

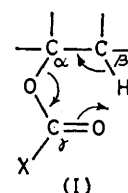
The Mechanism of the Gas-phase Pyrolysis of Esters. Part 5.¹ Pyrolysis of 1-Arylethyl Phenyl Carbonates; the Origin of the Kinetic Isotope Effect

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Rates of gas-phase thermal decomposition of a range of 1-arylethyl phenyl carbonates have been measured between 552.7 and 637.8 K. The rate data correlate with σ^+ values giving $\rho = -0.84$ at 600 K confirming that the transition state for phenyl carbonate pyrolysis is more polar (more *E1*-like) than for acetate pyrolysis, for which the corresponding ρ factor is -0.66 . The Hammett plot shows slight curvature attributable to substituent dependence of the transition state structure. The greater polarity of the carbonate transition state relative to that for acetates is confirmed by the kinetic isotope effect ($k_H : k_D$ at 600 K) which is substantially smaller for 1-phenylethyl phenyl carbonate (2.11) than for 1-phenylethyl acetate (2.32). For the corresponding tertiary esters the kinetic isotope effects are more nearly equal, being 2.19 (phenyl *t*-butyl carbonate) and 2.285 (*t*-butyl acetate) the former value being *greater* than for the secondary carbonate. These results demonstrate that the kinetic isotope effect in ester pyrolysis is a composite value, being a summation of the primary effect arising from β -hydrogen-carbon bond breakage (and which *decreases* as the transition state becomes more *E1*-like) and a secondary hyperconjugative effect (which *increases* as the transition state becomes more *E1*-like); the importance of the latter in affecting elimination rates is greatest for tertiary esters and least for primary esters. A new value of 0.73 for $\sigma^+_{m-\text{NO}_2}$ is derived from the elimination and shown to be more satisfactory for correlating all electrophilic aromatic substitution data than the literature value (0.674) derived from solvolysis of 2-aryl-2-chloropropanes.

THE current consensus of opinion relating to the mechanism of ester pyrolysis is that it is best described as a cyclic process in which there is some charge separation in the transition state, *i.e.*, the process is semi-concerted.² In the research programme described in this series we have set out to determine with some precision, the extent of this charge separation. This is achieved by (amongst other means) placing aryl groups at each of the carbon atoms which form three members of the six-membered cyclic transition state (I), and evaluating the sign and magnitudes of the Hammett ρ factors which are obtained. So far we have shown that: (i) the amount of positive charge which develops at C_α is greater than at C_γ ; (ii) the magnitude of these charges increases along the series primary < secondary < tertiary; (iii) the magnitude of these charges increases along the following series

of ester types: acetate < phenylacetate < benzoate < carbamate < carbonate, *i.e.* as the electron-withdrawing ability of the group X in (I) increases. Along this series



therefore, the increase in positive charge at C_α should be matched by a corresponding increase in negative charge at C_γ .

Our view then is that the reaction becomes less concerted, *i.e.* slightly more *E1*-like along the above series

¹ Part 4, S. de Burgh Norfolk and R. Taylor, *J.C.S. Perkin II*, 1976, 280.

² R. Taylor in 'The Chemistry of Functional Groups. Supplementary Volume B: Acid Derivatives,' ed. S. Patai, Wiley, in the press.

of esters. Accordingly the breaking of the β -C-H bond should become less kinetically significant along these series, leading to a diminishing β -deuterium isotope effect. On the other hand the secondary effect (due to hyperconjugative stabilisation of the incipient carbocation by the electrons of the neighbouring C-H bond) should become more important as the transition state becomes more *EI*-like. This latter point was not considered by Kwart and Slutsky who concluded that since the isotope effects for pyrolysis of primary acetates

against σ^+ values^{11,12} gives a good correlation with $\rho = -0.84$ (Figure). This is greater than that obtained for acetate pyrolysis at the same temperature and shows that more charge develops at the α -carbon for phenyl carbonate pyrolysis than for acetate pyrolysis. This confirms the conclusion reached by one of us from analysis of rate data for pyrolysis of aliphatic esters.¹³ The reason for the increase in polarity is the greater electron withdrawal (at the γ -carbon) of the PhO group (in phenyl carbonates) relative to Me (in acetates).

