

The Effect of Steric Crowding on the Structures of Solvolytically Reactive Arylvinyl Systems

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The structures of 1-anisyl-2,2-diphenylvinyl bromide (**4a**), α -bromo- and α -tosyloxy-9-(*p*-methoxybenzylidene)anthrone, (**5a**) and (**5b**), and *p*-acetamido- α -bromostyrene, (**6**), were determined by X-ray crystallography. Most of the torsional angles of the aryl groups with the double bond are $44.3 \pm 3.3^\circ$, except that for the angle of the β -ring *cis* to Br in (**4a**) which is 68.6° and that for the α -ring in (**5a**) which is 75.6° . The central rings of the anthronylidene moiety in (**5a**) and (**5b**) are puckered. The C–Br bond lengths in (**4a**) (1.927 Å) and (**5a**) (1.923 Å) are longer than in (**6**) (1.907 Å) and than the mean value for other =C–Br bonds. The XC=C angle is wider for (**5a**) (X = Br) than for (**5b**) (X = O). The geometric parameters obtained from the crystal structure determination were discussed in relation to the contribution of steric crowding to the relative solvolysis rates and $k_{\text{Br}}/k_{\text{OTs}}$ ratios of the corresponding compounds.

The solvolysis reactions of α -arylvinyl bromides and tosylates (**1**) to form intermediate vinyl cations (**2**) [equation (1)] show several unique features, which depend primarily on the steric bulk of the β -substituents.¹

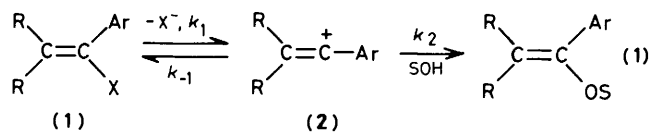
Firstly, when Ar = *p*-anisyl (An), the Winstein–Grunwald *m* values, which measure the response of the solvolysis rate to a change of the solvent,² decrease from a value of 0.77 for (**3**),³ to 0.34 and 0.42 for trianisylvinyl bromide⁴ and tosylate⁵ and to 0.28 for (**5b**).⁶ Whereas the first value is characteristic of an $S_{\text{N}}1$ mechanism,² the last value is one of the lowest known for this process.

Secondly, the solvolytic reactivity ratios of a vinyl tosylate compared with the corresponding vinyl bromide ($k_{\text{OTs}}/k_{\text{Br}}$) decrease from 335 for 2,4,6-Me₃C₆H₂C(X)=CH₂ in 80% EtOH,⁷ *via* 25.1 for compounds (**4**) in 70% Me₂CO,^{5a} to 3.8 and 0.16 for compounds (**5**) in 80% EtOH and tetrafluoroethylene (TFE).⁸ The last value is the lowest known for $S_{\text{N}}1$ reactions.

Thirdly, the selectivity of the vinyl cations (**2**) towards capture by the leaving group X⁻ and the solvent SOH, as measured by k_{-1}/k_2 increase from an apparent value of 0 (in 80% EtOH)^{3,9} for the ion derived from (**3**) *via* 78 (in TFE)¹⁰ for the trianisylvinyl cation to the high value of 381 (in TFE) for the ion derived from (**5**).¹¹

All these phenomena are believed to result from steric crowding in the vinylic system.¹ Thus, increased hindrance to solvent approach by the β -substituents reduces the *m* values. Increased steric interactions of the β -substituent *cis* to the leaving group increase the solvolysis rates of the bromides compared with the tosylates, thus reducing the $k_{\text{OTs}}/k_{\text{Br}}$ ratio. Similarly, steric inhibition by the β -substituents to approach of X⁻ and SOH to the vacant orbital of the ions increase the ions, selectivities. These arguments regarding steric effects in the ground states were evaluated by inspection of space-filling molecular models.¹ A much better and more quantitative understanding of these effects can be gained through the accurate knowledge of bond lengths and angles in some of these compounds.

We have therefore determined the structures of (**4a**), (**5a**), (**5b**), and (**6**) by X-ray diffraction. Unfortunately, the low melting (33 °C) and highly sublimable crystals of (**3**)³ strongly influenced its crystal structure refinement. The most relevant atoms suffer from very large thermal motions and the geometric parameters obtained are of no significance for the desired comparison of this least substituted bromide with the other



(1)

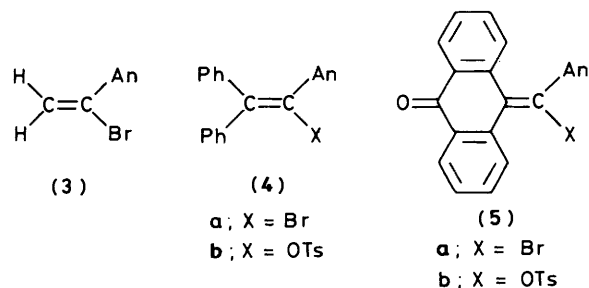
(2)

X = Br, OTs

a; R = H

b; R = Ph

c; R₂C = 9-anthronyl

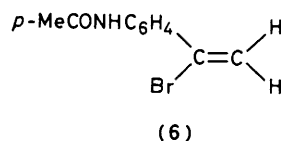


a; X = Br

b; X = OTs

a; X = Br

b; X = OTs



vinyl bromides studied. The structure of the closely related vinyl bromide (**6**) was therefore determined instead. It is assumed that the substitution of the *p*-methoxy substituent by a *p*-acetamido group will have a very small effect on the geometry around the vinylic carbons.

These particular compounds were chosen for the following reasons. (a) They form a short series of α -arylvinyl bromides where the steric bulk of the β -substituents apparently changes gradually from small in (**6**), to medium in (**4a**), and to large in (**5a**). This series allows the study of the effect of steric crowding on the geometries around the double bond. It was hoped that if steric interactions between X and the *cis*- β -aryl group are indeed important then this will be reflected in elongation of the C=C or C–Br bonds as the crowding increases, or in rotation of the aryl

Table 1. Crystallographic and experimental details for (4a), (5a and b), and (6)

