pyridine was heated under reflux for 30 min. The mixture was poured into 2 *N* acetic acid and the yellow precipitate was collected and recrystallized from 1-butanol. The oxime (67 mg.) melted at 247–250° dec., and had λ_{max} 280 mμ (log ε 4.47), 376 sh (3.78), and 410 (3.92).

Anal. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75. Found: C, 67.32, 67.48; H, 4.12, 3.90; N, 8.86.

Oxidation of Guatterine to Atherospermidine.—A mixture of 412 mg. of colorless guatterine and 416 mg. of chromium trioxide in 6 ml. of pyridine was allowed to stand for 18 hr. Ethanol (1.5 ml.) and pyridine (2 ml.) were added and the mixture was stirred and diluted with water (60 ml.). The aqueous solution was extracted repeatedly with chloroform until the extracts were no longer fluorescent. The extract was dried over sodium sulfate and evaporated, and the yellow-brown residue was recrystallized from chloroform to yield 122 mg. of golden yellow needles of atherospermidine, identical with the compound isolated from the plant extracts.

Acetylation of Guatterine. A. Acetate III.—A mixture of 200 mg. of guatterine, 200 mg. of anhydrous sodium acetate, and 2.5 ml. of acetic anhydride was heated under reflux for 90 min. After the addition of 10 ml. of water and heating for a further 30 min., the solution was cooled, made basic with ammonia and extracted with chloroform. The dried chloroform solution was evaporated and the residue was crystallized from acetone–water. The colorless needles melted at 190–192°.

Anal. Calcd. for $C_{23}H_{23}NO_6$: C, 67.46; H, 5.66; N, 3.42. Found: C, 67.42; H, 5.84; N, 3.20.

The infrared spectrum showed characteristic absorption at 1750 (O-acetyl) and 1645 cm.$^{-1}$ (N-acetyl). The ultraviolet spectrum had λ_{max} 252 mμ (log ε 4.57), 284 sh (4.31), 324 (3.87), and 364 (3.10).

B. Acetate IV.—In another experiment, a mixture of 300 mg. of guatterine, 320 mg. of sodium acetate, and 3.5 ml. of acetic anhydride was refluxed for 2 hr. The excess acetic anhydride was removed by heating under vacuum and the residue was taken up in ethyl acetate. The filtered solution was evaporated to dryness and the residue was dissolved in acetone. After treatment with charcoal the solution was diluted with water and allowed to stand. The product (83 mg.) separated as tiny white needles, m.p. 222–223°.

Anal. Calcd. for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11. Found: C, 71.15; H, 5.85.

The ultraviolet spectrum showed λ_{max} 262 mμ (log ε 4.85), 286 (4.58), 320 (4.08), 330 (4.08), and 368 (3.23). The infrared spectrum showed a peak at 1663 cm.$^{-1}$ (N-acetyl).

Repeated attempts to reproduce the preparation of the acetate (m.p. 223°) were fruitless; the 192° acetate was always the product isolated. Although the carbon–hydrogen analysis was imperfect (the single analytical result agrees with $C_{20}H_{19}NO_4$—calcd.: C, 71.21; H, 5.68), the integration of the n.m.r. spectrum shows the required 17 protons, all of them accounted for in the interpretation of the spectrum based upon the structure IV.

Oxidation of Atherospermidine. 1-Azaanthraquinone-4-carboxylic Acid.—To a solution of 176 mg. of atherospermidine in 12 ml. of 13 *N* sulfuric acid was added a solution of 204 mg. of chromium trioxide in 5 ml. of 14 *N* sulfuric acid. The mixture was allowed to stand for 16 hr. and, after dilution with 40 ml. of water, heated for 1 hr. on the steam bath. The solution was filtered and the yellow precipitate was washed with water and purified by solution in aqueous ammonia and reprecipitation with acid. There was obtained 53 mg. of pale yellow 1-azaanthraquinone-4-carboxylic acid, m.p. 327–328° dec. The compound decomposed on melting and a sublimate of golden yellow needles of 1-azaanthraquinone formed on the walls of the capillary tube.