TABLE I
Pyrolysis of compounds $\text{RC}_6\text{H}_4\text{CH}(\text{OCOPh})\text{CH}_3$

R	T/K	$10^3 k/s^{-1}$						log (A/s^{-1})	E kcal mol ⁻¹	ΔS^\ddagger ^a cal mol ⁻¹ K ⁻¹	Corr. coeff.	log k/k_0 ^a
		570.7	571.4	587.1	587.5	604.8	623.9					
<i>p</i> -Me		8.18			20.7	58.0	161	13.17	39.86	0.5	0.999 67	0.298
<i>m</i> -Me			5.31	13.95	14.3	38.9	100	12.89	39.63	-0.9	0.999 73	0.112
H ^b		3.89		10.4	10.5	29.7	82.3	13.21	40.80	0.5	0.999 90	0
<i>p</i> -Cl		3.38		8.67		24.3	68.7	12.90	40.16	-0.9	0.999 87	-0.076
<i>m</i> -Cl			1.97	5.17		14.5	40.8	12.94	40.91	-0.9	1.000 00	-0.305
<i>p</i> -CF ₃			1.25	3.41		9.59	27.6	12.99	41.54	-0.4	0.999 99	-0.486
<i>m</i> -NO ₂				2.78		7.60	22.5	12.81	41.29	-1.3	0.999 92	-0.577
<i>p</i> -NO ₂				2.48		7.10	20.9	13.05	42.06	0	0.999 99	-0.616

^a At 600 K. ^b The [2,2,2-³H₃] isomer which n.m.r. showed to contain 95% β -deuterium gave values of $10^3 k/s^{-1}$ (K in parentheses) as follows: 1.985 (571.3), 5.25 (587.4), 14.3 (604.6), 33.7 (620.2), 80.1 (635.9), $\log(A/s^{-1}) = 13.07$, $E/\text{kcal mol}^{-1} = 41.24$, $\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1} = 0$, corr. coeff. = 0.999 93, and $\log k/k_0 = -0.301$.

and tertiary carbamates were fairly similar, that 'their respective thermolytic transition states have similar structures and possess the same degree of double bond development'.³ As we shall show, neglect of this factor and failure to compare esters of the same type cause this conclusion to be in error.

In Part I, we proposed that the overall isotope effect would be a composite of the primary and secondary (hyperconjugative) effects,⁴ but the evidence that we obtained for the latter was small and within the limits of experimental error. However, our models were secondary esters and therefore not ideal for detecting hyperconjugative effects. So far, Hammett correlations are available for pyrolysis of ethyl,⁵ isopropyl,⁵ and *t*-butyl⁶ benzoates, ethyl carbonates,⁷ 2-aryl¹ and 1-aryl-ethyl⁸ acetates, and *t*-butyl carbamates;⁹ the kinetic isotope effects have been measured for the last two series of compounds. In this paper we report rate data for pyrolysis of 1-arylethyl phenyl carbonates, and the kinetic isotope effect at 600 K for 1-phenylethyl phenyl carbonate, 1-phenylethyl acetate, phenyl *t*-butyl carbonate, and *t*-butyl acetate, each measured by the very accurate static method.¹⁰

RESULTS AND DISCUSSION

The kinetic data for the 1-arylethyl phenyl carbonates are given in Table I. A plot of the $\log k_{\text{rel}}$ values

³ H. Kwart and J. Slutsky, *J.C.S. Chem. Comm.*, 1972, 1182.

⁴ R. Taylor, *J.C.S. Perkin II*, 1972, 165.

