[COMMUNICATION NO. 1910 FROM THE KODAK RESEARCH LABORATORIES]

Disproportionation of Unsymmetrical Carbonates

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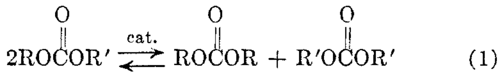
Received August 16, 1957

Mixed ethyl and aryl or aralkyl carbonates disproportionate when heated with suitable catalysts, particularly metal alkoxides. Usually, diethyl carbonate is formed, and often the other symmetrical carbonate can be isolated. However, loss of carbon dioxide and other side reactions can take place. The course of the reactions depends on the structure of the carbonates and on the catalyst.

Side reactions of the symmetrical carbonates include polymerization, loss of carbon dioxide, and formation of olefins, alcohols, and ethers. Of the carbonates, the benzyl structure is the one most prone to side reactions. While the β-phenylethyl unit is somewhat more stable, it will degrade to styrene during long reaction times. Phenyl carbonates are also unstable. Cinnamyl and furfuryl derivatives are exceptionally unstable, and readily yield polymers. Tetrahydrofurfuryl carbonates are stable to polymerization, and the symmetrical carbonate is obtained in this case. The allyl system does not disproportionate at its boiling point. It was expected that the 3-phenylpropyl unit would possess enhanced stability, but it was cleaved to the alcohol. The β-phenoxyethyl unit is the most stable carbonate studied with regard to degradation, both during and after the formation of the symmetrical carbonate.

The more alkaline catalysts, such as sodium methoxide and lithium aluminum ethoxide, promote more side reactions than does titanium butoxide, the catalyst of choice.

Symmetrical carbonates have been most often prepared by reaction of an alkoxide with phosgene. We decided to study their formation by ester interchange (Reaction 1).

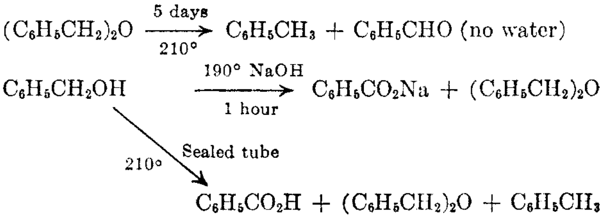


$$2\mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'} \overset{\text{cat.}}{\rightleftarrows} \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR} + \mathrm{R'O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'} \qquad (1)$$

In general, our hope to develop a workable synthesis of symmetrical carbonates was realized. It is more convenient to discuss the detailed behavior of the compounds separately.

Ethyl benzyl carbonate, when treated with lithium aluminum ethoxide, produced diethyl carbonate, dibenzyl ether, and carbon dioxide. No symmetrical carbonate was isolated. Using lithium methoxide catalyst, a small amount of the symmetrical dibenzyl carbonate was obtained. The major product was dibenzyl ether. Sodium methoxide, titanium tetrachloride, titanium butoxide, sodium hydrogen titanium butoxide, strontium methoxide, magnesium methoxide, aluminum isopropoxide, tetraethyl tin, lead borate, and sodium phenoxide produced dibenzyl carbonate, diethyl carbonate, and no dibenzyl ether.

Dibenzyl carbonate, treated with lithium methoxide, produced dibenzyl ether, benzyl alcohol, and water. Lithium aluminum ethoxide produced only dibenzyl ether. On the other hand, magnesium methoxide, during much longer reaction times, produced benzaldehyde, toluene, dibenzyl ether, water, and carbon dioxide. Shorter reaction times, comparable to those used for the first two catalysts, yielded only dibenzyl carbonate. Apparently, degradation reactions of dibenzyl ether were much slower in the presence of magnesium methoxide than with either lithium aluminum ethylate or lithium methoxide. When dibenzyl ether itself was treated with lithium methoxide under the same reaction conditions, a small amount of benzaldehyde and toluene was noted. The identity and appearance of degradation products of benzyl alcohol, which were particularly noticeable during the longer heating times and with the more alkaline catalysts, are related to the work of Lachman,[1] who studied the decomposition of dibenzyl ether and benzyl alcohol at elevated temperatures.



