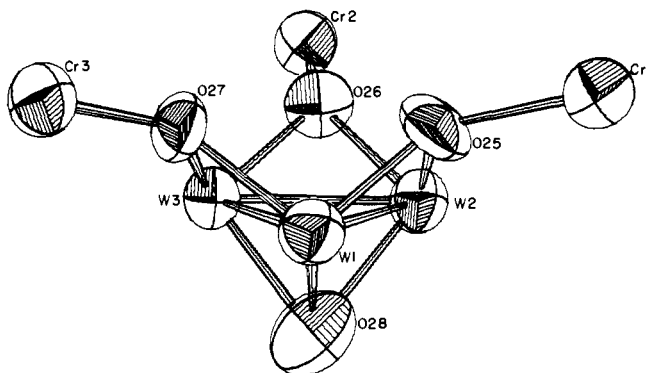


**Figure 1.** Structure and labeling scheme for the molecular unit  $W_3(OCH_2C(CH_3)_3)O_3Cr_3(O_2CC(CH_3)_3)_{12}$ , with all C(methyl) atoms of the carboxylate ligands omitted for clarity. Thermal ellipsoids enclose 50% of the electron density.



**Figure 2.** A view of the  $W_3$  cluster showing the triply bridging alkoxo (O28) and doubly bridging oxo O atoms, and the nonplanarity of the three oxo O atoms with the metals to which they are bonded.

within either the W or Cr set; the average bond distances are  $d(W-O) = 2.07$  (1) and  $d(Cr-O) = 1.97$  (2) Å. The small range of the Cr-O distances, e.g., 1.92–2.00 Å about Cr1, clearly indicates Cr(III), rather than Cr(II) which would be expected to show a much larger range because of Jahn-Teller distortion.<sup>10</sup> Another perspective of the structure is gained by viewing the cluster of W atoms and their bonded O atoms as a  $W_3O_{13}$  unit. The bonded O atoms form two closest packed layers, six atoms in one and seven in the other, between which the W atoms occupy adjacent octahedral sites. This structure then is analogous to the triangular clusters found in  $Zn_2Mo_3O_8$ <sup>11</sup> and  $Nb_3Cl_8$ ,<sup>12</sup> but represents the first molecular example of this type.

Assessment of oxidation state as 3+ for chromium is confirmed by the magnetic susceptibility. Over the range 77–300 K the temperature independent molecular moment of  $6.44 \mu_B$  indicates the paramagnetism arises entirely from Cr(III), i.e.,  $6.44 (3^{-1/2}) = 3.72 \mu_B$  per Cr atom, and that all electrons in the tungsten cluster are paired. Thus, by deduction the average oxidation state of W is 3.33+, and a total of four electron pairs are involved in the W-W interactions of the cluster. According to Cotton's MO results for clusters of this type<sup>13</sup> six electrons clearly occupy the bonding orbitals  $a_1^{(1)}$  and  $e^{(1)}$ . The next two electrons must reside in an  $a_1^{(2)}$  orbital, but the bonding character is uncertain. A comparison of average metal-metal bond distances, 2.610 (1) Å in this compound vs. 2.53 (1) Å in  $Zn_2Mo_3O_8$ <sup>11</sup> and 2.52 Å in  $W_3O_4F_9^{5-}$ ,<sup>14</sup> each with six

electrons, strongly suggests the last two electrons have anti-bonding character.

In previous studies of the reaction between  $W(CO)_6$  and acetic acid amorphous trimeric products were obtained and variously formulated as  $W_3O(O_2CCH_3)_9^2$  or  $W_3O(O_2CCH_3)_8(OH) \cdot H_2O$ ,<sup>1</sup> each with W in the average oxidation state 3.67+. If these products are diamagnetic as reported, then their identification as derivatives of W (3.67+) cannot be correct. Yet it is clear that oxygen is indeed abstracted from the carboxylic acid in these reactions, for not only the abstracted O atoms but also an alkoxy radical formed thereby is trapped and incorporated in the molecule reported here. This is an important feature because the enhanced ability of W to abstract O atoms may prevent formation of the quadruply bonded  $W_2(O_2CR)_4$ , in marked contrast to the ready formation of  $Mo_2(O_2CR)_4$  in the related reactions of  $Mo(CO)_6$ .