Anal. Calcd. for $C_{14}H_7NO_4$: C, 66.41; H, 2.79; N, 5.53. Found: C, 66.44; H, 2.80; N, 5.88.

The ultraviolet spectrum showed λ_{max} 252 mμ (log ε 4.54) and 317 (3.73). The infrared spectrum (KBr) showed broad absorption in the 3350–3500-cm.$^{-1}$ region (carboxyl-OH) and peaks at 1670 and 1708 cm.$^{-1}$.

1-Azaanthraquinone.—A sample of 61 mg. of 1-azaanthraquinone-4-carboxylic acid was mixed with 60 mg. of calcium oxide and heated in a metal bath until a sublimate of yellow needles had formed on the walls of the tube. The sublimate was recrystallized from chlorobenzene, forming yellow needles, m.p. 281–283°, undepressed upon admixture with a synthetic specimen. The ultraviolet absorption spectra of the compound from atherospermidine and that prepared synthetically (see below) were identical.

1-Azaanthraquinone was prepared starting from 1-chloro-2-acetnaphthalide[14] by way of 10-chloro-1-azaanthracene.[15,16] The ultraviolet spectrum showed λ_{max} 249 mμ (log ε 4.53) and 324 (3.51). The infrared spectrum (KBr) showed peaks at 1665 and 1685 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_7NO_2$: C, 74.64; H, 3.37; N, 6.70. Found: C, 74.88; H, 3.54; N, 6.90.

(14) A. P. J. Hoogeveen, *Rec. trav. chim.*, **50**, 37 (1931).

(15) A. Etienne, *Ann. chim.* (Paris), [12] **1**, 5 (1946). Numbered here according to "The Ring Index" (A. M. Patterson, L. T. Capell, and D. F. Walker, American Chemical Society, Washington, D. C., 1959, p. 456). In the original publication the compound is named meso(9)chloroazanthracene-α.

(16) A. Etienne and M. Legrand, *Bull. soc. chim. France*, [5] **20**, 110 (1953).

Pyrolysis Studies. XIII.[1a] Kinetics of the Vapor Phase Pyrolysis of Arylethyl Methyl Carbonates. A Linear Free-Energy Relationship for *ortho* Substituents

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The absolute reaction rate constants in the pyrolysis of a series of *ortho*-, *meta*-, and *para*-substituted 1-arylethyl methyl carbonates and some *ortho*-substituted 1-arylethyl acetates have been determined. The mechanism of the pyrolysis of the carbonates is discussed. Even in the pyrolysis of the *ortho*-substituted esters, proximity effects are at a minimum for it is found that a linear free-energy relationship is obeyed between the pyrolysis of the *ortho*-substituted acetates and carbonates. Important differences are found between this relationship and the linear free-energy relationship obeyed by the *meta*- and *para*-substituted isomers.

Because of the general proximity of *ortho* substituents to the reaction center, their substituent effects have proved to be more complex than those of *meta* and *para* substituents, so that it has been found difficult in the past to correlate *ortho*-substituent effects by means of linear free-energy relationships based on *meta*- and *para*-substituent constants. This complexity is due, in part, to the fact that most of the reaction systems studied so far have involved bimolecular reactions in the condensed phase with the attendant problems, amongst others, primary steric effects and steric inhibition of solvation. However, from a study of gas phase unimolecular elimination reactions information can be obtained about *ortho*-substituent effects free from these complications. Previous papers concerned with *ortho*-substituent effects in the gas phase dealt with *ortho*-

(1) (a) Paper XII: G. G. Smith and D. V. White, *J. Org. Chem.*, **29**, 3533 (1964). (b) Postdoctoral research associate, 1963–1964.