$$(C_6H_5CH_2)_2O \xrightarrow[210°]{\text{5 days}} C_6H_5CH_3 + C_6H_5CHO \text{ (no water)}$$

$$C_6H_5CH_2OH \xrightarrow[\text{1 hour}]{190° \text{ NaOH}} C_6H_5CO_2Na + (C_6H_5CH_2)_2O$$

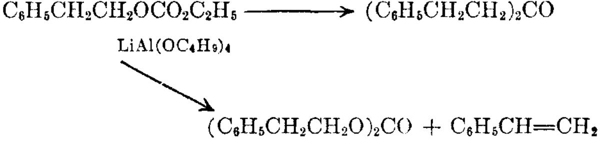
$$C_6H_5CH_2OH \xrightarrow[210°]{\text{Sealed tube}} C_6H_5CO_2H + (C_6H_5CH_2)_2O + C_6H_5CH_3$$

Related studies by Cannizzaro[2] and Lowe[3] illustrated the disproportionation of benzyl alcohol.

$$C_6H_5CH_2OH \xrightarrow[\text{Boric anhydride}]{} C_6H_5CH_2OCH_2C_6H_5$$

$$C_6H_5CH_2OH \xrightarrow[\substack{H_2O \\ \text{reflux}}]{\text{NaOH}} C_6H_5CH_2OCH_2C_6H_5$$

Ethyl β-phenylethyl carbonate, smoothly disproportionated in the presence of titanium butoxide yielded 82% of the desired product. Lithium aluminum butoxide yielded 74%, along with some carbon dioxide and styrene.



$$C_6H_5CH_2CH_2OCO_2C_2H_5 \xrightarrow{Ti(OC_4H_9)_4} (C_6H_5CH_2CH_2)_2CO$$

$$C_6H_5CH_2CH_2OCO_2C_2H_5 \xrightarrow{LiAl(OC_4H_9)_4} (C_6H_5CH_2CH_2O)_2CO + C_6H_5CH{=}CH_2$$

Previous work[4] indicated that only small amounts of styrene were produced by the noncatalyzed pyro-

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[1] A. Lachman, *J. Am. Chem. Soc.*, **45**, 2356 (1923).

[2] S. Cannizzaro, *Ann.*, **92**, 113 (1854).

[3] C. W. Lowe, *Ann.*, **241**, 374 (1887).

[4] J. L. R. Williams, K. R. Dunham, and T. M. Laakso, *J. Org. Chem.*, **23**, 676 (1958).

lytic decomposition of ethyl β-phenylethyl carbonate at 250°.

Di(β-phenylethyl) carbonate, heated to 250°, with no catalyst, yielded 1.4% of styrene and 78% recovered carbonate. Lithium aluminum ethoxide produced 50% styrene, some polystyrene, and 2% of the starting material. Titanium butoxide gave no styrene, and 84% of the carbonate was recovered.

γ-Phenylpropyl ethyl carbonate, heated with lithium aluminum ethoxide, yielded 59% of γ-phenylpropyl alcohol, and no high-boiling fraction was detected. This result is in accord with the work of Ritchie,[5] who described experiments dealing with the pyrolysis of carbonic esters, in which alkyl carbonates produced an alcohol, an olefin, and carbon dioxide. Unsymmetrical carbonates gave mixtures of all possible alcohols and olefins.

Bis(γ-phenylpropyl) carbonate suffered little degradation in the presence of sodium hydrogen titanium butoxide or titanium butoxide, having been recovered in 84 and 83% yield.

Allyl ethyl carbonate, refluxed with lithium aluminum ethoxide, was unchanged; 94% of the starting material was recovered.

Cinnamyl ethyl carbonate, treated either with lithium aluminum ethoxide or strontium methoxide, lost carbon dioxide. The rate of release of carbon dioxide, however, was much more rapid in the case of lithium aluminum ethoxide. Unfortunately, further decomposition and polymerization occurred during distillation, and no identification of the products was possible.

