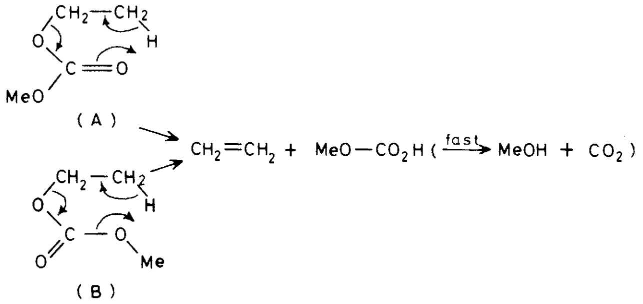
The Mechanism of Thermal Eliminations. Part 15.[1] Abnormal Rate Spread in Pyrolysis of Alkyl Methyl Carbonates and *S*-Alkyl *O*-Methyl Carbonates due to Enhanced Nucleophilicity of the Carbonyl Group

Roger Taylor
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

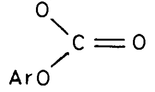
Rate coefficients for pyrolytic elimination of ethyl, isopropyl, and t-butyl carbonates, and of di-t-butyl carbonate have been measured over a 50 K range for each compound. The relative rates at 600 K are 1 : 29.6 : 2 934 : 3 526 and the rate spread for the primary, secondary, and tertiary compounds is inconsistent with that obtained from elimination of a range of other esters including alkyl phenyl carbonates. The least reactive compounds are found to be more reactive than predicted, probably owing to a combination of the greater E_i character of their transition states and the high nucleophilicity of the carbonyl group in dialkyl carbonates. Rate data for pyrolysis of *S*-ethyl, *S*-isopropyl, and *S*-t-butyl *O*-methyl carbonates give the relative rates at 600 K as 1 : 22 : 1 074. The Bu$^\mathrm{t}$: Pr$^\mathrm{i}$ rate ratio (49 : 1) is therefore greater than the Pr$^\mathrm{i}$: Et ratio, as it is for all other related eliminations; this confirms that the literature results (which show the converse) are in error. The seemingly anomalous relative reactivities of thiolacetates and thiolcarbonates as compared with their oxygen-containing analogues is also shown to be consistent with the effect of variable polarity of the transition state in ester pyrolysis upon the importance of carbonyl group nucleophilicity, and this also accounts for the relative reactivities of thiol-, thion-, and dithio-acetates. Steric acceleration appears less important for carbonates than for acetates, since the rate for di-t-butyl carbonate (statistically corrected) is lower than for t-butyl methyl carbonate, whereas pivalates are more reactive than acetates.

Carbonates can in principle undergo pyrolysis by two mechanisms, (A) or (B),[2] and although there have been a number of studies of carbonate pyrolysis, none has revealed any evidence for the involvement of (B). Indeed, all the evidence has firmly confirmed process (I), as follows.



(i) Pyrolysis of aryl ethyl carbonates (1) gave a Hammett correlation with a positive ρ-factor of 0.19.[3] Thus electron-withdrawing substituents in the aryl ring increase the rate (through aiding polarisation of the C_α–O bond), exactly the opposite of that which would be obtained if (B) was involved, since electron withdrawal would make the ethereal oxygen less nucleophilic thereby lowering the reaction rate.

(ii) Pyrolysis of t-butyl *N*-arylcarbamates gives a similar correlation, showing that both carbonates and carbamates are pyrolysed *via* the same mechanism.[4] However, carbamates are less reactive than carbonates [5] yet the amino group is much more nucleophilic than the ethereal oxygen in carbonates. Thus both must undergo pyrolysis *via* (A).



