82482-65-3; **21**, 74272-43-8; **22**, 62907-50-0; **23**, 62907-52-2; **24**, 82482-66-4; **25**, 70412-26-9; **26**, 70412-27-0; **27**, 66221-05-4; **28**, 82482-67-5; **29**, 74964-29-7; **30**, 82482-68-6; **31**, 82494-80-2; **32**, 62907-51-1; **33**, 62907-54-4; **34**, 71956-72-4; **35**, 70412-29-2; **36**, 82482-69-7; **37**, 70412-28-1; **38**, 82482-70-0; **39**, 82482-71-1; **40**, 66221-12-3; **41**, 73377-61-4; **42**, 66221-10-1; **43**, 73464-49-0; triphenylcyclopropenyl perchlorate, 51778-20-2; benzylmagnesium chloride, 6921-34-2; 2,3-diphenylindanone, 7474-64-8; 2-methylindanone, 17496-14-9; 3-benzyl-2-phenylindanone, 10273-47-9; phenylmagnesium bromide, 100-58-3; silver perchlorate, 7783-93-9.

Effect of Remote Substituents upon the Long-Range Aryl Migration and Electrocyclic Ring Opening of *exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-yl Tosylates in Solvolysis[1,2]

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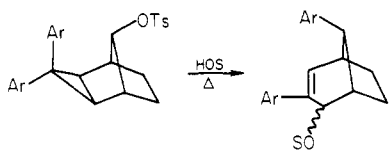
The processes of long-range aryl migration (LRAM) and electrocyclic ring opening (ERO) that occur in the solvolysis of the title substrates have been investigated with respect to their relative timing. By substituting an electron-withdrawing group (CN) or an electron-donating group (Et) in these substrates at the site of potential cationic charge development as ERO occurs, it has been determined that large rate differences in such substituted substrates are observed (>10^3). Moreover, the rate ratios of *p*-tolyl substrates to phenyl substrates in migration (LRAM) are not constant but rather increase as ERO becomes more facile. The mechanistic conclusion drawn from these results is that LRAM and ERO do occur in concert (LRAMERO) but not in synchrony in all cases. Instead, a continuum of LRAMERO transition states is proposed, with an approach to synchrony as ERO becomes more and more facile. Additionally, the synthesis and characterization of the title compounds and the intermediates involved in their (at times lengthy) synthesis are described.

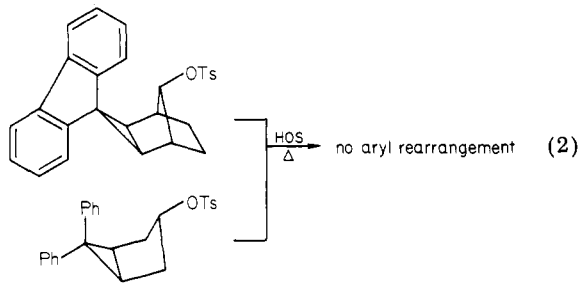
Introduction

The solvolytic rearrangement shown in eq 1 presents



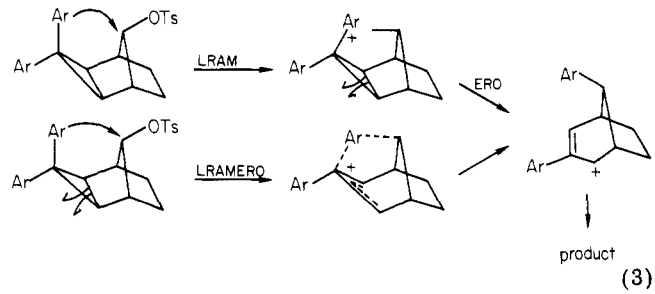
(1)

some fascinating problems in mechanistic investigation. Earlier work from this laboratory has delineated reasonably clearly the overall course of the reaction: anchimeric participation of the Ar_1-5 type is involved; the reaction is clean, with essentially total conversion to the rearranged epimers shown;[4] a change to the fluorenylidene group or to a less rigid alicyclic framework (eq 2) eliminates the



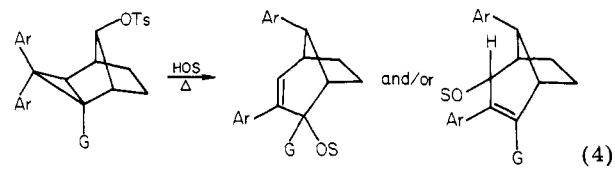
(2)

rearrangement.[5] But a vexing question remained. Is the long-range aryl migration (LRAM) antecedent to or concomitant with the disrotatory electrocylic ring opening (ERO) of the cyclopropane moiety (eq 3)? The suggestion



(3)

was previously advanced that the two processes are in concert (LRAMERO), based upon the rather low ρ^+ values for the process (−1.68 for hydrolysis at 112 °C, −1.30 for acetolysis at 110.5 °C) and the slight retardation in solvolysis rate exhibited by the analogous tosylate possessing a Δ^6 double bond.[4] In the present study, this question has been pursued in another way. Placement of electron-donating or electron-withdrawing groups at putative cationic centers has long been a favorite probe for mechanistic study.[6] It was therefore hoped that LRAMERO could be distinguished from LRAM/ERO (the stepwise alternative) by noting the effect of such groups G upon the rate of solvolysis of compounds shown in eq 4. In principle, an



(4)

(1) Electrocyclic Effects in Solvolysis. 5. Part 4: Wilt, J. W.; Niinemae, R. *J. Org. Chem.* **1980**, *45*, 5402.

(2) Taken in part from the Dissertation of C.O-Y., Loyola University of Chicago, Dec 1979.

(3) Petroleum Research Fund Fellow, 1976-1978.

(4) Wilt, J. W.; Malloy, T. P.; Mookerjee, P. K.; Sullivan, D. R. *J. Org. Chem.* **1974**, *39*, 1327.

(5) Wilt, J. W.; Kurek, J.; Roberts, W. N. *J. Org. Chem.* **1980**, *45*, 4243.

(6) Such a probe forms the basis for the structure-reactivity concept developed for essentially all carbocationic reactions.

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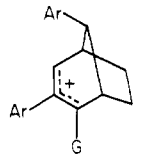
electron-withdrawing group G should retard LRAMERO because the ionic intermediate shown below, the "product ion", would be destabilized relative to the parent product

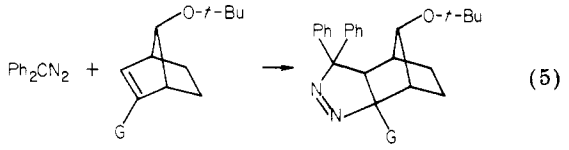


"product ion"

ion (G = H), forcing a higher activation energy on the process. The opposite effect would be expected for an electron-donating group G, and rate acceleration for LRAMERO should be observed. Coupled with this aspect of the investigation, it was considered potentially useful to compare the rate ratio for the tosylates in eq 4 where Ar = *p*-tolyl (T series) vs. Ar = Ph (P series) for each of the classes of G. As aforementioned, it was reasoned that LRAMERO would be further advanced with an electron-donating G group present. This in turn would increase the total electron deficiency at the transition state. Such an outcome would lead to an increased *p*-Tol/Ph rate ratio.[7] Again, the opposite would be expected for an electron-withdrawing G group. The ongoing gives the results of this attempt to unravel the timing of the steps in this rearrangement.

Synthesis

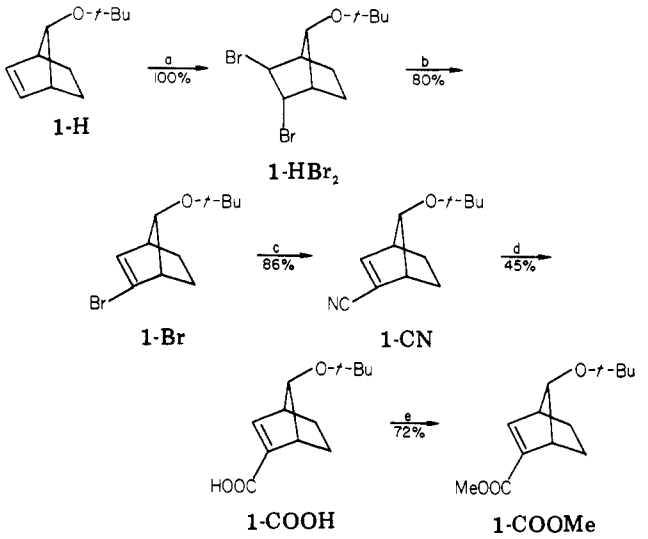
The syntheses of the requisite tosylates eventually proved to be no small task. A modification of the original procedure used to prepare the parent system[4] was deemed best. However, attempts to add diphenyldiazomethane to 2-substituted norbornenes 1-G via 1,3-dipolar cycloaddition (eq 5), a reaction so successful when G = H,[4] failed com-



1-G 2P-G[8] (5)

pletely with G = Me, Ph. Two possible explanations seem reasonable. First, 1,3-dipolar cycloaddition of diazoalkanes is a dipole-HO controlled cycloaddition and the rate is retarded with electron-rich dipolarophiles.[9] Second, the size of G engenders steric compression in the addition transition state as G crowds the endo hydrogen at C-9 of the adduct 2P-G. Both of these factors presumably slowed the addition to the point where self-destruction of the diazoalkane to azine was favored instead. Although not thoroughly investigated, attempts to bypass pyrazoline 2P-G by a diaryl carbene (carbenoid) addition to 1-G to form cyclopropyl adducts were also unrewarding.[10] Successful addition was, however, accomplished with 1-CN and 1-COOMe, examples of electron-poor dipolarophiles where the above problems would be removed or reduced.[9] The synthesis of 1-CN and 1-COOMe are shown in Scheme I. Use was made in this synthesis of the novel *radical* addition of bromine to 1-H via 1,2-dibromotetrachloroethane. Earlier work from this laboratory[11] had established that this reaction is valuable because the Wagner–Meerwein rearrangement, so common in the case of norbornenes and benzonorbornadienes with other bromine addition modes, is avoided. The sequence, otherwise quite successful, was marred only by the poor conversion of 1-CN to 1-COOH. A number of procedures were tried for this hydrolysis, but some polymerization and decarboxylation plagued all of the processes attempted. Esterification to 1-COOMe was achieved by a nonacidic technique involving displacement by carboxylate ion upon methyl iodide.[12] This effective method, though less commonly used than acid-catalyzed esterification, is useful when an acid-sensitive function, in this case the *tert*-butoxy group, is present. The 1,3-dipolar cycloaddition of either diphenyl- or di-*p*-tolyldiazomethane to 1-CN and 1-COOMe to form 2PT-CN and 2PT-COOMe, respectively, was best achieved by the "leave it alone" method, whereby the olefin and diazo components were mixed in a 1:1 ratio and allowed to stand undisturbed for several weeks. At times a small volume of petroleum ether or ether together with a trace of hydroquinone was used as a solvent for the reaction.[13] The purple mix eventually solidified and largely decolorized as the adducts 2PT-CN and 2PT-COOMe formed. The ketazine from the diazoalkanes was a troublesome contaminant in this process, however. The addition appeared to be regiospecific for 1-CN, because 2PT-CN were the only adducts observed, in complete accord with FMO predictions.[9] With 1-COOMe, however, the "abnormal" adducts 3PT-COOMe were formed (in small amount) in addition to the expected

Scheme I



a, $Br_2C_2Cl_4$, CCl_4, $h\nu$; b, KOt-Bu, *t*-BuOH, Δ; c, NaCN, CuCN, DMF, Δ; d, KOH, H_2O, Δ; e, NaOH, CH_3I, HMPA, 25 °C

(7) As the log, this rate ratio is actually a two-point Hammett plot, which though crude would show a dependence upon the G group and allow a semiquantitative measure of the extent of LRAMERO.