Ethyl phenyl carbonate, treated with lithium aluminum ethoxide or strontium methoxide, produced low yields of symmetrical carbonate. The odor of phenol was noted in both cases. Phenetole was isolated in 30% yield from the first run, and may have been present in the second. Formation of phenetole is analogous to the conversion of β-napthyl ethyl carbonate by heating, to β-ethoxynaphthalene.[6]

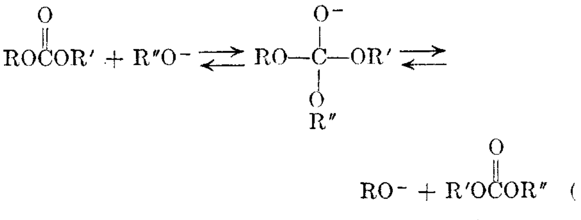
Ethyl furfuryl carbonate, treated with titanium butoxide, strontium methoxide, or lithium aluminum ethoxide, yielded polymers. Small amounts of a mixture of diethyl carbonate, ethanol, and furfuryl alcohol were obtained.

Ethyl tetrahydrofurfuryl carbonate, with either strontium methoxide or lithium aluminum ethoxide, gave 69.8 and 62.8% yields of the symmetrical carbonate, with no evidence of release of carbon dioxide.

Ethyl β-phenoxyethyl carbonate yielded 76 to 92% of the symmetrical carbonate with the four catalysts studied: strontium methoxide, titanium butoxide, lithium aluminum ethoxide, and sodium hydrogen titanium butoxide. No carbon dioxide was formed, and the material balance was the best in the study.

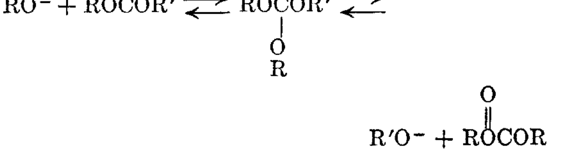
It is thus obvious that structure and catalyst exert important influences on the course of the interchange reaction.

A general mechanism for base-catalyzed interchange is suggested in Equations 1 to 3. The catalyst ion is R″O⁻.



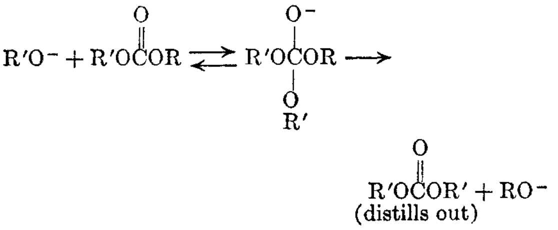
$$\mathrm{RO\overset{O}{\overset{\|}{C}}OR' + R''O^- \rightleftharpoons RO-\underset{\underset{R''}{O}}{\overset{O^-}{C}}-OR' \rightleftharpoons RO^- + R'O\overset{O}{\overset{\|}{C}}OR''} \quad (1)$$

Equation 1 describes the equilibrium of the catalyst with the first of the radicals of the unsymmetrical carbonate; Equation 2 that with the second, and equation 3 shows a third equilibrium.



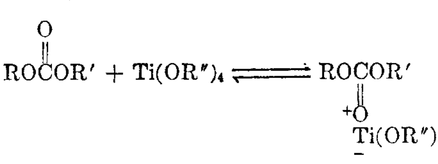
$$\mathrm{RO^- + RO\overset{O}{\overset{\|}{C}}OR' \rightleftharpoons RO\underset{\underset{R}{O}}{\overset{O^-}{C}}OR' \rightleftharpoons R'O^- + RO\overset{O}{\overset{\|}{C}}OR} \quad (2)$$

If one symmetrical carbonate is removed as it forms, the equilibrium will be shifted towards formation of the two symmetrical carbonates, and the residue will be the pure, high-boiling symmetrical carbonate.