TABLE I

ARYLETHYL METHYL CARBONATES

Substituent	M.p. or b.p., °C. (mm.)	$n^{20}D$	Formula	Calcd., % C	Calcd., % H	Calcd., % X	Found, % C	Found, % H	Found, % X
			1-Arylethyl Methyl Carbonates						
H	85 (0.4)	1.4930	$C_{10}H_{12}O_3$	66.7	6.71	...	66.6	6.55	...
o-F	62.4 (0.1)	1.4764	$C_{10}H_{11}FO_3$	60.6	5.60	9.58	60.6	5.55	9.71
p-F	75.6 (0.5)	1.4769	$C_{10}H_{11}FO_3$	60.6	5.60	9.58	60.7	5.48	9.72
o-Cl	74–75 (0.5)	1.5068	$C_{10}H_{11}ClO_3$	55.9	5.17	16.5	55.9	5.31	16.6
m-Cl	80–82 (0.1)	1.5074	$C_{10}H_{11}ClO_3$	55.9	5.17	16.5	56.0	5.19	16.5
p-Cl	79–80 (0.1)	1.5051	$C_{10}H_{11}ClO_3$	55.9	5.17	16.5	55.8	5.14	...
o-Br	78–80 (0.05)	1.5271	$C_{10}H_{11}BrO_3$	46.3	4.27	30.8	46.2	4.15	30.8
p-Br	80–81 (0.1)	1.5264	$C_{10}H_{11}BrO_3$	46.3	4.27	30.8	46.3	4.41	30.7
m-NO_2	39–40	...	$C_{10}H_{11}NO_5$	53.3	4.93	6.21	53.5	4.75	6.46
o-Me	79–80 (0.4)	1.4970	$C_{11}H_{14}O_3$	68.0	7.27	...	68.0	7.15	...
p-Me	62–64 (0.3)	1.4920	$C_{11}H_{14}O_3$	68.0	7.27	...	68.0	7.17	...
o-MeO	76–77 (0.1)	1.5078	$C_{11}H_{14}O_4$	62.8	6.71	...	63.0	6.67	...
p-MeO	88 (0.2)	1.5021	$C_{11}H_{14}O_4$	62.8	6.71	...	62.8	6.58	...
			2-Arylethyl Methyl Carbonates						
H	85 (0.6)	1.4952	$C_{10}H_{12}O_3$	66.7	6.71	...	66.7	6.83	...
p-Cl	87 (0.1)	1.5062	$C_{10}H_{11}ClO_3$	55.9	5.17	16.5	56.1	5.27	16.72
p-MeO	106–108 (0.5)	1.5040	$C_{11}H_{14}O_3$	62.8	6.71	...	63.0	6.86	...

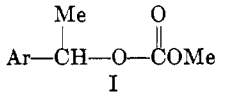
TABLE II

ARYLETHYL ACETATES

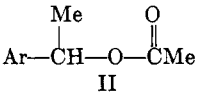
Substituent	B.p., °C. (mm.)	$n^{20}D$	Formula	Calcd., % C	Calcd., % H	Calcd., % X	Found, % C	Found, % H	Found, % X
o-F	49 (0.1)	1.4790	$C_{10}H_{11}FO_2$	65.9	6.03	10.5	65.9	5.93	10.3
o-Cl	64–65 (0.05)	1.5011	$C_{10}H_{11}ClO_2$	60.5	5.53	17.9	60.6	5.52	17.8
o-Br	83–84 (0.3)	1.5315	$C_{10}H_{11}BrO_2$	49.4	4.52	32.9	49.5	4.39	32.8

substituent effects in the pyrolysis of ethyl benzoates,[2] and isopropyl benzoates,[3a] and phenyl ethyl carbonates.[3b]

We now report the effects of *ortho* substituents in the pyrolysis of 1-arylethyl methyl carbonates I and 1-arylethyl acetates II.[4]



I



II

Since the mechanisms of pyrolysis of these two classes of compounds are believed to be very similar[5] and because in both reactions steric effects are at a minimum (although the reaction site is close to the *ortho* substituent) it is expected that a linear free-energy relationship can be obtained for *ortho*-substituent effects in the two series. If this is the case it may be that in other reactions carried out under similar conditions *ortho*-substituent effects will also follow a linear free-energy relationship. In this way Hammett relationships can be established for *ortho* substituents. Comparisons can then be made with *meta*- and *para*-substituent effects and with *ortho*-substituent effects in other reactions. In this manner a suitable explanation can be given why *ortho* substituents in many reactions do not often follow a linear free-energy relationship.