(8) Because a number of intermediates are involved in the syntheses devised, the following abbreviations have been employed: The *initial number* indicates simply a consecutive order of compounds related by some chemical process; the *letter* P (phenyl series) or T (*p*-tolyl series) then follows, and the last *chemical symbol* shows what G group is present. The letters PT indicate that both the phenyl and *p*-tolyl series were employed as reactants or formed as products in analogous processes.

(9) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; pp 148 ff.

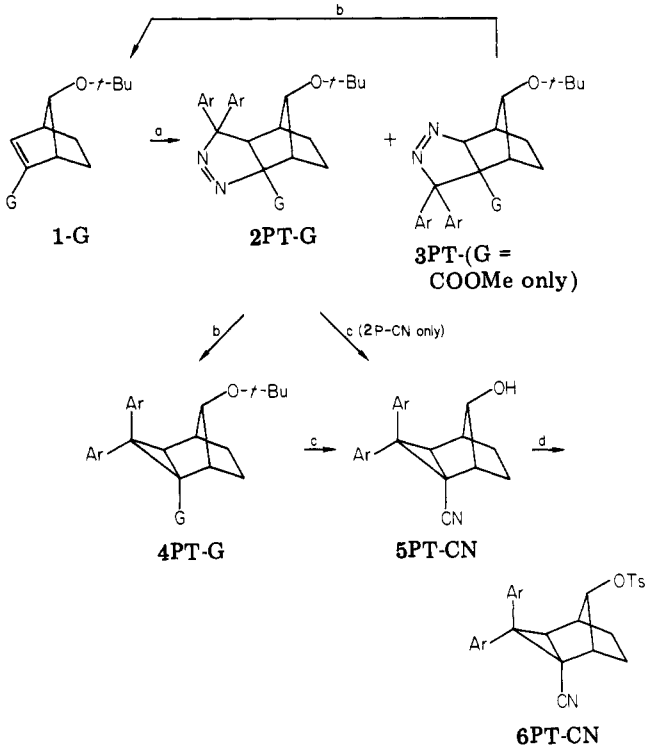
(10) Carbene (carbenoid) additions are generally more favorable with electron-rich double bonds. The failure to obtain good results in the present case may reflect the steric crowding problem that remains regardless of the mode of addition. Further, more detailed, investigation of such additions in the present substrates is planned.

(11) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1562.

(12) Shaw, J. E.; Kunerth, D. C.; Sherry, J. J. *Tetrahedron Lett.* **1973**, 689.

(13) A somewhat similar technique was reported during the course of this work. Diphenyldiazomethane was added to 3-cyanocyclopent-2-enone over a 45-day period at 25 °C. Curiously, the product was the diphenylcyclopropyl adduct and not the pyrazoline; Zimmerman, H. E.; Pasteris, R. J. *J. Org. Chem.* **1980**, *45*, 4864.

Scheme II

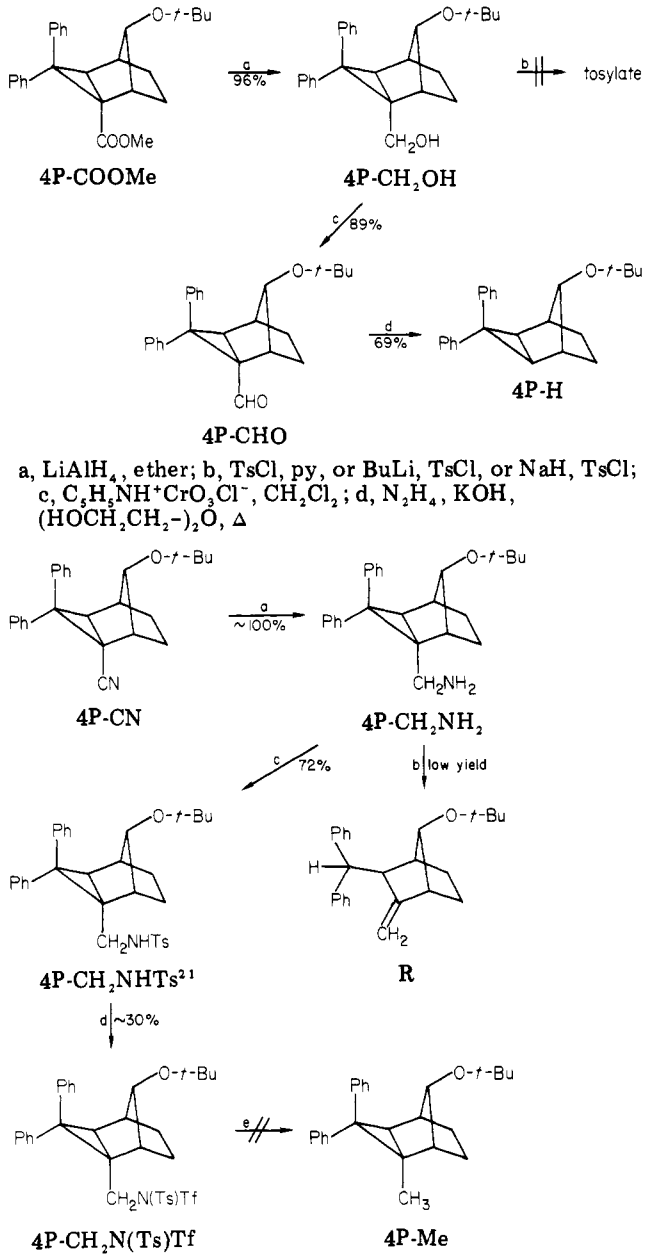


a, Ar_2CN_2, 25 °C, petroleum ether, 2-3 weeks; b, 160-165 °C, 1 h, neat, or toluene, Δ, 6-22 h; c, toluene, HOTs (trace), Δ (on G = CN only); d, TsCl, pyridine

2PT-COOMe products.[14] Upon being heated, 3P-COOMe was observed by NMR analysis to revert (at least partially) to 1-COOMe and the diazoalkane, thereupon to reform the 2P-COOMe adduct and then the cyclopropyl product 4P-COOMe.[15] These cyclopropyl-type products formed uneventfully upon thermolysis of either 2PT-CN or 2PT-COOMe. Conversion of the nitriles 4PT-CN to the alcohols 5PT-CN was accomplished by heating in toluene containing a small amount of *p*-toluenesulfonic acid. Alternatively, alcohol 5P-CN could be obtained from *pyrazoline* 2P-CN by the same treatment. The formation of tosylates 6PT-CN was readily accomplished in the usual manner. These reactions are shown in Scheme II.

The availability of the 6PT-CN tosylates completed one-half of the projected goal of the study, viz., that of an electron-withdrawing group positioned to affect LRAME-RO. It was our hope to proceed from either of the pairs 4PT-CN or 4PT-COOMe to 4PT-Me via one of several potential routes. In brief, none of the projected routes, pursued only in the diphenyl (P) series, succeeded and the sequences will therefore be described succinctly. Reduction of 4P-COOMe to 4P-CH_2OH was straightforward, but its subsequent conversion to a tosylate for a contemplated

Scheme III



reduction to 4P-Me failed under a variety of conditions. Oxidation of 4P-CH_2OH to 4P-CHO was accomplished, but its attempted reduction by a Huang-Minlon reaction led to deformylation to 4P-H, a rare but known calamity.[18] Reduction of 4P-CN to 4P-CH_2NH_2 was successful, but deamination to 4P-Me by several methods failed,[19] and with hydroxylamine-*O*-sulfonic acid[20] appeared to open the cyclopropyl ring in an interesting manner to form the

(14) The reason(s) for the formation of the reversed cycloadduct with 1-COOMe is unclear. Its cycloaddition is, interestingly, considerably slower than with 1-CN, probably reflecting both the difference in electron deficiency of the double bonds involved and steric effects in the adducts formed. In fairness to the FMO approach, it is known to be less definite with respect to 1,3-dipolar cycloadditions than to Diels–Alder reactions[9] and, in any case, has correctly predicted the *major* product from both 1-CN and 1-COOMe.

(15) While not studied separately, the *p*-tolyl abnormal ester 3T-COOMe would undoubtedly undergo the same cycloreversion. Although, 1,3-dipolar cycloreversions are known, the literature examples do not appear to be related to the present case. Either the dipole was not a diazoalkane,[16] or the adduct reverted to products different from the original dipole and dipolarophile.[17] We believe that the course of the cycloreversion of 3P-COOMe is of interest to the theory of cycloadditions and it will be investigated thoroughly in the near future.

(16) Ainsworth, C. *J. Heterocycl. Chem.* **1966**, *3*, 470.

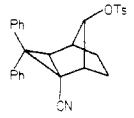
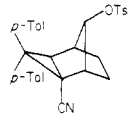
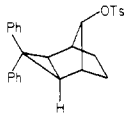
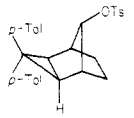
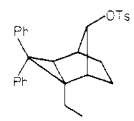
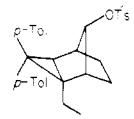
(17) Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1969**, 2659. White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1348. Gassman, P. G.; Greenlee, W. J. *Ibid.* **1973**, *95*, 980. Wilt, J. W.; Niinemae, R. ref 1.

(18) Todd, D. *Org. React.* **1948**, *4*, 381.

(19) Most work was done on deamination *via* hydride displacement on *N,N*-disulfonimides, a route developed with considerable success in other systems by Hutchins, R. O.; Cistone, F.; Goldsmith, B.; Heuman, P. *J. Org. Chem.* **1975**, *40*, 2018. Cf. also Curtis, V. A.; Knutson, F. J.; Baumgarten, R. J. *Tetrahedron Lett.* **1981**, 199.

(20) Nickon, A.; Hill, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 1153.

