

moderately low and distributions are broad (as will frequently be the case) there may be no satisfactory method for direct determination of number aver-

ages. In such cases, separation into low and high fractions and separate determination by appropriate procedures may be necessary.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH., AND UTAH STATE UNIVERSITY, LOGAN, UTAH]

## Substituent Effects in Pyrolysis. V.<sup>1,2</sup> A $\rho$ - $\sigma^+$ Correlation in the Pyrolysis of 1-Arylethyl Acetates

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A kinetic study of the gas-phase thermal decomposition of a number of 1- and 2-arylethyl acetates has been made between 297.8° and 409.2°. Each ester was pyrolyzed at four different temperatures and over a temperature range of not less than 50° in a static system at reactant pressures of 6 to 200 mm.; the energies and entropies of activation range, respectively, from 41.7 to 44.7 kcal./mole and +0.34 to -2.66 e.u. for the 1-arylethyl acetates, and from 44.8 to 45.9 kcal./mole and -3.24 to -3.67 e.u. for the 2-arylethyl acetates. A plot of  $\log k_{rel}$  for the effects of the substituents in the 1-aryl series at 600°K. against  $\sigma^+$ -constants (Brown and Okamoto<sup>4</sup>) gives an excellent correlation ( $\rho = -0.66$ ) thus proving that the elimination of acetic acid proceeds *via* a mechanism in which some charge separation occurs, as has recently been suggested.<sup>5</sup> The importance of the breaking of the carbon-hydrogen and single carbon-oxygen bonds in the reaction mechanism has been further evaluated.

It has been recently emphasized by the work of Brown,<sup>4</sup> Bartlett,<sup>6</sup> Lossing<sup>7</sup> and others<sup>8</sup> that reactions which follow a  $\rho$ - $\sigma^+$  relationship must involve an electron-deficient intermediate, transient or otherwise, which can be stabilized in the rate-determining transition state by electron release from an aromatic ring. If a reaction involves an electron deficient center, such as a fully or partially formed carbonium ion, the correlation between the logarithms of the relative rates and Hammett's  $\sigma$ -constants is unsatisfactory.

In a recent study of the gas-phase thermal decomposition of 1,2-diarylethyl acetates, Smith,

(1) Part IV, G. G. Smith, F. D. Bagley and R. Taylor, *J. Am. Chem. Soc.*, **83**, 3647 (1961).

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(4) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

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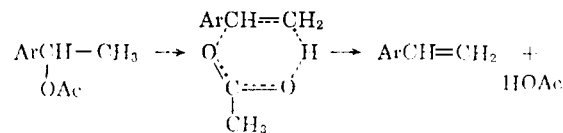
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(8) (a) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); D. E. Pearson and J. D. Burton, *ibid.*, **19**, 957 (1954); (b) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Am. Chem. Soc.*, **76**, 4525 (1954); (c) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953); G. S. Hammond, *et al.*, *ibid.*, **80**, 563, 568, 573 (1958); (d) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955); (e) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957); (f) J. Miller, *Austral. J. Chem.*, **9**, 61 (1956); (g) Y. Tsuno, T. Iyata and Y. Yukawa, *Bull. Chem. Soc. Japan*, **32**, 960, 965 (1959); (h) Y. Ogata and I. Tabushi, *J. Am. Chem. Soc.*, **83**, 3440, 3444 (1961).

Bagley and Taylor<sup>1</sup> showed that substituents in the 1-aryl ring caused a greater change in the rate of pyrolysis than substituents in the 2-aryl ring. A plot of  $\log k_{rel}$  ( $\log k/k_0$ ) for the effects of substituents in the 1-aryl ring at 600°K. against Hammett's  $\sigma$ -constants gave a poor correlation.<sup>1</sup> However, when the values of  $\log k_{rel}$  are plotted against  $\sigma^+$ -constants (Brown and Okamoto<sup>4</sup>) a very satisfactory correlation is obtained (see Fig. 1), with  $\rho = -0.62$ .

A series of 1-arylethyl acetates have been prepared and pyrolyzed in order to evaluate the effects of a large number of substituents in the gas phase for the following three reasons: (a) The small  $\rho$ -factor for the reaction permits examination of the effects of substituents with a wide range of reactivities all under identical conditions. (b) The results from this gas phase study can be readily compared with condensed phase electrophilic aromatic substitution since they are all correlated by  $\sigma^+$ -values. (c) The preparation of the 1-arylethyl acetates involve simpler preparative procedures than the 1,2-diarylethyl acetates. For comparative purposes, studies were made on four 2-arylethyl acetates.



The thermal decomposition of esters into olefins and acids has been shown to be a first-order reaction which is unimolecular, homogeneous, and generally has a negative entropy of activation.<sup>5,9</sup> The thermal stability of the esters has been shown to be a function of molecular weight<sup>10</sup> and substit-

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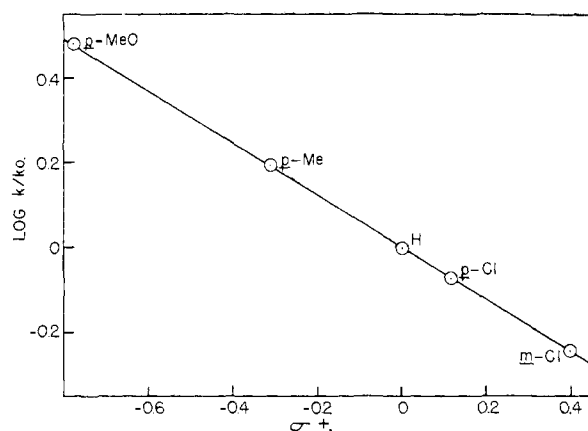


Fig. 1.—Hammett  $\rho\text{-}\sigma^+$  plot of 1-aryl-2-phenylethyl acetates at 600°K.