Parameter Formula	(4a) C ₂₁ H ₁₇ BrO	(5a) C ₂₂ H ₁₅ BrO ₂	(5b) C ₂₉ H ₂₂ SO ₅	(6) C ₁₀ H ₁₀ BrNO
Mol. wt.	365.28	391.27	484.31	240.11
a (Å)	5.644(3)	12.550(7)	15.118(8)	11.151(6)
b (Å)	17.678(9)	6.824(3)	10.813(5)	9.237(5)
c (Å)	17.431(9)	10.715(5)	14.850(7)	10.142(5)
β (°)	97.80(2)	109.93(2)	96.14(2)	106.19(2)
U (Å ³)	1 728.08	862.69	2 413.62	1 003.22
Z	4	2	4	4
Space group	P2 ₁ /C	P2 ₁	P2 ₁ /C	P2 ₁ /C
D _x (g cm ⁻³)	1.404	1.506	1.333	1.589
Scan mode	ω/θ	ω/θ	ω/θ	ω/θ
Δω (°)	1.2	1.4	1.2	1.2
Scan time (s)	24.0	28.0	24.0	24.0
Background time (s) ^a	20.0	28.0	24.0	20.0
θ _{max.} (°)	25.0	25.0	24.0	25.0
Reflections measured	3 132	1 642	3 779	1 701
Significant	2 371	1 634 ^b	2 568	1 412
[F _o > 1.5σ(F _o)]				
Weighting coefficients (k; g) ^c	1.3402	0.4197	1.4507	1.2993
R _w	0.0037	0.0028	0.000	0.0036
R	0.073	0.035	0.060	0.068
	0.065	0.031	0.073	0.057

^a Total background counting time. ^b F_o > 0.0. ^c w = k/[σ²(F_o) + gF_o²].

groups out of the plane of the double bond. Furthermore, if the $k_{\text{OTs}}/k_{\text{Br}}$ ratios reflect a higher steric crowding in the bromide, this should be revealed in a comparison of the structures of (5a) and (5b). (b) Kirby and co-workers recently reported that an interesting relationship exists between the length of a bond that is cleaved hydrolytically and its hydrolysis rate, or the pK_a of the leaving group.^{12a-c} A similar relationship was implied recently between the C-OTs bond lengths and the solvolysis rates of several tosylates.¹³ We wondered whether a similar qualitative correlation (or even a quantitative one) would be observed in our systems for the C-Br bond. (c) The tosylate (5b) was prepared from (5a) and silver tosylate,⁸ and the remote possibility that the reaction proceeds with rearrangement and that the product is an isomer of (5b) could not be ruled out entirely. If this is the case the $k_{\text{OTs}}/k_{\text{Br}}$ ratio will be irrelevant to the question of steric crowding. We have therefore sought unequivocal proof that this tosylate is indeed (5b).

Experimental

Preparation of Compounds.—1-Anisyl-2,2-diphenylvinyl bromide (4a),⁴ 9-(α-bromoanisylidene)anthrone (5a),¹⁴ the corresponding tosylate (5b),^{6,8} and *p*-acetamido-α-bromostyrene (6)¹⁵ were prepared according to the literature. The formation of the tosylate (5b) from (5a) and silver tosylate is reported in reference 6, and discussed briefly in reference 8. Crystals that are suitable for X-ray analysis were obtained by crystallization of (4a) from 95% EtOH, of (5a, and b) from MeOH, of (4b) from cold methanol, and of (6) from nitromethane.

Crystal Structure Analysis.—Crystallographic data and details of intensity measurements and structure refinement are given in Table 1. The intensities were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). The crystal structures were solved by MULTAN 77¹⁶ and

refined by full-matrix least-squares procedures¹⁷ with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. Scattering factors for the non-hydrogen atoms were taken from Cromer and Mann¹⁸ and for H from Steward *et al.*¹⁹ Final positional parameters for (4a), (5a), (5b), and (6) are given in Tables 2–5, respectively. In the stereoviews (Figures 1–4), vibration ellipsoids are drawn at the 50% probability level.²⁰ The list of observed and calculated structure factors as well as thermal parameters are contained in Supplementary Publication No. SUP 56079 (52 pp).^{*} The atomic notation used in Tables 2–11 is given in Figure 5.

Results

Structural Commentary.—**Compound (4a).** The refinement was carried out in two separate blocks, the non-hydrogen atom parameters in one, the H parameters in the other. Bond lengths and angles are given in Tables 6 and 7; the C–H bond distances (not given in Table 6) lie in the range 0.84–1.05 Å. The e.s.d.s of the bond distances are typically 0.005–0.010 Å, and of the bond angles, 0.3–0.6°.

Compound (5a). The refinement was carried out in two blocks, the non-hydrogen atom parameters in one, the H parameters in the other. Bond lengths and angles are given in Tables 8 and 9, respectively; the C–H distances (not given in Table 8) lie in the range 0.93–1.19 Å. The e.s.d.s of the bond distances are typically 0.003–0.007 Å, and of the bond angles, 0.3–0.5°.

Compound (5b). The refinement was carried out in two blocks, non-hydrogen atom parameters in one, H parameters in the other. Bond lengths and angles are given in Tables 8 and 9, respectively; the C–H bond distances (not given in Table 8) lie in the range 0.90–1.05 Å. The e.s.d.s of the bond distances are typically 0.003–0.010 Å, and of bond angles, 0.2–0.6°.

Compound (6). Bond lengths and angles are given in Table 10. Although the position of the H atoms were located from the difference Fourier maps and were refined, the e.s.d.s are too large for any significant consideration. The e.s.d.s of the bond distances are typically 0.005–0.008 Å, and of bond angles, 0.5–

* For details of the Supplementary Publication Scheme, see Instructions for Authors *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

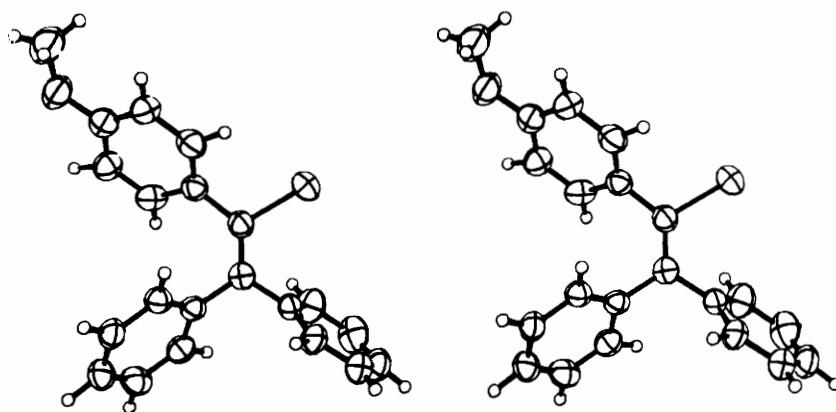


Figure 1. Stereodiagram of (4a)