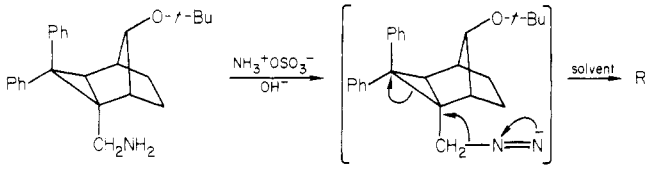
Table I. Solvolytic Data[a]

tosylate	temp, °C	10^5k, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
	111.0 ± 0.5	0.91 ± 0.40		
	120.0 ± 0.5	2.30 ± 0.11		
	132.0 ± 0.5	5.25 ± 0.19		
	(25)[b]	(6.31×10^{-10})[c]	24.8 ± 1.9	−17.4 ± 4.9
6P-CN				
	99.0 ± 0.2	1.27 ± 0.02		
	110.0 ± 0.2	3.16 ± 0.07		
	119.0 ± 0.2	7.45 ± 0.21		
	(25)[b]	(2.26×10^{-9})[c]	24.7 ± 1.0	−15.2 ± 2.7
6T-CN				
	63.5 ± 0.2	0.81 ± 0.01		
	75.0 ± 0.5	2.84 ± 0.04		
	85.4 ± 0.2	8.02 ± 0.09		
	(25)[b]	(5.87×10^{-8})[c]	24.5 ± 0.1	−9.4 ± 0.4
6P-H				
	55.5 ± 0.2	1.25 ± 0.02		
	65.0 ± 0.2	3.21 ± 0.05		
	76.0 ± 0.2	10.8 ± 0.3		
	(25)[b]	(2.60×10^{-7})[c]	23.4 ± 0.9	−10.1 ± 2.6
6T-H				
	38.8 ± 0.2	1.09 ± 0.02		
	48.8 ± 0.2	3.30 ± 0.09		
	55.0 ± 0.2	7.60 ± 0.05		
	63.1 ± 0.2[d]	13.0 ± 0.4		
	63.4 ± 0.2[d]	14.1 ± 0.4		
6P-Et	(25)[b]	(2.41×10^{-6})[c]	20.9 ± 1.0	−14.1 ± 3.2
	35.2 ± 0.2	5.06 ± 0.08		
	45.5 ± 0.2	16.3 ± 0.3		
	50.6 ± 0.2	26.8 ± 0.4		
	(25)[b]	(1.38×10^{-5})[c]	21.0 ± 0.40	−10.3 ± 1.4
6T-Et				

[a] For details, see the Experimental Section. [b] Extrapolated value from data at other temperatures. [c] These values are k, *not* 10^5k. [d] Duplicate runs, performed to establish the precision of the technique.

rearranged product **R**. Although unsuccessful for our purposes these reactions are of some interest in the general chemistry of this tricyclic system. They are therefore shown in Scheme III.

From these results it seemed clear that reaction intermediates that placed anionic charge adjacent to the cyclopropyl ring led to cleavage as in eq 6, shown for the



4P-CH_2NH_2 (6)

hydroxylamine-O-sulfonic acid deamination reaction.

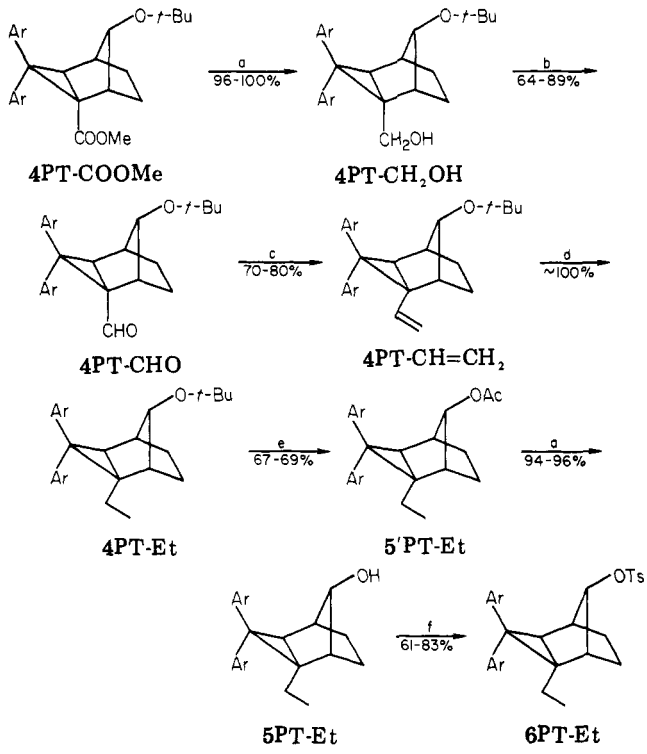
Frustrated in these attempts to position a methyl group in the tricyclic system, we considered an ethyl group instead. An analogous series of steps that led to 4P-CHO (Scheme III) was therefore performed, converting 4T-COOMe to 4T-CHO. Both series (PT) were then used in the subsequent transformations. A Wittig reaction on the aldehydes 4PT-CHO, although initially unsuccessful, was eventually found to succeed with extended reaction time to afford the vinyl compounds 4PT-CH=CH_2. Although the reaction was slow, heterogeneous catalytic hydrogenation was forced upon 4PT-CH=CH_2 and the ethyl derivatives 4PT-Et were obtained. Homogeneous catalytic hydrogenation using Wilkinson's catalyst was much more effective. Subsequent conversions to the alcohols 5PT-Et and their tosylates 6PT-Et were more or less routine. The T series was much more prone to the problem of cyclopropyl ring opening, undoubtedly because the di-*p*-tolyl functionality made such an opening more facile by the extra electron donation available. In any event, whereas the routes to the methyl analogue were marked by failure and side reactions, removal of the reaction site to a position one more carbon distant from the cyclopropyl ring removed the problems. Scheme IV shows these reactions. Relevant characterization data for the compounds shown in the schemes are reserved for the Experimental Section, but the microanalyses and/or spectra supported the assigned structures. With the synthesis of the ethyl-substituted tosylates 6PT-Et, the goal of the research could now be pursued.

(21) For an X-ray crystallographic study of this sulfonamide, see Pavkovic, S. F.; Santangelo, P. G. *Acta Crystallogr., Sect. B* **1981**, *37*, 1762. We thank Professor Pavkovic of this department for his interest and time to confirm the structure of this compound and to give us detailed X-ray structural information on the tricyclic ring system present. Cf. also Macdonald, A. C.; Trotter, J. *Acta Crystallogr.* **1965**, *18*, 243.

(22) Oxidation with pyridinium chlorochromate gave some cyclopropyl ring opening in the T series, and the use of Sarett's reagent was preferable here.

(23) Olefins 4PT-CH=CH_2 were sensitive substances. On occasion, chromatography (even on Florisil) led to some cyclopropyl ring opening. Such a result again implicates some cationic intermediates with charge adjacent to the ring, perhaps caused by acidic impurities in the column substrate.

Scheme IV



a, $LiAlH_4$, ether; b, $C_5H_5NH^+CrO_3Cl^-$, CH_2Cl_2 or CrO_3, pyridine;[22] c, $Ph_3P{=}CH_2$, ether, 72 h;[23] d, $(Ph_3P)_3RhCl$, H_2, PhH, 5 days; e, HOAc, Ac_2O, $HClO_4$; f, TsCl, pyridine

Table II. Rate Comparisons among Systems at 25 °C

tosylate	k^T/k^P [a] (ρ^+) [b]	k_{rel}	
6P-CN		1.00	
6T-CN	3.58 (−2.16)		1.00
6P-H		93.0	
6T-H	4.43 (−2.52)		115
6P-Et		3820	
6T-Et	5.73 (−2.96)		6110

[a] The ratio of the rate constants for the *p*-tolyl (T) analogue and the phenyl (P) analogue, taken from Table I. [b] Calculated by the equation $\log (k^T/k^P) = \rho^+\sigma^+$, for which $\sigma^+ = -0.256$ (*p*-Me) was used.

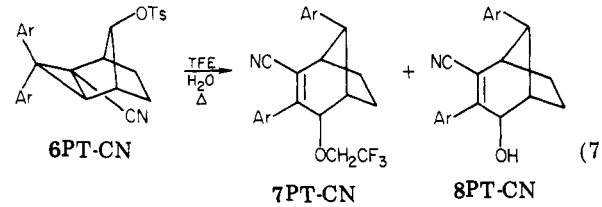
Solvolytic Reactivity

The four tosylates, pairs 6PT-CN and 6PT-Et, were solvolyzed in 2,2,2-trifluoroethanol (TFE)–water (97:3, v/v), a solvent of high ionizing power and low nucleophilicity, which has served usefully in other studies where participation phenomena were of interest.[24] Because our earlier studies of the parent system 6PT-H had used other solvolytic media,[25] this pair was also studied in the present medium so that comparisons among the three systems could be made. The titrimetric rate data and activation parameters are given in Table I. Comparisons among the systems are gathered in Table II.

The use of TFE/H_2O was indeed effective in promoting both the solvolytic participation and rates, as hoped. From earlier data[4] it may be calculated that at 25 °C in dioxane/water (80:20, v/v), k(6P-H) = 4.66×10^{-10} s^{-1} and k(6T-H) = 1.82×10^{-9} s^{-1}. This gives a value of k^T/k^P = 3.91, compared to 4.43 in TFE/H_2O, indicating more participation by *p*-tolyl in the latter solvent. The rate constants themselves are increased 126-fold for 6P-H and 143-fold for 6T-H with the change in solvent. The choice to avoid acetic acid as the solvolysis medium was also beneficial. A comparison of rates for 6T-H in dioxane/water and acetic acid at 25 °C from the earlier data indicates that k^T(HOAc)/k^T(dioxane/water) = 1.07, only a small increase. Clearly, neither of the earlier used solvents would have been as effective in uncovering the participation phenomena as was TFE/H_2O.

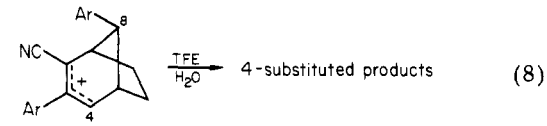
Solvolysis Products

Notwithstanding the considerable spread of reactivities among them, all the tosylates underwent the LRAM–ERO process involving the transannular aryl group migration and opening of the cyclopropane ring. The solvolysis products from 6PT-H in other media have been described earlier[4] and they were not further characterized here, although spectral analysis clearly showed that the expected products were formed. The major products from tosylates 6PT-CN, formed in >80% isolated yield, were the trifluoroethyl ethers and alcohols (eq 7) also anticipated from the earlier work.