Experimental

Preparation of Arylethyl Methyl Carbonates and 1-Arylethyl Acetates.—The carbonates were prepared by treatment of the appropriate alcohols by either method A or B given below. The acetates were prepared in 70–80% yield by acetylation of the appropriate alcohols by the method of Shriner and Fuson.[6] Those alcohols which were not commercially available were prepared by sodium borohydride reduction of the acetophenone, or treatment of the arylmagnesium bromide with acetaldehyde, or reduction of the corresponding phenylacetic acid with lithium aluminum hydride.

Method A.—The carbonate was prepared by the method of Smith and Kösters[7] except that after the addition of all the methyl chloroformate the mixture was stirred and refluxed for 24 hr. This method was used for the unsubstituted methyl and methoxy-substituted carbonates giving yields of pure carbonate of 35–45%.

Method B.—The carbonate was prepared according to the method of Woodward, Kohman, and Harris[8] and isolated as in method A. This method was found satisfactory for the nitro- and halogen-substituted carbonates, giving yields of pure compounds of 70–80%. However, this method, when applied to *p*,α-dimethylbenzyl alcohol, gave a mixture of *p*,α-dimethylbenzyl chloride and *p*-methylstyrene with very little carbonate formation.

Physical constants and analyses of the esters and carbonates are listed in Tables I and II.

Method of Pyrolysis.—All of the esters were pyrolyzed at temperatures ranging from 288.4 to 383.5° in a stainless steel static reactor of constant volume (200 ml.) whose design and operation have been described.[9] The reaction was followed by automatically measuring the increase in pressure inside the reactor by means of a pressure transducer connected to a strip chart recorder. The temperature was maintained to within 0.02° with a large glass wool lagged aluminum block electrically heated. The surface of the reactor was deactivated by leaving the products from the pyrolysis of 3-butenoic acid at 400° for several days in the reactor, and by pyrolyzing the ester being studied until reproducible results were obtained. Precautions were taken to exclude air from the reactor, since air reactivates the surface.

(2) G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963).

(3) (a) G. G. Smith and D. A. K. Jones, *ibid.*, **28**, 3499 (1963). (b) G. G. Smith, D. A. K. Jones, and R. Taylor, *ibid.*, **28**, 3547 (1963).

(4) The rates of pyrolysis of *meta*-, *para*-, and some *ortho*-substituted 1-arylethyl acetates have been determined by R. Taylor, G. G. Smith, and W. H. Wetzel [*J. Am. Chem. Soc.*, **84**, 4817 (1962)].

(5) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(6) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 165, method B.

(7) G. G. Smith and B. Kösters, *Ber.*, **93**, 2400 (1960).

(8) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).

(9) G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963).

Since all esters could be injected into the evacuated reactor as liquids it was not necessary to dissolve them in an inert solvent. All of the rate constants were determined at least in triplicate.

Product Analysis.—The products from several pyrolyses of 1-phenylethyl methyl carbonate and 1-phenylethyl acetate were trapped in a liquid nitrogen trap and analyzed by v.p.c. on a Dow silicone 710 column. Only three peaks were obtained corresponding in retention times to carbon dioxide, methanol, and styrene from the carbonate and one peak corresponding to styrene was obtained from the acetate. Acetic acid did not come through the column.

Results

Rates of pyrolysis of 1-arylethyl methyl carbonates, 1-arylethyl acetates, and 2-arylethyl methyl carbonates are given in Tables III, IV, V, and VI. For all the esters except the *m*-nitro, plots of log $(P_\infty - P)$ against time were linear at least up to 90% decomposition, and P_∞ was three times the extrapolated P_0, thus giving reproducibility of ±2% in the rate constants. For the *m*-nitro ester, secondary decomposition made it impossible to determine P_∞ and the rate constant was calculated by the method of Guggenheim[10] giving a reproducibility of ±3% in the rate constants. Determinations of the rate constant were carried out at least three times for each compound. The Arrhenius plots were linear for all the compounds studied and the derived energies and entropies of activation are given in Table IV.

