results show that the main reaction is H abstraction from SH.[13] The partial rate for this abstraction is 2.7 × 10^9 M^{-1} $\sec^{-1}$, similar to that observed for thiophenol (Table I). Some abstraction of the SH group to form H_2S also takes place.[11-13] However, H abstraction from C–H bonds is negligible in cysteine. Other sulfur compounds which do not contain an SH group also react with hydrogen atoms very rapidly but in these cases no H_2 formation beyond the molecular yield is observed and the reaction must involve addition of H on the sulfur to rupture the C–S or S–S bonds as previously suggested.[7]

With nitromethane and histidine little abstraction is detected, confirming previous suggestions[4,7] based on the measured total rate constants.

In conclusion, measurement of hydrogen yields allows us to distinguish between the various modes of reaction of hydrogen atoms with organic compounds. Supplemented by rate-constant data it gives some insight into the structure of molecules. General patterns of reactivity have been summarized[3] and the present study gives additional information, mostly on the reactivities of benzylic and allylic hydrogens and of carbonyl compounds, and assigns a partial rate constant of 1 × 10^8 M^{-1} $\sec^{-1}$ for H addition to an enol site.

Registry No.—Hydrogen, 12184-88-2.

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Reactions of Polyarylated Carbinols. II.[1] Kinetic Study of a Suprafacial [1,5]-Sigmatropic Rearrangement[2]

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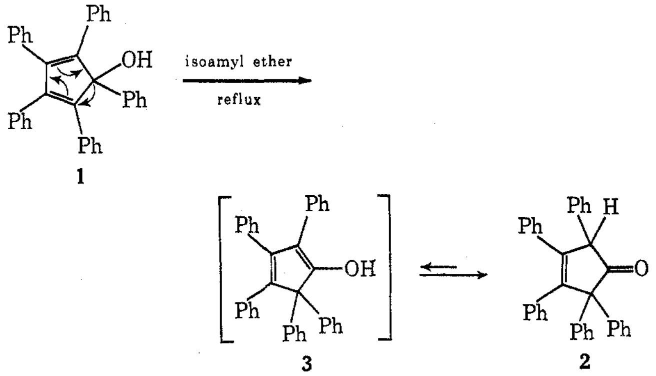
A kinetic study of the suprafacial [1,5]-sigmatropic phenyl rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2) has been performed at 173° in isoamyl ether and at 173, 180, 190, and 200° in diphenyl ether. The rearrangement is observed to be first order throughout the temperature range investigated, and the rate constants (k) at the temperatures used were found to be 0.28, 0.40, 1.09, and 2.7 × 10^{-2} hr^{-1}, respectively. Calculation of the activation energy of this phenyl [1,5]-sigmatropic shift from the Arrhenius equation gave 36.1 ± 3.6 kcal/mol, while $\Delta S^{\ddagger}$ for this phenyl migration is −7 eu. These results are used to discuss both the mechanism of this rearrangement and the transition state for rearrangement in the pentaphenylcyclopentadienol system.

Since the initial work of Mironov[4] on methyl-substituted cyclopentadienes and on 5-deuteriocyclopentadiene several thermal sigmatropic reactions of cyclopentadiene systems have recently been discovered. McLean and Haynes[5] studied the [1,5]-hydrogen rearrangement of 1-methylcyclopentadiene and 1,2-dimethylcyclopentadiene, and Roth[6] has investigated the rearrangement of isotopically labelled 5*H*-perdeuteriocyclopentadiene, while Backes[7] has reported on [1,5]-ester migrations in the cyclopentadiene system. Work on the unsubstituted indene system has been performed by Roth,[6] Alder,[8] Berson,[9] and Isaacs,[10] while Koelsch and Johnson,[11] and more recently Miller,[12] have reported studied on substituted indene systems. More recently Wawzonek[13] has reported on the thermal sigmatropic rearrangement of 3a,7a-dihydro-3,3a,5,6-tetraphenylinden-1-one. Our recent report[1] that 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) undergoes a thermally induced, symmetry allowed, suprafacial [1,5]-sigmatropic phenyl shift to produce 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2) has extended these initial observations concerning sigmatropic shifts in cyclopentadiene, indene, and indenone systems to the cyclopentadienol system.

