The Solvolysis of Bromonorbornenotropenium Hexafluoroantimonates. Anchimeric Participation by the Tropenium Group[1]

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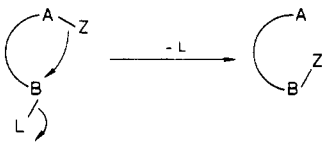
A series of tropenium ion analogues of bromobenzonorbornenes have been synthesized as their hexafluoroantimonate salts. The salts were studied in solvolytic media containing silver ion to determine rates and products. The exo-2- and anti-7-bromo salts exhibited modest solvolytic reactivity, characterized by significantly high epimeric rate ratios and clean retention in stereochemical control of product. The endo-2-bromo salt was quite slow, but it too showed clean stereochemical product formation, in its case total inversion. The syn-7-isomer was inert. The data are best interpreted in terms of anchimeric participation by the tropenium moiety in these salts. This work appears to be the first to establish the participation potential of this aromatic system.

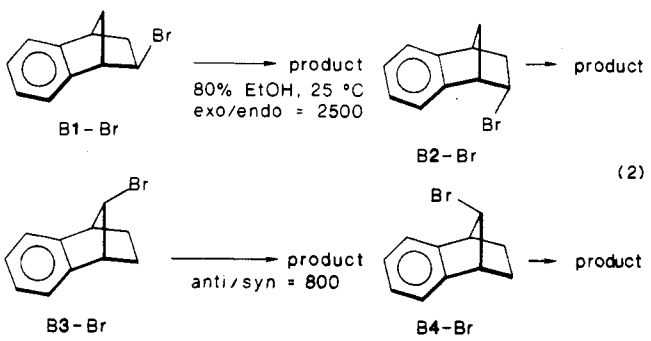
Introduction

"Anchimeric participation" in solvolysis connotes a rate enhancement due to some function Z in the displacement of some leaving group L. Often but not necessarily such participation occurs with migration, as shown in eq 1.[2]



(1)

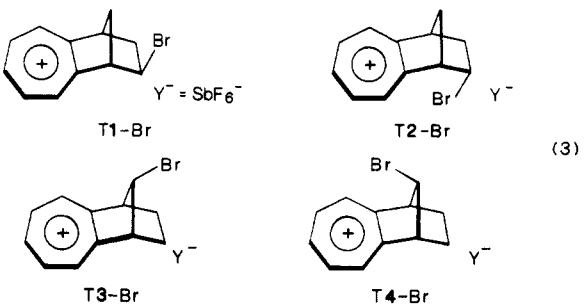
This widespread phenomenon involves examples of n-, π-, and σ-electron participation by Z. An initially uncharged Z acting as an internal nucleophile must develop some degree of cationic character at the transition state. Certainly π participation by neutral aromatic rings fits this description. From the many examples known, note the solvolyses of the bromides shown below,[3,4] where the epimeric rate ratios reflect the impact of such aromatic π participation (eq 2). Also well-known is the "aromatic"



(2)

kinship of the six π-electron trio, cyclopentadienide anion, benzene, and tropenium ion.[5] Again using the Z-A-B-L notation as above, if a cyclopentadienide anion moiety were Z, elimination of L would probably be too fast for typical solvolysis conditions.[6] Consequently it was thought preferable as an entry to this area to examine the tropenium ion system. It appears that this is the first study to probe this point or even to mention it. We chose to study the tropenium ion analogues of the bromides shown above, namely the salts shown in eq 3.[7,8] These "bromonorbornenotropenium" salts are especially intriguing because any potential anchimeric participation in their solvolysis would require the tropenium ion ring to behave as a cationic nucleophile.

Although these structures would be the first of their kind to be used in solvolytic studies, others have investigated



(3)

the possibility of electron-poor aryl participation in solvolysis. Acetolysis of 2- and 7-substituted benzonorbornenyl sulfonate esters is subject to benzo substituent effects.[9] The normally pronounced aryl anchimeric participation can be diminished or even cancelled by appropriate deactivating substituents, as can the control of product stereochemistry. Particularly effective are two nitro groups[9b,d] or an exo-coordinated chromium tricarbonyl ligand.[10] Such results are most emphatic in the exo-2-esters where participation is most developed but less so in the anti-7-, endo-2-, and syn-7-analogues. In con-

† Died May 13, 1987.
‡ In part.

(1) Taken from the dissertation of C. G., Loyola University of Chicago, 1985. For a preliminary account, cf.: Wilt, J. W.; George, C. *J. Org. Chem.* **1984**, *49*, 2298.
(2) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1.
(3) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1571.
(4) The notation used is as follows: B = benzonorbornene derivative substituted as indicated; T = the corresponding norbornentropenium derivative. The substitution patterns are: 1 = exo-2; 2 = endo-2; 3 = anti-7; 4 = syn-7. The skeletal numbering system employed for benzonorbornene (there are several used) is that of: Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240. It has been kept for the tropenium analogues as well.
(5) For a review of tropenium ion and related compounds, cf.: Pietra, F. *Chem. Rev.* **1973**, *73*, 293.
(6) Efforts to prepare and study such cases are planned.
(7) The choice of anion, which must be nonnucleophilic, was dependent upon the mode of synthesis. The hexafluoroantimonate salts were chosen for their stability, solubility properties, and ease of isolation. See ref 15.
(8) Although not germane to solvolysis, cyclopentadienide and tropenium ion analogues of another benzo system have been investigated. Thus, the cyclopentadienide anion of triptycene ("triptycepide") has been made by: Butler, D. N.; Gupta, I. *Can. J. Chem.* **1978**, 56, 80. The tropenium ion analogue of triptycene ("triptopylium") has also been prepared, both by Butler and Gupta above and a bit earlier by: Nakazawa, T.; Murata, J. *J. Am. Chem. Soc.* **1977**, *99*, 1996. See also: Nakazawa, T.; Abe, N.; Kubo, K.; Murata, I. *Tetrahedron Lett.* **1979**, 4995.
(9) (a) Tanida, H.; Tsuji, T.; Ishitobi, H. *J. Am. Chem. Soc.* **1964**, *86*, 4904. (b) Brown, H. C.; Tritle, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 1320; **1968**, *90*, 2689. (c) Tanida, H.; Hata, Y.; Ikegami, S.; Ishitobi, H. *J. Am. Chem. Soc.* **1967**, *89*, 2928. (d) Tanida, H.; Ishitobi, H.; Irie, T. *J. Am. Chem. Soc.* **1969**, *91*, 4512. (e) Tanida, H.; Irie, T.; Tsushima, T. *J. Am. Chem. Soc.* **1970**, *92*, 3404. For a review of early work, cf.: Tanida, H. *Acc. Chem. Res.* **1968**, *1*, 239.
(10) Bly, R. S.; Strickland, C. R. *J. Am. Chem. Soc.* **1970**, *92*, 7459. Wells, K. D.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1970**, *92*, 7461.