The reaction was shown to be homogeneous by inserting a stainless steel sponge (Gottschalk No. 725) into the reactor which increased the surface area ten times. After complete deactivation of the new surface, a rate constant of 1.91×10^{-3} was obtained for the pyrolysis of 1-phenylethyl methyl carbonate at 580.4°K. The rate for this reaction at this temperature in the unpacked reactor was 1.85×10^{-3}.

TABLE III

RATES OF PYROLYSIS OF 1-ARYLETHYL METHYL CARBONATES AT 307.2°

Substituent	$k \times 10^3$, sec.$^{-1}$	Substituent	$k \times 10^3$, sec.$^{-1}$
H	1.85	*o*-Br	0.735
o-F	0.965	*p*-Br	1.35
p-F	1.94	*m*-NO_2	0.426
o-Cl	0.754	*o*-Me	3.22
m-Cl	0.842	*p*-Me	3.92
p-Cl	1.52	*o*-MeO	3.94
		p-MeO	10.6

TABLE IV

ARRHENIUS PARAMETERS FOR 1-ARYLETHYL METHYL CARBONATES

	$k \times 10^3$, sec.$^{-1}$					
Substituent	288.4°	307.2°	325.4°	341.4°	E_a, kcal./mole	ΔS^*, e.u.
H	..	1.85	5.40	12.3	39.9	−3.6
o-Cl	..	0.754	2.57	5.86	41.9	−1.9
m-Cl	..	0.842	2.86	7.08	41.5	−2.3
p-Me	1.28	3.92	10.4	...	38.8	−3.9

TABLE V

RATES OF PYROLYSIS OF 2-ARYLETHYL METHYL CARBONATES AT 383.5°

Substituent	$k \times 10^3$, sec.$^{-1}$
H	7.31
p-Cl	7.59
p-MeO	6.79

TABLE VI

RATES OF PYROLYSIS OF 1-ARYLETHYL ACETATES AT 369.0°

Substituent	$k \times 10^3$, sec.$^{-1}$	Substituent	$k \times 10^3$, sec.$^{-1}$
H	8.22[a]	*o*-Br	3.88[a]
o-F	4.78[a]	*p*-Br	6.64[b]
p-F	8.81[b]	*m*-NO_2	3.33[b]
o-Cl	3.92[a]	*o*-Me	13.5[b]
m-Cl	4.92[b]	*p*-Me	12.6[b]
p-Cl	7.25[b]	*o*-MeO	15.3[b]
		p-MeO	22.5[b]

[a] Rate data obtained in this study. [b] Rate constants calculated using the Arrhenius equation based on the data reported by Taylor, Smith, and Wetzel.[4] The calculated rate of pyrolysis of 1-phenylethyl acetate from their data is 8.28×10^{-3} at 369.9°.

(10) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

Discussion

Mechanism of the Pyrolysis of the 1-Arylethyl Methyl Carbonates.—The present study demonstrates the similarities between the pyrolyses of arylethyl methyl carbonates and arylethyl acetates. Both esters decompose thermally by a first-order homogeneous reaction with negative entropies of activation and energies of activation that are similar. This suggests a unimolecular reaction for both proceeding through a cyclic transition state. Furthermore, a plot of the logarithms of the relative rate of pyrolysis at 580.4°K. of *meta*- and *para*-substituted 1-arylethyl methyl carbonates against the σ^+-values tabulated by Brown and Okamoto[11] gives a good straight line ($r = 0.999$, $s = 0.025$, $n = 8$) of slope of 0.97. A similar result was obtained for 1-arylethyl acetates at 600°K. ($r = 0.999$, $s = 0.012$, $n = 8$, slope = 0.66).[4] The $\rho\sigma^+$-relationship indicates that the transition state for the pyrolysis of both classes of compounds involves a partial positive charge being formed on the α-carbon atom; the greater ρ-factor for the 1-arylethyl methyl carbonate is indicative of a greater positive charge being formed during their pyrolysis. For one-step reactions not involving pre-equilibria this is a sound conclusion.[12]