(7)

As would be expected, the product ion shown in eq 8 was



(8)

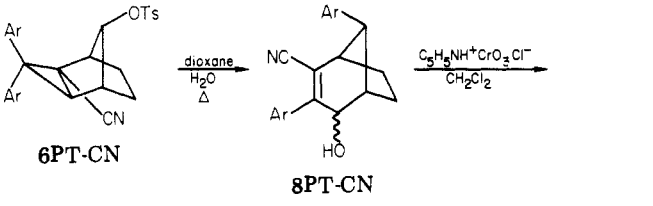
captured by the solvent at C-4 of the allylic ion (primarily from the endo side, from spectral data). Such a regiospecific and stereoselective capture by solvent is a consequence of the conjugation possible between the aryl and cyano groups in the adduct coupled with the steric hindrance to exo capture due to the syn 8-aryl group overhanging the reaction zone. No evidence for cyanohydrin or α-cyano ether products was found. For confirmation of the latter point, tosylates 6PT-CN were individually solvolyzed in aqueous dioxane as well. The epimeric alcohol products 8PT-CN, (exo/endo = 15:85) were then oxidized in each case to a *cyano* ketone, 9PT-CN, ν_{CO} 1680 cm^{-1}, establishing the α,β-unsaturated nature of the ketone and the site of the capture by solvent (eq 9).[26]

The solvolysis product from tosylate 6P-Et was a complex mixture that was only partly characterized. Among the products were the anticipated ether 7P-Et and alcohol 8P-Et, but deprotonation of the product ion also afforded a conjugated diene(s) **10P**, as shown in eq 10. This manifold of products is of course different from the -CN and -H series because such deprotonation is impossible in the latter cases. Due to scarcity of material, the products from 6T-Et were examined less intensively, but their spectral similarity to those above was clear.

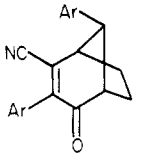
(24) Inter alia, cf. Scott, F. L. *Chem. Ind. (London)* **1959**, 224. Trahanovsky, W. S.; Doyle, M. P. *Tetrahedron Lett.* **1968**, 2155. Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838. Noyce, D. S.; Castenson, R. L.; Meyers, D. A. *J. Org. Chem.* **1972**, *37*, 4222.

(25) The earlier work[4] had used dioxane/water (80:20) and acetic acid. The cyanotosylates 6PT-CN were poorly soluble in the former and the latter is less useful in accentuating participation phenomena compared to TFE.

(26) The oxidation to an α,β-unsaturated ketone was used earlier[4] to establish the allylic alcohol nature of the solvolysis product.

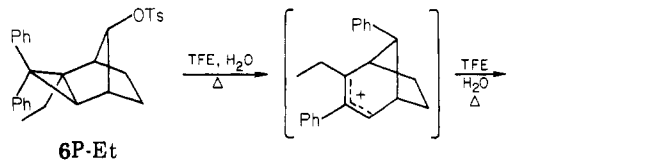


6PT-CN 8PT-CN

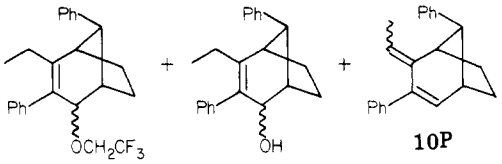


9PT-CN

(9)



6P-Et



7P-Et 8P-Et 10P

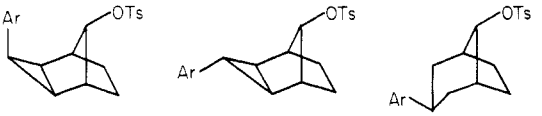
(10)

Discussion of Results

The nature of the intermediate (or transition state) is the deciding factor in this question of the timing of the parts in LRAMERO, viz., a typical phenonium ion vs. an atypical phenonium ion with partial opening of the cyclopropyl ring (see eq 3). The response of solvolytic rate to the G group is substantial (Tables I and II) and in our view represents a clear decision *favoring concerted aryl migration and ring opening*, the view originally espoused.[4] Both the *p*-tolyl/phenyl rate ratios (k^T/k^P) and the overall rate spread (k_{rel})among the tosylates supports this contention. Nevertheless, the *extent of ERO is variable*, a mechanistic feature *not* considered in the earlier conclusions. As the migration origin is stabilized by ring opening, more concertedness develops. One may view the process as a mechanistic continuum, with the contribution of ERO to its combination with LRAM increasing as the allylic ion stabilization in the product ion increases. Correspondingly, with increased allylic ion stabilization in the series -CN[27] < -H <Et, anchimeric participation is likewise enhanced, resulting in faster rates in the series and increased charge development at the transition state, a condition that engenders the increased *p*-tolyl/phenyl rate ratios (T vs. P series). This point is further reflected in the increased Hammett–Brown ρ^+ values observed.

An alternative view of these reactions would be the maintenance of LRAM separate from ERO, explaining the rate difference in terms of pure inductive effects of the G substituents upon a typical phenonium ion. This view seems less attractive in light of the earlier work[4] supporting LRAM and ERO acting in concert and because, in the present study, the G group is remote from the reaction center and the rate differences appear to be too large for such an explanation.

A remaining question to be answered centers upon the importance of the *nonmigrating* aryl group upon the course of LRAMERO. This matter was addressed earlier[4] to some degree, when it was suggested that the effect of the nonmigrating aryl group should be minimal in LRAMERO because it is positioned at the central carbon atom of the developing allylic cation. This central atom represents a nodal position in the nonbonding MO of an allylic ion, and a substituent at this position should not contribute significantly to its stabilization by lowering the energy of this orbital. Moreover, the substituent could affect the bonding MO only by cross conjugation, which again should be a minimal effect. However, the *steric* influence of this aryl group on the course of LRAMERO has not been evaluated, so the question remains one to be investigated more directly. For this purpose, the substrates shown below will be needed. A comparison of these three



systems among themselves and with the diaryl cases described in the present work is underway[28] and will be the subject of the next paper in this series.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Boiling points are uncorrected. Spectra were recorded on the following instruments: IR, Perkin-Elmer Model 700; ^{1}H NMR, Varian EM-360. For the former only structurally significant absorptions (in reciprocal centimeters) are given. Liquids were run as neat samples and solids as 1% mixtures in KBr disks. For the latter, the usual abbreviations are employed for the multiplicities of the resonances; defined multiplets are listed at their centers, otherwise the range is given. The reference standard was Me_4Si (δ 0.00) and the solvent was deuteriochloroform. Gas–liquid chromatography was carried out on a Gow-Mac Model 550 thermal conductivity instrument using helium as the carrier gas. High-pressure liquid chromatography was performed on a Gow-Mac Model 80-600 instrument. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, IL. The petroleum ether used was 30–60 °C boiling material.

***trans*- and *exo-cis*-2,3-Dibromo-*anti*-7-*tert*-butoxynorbornane (1-HBr$_2$).** A solution of *anti*-7-*tert*-butoxynorbornene[29] (15 g, 90 mmol) and 1,2-dibromotetrachloroethane[11] (30 g, 90 mmol) in carbon tetrachloride (160 mL) was irradiated with a 275-W sunlamp positioned so as to cause gentle reflux of the solvent. After 10 h of irradiation the solvent and tetrachloroethylene (formed in the reaction) were removed to leave the dibromides 1-HBr$_2$ as a pale-colored oil in quantitative yield: ^{1}H NMR of the predominant trans dibromide (CCl_4) δ 4.48 (t, 1, exo H-2), 4.20 (br s, 1, H-7), 3.83 (d, 1, endo H-3), 2.20 (m, 2, H-1, -4), 2.0–1.60 (m, 4, H-5, -6), 1.20 (s, 9, *t*-Bu). A small amount (~10%) of the exo-cis dibromide was evidenced by a doublet at δ 4.10 for the H-2, -3 resonance. The crude dibromide was used directly in the next step.

(27) The destabilization of cations by a cyano group has recently been shown to be less than expected on the basis of the supposed electron-withdrawing power of this group: Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *Ibid.* **1980**, *102*, 3957. Gassman, P. G.; Talley, J. J. *Ibid.* **1980**, *102*, 4138. Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613. This less-than-expected destabilization of cationic centers by cyano probably contributes to the present observation that LRAMERO still occurs with 6PT-CN and that the k_{rel} for the group is only ca. 10^{-2} compared to that of 6PT-H. Gassman and Talley (references above) suggest that a *minimal* inductive destabilization free from resonance stabilization by cyano on a cationic center should be ca. 10^{-6} relative to hydrogen.

(28) Wilt, J. W.; Curtis, V. A.; Congson, L., work in progress.

(29) Franzus, B.; Snyder, E. I. *J. Am. Chem. Soc.* **1965**, *87*, 3423. This reduction is capricious, at times giving unreduced and overreduced product. The best conditions we found employed 30 g of 7-*tert*-butoxynorbornadiene (Frinton Laboratories) in dry THF (350 mL) with a 2:1 molar excess of $LiAlH_4$ under reflux overnight. Even so, ~20% 7-*tert*-butoxynorbornane accompanied the desired monoene. The saturated ether is of course inert in the subsequent reactions and is removed in the purification steps.

2-Bromo-*anti*-7-*tert*-butoxynorbornene (1-Br). The above mixture of dibromides was heated under reflux (nitrogen blanket) for 19 h with potassium *tert*-butoxide (12 g) in dry *tert*-butyl alcohol (150 mL). The solvent was removed and the residue treated with water (100 mL). The organic material was taken up into ether (3 × 100 mL) and washed with hydrochloric acid (10%, 2 × 100 mL), sodium bicarbonate solution (5%, 2 × 100 mL), and brine (2 × 100 mL). After the material was dried (Na_2SO_4), the ether was removed and the residue was distilled to afford 1-Br 15.3 g, 80%, bp 90–96 °C (4 mm) contaminated with 7-*tert*-butoxynorbornane and *anti*-7-*tert*-butoxynorbornene (5% and 7%, respectively, from GLC analysis): IR $\nu_{C=C}$ 1580 cm^{-1}; ^{1}H NMR δ 6.0 (d, 1, H-3), 3.4 (br s, 1, H-7), 2.5 (m, 2, H-1, -4), 0.8–0.2 (m, 4, H-5, -6), 1.2 (s, 9, *t*-Bu). Anal. Calcd for the composition indicated by GLC: C, 55.99; H, 7.28. Found: C, 55.93; H, 7.26.