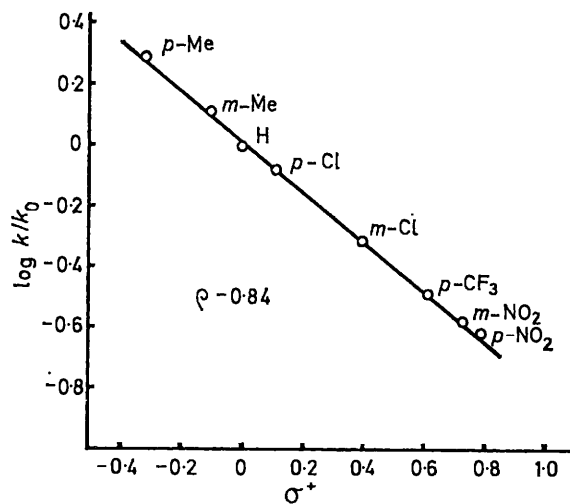
⁵ G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403; G. G. Smith and D. A. K. Jones, *ibid.*, p. 3896.

⁶ H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1975, 1802.

⁷ G. G. Smith, D. A. K. Jones, and R. Taylor, *J. Org. Chem.*, 1963, **28**, 3547.

⁸ R. Taylor, G. G. Smith, and W. H. Wetzell, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

Consequently the ρ factor for pyrolysis of 1-arylethyl methyl carbonates (I; X = OMe) should be less than -0.84 , and indeed, Smith *et al.*¹⁴ reported a value of



Hammett correlation for pyrolysis of 1-arylethyl phenyl carbonates at 600 K

ca. -0.74 (corrected to 600 K) for these esters. These results confirm our belief¹³ that the more reactive an ester is towards elimination, the more polar is the transition state, since the relative rates of elimination of acetates: methyl carbonates: phenyl carbonates is *ca.* 1:10:25.

⁹ R. Taylor and M. P. Thorne, *J.C.S. Perkin II*, 1976, 799.

¹⁰ R. Taylor, *J. Chem. Soc. (B)*, 1968, 1397.

¹¹ L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

¹² E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1463.

¹³ R. Taylor, *J.C.S. Perkin II*, 1975, 1025.

¹⁴ G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, 1969, **34**, 2091.

With regard to the Hammett correlation, three points may be noted. (i) The *m*-NO₂ substituent effect is not correlated by the σ^+ value of 0.674 derived from solvolysis of 2-aryl-2-chloropropanes¹¹ and our plot shows that a new value of 0.73 is required for the best fit of the log k_{rel} value to the mean slope; this is confirmed by data in the following paper. The new value gives a better correlation of *all* electrophilic aromatic substitutions and related reactions than does the old value; we discuss this in detail elsewhere.¹⁵ (ii) The Hammett correlation is in fact slightly curved, with electron-supplying substituents activating more, and electron-withdrawing substituents deactivating less than predicted. Recently one of us observed the same pattern in pyrolysis of 1-arylethyl acetates containing two or more activating, or two or more deactivating substituents, due to the transition state polarity being increased or decreased, respectively.¹⁶ It follows that the same variation in transition state polarity occurs within a series of monosubstituted 1-arylethyl acetates, and the observed ρ factor is an average value representing the range of transition state structures. Nevertheless a precise correlation with σ^+ values is obtained because in effect this is a correlation with the Yukawa-Tsuno equation (1)¹⁷ in which $r = 1.0$ and the value of r is artificially high relative to ρ as a con-

$$\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)] \quad (1)$$

sequence of this variation in transition state structure. (Another contributing factor is the absence of solvent which means that there can be no solvent-assistance in stabilising the transition state¹⁸). For the 1-arylethyl phenyl carbonates, the greater charge in the transition state causes the deviations to be more apparent, though again they can largely be removed through use of equation (1) with $r = 1.3$ and $\rho = -0.80$. (iii) The data confirm the findings of one of us¹² that the correct σ^+ value for the *m*-methyl substituent is considerably more negative than that derived from solvolysis of 2-aryl-2-chloropropanes.¹¹ From pyrolysis of 1-arylethyl acetates a value of -0.10 was indicated and the present results are best fitted by an even higher value of -0.130 . Discussion of the significance of this is deferred to a later paper in which the results from a number of other reactions will be considered.