uents in the acyl group of the ester.<sup>9b,10b,11</sup> Where more than one olefin may arise because of elimination of a hydrogen atom from different  $\beta$ -carbon atoms, the direction of elimination is thought to be governed by the number of *cis*-hydrogens,<sup>12</sup> crowding in the transition state<sup>9c,12h</sup> by the stability of the forming olefin as measured by the thermodynamic stability of the olefin produced,<sup>12k,13</sup> and the acidity of the  $\beta$ -hydrogen atom.<sup>12k,13,14</sup> A study of the  $\beta$ -deuterium isotope effect has shown the carbon-hydrogen bond is likely to be broken in the rate-determining transition state of the reaction. In our previous paper we showed that in the pyrolysis of 1,2-diarylethyl acetates, substituents in the 1-aryl ring had a greater effect on the rates of pyrolysis than substituents in the 2-aryl ring.<sup>1</sup> In this paper we have compared the effects of substituents on the rates of pyrolysis of 1- and 2-arylethyl acetates to determine further which of the single carbon-oxygen and carbon-hydrogen bond-breaking processes appears to be the most important in the rate-determining stage of the reaction. Substituents in the aryl ring of the 1-arylethyl acetates will affect the breaking of the single carbon-oxygen bond, while substituents in the aryl ring of the 2-arylethyl acetates will affect the breaking of the carbon-hydrogen bond. Further, we have compared the pyrolysis rates of the 1- and 2-arylethyl acetates with the pyrolysis rates previously obtained for the corresponding 1,2-diarylethyl acetates, in order to determine the effect of a phenyl group attached directly to

the carbon atoms possessing the single carbon-oxygen, and carbon-hydrogen bonds under discussion.

### Experimental

**Ester Preparations.**—The esters were prepared from the appropriate alcohols according to procedures A or B. These alcohols which were commercially unavailable were prepared by sodium borohydride reduction of the alkyl ketones (method C), or by the reaction of the appropriate aryl magnesium bromide with acetaldehyde or ethylene oxide according to the method of Grignard<sup>15</sup> (method D). Physical constants of the esters are listed in Table I. Intermediates were prepared by known procedures and their physical constants agreed with those reported.

**Method A.**—The appropriate aryl ethanol was acetylated by the method of Shriner and Fuson.<sup>16</sup>

**Method B.**—A slight molar excess of acetyl chloride was added to the appropriate aryl ethanol cooled in an ice-bath. After the exothermic reaction had ceased, the mixture was gently refluxed for 5 minutes, cooled, and dissolved in ether. The ethereal solution was washed successively with water, 5% sodium carbonate solution and water, dried over anhydrous magnesium sulfate, and fractionated.

**Method of Pyrolysis.**—The method and apparatus used for determining the reaction kinetics have previously been described.<sup>1,17</sup> All samples, with the exception of the *p*-acetylamino, *o*-biphenyl and 2-fluorenyl esters, were liquids and were injected into the furnace as such (25–250- $\mu$ l. samples); these three esters were injected into the furnace as solutions in chlorobenzene, this solvent having been observed to be stable under the reaction conditions.

Reaction rates were determined for each ester at four different temperatures and over a temperature range of not less than 50°.

### Results

The rates of pyrolysis of 1-arylethyl acetates at various temperatures are given in Table II. For most esters,  $\log (P_\infty - P_t)$  vs. time plots are linear to beyond 95% of reaction, which indicated that the reactions followed first-order kinetics, and rates could be duplicated to better than  $\pm 2\%$ . However, for the *m*-nitro ester, a secondary reaction took place which gave an over-all reaction stoichiometry of three instead of the value two obtained with the other esters. The secondary reaction appeared to be slower than the elimination reaction, and therefore  $P_\infty$  for the elimination reaction was taken as two-thirds of the value of  $P_\infty$  actually obtained in each run. The value of  $k$ , the rate constant, for the *m*-nitro ester only was calculated from the initial slope of the  $\log (P_\infty - P_t)$  vs. time plot so obtained. The rate constants for this ester are not considered to be accurate, therefore, to better than  $\pm 10\%$ . The *m*-bromo ester exhibited a fall-off in rate with time for a reason which could not be ascertained but was possibly due to the presence of a trace impurity since the ester was slightly colored. Rates calculated from the initial slopes of the  $\log (P_\infty - P_t)$  vs. time plots were identical (within experimental error) with rates interpolated from the Arrhenius plot for the *m*-chloro ester. However, in view of the uncertainty of the accuracy of the results obtained with this ester, they are not given in Table II. From the kinetics obtained with the *p*-acetylamino ester, a scatter was obtained on the Arrhenius plot and the slope of the best straight line through

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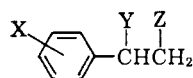
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TABLE I  
ARYLETHYL ACETATES