**Acknowledgments.** We express our appreciation to Professor R. A. Jacobson for his valuable advice and assistance during the x-ray structure determination, and to Mr. James Benson for his aid during x-ray data collection.

## References and Notes

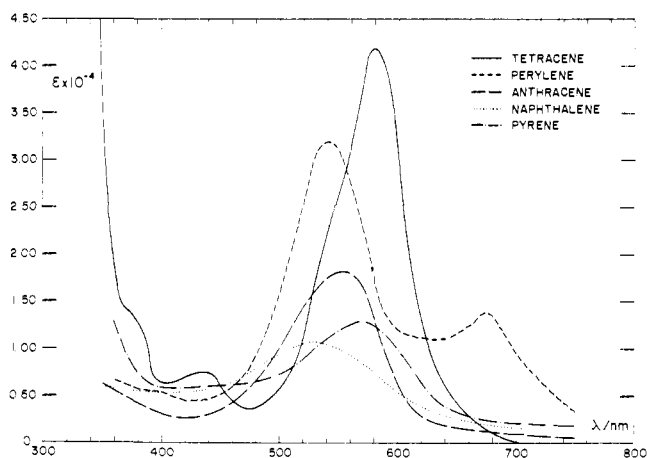
- (1) T. A. Stephenson and D. Whittaker, *Inorg. Nucl. Chem. Lett.*, **5**, 569 (1969).
- (2) F. A. Cotton and M. Jeremic, *Synth. Inorg. Metal-Org. Chem.*, **1**, 265 (1971).
- (3) G. Holste, *Z. Anorg. Allg. Chem.*, **398**, 249 (1973).
- (4) T. A. Stephenson, E. Bannister and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964); D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965); A. B. Brignole and F. A. Cotton, *Inorg. Synth.*, **13**, 87 (1972); S. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969).
- (5) V. Katovic, J. L. Templeton, R. J. Hoxmeier, and R. E. McCarley, *J. Am. Chem. Soc.*, **97**, 5300 (1975).
- (6) C. D. Garner and R. G. Senior, *J. Chem. Soc., Chem. Commun.*, 580 (1974).
- (7) The crystal selected is monoclinic:  $a = 23.479$  (10),  $b = 18.395$  (9),  $c = 23.535$  (9) Å;  $\beta = 99.59$  (3)°; space group  $P2_1/n$ ;  $Z = 4$ . Of the total 13 682 independent reflections monitored for intensity measurements, 7555 with  $I \geq 3\sigma(I)$  were used in the structure solution and refinement. The positions of the six metal atoms in the molecular unit were located from analysis of a sharpened three-dimensional Patterson function. All remaining nonhydrogen atoms were located by successive structure factor and electron density map calculations. In the final refinement cycles all atoms were refined with anisotropic temperature factors except the methyl carbon and atoms of the dichlorobenzene which were restricted to isotropic. Refinement converged to 0.090 and 0.105 for  $R$  and  $R_w$ , respectively.
- (8) Full details of the x-ray structure determination will be included in a subsequent publication.
- (9) S. C. Chang and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, **26**, 673 (1970).
- (10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N.Y., 1962, p 240.
- (11) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).
- (12) H. Schafer and H-G. Schnering, *Angew. Chem.*, **76**, 833 (1964).
- (13) F. A. Cotton, *Inorg. Chem.*, **3**, 1217 (1964).
- (14) K. Mennemann and R. Mattes, *Angew. Chem., Int. Ed. Engl.*, **15**, 118 (1976).
- (15) On leave from the University of Zagreb, Zagreb, Croatia, Yugoslavia.

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## Disproportionation of Lithium Salts of Radical Anions of Planar Aromatic Hydrocarbons in Diethyl Ether. Its Large Magnitude and Correlation with the Cation-Anion Coulomb Energy

Sir:

Radical anions may disproportionate into dianions in a reaction described by the equation  $2A^{\cdot-} \rightleftharpoons A + A^{2-}$ . In this process the two electrons moving in two separated orbitals, each associated with a molecular entity independent of the



**Figure 1.** Absorption spectra of lithium salts of the dianions in diethyl ether at ambient temperature. The extinctions of naphthalene<sup>2-</sup>·2Li<sup>+</sup> are magnified by 1.8.

other, are forced into a common orbital. The resulting electron–electron repulsion greatly increases the energy of the system and therefore the disproportionation has been expected to be a highly endothermic and greatly unfavorable reaction. Are there any factors favoring this process?