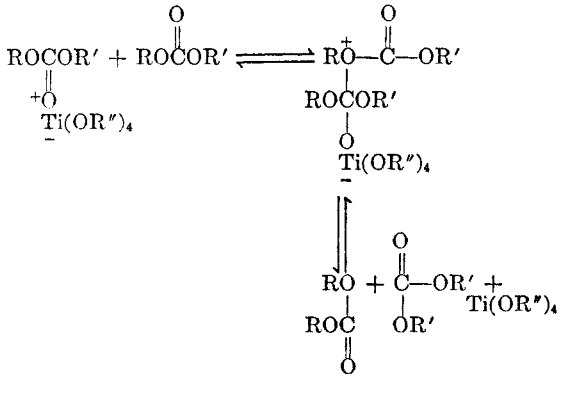


$$\mathrm{R'O^- + R'O\overset{O}{\overset{\|}{C}}OR \rightleftharpoons R'O\underset{\underset{R'}{O}}{\overset{O^-}{C}}OR \longrightarrow \underset{\text{(distills out)}}{R'O\overset{O}{\overset{\|}{C}}OR'} + RO^-} \quad (3)$$

With a Lewis acid (for instance, titanium alkoxide) the reaction path could proceed similarly (Equations 4 and 5).



$$\mathrm{RO\overset{O}{\overset{\|}{C}}OR' + Ti(OR'')_4 \rightleftharpoons RO\underset{\underset{Ti(OR'')_4^-}{{}^+O}}{\overset{}{C}}OR'} \quad (4)$$



$$\mathrm{RO\underset{\underset{Ti(OR'')_4^-}{{}^+O}}{C}OR' + RO\overset{O}{\overset{\|}{C}}OR' \rightleftharpoons \underset{\underset{\underset{Ti(OR'')_4^-}{O}}{ROCOR'}}{R\overset{+}{O}}-\overset{O}{\overset{\|}{C}}-OR'} \quad (5)$$

$$\mathrm{\Downarrow\Uparrow \quad \underset{\underset{O}{\overset{\|}{ROC}}}{RO} + \underset{OR'}{\overset{O}{\overset{\|}{C}}}-OR' + Ti(OR'')_4}$$

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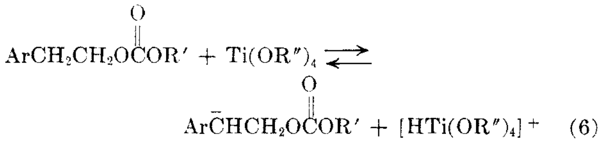
(5) P. D. Ritchie, *J. Chem. Soc.*, 1054 (1935).

(6) K. C. Tsou and A. M. Seligmann, *J. Am. Chem. Soc.*, **76**, 3704 (1954).