X	Y	Z	Method of prepn. <sup>b</sup>	Over-all yield, %	M.p. or b.p. °C. (mm.)	n <sub>D</sub> <sup>20</sup>	Carbon, % <sup>a</sup>		Hydrogen, % <sup>a</sup>	
							Calcd.	Found	Calcd.	Found
<i>p</i> -OCH <sub>3</sub>	H	AcO	A	67	158–159 (27) <sup>c</sup>	1.5070	68.02	68.00	7.27	7.26
<i>p</i> -CH <sub>3</sub>	H	AcO	B	61	121–121.5 (11) <sup>d</sup>	1.4976	74.13	73.91	7.91	7.87
H	H	AcO	A	74	118 (17) <sup>e</sup>	1.4968				
<i>m</i> -Cl	H	AcO	B	69	132–133 (11)	1.5123	60.46	60.44	5.58	5.66
<i>m</i> -NO <sub>2</sub>	AcO	H	C	71	131 (1.6)	1.5225	57.41 <sup>aa</sup>	57.55	5.30	5.36
<i>p</i> -F	AcO	H	D <sup>f</sup>	35	76 (2.0)	1.4802	65.91	66.00	6.08	6.23
<i>m</i> -F	AcO	H	D <sup>g</sup>	32	70 (1.1)	1.4799	65.91	66.08	6.08	6.28
<i>p</i> -Cl	AcO	H	C <sup>h</sup>	62	88 (1.1)	1.5087	60.46	60.51	5.58	5.68
<i>m</i> -Cl	AcO	H	B <sup>i</sup>	72	65–66 (0.5)	1.5116	60.46	60.53	5.58	5.66
<i>p</i> -Br	AcO	H	D <sup>j</sup>	44	108 (2.0)	1.5351	49.40	49.79	4.56	4.56
<i>m</i> -Br	AcO	H	D <sup>k</sup>	29	96 (1.1)	1.5295	49.40	49.61	4.56	4.62
<i>p</i> -I	AcO	H	C	85	114 (1.1)	1.5647	41.40	41.17	3.83	3.79
<i>m</i> -I	AcO	H	C	80	112 (1.0)	1.5653	41.40	41.36	3.83	3.81
H	AcO	H	A	67	105–108 (15) <sup>l</sup>	1.4998				
<i>o</i> -Ph	AcO	H	D <sup>m</sup>	54	134 (0.8)		79.97	79.96	6.71	6.82
					M.p. 54					
<i>m</i> -Ph	AcO	H	D <sup>n</sup>	46	145 (1.0)	1.5840	79.97	79.73	6.71	6.68
<i>p</i> -Ph	AcO	H	C <sup>o</sup>	76	165 (1.5)	1.5735	79.97	79.90	6.71	6.56
3,4-C <sub>7</sub> H <sub>5</sub> <sup>p</sup>	AcO	H	C <sup>q</sup>	75	52–53		80.93	81.09	6.39	6.38
2,3-C <sub>4</sub> H <sub>4</sub> <sup>r</sup>	AcO	H	C <sup>s</sup>	53 <sup>t</sup>	126 (0.8)	1.5758	78.48	78.08	6.58	6.48
3,4-C <sub>4</sub> H <sub>4</sub> <sup>u</sup>	AcO	H	C <sup>v</sup>	86	130 (0.9)	1.5734	78.48	78.10	6.58	6.63
<i>o</i> -CH <sub>3</sub>	AcO	H	D <sup>w</sup>	52	80 (2)	1.4991	74.13	74.40	7.91	7.96
<i>p</i> -CH <sub>3</sub>	AcO	H	A	69	105–106 (21)	1.4934	74.13	74.04	7.91	7.82
<i>o</i> -OCH <sub>3</sub>	AcO	H	D <sup>x</sup>	53	105 (2.2)	1.5050	68.02	68.27	7.27	7.23
<i>p</i> -OCH <sub>3</sub>	AcO	H	C <sup>y</sup>	65	153–154 (27)	1.5039	68.02	67.93	7.27	7.27
<i>p</i> -NHCCH <sub>3</sub>	AcO	H	C	67	102 <sup>z</sup>		65.13 <sup>bb</sup>	65.08	6.83	6.60
<i>p</i> - <i>t</i> -Bu	AcO	H	D	45	96 (2.0)	1.5011	76.33	76.30	9.15	9.04

<sup>a</sup> Analyses were made by A. Bernhardt, Mülheim, Germany. <sup>b</sup> The general methods of preparation, A, B, C and D are given in the Experimental section. <sup>c</sup> N. Tiffeneau, *Ann. chim. phys.*, 10, 350 (1907), gave b.p. 156–157° (11). <sup>d</sup> K. Kindler and L. Blaas, *Ber. deut. chem. Ges.*, 77B, 585 (1944), gave b.p. 119–122° (12). <sup>e</sup> Br. Rodzrogowski, *ibid.*, 9, 373 (1876), gave b.p. 212°. G. H. Gladstone, *J. Chem. Soc.*, 45, 246 (1884), gave *n*<sub>D</sub><sup>20</sup> 1.5108. <sup>f</sup> Prepared from Eastman Kodak Co. *p*-bromofluorobenzene. <sup>g</sup> Prepared from Eastman Kodak Co. *m*-bromofluorobenzene. <sup>h</sup> Prepared from Eastman Kodak Co. *p*-chloroacetophenone. <sup>i</sup> The intermediate alcohol was purchased from the Aldrich Chemical Co. <sup>j</sup> Prepared from Eastman Kodak Co. *p*-dibromobenzene. <sup>k</sup> Prepared from Eastman Kodak Co. *m*-dibromobenzene. <sup>l</sup> J. Marshall, *J. Chem. Soc.*, 107, 523 (1915), gave b.p. 105–108° (15). <sup>m</sup> Prepared from Eastman Kodak Co. *o*-bromobiphenyl. <sup>n</sup> The intermediate *m*-bromobiphenyl was prepared in over-all yield of 70% from *m*-aminobiphenyl (Aldrich Chemical Co.) by the method of W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, *J. Am. Chem. Soc.*, 68, 1111 (1946). <sup>o</sup> Prepared from Eastman Kodak Co. *p*-phenylacetophenone. <sup>p</sup> 1-(2-Fluorenyl)-ethyl. <sup>q</sup> The intermediate 2-acetylfluorene, m.p. 123°, was prepared in 71% yield from fluorene (Eastman Kodak Co.) by the method of F. E. Ray and G. Rieveschl, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 23. <sup>r</sup> 1-( $\alpha$ -Naphthyl)-ethyl. <sup>s</sup> Prepared from Eastman Kodak Co. 1-acetonaphthone. <sup>t</sup> After suffering mechanical loss. <sup>u</sup> 1-( $\beta$ -Naphthyl)-ethyl. <sup>v</sup> Prepared from Eastman Kodak Co. 2-acetonaphthone. <sup>w</sup> Prepared from Eastman Kodak Co. *o*-bromotoluene. <sup>x</sup> Prepared from Eastman Kodak Co. *o*-bromoanisole. <sup>y</sup> Prepared from Eastman Kodak Co. *p*-methoxyacetophenone. <sup>z</sup> M. L. Rousset, *Bull. soc. chim. France*, 11, 322 (1894), gave 192° for m.p. <sup>aa</sup> Nitrogen, %, calcd., 6.69; found, 6.79. <sup>bb</sup> Nitrogen, %, calcd., 6.33; found, 6.33.