(1)

(iii) Methyl alkyl carbonates should be less reactive than phenyl alkyl carbonates; our data on 1-phenylethyl phenyl carbonates [6] and 1-phenylethyl methyl carbonates [7] indicate this to be so, the respective values of $10^3 k/\mathrm{s}^{-1}$ at 600 K being 22.2 and 6.98. We would therefore expect ethyl phenyl carbonate [$10^4 k/\mathrm{s}^{-1}$ (629 K) = 6.79] [5] to be more reactive than ethyl methyl carbonate. However two widely differing values for the rate coefficient of the latter at this temperature are given in the literature. Al-Awadi and Bigley [8] quote 6.9 and Gordon and Norris [9] quote 52, so both are *higher* than that for the phenyl compound but differ considerably. Re-investigation of the rates for the ethyl methyl carbonates as well as for the secondary and tertiary compounds, under the same conditions as those used for ethyl phenyl carbonate seemed necessary.

During the course of preparing t-butyl methyl carbonate, di-t-butyl carbonate was obtained as a by-product from the reaction of potassium t-butoxide with methyl chloroformate, through nucleophilic displacement of both Cl^- and MeO^-. We therefore pyrolysed this compound because we expected comparison with the rate of elimination of t-butyl methyl carbonate to give information concerning the effect of steric acceleration. We previously showed steric acceleration to be an important factor governing the rates of ester pyrolysis [10–13] and this has been confirmed by Smith and co-workers.[14]

Rate data from a recent study of the gas-phase elimination of *S*-alkyl *O*-methyl carbonates [8] give the relative rates for the ethyl, isopropyl, and t-butyl compounds at 600 K as 1 : 74.5 : 2 531, and we have argued [15] that these must be incorrect since the Bu$^\mathrm{t}$: Pr$^\mathrm{i}$ rate ratio (34 : 1) is *less* than the Pr$^\mathrm{i}$: Et ratio; this contrasts both with the rate spreads for all other related compounds, and with predictions based on transition state polarities. The corresponding Arrhenius parameters [E/kJ mol^{-1}, log (A/s^{-1})] were 226, 12.65; 203, 12.52; 176, 11.70,[8] and comparison with the wide range of values now available for related compounds suggested that those parameters were too small for the t-butyl compound and too large for the ethyl one. Since it is important for further development of gas-phase elimination theory to know whether this is a real

Table 1. Rate data for pyrolysis of carbonates RO·CO·OR′

R	R′	T/K	10^3k/s^{-1}	E/kJ mol^{-1} [a]	log(A/s^{-1}) [a]	Correlation coefficient	10^3k/s^{-1} at 600 K
Me	Et	626.1	0.365	187.45	12.202	0.999 87	0.076
		636.4	0.666				
		645.8	1.07				
		660.7	2.35				
		666.1	3.18				
		681.9	7.03				
Me	$\mathrm{Pr^i}$	594.5	1.58	180.14	13.037	0.999 87	2.23
		626.1	10.5				
		636.4	17.8				
		645.8	29.05				
		660.7	61.0				
Me	$\mathrm{Bu^t}$	546.4	10.3	156.06	12.937	0.999 98	222
		560.9	25.4				
		575.8	59.7				
		585.3	102				
		592.1	146				
		594.5	168				
		597.5	195				
$\mathrm{Bu^t}$	$\mathrm{Bu^t}$	546.4	12.6	155.07	12.930	0.999 63	268
		560.9	30.7				
		575.8	77.5				
		585.3	122				
		592.1	175				
		594.5	201				

[a] These values are not rounded off, in order that the rate coefficients calculated at 600 K may be verified.

Table 2. Rate coefficients (10^3 k/s^{-1}) for pyrolysis of carbonates RO·CO·OR′ at 600 K

R′	R = Me	R = Ph	$k_{\mathrm{rel.}}$
Et	0.076	0.12	1.58
$\mathrm{Pr^i}$	2.25	4.78	2.12
$\mathrm{Bu^t}$	223	601	2.70
CHMe(Ph)	6.98	22.2	3.18

Table 3. Relative rates of ethyl, isopropyl, and t-butyl esters of acids RCO_2H at 600 K

R	$\mathrm{Pr^i}$/Et	$\mathrm{Bu^t}$/$\mathrm{Pr^i}$	$\mathrm{Bu^t}$/Et	k_{tel}(Et) [a]	k_{tel}($\mathrm{Bu^t}$) [b]	ρ [c]
Me	28.8	115	3 312	1	1	−0.66
$PhCH_2$	32.3	121	3 910	1.26	1.55	
Ph	36.3	125	4 538	1.72	2.22	−0.72
MeO	29.6	99.1	2 934	7.75	6.86	−0.71
PhO	39.8	126	5 015	12.9	17.8	−0.84

[a] Relative rates of ethyl esters. [b] Relative rates of t-butyl esters. [c] For 1-arylethyl esters.

deviation or simply experimental error, we have made all of the compounds and measured their elimination rates.