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Table I. Yields and Physical Properties of Bromonorbornenotropenium Hexafluoroantimonates

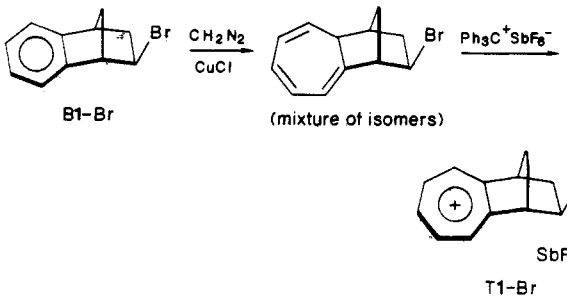
salt	yield, %[a]	mp, °C[b]	anal.[c] found C	H
T1-Br	40 (25)	173–174	31.06	2.45
T2-Br	21 (54)	160–162	31.42	2.43
T3-Br	32 (35)	178–184	30.82	2.23
T4-Br	29 (49)	185–186	31.20	2.32

[a] Based upon the amount of tropilidenes present. The percentage conversion to the tropilidene from the initial bromo compound is in parentheses. [b] These values are dependent upon the rate of heating. Prior darkening and sintering was observed from ca. 140 °C. [c] Calcd for $C_{12}H_{12}BrF_6Sb$: C, 30.54; H, 2.56.

formity with the decreasing trend toward participation in such substrates.[9] From these earlier studies one would conclude that the tropenium substituent, being the extreme of such deactivated benzo systems,[11] should exhibit little or probably no anchimeric assistance or control of product stereochemistry in the solvolysis of, for example, T1-Br or T3-Br. Stunningly, this conclusion would appear to be totally wrong.

Results.

Synthesis and Characterization Studies. The tropenium systems, as shown for the case of T1-Br (eq 4), were prepared by the method of Redecker and Grimme,[14] as modified by Thummel and Chayangkoon.[15] In brief,

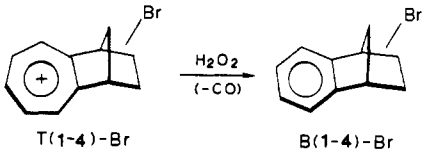


(4)

the sequence uses the long-known expansion of benzene rings to tropilidenes by diazo compounds,[16] here diazomethane,[17] followed by hydride abstraction by potent carbocation salts, in this case trityl hexafluoroantimonate.[18] Conversion to the mixture of tropilidene isomers must be monitored lest overexpansion to larger ring byproducts becomes significant. Normally 25–60% conversions were found to be acceptable. Neither separation nor isolation of the individual tropilidenes was required because all such isomers afford the desired tropenium product upon hydride loss. This sequence was applied to the appropriate bromobenzonorbornene[19] to obtain the crystalline hexafluoroantimonate salt. Some data for these salts are given in Table I.

The salts varied in appearance from white to dark microcrystalline solids, easily soluble in acetonitrile but particularly insoluble in nonpolar solvents as expected. Their NMR spectra (see Experimental Section) were largely predictable, with the tropenium aromatic proton resonance centered at ca. δ 9 and the carbon resonances from δ 146 to 180.[20,22]

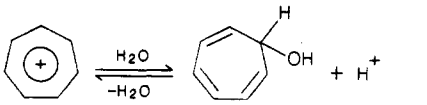
To study the tropenium salts in solvolysis, a procedure for establishing the structure of the products needed to be determined. The oxidation of tropenium salts to their benzene analogues by aqueous hydrogen peroxide[23] was selected as a suitable procedure. To ensure the integrity of this method, the tropenium salts were themselves investigated (eq 5). In each case the bromobenzonorbornene



(5)

used initially to prepare the tropenium salt was isolated in high yield (>80%). The oxidation was performed upon calibrated mixtures of epimeric salts, T1-Br with T2-Br and T3-Br with T4-Br. Gas chromatographic analysis of the benzo products showed that small amounts (<1%) of one epimer contaminant was detectable in the other.

Solvolysis Studies. Rates. Tropenium ion equilibrates with tropyl alcohol in water (eq 6).[24] Therefore,



(6)

any solvolysis study of the tropenium salts must be performed in acidic media in order to suppress this side reaction. Acetic or trifluoroacetic acid containing acetonitrile as a minor cosolvent was selected for use. Preliminary studies showed that none of the tropenium salts liberated bromide ion at practical rates in these solvents. Consequently, electrophilic assistance was employed. When equimolar silver acetate or trifluoroacetate was present, solvolysis occurred at measurable rates and followed apparent second-order kinetics (see Discussion) past two half-lives.[25] Kinetic data are presented in Table II.

(11) Tropenium ion is relatively unaffected in water (k for decomposition = 1 s^{-1})[12] and does not undergo electrophilic substitutions such as nitration, sulfonation, or Friedel–Crafts reactions.[13]

(12) Winstein, S. *Carbonium Ions*; Olah, G. R., Schleyer, P. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 966.

(13) Noller, C. R. *Chemistry of Organic Compounds*, 3rd ed.; Saunders: Philadelphia, PA, 1965; p 944.

(14) Redecker, K. Diplomarbeit, University of Cologne, Cologne, 1967; quoted in ref 15.

(15) Thummel, R. P.; Chayangkoon, P. *J. Org. Chem.* **1983**, *48*, 596. This paper was the fountainhead of the synthetic aspect of the present study. Various other approaches to these systems tried by us failed. These authors discuss the choice of counterion and cite reasons for the preference for hexafluoroantimonate.

(16) Buchner, E.; Curtius, T. *Chem. Ber.* **1885**, *18*, 2379. Braren, W.; Buchner, E. *Chem. Ber.* **1901**, *34*, 989. Loose, A. *J. Prakt. Chem.* **1909**, *79*, 509.

(17) Muller, E.; Fricke, H. *Justus Liebigs Ann. Chem.* **1963**, *661*, 38.

(18) Holmes, J.; Pettit, R. *J. Org. Chem.* **1963**, *28*, 1695.

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

(20) The parent tropenium hexafluoroantimonate exhibits singlets at δ (CH_3CN) 9.33 for its protons and δ (CD_3NO_2) 160.62 for its carbons (proton-decoupled).[21]

(21) Volz, H.; Volz de Lecca, M. J. *Justus Liebigs Ann. Chem.* **1971**, *750*, 136.