these points was very different from the slopes obtained with the other esters. Further, the reactivity of the *p*-acetylamino ester at 600°K. was very much greater than would be expected from a consideration of the  $\sigma^+$ -value of the *p*-acetylamino group. The reason for this behavior was not clear, but it was not due to the *p*-acetylamino ester being injected into the furnace as a solution in chlorobenzene, for solutions of other esters in this solvent gave rate constants identical, within experimental error, with those obtained with the pure liquids. In some preliminary runs, surface reactions were obtained, particularly with those

esters which are strongly activated by time-variable electron release from the substituent. Surface reactions were manifest in reaction orders of between zero and one, the pyrolysis rates being non-reproducible and considerably faster than those which were subsequently obtained by the first-order reaction; under these conditions the pressure in the reactor rose to a maximum and then slowly decreased, indicating that a surface-catalyzed polymerization of the reaction products was taking place. It was discovered that 3-butenic acid, injected into the reactor at 400°, pyrolyzed very rapidly in a reaction of

TABLE II  
KINETIC DATA FROM PYROLYSIS OF 1-ARYLETHYL ACETATES,  
 $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OCOCH}_3$

X	Temp., °C.	$10^4k$ , sec. <sup>-1</sup>	$E_a$ , kcal./ mole	$\Delta S^\ddagger$ , e.u. at 600°K.	$\log$ $k/k_0$ at 600°K.
<i>p</i> -MeO	343.5	5.78	41.7	-2.66	0.500
	328.6	2.38			
	312.0	0.930			
	297.8	0.403			
3,4-C <sub>2</sub> H <sub>5</sub>	365.3	14.8	43.4	-0.08	.395
	349.7	6.65			
	336.0	3.20			
	315.0	0.820			
<i>o</i> -MeO	366.6	12.9	43.6	- .33	.260
	343.4	3.44			
	331.7	1.69			
	308.5	0.404			
<i>o</i> -Ph	369.0	13.6	44.1	.34	.235
	343.8	3.50			
	331.3	1.60			
	318.4	0.686			
<i>p</i> - <i>t</i> -Bu	369.0	12.9	43.4	- .82	.220
	345.0	3.58			
	331.2	1.50(5)			
	315.9	0.598			
<i>o</i> -Me	369.0	12.7	43.6	- .56	.215
	345.0	3.40			
	331.2	1.47			
	313.9	0.506			
<i>p</i> -Me	364.3	9.32	43.2	-1.32	.190
	345.2	3.41			
	325.5	1.01			
	312.0	0.445			
2,3-C <sub>2</sub> H <sub>5</sub>	368.6	10.5	43.8	-0.60	.140
	344.4	2.84			
	327.9	0.986			
	314.2	0.445			
<i>p</i> -Ph	368.6	10.5	43.8	- .60	.140
	343.0	2.47			
	327.9	1.01			
	313.7	0.430			
3,4-C <sub>2</sub> H <sub>5</sub>	368.6	9.80	43.8	- .70	.115
	344.4	2.67			
	327.6	0.953			
	312.7	0.384			
<i>p</i> -F	384.0	18.5	43.6	-1.36	.035
	363.4	6.48			
	343.2	2.01			
	329.8	0.940			
H	367.5	7.25	43.7	-1.25	.000
	345.2	2.14			
	327.9	0.760			
	311.5	0.274			
<i>m</i> -Ph	384.7	17.6	43.7	-1.25	.000
	363.8	6.33			
	343.5	1.84			
	329.8	0.881			
<i>p</i> -Cl	364.0	5.17	44.1	-1.20	- .070
	343.7	1.65			
	331.9	0.793			
	311.5	0.238			
<i>p</i> -I	384.9	16.0	44.6	-0.38	- .080
	366.2	5.72			
	342.0	1.45			
	329.5	0.725			
<i>p</i> -Br	385.6	14.95	44.1(5)	-1.07	- .110
	365.5	5.48			
	342.9	1.43			
	330.0	0.700			
<i>m</i> -I	385.1	11.5(5)	44.4	-1.21	- .230
	365.9	4.21			
	341.8	1.02			
	330.7	0.560			
<i>m</i> -Cl	381.0	8.70	44.4	-1.22	- .245
	364.0	3.53			
	345.2	1.18			
	329.5	0.475			
<i>m</i> -F	384.2	10.5	44.7	-0.96	- .245
	363.0	3.38			
	345.2	1.20			

<i>m</i> -NO <sub>2</sub>	325.9	0.374	44.5	-1.88	- .420
	384.2	7.05			
	364.3	2.53			
	345.6	0.750			
<i>m</i> -Br	327.5	0.296	See text		
	<i>p</i> -NHCOCH <sub>3</sub>	See text			

stoichiometry *ca.* three and coated and deactivated the reactor surface. On fresh stainless steel, four separate 100- $\mu$ l. samples of this acid injected at 400° were sufficient to deactivate completely the surface of a reactor of *ca.* 185-ml. capacity, as shown by the fact that repeated injections of this acid produced no further decrease in the pyrolysis rates of the esters, and the reaction kinetics were first order. The indications were that the *p*-acetylamino ester was extremely sensitive to surface reactions, since it has an activation energy considerably lower than the other esters; however, repeated injections of 3-butenic acid into the reactor failed to produce any noticeable effect on the rates of pyrolysis of the *p*-acetylamino ester. The cause for the abnormal kinetics obtained with this ester was not investigated further.

The rates of pyrolysis of the 2-arylethyl acetates are given in Table III. These pyrolyzed much more slowly than the 1-arylethyl acetates in the time normally taken as  $P_\infty$  (ten times the half-life), decomposition of the acetic acid produced in the reaction was appreciable, and the reaction stoichiometry was slightly greater than two in this time. Rate constants were therefore obtained by using the  $P_\infty$  value calculated from  $P_0$ , ( $P_\infty = 2P_0$ ) and the values of  $k$  were calculated from the initial slopes of the  $\log(P_\infty - P_t)$  vs. time plots so obtained. In the two aryl series rate constants were considered to be accurate to only  $\pm 4\%$  because of the complication from the secondary reaction.