Results and Discussion

(1) *Pyrolysis of Carbonates.*—All the carbonates exhibited excellent first-order kinetics (linear to at least 99% reaction); the rate coefficients were readily reproducible, and the derived Arrhenius plots have excellent correlation coefficients (Table 1). The Arrhenius parameters are almost identical with those for alkyl phenyl carbonates.[5] The rate of elimination is in each case lower than for the corresponding phenyl carbonate (Table 2), and the relative rates are close to those previously observed for 1-phenylethyl methyl and phenyl carbonates. All these results therefore confirm that mechanism (A) operates. Our data predict a rate coefficient for pyrolysis of ethyl methyl carbonate at 629 K of 4.3×10^{-4} s^{-1}, close to that given by Al-Awadi and Bigley[8] (and in excellent agreement with their unpublished[15] value of 3.6×10^{-4} s^{-1}). The results of Gordon and Norris are therefore confirmed as being substantially in error, as predicted by Richardson and O'Neal.[17]

The relative Et : $\mathrm{Pr^i}$: $\mathrm{Bu^t}$ elimination rates are 1 : 29.6 : 2 934 so that the $\mathrm{Bu^t}$: $\mathrm{Pr^i}$ rate ratio is 99.1 : 1. These values are assembled in Table 3 along with those for other esters,[5] the compounds being placed in order of increasing polarity of the transition states as indicated by the rate coefficient for the t-butyl compound,[5] and confirmed by the ρ-factors for pyrolysis of 1-arylethyl derivatives.[7,18,19] Two features are evident. First the $\mathrm{Bu^t}$: $\mathrm{Pr^i}$ and $\mathrm{Pr^i}$: Et rate ratios are inconsistent with those for other compounds in the series (and indeed for other compounds as well).[15] Secondly, although both the t-butyl rates and the ρ-factors indicate that methyl carbonate pyrolysis has similar transition state polarity to that of benzoates, the relative rates of the ethyl compounds indicate the polarity to be nearer to that of the phenyl carbonates. Both anomalies arise from the rates of the ethyl and isopropyl compounds being higher than expected, and by *ca.* 60% and 25%, respectively. Two interpretations of this are possible.

(i) For the least reactive compounds mechanism (B) is partly occurring, leading to enhanced rates. This is feasible because any alternative mechanism which could be involved would have to have a lower energy pathway and such a pathway would of course be most attractive to the least reactive compound; this possibility cannot be discounted by our data, though we consider it much less likely than the alternative explanation.

(ii) The rate for the least reactive compounds is being enhanced as a result of the difference in polarities of the transition states for primary, secondary, and tertiary compounds. We have previously shown by various means that along this series there is an increase in $E1$ character of the E_i reaction.[5,10,12,19,20] For primary compounds, β-C–H bond breaking will be relatively more important kinetically, and consequently the importance of nucleophilic attack upon the β-hydrogen will be greater. Now for alkyl methyl carbonates the carbonyl group must be exceptionally nucleophilic because of

Table 4. Rate data for pyrolysis of thiolcarbonates RS·CO·OMe

R	T/K	10^3k/s^{-1}	E/kJ mol^{-1} [a]	log(A/s^{-1}) [a]	Correlation coefficient	10^6k/s^{-1} at 600 K
Et	724.9	1.01	212.31	12.299	0.999 94	0.651
	728.6	1.18				
	743.2	2.35				
	755.1	4.09				
	775.0	9.74				
Pr^i	669.7	0.987	202.56	12.792	0.999 95	14.3
	680.8	1.74				
	693.0	3.34				
	708.1	7.02				
	721.1	13.1				
Bu^t	658.2	17.2	180.56	12.566	0.999 66	699
	669.7	31.1				
	680.7	50.2				
	693.0	86.3				
	708.1	182				
	714.0	231				
	721.7	308				

[a] These values are not rounded off, in order that the rate coefficients calculated at 600 K may be verified.