Another similarity between the pyrolysis of carbonates and acetates is shown by the fact that the strength of the single carbon–oxygen bond is much more important than the acidity of the β-carbon–hydrogen bond in determining the stability of these esters. The ρ-factor in the pyrolysis of both carbonates and acetates in the 2-aryl series is much smaller than those for the 1-aryl series ($\simeq$1.0 *vs.* $\simeq$0.1). Both 1-phenylethyl acetate and 1-phenylethyl methyl carbonate pyrolyze 11–12 times faster than their 2-phenyl isomers. For the phenylethyl acetates, it has been postulated[4] that the size of this ratio is due to the greater stabilization of the carbonium ion by the adjacent phenyl and methyl groups in 1-phenylethyl acetate than by the benzyl group in 2-phenylethyl acetate. A similar explanation must also hold for the differences in the rate of pyrolysis of 1- and 2-phenylethyl methyl carbonates.

Two mechanisms have been proposed for the pyrolysis of carbonates with β-hydrogen.[13,14] Based on the

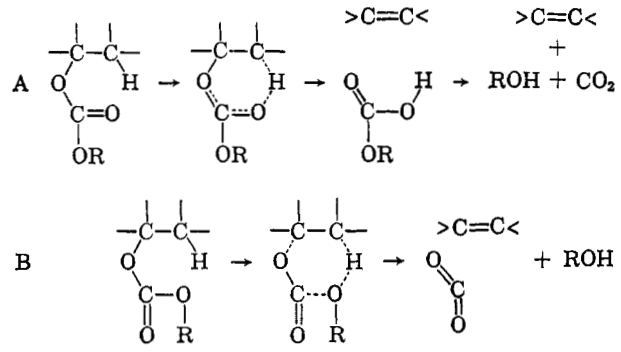
(11) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(12) Application of the Yukawa and Tsuno treatment [Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959)] to the kinetic data gives a value of approximately 1.2 and 1.0 for the value of r for the carbonate and acetate pyrolysis, respectively, indicating slightly more resonance interaction between the substituent and the reaction center during the carbonate reaction.

(13) G. L. O'Conner and H. R. Nace, *J. Am. Chem. Soc.*, **75**, 2118 (1953).

(14) K. C. Tsuo and A. H. Seligman, *ibid.*, **76**, 3404 (1954).

similarity of the pyrolyses of carbonates and acetates, mechanism A is favored; however, final selection must await a kinetic isotope effect study.



ortho-**Substituent Effects.**—In view of the close similarity in the structures of 1-arylethyl methyl carbonates and 1-arylethyl acetates and the absence of primary steric or solvation effects in the pyrolysis of these esters it was hoped that *ortho*-substituent effects in the two reactions would obey a linear free-energy relationship.

Figure 1 shows the free-energy relationship which is obtained when the log k/k_0 is plotted for acetate *vs.* carbonate pyrolysis. The *ortho*-substituent points are essentially in as good agreement with one another (r = 0.994, s = 0.042, n = 6) as are the *meta*- and *para*-substituent points (r = 0.999, s = 0.019, n = 8). This excellent correlation for *ortho* substituents is confirmation of our view that in these pyrolytic reactions, *ortho*-substituent effects are considerably less complicated than in condensed phase reactions. A linear free-energy relationship for a reaction involving *ortho* substituents is unusual, particularly when the reaction center is as close to the substituent as in the present case. Charton[15] has shown that, although *ortho*-substituent effects in some condensed phase reactions can be correlated by the σ-constants for *para* substituents, the correlation only holds when there are at least two atoms between the ring and the reaction center.

Having obtained a linear free-energy relationship for *ortho*-substituent effects, directly from experimental results without any recourse to calculations for steric effects, it is now possible to compare the linear free-energy relationship for *ortho*-substituent effects with that for *para*-substituent effects. It is immediately obvious that the two relationships have a different slope, although they do intersect at a point equivalent to the unsubstituted compound. No simple explanation can be offered for this behavior although it would appear that it is something to do with the electrical effect of *ortho* substituents. It is hard to see how any steric effect could account for it because it is difficult to conceive of a steric effect greater in one series than in the other which could alter the polar effects of each substituent so that a free-energy relationship is obeyed, particularly in view of the wide range of substituent sizes studied. Also, it is difficult to see why this steric effect would be different in the pyrolysis of the carbonates than in that of the acetates, because in the transition state for these reactions, the methyl or methoxy group, whichever the case may be, attached to the carbonyl group is several atoms

(15) M. Charton, *Can. J. Chem.*, **38**, 2493 (1960).