TABLE III  
KINETIC DATA FROM PYROLYSIS OF 2-ARYLETHYL ACETATES,  
 $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OCOCH}_3$

X	Temp., °C.	$10^4k$ , sec. <sup>-1</sup>	$E_a$ , kcal./mole	$\Delta S^\ddagger$ , e.u., at 650°K.	$\log k/k_0$ at 650°K.
<i>m</i> -Cl	409.2	6.95	44.8	-3.43	0.13
	381.0	1.88(5)			
	364.9	0.730			
H	409.2	5.57	45.4	-3.67	.00
	381.0	1.47			
	367.5	0.650			
<i>p</i> -Me	409.2	5.45	45.4	-3.67	.00
	381.0	1.50			
	366.5	0.65			
<i>p</i> -MeO	405.0	3.93	45.9	-3.24	- .08
	382.3	1.16			
	364.6	0.460			
	343.0	0.121			

The Arrhenius diagrams on 1- and 2-arylethyl acetates were linear for all of the compounds which were studied. The energies and entropies of activation and the logarithms of the relative reaction rates  $\log k_{\text{rel}}$  given in Tables II and III were calculated from Arrhenius diagrams at 600°K. for the 1-arylethyl acetates, and at 650°K. for the 2-

arylethyl acetates, respectively. In calculating the entropy it was assumed that  $E_a$  was equal to  $\Delta H^\ddagger$  and that the transmission coefficient was equal to one. The maximum errors which can arise from calculating the energies and entropies of activation over a 50° range are  $\pm 0.6$  kcal. and  $\pm 1.0$  e.u., respectively, for esters whose rates are determined to  $\pm 2\%$  accuracy;  $\pm 1.2$  kcal. and  $\pm 1.9$  e.u., respectively, for esters whose rates are determined to  $\pm 4\%$  accuracy; and  $\pm 2.9$  kcal., and  $\pm 4.5$  e.u., respectively, for the *m*-nitro ester.

### Discussion

As expected from the results obtained with the 1,2-diarylethyl acetates (Fig. 1), a plot of the logarithms of the relative rates of pyrolysis of the *meta* and *para* 1-arylethyl acetates against  $\sigma^+$ -constants<sup>4</sup> gives a straight line (Fig. 2); the  $\rho$ -value of  $-0.66$  at 600°K. agrees within experimental error with the value (0.62) obtained from the pyrolysis of 1,2-diarylethyl acetates. In both series  $\rho$  decreases with increasing temperature. The sign and magnitude of the  $\rho$ -factor of a reaction is considered to be a measure of the charge separation in the rate-determining transition state, and our value of  $-0.66$  therefore indicates a small degree of charge separation in the transition state, in agreement with the prediction of DePuy and King.<sup>5</sup> The decrease in the value of  $\rho$  on going to a higher temperature may be explained on the basis of the selectivity-reactivity theory of Brown, *et al.*<sup>18</sup> Ester pyrolysis takes place more readily at higher temperatures, and thus there is less selectivity between the substituted and unsubstituted esters.

It is noted that in each series of esters the activation energies of the esters increase as the reaction rate decreases while the entropies of activation are constant within experimental error (see Tables II and III, and Table III, ref. 1). This is as one would expect for a reaction largely controlled by activation energies.

**Relative Importance of the Single Carbon-Oxygen and Carbon-Hydrogen Bond-breaking Processes.**—The  $\rho$ -factor for the effects of substituents in the pyrolysis of 2-arylethyl acetates at 650°K. (Table III) is *ca.* 0.3; *i.e.*, substituents which withdraw electrons and hence increase the acidity of the  $\beta$ -hydrogen increase the rate of pyrolysis. This  $\rho$ -factor is numerically less than that obtained ( $-0.66$ ) for the effects of substituents in the pyrolysis of 1-arylethyl acetates and thus these results are in agreement with our previous observations<sup>1</sup> with the 1,2-diarylethyl acetates, *viz.*, that substituents in the 2-aryl ring have a smaller effect on the rate than substituents in the 1-aryl ring. It is therefore apparent that the strength of the carbon-oxygen bond (which is reflected in the stability of the partially-formed carbonium ion) is more important in determining the stability of the ester, than the strength of the carbon-hydrogen bond. Macoll's suggestion that the stability of esters in pyrolysis is primarily determined by nucleophilic attack of the acyl group

(18) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **75**, 6292 (1953); **76**, 605 (1954); **77**, 2300 (1955); **78**, 6255 (1956); **80**, 4046 (1958); **81**, 3323, 3315 (1959).

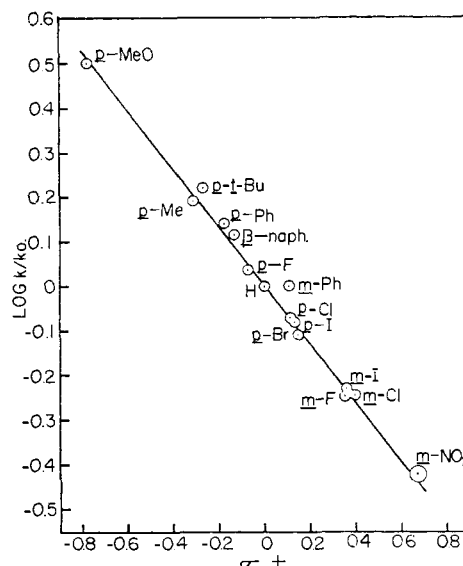
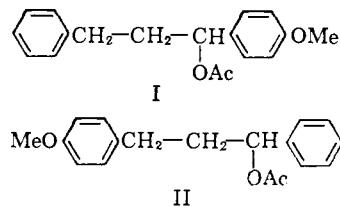


Fig. 2.—Hammett  $\rho$ - $\sigma^+$  plot for pyrolysis of 1-arylethyl acetates at 600°K.

upon the  $\beta$ -hydrogen atom<sup>19</sup> does not seem justified in the light of our results.

Although DePuy and Leary have proposed that the strength of the forming olefinic bond is an important factor in determining the direction of elimination,<sup>13</sup> from the results reported on the pyrolysis of 1,2-diarylethyl acetates<sup>1</sup> and the discussion below, the effect of olefin stability on the ease of pyrolysis of esters is not thought to be significant. Regardless of the importance of the olefin stability on the ease of pyrolysis, the relative importance of the carbon-hydrogen and single carbon-oxygen bond-breaking processes would be unaffected since the olefins formed from the isomeric 1- and 2-arylethyl acetates are identical. (Likewise the olefins formed from the isomeric 1,2-diarylethyl acetates were identical for a given substituent.)