(22) A curious concentration dependence of the chemical shift for the anti-7 and exo-3-protons in salt T1-Br, as well as its acetoxy analogue (T1-OAc), was observed. It is unlikely that this spectral feature was an anisotropic effect due to the acetonitrile solvent because only the aforementioned protons were affected and only in salts T1-Br and -OAc. It is believed that the effect is due to coordination of the tropenium moiety of one salt with the n electrons of the Br or OAc substituents on another. From inspection of models, such coordination would position the anti-7- and exo-3-protons in the deshielding zone of the tropenium ring and cause their downfield shift, as observed. Dilution would reverse both the association and the shift. Such coordination would be electrostatically disfavored in salts T2-Br and T4-4 and be too remote for significant shifts in salt T3-Br, none of which showed the concentration dependence as stated.

(23) Volpin M. E.; Kursanov, D. N.; Dulova, V. G. *Tetrahedron* **1960**, *8*, 33.

(24) Doering, W. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203. For an account for the association–dissociation reactions of tropenium ions with nucleophiles, cf.: Kessler, H.; Feigel, M. *Acc. Chem. Res.* **1982**, *15*, 2. It should be noted, however, that this account deals with reactions in aprotic media, and, as the authors state, it gives no information for these reactions in protic media such as used here.

Table II. Summary of Solvolysis Data

salt	solv[a]	T, °C (± 0.5 °C)	10^5k,[b] M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
T1-Br	A	30.5	3.71 ± 0.08[c]		
		56.0	73.7 ± 1.3		
		76.0	377 ● 17	20.9 ± 0.9[d]	−9.9 ± 2.8
	B	36.0	37.7 ± 2.9		
		46.5	78.6 ± 3.9		
		56.0	196 ± 5.0		
		(76.0)[e]	786	15.9 ± 1.3	−22.8 ± 4.0
	C	76.0	0.189		
	D	76.0	0.02[f]		
T2-Br	A	76.0	0.286		
T3-Br	A	56.0	12.4 ± 0.3		
		66.0	27.9 ± 1.0		
		76.0	67.5 ± 1.3	18.7 ± 0.6	−20.0 ± 1.7
	B	56.0	26.4 ± 0.5		
T4-Br	A	76.0	*g*		

[a] A = 75:25 (v/v) HOAc/MeCN, AgOAc (1 equiv). B = 95:5 (v/v) HOAc/MeCN, AgOAc (1 equiv). C = 75:25 (v/v) HOTFA/MeCN, AgOTFA (1 equiv). D = 95:5 (v/v) HOAc/MeCN, NaOAc (1 equiv). [b] Calculated by computer from the equation $10(a-x) - 1/a$ vs. t. [c] All error limits are one standard deviation of the least-squares slope. [d] Calculated from the Eyring plot. [e] Calculated from data at other temperatures. [f] First order, 10^5k in s^{-1}. [g] No reaction was observed even after 105 days.

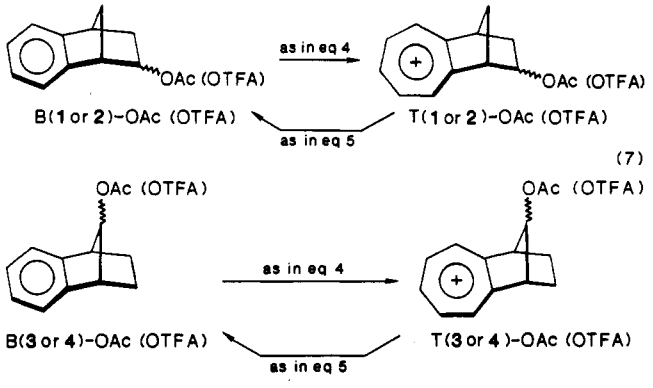
Additional studies were performed as indicated.[26]

(1) The effect of added *sodium* acetate on the solvolysis was studied. The reaction of salt T3-Br with equimolar silver acetate in solvent A (Table II) showed essentially no change over a 5.5-h period at 76 °C when 0, 0.1, 1, or 10 equiv of sodium acetate were present (13 ± 3% reaction).

(2) Added sodium acetate (1 or 10 equiv) produced no change in the UV spectrum of salt T2-Br alone in 75:25 v/v HOAc/MeCN.

(3) The extent of reaction of salt T1-Br at 76 °C in solvent B (Table II) with sodium acetate instead of silver acetate did depend upon acetate concentration. Nonetheless, the reactions were very slow (reaction time was 27 days). A 100-fold change in acetate (0.1–10 equiv) produced a 6-fold change in the extent of reaction (14–87%).

Products. The expected products of these solvolyses are obviously the acyloxy derivatives of the starting bromo salts. Therefore, as control studies, the acetoxy (OAc) and trifluoroacetoxy (OTFA)norbornenotropenium salts shown below were also synthesized by the sequence in eq 4. These salts were oxidized with hydrogen peroxide as mentioned above. Again this process formed only the benzo starting materials (eq 7), with yields consistently >80% in all cases.



(25) With such solvents containing silver acetate (trifluoroacetate) or sodium acetate the initially slightly colored tropenium salt solutions became green or red, respectively, as the reaction proceeded, sometimes requiring a special end point detection method (see Experimental Section). In nonacidic, aqueous acetonitrile solvent with no added salts, an immisicible *blue* oil formed upon heating. The origin of these colors is unknown, but the latter may represent formation of cycloheptatrienyl byproduct(s).

(26) These experiments were performed to answer the claim of a referee that a neutral intermediate (such as I in the text) was the actual reactant in these reactions.

Table III. Products and Stereochemical Course of Solvolysis[a]

salt	solv[b]	product: solvolysis	product: oxidation[c]	stereochemical course
T1-Br	A, B[d]	T1-OAc	B1-OAc	retention
T1-Br	C	T1-OTFA	B1-OTFA	retention
T2-Br	A	T1-OAc	B1-OAc	inversion
T3-Br	A, B	T3-OAc	B3-OAc	retention
T4-Br	A	*e*	B4-Br	*e*

[a] At 76.0 °C. [b] See Table II. Use of NaOAc in place of AgOAc in the solvents A and B gave the same results. [c] Via oxidation of the solvolysate with H_2O_2. See eq 7. The only other product detected was the bromobenzonorbornene derived from unreacted tropenium salt. The products were free of epimers within 1%. [d] With solvent B at 56.0 °C. [e] No solvolysis detected after 105 days.

By use of calibrated mixtures the presence of contaminating epimers was detectable at levels <1%. Because this expansion–contraction sequence (eq 7) was thus demonstrated to be stereospecific, its use to establish the course of the solvolyses was warranted. The results are given in Table III. As seen in Table III, where solvolysis proceeded only two products were observed upon oxidation, the *starting* bromide and an acetate or trifluoroacetate ester.