2-Cyano-*anti*-7-*tert*-butoxynorbornene (1-CN). A mixture of 1-Br (88% pure, 17.8 g, 73 mmol), copper(I) cyanide (Fisher; 13.1 g, 146 mmol), and sodium cyanide (7.15 g, 146 mmol) in reagent-grade dimethylformamide (350 mL) was heated under reflux with vigorous stirring under a nitrogen blanket for 11 h.[30] The dark material was cooled and then shaken with a saturated aqueous solution of sodium cyanide (500 mL) and ether (1 L). The layers were separated, and the aqueous phase extracted with ether (3 × 200 mL). The combined ether material was washed with water (2 × 200 mL), brine (3 × 200 mL), then dried ($MgSO_4$), and evaporated. The residual oil was distilled to afford 1-CN, 12 g, 86%, bp 105–110 °C (4 mm). The analytical sample was collected by GLC at 210 °C (Carbowax 20 M): IR ν_{CN} 2250, $\nu_{C=C}$ 1580 cm^{-1}; ^{1}H NMR δ 6.8 (d, 1, H-3), 3.4 (br s, 1, H-7), 2.7 (m, 2, H-1, -4), 2.0–0.9 (m, 4, H-5, -6), 1.1 (s, 9, *t*-Bu). Anal. Calcd for $C_{12}H_{17}ON$: C, 75.35; H, 8.96. Found: C, 75.09; H, 9.07.

***anti*-7-*tert*-Butoxynorbornene-2-carboxylic Acid (1-COOH).**[31] Nitrile 1-CN (7 g, 37 mmol) and potassium hydroxide (85% material, 15 g) were suspended in water (100 mL). The solution was heated under reflux for 24 h, poured into ice–water (100 mL), and extracted with petroleum ether to recover unchanged nitrile. The aqueous solution was acidified with hydrochloric acid (10%) and extracted with ether (3 × 100 mL). The extracts were washed with water (3 × 75 mL), dried ($MgSO_4$), and freed of solvent to produce the acid 1-COOH, 3.2 g, 45%, bp 140–146 °C at 4 mm with decomposition and polymerization: IR ν_{CO} 1720–1670, ν_{OH} 3500–2400, $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR δ 10.8 (s, 1, COOH), 7.0 (d, 1, H-3), 3.4 (br s, 1, H-7), 2.9 (m, 1, H-1), 2.6 (m, 1, H-4), 2.3–0.9 (m, 4, H-5, -6), 1.16 (s, 9, *t*-Bu). The acid was used directly in the next step.

Methyl *anti*-7-*tert*-Butoxynorbornene-2-carboxylate (1-COOMe). To a solution of acid 1-COOH (1.8 g, 37 mmol) in hexamethylphosphoramide (HMPA, Aldrich; **caution: cancer suspect agent**; 130 mL) was added aqueous sodium hydroxide (25%, 10 mL). The solution was stirred at 25 °C for 2 h and methyl iodide (**caution: cancer suspect agent**; 10 mL, 160 mmol) was then added.[12] The solution was again stirred at 25 °C for another 6 h. The material was then poured into hydrochloric acid (10%, 80 mL) and the ester was taken up into petroleum ether (3 × 100 mL). The petroleum ether material was washed with water (3 × 100 mL), dried (Na_2SO_4), and evaporated to provide 1-COOMe, 6.2 g, 72%, bp 100–105 °C (2 mm) (Hickman still bath temperature): IR ν_{CO} 1720, $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR δ 6.75 (d, 1, H-3), 3.63 (s, 3, COOMe), 3.32 (br s, 1, H-7), 2.83 (m, 1, H-1), 2.57 (m, 1, H-4), 1.83 (m, 2, exo H-5, -6) 1.0 (m, 2, endo H-5, -6), 1.16 (s, 9, *t*-Bu). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.44; H, 9.01.

1,3-Dipolar Cycloadditions. Several lots of equimolar quantities (ca. 1 g)[32] of the diaryldiazoalkane (diphenyl- or di-*p*-tolyl-) and 1-CN or 1-COOMe were mixed in petroleum ether or ether, ca. 5 mL, together with hydroquinone (50 mg)[33] in small test tubes, which were then corked, and the mixtures were allowed to stand in the dark at room temperature for 2–3 weeks. The initially intensely colored solutions gradually decolorized and solidified during this time. Additional petroleum ether was then added and the insoluble material was collected by filtration. Diaryl ketone azine was a significant and persistent contaminant in the colorless, crystalline, pyrazoline adducts. Attempted recrystallization or column chromatography often led to the loss of nitrogen. The best method for purification of the pyrazolines was to dissolve them in hot chloroform (the ketazine impurity was easily detected by the yellow color acquired by the chloroform[34]) and then to add petroleum ether until cloudiness appeared. The cooled solution then deposited pyrazoline largely free of azine. Nonetheless, some of the pyrazolines were simply characterized by spectra and used directly in the next step (pyrolysis).

Adduct of Diphenyldiazomethane and 1-CN, *endo*-2-Cyano-*exo*-(3,4-diaza-5,5-diphenyl)-*anti*-10-*tert*-butoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (2P-CN): 75%, mp 150–151 °C dec (from cyclohexane); IR ν_{CN} 2250, $\nu_{N=N}$ 1560 cm^{-1}; ^{1}H NMR δ 7.37–7.32 (sh m, 10, Ph H), 3.0–2.8 (m, H-1, -7, -10), 2.0–1.0 (m, 5, H-6, -8, -9), 0.8 (s, 9, *t*-Bu).

Adduct of Di-*p*-tolyldiazomethane and 1-CN, *endo*-2-Cyano-*exo*-(3,4-diaza-5,5-di-*p*-tolyl)-*anti*-10-*tert*-butoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (2T-CN): 60%, not purified; IR ν_{CN} 2250, $\nu_{N=N}$ 1560 cm^{-1}; ^{1}H NMR δ 7.22 (sh m, 8, Ar H), 2.98–2.83 (m, 3, H-1, -7, -10), 2.33 (s, 3, Ar CH_3), 2.27 (s, 3, Ar CH_3), 1.97–1.25 (m, 5, H-6, -8, -9), 0.83 (s, 9, *t*-Bu).

Adducts of Diphenyldiazomethane and 1-COOMe. *endo*-2-(Carbomethoxy)-*exo*-(3,4-diaza-5,5-diphenyl)-*anti*-10-*tert*-butoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (2P-COOMe): 70%, mp 136–137 °C (from petroleum ether); IR ν_{CO} 1710, $\nu_{C=C}$ 1550 cm^{-1}; ^{1}H NMR δ 7.37 (m, 10, Ph H), 3.77 (s, 3, COOMe), 3.2 (s, 1, H-10), 3.03 (m, 1, H-1), 2.9 (m, 1, H-7), 1.92–1.27 (m, 5, H-6, -8, -9), 0.82 (s, 9, *t*-Bu). Anal. Calcd for $C_{26}H_{30}N_2O_3$: C, 74.61; H, 7.22. Found: C, 74.53; H, 7.26.

***endo*-6-(Carbomethoxy)-*exo*-(3,4-diaza-5,5-diphenyl)-*anti*-10-*tert*-butoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (3P-COOMe):** 10%, mp 155.5–156 °C (from hexane). This adduct was more soluble in the petroleum ether wash of the adduct material than 2P-COOMe and could be isolated from the filtrate of the reaction material; IR ν_{CO} 1710, $\nu_{N=N}$ 1550 cm^{-1}; ^{1}H NMR δ 8.17–6.63 (m, 10, Ph H), 5.43 (sh m, 1, H-2), 3.20 (s, 3, COOMe), 2.93 (sh m, 1, H-10), 2.73 (m, 1, H-1), 2.33 (m, 1, H-7), 2.03–0.90 (m, 4, H-8, -9), 0.67 (s, 9, *t*-Bu). Anal. Calcd for $C_{26}H_{30}N_2O_3$: C, 74.61; H, 7.22. Found: C, 74.66; H, 7.32.

Adducts of Di-*p*-tolyldiazomethane and 1-COOMe.[35] ***endo*-2-(Carbomethoxy)-*exo*-(3,4-diaza-5,5-di-*p*-tolyl)-*anti*-10-*tert*-butoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (2T-COOMe):** ~30% contaminated with di-*p*-tolylketazine and unchanged 1-COOMe, mp ~144 °C dec; ^{1}H NMR (partial) δ 3.80 (s, 3, COOMe), 3.02 (br s, 1, H-10), 2.28 (s, 3, Ar CH_3), 2.25 (s, 3, Ar CH_3), 0.83 (s, 9, *t*-Bu). This adduct was not purified but was used directly in the next step.

The "abnormal" adduct, *endo*-6-(carbomethoxy)-*exo*-(3,4-diaza-5,5-di-*p*-tolyl)-*anti*-10-*tert*-butoxytricyclo-[5.2.1.0^{2,6}]dec-3-ene (3T-COOMe) was observed in the crude adduct (<5%). Although never isolated in pure form, its presence was evident by the sharp multiplet resonance at δ 5.25 (H-2) and by its upfield position for the *tert*-butoxy group at δ 0.67. It was likewise allowed to remain in the crude adduct in the subsequent pyrolysis.

Pyrolysis of Adducts. Heating the above adducts neat at 160–165 °C until the evolution of nitrogen ceased, as described earlier,[4] or (preferably) heating the adducts in toluene (10 mL/g) under reflux for 6–24 h, followed by evaporation of the solvent and recrystallization of the residual solid led to the tricyclic ethers, as detailed below.

***endo*-2-Cyano-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-CN):** 90%, mp 158.5–159 °C (from hexane); IR ν_{CN} 2250 cm^{-1}; ^{1}H NMR δ 7.27 (m, 10, Ph H), 3.14

(30) The procedure followed was that of Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3734.

(31) Attempts to form the organolithium or Grignard reagents from 1-Br in the hope of obtaining 1-COOH by carbonation were unsuccessful.

(32) Larger amounts in fewer batches gave less favorable results.

(33) The lengthy reaction time allows some polymerization and/or oxidation of 1-CN and (particularly) 1-COOMe, a deleterious side reaction minimized by the addition of an antioxidant.

(34) The cause for this coloration is not known, but it is a sensitive method to detect azine in these adducts.

(35) The assistance of Mr. Michael Merry (undergraduate research scholar) in these preparations is gratefully acknowledged.

(br s, 1, H-8), 2.47–1.20 (m, 7, H-1, -4, -5, -6, -7), 0.70 (s, 9, *t*-Bu). Anal. Calcd for $C_{25}H_{27}NO$: C, 83.99; H, 7.61. Found: C, 84.18; H, 7.61.

***endo*-2-Cyano-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4T-CN)**: 91%, mp 170–171 °C (from hexane); IR ν_{CN} 2250 cm^{-1}; ^{1}H NMR 7.57–7.0 (m, 8, Ar H), 3.17 (br s, 1, H-8), 2.27 (br s, 6, Ar CH_3), 2.43–1.23 (m, 7, H-1, -4, -5, -6, -7), 0.7 (s, 9, *t*-Bu). Anal. Calcd for $C_{27}H_{31}NO$: C, 84.11; H, 8.11. Found: C, 84.29; H, 8.17.