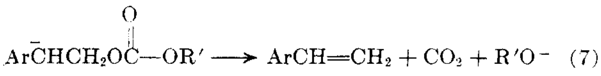
TABLE I. REACTIONS OF CARBONATES

Class	Compound	Run	Catalyst	Amount	Time (Min.)	Products
A	$C_6H_5CH_2OCO_2C_2H_5$[g]					$(C_6H_5CH_2)_2O$
	100 g. (0.55 mole)	1	$LiAl(OC_2H_5)_4$[a]	1.0 ml.	1.95	79
		2	$LiOCH_3$[b]	10.0 ml.	120	57.5
		3	$NaOCH_3$[f]	0.1 g.	155	–
		4	$TiCl_4$	0.5 ml.	105	–
		5	$Ti(OC_4H_9)_4$	0.1 ml.	100	–
		6	$NaHTi(OC_4H_9)_6$[c]	10.0 ml.	180	–
		7	$Sr(OCH_3)_2$[d]	10.0 ml.	90	–
		8	$Mg(OCH_3)_2$[e]	10.0 ml.	22	–
		9	$Al(OC_3H_7)_3$[f]	0.1 g.	75	–
		10	$(C_2H_5)_4Sn$	3.0 ml.	360	–
		11	Lead borate	0.1 g.	50	–
		12	$NaOC_6H_5$	1.0 g.	90	–
	$(C_6H_5CH_2O)_2CO$[h]					
	50 g. (0.21 mole)	13	$LiOCH_3$[b]	10.0 ml.	165	28.8
		14	$LiAl(OC_2H_5)_4$[a]	4.0 ml.	130	99
		15	$Mg(OCH_3)_2$[a]	10.0 ml.	1080	58.5
	$(C_6H_5CH_2)_2O$[i]					C_6H_5CHO
	40 g. (0.2 mole)	16	$LiOCH_3$[b]	10.0 ml.	195	Trace
B	$C_6H_5CH_2CH_2OCO_2C_2H_5$[j]					$(C_6H_5CH_2CH_2O)_2CO$
	100 g. (0.52 mole)	17	$LiAl(OC_2H_5)_4$[a]		120	61
		18	$Ti(OC_4H_9)_4$	0.3 ml.	120	64
	$(C_6H_5CH_2CH_2O)_2CO$					$(C_6H_5CH_2CH_2O)_2CO$
	50 g. (0.26 mole)	19	Nil		420	78
		20	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	420	2
		21	$Ti(OC_4H_9)_4$	0.3 ml.	180	84
C	$C_6H_5CH_2CH_2CH_2OCO_2C_2H_5$					$(C_6H_5CH_2CH_2CH_2O)_2CO$
	100 g. (0.48 mole)	22	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	60	–
		23	$Ti(OC_4H_9)_4$	0.1 ml.	60	84.5
		24	$NaHTi(OC_4H_9)_6$	10.0 ml.	50	83
D	$CH_2{=}CHCH_2OCO_2C_2H_5$[k]					$CH_2{=}CHCH_2OCO_2C_2H_5$
	100 g. (0.77 mole)	25	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	70	94 (recovery
E	$C_6H_5CH{=}CH{-}CH_2OCO_2C_2H_5$[g]					
	100 g. (0.48 mole)	26	$Sr(OCH_3)_2$[d]	10.0 ml.	175)	No clear fractions, polymer-
		27	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	40)	with loss of CO_2
F	$C_6H_5OCO_2C_2H_5$[l]					C_6H_5OH
	100 g. (0.62 mole)	28	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	180	Trace
		29	$Sr(OCH_3)_2$[d]	10.0 ml.	200	Trace
G	$C_4H_3OCO_2C_2H_5$[o]					$C_4H_3OCH_2OH$
	100 g. (0.54 mole)	30	$Sr(OCH_3)_2$[d]	10.0 ml.	85)	+
					)	Polymer on distillation
		31	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	70)	+
		32	$Ti(OC_4H_9)_4$	0.3 ml.		
H	$C_4H_7OCH_2OCO_2C_2H_5$[m]					$(C_4H_7OCH_2O)_2CO$[m]
	100 g. (0.56 mole)	33	$Sr(OCH_3)_2$[d]	10.0 ml.	15	69.8
		34	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	75	62.8
I	$C_6H_5OCH_2CH_2OCO_2C_2H_5$[n]					$(C_6H_5OCH_2CH_2O)_2CO$[n]
	100 g. (0.48 mole)	35	$Sr(OCH_3)_2$[d]	10.0 ml.	65	60.8
		36	$Ti(OC_4H_9)_4$	0.6 ml.	45	62.7
		37	$LiAl(OC_2H_5)_4$[a]	10.0 ml.	75	65.5
		38	$NaHTi(OC_4H_9)_6$[c]	10.0 ml.	90	73.0

Equations 1 to 5 fail to explain the side reactions of many of the carbonates. These may arise as a consequence of subsequent reactions of carbanions formed as shown in Equations 6 to 8.



$$ArCH_2CH_2O\overset{\overset{\Large O}{\|}}{C}OR' + Ti(OR'')_4 \rightleftarrows Ar\bar{C}HCH_2O\overset{\overset{\Large O}{\|}}{C}OR' + [HTi(OR'')_4]^+ \quad (6)$$



$$Ar\bar{C}HCH_2O\overset{\overset{\Large O}{\|}}{C}{-}OR' \longrightarrow ArCH{=}CH_2 + CO_2 + R'O^- \quad (7)$$

$$R'O^- + [HTi(OR'')_4]^+ \longrightarrow R'OH + Ti(OR'')_4 \quad (8)$$

EXPERIMENTAL

Decomposition studies. Samples of various carbonates were heated in glass equipment consisting of flask, Vigreux column, and partial take-off head. Silicone oil baths were used, and held throughout the decomposition period at 250°. Heating mantles were used to distill the products from the reaction flask. The results are summarized in Table I.