The Kinetic Isotope Effect.—Preparation of [2,2,2-²H₃]-1-phenylethyl phenyl carbonate gave a product containing 95% of β -deuterium per molecule and the kinetic isotope effect obtained with this ester (Table 1) was 2.00. Correction for the incomplete deuteration gives a true isotope effect of 2.11. We have also measured the isotope effects for 1-phenylethyl acetate between 656.1 and 600.8 K (Table 3), for phenyl t-butyl carbonate between 574.7 and 519.0 K (Table 4), and for t-butyl acetate between 609.2 and 518.8 K (Table 4); each deuterated compound was shown by

n.m.r. to contain >99.5% deuterium in the β -position. This, the most detailed examination yet made of the kinetic isotope effect in thermal eliminations was carried out over these wide temperature ranges to ascertain if each pair of deuterated and undeuterated isomers would give a constant log A value. Such constancy is a necessary consequence of the requirement¹⁹ that the isotope effect should vary as a function of $e^{-1/RT}$ or, put another way, that $\log (k_{\text{H}}/k_{\text{D}})_1 T_1 = \log (k_{\text{H}}/k_{\text{D}})_2 T_2$. The data in Tables 1, 3, and 4 show this constancy so that we may use the Arrhenius equation to calculate with complete confidence the isotope effects at temperatures outside the range measured. Such confidence is necessary because the widely differing reactivities of the esters examined did not permit measurement of the elimination rates for all of them at a common temperature. The derived isotope effects are summarised in Table 2.

TABLE 2

β -Deuterium isotope effects ($k_{\text{H}}/k_{\text{D}}$) in ester elimination at 600 K

	Acetate	Phenyl carbonate
1-Phenylethyl	2.32(1) ^a	2.11(24) ^a
t-Butyl	2.285(55) ^a	2.19(1030) ^a

^a Relative reactivity of the protium-containing ester at 600 K.

Consider first the secondary (1-phenylethyl) esters. We have shown that the transition state for phenyl carbonate pyrolysis is more polar than that for acetate pyrolysis by virtue of the greater rate spread between primary, secondary, and tertiary phenyl carbonates than between the corresponding acetates,¹³ and because, as shown above, the Hammett ρ factor is larger for 1-arylethyl phenyl carbonates than for 1-arylethyl acetates. Accordingly the transition state for the elimination from phenyl carbonates will be slightly less E_i -like and slightly more $E1$ -like so that β -carbon-hydrogen bond breaking is predicted to be less kinetically important; this is experimentally observed, the isotope effects being 2.11 (phenyl carbonates) and 2.32 (acetates).

Consider next the tertiary (t-butyl) esters. These are much more reactive than the secondary esters and consequently should have a much more polar transition state. This we have confirmed by the fact that the ρ -factors for pyrolysis of ethyl, isopropyl, and t-butyl benzoates at 600 K are 0.26, 0.335, and 0.58, respectively.⁶ From a comparison of the relative reactivities of t-butyl acetate and 1-phenylethyl phenyl carbonate (Table 2) the kinetic isotope effect for the former could be expected to be *ca.* 2.10. The observed value is substantially higher and this must arise because of secondary isotope effects due to hyperconjugative stabilisation of the incipient α -carbocation; this will be much more important for the tertiary esters (which have nine β -carbon-hydrogen bonds) than for the 1-phenylethyl esters (which have only three). The secondary hyperconjugative effect should become more

¹⁵ H. B. Amin and R. Taylor, *Tetrahedron Letters*, 1978, 267.

¹⁶ E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 1537, 1541.

¹⁷ Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

¹⁸ R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937.

¹⁹ K. Wiberg, *Chem. Rev.*, 1955, **55**, 713.

pronounced the more polar the transition state, and this is also observed. Whereas the overall isotope effect for t-butyl acetate is slightly less than that for 1-phenylethyl

Quantitative evaluation of the magnitude of the secondary effect is not possible because it will vary with ester reactivity, but a reasonable estimate may be made.