Disproportionation of some radical anions induces changes in the molecular framework of the reacting species, the radical ions of tetraphenylethylene or cyclooctatetraene providing the most striking examples of such a behavior. It was shown<sup>1</sup> that the changes in the geometry of the reagents taking place in these disproportionations are favorable for the forward reaction, and therefore the disproportionation constants were found to be large for these systems. However, the geometrical changes, if any, are insignificant in the disproportionation of planar radical anions of aromatic hydrocarbons, and hence it was generally believed that such reactions would be always unfavorable and their equilibrium constants should be substantially smaller than unity.

There were some indications that the problem may be more complex than anticipated. Dieleman<sup>2</sup> found the disproportionation constant of sodium salt of *p,p'*-quaterphenylide to be 6.9 in 2-methyltetrahydrofuran, and Shatenstein<sup>3</sup> observed spontaneous disproportionation of lithium naphthalenide in diethoxyethane. Recently we reported the disproportionation constant of lithium tetracenide to be about 16 in diethyl ether<sup>4</sup> while its value in tetrahydrofuran is  $\sim 10^{-9}$ . Still larger values were found<sup>5</sup> for the equilibrium constant of sodium tetracenide disproportionation in benzene containing small amounts of tetrahydrofuran. These results raised the question of what are the factors that shift so enormously the equilibrium of these disproportionations.

Hush<sup>6</sup> was probably the first to discuss the energetics of the disproportionation of aromatic radical ions. In his treatment he looked upon these species as free  $A^{\cdot-}$  ions yielding on their disproportionation free  $A^{2-}$  dianions. Born's approach<sup>7</sup> predicts the solvation energy of dianions to be twice as large as that of two radical anions, and hence Hush concluded that the disproportionation should be more extensive in solvents of high dielectric constants than in those of low polarity. The experimental evidence contradicts this prediction since, as mentioned before, the disproportionation constant of lithium tetracenide is by ten orders of magnitude greater in the less polar diethyl ether than in the more polar tetrahydrofuran.

Many investigators overlooked an essential point. In ethereal solvents radical anions are mainly present in the form of ion pairs and not as free ions. Hence, the disproportionation observed in such media is represented by the equation,  $2A^{\cdot-}, Cat^+ \rightleftharpoons A + A^{2-}, 2Cat^+$ . The Coulombic interaction between the anions and cations in  $A^{2-}, 2Cat^+$  is twice as strong as in the two

**Table I.** The  $\lambda_{max}$ 's and  $\epsilon$ 's of Lithium Salts of Dianions in Diethyl Ether

Hydrocarbon	$\lambda_{max}/nm$	$\epsilon \times 10^{-4}$
Naphthalene	530	0.63
Anthracene	554	1.8
Tetracene	580	4.2
Perylene	552	3.2
Pyrene	569	1.3

$A^{\cdot-}, Cat^+$ , and the respective energy difference may be even larger if the association of the oppositely charged ions is tighter in the  $A^{2-}, 2Cat^+$  aggregates than in the  $A^{\cdot-}, Cat^+$  ion pairs. The resulting decrease in Coulombic energy is extremely large, often exceeding 35 kcal/mol.<sup>8</sup>

To better assess the magnitude of this electrostatic factor and its correlation with the structure of the parent hydrocarbon, we determined the equilibrium constants of the disproportionation of lithium salts of naphthalenide, anthracenide, tetracenide, perylenide, and pyrenide in diethyl ether at ambient temperature.