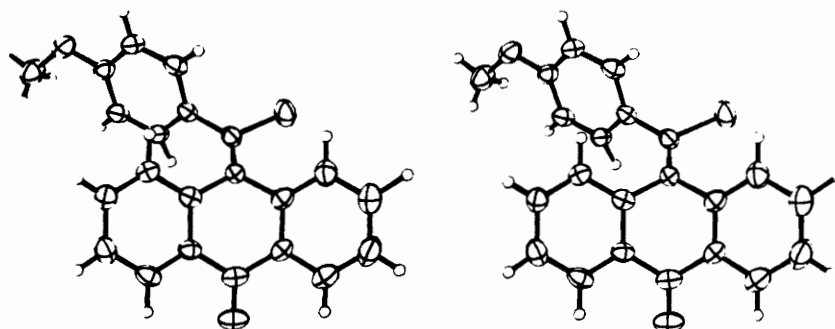


Figure 2. Stereodiagram of (5a)

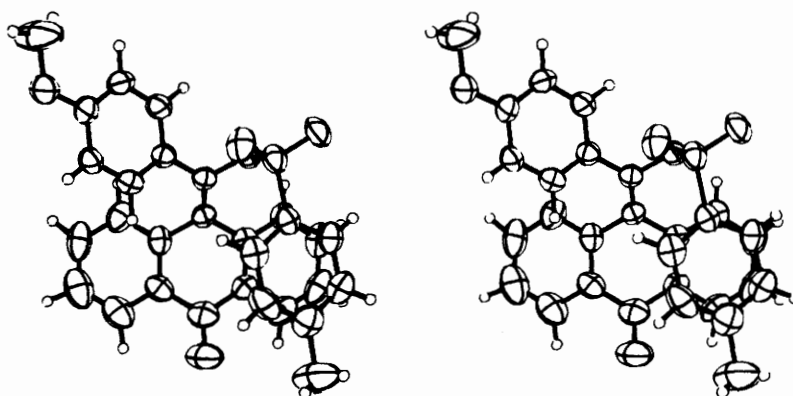


Figure 3. Stereodiagram of (5b)

0.6° . The molecules are packed in the unit cell with the hydrogen bonds between the amide groups related by a two-fold screw axis. The $N(1) \cdots O(1)$ distance is 2.984 \AA .

Discussion

One of our goals was immediately fulfilled. The X-ray diffraction data show unequivocally that the tosylate formed from (5a) and AgOTs is indeed (5b) and not the alternative isomeric structure (7), which was discarded previously for other reasons.⁸ The geometric parameters of interest for compounds (4), (5), and (6) are now discussed in relation to the general structure (8).

Structure.—(a) *Puckering of the double bond and the central ring of (5a and b).* The most relevant torsion angles of

compounds (4)—(6) are presented in Table 11. The puckering of the double bond is given by the *cis*-torsion angle, $C(3)-C(1)-C(2)-C(10)$. The double bond is slightly puckered in systems (4) and (5); *i.e.*, -8.1° for (4a), 4.8° for (5a), and 2.3° for (5b). The puckering values for (4a) and (5) are within the range of $2.3-11.4^\circ$ found for other triarylvinyl propellers²¹ and they reflect the mutual steric interactions of neighbouring bulky aryl groups on the double bond. The puckering of the double bond in (6) cannot be described by the *cis*-torsion angle because it involves the positions of the vinylic hydrogens that could not be refined to a significant level (see above).

The α -aryl rings in all the compounds and the β -phenyl groups of (4a) are planar. The central ring of the anthronylidene moiety in (5a) and (5b) has a boat geometry and it is strongly puckered. This conformation involves a bend of 139.6° and 148.6° in the skeleton of the central ring of (5a) and (5b), respectively. The

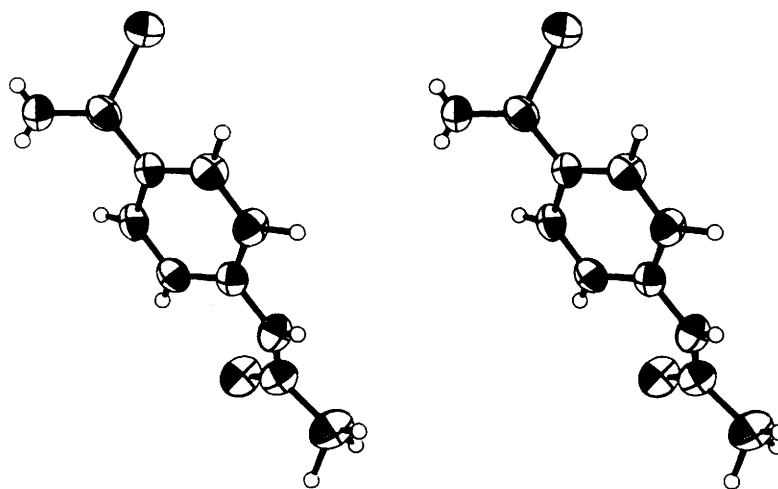


Figure 4. Stereodiagram of (6)

Table 2. Positional parameters of (4a), for non-hydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^3$), with estimated standard deviations in parentheses

	x	y	z		x	y	z
Br	5 245(1)	3 848(0)	223(0)	C(19)	8 458(12)	6 159(3)	1 674(4)
O(1)	5 609(8)	175(2)	1 102(2)	C(20)	9 880(11)	5 674(4)	1 332(4)
C(1)	6 417(9)	3 359(3)	1 188(3)	C(21)	9 513(11)	4 890(3)	1 356(4)
C(2)	7 271(8)	3 773(3)	1 789(3)	H(4)	270(9)	250(3)	53(3)
C(3)	6 128(8)	2 523(3)	1 138(3)	H(5)	221(12)	116(3)	61(4)
C(4)	4 033(10)	2 175(3)	809(3)	H(7)	900(9)	85(3)	163(3)
C(5)	3 765(10)	1 396(3)	785(3)	H(8)	938(7)	228(3)	163(3)
C(6)	5 668(10)	947(3)	1 101(3)	H(91)	374(11)	-64(4)	94(3)
C(7)	7 771(10)	1 275(3)	1 428(3)	H(92)	280(9)	-1(3)	29(3)
C(8)	8 034(9)	2 051(3)	1 448(3)	H(93)	201(12)	-6(3)	114(4)
C(9)	3 388(14)	-192(4)	824(4)	H(11)	476(7)	286(2)	263(2)
C(10)	7 832(8)	3 442(3)	2 582(3)	H(12)	567(9)	236(3)	386(3)
C(11)	6 217(8)	2 981(3)	2 896(3)	H(13)	923(9)	269(3)	463(3)
C(12)	6 730(10)	2 703(3)	3 645(3)	H(14)	1 190(11)	345(4)	409(4)
C(13)	8 867(10)	2 875(3)	4 090(3)	H(15)	1 094(10)	396(3)	279(3)
C(14)	10 485(9)	3 326(3)	3 787(3)	H(17)	507(9)	490(3)	241(3)
C(15)	9 969(9)	3 616(3)	3 045(3)	H(18)	552(12)	618(3)	229(4)
C(16)	7 704(8)	4 603(3)	1 737(3)	H(19)	886(11)	669(4)	169(4)
C(17)	6 326(10)	5 108(3)	2 093(3)	H(20)	1 121(12)	579(4)	108(4)
C(18)	6 682(12)	5 876(3)	2 049(3)	H(21)	1 047(10)	450(4)	112(4)

