orange solution. Heating was stopped after 20 min., the mixture was cooled to room temperature, and the precipitates were filtered. The precipitates were heated with 20 ml. of benzene and filtered hot with suction. Insoluble matter was washed with benzene and dried, m.p. 115–117°, yield, 1 g. (11%). After five successive crystallizations from benzene, white needles melting with decomposition at 110–114° were obtained.

The acid hydrolysis of ethylenedi-*p*-toluenesulfonamide was worked up as described previously. Acetaldehyde 2,4-dinitrophenylhydrazone and *p*-toluenesulfonamide (85.8%) were obtained.

N-α-Butoxyethyl-N-methyl-p-toluenesulfonamide (IX). A mixture of 111 g. (0.6 mole) of *N*-methyl-*p*-toluenesulfonamide, 240 g. (2.4 moles) of *n*-butyl vinyl ether and 0.6 ml. of concentrated hydrochloric acid was heated at 60° for 2.5 hr., allowed to cool, washed successively with 5% sodium hydroxide solution and water, and dried over sodium sulfate overnight. Vacuum distillation under nitrogen yielded 144.2 g. (84%) of product, b.p. 162–184° (5.5 mm.). During the distillation, slight decomposition was observed. An analytical sample was prepared by redistillation, b.p. 160–164° (4 mm.).

The same procedure was used for the acid hydrolysis of (IX) as described previously. Acetaldehyde 2,4-dinitrophenylhydrazone (91%) and *N*-methyl-*p*-toluenesulfonamide (77%) were identified.

N-Vinyl-N-methyl-p-toluenesulfonamide. A sample of 144 g. (0.505 mole) of *N*-α-butoxyethyl-*N*-methyl-*p*-toluenesulfonamide was heated in a Claisen flask under a pressure of 22–30 mm. The bath temperature was maintained at 250–260°. The imidoether distilled with decomposition to give 1-butanol and a yellow, oily fraction, b.p. 196–198° (22–30 mm.). Redistillation of the oil yielded 93 g. (87%) of crude product, b.p. 150–157° (4 mm.), which was recrystallized from petroleum ether-benzene to give white crystals, m.p. 56–57.7°.

Anal. Calcd. for $C_{10}H_{13}O_2NS$: C, 56.84; H, 6.20; N, 6.63. Found: C, 56.92; H, 6.31; N, 6.57.

Polymerization. *N*-Vinyl-*N*-methyl-*p*-toluenesulfonamide was heated with 2% benzoylperoxide for 7 hr. on a boiling water bath, but failed to polymerize. On the other hand, when a few drops of an ether solution of boron trifluoride etherate were added to an ether solution of the vinyl sulfonamide, a white polymer deposited, which was insoluble in ether, acetone, and benzene.

N-α-Ethoxyethylcarbazole. A 13.4 g. (0.08 mole) sample of carbazole was treated with 34.6 g. (0.48 mole) of ethyl vinyl ether for 5 hr. at 180° by the same procedure as in the case of dicarboxylic acid imide. There was obtained 8.8 g. (54%) of crude product, b.p. 163–169° (3 mm.). After recrystallization from ethanol, it melted at 74–74.5°.

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KYOTO UNIVERSITY, JAPAN

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Pyrolysis of Organic Carbonates

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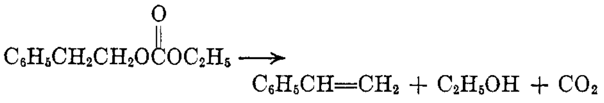
A study of the pyrolysis of organic carbonates in a flow system has been carried out to determine the utility of the reaction for the introduction of unsaturation into aliphatic chains.

A comparison of the ease of decomposition of ethyl carbonates and acetates of α-phenethyl alcohol and β-phenethyl alcohol has indicated that the four esters can be arranged into the following order of pyrolytic instability: 300°: β-acetate ≃ β-carbonate ≃ α-acetate ≃ α-carbonate; 400°: β-acetate < β-carbonate < α-acetate < α-carbonate; 500°: β-acetate < β-carbonate < α-acetate = α-carbonate. Pyrolysis of aliphatic bis(ethyl carbonates) led to the formation of dienes as well as a number of intermediate products.