Table 5. Arrhenius parameters for pyrolysis of carbonates RO·CO·OMe and thiolcarbonates RS·CO·OMe

	E/kJ mol^{-1}, log(A/s^{-1}) [a]		
	Et	Pr^i	Bu^t
Carbonate	201.0, 12.5	192.3, 13.2	169.6, 13.3
Thiolcarbonate	212.3, 12.3	202.6, 12.8	180.6, 12.6
δ(E)	11.3	10.3	11.0
δ(log A)	0.2	0.4	0.7

[a] Parameters rounded off.

resonance with both *O*-alkyl groups. By contrast in phenyl carbonates, one lone pair on oxygen will be strongly delocalized into the adjacent phenyl ring, making these electrons relatively unavailable for conjugation with carbonyl. We therefore believe that the enhanced reactivity of the ethyl compound arises from the combination of enhanced nucleophilicity of the carbonyl group and the greater importance of attack of this group upon the β-hydrogen. For the isopropyl compound, the transition state for which is more *E*1-like, β-C–H bond breaking is kinetically less important, and so consequently is the result of this enhanced nucleophilicity.

(2) *Pyrolysis of Thiolcarbonates.*—Both the t-butyl and isopropyl compounds exhibited excellent first-order kinetics, readily reproducible rate coefficients, and no deviant runs on the Arrhenius plots, which have excellent correlation coefficients (Table 4). However, below 715 K the ethyl compound showed a tendency to undergo some decomposition by a pathway which probably involves radical chains. These runs were initially rapid (*ca.* 2—3 times the subsequent rate) but this stage ceased after *ca.* 5% of reaction had taken place, and the usual first-order kinetic form was then obtained. Nevertheless anomalously low Arrhenius data (670—710 K) were obtained with both *E* and log *A* much too small (188 kJ mol^{-1} and 10.5 s^{-1}, respectively). The incursion of a radical mechanism is entirely consistent with the difficulty in the primary ethyl compound of heterolytic cleavage of the relatively non-polar C–S bond, so that some homolytic cleavage occurs. At higher temperatures this problem became insignificant as expected, and rate data were therefore obtained between 725 and 775 K. However, in this range a second, but minor, problem was encountered, namely secondary decomposition of methanol. The extent of this in ten times the half-life of the primary elimination was, for example, 3.4% at 725 K and 6.3% at 755 K. It was therefore easy to obtain the rate coefficients for the primary elimination by the usual procedures, and these data were reproducible and also gave an excellent Arrhenius correlation (Table 4).

The Arrhenius parameters for the thiolcarbonates are compared with those for the carbonates in Table 5, from which it is apparent that there is a close parallel between corresponding sets of data. In general the thiolcarbonates have the higher activation energies (by a constant amount) and which reflects the lower polarity of the C–S than of the C–O bond. (In general, ester elimination rates parallel the polarity of the C_α–X bond.[5]) The thiolcarbonates also have the lower log *A* values, which may reflect a larger distance between the carbonyl oxygen and the β-hydrogen, arising from the presence of the larger sulphur atom.

Comparison with the literature data [8] (see Introduction) shows good agreement with the isopropyl data, but confirms that the previous t-butyl and ethyl data were anomalous. The low parameters for the former compound strongly suggests the incursion of surface catalysis (which is always more likely to affect the most reactive compound in a series) because the rates were measured at lower temperatures where decomposition routes of lower activation energy become more significant. The literature ethyl ester data were obtained at higher temperatures than those used in the present work, so it is possible that secondary decomposition of methanol (which would have been more severe) caused the erroneously high *E* and log *A* values. The new data give Pr^i : Et and Bu^t : Pr^i values of 22 : 1 and 49 : 1, respectively, and these are now as expected, the latter being the greater of the two ratios.