All the investigated hydrocarbons were purchased from Aldrich Chemicals and claimed to be 99% pure. They were recrystallized and eventually vacuum sublimed before being used. Their reduction was performed in diethyl ether, using lithium metal as the reducing agent. Chunks of lithium metal were introduced into a flask connected through a constriction to a side bulb. After its evacuation a purified, dry diethyl ether was distilled into it on a vacuum line and a small amount of perylene was added by crushing a breakseal of an attached ampoule containing that hydrocarbon. The resulting reaction "cleans" the surface of the metal and removes the layer of the oxide. Thereafter, the perylene solution was poured into the side bulb and the ether distilled back into the main flask. The metal was stirred with the distilled ether, the liquid poured again into the side bulb and this "washing" procedure repeated three times. Finally, the contents of the main flask were cooled with liquid nitrogen and the side bulb sealed off at the constriction. By crushing an appropriate breakseal a known amount of the investigated hydrocarbon was introduced into the flask. Its reduction was carried out for a desired time, the resulting solution was transferred into an optical quartz cell and an ESR tube, both were attached to the main flask, and the optical spectrum and the overmodulated ESR spectrum were recorded. The solution was brought then back into the main flask and the hydrocarbon reduced further. Thus, the optical and ESR spectra of the studied solution could be determined at various stages of reduction.

Complete reduction of the investigated hydrocarbon, indicated by the virtual disappearance of the ESR signal, afforded the solution of its pure dianions. Their spectra were recorded and their concentration was determined by adding an excess of tetracene to the investigated solutions. The dianions were converted then into radical anions of tetracene, the concentration of the latter being calculated from their optical density because the pertinent extinction coefficient is known<sup>2</sup> ( $\lambda_{max}$  580 nm,  $\epsilon$   $4.3 \times 10^4$ ). Thus the extinction coefficients of the other dianions were obtained and these are listed in Table I. The relevant spectra are displayed in Figure 1.

Disproportionation constants were calculated as  $[A] \cdot [A^{2-}, 2Cat^+] / [A^{\cdot-}, Cat^+]^2$  utilizing the data pertaining to the solutions in which the concentration of radical anions was low. For perylene and pyrene systems the concentration of the unreduced hydrocarbon was determined spectrophotometrically, whereas for other solutions it was obtained as the difference  $[A]_0 - [A^{2-}, 2Cat^+]$ . Typical results are shown in Table II, and the calculated disproportionation constants of the studied systems are collected in Table III.

**Table II.**  $K_{\text{disp}} = [A][A^{2-}, 2Li^+]/[A^{\cdot-}, Li^+]^2$  in Diethyl Ether

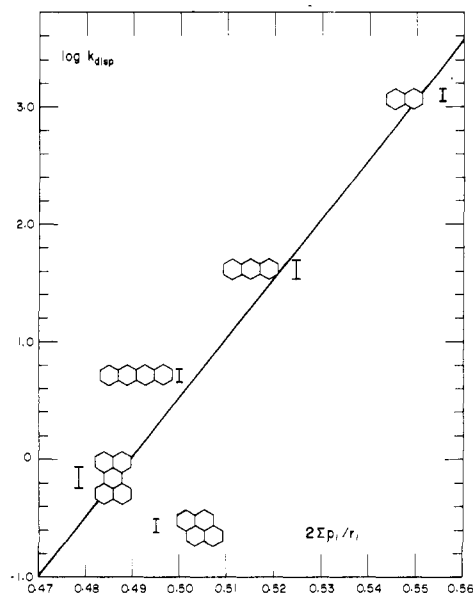
$10^4$ [Hydrocarbon]/ M	$10^4$ [Dianion]/ M	$10^4$ [Radical anion]/ M	$K_{\text{disp}}$
Naphthalene			
23.0	6.73	0.35	1250
21.1	5.48	0.32	1100
16.5	13.2	0.40	1370
9.8	19.9	0.38	1350
			Average $1270 \pm 120$
Anthracene			
21.8	1.08	0.81	36
20.2	1.14	0.68	50
20.7	2.35	1.20	34
18.4	1.95	0.87	47
14.5	3.46	1.04	46
14.5	4.54	1.33	37
			Average $42 \pm 7$
Pyrene			
8.44	29.9	29.9	0.29
4.39	39.7	24.9	0.28
1.97	49.7	20.	0.24
18.4	17.4	32.5	0.30
			Average $0.27 \pm 0.03$

**Table III.** Disproportionation Constants  $K_{\text{disp}}$  of Lithium Salts of Aromatic Radical Anions in Diethyl Ether at Ambient Temperature