In our initial publication[1] we postulated that the conversion of 1 to 2 proceeds through the keto–enol tautomerization of the dienol intermediate 3. Since the rearrangement of 1 to 2 proceeds so cleanly and because this is the first observation of a sigmatropic phenyl shift in a cyclopentadienol system, a kinetic study of this rearrangement was undertaken to establish that this is indeed a true sigmatropic rearrangement and to obtain some information about the activation energy and the entropy of activation for this rearrangement.



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[1] For paper I in this series, see A. K. Youssef and M. A. Ogliaruso, *J. Org. Chem.*, **37**, 2601 (1972).

[2] Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

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TABLE I
THE ISOMERIZATION REACTION OF 1,2,3,4,5-PENTAPHENYL-2,4-CYCLOPENTADIEN-1-OL AT DIFFERENT TEMPERATURES AND IN DIFFERENT SOLVENTS

Reaction time	% Ratio	
	Alcohol	Ketone
0.5[a,b,c]	89.5	10.5
1.0	85.0	15.0
2.0	70.9	29.1
2.5	65.5	34.5
3.0	60.8	39.2
3.5	55.9	40.1
4.0	49.5	50.5
4.5	46.7	53.3
5.0	44.0	56.0
5.5	39.5	60.5
6.0	36.0	64.0
6.5	33.0	67.0
7.0	30.8	69.2
8.2	24.0	76.0
9.0	22.5	77.5
10.0	17.5	82.5
11.0	15.4	84.6
11.5	14.0	86.0
15[d,e,f]	91.2	8.8
30	88.4	11.6
50	85.0	15.0
65	78.6	21.4
110	66.5	33.5
140	57.7	42.3
170	48.8	51.2
235	39.5	60.5
295	25.0	75.0
475	16.6	83.4
15[d,f,g]	91.1	8.9
30	82.3	17.7
45	73.3	26.7
60	63.0	37.0
90	48.1	51.8
120	34.5	65.5
180	17.0	83.0
240	7.7	92.3
10[d,f,h]	82.5	17.5
20	66.0	34.0
30	51.3	48.7
40	37.3	62.7
60	22.2	77.8
80	13.5	86.5
110	4.0	96.0
140	2.6	97.4

[a] Solvent is either isoamyl ether or diphenyl ether. [b] Temperature is 173°. [c] Time is in hours. [d] Solvent is diphenyl ether. [e] Temperature is 180°. [f] Time is in minutes. [g] Temperature is 190°. [h] Temperature is 200°.

TABLE II
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THERMOLYSIS OF 1,2,3,4,5-PENTAPHENYL-2,4-CYCLOPENTADIEN-1-OL IN DIPHENYL ETHER

Temp, °C	$10^2\,k$, hr^{-1}	$\Delta S^{\ddagger}$,[a] eu	E_a,[a] kcal/mol
173	0.28	−7.5	36.1
180	0.40		
190	1.09		
200	2.79		

[a] Calculated at 173°.

