Pyrolysis Study. XX. Substituent Effects of 3-Aryl-3-buten-1-ols[1]

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The homogeneous unimolecular pyrolyses of seven 3-aryl-3-buten-1-ols have been studied in a deactivated constant-volume stainless steel reactor. Arrhenius parameters have been calculated over the temperature range 619.5–656.9°K. A value of $\rho = -0.59$ evaluated from the Hammett plot indicates modest substituent effects with little or no charge developing at the 3 position in the proposed concerted six-membered transition state. Conjugation of the olefin produced from the pyrolysis and the acidity of the alcohol hydrogen have been postulated as the major factors in controlling the rate of pyrolysis.

β-Hydroxy olefins have been reported to pyrolyze to a simpler olefin and carbonyl compounds by a unimolecular, homogeneous process, likely through a six-membered transition state.[3,4] Recently,[1] the nature of the transition state was studied using substituent effects in 1-aryl-3-buten-1-ol. Earlier Smith and Yates[5] reported the investigation of the influence of a phenyl group at the 3 and 4 positions and alkyl substituents at the 1 position on the ease of thermolysis of 3-buten-1-ol. They found that a π contribution at the 3 position increased the rate of pyrolysis, whereas it decreased the rate at the 4 position of 3-buten-1-ol. They observed the following order of reactivity, tertiary > secondary > primary alcohols, and proposed a transition state consisting of a polarized bond between C-3 and C-4 with a slight positive charge at the 3 position and a small negative charge at the 4 position. Smith and Voorhees recently reported substituent effects in the thermolysis of 1-aryl-3-buten-1-ols.[1] The present study provides quantitative information in the 3-aryl series which also supports the cyclic transition state mechanism with modest charge separation. It is particularly interesting that 1-aryl-3-buten-1-ols were shown to pyrolyze at a rate twice as fast as the most reactive previously reported β-hydroxy olefin;[5] yet the rate follows a regular Hammett $\sigma\rho$ relationship with only modest substituent effects, $\rho = -0.26$.[1]

Results

The 3-aryl-3-buten-1-ols were pyrolyzed in a deactivated stainless steel reactor[6] over a temperature range of 619.5–656.9°K, and the products, formaldehyde and a substituted α-methylstyrene, were identified by mass spectroscopy and nmr analyses, respectively. Table I summarizes the first-order rate constants, temperature, and $1/T$ for the pyrolyses. The first-order rate constants, which were reproducible to ±2%, were obtained over 90% of the reaction. The stoichiometry was determined to be 1:1.95 by a ratio of P_0/P_∞.

Rates were measured under various conditions to test the unimolecularity and homogeneity of the reaction. Radical chain mechanisms were ruled out as cyclohexene, a radical inhibitor, had no effect on the rate of pyrolysis (*e.g.*, k for 3-phenyl-3-buten-1-ol was 8.60×10^{-3} with cyclohexene, compared to 8.60×10^{-3} without cyclohexene at 636.2°K). Surface catalysis for 3-phenyl-3-buten-1-ol was shown to be absent as a tenfold increase in surface to volume ratio had little effect on the rate (*e.g.*, k for 3-phenyl-3-buten-1-ol was 8.98×10^{-3} in an unpacked reactor, compared to 8.61×10^{-3} in a packed reactor at 6.36.2°K). Variation of the sample size (50–200 ml) and initial pressure (80–200 mm) was used for each compound with no effect on the rate or reproducibility between runs.