Hydrocarbon	$K_{\text{disp}}$	$\Delta E$
Biphenylene	1270	0.5574
Naphthalene	$1270 \pm 120$	0.5558
Anthracene	$42 \pm 7$	0.5244
Tetracene	$16 \pm 1$	0.5000
Perylene	$0.76 \pm 0.11$	0.4780
Pyrene	$0.27 \pm 0.03$	0.4948

The magnitudes of the disproportionation constants listed in Table III are astonishing. It is obvious that the interaction of lithium cations with the dianions is an important factor favoring the reaction. A naive approach led to an interesting correlation of the observed  $K_{\text{disp}}$  with the calculated difference of the electrostatic energies. The  $Li^+$  cations were assumed to be located 3 Å above the centers of the relevant radical anions and again 3 Å above and below the centers of the corresponding dianions. The Coulombic interaction was calculated as the sum  $\Sigma e^2 \rho_i / r_i$ , where  $\rho_i$  denotes the odd electron's density on the appropriate aromatic carbon atom and  $r_i$  is its distance from the cation. The  $\rho_i$ 's were computed using the conventional Hückel approach.<sup>9</sup> On this basis  $2\Sigma \rho_i / r_i$  is proportional to the anticipated difference of electrostatic energies in the dianion and two radical anions. The results of such calculations are included in Table III, and the plot of  $\log K_{\text{disp}}$  vs.  $2\Sigma \rho_i / r_i$  is shown in Figure 2.

The linear relation seen in Figure 2 demonstrates that the increase in the Coulombic energy of  $Li^+$ -anion interaction, arising from the conversion of two radical anions into dianion, is the crucial factor facilitating the disproportionation of lithium salts of planar aromatic radical anions in diethyl ether. The simplicity of the model calls for some comments. The solvation of  $Li^+$  cations in diethyl ether is apparently poor, and hence their association with anions is tight in this medium. This magnifies the Coulombic interaction and makes it a dominant factor in the studied reaction. Certainly, our model is simplistic and its improvement could be contemplated. For example, electron-electron repulsion in the dianions varies with the structure of the parent hydrocarbon (see ref 4). The increase

**Figure 2.** Correlation of  $\log K_{\text{disp}}$  with  $2\Sigma \rho_i / r_i$ . (Correction added in proof. The point for tetracene shown in the figure was incorrectly plotted ( $K \sim 5$ ,  $\log K \sim 0.7$ ). It should be raised to  $K = 16$   $\log K = 1.2$ .)

in the repulsion opposes the effect of the cation-anion interaction, but apparently both increase with decreasing size of the hydrocarbon in a somewhat similar fashion. The decreasing size of the parent hydrocarbon should tighten the aggregates. This would amplify the observed effects, without affecting, however, the trends.

It should be stressed that the simple relation revealed by Figure 2 applies best to structurally similar hydrocarbons; hence, not surprisingly, the points for perylene and pyrene deviate somehow from the line determined by naphthalene, anthracene, and tetracene. The relation breaks down if applied to a different type of hydrocarbon, e.g., the disproportionation constant of lithium salt of stilbene radical anions in diethyl ether is  $8 \times 10^4$ , whereas  $2\Sigma \rho_i / r_i = 0.5252$  is much too small. This study has not been extended yet to other cations or solvents.

**Note Added in Proof.** Our calculations of the disproportionation constants implicitly assume that the investigated salts remain unaggregated; i.e., species such as  $(A^{\cdot-}, Li^+)_n$  or  $(A^{2-}, 2Li^+)_m$  are not present in diethyl ether, at least in the investigated concentration range. To confirm this assumption we determined (spectrophotometrically) the effect of 500-fold dilution on the equilibrium constant of  $2Pe^{\cdot-}, Li^+ \rightleftharpoons Pe + Pe^{2-}, 2Li^+$ . The results given below fully demonstrate the absence of any aggregation.

