the product crystallized from EtOH to give 0.45 g (91%) of **6** identical with material described above.

Oxidation of 6 to 2,5-Diphenyl-1,6-dioxa-$6a\lambda^4$-thia-3,4-diazapentalene (1). General Method. To a solution of 0.284 g (1 mmol) of **6** in 10 mL of $CHCl_3$ containing 0.3 mL (2 mmol) of triethylamine at room temperature was added dropwise 2 mL of a 0.5 N solution of Br_2 in $CHCl_3$. The Br_2 color immediately discharged, and after the addition was complete the solvent was removed and the residue partitioned between H_2O and CH_2Cl_2. The organic layer was dried and passed through a pad of silica gel and the product crystallized from acetone to give 200 mg (73%) of **1**: mp 193.5–194.0 °C (lit. mp 195–197 °C,[3] 189–190 °C[2]); mass spectrum, m/e 282 (M^+).

2,5-Dimethyl-1,6-dioxa-$6a\lambda^4$-thia-3,4-diazapentalene (4). In an analogous manner to the preparation of **1** from **6**, 1.6 g of **7**[6] gave 0.9 g (58%) of **4** crystallized from CH_2Cl_2/hexane. The material was difficult to crystallize, and TLC showed the liquors to contain essentially pure **4**: mp 57.5–59.5 °C; NMR δ 2.63 (s); mass spectrum, m/e 158 (M^+). Anal. Calcd for $C_5H_6N_2O_2S$: C, 37.97; H, 3.82; N, 17.71; S, 20.27. Found: C, 37.91; H, 3.86; N, 17.63; S, 19.92.

2-Methyl-5-phenyl-1,6-dioxa-$6a\lambda^4$-thia-3,4-diazapentalene (5). In an analogous manner to the preparation of **1** from **6**, 0.22 g of **8**[7] gave 0.09 g (41%) of **5** crystallized from Et_2O/hexane: mp 102.5–103.5 °C; NMR δ 2.63 (3 H, s), 7.4–7.7 (3 H, m), 8.3–8.5 (2 H, m); mass spectrum, m/e 220 (M^+). Anal. Calcd for $C_{10}H_8N_2O_2S$: C, 54.53; H, 3.66; N, 12.72; S, 14.56. Found: C, 54.39; H, 3.33; N, 12.36; S, 14.11.

Registry No. 1, 62302-08-3; 2, 62337-60-4; 3, 17280-68-1; 4, 74346-71-7; 5, 74346-72-8; 6, 74346-73-9; 7, 4984-27-4; 8, 74346-74-0.

Reactions of Polyarylated Carbinols. 6.[1a] Kinetics of the Thermal [1,5] Sigmatropic Phenyl and Para-Substituted-Phenyl Rearrangements in 3,4-Bis[*p*-substituted-phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ols and 1-[*p*-Substituted-phenyl]-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols

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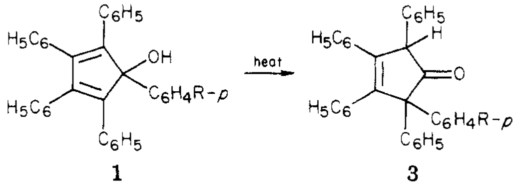
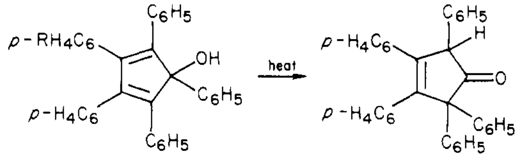
During our continuing research on 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol[1b] and its derivatives,[2] we became interested in using this system to establish the limits for electronic-effect involvement in its thermal [1,5] sigmatropic phenyl rearrangement. This interest stemmed from the meager data that has accompanied theoretical predictions of the electronic effects involved in neutral [1,5] sigmatropic phenyl rearrangements.[3] The pentaphenylcyclopentadienol system is particularly attractive for such a study because it is free from competing shifts of species with migratory aptitudes greater then phenyl;[3,4] thus, this system could be used to establish both the limits of electronic-effect involvement in [1,5] sigmatropic rearrangements and the applicability of using a mechanistic probe of the Hammett type[5] to establish such electronic-effect involvement. In addition, since the cyclopentadiene nucleus is substituted with phenyl groups at all five positions, the opportunity presents itself to probe both at the migration center and on the backbone of the migration framework. To date no investigation has been reported where electronic effects at the migration center of such a rearrangement have been responsive to a Hammett probe.