Experimental Section

General.—Gas–liquid partition chromatography (glpc) was conducted using a Bendix Model 2600 gas chromatograph and a Bendix Model 1200 recorder. The glpc was equipped with a 3 ft × 0.25 in. column packed with 3% QF-1 on Chromosorb W (H. P., mesh 100/120) support. Operating conditions were as follows: temperature of inlet 210°, detector 255°, injector 255°, column 210°, and a He carrier gas flow rate of 80 ml/min. Analysis of each sample taken showed only three peaks, corresponding to the solvent, the remaining unreacted alcohol **1**, and the ketone product **2**. Retention time of the alcohol **1** was 6 min 15 sec; of the ketone, 13 min 45 sec. In order to study the kinetics at temperatures higher than 173° it was necessary to change the solvent from isoamyl ether to diphenyl ether (bp 259°), which was found to be satisfactory. To establish that changing to this solvent did not in any way affect the results, the kinetic study performed at 173° in isoamyl ether was again performed at 173° in diphenyl ether. The results obtained in both solvents at 173° were exactly the same. The solvents isoamyl ether and diphenyl ether were both purified by two distillations before use. The alcohol **1** was synthesized as previously described.[1] The temperature of the reaction mixture was maintained at the temperature reported ±1°, by means of a thermostatically controlled oil bath.

Kinetic Runs.—Into a 100-ml, two-necked, round-bottomed flask equipped with a reflux condenser, a serum cap, and a magnetic stirrer was placed 75 ml of the solvent (either isoamyl or diphenyl ether), which was then heated to the appropriate temperature (173° when isoamyl ether was used, and in separate kinetic runs 173, 180, 190, and 200° when diphenyl ether was used). At this point 2.0 g (0.0042 mol) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (**1**) was added as a solid all at once. While the mixture was refluxing, samples of 5 ml each were taken at various times (Table I) by inserting a hypodermic syringe through the serum cap. The samples thus removed were placed in separate containers and cooled by means of an ice–water bath. After all the required samples were collected, glpc analysis was carried out using the instrument and conditions described above. For each kinetic run the peak areas of the two peaks corresponding to the alcohol **1** and the ketone **2** were determined by triangulation[14] and the per cent concentrations represented by these peak areas were then calculated (Table I) and the logarithm of the concentrations was determined. For each kinetic run the concentration of both the starting alcohol **1** and the product ketone **2** were separately plotted *vs.* time, and the logarithm of the concentration of the starting alcohol **1** *vs.* time was plotted.

Results

Plotting the logarithm of the concentration of the starting alcohol **1** only at the different temperatures *vs.* time afforded the curve shown in Figure 1. This curve illustrates that the slopes increase as the temperature is increased, which is in accord with increases in the rate of the reaction with increasing temperature. It can be readily seen from these plots in Figure 1 that at 200° the reaction goes to completion in less than 3 hr, whereas at 173° less than 90% of the starting alcohol **1** has reacted in 12 hr. Since a straight line is obtained at every temperature when the logarithm of the concentration of the starting alcohol **1** (the disappearance of alcohol **1** with time) is plotted *vs.* time, this indicates that the sigmatropic rearrangement of **1** is a first-order reaction throughout the temperature range investigated.

Using a least square program to calculate the slope of the curves in Figure 1, it was possible to calculate the rate constants (k) for each individual run, which are recorded in Table II. The activation energy of this sigmatropic rearrangement was then calculated by plotting log k *vs.* $1/T$ (°K), which gave an Arrhenius plot. Again using the least square program to calculate the slope of this plot afforded a value of 0.78863 × 10^4 for the slope. Using the standard Arrhenius

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(14) As described in H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Varian Associates, Palo Alto, Calif., 1969, p 154.

equation[15] gave an activation energy of 36.1 ± 3.6 kcal/mol for this rearrangement. Calculation of the entropy of activation[16] using this activation energy gave -7.5 cal deg^{-1} mol^{-1}.