Discussion

From the results given above it may be concluded that *anchimeric participation is involved* in the solvolysis of these norbornenotropenium salts. This conclusion rests upon three time-tested characteristics for such participation:[2,3,9] (i) high epimeric rate ratios; (ii) greater participation at position 2 than at 7; (iii) stereochemical outcome.[27]

(i) The exo/endo rate ratio is >1300 at 76 °C in solvent A, while the anti/syn rate ratio is also quite large, albeit incalculable due to the inertness of the syn epimer.

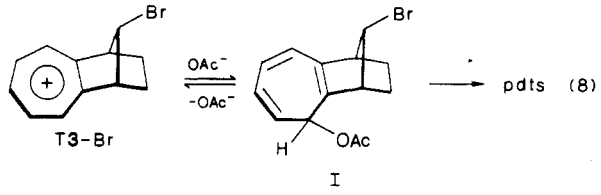
(ii) T1-Br (exo-2-bromide) is >5-fold more reactive than is T3-Br (anti-7-bromide) under the above conditions.

(iii) The faster substrates solvolyzed with apparently complete retention, while the slower T2-Br solvolyzed with total inversion.

(27) The referee mentioned[28] found these results more compatible with intervention by a neutral intermediate, particularly in relation to the literature data on benzonorbornenyl substrates. We hesitate to compare our data in this way because the literature work involved no Ag^+ assistance. Moreover, there is evidence against a neutral intermediate (see text).

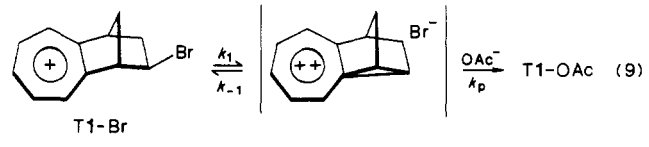
Although electrophilic assistance by silver ion (Ag^+) was necessary for practical rates, no such assistance was necessary for the stereochemical results. Data in Table II show that T1-Br was over (4×10^4)-fold faster when Ag^+ was present compared to sodium ion. Yet in each case total retention was the outcome. This fact is important because Ag^+ definitely enters the mechanism and the apparent second-order kinetics followed might be contrasted to the normal pseudo-first-order kinetics commonly associated with the solvolysis of neutral substrates. Evidence exists that soluble Ag^+ and Ag^+ absorbed on solid silver salt are the actual reactants. Although the processes undoubtedly differ in certain respects, the literature is clear that Ag^+-assisted reactions mirror those commonly ascribed to carbocation intermediates.[28] This work was not intended to unravel the complexities inherent in Ag^+-promoted reactions of this type. The cogent points are that all the salts were compared under the same conditions and that Ag^+, while needed for practical rates, was not needed for the clean stereochemical results observed.

Although participation is evident, is it due to the tropenium ion? The constancy of the Ag^+-assisted solvolysis of salt T3-Br in the presence of added sodium acetate argues powerfully against prior formation of a neutral intermediate (**I**, eq 8),[29] which would then undergo reaction as expected for such an *anti*-7-norbornenyl analogue.[30]



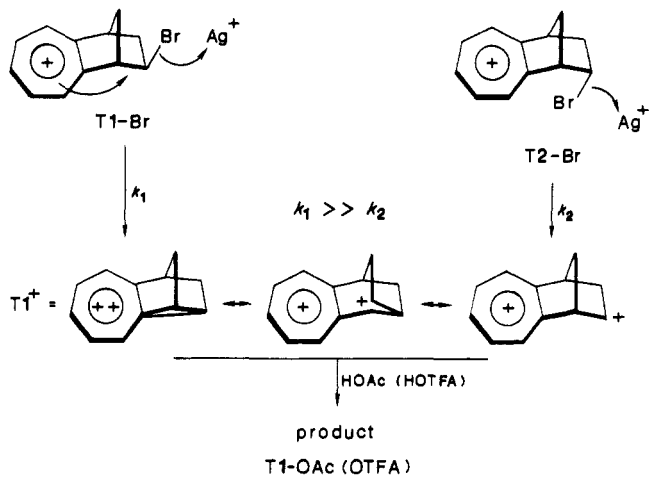
I

Moreover, intermediates like I should be detectable by changes in UV spectra as the strongly absorbing tropenium chromophore is diluted by added acetate. As mentioned, no change was observed. The rate dependence of the Ag^+-free solvolysis of salt T1-Br upon added sodium acetate does not implicate a neutral intermediate either. Without Ag^+, which precludes ion pairs by irreversible capture of bromide ion, reversible ion pair formation in acetic acid is a documented fact.[31] The added acetate salt simply destroys these ion pairs faster than does acetic acid itself (eq 9). The rate $v = 1/(1 + (k_{-1}/k_p))[OAc^-]k_1[$tropenium salt$]$, and it increases with added acetate but obviously not linearly. It should be noted that the slow step itself (k_1) undoubtedly varies with changes in the medium caused by the added salt.[32]

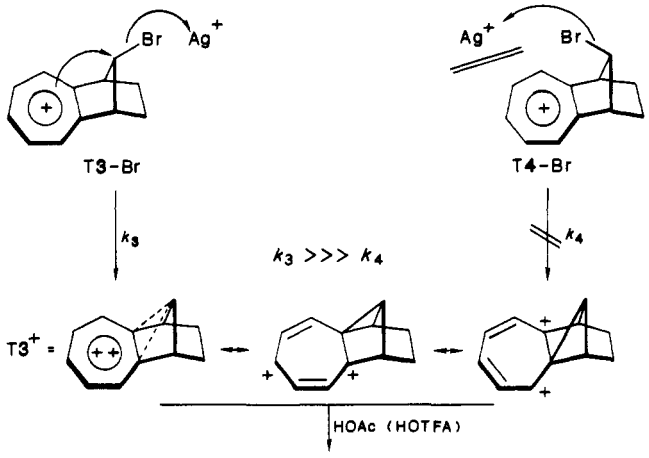


An aspect in the work that has not been addressed is the role of the hexafluoroantimonate counterion. No evidence was obtained that this ion was involved chemically,

Scheme I



Scheme II



(28) For discussion of electrophilic "catalysis" in substitution reactions of halides, cf.: Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell University: Ithaca, NY, 1953; pp 357–360. For evidence of "hard–soft" features to such reactions, cf.: Clark, H. R.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 4302.

(29) Other isomers would presumably form as well.