[Pe]	[ $Pe^{\cdot-}, Li^+$ ]	[ $Pe^{2-}, 2Li^+$ ]	$K_{\text{dispr}}$
$4.1 \times 10^{-4}$	$3.1 \times 10^{-4}$	$4.8 \times 10^{-4}$	0.56
$6.2 \times 10^{-7}$	$4.7 \times 10^{-7}$	$5.8 \times 10^{-7}$	0.88
$1.0 \times 10^{-4}$	$4.35 \times 10^{-4}$	$2.4 \times 10^{-4}$	0.75
$2.0 \times 10^{-7}$	$5.1 \times 10^{-7}$	$3.3 \times 10^{-7}$	0.92
$1.3 \times 10^{-4}$	$1.3 \times 10^{-3}$	$4.7 \times 10^{-4}$	0.77
$2.2 \times 10^{-7}$	$1.8 \times 10^{-6}$	$6.9 \times 10^{-7}$	0.81

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#### References and Notes

- (1) See for the discussion of this topic, M. Szwarc and J. Jagar-Grodzinski in "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed., Wiley, New York,

- N.Y., 1974, pp 90–106.  
 (2) J. Dieleman, Thesis, Free University, Amsterdam (1962).  
 (3) A. I. Shatenstein, *Org. React. (USSR)*, 1, 191 (1964).  
 (4) G. Levin and M. Szwarc, *J. Am. Chem. Soc.*, **98**, 4211 (1976).  
 (5) J. Pola, G. Levin, and M. Szwarc, *J. Phys. Chem.*, **80**, 1690 (1976).  
 (6) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).  
 (7) M. Born, *Z. Phys.*, 1, 45 (1920).  
 (8) The importance of cations in determining the degree of disproportionation of radical anions was clearly recognized by Garst; see J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962), and also the discussion in ref 1.  
 (9) C. A. Coulson and A. Streitwieser, "Dictionary of  $\pi$ -Electron Calculation", W.H. Freeman, San Francisco, Calif., 1965.

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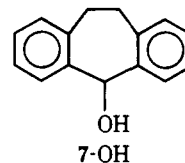
### Solvolysees of Pseudo-Geminal "Equatorial" and "Axial" Systems of Tris[2.2.2]paraxylylene and Related Compounds. An Extremely Large Difference in Rates Due to Phenyl Conjugation and Transannular Interaction

Sir:

Although recent molecular orbital calculations have predicted a very large difference in energy (e.g., by 22.3 kcal/mol according to the MINDO/3 method)<sup>1,2</sup> between coplanar and perpendicular conformations of benzyl cation, only a small decrease ( $<10^3$  times) in the solvolysis rate due to loss of conjugation has been reported for, e.g.,  $\alpha$ -alkylbenzyl systems.<sup>3</sup>

In this paper we wish to report an extremely large reduction of the ionization rate of the pseudo-geminal "equatorial" system of tris[2.2.2]paraxylylene (**2**) compared with the 5*H*-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-yl (**7**) system in connection with loss of conjugation, and also wish to describe a significant transannular effect on the rate and the reaction path in the solvolysis of the pseudo-geminal "axial" system of tris[2.2.2]paraxylylene (**3**).

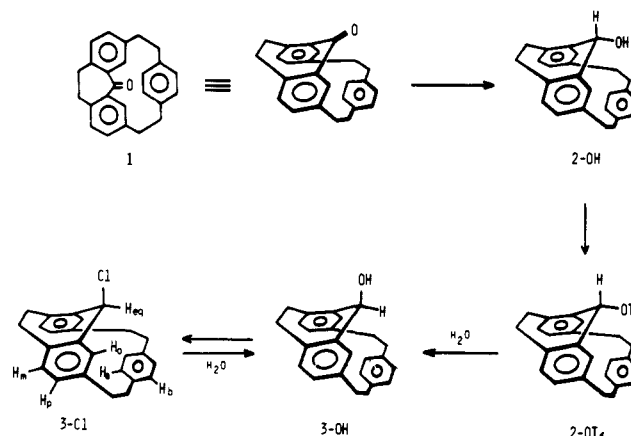
Based on spectral properties of the pseudo-geminal ketone of tris[2.2.2]paraxylylene (**1**) compared with those of 5*H*-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (**6**), very slow ionization at the pseudo-geminal bridge position has been expected.<sup>4</sup> Borohydride or alkaline zinc reduction of **1** gave the "equatorial" alcohol (**2-OH**) stereospecifically.<sup>5</sup> The "axial" alcohol (**3-OH**) was obtained from hydrolysis of the "equatorial" trifluoromethanesulfonate (triflate) (**2-OTf**) again stereospecifically.<sup>5</sup> In order to measure the ionization rates of **3** and **7**, pseudo-geminal "axial" chloride (**3-Cl**)<sup>6,7</sup> and the *p*-nitrobenzoate of **7-OH** (**7-OPNB**)<sup>8</sup> were prepared from **3-OH** and **7-OH**, respectively. On hydrolysis in 60% aqueous dioxane, all of the derivatives displayed good first-order kinetics up to 60–85% reaction. Only **3-OH**<sup>9</sup> was obtained from