The small  $\rho$ -factor for the pyrolysis of 1-arylethyl acetates shows that the rate-determining stage of the reaction occurs early along the reaction path. At this stage, however, the degree of olefin formation will be very small, and hence it is difficult to envisage that the stability of the forming olefin will influence the direction of elimination. In support of their hypothesis, DePuy and Leary<sup>13</sup> reported that 1-(4-methoxyphenyl)-3-phenyl-1-propyl acetate (I) pyrolyzed 3.7 times more rapidly than 3-(4-methoxyphenyl)-1-propyl acetate (II) under identical conditions, the olefin formed from I being known to be more stable than that formed

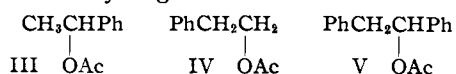


from II. This relative rate factor is very close to the values (3.03, 3.16) obtained by us for the in-

(19) A. Maccoll, *J. Chem. Soc.*, 3398 (1958).

crease in rates over those of the unsubstituted compounds, due to a *p*-methoxy group substituted in the 1-aryl ring in the pyrolysis of 1,2-diarylethyl and 1-arylethyl acetates, respectively. These factors in our work are accounted for *entirely* (by virtue of the correlation with  $\sigma^+$ -values) by the increased stabilization of the carbonium ion due to the *p*-MeO group in the 1-aryl ring, and it seems to us that this explanation will account very satisfactorily for the observations of DePuy and Leary.

DePuy, King and Froemsdorf<sup>12k</sup> reported that 1-phenylethyl acetate (III) pyrolyzes  $10.6 \pm 0.6$  times faster than 2-phenylethyl acetate (IV) at 400°, which is in good agreement with the value (10.85) obtained from our data by extrapolation of the  $\log k$  vs.  $10^3/T$  plot to 400°. This factor is greater than could arise solely from there being one more hydrogen atom available for elimi-



nation in III, than in IV, especially since the acidity of the hydrogen atoms in IV will be enhanced by the adjacent electron-withdrawing phenyl group. We ascribe the factor to increased stabilization of the carbonium ionic center in III due to the adjacent methyl and phenyl groups (this latter group supplying electrons by a +E effect which will outweigh its electron-withdrawing -I effect in this situation). By contrast, the carbonium ionic center in IV only has a benzyl group adjacent to it, and this group will, at most, be weakly electron supplying.

Further evidence that the single carbon-oxygen bond-breaking process is more important in determining the stability of the esters than the carbon-hydrogen bond-breaking process can be obtained by considering the data in Table IV. (The relative rate for 2-phenylethyl acetate is obtained by making a slight extrapolation of the  $\log k$  vs.  $10^3/T$  plot.)

TABLE IV

RELATIVE RATES OF ESTER PYROLYSIS AT 600°K.

Compound, acetate	Relative rate	$E_a$ , kcal./mole
2-Phenylethyl (IV)	1.0	45.4
1-Phenylethyl (III)	12.3	43.7
1,2-Diphenylethyl (V)	32.4	43.3

The difference in the reactivities of 1-phenylethyl acetate (III) and 1,2-diphenylethyl acetate (V) is to be compared. One might argue that the diaryl ester should be the least stable by virtue of its greater molecular weight. However, this effect is very small, and probably non-existent in our static system. These esters do not form isomeric olefins; however, as has been shown above, the stability of the forming olefin is not an important factor in determining the stability of esters. Thus the difference in reactivity, a factor of 2.6, arises from the increased acidity of the  $\beta$ -hydrogen atoms in V due to the presence of the adjacent phenyl group. It is noted that the factor 2.6 does not give an accurate measure of the effect of the increased acidity of the hydrogen atoms since there is one fewer available for elimination in V than in III.

The factor is, however, very much less than that (12.3) which arises from replacing a hydrogen atom adjacent to the carbonium ionic center by a phenyl group, as seen from a comparison of the rates of 2-phenylethyl acetate (IV) and 1,2-diphenylethyl acetate (V). These two esters have an equal number of equally acidic hydrogen atoms and the difference in rate can *only* arise from increased stabilization of the carbonium ionic center by the adjacent phenyl group (which will be strongly electron supplying in this situation). Hence the observed reactivities of these esters can be accounted for by the knowledge that the C-H and C-O bond-breaking processes are both important in the rate-determining stage of the reaction, the strength of the latter bond being the major factor in determining the stability of the ester.

The carbonium ionic character of the transition state accounts very satisfactorily for the increase in rate due to  $\alpha$ -methylation of alkyl acetates. Table V gives the relative rates of pyrolysis of ethyl, isopropyl and *t*-butyl acetates at 400°, calculated by DePuy and King,<sup>5</sup> and Maccoll,<sup>20</sup> from data of Blades,<sup>9e</sup> and Rudy and Fugassi.<sup>9a</sup>

TABLE V

EtOAc	<i>i</i> -PrOAc	<i>t</i> -BuOAc	$\frac{\log f_{\text{Bu}^t}}{\log f_{\text{Pr}^i}}$	Ref.
1	19	1170	2.40	5
1	25	1660	2.30	20

Though there seems to be some disagreement about the relative rates in this reaction, there is little question that the increase in rate due to  $\alpha$ -methylation is greater than that which could arise solely from the statistical effect of the increased number of  $\beta$ -hydrogen atoms, and must be attributed to the increased stabilization of the carbonium ionic center by electron supply from the adjacent methyl group.

Emovon and Maccoll have recently shown<sup>21</sup> that  $\beta$ -methylation of *t*-butyl acetate, while *reducing* the number of  $\beta$ -hydrogen atoms available for elimination, actually *increases* the rate of pyrolysis and reported that "in the tertiary series the electron demands are becoming more like those in the transition states of the halides" (which pyrolyze *via* a carbonium ion mechanism) which is in accord with our hypothesis of increased stabilization of the carbonium ionic center.