For these studies two series of compounds were synthesized: the 1-[*p*-substituted-phenyl]-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol series (**1**) and the 3,4-bis[*p*-substituted-phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ol series (**2**). This paper discusses the results of the investigations of the kinetics of the thermal rearrangements for both these systems to ketones **3** and **4**, respectively.



1 **3**

R = OCH_3, $C(CH_3)_3$, CH_3, H, C_6H_5, Cl, Br, CF_3



2 **4**

R = $C(CH_3)_3$, CH_3, H, Cl, Br

Experimental Section

Preparation of Carbinols 1. These carbinols were prepared in the normal manner[2] by Grignard addition of the appropriate para-substituted phenylmagnesium bromides to tetracyclone.

Preparation of Carbinols 2. These carbinols were prepared[2] by Grignard addition of phenylmagnesium bromide to the appropriate 3,4-bis(*p*-substituted-phenyl)-2,5-diphenyl-2,4-cyclopentadien-1-ones.

Kinetic Runs. All solvents were of spectral-grade quality and were used without further purification. The kinetic studies of the sigmatropic rearrangements of the polyarylated alcohols were performed as follows. Into a 50-mL, two-necked, round-bottomed flask equipped with a reflux condenser, a serum cap, and a magnetic stirrer was placed 20 mL of tetraethylene glycol, which was then heated to the appropriate temperature (for carbinols **1**, 150, 165, 180, 190, and 200 °C in separate kinetic runs; for carbinols **2**, 180, 190, 200, and 210 °C in separate kinetic runs). The temperature of the reaction mixture was maintained at the temperature reported (±0.2 °C) by means of a thermostatically controlled oil bath. At this point 150 mg of the substituted polyarylated carbinol to be studied was added as a solid all at once to the solvent. While the mixture was stirring, samples of 0.5 mL each were taken at various times by inserting a hypodermic syringe through the serum cap. The samples thus obtained were placed in separate containers and cooled by means of an ice–water bath to room temperature. These samples were then separately injected into a Molecular Separations, Inc., B500, high-performance LC. The mobile phase used was methanol/*n*-hexane (0.01% to 99.99%), flowing at 1.4 mL/min through a 2 ft x 2.1 mm (i.d.) stainless-steel column packed with Vydac absorbant. Peaks were recorded on a 10-mV recorder and the peak heights were used as a measure of concentration.[6] This same procedure was used for all the kinetic investigations.

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(1) (a) Part 5: J. G. Mason, A. K. Youssef, and M. A. Ogliaruso, *J. Org. Chem.*, **40**, 3015 (1975). (b) Previous papers in the series referenced in footnote 1a.

(2) T. A. Perfetti and M. A. Ogliaruso, *J. Org. Chem.*, **43**, 884 (1978).

(3) C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).

(4) W. R. Dolbier, Jr., K. E. Anapolle, L. McCullagh, K. Matsui, J. M. Riemann, and D. Rolison, *J. Org. Chem.*, **44**, 2845 (1979).

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(6) D. L. Johnson and R. Stevenson, "Basic Liquid Chromatography", Varian Associates, Inc., Palo Alto, CA, 1978, p 227.

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Table I. Activation Parameters for Thermolysis of Substituted Alcohols 1 and 2 in Tetraethylene Glycol

alcohol	substituent (R =)	temperature range, °C	$\Delta S^{\neq}$, eu	E_a, kcal/mol
1	CF_3	150-200	-11.6	30.9
1	Br	150-200	-3.8	34.8
1	Cl	150-200	-7.0	33.1
1	C_6H_5	150-200	-6.0	33.2
1 or 2	H	150-210	-2.6	34.7
1	CH_3	150-200	-8.6	32.4
1	$C(CH_3)_3$	150-200	+0.2	36.0
1	OCH_3	150-200	-6.5	33.6
2	Br	180-210	-17.8	26.5
2	Cl	180-210	-14.0	29.3
2	CH_3	180-210	-13.1	30.3
2	$C(CH_3)_3$	180-210	-16.6	28.7

Preparation of Ketones 3 and 4. Preparative-scale (5 g) conversions of alcohols 1 to ketones 3 and alcohols 2 to ketones 4 were performed to obtain pure samples of the ketones for analysis and spectroscopic identification. All ketones prepared gave satisfactory analyses and expected spectroscopic data.