In another study,[1] the disproportionation of unsymmetrical carbonates to form symmetrical carbonates was studied. Formation of the symmetrical carbonates depended on the nature of the group, Ar, and the catalyst.

$$2ArOCO_2C_2H_5 \xrightarrow[\text{catalyst}]{} ArOCO_2Ar + (C_2H_5O)_2CO$$

Ethyl β-phenethyl carbonate underwent a side reaction to form considerable amounts of styrene, rather than the symmetrical carbonate. The catalyzed disproportionations were carried out at 250°, a temperature approaching the range in which esters pyrolyze to form olefins and acids. It was decided to investigate to what extent the formation of styrene was due to the noncatalyzed pyrolysis reaction.



$$C_6H_5CH_2CH_2O\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow C_6H_5CH{=}CH_2 + C_2H_5OH + CO_2$$

This route is apparently favored over formation of ethylene and β-phenethyl alcohol, since no β-phenethyl alcohol was isolated from the pyrolyses mixtures.

A comparison of acetate and carbonate pyrolyses has been included in this work. It is hoped that carbonic ester pyrolysis will serve as an acid-free pyrolysis system, for use in the preparation of unsaturates bearing acid sensitive functional groups.

A. Pyrolyses of phenethyl alcohol esters. Pyrolyses of the acetates and ethyl carbonates of α-phenethyl alcohol and β-phenethyl alcohol indicate that the carbonate structure undergoes pyrolytic rupture under conditions similar to those used for the acetate unit. Both the α- and β-esters of the two al-

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[1] J. L. R. Williams, D. D. Reynolds, K. R. Dunham, and J. F. Tinker, unpublished results.

cohols pyrolyze only very slowly in the vicinity of 300° while the pyrolysis rates of both the acetates and the carbonates of the α-alcohol increase more rapidly with increase in temperature than do the β-alcohol esters. The four esters can be arranged into the following order of pyrolytic instability:

$$300^\circ\ \beta\text{-acetate} \approx \beta\text{-carbonate} \approx \alpha\text{-acetate} \approx \alpha\text{-carbonate}$$
$$400^\circ\ \beta\text{-acetate} < \beta\text{-carbonate} < \alpha\text{-acetate} < \alpha\text{-carbonate}$$
$$500^\circ\ \beta\text{-acetate} < \beta\text{-carbonate} < \alpha\text{-acetate} = \alpha\text{-carbonate}$$

These relationships indicate that at 300° there is very little difference in pyrolytic stability between the carbonates and the acetates of α-phenethyl alcohol and β-phenethyl alcohol since all four esters decompose to the extent of less than one per cent. In the presence of catalysts, considerable decomposition has been shown to occur[1] at 250°. At 400°, however, the esters decompose at different rates as a result of two structural features: (*1*) acetate *vs.* carbonate structure, and (*2*) primary alcohol ester *vs.* a secondary alcohol ester. The 400° pyrolyses indicate that although the primary esters are more stable than the secondary esters, there is, nevertheless, a difference between the stability of the carbonate structure and the acetate structure in both the α- and the β-series. At 500°, the secondary ester structure contributes much more to the instability than does the difference between carbonate and acetate structures. However, in the primary ester system at 500°, the carbonate structure causes greater instability than does the acetate.

The pyrolyses work was extended to other carbonic esters to investigate the effect of structure and the general synthetic utility.

B. Pyrolysis of 1,5-bis(ethoxycarbonyloxy)pentane. Following are the products isolated from the pyrolysis of 1,5-bis(ethoxycarbonyloxy)pentane:

$C_2H_5OCO_2(CH_2)_5OCO_2C_2H_5 \longrightarrow$

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$	8.6%
$CH_2{=}CH_2$	no recorded yield
C_2H_5OH	23.5%
$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}OH$	30.2%
$HO{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH$	7.6%
CO_2	no yield

During the pyrolysis of 1,5-bis(ethoxycarbonyloxy)pentane, there is competition between the two reaction sequences which can introduce double bonds into either the five-carbon chain or the two-carbon chain. Formation of ethylene will lead to the formation of the alcohol or diol in the five-carbon chain.

$$2CH_2{=}CH_2 + HOCH_2(CH_2)_3CH_2OH$$
$$C_2H_5OCO_2CH_2(CH_2)_3CH_2OCO_2C_2H_5 \begin{matrix}\nearrow \\ \searrow\end{matrix} \qquad + CO_2$$
$$2C_2H_5OH + CH_2{=}CHCH_2CH{=}CH_2$$

extreme cases

Formation of ethanol requires introduction of double bonds into the five-carbon chain. In practice, however, both reaction sequences proceed simultaneously, leading to the products just outlined. It would be expected that, under different flow rates and temperatures, the ratios of the various products would be shifted.