(30) This pathway was advocated in a forceful manner by a referee.[26] In summary, this alternative view was predicated upon the following series of contentions. First, from the work of Kessler and Feigel cited in ref 24 it was claimed that significant association of the tropenium salts with acetate ion would occur and make I a real possibility. Second, the background concentration of acetate ion in the solvents used was claimed to be 0.008 M. On this basis, the effect of added sodium acetate upon the rate of solvolysis of T1-Br would appear to be a linear one and indeed implicate intermediate I. Such a background concentration of acetate *could* also explain the absence of change in the ultraviolet spectrum of T2-Br in the presence of added acetate. Third, the apparent absence of acceleration by added acetate salt upon the silver ion assisted processes was ascribed to various complications: a changed background acetate concentration due to a different solvent composition; decreased silver ion concentration through association with acetate ion; the degree of ionization of salts in the medium used. Other items of argument concerned the dielectric constant and acidity constant of the solvent used, the disconcerting similarity of our results with those from solvolysis of neutral benzonorbornenyl substrates and the apparent inconsistency of our data with that expected for such an electron-poor substituent when compared with others, such as the nitro-substituted benzonorbornenyl cases. With respect to the many comparisons made by the referee to solvolytic data from other substrates, the authors consider such comparisons inappropriate in that no data exists for such substrates in silver ion promoted solvolysis (see ref 27). Furthermore, the authors contend that the Kessler–Feigel work is not germane (see ref 24). From various literature sources, a value of ca. 2×10^{-4} M is more probable for the acetate background concentration in the solvents used. Therefore, both a kinetic effect and a spectral effect in the UV should have attended addition of added acetate salt. The complications noted by the referee in the silver ion promoted work are real, and the authors do not claim otherwise. Nonetheless, as noted, the effect of added acetate salt was *nil*, making these complications curiously effective in masking the intermediacy of I. In summary, every search for I was futile and the authors do not believe it plays a significant role, if any, in the present work.

(31) The solvents used (Table II) would vary in this regard. Ion pairing should decrease with increased solvent polarity, i.e., solvent D = B > A > C.

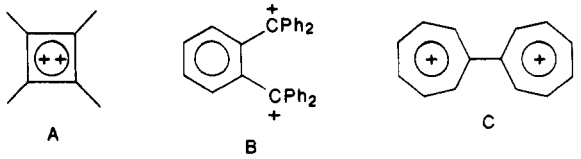
(32) Probably spuriously considering the nonaqueous medium, the increase in rate was nearly proportional to $\mu^{1/2}$ (μ = ionic strength), calculated for totally ionized added sodium acetate.

and it has been supposed that its presence was not a critical feature in either the kinetics or product formation.

The solvolyses of these tropenium salts clearly involved like-charge dispersal in the slow step. This is evidenced by the data for T1-Br in the increasingly polar media of solvents B, A, and C.[33] The rate of solvolysis of this salt *decreased* in the ratio >4000:2000:1 in these solvents, reflecting the established fact that more polar media retard the rate of reactions involving like-charge dispersal in the slow step. The less favorable activation entropy observed in solvent B compared to A is also in accord with a charge-dispersed transition state. Reactions of this sort typically exhibit less favorable activation entropies in less polar media.[35] Yet another indication of this aspect of these solvolyses is the reduced rate in trifluoroacetic acid, solvent C, one of the better "accelerating" solvents for charge-separation-type solvolyses.[36]

Schemes I and II show the course of these solvolyses according to the accumulated evidence.

With regard to these schemes, many dicarbocations are known,[37] among them those shown below.[38] So the di-



A B C

carbocations $T1^+$ and $T3,^+$ while unusual, are certainly not unimaginable. The extent of the tropenium bridging is, however, worth noting. The pure stereochemistry observed in product formation indicates that the electrostatically disfavored charge situation associated with the "bridged" character of these intermediates is important. From the nature of the "classical" contributors to $T3^+$, it is suggested that the double charge is more highly localized on the tropenium ring in this case, thereby accounting for the notably less favorable entropy found for this system. The assistance by silver ion pictured in the schemes would be diminished for T4-Br due to repulsion of the ion by the tropenium group. This is the presumed cause for the inertness of this salt. Even so it must be noted that B4-Br is the slowest of these bromides in "ordinary" solvolysis,[3] so it is the syn-7-position itself and its lack of potential assistance that are involved as well.

A detailed theoretical rationale for the participation by tropenium ion is beyond the intent of this work. Such rationales are numerous for phenyl participation, however,[39] and clearly the tropenium case would be modeled upon such treatments. A particularly intriguing one is based upon FMO theory.[40] Although developed for electrophilic aromatic substitution, the treatment is obviously applicable to aryl participation because the two processes are really the same. Briefly, this approach considers the sum of the HOMO π-electron energies (in terms of β) for the ground-state aromatic and the benzenonium ion, considered as a pentadienyl cation. Reactivity is then correlated with the difference in these sums. For substitution upon benzene the difference is 1.27β. If $T1^+$ and $T3^+$ are considered to be hexadienyl dications, this treatment gives a difference of 1.45β for the systems here. Although the treatment fails to account for charge differences between the aromatic models, nonetheless it does place participation by tropenium ion in a reasonable, albeit less favorable, position relative to phenyl itself. As such, the treatment lends its support to the results obtained in this study and justifies further attempts to refine it.

From simple Hückel theory, the atomic coefficients for the tropenium HOMO at C-5,6 in these norbornenotropeniums are probably close to those of tropenium ion itself (−0.48)[41] and thus close to those of the benzo HOMO at these sites in the benzonorbornenes (for benzene, −0.5).[41] From the present results, this local electron density seems available for participation by the troponium group, although the driving force is considerably reduced by the electron deficiency in the π-electron network. This last fact makes electrophilic assistance important if the participation is to be observed readily.

Experimental Section

General Comments. Melting points were taken on a calibrated Fisher-Johns block. The following instruments were used to determine spectra: Varian 360A (^{1}H NMR); FT-80 (^{13}C NMR); IBM FT 98 and Beckman Acculab 1 (IR); Hewlett-Packard 8451A (UV). All NMR spectra are given in δ values. The internal reference standard was Me_4Si ($\delta = 0$), and the solvent was either CD_3CN or $CDCl_3$. Integrations were within 10% of theory. Centers of defined multiplets or ranges of complex multiplets are given. All ^{13}C NMR spectra are proton-decoupled. UV spectra were taken in CH_3CN, and the values listed are for λ_{max} and (log ϵ). The IR spectra in cm^{-1} were taken on KBr disks (1%) for solids and neat for liquids. Rate constants were calculated by a computer using a least-squares program. Gas chromatography (GC) was performed on Gow-Mac Model 550 and Hewlett-Packard Model 5890A instruments. Microanalyses were performed by Micro-Tech Laboratories, Skokie, IL.