***endo*-2-(Carbomethoxy)-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-COOMe)**: 86%, mp 128.5–129 °C (from hexane); IR ν_{CO} 1730 cm^{-1}; ^{1}H NMR δ 7.2 (m, 10, Ph H), 3.32 (s, 3, COOMe), 3.17 (br s, 1, H-8), 2.57 (br s, 1, H-1), 2.27 (m, 2, H-4, -5), 1.93–1.20 (m, 4, H-6, -7), 0.7 (s, 9, *t*-Bu). Anal. Calcd for $C_{26}H_{30}O_3$: C, 79.97; H, 7.74. Found: C, 79.89; H, 7.80.

***endo*-2-(Carbomethoxy)-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-COOMe)**: 87%, mp 142.5–143 °C (from hexane): IR ν_{CO} 1730 cm^{-1}; ^{1}H NMR δ 7.47–6.8 (m, 8, Ar H), 3.37 (s, 3, COOMe), 3.20 (sh m, 1, H-8), 2.60 (m, 1, H-1), 2.30 (m, 1, H-5), 2.23 (s, 3, Ar CH_3), 2.17 (s, 3, Ar CH_3), 1.97–1.13 (m, 5, H-4, -6, -7), 0.70 (s, 9, *t*-Bu). Anal. Calcd for $C_{28}H_{34}O_3$; C, 80.35; H, 8.19. Found: C, 80.58; H, 8.10.

Synthesis of the Cyano System. Cleavage of Ethers to Alcohols. The tricyclic ethers **4PT**-CN (1 g) were heated under reflux in toluene (25 mL) containing *p*-toluenesulfonic acid (80 mg) for 18 h.[36] A solution of aqueous sodium carbonate (10%, 100 mL) was added and the material was extracted with ether (3 × 30 mL). The ether–toluene extracts were dried ($MgSO_4$) and evaporated. The residual alcohols were purified by recrystallization from benzene–hexane.

***endo*-2-Cyano-*exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (5P-CN)**: 81%, mp 200–202 °C dec; IR ν_{OH} 3475, ν_{CN} 2250 cm^{-1}; H NMR δ 7.27 (m, 10, Ph H), 3.31 (br s, 1, H-8), 2.8–2.5 (m, 2, H-1, -5), 2.4–1.2 (m, 6, H-4, -6, -7, OH). Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35. Found: C, 83.53; H, 6.27. This alcohol was also prepared in the same way from the pyrazoline 2P-CN (1.4 g) in toluene (35 mL) and *p*-toluenesulfonic acid (0.1 g) under reflux for 22 h.

***endo*-2-Cyano-*exo*-3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (5T-CN)**: 86%, mp 156–157 °C; IR ν_{OH} 3470–3120, ν_{CN} 2250 cm^{-1}; ^{1}H NMR δ 7.37–6.93 (m, 8, Ar H), 3.35 (br s, 1, H-8), 2.25 (s, 3, Ar CH_3), 2.22 (s, 3, Ar CH_3), 2.57–1.20 (m, 8, H-1, -4, -5, -6, -7, OH). Anal. Calcd for $C_{23}H_{23}NO$: C, 83.86; H, 7.04. Found: C, 83.88; H, 7.06.

Conversion of Alcohols to Tosylates. This conversion was performed in the standard fashion with recrystallized *p*-toluenesulfonyl chloride and dry pyridine. Reaction was allowed to proceed at room temperature for 5 days. The tosylates were recrystallized from benzene–petroleum ether.

***endo*-2-Cyano-*exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Tosylate (6P-CN)**: 76%, mp 225–227 °C dec; IR ν_{CN} 2250, ν_{SO_2} 1370, 1180 cm^{-1}; ^{1}H NMR δ 7.40–7.20 (m, 14, Ar H), 3.90 (br s, 1, H-8), 2.60 (m, 2, H-1, -5), 2.43 (s, 3, Ar CH_3), 2.38 (m, 1, H-4), 2.0–1.4 (m, 4, H-6, -7). Anal. Calcd for $C_{28}H_{25}NO_3S$: C, 73.82; H, 5.53. Found: C, 73.98; H, 5.57.

***endo*-2-Cyano-*exo*-3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Tosylate (6T-CN)**: 81%, mp 145–146 °C; IR ν_{CN} 2250, ν_{SO_2} 1365, 1175 cm^{-1}; ^{1}H NMR δ 7.38–7.05 (m, 12, Ar H), 3.97 (m, 1, H-8), 2.65 (m, 2, H-1, -5), 2.47 (s, 3, Ar CH_3), 2.35 (s, 3, Ar CH_3), 2.23 (s, 3, ArCH_3), 2.0–1.50 (m, 5, H-4, -6, -7). Anal. Calcd for $C_{30}H_{29}NO_3S$: C, 74.51; H, 6.04. Found: C, 74.78; H, 6.21.

Attempted Synthesis of the Methyl System. Reduction of ester 4P-COOMe with lithium aluminum hydride in dry ether (25 °C, 10 h) led to ***endo*-2-(hydroxymethyl)-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-CH_2OH)**: 96%, mp 134–135 °C (from hexane); IR ν_{OH} 3550–3200 cm^{-1}; ^{1}H NMR δ 7.53–7.00 (m, 10, Ph H), 3.35 (q, 2, CH_2OH, AB, J = 11 Hz), 3.23 (br s, 1, H-8), 2.63 (br s, 1, H-1), 2.10 (br s, 1, H-5), 1.77–1.30 (m, 6, H-4, -6, -7, OH), 0.8 (s, 9, *t*-Bu). Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.72; H, 8.49. Various methods to convert 4P-CH_2OH into its tosylate were unsuccessful. Oxidation of 4P-CH_2OH (1 g, 2.4 mmol) with pyridinium chlorochromate (0.6 g, 2.8 mmol) in methylene chloride in the usual manner[37] afforded ***endo*-2-formyl-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-CHO)**: 89%, mp 149–150 °C (from hexane); IR ν_{CHO} 2770, 1690 cm^{-1}; ^{1}H NMR δ 8.75 (s, 1, CHO), 7.27 (m, 10, Ph H), 3.22 (br s, 1, H-8), 2.62 (br s, 2, H-1, -5), 2.33 (br s, 1, H-4), 2.1–1.20 (m, 4, H-6, -7), 0.70 (s, 9, *t*-Bu). Anal. Calcd for $C_{25}H_{28}O$: C, 83.30; H, 7.83. Found C, 83.52; H, 7.94. Attempts to convert 4P-CHO to 4P-CH_3 by the Huang-Minlon reduction failed, resulting instead in the formation of the deformylated product 4P-H. Similarly, pyrazoline 2P-COOMe was reduced to the alcohol 2P-CH_2OH and then oxidized to the aldehyde 2P-CHO. As with 4P-CHO, Huang-Minlon reduction of 2P-CHO also produced 4P-H (69%, mp 118–119 °C, identical via mixture melting point and spectra with an authentic sample[4]).

To pursue a route via deamination, nitrile 4P-CN (4.0 g, 11.2 mmol) was reduced with lithium aluminum hydride (0.448 g, 11.5 mmol) in dry tetrahydrofuran (THF, 10 mL) under nitrogen (heated at reflux for 12 h). The reduction was processed with aqueous sodium hydroxide. After a workup in the usual fashion, there was obtained ***endo*-2-(aminomethyl)-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-CH_2NH_2)**: ~100%, mp 111–112 °C (from petroleum ether–chloroform). The amine colored by standing, so it was quickly converted to its ***p*-toluenesulfonamide 4P-CH_2NHTs**[21] by treatment first with sodium hydride in THF followed by *p*-toluenesulfonyl chloride, first at 0 °C and then under reflux overnight: 72%, mp 221–221.5 °C (hexane–chloroform); IR ν_{NH} 3600–3300, ν_{SO_2} 1320, 1150 cm^{-1}; ^{1}H NMR δ 7.8–7.0 (m, 14, Ar H), 5.03 (br t, 1, NH, J = 7 Hz), 3.60–3.10 (m, 2, AB, CH_2N), 3.22 (br s, 1, H-8), 2.40 (s, 3, Ar CH_3), 2.30–1.06 (m, 7, H-1, -4, -5, -6, -7), 0.63 (s, 9, *t*-Bu). Anal. Calcd for $C_{32}H_{37}NO_3S$: C, 74.53; H, 7.23. Found C, 74.81; H, 7.43. Reaction of 4P-CH_2NHTs with further sodium hydride in THF followed by additional *p*-toluenesulfonyl chloride or trifluoromethanesulfonyl chloride (the latter at −60 °C) led to crude di-*p*-toluenesulfonimide or *N*-*p*-toluene-*N*-trifluoromethanesulfonimide (4P-N(Tf)Ts), neither of which was obtained in pure enough form for adequate characterization. Attempted displacement on these sulfonimides at 100–110 °C with sodium borohydride in HMPA or with potassium iodide in DMF led only to monosulfonamide products. No evidence for deamination or displacement was found. Reaction of 4P-CH_2NH_2 (1.8 g, 5 mmol) in ethanol (80 mL) containing aqueous sodium hydroxide (10% 20 mL) with hydroxylamine-*O*-sulfonic acid (1.22 g) was performed at 0 °C with vigorous stirring.[20] When gas evolution ceased (ca. 30 min), further portions (2 × 0.53 g) of hydroxylamine-*O*-sulfonic acid were added each time. The material was added to ice–water (100 mL) and extracted with petroleum ether (2 × 50 mL). The petroleum ether extracts were washed with hydrochloric acid (5%, 2 × 100 mL), saturated sodium bicarbonate solution, and brine. The dried ($MgSO_4$) extracts were evaporated to leave a crude oil (0.4 g) which showed ^{1}H NMR resonances in the δ 5.4–4.0 region, indicating vinyl protons associated with compound R (Scheme III). Considerable unchanged amine 4P-CH_2NH_2 was recovered from the hydrochloric acid washes.

Synthesis of the Ethyl System. Reduction of ester 4T-COOMe with lithium aluminum hydride as described for the phenyl analogue led to ***endo*-2-(hydroxymethyl)-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4T-CH_2OH)**: ~100%, mp 120–121 °C (chromatographed on silica gel, recrystallized from hexane), IR ν_{OH} 3500 cm^{-1}; ^{1}H NMR δ 7.50–6.83 (m, 8, Ar H), 3.90, 3.00 (2 d, 2, AB, CH_2OH, J =12 Hz), 3.27 (br s, 1, H-8), 2.3 (m, 2, H-1, -5), 2.27 (s, 3, Ar CH_3), 2.20 (s, 3, Ar CH_3), 1.93–1.56 (m, 6, H-4, -6, -7, OH), 0.70 (s, 9, *t*-Bu). Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 83.21; H, 8.81.