Results

Plotting the logarithm of the percent concentration of the starting alcohols (1 or 2) at the temperatures (150, 165, 180, 190, 200, and/or 210 °C) investigated vs. time afforded a series of curves for each substitutent. All the plots showed an increase in the slope of the line as the temperature was increased, which is in accord with increases in the rate of the reactions with increasing temperature. Since a straight line was obtained in all the above described plots with each substituent, and at each temperature, this indicated that the sigmatropic rearrangement of all the substituted alcohols 1 and 2 was a first-order reaction throughout the temperature range investigated.

Using a least-squares program to calculate the slope of the curves obtained above, it was possible to calculate the rate constants (k) for each individual run for each substituent, which are recorded in Table I. The activation energy (Table I) of these sigmatropic rearrangements was then calculated by plotting log k vs. $1/T$ (K), which gave an Arrhenius plot for each substituent (alcohols 1, Figure 1; alcohols 2, Figure 2).). Using the standard Arrhenius equation[7] gave activation energies for each substituent, which are recorded in Table I, and the entropy of activation[8] for each substituent was then calculated by using these activation energies.

Discussion

The energy of activation (E_a = 34.7 kcal/mol) obtained in this study for the [1,5] sigmatropic phenyl rearrangement in the parent alcohol (1 or 2, R = H) was obtained via high-performance LC analysis of the kinetic runs and is consistent with the value previously reported[1b] which was obtained by using GC analysis of the kinetic runs. In retrospect, it appears that the GC analysis is relatively free of any predicted bias.[9]

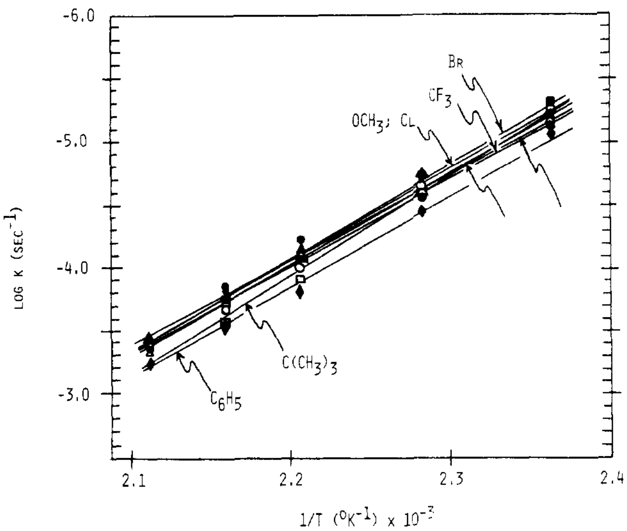

Figure 1. Variation of log k vs. $1/T$ over the temperature range 150.0 to 200.0 ± 0.2 °C for alcohols 1: ◇ (R = OCH_3); □ (R = $C(CH_3)_3$); △ (R = CH_3); ○ (R = H); ◆ (R = C_6H_5); ▲ (R = Cl); ■ (R = Br); ● (R = CF_3).

It is interesting to note that although the range of energies of activation obtained for the alcohols 2 (E_a = 26.5–30.3 kcal/mol) is slightly lower than the range of activation energies obtained for the alcohols 1 (E_a = 30.9–36.0 kcal/mol) they are very similar.

Since negative entropies of activation ($\Delta S^{\ddagger}$) are an established characteristic of sigmatropic rearrangements,[3] the negative entropies of activation obtained in this study are expected and are, with one exception, consistent with a transition state which is more ordered than the ground state of the reactants.

The value of +0.2 eu obtained for the entropy of activation of the *tert*-butyl-substituted alcohol 1 (R = *t*-Bu) is interesting because its near isentropicity argues for the reactant being slightly more ordered than the transition state. The steric bulk and entropic rotational demands of the phenyl-substituted alcohol (1, R = C_6H_5) should be comparable to the *tert*-butyl alcohol (1, R = *t*-Bu), but the phenyl-substituted alcohol displays a definite negative entropy of activation as do the other substituted alcohols (1 and 2) and the parent alcohol (1 or 2, R = H). The reason for the anomalous entropy of activation for the *tert*-butyl alcohol is unclear; however, it may be due to the *tert*-butyl group having less freedom in the ground state than in the transition state. At the other extreme are the substituted alcohols 2 which show entropies of activation lower ($\Delta S^{\ddagger}$ = -17.8 to -13.1 eu) than those for the alcohols 1 ($\Delta S^{\ddagger}$ = -11.6 to +0.2 eu).