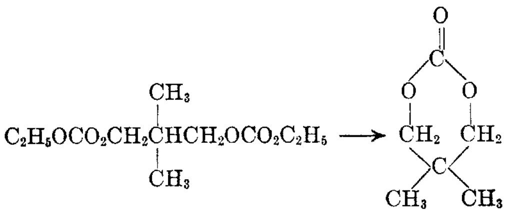
C. Pyrolysis of 1,10-bis(ethoxycarbonyloxy)decane. Pyrolysis of 1,10-bis(ethoxycarbonyloxy)decane under conditions identical with those used for 1,5-bis(ethoxycarbonyloxy)pentane led to the formation of two additional types of products, the mono-olefin-monocarbonate and the carbonate-carbinol.

$C_2H_5OCO_2(CH_2)_{10}OCO_2C_2H_5 \longrightarrow$

$C_2H_5OCO_2(CH_2)_8CH{=}CH_2$	3.4%
$C_2H_5OCO_2(CH_2)_{10}OH$	7.8%
$CH_2{=}CH(CH_2)_6CH{=}CH_2$	10.6%
$CH_2{=}CH(CH_2)_8OH$	27.4%
$HO(CH_2)_{10}OH$	18%
Ethylene	no recorded yield
Ethanol	4.7%

As in the case of 1,5-bis(ethoxycarbonyloxy)pentane, the major product (highest conversion) was the olefinic carbinol. The isolation of the mono-olefin-monocarbonate and the carbonate-carbinol would indicate a somewhat slower decomposition in the case of the ten-carbon system.

D. Pyrolysis of 1,3-bis(ethoxycarbonyloxy)-2,2-dimethylpropane. Pyrolysis of 1,3-bis(ethoxycarbonyloxy)-2,2-dimethylpropane caused cyclization of the carbonate structure with elimination of ethyl carbonate or its equivalents, to form 2,6-dioxa-4,4-dimethylcyclohexanone in 51.5% yield.



Ethylene—no recorded yield
Ethanol—no recorded yield

E. Pyrolysis of allyl ethyl carbonate. The reaction mixture produced by the pyrolysis of allyl ethyl carbonate failed to yield any clean-cut fractions upon distillation. The fractions were shown, by infrared spectroscopy and mass spectrometry, to consist of the following components:

$CH_2{=}CHCH_2OCO_2C_2H_5 \longrightarrow$

C_2H_5OH	5.5%
$CH_2{=}CHCH_2OH$	44.5%
$C_2H_5OCO_2C_2H_5$	2.2%
$CH_2{=}CHCH_2OCO_2C_2H_5$	45.5% recovery

TABLE I

STARTING MATERIALS

Compound	B.P. or M.P., °C.		Refractive Index and Density		Analysis	
	Found	Lit.	Found	Lit.	Calcd.	Found
α-Phenethyl acetate[a]	213–216		d_{17} 1.050			
β-Phenethyl acetate[b]	224		n_D^{25} 1.5108 d_{26} 1.029			
Ethyl α-phenethyl carbonate	72/0.5 mm.		n_D^{25} 1.4859 d_{26} 1.051		C—68.0 H— 7.3	67.8 7.4
Ethyl β-phenethyl carbonate[c]	99 (1.0 mm.)	140–141 (1.7 mm.)	n_D^{25} 1.4904 d_{26} 1.023	n_D^{22} 1.4889 d_{22} 1.063	C—69.9 H— 6.9	70.0 7.0
1,5-Bis(ethoxycarbonyloxy)-pentane[d]	138/2.5 mm.		n_D^{25} 1.4253			
1,10-Bis(ethoxycarbonyloxy)-decane[d]	176–178/1.3 mm. m.p. 17					
1,3-Bis(ethoxycarbonyloxy)-2,2-dimethylpropane	83–84/0.8 mm.				C—53.3 H— 8.0	53.1 7.7
Allyl ethyl carbonate[e]	148–149		n_D^{25} 1.4069 d_{26} 0.985	n_D^{25} 1.4095 d_{25} 0.98		

[a] Beilstein, **6,** 476 (1923). [b] Beilstein, **6,** 479 (1923). [c] P. Schviny and S. Sabetay, *Bull. soc. chim. France,* **43,** 859 (1928). [d] D. D. Reynolds and J. Van Den Berghe (Eastman Kodak Co.), U. S. Patent **2,789,968** (1957). [e] D. E. Adelson and H. Dannenberg, U. S. Patent **2,595,214** (1952).