Oxidation of 4T-CH_2OH with chromium trioxide in pyridine[22] in the literature fashion produced ***endo*-2-formyl-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4T-CHO)**: 64%, mp 138.5–139 °C (from petroleum ether); IR ν_{CHO} 2750, 1680 cm^{-1}; ^{1}H NMR δ 8.57 (s, 1, CHO), 7.43–6.78 (m, 8, Ar H), 3.17 (m, 1, H-8), 2.5 (br m, 1, H-1), 2.40 (sh m, 1, H-5), 2.23 (s, 3, Ar CH_3), 2.20 (s, 3, Ar CH_3), 1.93–1.03 (m, 5, H-4, -6, -7), 0.67 (s, 9,

(36) Loozen, H. J. J.; de Haan, J. W.; Buck, H. M. *J. Org. Chem.* **1977**, *42*, 419. This technique is *not* useful in the -H or -Et series, where LRAMERO was found to accompany the ether cleavage.

(37) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

t-Bu). The crude aldehyde was used directly in the Wittig reaction.

Wittig Reactions on 4PT-CHO. Methylenetriphenylphosphorane was generated from methyltriphenylphosphonium bromide and n-butyllithium in dry ether (ca. 25–35 mL) in the usual fashion[38] (nitrogen blanket, 2–4-mmol scale). To the yellow slurry was then added the appropriate aldehyde (1 equiv) in dry ether (ca. 25–35 mL), causing a decoloration and precipitate formation. The milky suspension was subsequently stirred under reflux for ca. 60 h.[39] Additional ether (30 mL) was then added and the solution was filtered free of the triphenylphosphine oxide precipitate. The filtrate was chromatographed on Florisil (*not* alumina, which caused ring opening in 4T-CH=CH_2), using 5% ether in hexane as the eluant. The colorless olefins that remained upon removal of the eluant were characterized only by their ^{1}H NMR spectra before being hydrogenated.

***endo*-2-Vinyl-3,3-phenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-CH=CH_2)**: 70%, oil (not distilled); ^{1}H NMR δ 7.50–6.87 (m, 10, Ph H), 5.5–4.70 (m, 3, CH=CH_2), 3.27 (br s, 1, H-8), 2.37 (br s, 1, H-1), 2.23 (br s, 1, H-5), 1.97–1.10 (m, 5, H-4, -6, -7), 0.70 (s, 9, t-Bu).

***endo*-2-Vinyl-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4T-CH=CH_2)**: 80%, oil (not distilled); ^{1}H NMR δ 7.4–6.7 (m, 8, Ar H), 5.4–4.60 (m, 3, CH=CH_2), 3.27 (br s, 1, H-8), 2.37–2.07 (obscured m, 2, H-1, 5), 2.17 (s, 3, Ar CH_3), 2.13 (s, 3, Ar CH_3), 1.93–1.03 (m, 5, H-4, -6, -7), 0.70 (s, 9, t-Bu).

Hydrogenation of Vinyl Compounds. Catalytic hydrogenaton of 4PT-CH=CH_2 (2–5-mmol scale) using palladium on charcoal catalyst (5% or 10%) in ethyl acetate or 95% ethanol (50 mL) at 25 °C (2 atm) was slow and erratic. Partial (40–65%) reduction occurred over a week's time, but the reaction was impractical. Use of Wilkinson's catalyst,[40] $(Ph_3P)_3RhCl$ (50–150 mg) in *degassed* benzene (50 mL) on the same scale led to complete reduction in 5 days (25 °C, 3 atm). The material was then passed through a short column of Florisil and the benzene was evaporated to afford the ethers as colorless oils in quantitative yield. Again these ethers were simply characterized by their ^{1}H NMR spectra and then cleaved to the corresponding acetate esters.

***endo*-2-Ethyl-*exo*-3,3-diphenyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4P-Et)**: ~100%, oil (not distilled); ^{1}H NMR δ 7.43–6.87 (m, 10, Ph H), 3.23 (br s, 1, H-8), 2.17 (br s, 2, H-1, -5), 1.97–0.83 (m, 10, H-4, -6, -7, CH_2CH_3), 0.70 (s, 9, t-Bu).

***endo*-2-Ethyl-*exo*-3,3-di-*p*-tolyl-*anti*-8-*tert*-butoxytricyclo[3.2.1.0^{2,4}]octane (4T-Et)**: ~100%, oil (not distilled); ^{1}H NMR δ 7.43–7.20 (m, 8, Ar H), 3.23 (br s, 1, H-8), 2.33–2.06 (obscured m, 2, H-1, -5), 2.23 (s, 3, Ar CH_3), 2.20 (s, 3, Ar CH_3), 1.93–0.83 (m, 10, H-4, -6, -7, CH_2CH_3), 0.70 (s, 9, t-Bu).

Cleavage of Ethers to Acetate Esters. The ethers 4PT-Et were converted to acetate esters with acetic acid, acetic anhydride, and perchloric acid as described in earlier work.[4] The reactions were performed on a 2–5-mmol scale. Cleavage of 4T-Et was very sensitive to reaction time. Only 2 min at 0 °C was used. Longer times led to a variety of products by ring opening. The short reaction time led to unchanged 4T-Et in the product and chromatography on silica gel was used to separate the materials.

***endo*-2-Ethyl-*exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Acetate (5P-Et)**: 69%, mp 129.5–130 °C (from methanol); IR ν_{OCOCH_3} 1738, 1244 cm^{-1}; ^{1}H NMR δ 7.46–6.9 (m, 10, Ph H), 4.13 (br s, 1, H-8), 2.50 (m, 2, H-1, -5), 1.80 (s, 3, $OCOCH_3$), 1.87–0.67 (m, 10, H-4, -6, -7, CH_2CH_3). Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.33; H, 7.60.

***endo*-2-Ethyl-*exo*-3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Acetate (5T-Et)**: 67%, mp 120–121 °C (from hexane); IR ν_{OCOCH_3} 1733, 1235 cm^{-1}; ^{1}H NMR δ 7.40–6.87 (m, 8, Ar H), 4.17 (br s, 1, H-8), 2.47 (m, 2, H-1, -5), 2.23 (s, 3, Ar CH_3), 2.20 (s, 3, Ar CH_3), 1.80 (s, 3, $OCOCH_3$), 1.83–0.83 (m, 10, H-4, -6, -7, CH_2CH_3). Anal. Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.62; H, 8.09.

Hydrolysis of Acetate Esters. The acetate esters above (the 5′T-Et used was contaminated with some 4T-Et) were treated with lithium aluminum hydride in ether in the customary fashion (2–5-mmol scale). Because alcohol 5T-Et was contaminated with ether 4T-Et, the alcohol was purified by a combination of chromatography on Florisil and repeated recrystallizations.

***endo*-2-Ethyl-*exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (5P-Et)**: 94%, mp 131.5–132.5 °C (from hexane); IR ν_{OH} 3640–3140 cm^{-1}; ^{1}H NMR δ 7.5–6.9 (m, 10, Ph H), 3.30 (br s, 1, H-8), 2.23 (br m, 2, H-1, -5), 1.97–0.70 (m, 11, H-4, -6, -7, CH_2CH_3, OH). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.86; H, 7.86.

***endo*-2-Ethyl-*exo*-3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (5T-Et)**: 96%, mp 84–86 °C (sinters); IR ν_{OH} 3600–3150 cm^{-1}; ^{1}H NMR δ 7.33–6.83 (m, 8, Ar H), 3.33 (br s, 1, H-8), 2.43 (br s, 2, H-1, -5), 2.23 (s, 3, Ar CH_3), 2.16 (s, 3, Ar CH_3), 1.8–0.83 (m, 11, H-4, -6, -7, CH_2CH_3, OH). Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.74; H, 8.68.

Formation of Tosylates. The above alcohols were converted to their tosylates with p-toluenesulfonyl chloride in dry pyridine in the usual manner (25 °C, 12–18 h).

***endo*-2-Ethyl-*exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Tosylate (6P-Et)**: 83%, mp 150–151 °C dec (from ether–petroleum ether); IR ν_{SO_2} 1355, 1175 cm^{-1}; ^{1}H NMR δ 7.4–6.97 (m, 14, Ar H), 4.0 (br s, 1, H-8), 2.4 (obscured s, 2, H-1, -5), 2.4 (s, 3, Ar CH_3), 2.2–0.77 (m, 10, H-4, -6, -7, CH_2CH_3). Anal. Calcd for $C_{29}H_{30}O_3S$: C, 75.95; H, 6.59. Found: C, 75.91; H, 6.57.

***endo*-2-Ethyl-*exo*-3,3-di-*p*-tolyltricyclo[3.2.1.0^{2,4}]oct-*anti*-8-yl Tosylate (6T-Et)**: 61%, mp 144.0–144.5 °C dec (from hexane); IR ν_{SO_2} 1355, 1185 cm^{-1}; ^{1}H NMR δ 7.33–6.73 (m, 12, Ar H), 4.1 (br s, 1, H-8), 2.50 (br s, 2, H-1, -5), 2.40 (s, 3, Ar CH_3), 2.30 (s, 3, Ar CH_3), 2.20 (s, 3, Ar CH_3), 1.93–0.73 (m, 10, H-4, -6, -7, CH_2CH_3). Anal. Calcd for $C_{31}H_{34}O_3S$: C, 76.51; H, 7.04. Found: C, 76.25; H, 6.91.

Solvolysis of Tosylates. 2,2,2-Trifluoroethanol (Aldrich Gold Label) was distilled immediately before use. It was added to deionized water (1.5 mL) and a measured amount of distilled 2,6-lutidine (Aldrich) to bring the total volume to 50.0 mL and ca. 0.03 M in the lutidine. The six tosylates 6PT-CN, 6PT-H, and 6PT-Et were solvolyzed as ca. 0.02 M solutions in this solvent. One-milliliter aliquots were employed, using the familiar sealed (under nitrogen) ampule technique. Large ampules (10 mL) were used. The kinetic baths were Vapo-stats, employing an appropriate pure solvent or appropriate azeotropic binary solvent.[41] The rates (2–3 half-lives) were followed by visual titration of the remaining 2,6-lutidine directly in an opened ampule at various times, using standardized hydrochloric acid (ca. 0.005 M). Bromphenol blue was the indicator. Good first-order behavior was observed. For 6P-H the visual technique was modified as follows. At the first sign of the color change (blue to green), a combination pH microelectrode (Sargent-Welch Model S-30070-05) was inserted into the ampule and all of the titrations were then continued to the same final pH (Sargent-Welch pH Meter, Model NX).

Treatment of Data. The first-order rate constants were obtained in standard fashion by computer, using $\ln a/(a-x) = kt$. The treatment gave the least-squares slope and its standard deviation. Activation parameters and their standard deviations were obtained from the Eyring equation, again by computer. The data is given in Table I.