Anomalous Reactivity of Acetates and Carbonates, and their Thiol Counterparts.—Recently it was proposed that mechanism (B) might be involved in the pyrolysis of thiolcarbonates because whereas carbonates (2) are more reactive than acetates (3), thiolcarbonates (4) are *less* reactive than thiolacetates (5).[8,*] It was argued that the carbonyl oxygen in thiolcarbonates does not have enhanced nucleophilicity through resonance with the ethereal oxygen (next to the ethyl

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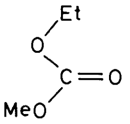
[*] The revised data for the thiolcarbonates makes the reactivity difference between them and thiolacetates less than described in ref. 8.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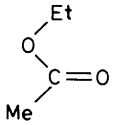
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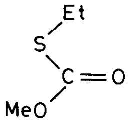
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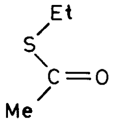
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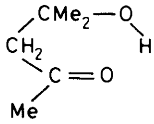
	(2)	(3)	(4)	(5)
$10^6k/s^{-1}$ at 600 K	76[21]	9.8[5]	0.65[22]	1.09[22]
$k_{rel.}$	7.76	1	1	1.68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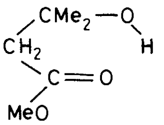
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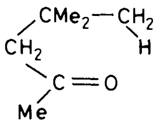
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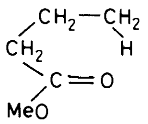
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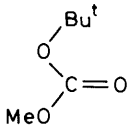
	(6)	(7)	(8)	(9)
$10^3k/s^{-1}$ at 600 K	223[21]	32.5[5]	0.70[21]	1.11[26,†]
$k_{rel.}$	6.86	1	1	1.59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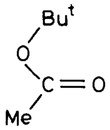
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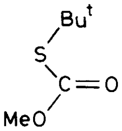
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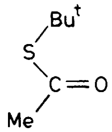
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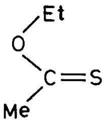
	(10)	(11)	(12)	(13)
k/s^{-1} at 600 K	295×10^{-3}	1.25×10^{-3}	5×10^{-10}	$<10^{-13}$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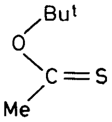
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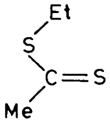
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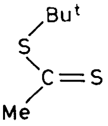
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	(14)	(15)	(16)	(17)
$10^3k/s^{-1}$ at 600 K	1.83	2700	0.343	73.2

group), as it does in acetates and carbonates, so that elimination takes place *via* attack of the ethereal oxygen. This interpretation can however be discounted for four reasons.

(i) This nucleophilic assistance is also absent in the thiolacetates, yet they are *more* reactive than the thiolcarbonates.

(ii) Nucleophilic assistance through resonance between the carbonyl group and the ether oxygen next to the methyl group *is* available to the thiolcarbonate but not the thiolacetate, yet the latter is the most reactive.

(iii) If attack by the ether oxygen of (4) were preferred, *i.e.* mechanism (B), then this would have to proceed *via* a lower energy pathway leading to an *increased* rate, the opposite of that observed.

(iv) Since in the thiolcarbonate there is only one ethereal oxygen (*cf.* two in the carbonate), this oxygen will be more involved in resonance with the carbonyl group than is the case in the carbonates, so that attack by the lone pair on the ethereal oxygen in thiolcarbonates (4) is *less* likely than in the case of the corresponding oxygen in carbonates, not more.