A number of facets of ester pyrolysis can now be summarized. The elimination of the acid takes place *via* a concerted mechanism with some charge separation resulting in the partial formation of a carbonium ion; this carbonium ion is stabilized or destabilized in the transition state of the reaction by electron release or withdrawal by substituents attached to the 1-carbon atom, as observed in the present and earlier work.<sup>1</sup> In the rate-determining step, the carbon-hydrogen and single carbon-oxygen bonds break simultaneously, and the reaction can therefore give rise to an isotope effect as experimentally observed when the

(20) A. Maccoll, in "Theoretical Organic Chemistry," papers presented to the Kekulé Symposium, London, 1958, p. 230; Butterworths Scientific Publications, London, 1958.

(21) E. V. Emovon and A. Maccoll, *J. Chem. Soc.*, 395 (1962).

$\beta$ -hydrogen atom is replaced by a deuterium atom<sup>19c,4</sup>; for the same reason an increased rate is observed when the acidity of the  $\beta$ -hydrogen is increased.<sup>20</sup> The relative rates of pyrolysis of esters, *viz.* tertiary > secondary > primary, is not only a consequence of the statistical effect of the number of hydrogen atoms available for elimination, but also partly results from a stabilization in the transition state of the positive charge which develops on the carbon atom by electron supply from the attached alkyl groups. Since the double bond of the olefin cannot have formed appreciably in the transition state of the reaction, the elimination cannot be influenced by the stability of the forming olefinic bond to any extent. There may, of course, be any number of transition states (and corresponding intermediates) leading to the rate-determining transition state. One of these could involve a suitable orientation of the atoms needed for a concerted reaction intermediate through which the acid is eliminated.

**Application of the Results to Current Theories of Electrophilic Aromatic Substitution.**—The excellent correlation of  $\log k/k_0$  vs.  $\sigma^+$ -constants<sup>4</sup> for the 1-arylethyl acetates is somewhat fortuitous, since a close correlation need not necessarily exist for reactions in which a positive center is stabilized by resonance from an aromatic ring. As pointed out by de la Mare<sup>22</sup> and others,<sup>8</sup> an exact correlation in each reaction series is not possible principally because the contribution from the time-variable resonance effect (+E) may be different in each series. Yukawa and Tsuno<sup>23</sup> have had considerable success in correlating the effects of substituents in reactions believed to involve a positively charged intermediate by means of the equation

$$\log k/k_0 = \rho(\sigma + r\Delta\sigma_{R^+})$$

where  $r$  is a measure of the resonance contribution to the reaction and  $\Delta\sigma_{R^+}$  is defined as  $\sigma^+ - \sigma$ .<sup>23</sup> Applying this treatment to our results we obtain a value of *ca.* 1.0 for  $r$ , and thus the amount of resonance stabilization of the rate-determining transition state in our reaction is approximately the same as in the solvolysis of the aryldimethylcarbinyl chlorides. This explains why we obtain such a good correlation against  $\sigma^+$ -constants in the first instance.

Knowles, Norman and Radda have recently suggested that substituent effects in aromatic substitution can be treated quantitatively.<sup>24</sup> The basis of their hypothesis is that the  $\rho$ -factor in an electrophilic substitution reaction is a measure of the activity of the attacking species and therefore of the degree of bond formation between the attacking species and the reaction center in the intermediate (assumed to be of the Wheland type). Since the amount of resonance interaction in the transition state was considered to be proportional to the extent of formation of the Wheland intermediate, then the amount of resonance interaction in the transition state should be proportional to  $\rho$ . For the electrophilic aromatic substitution reactions which were examined, this assumption appeared

to be true. However, a more extensive examination of these and related reactions by Yukawa and Tsuno shows that there is no over-all quantitative correlation between  $r$ , the resonance contribution to the reaction, and the  $\rho$ -factor of the reaction.<sup>23</sup> Our result clearly fits in with this latter observation, for although the resonance contribution in our reaction is the same as in the solvolysis of phenyldimethylcarbinyl chlorides (where  $\rho = -4.62$ ), our  $\rho$ -factor of  $-0.66$  is considerably different. The reason for the lack of a quantitative correlation between  $r$  and  $\rho$  is presently obscure but, as Yukawa and Tsuno have suggested, points to a difference in mechanism between one reaction and another. Influencing factors may be the dielectric constant of the medium (an increase in the dielectric constant of the medium will give increasing opportunities for charge separation) and the solvation power of the medium (an increase in the solvating power of the medium will give increasing opportunities for stabilization of the intermediates through the transition state). Also, the reactions considered are of widely differing types, *e.g.*, nitration<sup>8b,25</sup> in which hydrogen is displaced, desilylation<sup>26</sup> in which the trimethylsilyl group is displaced, solvolysis of aryldimethylcarbinyl chlorides<sup>4</sup> in which the positively charged reaction center is in the side chain, and the decomposition of 1-arylethyl chlorocarbonates (in solution)<sup>27</sup> which, like the pyrolysis of 1-arylethyl acetates (gas-phase), is a reaction involving a cyclic transition state where the positive reaction center is in the side chain. In these reactions, the number of atoms over which the positive charge may be spread and hence stabilized in the transition state is variable. For a correlation to exist between  $r$  and  $\rho$ , a transition state of given positive charge will always require the same amount of resonance stabilization by the substituents on the aromatic ring, regardless of the reaction taking place or the extent of solvation and this seems to us unreasonable. We feel it is necessary to emphasize at this stage that the  $\rho$ -factor of a reaction is a measure of the charge separation in the rate-determining transition state or the position of this transition state along the reaction coordinate. The resonance contribution, however, will not only be related to the  $\rho$ -factor, but also to the number of sites over which the positive charge can be spread and hence stabilized in the transition state. Solvation increases the number of such sites and thus in systems where the charged intermediate is stabilized through the transition state by solvation, for a given  $\rho$ -value, the extent of resonance stabilization (by electron release from substituents) is smaller than in gas-phase reactions of similar  $\rho$ . In solution reactions solvation is principally responsible for reducing the potential energy barrier of the rate-determining transition state.