Solvolysis Products. Tosylate 6P-CN (0.45 g, 1 mmol) was heated in the solvent (50 mL) at 130 °C for 10 days. The solvent was removed and the residue was taken up into ether. After processing, the residual oil was chromatographed on Florisil. Elution with hexane gave unidentified material (30 mg). Upon elution with 20% ether in hexane there was obtained ***endo*-4-(2,2,2-trifluoroethoxy)-2-cyano-3,*syn*-8-diphenylbicyclo[3.2.1]oct-2-ene (7P-CN)**, oil not purified, 0.145 g (41%); IR ν_{CN} 2225, $\nu_{C\text{-}F}$ 1160, 1120 cm^{-1}; ^{1}H NMR δ 7.28 (m, 10, Ph H), 3.93 (d, 1, H-4), 3.43–3.25 (m, 2, H-5, -8), 3.37 (q, 2, OCH_2CF_3, J =

(38) Wittig, G.; Schöllkopf, U., *Org. Synth.* **1960**, *40*, 66.
(39) Reaction times shorter than this led to mixtures containing appreciable quantities of unchanged aldehyde.
(40) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Chem. Commun.* **1965**, 131.
(41) The solvents used at reflux for the approximate temperatures (°C) indicated were as follows: methylene chloride, 39 °C; 1-chloropropane, 46 °C; acetone/hexane (59:41, v/v), 49 °C; water bath maintained at 51 °C; acetone, 56 °C; methanol, 65 °C; carbon tetrachloride, 76 °C; trichloroethylene, 86 °C; water, 100 °C; toluene, 111 °C; tetrachloroethylene, 120 °C; chlorobenzene, 135 °C.

9 Hz), 2.6-1.1 (m, 5, H-1, -6, -7). Elution with ether afforded **4-cyano-3,*syn*-8-diphenylbicyclo[3.2.1]oct-3-en-*endo*-2-ol (8P-CN)**, mp 139-140 °C (from benzene-petroleum ether), 0.120 g (41%); IR ν_{OH} 3545, ν_{CN} 2220 cm^{-1}; ^{1}H NMR δ 7.4 (sharp m, 10, Ph H), 4.2 (d, 1, H-2, J = 10 Hz), 3.4-3.2 (m, 3, H-1, -5, -8), 2.2-0.8 (m, 5, H-6, -7, OH). Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35. Found: C, 83.66; H, 6.40.

The endo alcohol 8P-CN and its exo epimer (85:15, respectively) were also obtained (quantitatively) by heating tosylate 6P-CN in 80% dioxane/20% water at 160 °C for 3 weeks. Oxidation of the alcohol mixture with pyridinium chlorochromate (methylene chloride, 25 °C, 3.5 h), followed by the usual workup,[37] led to **4-cyano-3,*syn*-8-diphenylbicyclo[3.2.1]oct-3-en-2-one (9P-CN)**, 65%, mp 154-156 °C (from benzene-petroleum ether); IR ν_{CN} 2250, ν_{CO} 1680 cm^{-1}; ^{1}H NMR δ 7.3-6.87 (m, 10, Ph H), 3.58 (br m, 3, H-1, -5, -8), 2.53-1.77 (m, 4, H-6, -7). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72. Found: C, 84.15; H, 5.83.

From tosylate 6T-CN in 80:20 dioxane/water (130 °C, 8 days) was similarly obtained a semisolid mixture of crude endo and exo alcohols 8T-CN (82%). Oxidation of the crude alcohols as before with pyridinium chlorochromate led to **4-cyano-3,*syn*-di-*p*-tolylbicyclo[3.2.1]oct-3-en-2-one (9T-CN)**, 80%, mp 176-177 °C from benzene-petroleum ether; IR ν_{CN} 2250, ν_{CO} 1680 cm^{-1}; ^{1}H NMR δ 7.12 (m, 8, Ar H), 3.57 (m, 2, H-1 (or -5), 8), 2.32 (s, 6, Ar CH_3), 2.72-1.73 (m, 5, H-5 (or -1), -6, -7). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46. Found: C, 84.39; H, 6.55.

Less material was available in the -Et series, particularly in the *p*-tolyl (T) case. For product analysis, therefore, all the titrated (ampule) material was pooled and processed. Because this material represented reactions carried out at different temperatures, the percentage of each component represents an average over the temperature range used. Removal of the solvent from the solvolysate of 6P-Et and a combination of chromatography of the residue on Florisil, using ether-petroleum ether mixtures (increasingly richer in the former) as eluants, and/or high-pressure liquid chromatography (25-cm Partisil PXS 10/25 column, hexane eluant) gave a series of fractions with the product composition described below (based upon peak area only). Elution with 5% ether in petroleum ether gave **2-ethylidene-3,*syn*-8-diphenylbicyclo[3.2.1]oct-3-ene (10P)**, *E* or *Z* nature unknown, 18%, waxy solid, mp 69.5-70 °C; IR $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR δ 7.33-6.77 (m, 10, Ph H), 5.70 (d, 1, H-4, J = ca. 7 Hz), 4.97 (q, 1, =CHCH$_3$, J = ca. 8 Hz), 3.63 (m, 1, H-1(5)), 3.23-2.87 (br m, 2, H-5(1), -8), 2.4-1.17 (br m, 4, H-6, -7), 1.70 (d, 3, CH_3, J = ca. 8 Hz). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 91.60; H, 7.83. Elution with 10% ether in petroleum ether led to **2-ethyl-4-*endo*-(2,2,2-trifluoroethoxy)-3,*syn*-8-diphenylbicyclo[3.2.1]oct-2-ene (7P-Et)**, oil, 14%, only partially characterized; ^{1}H NMR (partial) δ 3.54 (br s, 1, H-4), 3.23 (q, 2, OCH_2CF_3, J = 4.5 Hz). Finally, elution with 25% ether in petroleum ether afforded **4-ethyl-3,*syn*-8-diphenylbicyclo[3.2.1]oct-3-en-*endo*-2-ol (8P-Et)**, oil, 68%, only partially characterized; IR ν_{OH} 3585, $\nu_{C=C}$ 1593 cm^{-1}; ^{1}H NMR no vinyl protons.

An analogous product study on the solvolysate from 6T-Et was also performed, although even less material was available. The chromatographic fractions were therefore characterized only by spectra. The results indicated that 6T-Et had solvolyzed to a similar array of products as those mentioned above from 6P-Et.

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Registry No. 1-H, 3391-05-7; 1-HBr$_2$, 82521-65-1; 1-Br, 82521-66-2; 1-CN, 82521-67-3; 1-COOH, 82521-68-4; 1-COOMe, 82521-69-5; **2P**-CN, 82521-70-8; **2T**-CN, 82536-73-0; **2P**-COOMe, 82521-71-9; **2T**-COOMe, 82521-72-0; **3P**-COOMe, 82521-73-1; **3T**-COOMe, 82521-74-2; **4P**-CN, 82521-75-3; **4T**-CN, 82521-76-4; **4P**-COOMe, 82521-77-5; **4T**-COOMe, 82521-78-6; **4P**-CH_2OH, 82521-79-7; **4P**-CHO, 82521-80-0; **4P**-H, 50522-49-1; **4P**-CH_2NH_2, 82521-81-1; **4P**-CH_2NHTs, 82569-87-7; **4T**-CH_2OH, 82521-82-2; **4T**-CHO, 82536-74-1; **4P**-CH=CH_2, 82521-83-3; **4T**-CH=CH_2, 82521-84-4; **4P**-Et, 82521-85-5; **4T**-Et, 82521-86-6; **5P**-CN, 82521-87-7; **5T**-CN, 82521-88-8; **5P**-Et, 82521-91-3; **5T**-Et, 82521-92-4; 5′P-Et, 82521-89-9; 5′T-Et, 82521-90-2; **6P**-CN, 82521-93-5; **6T**-CN, 82521-94-6; **6P**-H, 29266-07-7; **6T**-H, 50522-61-7; **6P**-Et, 82521-95-7; **6T**-Et, 82521-96-8; **7P**-CN, 82521-97-9; **7P**-Et, 82522-02-9; **8P**-CN (isomer 1), 82521-98-0; **8P**-CN (isomer 2), 82522-04-1; **8P**-Et, 82522-03-0; **8T**-CN (isomer 1), 82522-05-2; **8T**-CN (isomer 2), 82522-06-3; **9P**-CN, 82521-99-1; **9T**-CN, 82522-00-7; **10P**, 82522-01-8; Ph_3P=CH_2, 3487-44-3; diphenyldiazomethane, 883-40-9; di-*p*-tolyldiazomethane, 1143-91-5.

Hydration of the Flavylium Ion. 2. The 4′-Hydroxyflavylium Ion

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An investigation of the transformations undergone by the 4′-hydroxyflavylium ion in aqueous solution is reported. A rapid initial deprotonation of the hydroxy group occurs, resulting in an anhydro base, the pK_a value associated with this ionization being 5.5. A slower transformation follows in which further equilibration occurs with a pseudobase and a ring-opened *cis*-chalcone. The stabilities of the neutral species are very similar, the mixture at equilibrium consisting of 37% pseudobase, 33% neutral chalcone, and 30% anhydro base. This equilibrium is displaced toward flavylium ion in acid solutions (pH <5) and is displaced toward chalcone in base due to the ionization of its phenolic hydroxyl groups. The pseudobase is formed in solutions with pH <8 by hydration of the flavylium ion, while in solutions with pH >8 direct hydration of the anhydro base occurs. In all solutions with pH >4 a very slow further reaction occurs, resulting in the irreversible formation of *trans*-2,4′-dihydroxychalcone, the product of thermodynamic control at all pHs.

Polyhydroxyflavylium ions form the nucleus of the anthocyanin pigments responsible for a large number of plant and flower colors.[1-3] While these highly colored cations are stable in relatively acidic solutions, they undergo a number of structural transformations in less acidic, neutral, and basic solutions, usually with substantial color changes or color disappearance.[1-3] The chemistry associated with these changes has been examined in varying degrees with several naturally occurring anthocyanins and some model flavylium salts.[1-11] We recently reported[12] a detailed study

(1) Hayashi, K. In "The Chemistry of Flavanoid Compounds"; Geissman, T. A., Ed.; Pergamon Press: Oxford, 1962; pp 248-285.
(2) Jurd, L. In "The Chemistry of Plant Pigments"; Chichester, C. O., Ed.; Academic Press: New York, 1972; p 123.
(3) Jurd, L. *Recent Adv. Phytochem.* **1972**, 135.
(4) Sondheimer, F. *J. Am. Chem. Soc.* **1953**, *75*, 1507.
(5) Jurd, L. *J. Org. Chem.* **1963**, *28*, 987.

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