Bromobenzonorbornenes. These bromides were prepared as described.[19] For B3-Br the reported yield of 34% was bettered to 64%. Bromide B4-Br could not be obtained as described. Use of aqueous dioxane (1:3 v/v) for the reduction medium did, however, afford the compound. The physical properties observed agreed with those reported.[19] The ^{13}C NMR data are summarized here:[42] B1-Br, 149.6, 145.6, 128.4, 127.7, 123.6, 122.4, 55.2, 51.5, 48.4, 45.7, 42.7; B2-Br, 147.3, 143.1, 126.6, 125.3, 124.0, 120.1, 51.3, 48.7, 48.3, 43.8, 39.1; B3-Br, 144.5, 126.5, 120.7, 58.9, 49.4, 24.1; B4-Br, 144.7, 126.4, 122.1, 65.3, 51.1, 25.2.

(Acyloxy)benzonorbornenes. These esters were prepared from the known alcohols[43] by treatment with acetic or tri-

(33) This statement, reflects the *Y* values of the acids in the solvent: HOAc, −1.64; HOTFA, +1.84. A high polarity has been assumed for acetonitrile because, although its *Y* value is apparently unreported, its mixtures with water have *Y* values ranging from +0.73 (60:40, acetonitrile/water) to +3.18 (10:90).[34]

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(37) Cf.: le Noble, W. J. *Highlights of Organic Chemistry*; Dekker: New York, 1974; pp 806–811. It should be noted that some early claims for such species were incorrect.

(38) A: Olah, G. R.; Bollinger, J. M.; White, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 3667. B: Hart, H.; Sulzberg, T.; Rafos, R. R. *J. Am. Chem. Soc.* **1963**, *85*, 1800. C: Akhrem, I. S.; Fedin, E. I.; Kvasov, B. R.; Vol'pin, M. E. *Tetrahedron Lett.* **1967**, 5265.

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(41) Heilbronner, E.; Straub, P. *HMO (Tables)*: Springer Verlag: New York, 1966.

(42) For assignment of all spectra, contact the senior author or consult the dissertation of C.G. cited in ref 1.

(43) B1-OH, B2-OH, and B3-OH: Bartlett and Giddings, ref 4. B4-OH: Tanida et al., ref 9a.

fluoroacetic anhydride in pyridine. Where previously reported, the physical properties of these esters were consonant with the literature values. Certain new NMR and other appropriate data are summarized here.

B1-OAc:[3] ^{1}H NMR 7.03 (m, 4 H), 4.8–4.57 (m, 1 H), 3.43–3.17 (m, 2 H), 2.03 (s, 3 H), 2.17–1.67 (m, 4 H); ^{13}C NMR 170.1, 148.9, 126.1, 125.4, 122.1, 120.3, 75.4, 48.9, 46.2, 42.4, 36.9, 20.8.

B1-OTFA: ^{1}H NMR 7.2 (m, 4 H), 4.93 (t, 1 H), 3.6–3.3 (m, 2 H), 2.1–1.8 (m, 4 H); IR 1780 (C=O); UV 268 (2.83), 274 (2.79). Anal. Calcd for $C_{13}H_{11}O_2F_3$: C, 60.94; H, 4.32. Found: C, 60.70; H, 4.35.

B2-OAc: ^{1}H NMR 7.1 (m, 4 H), 5.3 (dt, 1 H), 3.73–3.50 (m, 1 H), 3.3–3.13 (m, 1 H), 2.3 (ddd, 1 H), 2.07–1.6 (m, 2 H), 1.7 (s, 3 H), 1.0 (dt, 1 H); ^{13}C NMR 169.8, 147.5, 141.9, 125.6, 125.0, 122.7, 119.8, 73.6, 47.5, 47.2, 42.8, 35.0, 20.0.

B2-OTFA: ^{1}H NMR 7.2 (m, 4 H), 5.57 (dt, 1 H), 3.9–3.67 (m, 1 H), 3.43–3.27 (m, 1 H), 2.43 (ddd, 1 H), 2.13–1.57 (m, 2 H), 1.2 (dt, 1 H); IR 1760 (C=O); UV 266 (2.82), 272 (2.76). Anal. Calcd for $C_{13}H_{11}O_2F_3$: C, 60.94; H, 4.32. Found: C, 60.74; H, 4.45.

B3-OAc:[44] ^{1}H NMR 7.1 (m, 4 H), 4.5 (m, 1 H), 3.3 (dd, 2 H), 2.27–1.9 (m, 2 H), 2.03 (s, 3 H), 1.33–1.0 (m, 2 H); ^{13}C NMR 170.1, 143.7, 126.3, 121.1, 82.6, 45.4, 23.9, 20.8.

B4-OAc:[9a] ^{1}H NMR 7.23 (sharp m, 4 H), 4.87 (t, 1 H), 3.4 (dd, 2 H), 2.30–1.80 (m, 2 H), 1.87 (s, 3 H), 1.40–0.80 (m, 2 H); ^{13}C NMR 171.2, 144.3, 126.2, 121.7, 88.9, 46.2, 23.9, 20.8.

Preparation of the Bromo- and (Acyloxy)norbornenotropenium Hexafluoroantimonates. The literature procedure[15] was followed closely. All operations were done behind a safety shield in a well-ventilated hood. All glass openings were fire-polished. Diazomethane (**CAUTION: carcinogen, explosion hazard**) was generated from *N*-nitroso-*N*-methylurea (NMU, **CAUTION: carcinogen, wear gloves**). Particular care was given to the KOH drying tube which tended to clog easily. Two explosions were caused from such blockage! The process involving the benzo compound (2.5–4 mmol), copper(I) chloride (30 mg), freshly made,[45] and diazomethane from NMU (2.5–4 g) was normally conducted in dry methylene chloride solvent at 25 °C for 1.5–2.5 h. Analysis by ^{1}H NMR of an aliquot indicated 25–50% conversions of the benzo reactant to tropilidene mixtures over these times. The heterogeneous material was filtered and trityl hexafluoroantimonate[15] in further methylene chloride was added. The trityl salt was used in ca. 35% excess relative to the tropilidenes present. The dark solution was allowed to stand at room temperature overnight. Ether/hexane (1:1 v/v, 75 mL) was then added, and the solution was refrigerated for 24 h to precipitate the tropenium salt completely. The dark salt was collected, dissolved in dry acetonitrile to remove some insoluble polymethylene and then freed of solvent by rotary evaporation. Repeated reprecipitation of the salt from solutions in dry methylene chloride with ether/hexane was continued until no further changes in physical properties were noted.