Table 3. Positional parameters of (5a), for non-hydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^3$), with estimated standard deviations in parentheses

	x	y	z		x	y	z
Br	5 084(0)	2 180	8 844(0)	C(18)	3 401(4)	-1 503(8)	4 231(4)
O(1)	1 409(3)	6 849(6)	11 012(3)	C(19)	4 286(4)	-2 747(11)	4 853(5)
O(2)	1 630(3)	1 345(6)	3 131(3)	C(20)	4 723(4)	-2 819(13)	6 247(4)
C(1)	3 455(3)	2 098(8)	8 174(3)	C(21)	4 291(4)	-1 572(7)	6 987(4)
C(2)	2 876(3)	1 011(6)	7 105(3)	C(22)	1 915(4)	861(7)	4 301(4)
C(3)	2 962(3)	3 410(6)	8 938(3)	H(4)	324(5)	156(7)	1 047(5)
C(4)	2 931(4)	2 844(6)	10 181(4)	H(5)	236(4)	366(7)	1 170(4)
C(5)	2 412(4)	4 042(7)	10 851(4)	H(7)	176(4)	768(8)	878(4)
C(6)	1 930(3)	5 806(7)	10 295(4)	H(8)	272(5)	574(9)	765(5)
C(7)	2 017(4)	6 417(6)	9 091(4)	H(91)	140(4)	944(7)	1 034(4)
C(8)	2 519(3)	5 223(7)	8 423(3)	H(92)	22(6)	833(12)	957(7)
C(9)	781(5)	8 520(8)	10 422(5)	H(93)	42(5)	896(9)	1 103(5)
C(10)	1 626(3)	1 143(6)	6 499(3)	H(11)	119(4)	106(8)	818(4)
C(11)	876(4)	1 232(6)	7 202(4)	H(12)	-77(4)	123(7)	705(4)
C(12)	-283(4)	1 264(7)	6 563(6)	H(13)	-152(4)	128(7)	470(4)
C(13)	-735(4)	1 305(7)	5 176(5)	H(14)	-33(5)	130(9)	350(5)
C(14)	3(4)	1 288(6)	4 457(4)	H(18)	309(5)	-146(9)	329(5)
C(15)	1 159(3)	1 161(6)	5 093(3)	H(19)	457(5)	-356(9)	434(5)
C(16)	3 416(3)	-294(6)	6 371(4)	H(20)	541(6)	-401(13)	682(6)
C(17)	2 946(3)	-278(6)	4 977(4)	H(21)	458(3)	-169(6)	797(3)

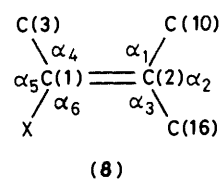
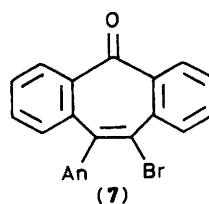
Table 4. Positional parameters of (5b), for non-hydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^3$), with estimated standard deviations in parentheses

	x	y	z		x	y	z
S	3 305(1)	3 848(1)	1 696(1)	C(24)	2 116(3)	2 011(4)	1 291(3)
O(1)	3 855(2)	9 811(3)	1 294(3)	C(25)	1 276(4)	1 550(5)	1 010(3)
O(2)	332(2)	3 762(4)	-1 708(3)	C(26)	572(4)	2 336(6)	796(4)
O(3)	3 709(2)	4 019(3)	736(2)	C(27)	715(9)	3 601(3)	903(3)
O(4)	3 239(2)	5 027(3)	2 107(2)	C(28)	1 538(4)	4 071(5)	1 198(3)
O(5)	3 865(2)	2 917(3)	2 125(2)	C(29)	-356(4)	1 853(7)	431(5)
C(1)	3 313(3)	4 900(4)	105(3)	H(4)	481(2)	594(3)	82(2)
C(2)	2 847(3)	4 475(4)	-649(3)	H(5)	510(2)	797(3)	133(2)
C(3)	3 474(3)	6 200(4)	403(3)	H(7)	246(2)	881(3)	65(2)
C(4)	4 308(3)	6 574(4)	776(3)	H(8)	215(2)	682(3)	7(2)
C(5)	4 464(3)	7 774(5)	1 081(3)	H(91)	504(4)	994(5)	187(4)
C(6)	3 773(3)	8 603(4)	1 013(3)	H(92)	507(5)	1 009(7)	111(5)
C(7)	2 930(3)	8 249(4)	649(3)	H(93)	451(4)	1 093(7)	198(4)
C(8)	2 790(3)	7 060(4)	358(3)	H(11)	350(2)	659(3)	-144(2)
C(9)	4 695(5)	10 214(7)	1 718(6)	H(12)	278(3)	798(4)	-236(3)
C(10)	2 428(3)	5 351(4)	-1 350(3)	H(13)	128(3)	773(5)	-292(3)
C(11)	2 860(3)	6 397(5)	-1 624(3)	H(14)	46(3)	567(4)	-253(3)
C(12)	2 408(5)	7 237(5)	-2 228(4)	H(21)	375(2)	233(3)	-32(2)
C(13)	1 539(6)	7 026(7)	-2 547(4)	H(20)	330(3)	35(4)	-68(3)
C(14)	1 113(4)	5 973(6)	-2 310(4)	H(19)	188(3)	-10(4)	-129(3)
C(15)	1 563(3)	5 118(5)	-1 724(3)	H(18)	87(2)	163(3)	-167(2)
C(16)	2 598(3)	3 160(4)	-820(3)	H(24)	256(2)	146(3)	142(2)
C(17)	1 750(3)	2 913(4)	-1 235(3)	H(292)	-35(5)	132(8)	78(5)
C(18)	1 473(4)	1 688(6)	-1 395(4)	H(291)	-78(5)	233(7)	69(5)
C(19)	2 044(5)	739(5)	-1 176(4)	H(28)	163(2)	499(3)	127(2)
C(20)	2 904(4)	974(5)	-780(3)	H(27)	24(2)	413(3)	84(2)
C(21)	3 168(3)	2 174(4)	-591(3)	H(25)	119(2)	65(3)	94(2)
C(22)	1 134(4)	3 921(5)	-1 550(3)	H(293)	-39(6)	145(9)	-13(8)
C(23)	2 244(3)	3 269(4)	1 377(3)				