Preparation of carbonate intermediates. Compounds not previously reported in the literature were prepared as in the following example:

Ethyl tetrahydrofurfuryl carbonate. To a stirred mixture of 500 g. (5.0 moles) of tetrahydrofurfuryl alcohol in 500 g. of pyridine, was added 600 g. (5.5 moles) of ethyl chlorocarbonate at 10–20°. After the addition was complete, the mixture was stirred for 1 hr. One liter of benzene was added,

TABLE I. Reactions of Carbonates (*Continued*)

Conversion (%) and Recoveries						
$(C_6H_5CH_2O)_2CO$	$(C_2H_5O)_2CO$	CO_2				
–	+	+				
Trace	+	+				
70.5	+	–				
89	+	–				
90	+	–				
88	+	–				
81.8	+	–				
79.5	+	–				
49	+	–				
72	+	–				
75	+	–				
75	+	–				
			$C_6H_5CH_2OH$	C_6H_5CHO	$C_6H_5CH_3$	H_2O
41		+	–	–	–	–
–		+	–	–	–	–
–		+	–	18	23.8	0.5
$C_6H_5CH_3$						
Trace						
$C_2H_5CH_2CH_2OCO_2C_2H_5$		$C_6H_5CH{=}CH_2$		$(C_2H_5O)_2CO$	CO_2	
18		Trace		+	Trace	
22	–	–		+	–	
$C_6H_5CH{=}CH_2$	$(C_2H_5O)_2CO$	CO_2				
1.4	+	+				
>50	+	+				
–	+	+				
$C_6H_5CH_2CH_2CH_2OH$						
59	+	–				
		–				
		–				
after heating at its boiling point)						
ised during distillation						
$C_6H_5OC_2H_5$	$(C_6H_5O)_2CO$					
–	36.8					
30	28					
$(C_2H_5O)_2CO$	CO_2	C_2H_5OH				
+	+	+				
+	+	+				
+	+	+				
$(C_2H_5O)_2CO$	CO_2					
+	+					
+	+					
C_6H_5[n]$OCH_2CH_2OCO_2C_2H_5$						
20						
32						
20						
15						

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[a] Lithium aluminum hydride, 1.0 g. in 100 ml. of absolute ethanol. [b] Lithium methoxide, 1.0 g. in 100 ml. of absolute ethanol. [c] Solution of 0.5 g. of sodium and 7.8 g. of titanium butoxide in 200 ml. of *n*-butyl alcohol. [d] Solution of 1.0 g. of strontium in 100 ml. of methanol. [e] Solution of 1.0 g. of magnesium in 100 ml. of methanol. [f] Catalyst was not completely soluble. [g] P. Schving and S. Sabetay, *Bull. Soc. Chim.*, **43**, 857 (1928). [h] C. A. Bischoff, *Ber.*, **36**, 159 (1903). [i] G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 2305 (1928). [j] P. Schving and S. Sabetay, *Bull. Soc. Chim.*, **43**, 1341 (1928). [k] D. E. Adelson and H. Dannenberg, U. S. Pat. **2,595,214** (1952). [l] L. Claisen, *Ber.*,**27**, 3182 (1894). [m] Tetrahydrofurfuryl. [n] Phenyl. [o] Furyl.

TABLE II. Unsymmetrical Carbonates $C_2H_5OCO_2R$

					Analysis			
					Calcd.		Found	
R	Yield, %	B.P.	M.P.	n_D^{25}	C	H	C	H
$C_6H_5OCH_2CH_2$—	86		45°		62.9	6.7	63.3	6.7
$C_6H_5(CH_2)_3$—	83	130° (2 mm.)		1.4860	69.2	7.8	69.7	8.2
$C_4H_3OCH_2$—[a]	77	66° (0.6 mm.)		1.4370	56.5	5.6	55.6	5.8
$C_4H_7OCH_2$—[b]	76	70° (1 mm.)		1.4560	55.2	8.0	54.8	8.4

[a] Furfuryl. [b] Tetrahydrofurfuryl.