All the entropies of activation obtained in this study, however, are higher than those reported by Miller and Boyer[10] for the [1,5] sigmatropic phenyl rearrangement in substituted indenes ($\Delta S^{\ddagger}$ = -27 eu), where the rearrangement displayed solvent effects which implicated the contribution of polar transition states. To date no neutral sigmatropic *phenyl* rearrangement has afforded a linear free-energy relationship,[11] while only one neutral sigma-

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[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, 1965, p 23.

[8] J. H. Bunnett in "Technique of Organic Chemistry", Vol. VIII, Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Eds., Interscience, New York, 1961, p 201.

[9] It was theorized that further rearrangement of the alcohols 1 and 2 would occur on the heated column of the GC during the approximately 30 min required for elution. This would yield measured rates greater than the true rates and energies of activation less than the actual energies of activation.

[10] L. L. Miller and R. F. Boyer, *J. Am. Chem. Soc.*, **93**, 650 (1971).

[11] All attempts to establish a linear free-energy relationship for alcohols 1 or 2 failed. The parameters investigated were Hammett's σ_p, σ_p^+, σ_p^-,[12] Taft's E_s,[13] and Swain and Lupton's $\mathcal{F}$ and $\mathcal{R}$.[14] The futility of these searches is clear in light of the bimodal distribution both alcohols 1 and 2 take when their activation parameters are compared.

[12] C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).

[13] R. W. Taft, Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., John Wiley and Sons, New York, 1956, pp 556–675.

[14] C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

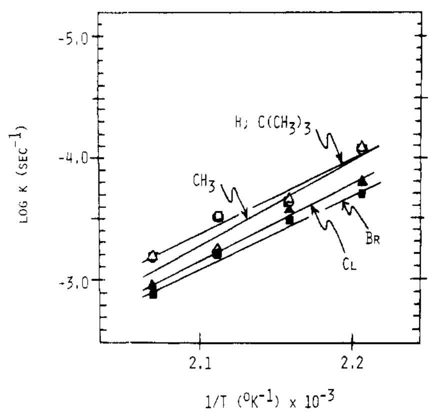

Figure 2. Variation of log k vs. $1/T$ over the temperature range 180.0 to 210.0 ± 0.2 °C for alcohols **2**: □ (R = $C(CH_3)_3$); △ (R = CH_3); ○ (R = H); ▲ (R = Cl); ■ (R = Br).

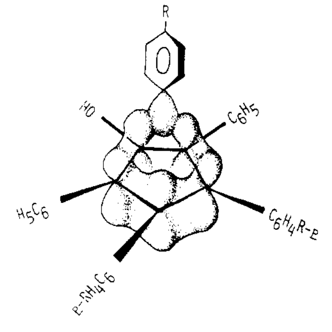

Figure 3. Transition state devoid of charge separation.

tropic *hydrogen* rearrangement, in a substituted isoindene system,[15] has afforded such a relationship.

A number of workers[16-20] have offered explanations for electronic effects observed in neutral sigmatropic reactions, but given the limited number of systems studied and the fact that only one has afforded a linear free-energy relationship, it appears to be premature to offer a comprehensive theory to account for such effects. Indeed, each system appears to be unique and given the situation that electronic effects have been observed in neutral sigmatropic rearrangements but have resisted a predictive theory, optimism suggests a spectrum of reactivity to account for the observed variability among neutral systems which rearrange by a sigmatropic mechanism. In this scheme, the rearrangement of the alcohols **1** and **2** should be placed at one end of the spectrum, where rearrangements occur by a *purely* concerted mechanism having a transition state devoid of charge separation (Figure 3).

The possibility certainly exists that the steric constraints of this system are so great that the individual members of the system are reduced to energetic equivalence.