TABLE I

RATE CONSTANTS, TEMPERATURES, AND $1/T$ FOR THERMOLYSIS OF 3-ARYL-3-BUTEN-1-OLS

Compound	No. of runs	10^2k, sec^{-1}	Temp, °K	$1/T \times 10^3$
3-Phenyl-3-buten-1-ol	2	1.50	649.4	1.540
	3	1.14	641.7	1.558
	3	0.720	631.6	1.583
	2	0.411	620.1	1.613
3-*p*-Fluorophenyl-3-buten-1-ol	3	1.35	649.4	1.540
	3	0.923	640.8	1.561
	3	0.560	632.2	1.582
	3	0.502	626.3	1.597
3-*m*-Methylphenyl-3-buten-1-ol	3	1.33	646.3	1.547
	3	1.00	639.1	1.564
	3	0.749	631.9	1.582
	3	0.452	622.3	1.606
3-*p*-Methylphenyl-3-buten-1-ol	3	1.53	645.9	1.548
	3	1.15	639.2	1.564
	3	0.786	630.4	1.587
	2	0.446	619.5	1.614
3-*m*-Bromophenyl-3-buten-1-ol	3	0.822	650.1	1.538
	3	0.622	642.2	1.557
	3	0.337	631.0	1.585
	3	1.06	656.9	1.528
3-*m*-Methoxyphenyl-3-buten-1-ol	3	1.26	649.3	1.540
	3	0.887	640.6	1.561
	3	0.458	627.0	1.595
3-*p*-Chlorophenyl-3-buten-1-ol	3	1.51	653.6	1.530
	2	0.897	643.5	1.554
	2	0.620	634.8	1.575
	3	0.443	627.7	1.593

Table II is a summary of the Arrhenius parameters for the 3-aryl-3-buten-1-ols obtained by a linear regression analysis of the rate data. The correlation coefficient (> ±0.98) indicates that each compound essentially fit a straight line.

Figure 1 is a Hammett $\sigma\rho$ plot resulting in a ρ value of -0.59 calculated using a linear regression analysis.

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[1] Part XIX: G. G. Smith and K. J. Voorhees, *J. Org. Chem.*, **35**, 2182 (1970).

[2] National Defense Education Act Predoctoral Fellow, 1968–1970.

[3] R. T. Arnold and G. Smolinsky, *J. Org. Chem.*, **25**, 129 (1960).

[4] G. G. Smith and R. Taylor, *Chem. Ind. (London)*, **35**, 949 (1961).

[5] G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

[6] G. G. Smith and J. A. Kirby, *Analyst (London)*, **94**, 242 (1969).

TABLE II
ACTIVATION PARAMETERS FOR 3-ARYL-3-BUTEN-1-OLS

Compound	E_a, kcal	10^3k (619°K)	$\Delta S^{\ddagger}$ (619°K)	Log *A*	Correlation coefficient
3-Phenyl-3-buten-1-ol	35.5	3.98	−13.6	10.1	−0.999
3-*p*-Fluorophenyl-3-buten-1-ol	36.3	3.34	−12.6	10.4	−0.988
3-*m*-Methylphenyl-3-buten-1-ol	35.8	3.89	−13.2	10.2	−0.997
3-*p*-Methylphenyl-3-buten-1-ol	36.7	4.44	−11.4	10.6	−0.998
3-*m*-Methoxyphenyl-3-buten-1-ol	36.8	3.15	−11.9	10.5	−0.999
3-*m*-Bromophenyl-3-buten-1-ol	38.9	1.88	−9.5	11.0	−0.997
3-*p*-Chlorophenyl-3-buten-1-ol	38.4	2.82	−9.5	11.0	−0.999

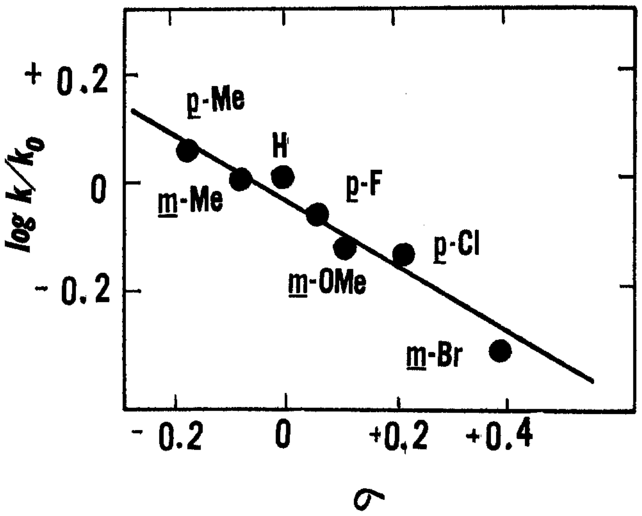

Figure 1. Hammett plot of 3-aryl-3-buten-1-ols at 619°K, $\rho = -0.59$.