These results are however nicely consistent with our variable transition state theory.[13] For carbonates and acetates, the C_α–O bond is fairly polar and breaking of this is the principal rate-determining step. Electron withdrawal at the acyl carbon aids polarisation of this bond and since OMe has a $-I$ effect and Me has a $+I$ effect the relative reactivities then follow.* For thiolesters the transition state will be less $E1$-like, *i.e.* C_α–S bond breaking will be less important (shown by the smaller spread of primary, secondary, and tertiary rates), and β-C–H bond breaking more so. Consequently, attack upon the β-C–H bond and hence nucleophilicity of the carbonyl group becomes more important, and it appears that the $-I$ effect of OMe *vs.* the $+I$ effect of Me now has its primary effect upon this nucleophilicity. A similar result is obtained in pyrolysis of hydroxy-ketones [*e.g.* (6)] [23] *vs.* hydroxy-esters [*e.g.* (7)],[24] and possibly in pentan-2-one (8) *vs.* methyl butanoate (9) [25] (though because of the very low reactivity of these latter compounds the rate coefficients may be considerably in error [1]); for each of these compounds, nucleophilic attack on hydrogen is now the most important step of the reaction. Furthermore, attack by the ethereal oxygen would not give the observed products. Similar results are shown by the t-butyl derivatives of the acetates and carbonates (10)—(13).

These arguments may be extended to account for the reactivity differences of thionacetates [(14), (15)] [8,27] *vs.* acetates, and dithioacetates [(16), (17)] [8,27] *vs.* thiolacetates. For thionacetates the higher nucleophilicity of the C=S bond causes the rates of elimination to be higher. The advantage of this enhanced nucleophilicity will be greater the more E_1-like the transition state. Consequently the thionacetate : acetate rate ratio is higher for the ethyl compounds (187 : 1) than for the t-butyl compounds (83 : 1). This of course exactly parallels the methyl carbonate *vs.* acetate situation (Table 3) and the same explanation applies. The nucleophilicity effect will be all the more important the less polar the C_α–X bond, and should therefore be more important in dithioacetates than in thionacetates. This is precisely observed, the dithioacetate : thiolacetate rate ratio being higher for the ethyl compounds (315 : 1) than that noted above for ethyl thionacetates *vs.* ethyl acetate. By contrast the t-butyl compounds, with a more $E1$-like transition state, show a rate increase (66-fold) comparable with that for t-butyl thionacetate *vs.* t-butyl acetate.‡

Steric Acceleration.—Previously we showed that isopropyl

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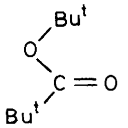
* There will of course be a contribution to the overall reactivity difference arising from the enhanced nucleophilicity of the carbonyl group in ethyl methyl carbonate, as described above.

† There is very marked disagreement between the Arrhenius parameters for pyrolysis of *S*-t-butyl thioacetate reported in refs. 22 and 26. We have attempted to resolve this problem by a further kinetic study which has revealed that the rate of decomposition of thioacetic acid, one of the products, is closely similar to that of *S*-t-butyl thioacetate. This made determination of rate data for the primary elimination impossible in our state system, and no doubt caused the discrepancies in the two previous studies, both of which used flow-tube techniques. For the ethyl and isopropyl compounds the secondary decomposition would be effectively instantaneous in the time of the primary elimination, giving 3.0 stoicheiometry (as for carbonates) and straightforward kinetics. Fortunately the two literature studies predict almost identical rate coefficients at 600 **K**, the temperature chosen for our comparison.

‡ The ratio is however smaller but the rate for t-butyl thionacetate is only an estimated [8] one and is based on assumptions of parallel behaviour for ethyl and t-butyl compounds, now seen to be incorrect.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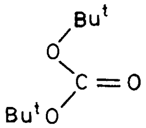
(19)

and t-butyl pivalates (18) were more reactive than the corresponding acetates, and interpreted this in terms of steric acceleration since electronic effects require the reverse order.[11] For carbonates however, the extra oxygen atom between the alkyl groups could mean that steric acceleration might be less or absent. Some indication that this might be so was provided by the data of Gordon and Norris[9] for the pyrolysis of methyl carbonate and diethyl carbonate, which gave k per β-hydrogen at 600 K as 2.9×10^{-4} and 2.3×10^{-4} s^{-1} respectively, though their abnormal Arrhenius data made any conclusions somewhat uncertain. The results for pyrolysis of methyl t-butyl carbonate and di-t-butyl carbonate (Table 1) give k per β-hydrogen at 600 K as 24.7×10^{-3} and 14.9×10^{-3} s^{-1}, respectively. Thus the bulkier di-t-butyl carbonate (19) is less reactive as expected from electronic considerations, and we may conclude that steric acceleration produced by bulky groups at the acyl carbon is unimportant for carbonates. This does not rule out the possibility of steric acceleration between components of the alkyl group, which should be much the same as for acetates, as we have described in detail elsewhere.[12,13]