Some data for the bromo salts are given in Table I. Their spectral data and those of the esters are summarized here.[42]

T1-Br: ^{1}H NMR 9.03 (sharp m, 5 H), 4.27–3.97 (m, 3 H), 2.83–2.1 (m, appearance concentration dependent,[22] 4 H); ^{13}C NMR, 179.3, 173.9, 154.5, 154.2, 150.2, 148.5, 147.4, 59.6, 51.3, 48.3, 44.7, 37.4; IR, 3117, 3067, 3014, 2947, 1454, 1342, 1304, 1273, 1155, 1148, 988, 966, 922, 808, 762, 654; UV 232 (4.40), 282, (3.69), 302 (3.66).

T2-Br: ^{1}H NMR 8.9 (sharp m, 5 H), 4.87 (dt, 1 H), 4.3–3.93 (m, 2 H), 3.0 (ddd, 1 H), 2.3–2.1 (m, 2 H), 1.47 (dt, 1 H); ^{13}C NMR, 178.4, 174.1, 154.0, 152.4, 150.4, 149.3, 147.3, 57.0, 50.8, 49.1, 43.4, 36.3; IR 3111, 3069, 3018, 2946, 1556, 1475, 1454, 1294, 1285, 1190, 1128, 1113, 962, 930, 874, 816, 760, 719; UV 232 (4.21), 280 (3.47).

T3-Br: ^{1}H NMR 8.93 (sharp m, 5 H), 4.33–4.17 (m, 1 H), 4.17–3.97 (dd, 2 H), 2.84–2.47 (m, 2 H), 1.53–1.17 (m, 2 H); ^{13}C NMR 174.4, 153.7, 150.9, 147.9, 56.9, 55.8, 21.9; IR 3018, 2972, 2953, 1456, 1344, 1308, 1242, 1163, 1084, 945, 837, 824, 770; UV 234 (4.32), 290 (3.54).

T4-Br: ^{1}H NMR 9.0 (sharp m, 5 H), 4.47 (t, 1 H), 4.28 (dd, 2 H), 2.82–2.22 (m, 2 H), 1.62–1.18 (m, 2 H); ^{13}C NMR 175.3, 154.1, 150.1, 148.4, 63.4, 57.9, 22.7; IR 3077, 3022, 2956, 1560, 1468, 1310, 1292, 1242, 993, 964, 839, 814, 739; UV 234 (4.41), 288 (3.67).

T1-OAc:[46] ^{1}H NMR 8.87 (sharp m, 5 H), 4.90–4.67 (m, 1 H), 4.0 (br s, 2 H), 2.41 (br s, concentration dependent,[22] 2 H), 2.30 (br s, 2 H), 2.03 (s, 3 H); ^{13}C NMR 181.0, 174.6, 170.9, 154.3, 153.8, 150.0, 148.7, 147.1, 72.4, 56.3, 50.2, 48.2, 33.5, 20.8; IR, 2961, 1730, 1452, 1367, 1286, 1259, 1177, 1059, 1026, 968, 752, 660; UV 240 (4.29), 282 (3.47), 302 (3.51).

T1-OTFA: ^{1}H NMR 8.93 (sharp m, 5 H), 5.20–4.93 (m, 1 H), 4.27–3.93 (m, 2 H), 2.47–2.07 (m, 4 H); IR 3020, 1782, 1456, 1348, 1263, 1169, 1005, 752, 656; UV 238 (4.30), 282 (3.51), 298 (3.50).

T2-OAc: ^{1}H NMR 8.87 (sharp m, 5 H), 5.65 (dt, 1 H), 4.3–4.1 (m, 1 H), 4.1–3.87 (m, 1 H), 2.77 (ddd, 1 H), 2.40–2.0 (m, 2 H), 1.70 (s, 3 H), 1.20 (dt, 1 H); ^{13}C NMR 179.4, 174.6, 170.6, 153.9, 152.8, 149.9, 149.1, 146.9, 71.7, 54.7, 50.6, 48.7, 34.2, 20.2; IR, 2961, 1732, 1456, 1379, 1248, 1103, 1053, 966, 756; UV 232 (4.27), 280 (3.57), 300 (3.58).

T2-OTFA: ^{1}H NMR 9.0 (sharp m, 5 H), 5.98 (dt, 1 H), 4.43–4.23 (m, 1 H), 4.2–3.93 (m, 1 H), 3.17–2.03 (m, 3 H), 1.37 (dt, 1 H); IR 2957, 1784, 1558, 1456, 1391, 1344, 1298, 1227, 1167, 1101, 1007, 864, 775, 756, 663; UV, 238 (4.27), 280 (3.66).

T3-OAc: ^{1}H NMR 9.0 (sharp m, 5 H), 4.73 (m, 1 H), 4.0 (dd, 2 H), 3.07–2.33 (m, 2 H), 2.07 (s, 3 H), 1.27 (m, 2 H); ^{13}C NMR 173.9, 170.3, 153.5, 150.5, 148.4, 81.6, 52.4, 21.4, 20.4; IR 2953, 1742, 1466, 1454, 1366, 1281, 1111, 1069, 758, 663; UV 236 (4.30), 282 (3.64).

T4-OAc: ^{1}H NMR 8.97 (sharp m, 5 H), 5.03 (t, 1 H), 4.07 (dd, 2 H), 2.63–1.07 (m, 4 H), 1.70 (s, 3 H); ^{13}C NMR 175.2, 170.7, 153.6, 149.6, 148.1, 89.9, 53.4, 21.0, 20.1; IR 2957, 1744, 1454, 1381, 1296, 1261, 1159, 1105, 1054, 750, 663; UV 236 (4.34), 282 (3.66).

Solvolysis Studies. Solvents and Reagents. Acetic acid[47] and acetonitrile[48] were purified as described. Trifluoroacetic acid (>99%) and the various silver salts (>98%) were used as supplied (Aldrich). Aqueous potassium thiocyanate (9.43×10^{-3} M) was standardized with silver nitrate. The ferric ammonium sulfate indicator was made according to the literature method.[49] Solvents were made by mixing appropriate volumes of components and stored under nitrogen.

Procedure. A water bath or a "Vapostat" apparatus using an appropriately boiling liquid was used. Separate sealed ampules containing known equimolar concentrations (ca. 0.0125 M) of the bromo tropenium salt and silver salt (at times sodium salt) were heated for established times, opened, and titrated for silver ion with standardized potassium thiocyanate. Because the reaction contents were themselves colored, an aliquot (5–10 μL) of an opened ampule titrated nearly to the end point was added to the ferric ammonium sulfate indicator on a spotting plate, whence the red endpoint was easily seen. A plot of $1/(a-x) - 1/a$ vs. time gave excellent linearity past two half-lives. Duplicate runs were made in several cases. Agreement was within 5%. The Eyring parameters were calculated in the usual way. The kinetic data are presented in Table II.