TABLE III

SYMMETRICAL CARBONATES $ROCO_2R$

R	B.P.	M.P.	n_D^{25}	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
$C_6H_5OCH_2CH_2$—	180–183° (0.4 mm.)	92–93°		67.6	6.0	67.5	5.8
$C_6H_5(CH_2)_3$—	176° (0.4 mm.)		1.5318	76.5	7.4	76.9	6.9
$C_4H_7OCH_2$—[a]	114°		1.4658	55.5	7.5	55.9	7.7

[a] Tetrahydrofurfuryl.

and the mixture was washed successively with water, dilute hydrochloric acid, water, dilute sodium carbonate, and water. The organic material was dried over calcium chloride and distilled to give 658 g. (76.0% of theoretical) of ethyl tetrahydrofurfuryl carbonate. The physical properties are listed in Table II.

Table III summarizes the properties of new symmetrical carbonates isolated from the disproportionation reactions of the unsymmetrical carbonates.

Catalysts. The catalysts were prepared or purified in a nitrogen atmosphere under dry conditions.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, MCLAUGHLIN GORMLEY KING CO.]

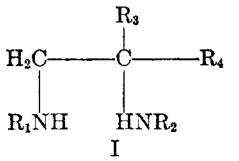
5-Membered Heterocyclic Compounds Derived from Piperonal. I. A Study of the Reactions between Piperonal and 1,2-Diamines

PETER F. EPSTEIN

Received August 19, 1958

A number of 1,2-diamines were allowed to react with piperonal. The nature of the products obtained varied with the type of amine used. When both the amine groups were primary, a di-Schiff's base was formed; with one primary and one secondary amine group the product was an imidazolidine; while in the case of a di-secondary amine there was either no reaction or an imidazolidine was formed, depending on the nature of the substituent groups.

Riebsomer[1] described the formation of some imidazolidines derived from benzaldehyde and furfural. Other workers[2–6] have reported similar results. It seemed to the author to be of interest to discover if the less reactive piperonal would behave in a similar manner, and accordingly attempts were made to condense piperonal with a number of 1,2-diamines of the general Formula I.



$$\begin{array}{ccc} & R_3 & \\ H_2C - & C & - R_4 \\ | & | & \\ R_1NH & HNR_2 & \end{array}$$

I

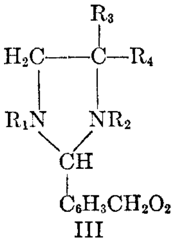
In the simplest case of all, using 1,2-diaminoethane (I; $R_1 = R_2 = R_3 = R_4 = H$) the only product which could be isolated was the di-Schiff's base *N,N'*-di(3,4-methylenedioxybenzal)-1,2-diaminoethane (II).

$CH_2O_2C_6H_3CH{=}NCH_2CH_2N{=}CHC_6H_3CH_2O_2$

II

This result was obtained regardless of the proportions of reagents used, and in no case could any of the imidazolidine be isolated. These findings agree with the work of van Alphen[5] regarding the corresponding benzaldehyde compounds.

In the case of diamines with one primary and one secondary group, of the type used by Riebsomer[1] the reaction proceeded smoothly to give imidazolidines. Thus, for example, N_1-phenyl-2-(3,4-methylenedioxyphenyl)-4,4-dimethylimidazolidine.



III

(II; R_1 = Ph, R_2 = H, $R_3 = R_4$ = Me) was prepared in 89% yield from piperonal and 1-phenyl-

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(3) C. A. Bischoff, *Ber.*, **31**, 3248 (1898).
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(5) J. van Alphen, *Rec. Trav. Chim.*, **54**, 93 (1935).
(6) W. L. C. Veer, *Rec. Trav. Chim.*, **57**, 989 (1938).