TABLE II

PYROLYSIS PRODUCTS

Compound	B.P. or M.P., °C.		Refractive Index and Density		Analysis	
	Found	Lit.	Found	Lit.	Calcd.	Found
1,4-Pentadiene[a]	25.5	25.8–26.2	n_D^{25} 1.3890	n_D^{20} 1.3883		
5-Hydroxy-1-pentene[b]	53 (17 mm.)	53 (17 mm.)	n_D^{25} 1.4320	n_D^{15} 1.4305		
5-Ethoxycarbonyloxy-1-pentene	42 (0.2 mm.)		n_D^{25} 1.4198		C—60.7 H— 8.8	61.1 9.2
1,5-Pentanediol[c]	238–239		n_D^{25} 1.4470			
Ethylene dibromide[d]	131.5	131.6	n_D^{25} 1.5337	n_D^{25} 1.5379	Br—85.2	85.2
1,9-Decadiene[e]	60 (15 mm.)	165	n_D^{25} 1.4297	n_D^{20} 1.4300		
10-Hydroxy-1-decene[f]	85–86 (2 mm.)	234–238	n_D^{25} 1.4454	n_D^{25} 1.4480		
10-Phenylureido-1-decene	49–50 m.p.	49–50 m.p.				
10-Ethoxycarbonyloxy-1-decene	106 (0.5 mm.)		n_D^{25} 1.4362 $d_{20/4}$ 0.937		C—69.0 H—10.5	68.5 10.8
1-Hydroxy-10-ethoxycarbonyl-oxydecane	170–175 (0.5 mm.)		n_D^{25} 1.4410 $d_{26/4}$ 0.997		C—63.5 H—10.6	63.8 10.5
1-Phenylureido-10-ethoxy-carbonyloxydecane	65–67 m.p.				C—65.8 H— 8.8 N— 3.8	65.3 8.8 3.8
1,10-Decanediol[g]	70–71 m.p.	70.5				
1,10-Bis(phenylureido)decane	166–167 m.p.				C—70.0 H— 7.8 N— 6.8	70.1 7.5 6.7
2,6-Dioxa-4,4-dimethylcyclo-hexanone	109–110 m.p.				C—55.3 H— 7.7	54.9 7.9
Allyl alcohol[h]		96–97		n_D^{25} 1.4135		
Diethyl carbonate[i]	128–129	127–129 (760 mm.)	n_D^{25} 1.3850	n_D^{20} 1.3852		

[a] P. Krogerman, *J. Am. Chem. Soc.,* **52,** 5060 (1930). [b] *Org. Syntheses,* **25,** 84 (1945). [c] N. Demjanow and M. Dojarenko, *Ber.,* **40,** 2589 1907). [d] V. Meyer and P. Petrenko-Kritschenko, *Ber.,* **25,** 3304 (1892). [e] J. L. Everett and G. A. R. Kon, *J. Chem. Soc.,* 3131 (1950). [f] J. W. Hill and W. A. Carothers, *J. Am. Chem. Soc.,* **55,** 5031 (1933). [g] L. Bouveault and G. Blanc, *Comp. rend.,* **137,** 328 (1903). [h] L. Henry, *Comp. rend.,* **145,** 1247 (1907). [i] W. H. Perkin, *J. Chem. Soc.,* **65,** 402 (1894).

Pyrolytic decomposition of allyl ethyl carbonate apparently proceeds more easily through the route involving formation of ethylene and allyl alcohol than that of ethyl alcohol and allene since no allene was found to be present in the pyrolyzate. Formation of diethyl carbonate in small amounts can only be explained by the possibility of the interchange of ethanol with allyl ethyl carbonate. Such an equilibrium would not be favored on the basis of volatility at the temperature of pyrolysis, but may possibly have occurred during the distillation of the products. The isolation of ethanol would indicate that allene may be formed in very small amounts or, more probably, that diethyl carbonate was decomposed.

EXPERIMENTAL

Apparatus and procedure. Pyrolysis of the carbonates was carried out by passing the compound through a 25-mm. o.d. Pyrex tube packed for a distance of 30 inches with Pyrex helices and heated to the desired temperature by means of an electrically controlled furnace. The reactants were pumped into the reaction zone by means of a Corsen-Ceverni bellows pump. The pyrolyzates were collected in traps cooled by Dry Ice and distilled through either a 12-inch Vigreux-type column or a 12-inch helices-packed column, depending on the boiling points of the products. Ethylene was detected by means of a gas trap containing a carbon tetrachloride solution of bromine. Carbon dioxide was detected using a lime-water trap. The percentage figures represent the composition of the pyrolyzates.