Characterization of Products. The titrated ampule contents from the kinetic study of each salt were pooled and treated with water (20 mL) and hydrogen peroxide (30%, 10 mL) with cooling. After 2 h the material was extracted thoroughly with ether. The combined ether extracts were washed with aqueous sodium bicarbonate (5%), water, and brine and then dried over $MgSO_4$. Evaporation of the ether left a residual oil, which was characterized by ^{1}H NMR and GC analysis to establish detection limits. Only one bromobenzonorbornene (that corresponding to the starting salt) and one (acyloxy)benzonorbornene were observed. These results are given in Table III.

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(46) All the (acyloxy)norbornenotropenium salts were off-white to dark grey microcrystalline solids that decomposed on heating with no definite melting point. IR analysis indicated that each was slightly contaminated with the corresponding alcohol salt, probably formed during the preparation. Because of this, no microanalytical data was obtained. Their structures are based upon spectra and their oxidation to the characterized (acyloxy)benzonorbornenes.

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Effect of Added Sodium Acetate. Three samples of salt T1-Br (18 mg), each admixed with a different quantity of sodium acetate (0.31, 3.1, and 31 mg; 0.1, 1, and 10 equiv, respectively) were dissolved in 95:5 HOAc/MeCN (3 mL). The ampules were sealed and held at 76 °C for 27 days (648 h). Workup of the reactions (see above) showed only two products by GC, bromide B1-Br and acetate B1-OAc. The latter comprised 14%, 34%, and 87% of the product for the three respective acetate concentrations.

Four samples of salt T3-Br (18 mg) and silver acetate (6.5 mg), each admixed with a different quantity of sodium acetate (0.031, 3.1, and 31 mg; 0, 0.1, 1, and 10 equiv., respectively), were dissolved in 75:25 HOAc/MeCN (3 mL). The ampules were sealed and held at 76 °C for 5.5 h. Workup as before showed only bromide B3-Br and acetate B3-OAc. The latter comprised 13 ± 3% of the product in every case.

The UV spectra of salt T2-Br (5×10^{-5} M) was taken in 75:25 HOAc/MeCN: λ_{max} 252 nm (log ϵ 4.03). Addition of 1 or 10 equiv of sodium acetate showed λ_{max} 252 nm in each case, with log ϵ 4.03 and 4.01, respectively.

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Registry No. B1-Br, 23526-72-9; B1-OAc, 90364-56-0; B1-OTFA, 109010-22-2; T1-Br·SbF_6, 90270-04-5; T1-OAc·SbF_6, 90270-06-7; T1-OTFA·SbF_6, 108920-12-3; B2-Br, 23526-73-0; B2-OAc, 109009-40-7; T2-Br·SbF_6, 104714-31-0; T2-OAc·SbF_6, 109009-42-9; T2-OTFA·SbF_6, 109009-44-1; B2-OTFA, 108920-10-1; B3-Br, 7605-11-0; B3-OAc, 1207-28-9; T3-Br·SbF_6, 104648-80-8; T3-OAc·SbF_6, 108920-14-5; B4-Br, 23526-75-2; B4-OAc, 1207-27-8; T4-Br·SbF_6, 104714-33-2; T4-OAc·SbF_6, 109009-46-3; $Ph_3C^+ \cdot SbF_6^-$, 437-18-3.

Convergence with Mutual Kinetic Resolution. 1. Studies Defining Methodology for the Taxol C/D Ring Fragment and Synthesis of the A Ring Fragment

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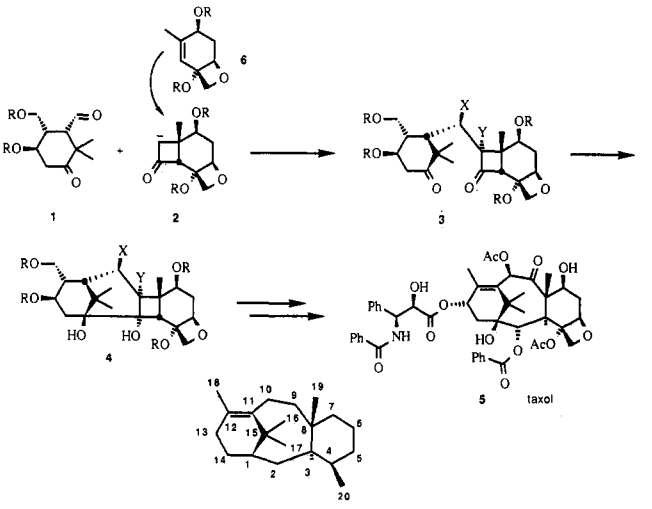
4-Exo-tet cyclization gives the alkoxyoxetane of the taxol C/D ring fragment if the tertiary alcohol is protected. Cycloaddition of dichloroketene and 1-[(*tert*-butyldimethylsilyl)oxy]-2-methylcyclohex-2-ene, a model for the allylic ether **6**, succeeds in the presence of DME. The synthesis of the A ring fragment relies on the Diels–Alder reaction of 1-ethoxy-3-[(trimethylsilyl)oxy]-2-methyl-1,3-butadiene with ethyl (*E*)-2-acetoxyacrylate and the axial conjugate addition of a vinyl Normant reagent.

Mutual kinetic resolution[1] in the aldol reaction of a cyclobutanone enolate[2] makes it possible in principle to couple A and C/D ring precursors **1** and **2** of the taxol skeleton for a convergent approach[3] to taxol[4,5] (Scheme I). This strategy complements the photochemical route outlined recently.[6] Our earliest experiments[2] were carried out with structurally simplified *racemic* A ring (aldehyde) and C/D ring (enolate) partners and gave within the limits of detection (^{1}H NMR at 300 MHz) only a single diastereomer in the aldol coupling reaction; efforts directed at generating fully functionalized A and C/D ring precursors are described herein. Model studies for generating the alkoxyoxetane unit[7] in the C/D ring precursor **2** and carrying out the [2 + 2] cycloaddition of dichloroketene[8] with an allyic ether precede the synthesis of complete A ring fragment.

Since **6** can aromatize with the formal loss of two water molecules, the alkoxyoxetane **8**, at a lower oxidation level, became the target of the model study. Using a ketone at C-4 (taxol numbering) as a precursor to the alkoxyoxetane unit was viewed a possible structural simplification.

As the first step in elaborating 3-methyl-2-cyclohexen-1-one, the methodology of Rubottom[9] afforded the ketol

Scheme I



9 (73% overall). Conversion of the ketol *tert*-butyldimethylsilyl ether **10** (obtained from **9** in quantitative yield

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