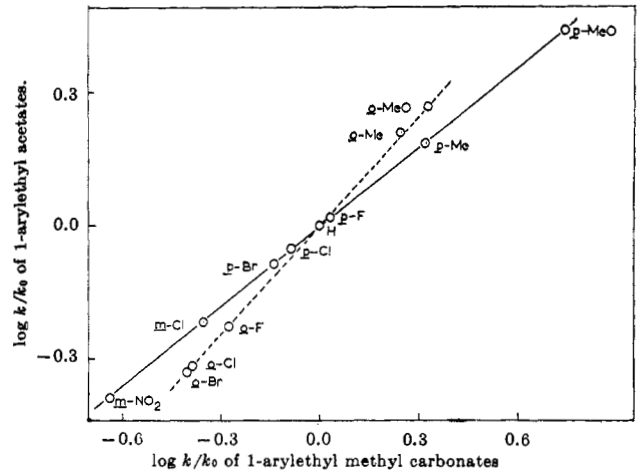


Figure 1.—Linear free-energy relationship for the pyrolysis of 1-arylethyl acetates *vs.* 1-arylethyl methyl carbonates: solid line, *meta* and *para* derivatives; dotted line, *ortho* derivatives.

removed from the *ortho* substituent. A further study involving larger ester groups will throw some light on the importance of steric effects.

A further proposition is that, for these two series at least, it is inherent in the nature of the polar effects of *ortho* substituents that they do not necessarily obey the same linear free-energy relationship as *meta*- and *para*-substituent effects. If, indeed, this is the cause and steric factors can be discounted as the cause of the existance of two lines in Figure 1, it would follow that for these two series the mechanism of transmission of substituent effects may be different from the *ortho* than from the *para* position. Therefore, the past procedure which has been attempted many times, of obtaining σ-constants for *ortho* substituents by fitting rate or equilibrium data for *ortho*-substituted compounds into the corresponding Hammett relationship for *meta*- and *para*-substituted compounds, may not be a valid approach.

Polar Effects of Individual *ortho* **Substituents.**—*ortho* to *para* rate ratios are given in Table VII.

TABLE VII

VALUES OF *ortho* TO *para* RATIOS FOR THE PYROLYSIS OF 1-ARYLETHYL METHYL CARBONATES AND 1-ARYLETHYL ACETATES

Substituent	F	Cl	Br	Me	MeO
1-Arylethyl methyl carbonates	0.498	0.496	0.541	0.826	0.371
1-Arylethyl acetates	0.535	0.540	0.591	1.07	0.628

The *ortho* to *para* rate ratios for the methoxy and all three of the halogen substituents are much less than one. Taylor, Smith, and Wetzel[4] explained the reduction in the substituent effects of the *o*-methoxy group in acetate pyrolysis by postulating that the *o*-methoxy group is unable to lie in the plane of the benzene ring thus reducing its mesomeric electron release. This explanation has been given considerable support by a recent study of steric inhibition of resonance of a methoxy group in the vapor phase pyrolysis of acetates.[1] Methyl groups *ortho* to the methoxy substituent are apparently very effective in reducing the delocalization from a methoxy substituent. A similar explanation is equally valid for the carbonate pyrolysis.

The size of the *ortho* to *para* ratios for the halogens would seem to be indicative of a larger polar effect for the halogens from the *ortho* than from the *para* position. It is possible that the *ortho* halogen is bent out of the plane of the ring thus reducing its mesomeric electron release, but this cannot account for all of the effect since in both series an *o*-chloro substituent produces a greater retarding effect than the *m*-chloro (no mesomeric electron release is possible for this latter substituent). It is possible, therefore, that there is a considerable inductive and/or field effect from the *ortho* halogen, greater than that from the *para* halogens. Similarly, other workers[16] have noted that the polar effect of *ortho* halogens seems to be greater than those of the *para* halogens. The *ortho* to *para* ratio for the methyl substituent is essentially unity, a value to be expected of a substituent that does not have a strong inductive or resonance effect.