Discussion

The results from this study on the pyrolysis of 3-aryl-3-buten-1-ols add additional evidence to substantiate the unimolecularity and homogeneity of the pyrolysis of β-hydroxy olefins; it also supports a six-membered transition state.[1,3–5,7a–c]

The activation energies reported in Table II range between 35.5 and 38.9 kcal/mol with an estimated error of ±2 kcal/mol. The $\Delta S^{\ddagger}$ values, which were calculated assuming $E_a = \Delta H^{\ddagger}$, were −9.5 to −13.6 eu. The estimated error for $\Delta S^{\ddagger}$ was ±3.0 eu.[7d] Both E_a and $\Delta S^{\ddagger}$ were in the expected range based on previously reported values[1,5] and substantiate a cyclic unimolecular process.[7d]

The calculated rate at 619°K for the thermolysis of 3-phenyl-3-buten-1-ol from data reported in this paper is 3.98×10^{-3} compared to 5×10^{-3}, the value reported earlier[5] for this compound. These rates are in reasonable agreement considering the problems associated with maintaining the temperature. The thermocouples used to measure the temperature were located in the thermostat and not directly in the reaction chamber. Although the thermocouples were frequently standardized using a National Bureau of Standards calibrated platinum resistance thermometer, a temperature gradient between the reactor and the thermostat was difficult to evaluate because of a minor but significant difference in insulation of the thermostat.

Knowing this, all substituent effect studies were referred to a standard (3-phenyl-3-buten-1-ol) run under identically the same conditions. The energy and entropy of activation for the unsubstituted 3-phenyl compound were within experimental error (above) of the values reported by Yates.

The results support only a slight charge separation in the transition state. As previously mentioned, Smith and Yates[5] postulated a slight positive charge at the 3 position. This is supported by the fact that the Hammett plot of log k/k_0 *vs.* σ for the 3-aryl-3-buten-1-ol thermolysis was linear, and the ρ was small, $\sigma = 0.59$. Furthermore a plot of Brown and Okamoto's[8] σ^+ *vs.* log k/k_0 gave more scattering of points and less statistical correlation. Even without a *p*-methoxy substituent study a curved plot was obtained when log k/k_0 was correlated with σ^+ substituent constants, particularly for the *p*-methyl substituent.

The 3 position apparently develops a slightly electron-deficient center in the transition state as noted by the size of ρ (−0.59), but the magnitude of this charge is modest. When the value of ρ is small, its sign may change with a change in temperature if the reaction is run near the isokinetic temperature.[8b] The isokinetic temperature for this reaction is 1100°K. This reaction, therefore, was carried out well below this temperature (650°) and the rate is most likely enthalpy controlled. The sign of ρ would not change over a large temperature range. Based on the comparative sizes of ρ, the magnitude of the charge at the 3 position is greater than the value of the charge at the 1 position ($\rho = -0.26$). Considering these two ρ values, it is of particular interest that the 1-aryl-3-buten-1-ols (Table III) have a faster rate of pyrolysis than the 3-aryl-3-buten-1-ol. Apparently, the increased rate of thermolysis by an aryl group at the 1 position cannot be explained by stabilization of the charge separation in the transition state. The 1-aryl substituent must also influence the acidity of the alcohol, along with influencing the rate.

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[7] (a) R. T. Arnold and G. Smolinksy, *J. Amer. Chem. Soc.*, **82**, 4919 (1960); (b) R. T. Arnold and G. Metzger, *J. Org. Chem.*, **26**, 5185 (1961); (c) R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **81**, 6443 (1959); (d) A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965).

[8] (a) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958); (b) J. E. Leffler, *J. Org. Chem.*, **20**, 1210 (1955).

TABLE III

RATE CONSTANTS AND RELATVE RATES FOR THE THERMOLYSIS OF β-HYDROXY OLEFINS

Compound	10^2k, sec^{-1} (619°K)	Rel rate
4-Phenyl-3-buten-1-ol	0.012	1.0
3-Buten-1-ol	0.053	4.4
4-Penten-2-ol	0.131	10.9
2-Methyl-4-penten-2-ol	0.280	23.3
3-Phenyl-3-buten-1-ol	0.50[a]	41.5
	0.40[b]	33.2
1-Phenyl-3-buten-1-ol	1.0	83.0

[a] From ref 5. [b] From this study.