TABLE 3
Kinetic data for pyrolysis of 1-phenylethyl acetates, PhCH(OAc)R

R	T/K =	$10^3 k/s^{-1}$				log (A/s ⁻¹)	E kcal mol ⁻¹	ΔS^\ddagger ^a cal mol ⁻¹ K ⁻¹	Corr. coeff.	k_H/k_D ^a
		656.1	637.5	622.8	600.8					
CH ₃	16.7	6.49	2.84	0.758	12.81	43.76	-1.3	0.999 90	2.32	
	16.8	6.45								
	17.0	6.51								
	16.8									
CD ₃	7.80	3.01	1.27	0.328	12.84	44.84	-1.2	0.999 86		
	7.79	2.94	1.26	0.328						
	7.81	2.98								
	7.75									

^a At 600 K.

acetates, the isotope effect for the very reactive phenyl t-butyl carbonate (in which the secondary effects will be the most significant), is significantly *greater* than that

From the difference in overall isotope effects for phenyl 1-phenylethyl carbonate and t-butyl acetate (which have fairly similar reactivities so that the primary effect

TABLE 4
Kinetic data for pyrolysis of phenyl t-butyl carbonate and t-butyl acetate ROCOR'

R'	R	T/K	$10^3 k/s^{-1}$	log(A/s ⁻¹)	E kcal mol ⁻¹	ΔS^\ddagger ^a cal mol ⁻¹ K ⁻¹	Corr. coeff.	k_H/k_D ^a
OPh	t-C ₄ H ₉	559.4	79.2	13.42	37.16	1.5	0.999 85	2.19
		557.9	73.4					
		557.5	71.8					
		553.3	56.4					
		544.4	32.1					
		542.7	27.4					
		529.8	12.4					
		522.6	7.65					
OPh	t-C ₄ D ₉	519.0	5.93	13.49	38.29	1.8	0.999 86	
		574.7	85.4					
		571.3	70.2					
		559.4	34.1					
		557.9	30.6					
		553.3	24.3					
		543.3	12.3					
		542.7	11.5					
		529.8	4.91					
		519.0	2.38					
CH ₃	t-C ₄ H ₉	609.2	67.4	13.06	39.69	-0.1	0.999 75	2.285
		608.1	62.0					
		599.9	41.4					
		588.2	20.55					
		587.4	19.9					
		585.5	17.75					
		575.2	9.21					
		571.3	7.50					
		559.4	3.37					
		557.9	3.15					
		553.3	2.35					
		543.3	1.19					
		518.8	0.237					
		519.0	2.38					
CH ₃	t-C ₄ D ₉	608.1	27.6	13.38	41.57	1.4	0.999 91	
		604.6	22.8					
		588.2	8.82					
		575.2	3.85					
		571.3	3.03					
		559.4	1.355					
		557.9	1.29					

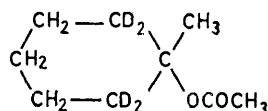
^a At 600 K

for phenyl 1-phenylethyl carbonate. The same argument accounts for the fact that although each phenyl carbonate is *ca.* 25 times more reactive than the corresponding acetate, the difference in kinetic isotope effect for the tertiary esters is smaller than for the secondary esters.

should be approximately constant) a value of *ca.* 0.03 per β -deuterium atom may be deduced. This shows that the effect must be hyperconjugative rather than inductive, since deuterium at the α -position (of 1-phenylethyl acetate) produces a rate retardation of 0.025 per deuterium,⁴ which would be equivalent to <0.01 at the

β -position if the effect were inductive. Moreover, one of us has shown that β -substituents do not modify pyrolysis rates through their inductive effect on the α -carbocation.¹ For phenyl *t*-butyl carbonate the secondary effect may be considerably greater, perhaps as much as 0.05 per β -deuterium.