Registry No. 1 (R = CF_3), 64706-20-3; **1** (R = Br), 19057-23-9; **1** (R = Cl), 15946-43-7; **1** (R = C_6H_5), 19209-97-3; **1** (R = H), 2137-74-8; **1** (R = CH_3), 64706-19-0; **1** (R = $C(CH_3)_3$), 64706-17-8; **1** (R = OCH_3), 64706-18-9; **2** (R = Br), 56549-00-9; **2** (R = Cl), 22926-90-5; **2** (R = CH_3), 19059-95-1; **2** (R = $C(CH_3)_3$), 64706-21-4.

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(15) K. K deFonseca, C. Manning, J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257 (1977).

(16) F. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun*, 716 (1972).

(17) R. Breslow, J. H. Hoffman, and C. Perchonock, *Tetrahedron Lett.*, 3723 (1973).

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(19) N. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **99**, 4936 (1977).

(20) W. A. Pettit and J. W. Wilson, *J. Am. Chem. Soc.*, **99**, 6372 (1977).

Polar Effect in Alkyl Radical Reactions. Carbon Kinetic Isotope Effects in Halogen Atom Transfer to Tin(III) and Chromium(II)

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Halogen atom transfer from organic halides is an important process in free-radical chemistry, and it can be effected by a variety of reagents, foremost of which are organometallic radicals and transition metal complexes, e.g., eq 1, where X = Cl, Br, and I.[1,2] Halogen atom

$$CH_3X + M^{n+} \rightarrow CH_3\cdot + XM^{n+1} \qquad (1)$$

transfer is accompanied by a change in the formal oxidation state of the metal center by one unit, as indicated by the superscripts in eq 1.

The transition state for halogen atom transfer may be qualitatively described in the context of the polar effects by involving various canonical forms, as in Figure 1.[3]

Indeed in a recent study,[4] Blackburn and Tanner reported that halogen atom transfer from a series of substituted benzyl chlorides, bromides, and iodides to tri-*n*-butyltin radicals, i.e., eq 2, showed excellent Hammett

$$ArCH_2X + n\text{-}Bu_3Sn^{III} \rightarrow ArCH_2\cdot + n\text{-}Bu_3Sn^{IV}X \qquad (2)$$

correlations. The variation in the postive ρ values and the use of σ^- substituent constants accorded with the importance of bond breaking and electron transfer in the transition state, as depicted by the contributions from the forms II and III, respectively, in Figure 1.

The relative reactivities of benzylic bromides to *n*-butyltin radicals in eq 2 compare favorably with those measured earlier for bromine atom transfer to the transition metal complexes of chromium(II),[5,6] i.e., eq 3. The

$$ArCH_2Br + Cr^{II} \rightarrow ArCH_2\cdot + BrCr^{III} \qquad (3)$$

latter was made in connection with a comparison of the polar effects in hydrogen atom and halogen atom transfers in the formation of benzylic radicals.[7]

In this report we present our initial efforts in the measurement of the kinetic isotope effects (KIE) as a complementary approach to ascertaining the extent of bond breaking and electron transfer in the transition state for halogen atom transfer. In particular, the availability of a sensitive isotope-ratio mass spectrometer capable of measuring $^{13}C/^{12}C$ to ±0.0005[8] allowed us to establish the carbon-13 KIE (in natural abundance) for chlorine, bromine, and iodine atom transfers in eq 1, using the tri-

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(1) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: London, 1974; pp 296, 349ff.

(2) (a) Davies, A. G.; Roberts, B. P. *Free Radicals* **1973**, *1*, Chapter 10. (b) Poutsma, M. L. *Ibid.* **1973**, *2*, Chapter 14.

(3) For a general discussion of polar effects, see: Russell, G. A. in ref 2, Vol. 1, Chapter 7. To emphasize the negative charge on carbon in the electron-transfer canonical form III, it may be represented alternatively as $[CH_3\!:^- X\cdot M^{n+1}]$.

(4) (a) Blackburn, E. V.; Tanner, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 692. (b) See also: Grady, G. L.; Danyliw, T. J.; Rabideux, P. *J. Organomet. Chem.* **1977**, *142*, 67.

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(6) See also: Kochi, J. K.; Mocadlo, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 4094; *J. Org. Chem.* **1965**, *30*, 1134.

(7) Kochi, J. K.; Davis, D. D. *Nature (London)* **1964**, *202*, 690.

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