaction with formic acid and hydrogen peroxide was completed, the solution was refluxed for 30 min and then evaporated. The solid residue (0.59 g, 86%) was recrystallized from pentane–ether to give acid **10** as a colorless solid, mp 232.5–235.5° dec.[45] The

acid was identical with that produced from ketone **8**, as were the methyl esters.

Acknowledgment. The authors thank Drs. Henry F. Dabek, Jr., and John L. Huston for the mass spectra.

Registry No.—**1**-P, 50522,48-0; **1**-O-*t*-Bu, 50522-49-1; **1**-OAc, 50522-50-4; **1**-OH, 29266-06-6; **1**-OTs, 29266-07-7; **2**-P, 50522-52-6; **2**-O-*t*-Bu, 50522-53-7; **2**-OAc, 50484-72-5; **2**-OH, 50522-54-8; **2**-OTs, 50522-55-9; **3**, 50522-56-0; **3**-P, 51096-42-5; **3**-O-*t*-Bu, 50522-58-2; **3**-OAc, 50522-59-3; **3**-OH, 50522-60-6; **3**-OTs, 50522-61-7; **4**-P, 50522-62-8; **4**-O-*t*-Bu, 50522-63-9; **4**-OAc, 50522-64-0; **4**-OH, 50522-65-1; **4**-OTs, 50522-66-2; **5**, 29302-44-1; **5**-OH, 29266-08-8; **5**-OTs, 29302-43-0; **6**-OTs, 50522-70-8; *endo*-**7**-OH, 50522-71-9; *exo*-**7**-OH, 50522-72-0; **8**, 29283-01-0; **9**, 29266-12-4; **10**, 29266-10-2; **11**, 50522-76-4; *endo*-**12**, 50522-77-5; *exo*-**12**, 50522-78-6; *endo*-**13**, 50522-79-7; *exo*-**13**, 50522-80-0; *endo*-**14**, 50522-81-1; *exo*-**14**, 50522-82-2; **15**, 50522-83-3; **16**, 50522-84-4; **17**, 50522-85-5; **18**, 50522-86-6; **19**, 50522-87-7; **23**, 29283-02-1; **24**, 29283-03-2; **37**, 2040-61-1; **37**-OTs, 50522-91-3; **38**, 24218-05-1; **38**-OTs, 50522-93-5.

Supplementary Material Available. Melting point, combustion analytical data, significant ir, complete nmr, and pertinent mass spectral data (asterisked compounds) for **1**-P-**4**-P, **1**-O-*t*-Bu-**4**-O-*t*-Bu, **1**-OAc-**4**-OAc, **1**-OH-**4**-OH, **1**-OTs*-**6**-OTs (melting point and analysis only), **7**-OH,* **8**,* **9**–**14**, **16**, **18**, **23**, and **24** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-1327.

References and Notes

(1) (a) Studies on 3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]octanes. II. (b) Paper I: J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, **38**, 277 (1973).

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(15) *Cf.* B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

(16) A WAT IV program was used. We thank Professors A. K. Jameson and J. F. Reed of this department for their assistance.

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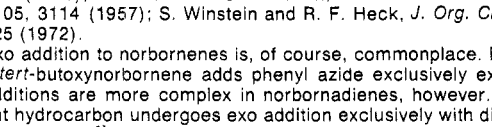
(18) For example, in iii and iv.[19]



iii iv

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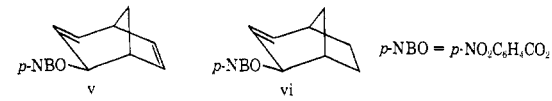

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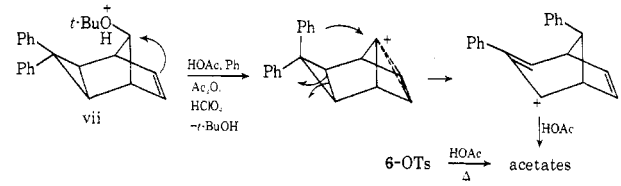

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Bridged Polycyclic Compounds. LXXX. Rearrangements in the Dibenzobicyclooctadiene Systems. Higher Energy Carbocations[1]

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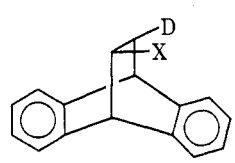
Treatment of 2-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (9) with acetic acid–sulfuric acid leads to equilibration with 1-deuterio-2-dibenzobicyclo[2.2.2]octadienol (10). Similar treatment of 1,*cis*-3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (13) gives both 1,*trans*-3-dideuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (14) and the 2,*trans*-3-dideuterio ester (15), with the former being produced two or three times as fast as the latter. These results demonstrate the existence of 2-dibenzobicyclo[2.2.2]octadienyl cation (6) and 1-protonated dibenzotricyclo[3.3.0.0^{2,8}]octadiene (7) as high-energy carbocations available in such rearranging systems.