Discussion

McLean and Haynes[5] have previously reported $\Delta S^{\ddagger} = -10$ eu for the [1,5]-hydrogen rearrangement of 1-methylcyclopentadiene and a $\Delta S^{\ddagger} = -4$ eu for the hydrogen migration process in 1,2-dimethylcyclopentadiene, while Roth[6] reported $\Delta S^{\ddagger} = -12$ eu for 5*H*-perdeuteriocyclopentadiene. Although phenyl migrations have not been studied kinetically in the cyclopentadiene system, there should be similar $\Delta S^{\ddagger}$ values observed for phenyl migrations in this system as have been observed for hydrogen migrations. Studies performed on hydrogen and phenyl migrations in substituted indene systems[12] have shown the need for justifying $\Delta S^{\ddagger}$ values obtained for phenyl migrations which differ drastically from the $\Delta S^{\ddagger}$ values obtained for hydrogen migrations in similar systems. In the cyclopentadienol system no kinetic studies have been performed on either hydrogen or phenyl migrations; however, it is expected that the values of $\Delta S^{\ddagger}$ observed in this system for hydrogen and/or phenyl migrations should correspond with the $\Delta S^{\ddagger}$ values reported in both the cyclopentadiene and indene systems for hydrogen and/or phenyl migrations. Thus the values of $\Delta S^{\ddagger} = -7.5$ eu reported here for [1,5]-phenyl migration in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol seems well within the region of $\Delta S^{\ddagger}$ values expected for rearrangements of hydrogen or phenyl in five-membered ring diene systems.[17]

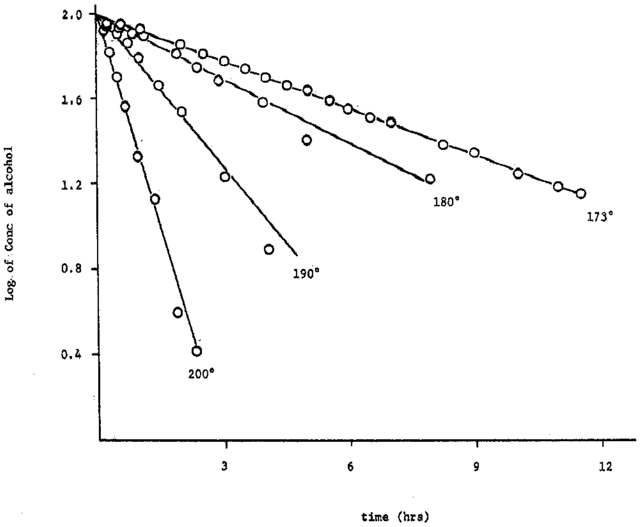

Figure 1.—Variation with time of the logarithm of the concentration of alcohol 1 at 173, 180, 190, and 200°.

The results reported here in isoamyl and diphenyl ether combined with our initial results in DMSO reported earlier[1] indicate that the observed phenyl migration is not solvent dependent. In addition, since previously reported results[1] indicate that this rearrangement proceeds without any ionic or radical character, it appears that the transition state for this phenyl shift is similar to the proposed transition state for sigmatropic hydrogen migrations[17,18] and that the phenyl rearranges *via* a true sigmatropic mechanism in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.

Registry No.—1, 2137-74-8; 2, 34759-47-2.

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The Mechanism of the Base-Catalyzed Prototropic Propargylic Rearrangement in Vicinal Diamines[1]

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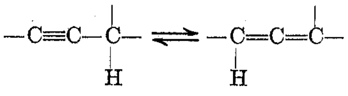
The relative rates of rearrangement of 3-hexyne with a strong base in various amines were ascertained, and vicinal diamines, particularly ethylenediamine (EDA), were found to be the most effective solvents. A concerted mechanism involving the EDA anion and the propargyl group in a nine-membered ring transition state is suggested. Since, in the presence of EDA-d_4, the rate of deuterium incorporation into the rearranged products parallels closely the rate of rearrangement, an intramolecular hydrogen transfer is not likely the preferred reaction path.

The base-catalyzed propargylic rearrangement is well known and documented.[2] Jacobs[3] equilibrated the isomeric pentynes with alcoholic potassium hydroxide at 175°. The reaction mixture consisted of 1.3% 1-pentyne, 3.5% 1,2-pentadiene, and 95.2% 2-pentyne.



$$-C{\equiv}C-\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}- \rightleftharpoons -C{=}C{=}\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}-$$

[1] Abstracted in part from the Ph.D. Thesis of Paul M. Barelski, Southern Illinois University, 1972.

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