hydrolysis of **3-Cl**, and **7-OH** was a sole product from **7-OPNB**.

Table I summarizes the results of the kinetic investigations on **2-OTf**, **3-Cl**, and **7-OPNB**. Thus, the relative rates of **2-OTf**, **3-OTf**, and **7-OTf** are estimated to be  $10^{-18.1}$ ,  $10^{-3.4}$ , and 1, respectively, using corrections for a triflate-tosylate reactivity difference of  $10^{4.8,10}$  for tosylate-*p*-nitrobenzoate of  $10^{9.1,11}$  and for tosylate-chloride of  $10^{5.7,12}$

Scheme I



The extremely large deceleration ( $10^{18.1}$  times) of the rate constant of **2-OTf** compared with **7-OTf** is mainly attributable to loss of conjugation due to lack of coplanarity between the incipient carbonium ion and the substituted phenyl rings,<sup>13</sup> because based on the Dreiding model of pseudo-geminal methanotriss[2.2.2]paraxylylene (**4**) the "equatorial" C-H bond is inclined about  $20^\circ$  from coplanar (hence, about  $40^\circ$  for the "axial" C-H bond), whereas the corresponding C-H bond of 5*H*-10,11-dihydrodibenzo[*a,d*]cycloheptene (**8**) can take the perpendicular conformation easily. Angle strain about the carbonium ion center upon ionization<sup>14</sup> of **2** should be a minor factor, for a  $J(^{13}\text{C-H})$  value for the pseudo-geminal bridge carbon of **4** is 129 Hz<sup>15</sup> and that for the corresponding carbon of **8** is 126 Hz. Steric hindrance in ionization<sup>16</sup> by the "face" <sup>5</sup> ring or the ethano bridge in the seven-membered ring in **2** is considered also to be minor on the basis of the CPK model.

Since **3-OH** is the sole product from **2-OTf** and **3-Cl**, and both reactions obey the first-order kinetics, the reactions must proceed via the same intermediate (**5**), where the *p* orbital of the carbonium ion can transannularly interact with the  $\pi$

Table I. Kinetic Data for Solvolysis in 60% (v/v) Aqueous Dioxane<sup>a</sup>

Compd	Temp, °C <sup>b</sup>	$K_1$ , s <sup>-1</sup>	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu	$K_{rel}$
2-OTf	110.6	$(1.39 \pm 0.07) \times 10^{-4}$	28.0	-3.6	$10^{-18.1}$
	98.9	$(4.24 \pm 0.07) \times 10^{-5}$			
	25.0	$2.72 \times 10^{-9}$ <sup>c</sup>			
3-Cl	40.0	$(2.45 \pm 0.00) \times 10^{-4}$	23.2	-1.2	$10^{-3.4}$
	25.0	$(3.58 \pm 0.00) \times 10^{-5}$			
3-OTf	25.0	$1.3 \times 10^6$ <sup>d</sup>			
7-OPNB	35.0	$(1.62 \pm 0.00) \times 10^{-4}$	22.8	-2.0	1
	25.0	$(4.50 \pm 0.11) \times 10^{-5}$			
7-OTf	25.0	$3.4 \times 10^9$ <sup>d</sup>			

<sup>a</sup> Determined conductometrically. <sup>b</sup> All temperatures  $\pm 0.1^\circ$  or better. <sup>c</sup> Extrapolated from high temperatures. <sup>d</sup> Estimated with the appropriate corrections for reactivities of the leaving groups; see text.