Some time ago[2] we reported that acetolysis of the *p*-toluenesulfonate of *cis*-3-deuterio-2-dibenzobicyclo[2.2.2]octadienol (1-OTs) led stereospecifically (*i.e.*, with clean anti migration) to *syn*-8-deuterio-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (2-OAc), which was in turn cleanly transformed (through the endo epimer of 2-OAc) in acetic acid containing perchloric acid to *cis*-3-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (1-OAc). The *trans*-3-deuterio acetate 3-OAc was absent from the latter reaction mixture.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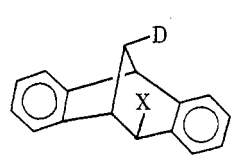
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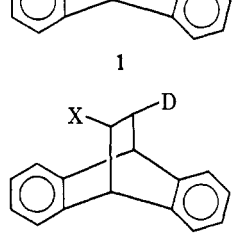
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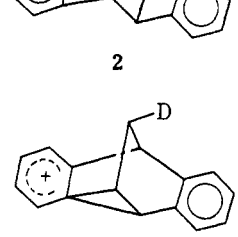
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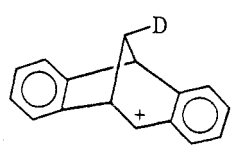
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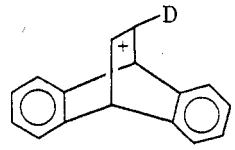
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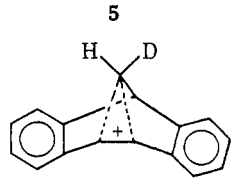
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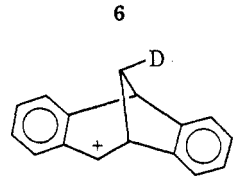
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These data were consistent with the intervention of some combination of the phenyl-bridged nonclassical ion (4) or some variant thereof[2,3] and that of the benzylic ion 5 or with that of the latter alone, including a geitonodesmic reaction.[3,4] The absence of 3-OAc made it clear that neither 2-dibenzobicyclo[2.2.2]octadienyl cation (6) nor the bridged ion 7 (1-deuterated dibenzotricyclo[3.3.0.0^{2,8}]octadiene) intervenes in these reactions (7 could be an intermediate or a transition state on the reaction coordinate between 5 and 8). Thus 6 and 7 are obviously of higher energy than 4 and/or 5, and the lower energy pathways involving the latter ions (or analogs) are transversed in these and in many similar reactions.[5] Species analogous to 7 have been shown to be involved as *low-energy* intermediates in reactions of bicyclo[3.2.1]octanyl systems,[6] but as discussed earlier,[7] geometric constraints not present in the latter system are present in 7.

When tetradeuterioacetic acid was added to dibenzobicyclooctatriene at 86° (catalyzed by 1 *M* D_2SO_4), the predominant kinetic product was the cis deuterio ester 1-OAc-d_3,[2] but the trans epimer 3 was also formed. Thus, when 10% of the olefin had been consumed, the ratio of 1-OAc-d_3 to 3-OAc-d_3 was approximately 86:14. By the time (10 hr) the addition was essentially complete, the ratio of 1 to 3 had dropped to 7:3. The isomerization of 1 to 3 obviously utilized one or both of the higher energy reaction channels described above (6 or 7), and it seemed of interest to determine which was utilized. We report now that processes involving both 6 and 7 occur at competitive rates.

Our first experiment was designed to test for the possible intervention of 7. To this end, we prepared 2-deuterio-2-dibenzobicyclo[2.2.2]octadienyl acetate (9). If 6 were the sole intermediate between 1-OAc and 3-OAc, then, in the time for the 1 ⇄ 3 equilibration, *dl*-9 would act as if it were inert, as its equivalent rearrangement would be degenerate. On the other hand, intervention of 7 (as either an intermediate or a transition state) would lead to scrambling of deuterium between C-2 and C-1, a process readily followed by pmr intensity measurements. (The C-1 proton absorbs at δ 4.50 and that at C-2 at δ 5.05.) This process is shown in Scheme I (in which we have omitted the intermediate phenyl-bridged cations analogous to 4). Bridge migration *via* 7, in the 1 to 3 rearrangement, is thus analogous to that *via* 7-*d* in the 9 to 10 rearrangement.

When 9 was heated in a 1.4 *M* sulfuric acid solution in acetic acid at 85°, it was found to rearrange toward its