Conjugation has been noted to be especially important in gas-phase reactions[9] and has been used to explain the relative rates for the 3-phenyl- and 4-phenyl-3-buten-1-ols.[5] The sharp increase in rate of pyrolysis. for the 1-aryl-3-buten-1-ols[1] seems to further exemplify the importance of conjugation in explaining the relative rates of pyrolysis for the phenyl-substituted β-hydroxy olefins. 1-Phenyl-3-buten-1-ol pyrolyzes 83 times faster than the 4-phenyl-3-buten-1-ol and almost twice as fast as the 3-phenyl-3-buten-1-ol. The products from these pyrolyses are benzaldehyde and propene from 1-phenyl, formaldehyde and 3-phenyl-propene from 4-phenyl, and formaldehyde and 2-phenylpropene from 3-phenyl-3-buten-1-ol. It is difficult to picture such a drastic change in rate unless the stabilization from conjugation of the products affects in some way the relative energy of the transition state. It also appears that the phenyl group stabilization is greater at the carbonyl position than at the olefinic position on the rate of pyrolysis. A requirement of a delicate balance between bond breaking and bond formation apparently must be present in the transition state of the thermolysis of 1- and 3-substituted 3-buten-1-ol, since data from these thermolyses follow a Hammett σp relationship appreciably better than a σ^+ relationship.

The concept of acidity of the alcohol hydrogen can also be used to explain the observed relative rates between 1-aryl- and 3-aryl-3-buten-1-ols. From the study of Smith and Yates,[5] a sequence of tertiary > secondary > primary was observed in the relative rates of thermolysis of 1-alkyl-substituted β-hydroxy olefins. This corresponds to the observed gas-phase acidity.[10] A similar comparison can be made to explain the difference in the rate of thermolysis for the 1-aryl- and 3-aryl-3-buten-1-ols. Here a comparison is being made also between a secondary and primary alcohol.

The idea of acidity fails to explain the slow rate for the 4-phenyl-3-buten-1-ol. The relative rates of thermolysis for 1-phenyl over 4-phenyl suggest that both conjugation and acidity could be operating as additive factors.

The results from this study have shown the thermolysis of β-hydroxy olefins proceeds through a highly concerted electrocyclic process with no substantial charge separation at any position. Because of the observed changes in the rate of thermolysis in chainging the position of the aryl group, it has been postulated that conjugation and the alcohol acidity are the most important factors in controlling the rate of thermolysis.

Experimental Section

Synthesis of 3-Aryl-3-buten-1-ols.—All of the 3-aryl-3-buten-1-ols were prepared using essentially the same sequence of reactions.[11,12] 3-*p*-Methylphenyl-3-buten-1-ol is given as a typical case. The synthesis of 2-*m*-bromophenylpropene is also included because of the special condition employed for dehydration. A list of yields and physical constants for the intermediates is given in Table IV, and information concerning the 3-aryl-3-buten-1-ols is given in Table V.

2-*p*-Methylphenylpropan-2-ol.—*p*-Methylacetophenone (68 g, 0.5 *M*) diluted by 100 ml of ethyl ether was added to 175 ml (0.5 *M*) of methylmagnesium bromide obtained commercially from Arapahoe Chemicals at −10° over a period of 3 hr. The mixture, which had stirred overnight, was hydrolyzed with a saturated solution of ammonium chloride. The ether layer was separated, dried with anhydrous magnesium sulfate, filtered, and evaporated. Distillation yielded 50 g of 2-*p*-methylphenylpropan-2-ol: bp 65–68° (1 mm); yield 66%; ir strong OH at 3300–3800 cm^{-1}.

2-*p*-Methylphenylpropene.—The 50 g (0.33 *M*) of 2-*p*-methylphenylpropan-2-ol was dissolved in 150 ml of acetic anhydride along with 1 g of sodium acetate and caused to reflux for 16 hr. After this period the excess acetic anhydride was hydrolyzed with a 6 *N* ammonium hydroxide solution and neutralized with a small excess of ammonium hydroxide. The solution was extracted with ether and the aqueous layer discarded. The ether solution was dried with anhydrous magnesium sulfate, filtered, and evaporated. Distillation yielded 31 g of 2-*p*-methylphenylpropene: bp 50–53° (0.65 mm); yield 73%; nmr δ 7.0 (m, aromatic), 4.9 (d, vinyl), 2.0 (s, $ArCH_3$), 1.8 ($CH_2{=}CArCH_3$); ir indicated hydrocarbon with terminal $C{=}CH_2$ at 1690 cm^{-1}.