Table 5. Positional parameters of (6), for non-hydrogen atoms ($\times 10^5$) and for hydrogen atoms ($\times 10^3$) with estimated standard deviations in parentheses

	x	y	z
Br	39 278(6)	10 513(9)	-29 294(7)
O(1)	105 698(40)	28 379(39)	19 959(42)
N(1)	96 090(48)	6 782(56)	16 696(53)
C(1)	55 539(51)	14 100(55)	-31 229(58)
C(2)	56 032(89)	18 199(69)	-43 539(68)
C(3)	65 997(49)	12 225(48)	-18 602(49)
C(4)	66 133(55)	1 114(56)	-9 290(56)
C(5)	76 269(51)	-626(56)	2 249(55)
C(6)	86 161(48)	8 987(48)	4 853(50)
C(7)	86 032(55)	20 050(57)	-4 298(56)
C(8)	76 075(50)	21 597(57)	-15 804(54)
C(9)	105 052(51)	15 709(55)	23 676(56)
C(10)	114 259(70)	9 665(73)	36 119(80)
H(N1)	960(4)	10(5)	194(4)
H(21)	615(5)	187(6)	-446(6)
H(22)	510(6)	184(6)	-494(7)
H(4)	589(6)	-34(7)	-105(6)
H(5)	769(5)	-85(6)	93(6)
H(7)	911(5)	261(6)	-31(5)
H(8)	749(7)	288(8)	-212(7)
H(101)	1 242(10)	126(9)	363(10)
H(102)	1 177(12)	153(14)	447(14)
H(103)	1 137(10)	-4(14)	379(10)

puckering is similar to that found in dianthronylidene^{22a} where the angle between the planes is 131.9°. The bent conformation is found in most dihydroanthracene derivatives^{22b} even when the crowding around the exocyclic carbon of the double bond is much lower than in our case, e.g., in 10-dicyanomethylene-anthrone.^{22c} However, in anthraquinone derivatives the central anthracene ring is found to be planar.^{22d}



(b) *Torsion angles of the aryl groups.* The torsion angle at the bond between the aryl groups and the vinylic double bond is a sensitive measure of the steric crowding in the system.²¹ This torsion angle is smallest in (6) where steric interactions between the aryl group and the *cis*-vinyl hydrogen are small. Steric interaction becomes appreciable when the double bond is substituted with two, three, and four aryl groups. The scattering of the torsion angles in polyarylviny propellers is discussed elsewhere²¹ but for most triaryl derivatives these angles are 39.7°–63.5°.²¹ Seven of the nine torsion angles of the three aryl groups in (4a), (5a and b) are 44.3 ± 3.3° (Table 11). However, the other two torsion angles are much larger: i.e., 68.6° for the β -ring *cis* to Br in (4a), and 75.6° for the α -ring in (5a).

Analysis of the torsion angles suggests that triarylviny propellers are less flexible than similar substituted diarylviny systems.²¹ The conformational parameters of triarylviny propellers are therefore expected to be fixed rigidly at their optimum values and to be similar in the solid state and in solution.

Differences in torsion angles should be interpreted with caution. Large differences between the torsional angles of the three rings were previously observed in several, but not in all,²¹ substituted triarylethylenes. For example, in one polymorphic form of *Z*-PhC(Et)=C(Ph)C₆H₄OCH₂CH₂NHMe₂-*p*-Br⁻ the aryl group *cis* to the Et substituent has a torsion angle of 59.7°, whereas the torsion angles of the other two rings are 48.3 ±

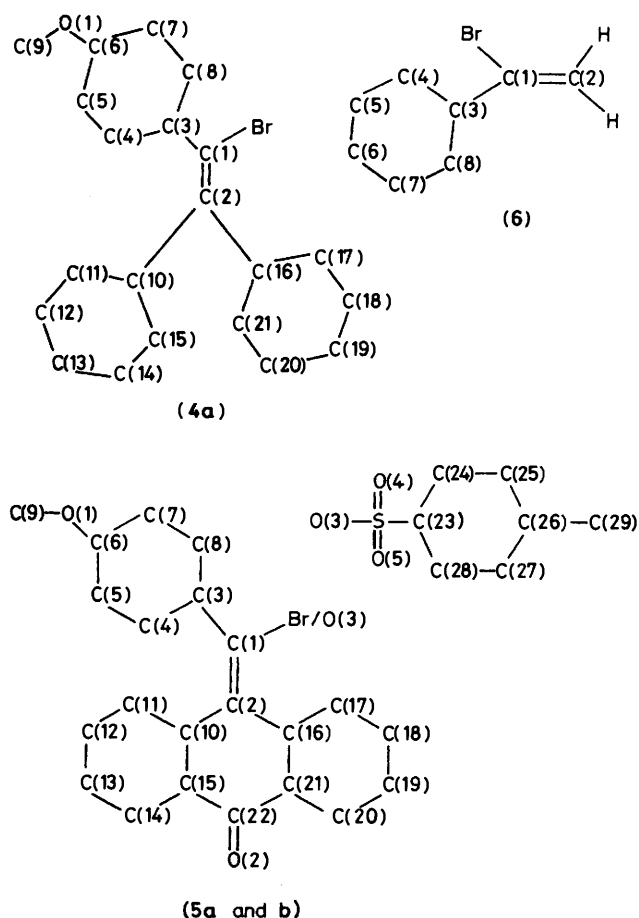


Figure 5. Atomic notation used in Tables 2—11

Table 6. Bond lengths for (4a)

Bond	Length (Å)	Bond	Length (Å)
Br—C(1)	1.927	C(11)—C(10)	1.389
C(6)—O(1)	1.366	C(15)—C(10)	1.392
C(9)—O(1)	1.436	C(12)—C(11)	1.389
C(2)—C(1)	1.314	C(13)—C(12)	1.377
C(3)—C(1)	1.490	C(14)—C(13)	1.371
C(10)—C(2)	1.495	C(15)—C(14)	1.385
C(16)—C(2)	1.493	C(17)—C(16)	1.384
C(4)—C(3)	1.386	C(21)—C(16)	1.387
C(8)—C(3)	1.409	C(18)—C(17)	1.375
C(5)—C(4)	1.385	C(19)—C(18)	1.364
C(6)—C(5)	1.388	C(20)—C(19)	1.366
C(7)—C(6)	1.374	C(21)—C(20)	1.402
C(8)—C(7)	1.380		