The above analysis is confirmed by the following. (i) De Puy *et al.*²⁰ measured the *exo* : *endo* product ratio by g.l.c. for pyrolysis of the tertiary cyclohexyl ester (II). This should give a reasonably accurate measure of the *product* isotope effect, which, corrected to 600 K was 2.02 ± 0.11 (error for $\pm 1\%$ error in g.l.c. analysis). This is significantly less than we obtain with *t*-butyl acetate (which is of comparable reactivity) and shows the presence of the secondary effect, and also indicates it to be *ca.* 0.03 per β -deuterium. (ii) Our belief that



(II)

the primary isotope effect decreases along the series of esters primary > secondary > tertiary is supported by the value given in (i) taken along with the product isotope effect for ethyl acetate of *ca.* 2.60 (corrected to 600 K).²¹ It is noteworthy that this was significantly less than the kinetic isotope effect (*ca.* 2.80 at 600 K)²¹ indicating that secondary isotope effects are appreciable even for the primary esters. However, they may here be derived to a significant extent from rehybridisation rather than hyperconjugative effects; rehybridisation alone cannot account for the secondary isotope effects because there is less rehybridisation at the β -position in the transition state for tertiary esters than for primary esters.

It is evident from the foregoing discussion that interpretation of transition state structure for ester pyrolysis from isotope effects alone is unsatisfactory since the two structurally dependent isotope effects have opposing dependencies. The conclusions of Kwart and Slutsky³ are therefore not valid.

Two other points may be noted. First, we previously attempted to detect the secondary effect by comparison of the isotope effects in 1-phenylethyl acetate and 1,2-diphenylethyl acetate which have three, and two β -hydrogens respectively. The small difference in isotope effect was not outside experimental error, though is significant (and in the required direction) if the Arrhenius effect is taken into account since the temperature used for each ester was not the same.

Secondly, one of us noted previously, that in pyrolysis of *t*-butyl *N*-*p*-tolylcarbamate, the isotope effect in the gas phase (1.78 at 569.2 K) was inconsistent with that determined in the liquid phase (2.56 at 468.7 K).⁹ The former value is also inconsistent with that which may

be estimated from the present work as being applicable to *t*-butyl *N*-arylcarbamates (which are *ca.* 3 times less reactive than phenyl carbonates). We have since found that the deuteriated carbamate was undergoing very *reproducible*, though surface-catalysed elimination (the tendency for carbamates to undergo surface-catalysed eliminations is very much greater than for other esters,¹³ probably because of the ease with which the nitrogen lone pair may be donated to Lewis acid sites on the surface). We plan to reinvestigate this particular isotope effect when a new type of reactor, presently under construction, becomes available, and using rates measured over a range of temperatures as in the present case. This provides an unambiguous method of determining surface-catalysed reactions. None of the conclusions given in our previous paper relating to isotope effects are fortunately affected since the present work provides a much more detailed confirmation of the views expressed in that paper.

EXPERIMENTAL

Kinetic studies were carried out in the manner previously described.¹⁰ All the esters gave excellent first-order kinetic plots with linearity to beyond 95% of reaction, and all rate coefficients could be duplicated to better than $\pm 1.5\%$. The absence of surface-catalysed reactions was established by the usual criteria and demonstrated also by the excellence of the correlation coefficients. For the 1-arylethyl phenyl carbonates, the log *A* values are slightly larger, and the activation energies slightly lower than for pyrolysis of the corresponding 1-arylethyl acetates.

1-Phenylethyl acetate,⁴ 1-phenyl[2,2,2-²H₃]ethyl acetate,⁴ *t*-butyl acetate,¹³ and phenyl *t*-butyl carbonate¹³ were available from previous studies. [²H₉]-*t*-Butyl acetate and phenyl [²H₉]-*t*-butyl carbonate were made by esterification of *t*-butyl alcohol (>99% deuterium in the alkyl group; Merck, Sharp, and Dohme, Ltd.) in pyridine with acetyl chloride or phenyl chloroformate, respectively.