3-*p*-Methylphenyl-3-buten-1-yl Acetate.—The 31 g (0.24 *M*) of 2-*p*-methylphenylpropene was added to a solution of 12.5 g (0.14 *M*) of paraformaldehyde in 150 ml of glacial acetic acid; the mixture refluxed for 3 hr; then 75 ml of acetic acid was distilled and replaced by 75 ml of acetic anhydride. The solution was neutralized with 6 *N* ammonium hydroxide solution and extracted with ether. The ether solution was dried, filtered, and evaporated. The resulting material was distilled: bp 85–94° (0.2 mm); 23 g; ir strong carbonyl band 1710 cm^{-1}, C–O band at 1030 cm^{-1}.

3-*p*-Methylphenyl-3-buten-1-ol.[9]—Hydrolysis of the 3-*p*-methylphenyl-3-buten-1-yl acetate was accomplished by refluxing 23 g (0.11 *M*) of the acetate with 5 g (0.13 *M*) of sodium hydroxide in 100 ml of 80% ethanol for 2 hr. After refluxing, the solution was cooled, washed with two 100-ml portions of water, and separated. Distillation yielded 20 g of material, bp 74–75° (0.15 mm), yield 25%, containing two products, identified from ir and nmr as 3-*p*-methylphenyl-2-buten-1-ol and 3-*p*-methylphenyl-3-buten-1-ol. Separation of 3-*p*-methylphenyl-3-buten-1-ol was accomplished (81% based on injection sample) by vpc using a 20-ft, 15% Carbowax 20M preparative column at 190° and flow rate of 26 cm^3/min: $n^{25}{}_D$ 1.5528; nmr δ 7.2 (m, aromatic) 5.1 (d, vinyl), 4.0 (t, CH_2CH_2OH), 3.0 (t, CH_2CH_2-OH), 2.6 (s, $ArCH_3$), 2.0 (s, CH_2OH); ir strong OH at 3400–3700 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.68; H, 8.86.

2-*m*-Bromophenylpropene.—*m*-Bromoacetophenone (75 g, 0.33 *M*) diluted with 100 ml of ethyl ether was added to 135 ml (0.33 *M*) of methylmagnesium bromide at −10° over a period of 2 hr. This mixture, which had stirred overnight, was hydrolyzed with a saturated solution of ammonium chloride. The ether layer was separated, dried, filtered, and concentrated on a rotoevaporator. The remaining organic portion was refluxed with 175 ml of acetic anhydride and 1 g of sodium acetate for 24 hr. At the end of this time the solution was hydrolyzed and neutralized with 6 *N* ammonium hydroxide solution. The solution was extracted with ether and the aqueous layer discarded. The ether layer was dried with anhydrous magnesium sulfate, filtered, and concentrated on a rotoevaporator. Distillation produced a compound, bp 110–112° (0.75 mm), that was later identified as 2-*m*-bromophenylpropan-2-yl acetate; the ir had a strong carbonyl band at 1730 cm^{-1}.

Since this method had not produced the desired substituted α-methylstyrene, the ester dissolved in 150 ml of cyclohexene

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(9) A. Maccoll and P. J. Thomas, *Progr. React. Kinet.*, **4**, 119 (1967).

(10) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968).

(11) C. C. Price, J. L. Benton, and C. J. Schmidle, *ibid.*, **71**, 2860 (1949).

(12) E. G. C. Hawkins and R. D. Thompson, *J. Chem. Soc.*, 370 (1961).

TABLE IV

SUMMARY OF INTERMEDIATES IN THE SYNTHESIS OF 3-ARYL-3-BUTEN-1-OLS[a,b]

		2-Aryl-2-propanol			2-Arylpropene			3-Aryl-3-buten-1-yl acetate		
Substituent	Compd no.	Registry no.	Bp, °C (mm)	Yield, g	Registry no.	Bp, °C (mm)	Yield, g	Registry no.	Bp, °C (mm)	Yield, g
H	10							7306-12-9	99–103 (0.1)	46.8
p-CH$_3$	11	1197-01-9	65–68 (1.0)	50	1195-32-0	50–53 (0.65)	31	29128-15-2	85–94 (0.2)	23
p-F	12	402-41-5	54–57 (0.8)	55	350-40-3	34–38 (0.7)	39.2	29128-16-3	103–109 (0.25)	29
m-CH$_3$	13				1124-20-5	44–46 (0.6)	52.9	29128-17-4	85–90 (0.38)	40.3
m-OCH$_3$	14				25108-57-0	54–56 (0.52)	30.5	29128-18-5	115–120 (0.2)	31.5
p-Cl	15	1989-25-9	70–75 (0.6)	46	1712-70-5	60–62 (0.1)	40	29128-19-6	104–110 (0.20)	16
m-Br	16				25108-58-1	63–64 (0.3)	31.1	29128-20-9	108–111 (0.53)	10.1