2.3°. In contrast, with *E*-PhC(Br)=C(Ph)C₆H₄Et-*p* the torsion angle of the α -aryl ring is the highest (62.1°),²⁴ and the same is also true for *E*-PhC(Et)=C(Ph)C₆H₄OCH₂CH₂NMe₂-*p* where this angle is 63.5°. Finally, the highest torsion angle (58.2°) in Ph₂C=C(Ph)C(=S)NHC₆H₁₁²⁶ is observed for the ring *trans* to the non-aryl substituent. The unavoidable conclusion from these data is that packing forces are partially responsible for the torsion angles of the rings. A recent study supports this conclusion. *trans*-Stilbene is planar in the solid phase but non-planar in the fluid and the gas phases.^{27a}

(c) *Bond lengths and bond angles.* The C—Br and the C=C bond lengths are of special interest. If steric interactions between the

Table 7. Bond angles for (4a)

Bond	Angle (°)	Bond	Angle (°)
C(9)—O(1)—C(6)	118.1	C(11)—C(10)—C(2)	121.7
C(2)—C(1)—Br	119.5	C(15)—C(10)—C(2)	120.6
C(3)—C(1)—Br	111.8	C(15)—C(10)—C(11)	117.6
C(3)—C(1)—C(2)	128.7	C(12)—C(11)—C(10)	120.9
C(10)—C(2)—C(1)	121.9	C(13)—C(12)—C(11)	120.4
C(16)—C(2)—C(1)	123.0	C(14)—C(13)—C(12)	119.3
C(16)—C(2)—C(10)	115.1	C(15)—C(14)—C(13)	120.5
C(4)—C(3)—C(1)	123.0	C(14)—C(15)—C(10)	121.1
C(8)—C(3)—C(1)	119.5	C(17)—C(16)—C(2)	120.0
C(8)—C(3)—C(4)	117.4	C(21)—C(16)—C(2)	121.7
C(5)—C(4)—C(3)	122.4	C(21)—C(16)—C(17)	118.2
C(6)—C(5)—C(4)	118.8	C(18)—C(17)—C(16)	121.1
C(5)—C(6)—O(1)	123.7	C(19)—C(18)—C(17)	120.8
C(7)—C(6)—O(1)	116.2	C(20)—C(19)—C(18)	119.4
C(7)—C(6)—C(5)	120.1	C(21)—C(20)—C(19)	120.7
C(8)—C(7)—C(6)	120.9	C(20)—C(21)—C(16)	119.8
C(7)—C(8)—C(3)	120.3		

bromide and the aryl group *cis* to it facilitate the cleavage of the C—Br bond, this may be reflected in a longer C—Br bond. Indeed, the C—Br bond lengths in both (4a) (1.927 Å) and in (5a) (1.923 Å) are 3—3.5 e.s.d.s. longer than in (6) (1.907 Å), and significantly longer than the mean value of 1.888 Å²⁸ of the C—Br bond lengths in other olefinic compounds; *i.e.*, 1.87(1) Å in *Z*-2,4-Me₂C₆H₃C(Ph)=CHBr,²⁹ 1.92(1) Å in Ph₂C=C(Br)Me,³⁰ and 1.911(9) Å in *E-p*-EtC₆H₄C(Ph)=C(Br)Ph.³¹ Note, however, that the C—Br bond lengths in (4a) and (5a) are essentially the same although we believe (see below) that steric interactions are more severe in the latter. Elongation of the C—Br bond is obviously not a very efficient mechanism for the relief of steric interactions. The energy loss that results from elongation and thus weakening of the C—Br bond outweighs the energy gain due to the relief of steric repulsions.

The C=C bond lengths are longer for the more crowded systems: *i.e.*, 1.350 Å in (5a) > 1.339 Å in (5b) > 1.320 Å in (6) and (4a) respectively. However, all these values are within the observed range of C=C bond lengths in other arylvinyl bromides.²¹

Most of the bond angles α_1 — α_6 around the central double bond in (4a), (5a and b), and (6) are remarkably similar. In *trans*-stilbene the C—C—C bond angle at the vinylic carbon is 125.8—127.0°. In *cis*-stilbene this angle is widened to 129.5° by steric repulsions between the *cis*-phenyl groups.^{32c} Values in all the compounds are similar and in the range 126.5—128.9°, close to that in *trans*- and *cis*-stilbene. The other angles are determined by steric repulsions between the various groups. α_2 Remains unchanged in (4a) and (5a and b) ($\alpha_2 = 114.0^\circ \pm 0.5^\circ$). In (6), $\alpha_6 = 116.0^\circ$ as a result of steric repulsions between the bromine and the geminal anisyl group. In (4a), the additional *cis* β -phenyl group causes a widening of α_6 to 119.5°. In the constrained and more sterically congested (5a), a further widening of α_6 to 122.0° occurs. In the tosylate (5b), however, α_6 is contracted to 117.9°, consistent with the smaller size of oxygen compared with bromine. In conclusion, both the slightly longer C=C bond length and the wider α_6 in (5a) compared with (4a), (5b) and (6) points to a higher steric congestion around the leaving group in (5a) compared with (4a), (5b) or (6).

Relation between the Solvolysis Rates and the Structures of Vinyl Derivatives.—Correlation between the chemical reactivity of a compound and its detailed structure in the solid state should be made with an important reservation concerning the validity of the assumption that the geometry of the molecule in the solid phase is similar to that in solution. This reservation is

Table 8. Bond lengths for (5a and b)

Bond	(5a) (Å)	(5b) (Å)	Bond	(5a) (Å)	(5b) (Å)
C(1)-Br/O(3)	1.923	1.424	C(15)-C(10)	1.418	1.387
C(2)-C(1)	1.350	1.339	C(12)-C(11)	1.380	1.402
C(3)-C(1)	1.483	1.486	C(13)-C(12)	1.399	1.368
C(10)-C(2)	1.482	1.497	C(14)-C(13)	1.392	1.372
C(16)-C(2)	1.495	1.486	C(15)-C(14)	1.379	1.397
C(4)-C(3)	1.401	1.383	C(22)-C(15)	1.487	1.482
C(8)-C(3)	1.391	1.387	C(17)-C(16)	1.407	1.387
C(5)-C(4)	1.388	1.386	C(21)-C(16)	1.381	1.391
C(6)-C(5)	1.387	1.372	C(18)-C(17)	1.405	1.401
C(7)-C(6)	1.395	1.385	C(22)-C(17)	1.472	1.477
O(1)-C(6)	1.368	1.373	C(19)-C(18)	1.378	1.358
C(9)-O(1)	1.407	1.423	C(20)-C(19)	1.396	1.391
C(8)-C(7)	1.371	1.365	C(21)-C(20)	1.392	1.378
C(11)-C(10)	1.393	1.389	O(2)-C(22)	1.226	1.223
O(3)-S		1.621	C(25)-C(24)		1.386
O(4)-S		1.421	C(26)-C(25)		1.372
O(5)-S		1.421	C(27)-C(26)		1.391
C(23)-S		1.741	C(29)-C(26)		1.541
C(24)-C(23)		1.378	C(28)-C(27)		1.371
C(28)-C(23)		1.379			