The 1-arylethyl phenyl carbonates were all prepared by dissolving the appropriate alcohol in pyridine and adding excess of phenyl chloroformate in portions to the cooled mixture. Normal work-up and fractional distillation yielded the following compounds: phenyl 1-phenylethyl carbonate (68%), b.p. 170–172° at 0.3 mmHg, *n*_D²⁰ 1.543 0 (Found: C, 74.5; H, 5.7. C₁₅H₁₄O₃ requires C, 74.4; H, 5.8%); 1-(*m*-methylphenyl)ethyl phenyl carbonate (37%), b.p. 132–134° at 0.4 mmHg, *n*_D²⁰ 1.541 0 (Found: C, 75.3; H, 6.5. C₁₆H₁₆O₃ requires C, 75.1; H, 6.3%); 1-(*p*-methylphenyl)ethyl phenyl carbonate (24%), b.p. 136° at 0.5 mmHg, *n*_D²⁰ 1.540 1 (Found: C, 75.1; H, 6.2%); 1-(*m*-chlorophenyl)ethyl phenyl carbonate (45%), b.p. 144–146° at 0.4 mmHg, *n*_D²⁰ 1.551 5 (Found: C, 65.0; H, 4.7. C₁₅H₁₃ClO₃ requires C, 65.1; H, 4.7%); 1-(*p*-chlorophenyl)ethyl phenyl carbonate (17%), b.p. 146–148° at 0.1 mmHg, *n*_D²⁰ 1.551 0 (Found: C, 65.15; H, 4.95%); phenyl 1-(*p*-trifluoromethylphenyl)ethyl carbonate (42%), b.p. 84–86° at 0.2 mmHg, *n*_D²⁰ 1.498 8 (Found: C, 62.0; H, 4.2. C₁₆H₁₃F₃O₃ requires C, 62.15; H, 4.2%); 1-(*m*-nitrophenyl)ethyl phenyl carbonate (26%), b.p. 110–142° at 0.05 mmHg, *n*_D²⁰ 1.560 3 (Found: C, 63.0; H, 4.6. C₁₅H₁₃NO₄ requires C, 62.7; H, 4.6%); 1-(*p*-nitrophenyl)ethyl phenyl carbonate

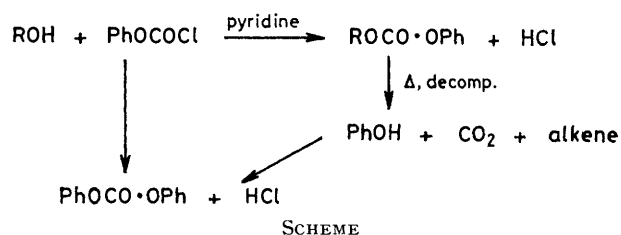
²⁰ C. H. De Puy, R. W. King, and D. H. Frosemendorf, *Tetrahedron*, 1959, 7, 123.

²¹ A. T. Blades and P. W. Gilderson, *Canad. J. Chem.*, 1960, 88, 1401, 1407.

(25%), b.p. 156—158° at 0.2 mmHg (Found: C, 62.9; H, 4.6%); *phenyl 1-phenyl[2,2,2-²H₃]ethyl carbonate* (60%), b.p. 104° at 0.1 mmHg, n_D^{20} 1.5431 (Found: C, 73.35, C₁₅H₁₁D₃O₃ requires C, 73.45%). The deuteriated alcohol precursor for this latter ester was made by reduction of acetophenone containing 98.5% deuterium in the methyl group [and itself made by repeated exchange (six times) of acetophenone with excess of D₂O in NaOD] with sodium borohydride. In a first preparation, substantial exchange was found to have occurred in this reduction step, presumably as a result of the presence of excess of borohydride and hence a very alkaline medium; the resultant ester contained only 77% deuterium in the methyl group. In a second batch, strongly alkaline conditions were avoided and the resultant alcohol (and ester) contained 95% deuterium in the methyl group; all deuterium contents were determined by n.m.r. and are considered accurate to $\pm 1\%$.

The low yields of esters was due in part to the formation

in each preparation of large amounts of diphenyl carbonate, m.p. 78—80° (lit.,²² 78°), which may have been formed as in the Scheme.



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²² C. A. Bischoff and A. von Hedenström, *Ber.*, 1902, **35**, 3434