[a] All reagents were used in the same molar ratios as for 3-*p*-methylphenyl-3-buten-1-ol. Reflux and reaction times were also simliar. [b] Spectra were recorded for all pure intermediates and were comparable to those described for 3-*p*-methylphenyl-3-buten-1-ol.

TABLE V

PHYSICAL CONSTANTS AND YIELDS OF 3-ARYL-3-BUTEN-1-OLS

					Calcd, %		Found, %		
Compound	Registry no.	Index of refraction, $n^{25}\text{D}$	Bp, °C (mm)	Yield,[a] %	C	H	C	H	Hal
3-Phenyl-3-buten-1-ol	3174-83-2	1.5557[b]	99–101 (0.10)	37.1	81.04	8.10	81.21	8.20	
3-*p*-Methylphenyl-3-buten-1-ol	29128-22-1	1.5528	74–75 (0.15)	20.3	81.44	8.70	81.68	8.86	
3-*p*-Fluorophenyl-3-buten-1-ol	29123-91-9	1.5324	107–108 (0.25)	22.1	72.29	6.63	72.51	6.80	11.31[c]
3-*p*-Chlorophenyl-3-buten-1-ol	29123-92-0	1.5699	121 (0.45)	5.7	65.76	6.07	65.54	6.01	19.15[d]
3-*m*-Methylphenyl-3-buten-1-ol	29123-93-1	1.5503	84–86 (0.36)	21.0	81.44	8.70	81.60	8.69	
3-*m*-Bromophenyl-3-buten-1-ol	29123-94-2		123–125 (0.26)	5.5	52.86	4.85	52.98	4.86	35.49[e]
3-*m*-Methoxyphenyl-3-buten-1-ol	29123-95-3	1.5554	108–109 (0.34)	14.7	74.13	7.92	74.27	7.86	

[a] Corrected for impurity. [b] Lit.[10] $n^{25}\text{D}$ 1.5580. [c] Calcd 11.31%. [d] Calcd 19.42%. [e] Calcd 35.24%.

was passed through a Pyrex tube packed with glass tubing under nitrogen at 500°. The product was collected in a Dry Ice–isopropyl alcohol cold trap and, after distillation of the cyclohexene, 31.1 g of 2-*m*-bromophenylpropene was collected: bp 63° (0.30 mm); yield 47%; nmr δ 7.4 (m, aromatic), 5.4 (d, vinyl), 2.1 (CH$_3$C=CH$_2$); ir had a terminal double bond at 1600 cm^{-1}.

Method of Pyrolysis.—The kinetics of thermolysis were done in a deactivated stainless steel reactor[6] fitted with a null point gauge and an exterior pressure measuring system. A small sample (100–150 μl) of the alcohol was injected into the system, the reactor sealed, and the pressure change followed with time. A pressure at $t = \infty$ was determined and a plot of $\ln (P_\infty - P_t)$ *vs.* time, where P_t is the pressure at time t, was used to obtain the first-order rate constants. The temperature of the pyrolysis thermostat was measured to ±0.1° by two chromel–alumel thermocouples, previously standardized against a National Bureau of Standards calibrated platinum resistance thermometer linked in series with an ice bath.

Product Analysis.—The pyrolysis products from three or four 0.3-ml injections were collected in a Dry Ice–isopropyl alcohol trap attached in the vacuum line directly behind the exhaust valve on the reactor. To ensure that all products were retained in the trap, the trap was kept at −78° until the gaseous material was distilled. Since the products from the pyrolysis of 3-aryl-3-buten-1-ol are formaldehyde and 2-arylpropene, it was necessary to distil the formaldehyde directly into a mass spectrometer gas cell and analyze directly by mass spectroscopy. The 2-arylpropenes were dissolved in Silinar C for nmr analysis.

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