Table 9. Bond angles for (5a and b)

Bond	(5a) (Å)	(5b) (Å)	Bond	(5a) (Å)	(5b) (Å)
C(2)-C(1)-Br/O(3)	122.0	117.9	C(12)-C(11)-C(10)	121.6	120.2
C(3)-C(1)-Br/O(3)	111.5	113.1	C(13)-C(12)-C(11)	120.3	119.9
C(3)-C(1)-C(2)	126.5	128.9	C(14)-C(13)-C(12)	118.8	120.6
C(10)-C(2)-C(1)	121.5	120.7	C(15)-C(14)-C(13)	120.9	119.9
C(16)-C(2)-C(1)	124.3	124.9	C(14)-C(15)-C(10)	120.6	120.3
C(16)-C(2)-C(10)	114.1	114.0	C(22)-C(15)-C(10)	119.5	120.0
C(4)-C(3)-C(1)	120.7	120.6	C(22)-C(15)-C(14)	119.7	119.6
C(8)-C(3)-C(1)	120.2	121.5	C(17)-C(16)-C(2)	116.9	117.8
C(8)-C(3)-C(4)	119.0	117.8	C(21)-C(16)-C(2)	123.7	123.6
C(5)-C(4)-C(3)	120.0	121.4	C(21)-C(16)-C(17)	119.3	118.7
C(6)-C(5)-C(4)	120.1	119.1	C(18)-C(17)-C(16)	119.7	120.2
C(5)-C(6)-O(1)	115.6	123.8	C(22)-C(17)-C(16)	120.4	121.3
C(7)-C(6)-O(1)	124.6	115.6	C(22)-C(17)-C(18)	119.6	118.5
C(7)-C(6)-C(5)	119.8	120.7	C(19)-C(18)-C(17)	120.1	120.2
C(9)-O(1)-C(6)	118.1	118.2	C(20)-C(19)-C(18)	120.2	120.3
C(8)-C(7)-C(6)	120.0	119.3	C(21)-C(20)-C(19)	119.7	119.7
C(7)-C(8)-C(3)	121.0	121.8	C(20)-C(21)-C(16)	120.9	120.9
C(11)-C(10)-C(2)	125.1	122.8	C(15)-C(22)-O(2)	121.7	122.2
C(15)-C(10)-C(2)	117.3	118.3	C(17)-C(22)-O(2)	123.1	122.4
C(15)-C(10)-C(11)	117.6	118.9	C(17)-C(22)-C(15)	114.6	115.3
C(1)-O(3)-S		118.9	C(28)-C(23)-C(24)		120.3
O(4)-S-O(3)		109.0	C(25)-C(24)-C(23)		119.9
O(5)-S-O(3)		102.3	C(26)-C(25)-C(24)		120.6
O(5)-S-O(4)		120.6	C(27)-C(26)-C(25)		118.4
C(23)-S-O(3)		103.0	C(29)-C(26)-C(25)		121.7
C(23)-S-O(4)		109.5	C(29)-C(26)-C(27)		119.9
C(23)-S-O(5)		110.7	C(28)-C(27)-C(26)		121.7
C(24)-C(23)-S		119.8	C(27)-C(28)-C(23)		119.1
C(28)-C(23)-S		119.9			

especially relevant in relation to conformational parameters, *e.g.*, torsion angles that may be changed by crystal packing forces.³³ We have no assurance that this assumption holds in our systems. However, there is evidence that at least in one related system, *i.e.*, trimesitylethenol [$\text{Mes}_2\text{C}=\text{C}(\text{OH})\text{Mes}$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$] the same propeller conformation exists both in the solid state²¹ and in solution.³⁴ In the following discussion we will examine the relation between the geometry of the molecules of interest and their reactivities, assuming that the conformations are the same in solution and in the solid phase.

Other conformational aspects of these molecules are discussed in detail in another paper, which analyses all the available data on the conformations of vinyl propellers.²¹

The major question that we seek to answer is whether the solvolysis rates can be related to a specific structural parameter of the vinyl derivatives. The most simplistic view, namely, that as the steric congestion increases the C-Br bond is elongated and thus weakened, and that this increases solvolysis rates is not verified by the crystallographic data. The C-Br bond lengths in (4a) and in (5a) are almost identical (Table 2) although the latter

Table 10. Bond lengths and angles for (6)

Br-C(1)	1.906	C(3)-C(8)	1.384
O(1)-C(9)	1.238	C(4)-C(5)	1.391
N(1)-C(6)	1.403	C(5)-C(6)	1.383
N(1)-C(9)	1.336	C(6)-C(7)	1.378
C(1)-C(2)	1.320	C(7)-C(8)	1.376
C(1)-C(3)	1.482	C(9)-C(10)	1.495
C(3)-C(4)	1.392		
C(6)-N(1)-C(9)	131.2	N(1)-C(6)-C(5)	117.9
Br-C(1)-C(2)	116.0	N(1)-C(6)-C(7)	122.8
Br-C(1)-C(3)	115.6	C(5)-C(6)-C(7)	119.3
C(2)-C(1)-C(3)	128.3	C(6)-C(7)-C(8)	120.2
C(1)-C(3)-C(4)	122.0	C(3)-C(8)-C(7)	121.7
C(1)-C(3)-C(8)	120.2	O(1)-C(9)-N(1)	121.4
C(4)-C(3)-C(8)	117.9	O(1)-C(9)-C(10)	121.7
C(3)-C(4)-C(5)	120.6	N(1)-C(9)-C(10)	116.9
C(4)-C(5)-C(6)	120.3		

solvolyses faster (see below). A simple correlation between bond lengths and reactivity, as found by Kirby and co-workers^{12a-c} or by Tidwell and co-workers^{12d} is not observed although our data are too limited for a reliable conclusion. A relationship between the solvolysis rates and other structural parameters should therefore be examined. The most relevant appears to be the bond angles around the C=C bond, and the torsion angles of the aryl groups.