Intermediates. The physical constants of the starting materials are listed in Table I, and those of the products in Table II. Literature values for both groups of known materials are listed therein, for convenience of comparison.

Pyrolyses

A. Pyrolysis of α-phenethyl acetate, β-phenethyl acetate, ethyl α-phenethyl carbonate, and ethyl β-phenethyl carbonate. Pyrolysis of the compounds was carried out at 300°, 400°, and 500° in the system described in the preceding paragraphs at the flow rates shown in Table III.

TABLE III

FLOW RATES FOR ESTER PYROLYSIS (MOLES PER HOUR)

Ester	Temperatures and Flow Rates		
	300°C.	400°C.	500°C.
α-Phenethyl acetate	0.50	0.50	0.50
β-Phenethyl acetate	0.50	0.43	0.54
Ethyl α-phenethyl carbonate	0.49	0.50	0.50
Ethyl β-phenethyl carbonate	0.42	0.47	0.38

Table IV lists the conversions to styrene per pass, determined by iodometric titration.

TABLE IV

PYROLYSIS OF ESTERS OF PHENETHYL ALCOHOLS

Ester	Temperature % Conversion to Styrene		
	300°C.	400°C.	500°C.
α-Phenethyl acetate	0.5	12.2	61.8
β-Phenethyl acetate	0.3	2.02	37.7
Ethyl α-phenethyl carbonate	0.6	26.9	62.2
Ethyl β-phenethyl carbonate	0.2	5.7	46.4

B. Pyrolysis of 1,5-bis(ethoxycarbonyloxy)pentane. Pyrolysis temperature, 500°; flow rate, 0.28 mole/hr.

Products: (1) 1,4-pentadiene, b.p. 25.5°, n_{D}^{25} 1.3890, 8.6%; (2) ethylene detected as the dibromide; (3) ethanol, b.p. 78.2°, n_{D}^{25} 1.3625, 23.5%; (4) 5-hydroxy-1-pentene, b.p. 37–39° (0.45 mm.), n_{D}^{25} 1.4230, 30.2%; (5) 1,5-dihydroxypentane, b.p. 86–91° (0.4 mm.), n_{D}^{25} 1.4470, 7.6%; (6) carbon dioxide.

C. Pyrolysis of 1,10-bis(ethoxycarbonyloxy)decane. Pyrolysis temperature, 500°; flow rate, 0.28 mole/hr.

Products: (1) ethylene, detected as the dibromide; (2) ethanol, b.p. 78.7°, n_{D}^{25} 1.3648, 4.7%; (3) 1,9-decadiene, b.p. 60° (15 mm.), n_{D}^{25} 1.4297, 10.6%; (4) 10-hydroxy-1-decane, b.p. 80–82° (0.8 mm.), n_{D}^{25} 1.4454, 27.4%; (5) 1,10-dihydroxydecane, m.p. 70–71°, 18% phenyl urethane, m.p. 166–167.5°; (6) 10-ethoxycarbonyloxy-1-decane, b.p. 106–117° (0.5 mm.); n_{D}^{25} 1.4365; 3.4%; (7) 10-ethoxycarbonyloxy-1-hydroxydecane, b.p. 155–175° (0.5 mm.); n_{D}^{25} 1.4412; 7.8%; phenylurethane, m.p. 48.5–49.5°; (8) 1,10-dihydroxydecane, m.p. 70–71°.

D. Pyrolysis of 1,3-bis(ethoxycarbonyloxy)-2,2-dimethylpropane. Pyrolysis temperature, 500°; flow rate, 0.27 mole/hr.

Products: (1) 2,6-dioxa-4,4-dimethylcyclohexanone, m.p. 109–110°, 51.5%; (2) ethanol, b.p. 78°, n_{D}^{25} 1.3647; (3) ethylene, detected as the dibromide.

E. Pyrolysis of allyl ethyl carbonate. Pyrolysis temperature, 500°; flow rate, 0.52 mole/hr.

Products: After distillation into 3 fractions: b.p. 72–88.5°, 88.5°, and 68–86° (105 mm.); the following components were determined by infrared and mass spectrometry: (1) ethanol, 5.5%; (2) allyl alcohol, 44.5%; (3) diethyl carbonate, 2.2%; (4) allyl ethyl carbonate, 47.8% recovery.

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