Experimental

Ethyl Methyl Carbonate.—Pyridine (10 ml) was added cautiously to ethanol (15 g, 0.33 mol) and methyl chloroformate (94.5 g, 1 mol) with cooling, and the mixture set aside for 48 h. Normal work-up followed by fractional distillation gave ethyl methyl carbonate (15 g, 52%), b.p. 105—107 °C at 760 mmHg, n_D^{20} 1.3771 (lit.,[28] 107.2—107.8 °C at 765 mmHg, n_D^{20} 1.3778).

Methyl Isopropyl Carbonate.—The same procedure applied to propan-2-ol gave methyl isopropyl carbonate (40%), b.p. 117—118 °C at 760 mmHg, n_D^{20} 1.3822 (lit.,[28] 115.6—116.4° at 757 mmHg, n_D^{20} 1.3856).

Methyl t-Butyl Carbonate and Di-t-butyl Carbonate.—attempted preparation of methyl t-butyl carbonate by the reaction of potassium t-butoxide with methyl chloroformate (the method of Oki and Nakanishi)[29] gave on work-up and fractional distillation, a variety of products. A first fraction, b.p. 40—55 °C at 100 mmHg, was indicated by n.m.r. and g.l.c. analysis to be a mixture of ethyl and t-butyl chloroformates; this may be a better route to the latter than the literature method which uses phosgene.[30] The next fraction was the required t-butyl methyl carbonate (30%), b.p. 84 °C at 100 mmHg, n_D^{20} 1.3898 (lit.,[29] b.p. 52—53 °C at 57 mmHg), and the final fraction was di-t-butyl carbonate, b.p. 105 °C at 85 mmHg, m.p. 39° (lit.,[29] b.p. 158°, m.p. 39.5—40.5 °C). Thus in this reaction all possible nucleophilic substitutions by Bu^tO^- had taken place.

S-*Ethyl* O-*Methyl Carbonate.*—Ethyl chloroformate was added in excess to ice-cold ethanethiol (12.4 g, 0.2 mol) and pyridine (20 ml). The mixture was then warmed during 1 h and set aside overnight. Addition of water followed by normal work-up (with at least three washings with water to remove most of the pyridine) gave, after fractional distillation, *S*-ethyl *O*-methyl carbonate (42%), b.p. 136 °C at 760 mmHg, n_D^{20} 1.4540 (lit.,[8] b.p. 35 °C at 29 mmHg, n_D^{23} 1.4530.

S-*Isopropyl* O-*Methyl Carbonate.*—The above procedure using propane-2-thiol (15.2 g, 0.2 mol) gave *S*-isopropyl *O*-methyl carbonate (60%), b.p. 90 °C at 160 mmHg, n_D^{20} 1.4482 (lit.,[8] b.p. 50.5 °C at 20 mmHg, n_D^{23} 1.4524; this may have contained a little pyridine, which raises the refractive index).

S-*Butyl* O-*Methyl Carbonate.*—The above procedure using 2-methylpropane-2-thiol (18.0 g, 0.2 mol) gave *S*-t-butyl *O*-methyl carbonate (68%), b.p. 105 °C at 160 mmHg, n_D^{20} 1.4502 (lit.,[8] b.p. 49 °C at 15 mmHg, n_D^{23} 1.4512); we found early fractions to give an exalted refractive index, again almost certainly due to traces of pyridine).

Kinetic Studies.—The general method, involving a static stainless steel reactor, has been described previously.[31]

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