The solvolysis rate is determined by the energy difference between the ground state (*e.g.*, the vinyl bromide) and the intermediate vinyl cation (2). In the ion (2) the α -ring is perpendicular to the double bond (*i.e.*, the torsion angle is 90°) in order to maximize the overlap between the empty cationic 2p orbital and the aromatic π -cloud.³⁵ This perpendicular conformation can be achieved in all compounds. Thus it is reasonable that the steric repulsions between the α -ring and the β -substituents are similar in all the cations (2). As the solvolysis of triarylvinyl systems is endothermic, the transition state should resemble the cations,³⁶ and it is therefore reasonable to assume that the steric repulsions are largely relieved also in the transition states.

The different solvolysis rates of the compounds of interest are therefore related primarily to their ground-state energies. Higher steric congestion is reflected in a higher ground-state energy and thus in a lower activation barrier (E_a) and a faster solvolysis rate.

The ground-state energies of the vinyl derivatives are determined primarily by two factors: (a) conjugation between the double bond and the aromatic rings [*i.e.*, $\pi(\text{Ar})-\pi(\text{C}=\text{C})$ conjugation] and (b) steric strain due mainly to steric interactions between the olefinic substituents. Styrene is planar and the barrier to rotation around the phenyl-olefin bond is 3 kcal mol⁻¹.^{27b} This barrier is probably even lower in *trans*-stilbene, which is found to be non-planar in both the vapour and the fluid phases with an angle of *ca.* 30° between the planes of each phenyl and the central ethylene groups.^{27a} Force-field calculations predict a barrier of only 0.5 kcal mol⁻¹.³⁷ By analogy, the energy barriers that are due to $\pi(\text{Ar})-\pi(\text{C}=\text{C})$ conjugation are expected to be close to zero in triarylethylenes.

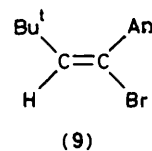
We therefore conclude that conjugation cannot be of major importance in determining the ground-state energies of the triarylvinyl bromides. Steric interactions between the olefinic substituents that are relieved in the transition state are of much greater importance. Structural manifestations of these steric interactions were discussed in detail above. Distortions of the bond angles around the C=C aryl bond, and in (5a and b) the puckering of the central ring, are particularly indicative of such

Table 11. Relevant torsion angles

Bond	(4a)	(5a)	(5b)
C(3)-C(1)-C(2)-C(10)	-8.1	4.8	2.3
C(3)-C(1)-C(2)-C(16)	173.2	-179.9	-169.4
O(3)/Br-C(1)-C(2)-C(16)	-8.9	2.9	8.6
O(3)/Br-C(1)-C(2)-C(10)	169.8	-172.5	-178.8
C(4)/C(8)-C(3)-C(1)-C(2) ^{a,b}	47.6	75.6	44.4
C(21)/C(17)-C(16)-C(2)-C(1) ^a	68.6	44.1	41.0
C(15)/C(11)-C(10)-C(2)-C(1) ^a	46.9	42.1	43.4

^a C(4), C(21), C(15) in (5a) and in (5b). C(8), C(17), C(11) in (4a). The torsion angles are given in absolute values. ^b The corresponding torsion angle in (6) is 37.1°.

steric strain. The structural data indicate that steric congestion decreases along the series (5a) > (4a) > (6). Hence, when other factors are identical, the solvolysis rates are expected to follow the same order. This is consistent with the two-fold higher acetolysis rate of (5a) compared with (4a), or with similar data in TFE,⁹ when the rate-reducing effect of the carbonyl group of (5a) is taken into account. Quantitative estimation of this retardation effect is difficult but we believe that it is larger than one order of magnitude. This estimation is based on the effect of β -aryl substituents on the solvolysis of triarylvinyl systems.^{1a,38} Compound (4a) also solvolyses 4.1 and 1.7 times faster than (3) in acetic acid and in 80% EtOH, respectively, in agreement with our hypothesis. However, in this case the analysis also is complicated by the estimation of the inductive effect of the β -aryl groups and by the different degrees of solvation of the resulting



ions. Similarly, owing to relief of ground-state steric strain the *E*-isomer of β -*t*-butyl- α -bromo-*p*-methoxystyrene, (9), solvolyses 1362 times faster in 80% EtOH than (3).³⁹ A better test of our suggestion is provided by a comparison of a vinyl bromide and vinyl tosylate in the same system: *i.e.* (5a and b).

The structural data indicate strongly that the bromide is considerably more strained than the tosylate. Thus, the torsion angle of the α -ring, α_6 , and the puckering of the central ring are substantially larger in (5a) than in (5b). The widening of α_6 by 4° in going from (5b) to (5a) signifies considerable increase in steric strain. While other effects contribute, it is clear that relief of steric strain is primarily responsible for the exceptionally low $k_{\text{OTs}}/k_{\text{Br}}$ ratio for the pair (5a and b).

Relevance to the Stability of (2).—The high selectivity of ion (2c) derived from (5a and b) was attributed to hindrance of nucleophilic approach to the vacant 2p(C⁺) orbital on C(1) (that lies in a plane perpendicular to the plane of the π -bond) by the *peri*-hydrogens of the anthronylidene moiety^{1,11} (see Figure 2). Although (2c) could not be isolated, a rough idea about the steric hindrance to nucleophilic approach to C(1) could be obtained from the distances of the *peri*-hydrogens from C(1) in the neutral precursors. The H(11)-C(1) and H(21)-C(1) distances are 2.93 and 2.99 Å in (5a) and 2.95 Å in (5b). The distances between C(1) and the *ortho*-hydrogens of the β -rings are much longer in (4a) (*i.e.*, 2.94–3.68 Å). Furthermore, ion (2c) is linear at C(1) (*i.e.*, $\alpha_4 = 180^\circ$) and in the absence of steric congestion around C(1), the anthronylidene

moiety is expected to adopt the more stable planar conformation as is commonly found in various anthrones.^{22d} In a planar conformation the *peri*-hydrogens are in the plane of the double bond and are therefore even closer (ca. 2.5 Å)^{22e} to C(1) than in (5a and b). These distances are shorter than the sum of the van der Waals radii of carbon and hydrogen (i.e., 2.9 Å) and thus confirm our assumption that the *peri*-hydrogens block very effectively the approach of nucleophiles to the 2p(C⁺) orbital (Figure 2). This steric hindrance to the approach of the nucleophile is much higher in (2c) than in (2b) where the β-rings can rotate freely out of the plane of the 2p(C⁺) orbital (Figure 2). As suggested earlier¹ an efficient bond formation between the nucleophile and C(1)⁺ should be easier for a soft (i.e., more polarizable) nucleophile such as Br⁻ than for the harder AcO⁻ ion, thus increasing the selectivity (i.e., the k_{Br}/k_{OAc} ratios) for (2c) relative to that of (2b). In (2b) selectivity is still observed but in the unhindered (2a) the apparent selectivity is zero.

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