This rather complete study of substituent effects on the ease of pyrolysis of esters has demonstrated the importance of using a homogeneous

(22) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

(23) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

(24) J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(25) C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *ibid.*, 1959 (1931); C. K. Ingold and F. R. Shaw, *ibid.*, 575 (1949); M. J. S. Dewar, T. Mole, D. S. Urch and E. W. T. Warford, *ibid.*, 3576 (1956).

(26) C. Eaborn, *ibid.*, 4858 (1956).

(27) K. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

gas-phase reaction in making a quantitative study of substituent effects in aromatic systems free from solvent complications. The discussion in this paper has been limited to elucidating the mechanism of ester pyrolysis. The significance and importance of using gas-phase reactions in quantitatively studying substituent effects, solvent partic-

ipation and the application of gas-phase studies to the current theories of electrophilic aromatic substitution is discussed elsewhere. From a comparison of the *ortho/para* ratios obtained in this and other aromatic reactions of the electrophilic type we propose to evaluate also the steric requirement of the present reaction.

[CONTRIBUTION NO. 1083 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, IND.]

## The Mechanism of Decarboxylation of Glycidic Acids<sup>1</sup>

BY V. J. SHINER, JR.,<sup>2</sup> AND BRIAN MARTIN

RECEIVED JULY 2, 1962

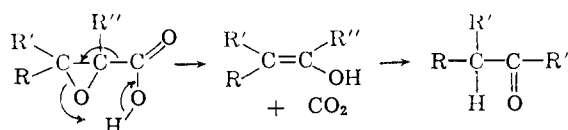
The decarboxylation of 3-phenyl-2,3-epoxybutanoic acid in "20%" aqueous dioxane has been shown to proceed without appreciable acid or base catalysis in the pH range 4.0–5.5. The reaction has further been shown to involve the production of the enol, 2-phenyl-1-propen-1-ol, as an intermediate. The rate of production of this enol in the decarboxylation reaction and the rate of its ketonization to 2-phenylpropanal have been measured in the pH range 0.5–5.5. Specific acid, water and general base catalysis were detected in the ketonization reaction. The general base catalysis is interpreted as involving general acid attack on the conjugate base of the enol. This is the reverse of the accepted mechanism for base-catalyzed enolization.

### Introduction

The Darzens glycidic ester condensation followed by hydrolysis to the glycidic acid and decarboxylation is a well-known synthetic route for the preparation of aliphatic aldehydes.<sup>3</sup> The condensation reaction has been studied and its mechanism reasonably well characterized.<sup>4</sup> The conversion of glycidic esters to glycidic acid salts is generally effected by simple aqueous alkaline hydrolysis. Glycidic acids produced by acidification of aqueous solutions of the salts are generally decarboxylated directly without purification either by warming the aqueous solution<sup>5</sup> or separating the acid and heating.<sup>6,7</sup>

However, in a few reported examples,<sup>6b,7</sup> the glycidic acids themselves have been isolated, purified by recrystallization and characterized, although they are apparently not particularly stable at room temperature and decarboxylate readily on heating. Dullaghan and Nord<sup>8</sup> report that some  $\alpha$ -alkylglycidic acids decarboxylate more readily than similar ones not having  $\alpha$ -alkyl substituents. These authors also report that acidification of the glycidic acid salts with acetic acid gives better yields of carbonyl (decarboxylation) products than acidification with phosphoric or hydrochloric acid or pyrolysis of the sodium salts.

Little, if any, further information relevant to the mechanism of the decarboxylation reaction is available, although Arnold<sup>9</sup> has suggested a cyclic

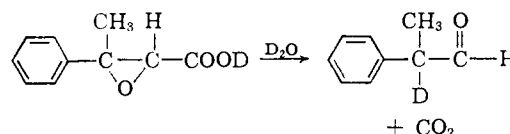


process producing the enol of the product as an intermediate.

Enol intermediates have been shown to be produced in the decarboxylation of  $\beta$ -keto acids and dimethylxaloacetic acid.<sup>10</sup>

### Results and Discussion

In the course of another investigation it was desired to prepare 2-phenylpropanal and 2-phenylpropanal-*d*. It was found that decarboxylation of 3-phenyl-2,3-epoxybutanoic acid in deuterium oxide gave the 2-deuterio compound. This result



is inconsistent with an *a priori* less likely mechanism involving the formation of the  $\alpha$ -keto acid by epoxide ring opening and rearrangement followed by decarboxylation. Some  $\alpha,\beta,\beta$ -trialkyl substituted glycidic acids were originally thought to decarboxylate to aldehydes, which would require an  $\alpha$ - $\beta$  shift of the alkyl group. These rearrangements have subsequently been shown not to take place in the manner originally suggested; the products are in all cases ketones and the  $\alpha$ -alkyl group does not migrate.<sup>6</sup> Thus all known glycidic acid decarboxylations seem to involve fundamentally the same structural alterations; carbon dioxide is lost, the epoxide ring opens and the new C–H bond is formed at the position  $\alpha$  to the carbonyl group in the product.

(10) (a) See J. Hine, "Physical Organic Chemistry," 2nd Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 303–304, for a summary of the information and references to the original literature. (b) R. Steinberger and F. H. Westheimer, *J. Am. Chem. Soc.*, **73**, 429 (1951).

(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September, 1962.

(2) Alfred P. Sloan Research Fellow.

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(4) M. Balaster, *Chem. Revs.*, **55**, 283 (1955).

(5) C. F. H. Allen and J. VanAllan in E. C. Horning, ed., "Organic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 733.

(6) (a) H. H. Morris and C. J. St. Lawrence, *J. Am. Chem. Soc.*, **77**, 1692 (1955). (b) H. H. Morris and R. H. Young, Jr., *ibid.*, **77**, 6678 (1955).

(7) F. F. Blicke and J. A. Faust, *ibid.*, **76**, 3156 (1954).

(8) M. E. Dullaghan and F. F. Nord, *J. Org. Chem.*, **18**, 878 (1953).

(9) R. T. Arnold, Abstracts of Papers Delivered at the Tenth National Organic Symposium of the American Chemical Society, Boston, Mass., 1947.