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(16) H. C. Brown, Y. Okamoto, and G. Ham, *J. Am. Chem. Soc.*, **79**, 1906 (1957).

4-Hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane 1-Sulfide and Derived Compounds

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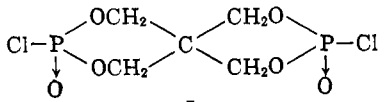
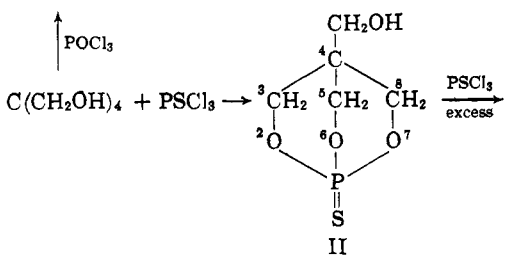
4-Hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane 1-sulfide (II), m.p. 161.0°, has been prepared in 63% yield from pentaerythritol and thiophosphoryl chloride. In an excess of the latter, however, O,O,O-tris(4-methoxy-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane 1-sulfide) phosphorothioate (III) forms. II was converted to the chloromethyl derivative by reaction with a solution of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide (I) in dimethylformamide; this solution acts as a new type of chlorinating agent. The primary hydroxyl of II is very reactive toward isocyanates, formaldehyde–HCl, and acyl halides, producing several series of hitherto unknown compounds.

We have previously reported that 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide (I) can be prepared by the interaction of excess phosphoryl chloride and pentaerythritol,[1] and have described some of its reactions.[2]

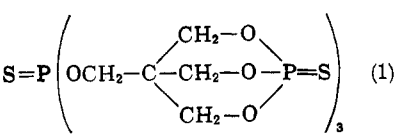
In continuation of this work we found that the reaction of pentaerythritol with excess thiophosphoryl chloride gave a chlorine-free product. Further investigation showed that 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane 1-sulfide[3] (II) had been first formed followed by conversion to O,O,O-tris-(4-methoxy-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane 1-sulfide) phosphorothioate (III). Use of an equal number of moles of reactants permitted isolation of II in 63% yield.



I



II



III

Thus, thiophosphoryl chloride forms with pentaerythritol a bicyclic cage structure readily, while phosphorus oxychloride uses only two phosphorus–chlorine functions to participate in ring formation. We have no entirely satisfactory explanation at present for the completely different behavior of the two phosphorus halides, though the hybridizations of the phosphorus–halogen bonds may be different in the two phosphorus halides. In the case of phosphoryl chloride, reaction might occur through the ionic species $(POCl_2)^+Cl^-$, a form in which its thio analog is not known to exist.[4] The bicyclic 4-methyl-substituted phosphite has been obtained by condensation of 1,1,1-tris(hydroxymethyl)-ethane with phosphorus trichloride in the presence of acid scavengers and in high dilution.[3,5] The latter condition favored ring closure.

The preparation of II has been reported in a recent patent,[6] by the transesterification of pentaerythritol with triethyl phosphite followed by sulfuration of the tervalent phosphorus under free-radical conditions with the use of octyl mercaptan. We have been unable to repeat the second step of this synthesis according to the description given, but have found that the bicyclic

(1) R. Rätz and O. J. Sweeting, *J. Org. Chem.*, **28**, 1608 (1963).

(2) R. Rätz and O. J. Sweeting, *ibid.*, **28**, 1612 (1963).

(3) An alternate system of numbering this ring system has been used [J. G. Verkade and L. T. Reynolds, *ibid.*, **25**, 663 (1960)]. According to that system, compound II would be 1-hydroxymethyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane 4-sulfide.

(4) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 255, 258.

(5) O. Neunhoeffer and W. Maiwald, *Ber.*, **95**, 108 (1962).

(6) W. S. Wadsworth, Jr., and W. D. Emmons, U. S. Patent 3,038,001 (June 5, 1962); *Chem. Abstr.*, **57**, 12322 (1962).