concentration cannot be explained if the acid form complexes (see text for the exceptional case of mannitol). The second assumption is that the change in concentration of acid form due to ionization (Equation 5) is negligible; such must be the case since the concentration of hydrogen ion never exceeded $10^{-6}M$.

From (5) $\log [H^+] = \log K_a + \log [BH] - \log [B^-]$

with polyol present,

$$-pH_f = -pK_a + \log [BH]_f - \log [B^-]_f$$

w/o polyol,

$$\underline{-pH_0 = -pK_a + \log [BH]_f - \log [B^-]_0}$$

and by addition,

$$pH_f - pH_0 = \Delta pH = \log [B^-]_f - \log [B^-]_0$$

Then $\Delta pH = \log \frac{[B^-]_f}{[B^-]_0}$ or

$$10^{\Delta pH} = \frac{[B^-]_f}{[B^-]_0} = \frac{[B^-]_0 - [BP_n^-]}{[B^-]_0} \quad (13)$$

by equation (9), and, $10^{\Delta pH} = 1 - \frac{[BP_n^-]}{[B^-]_n}$

by equation (6), $[BP_n^-] = K_c[B^-]_f[P]_f$

and $10^{\Delta pH} = 1 - K_c[P]_f \frac{[B^-]_f}{[B^-]_0} = 1 - K_c[P]_f\, 10^{\Delta pH}$

division by $10^{\Delta pH}$ gives $K_c = \frac{10^{-\Delta pH} - 1}{[P]_f}$

Measurements yield ΔpH; $[P]_f$ is found by correcting $[P]_0$ with the use of equations (10), (11), and (13).

Treatment of constants. $K_c = K_1$ if only "1:1 complex" is formed. K_c is then usually found to decrease slightly with polyol concentration increase, owing to decline in the dielectric constant; a standard value is obtained by extrapolation to $[P]_f = 0$.

When 2:1 complex (from two polyol molecules) is present,

$$K_c = \frac{[BP^-] + [BP_2^-]}{[B^-]_f[P]_f} = K_1 + K_{21}[P]_f, \text{ from (7) and } \quad (9)$$

K_1 and K_{21} ore obtained by plotting K_c, extrapolating to $[P]_f = 0$, and measuring the slope.

For a complex formed from two anions and one polyol molecule, reasoning is similar, and K_1 and K_{12} are obtained as above:

$$K_c = K_1 + 2K_{12}[B^-]_f$$

Relationship of K_2', K_2 and K_1. The formation constant for "2:1 complex" from "1:1 complex" is

$$K_2' = \frac{[BP_2^-]}{[BP^-][P]_f}$$

since $[BP^-] = K_1[B^-][P]_f$, it follows from (6) and (7) that

$$K_2' \cdot K_1 = \frac{[BP_2^-]}{[B^-][P]^2_f} = K_{21}$$

Acknowledgment. One of the authors (J.P.L.) expresses his gratitude to the Corporation of Brown University for a research assistantship.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Thermal Decomposition of Mixed Carboxylic-Carbonic Anhydrides; Factors Affecting Ester Formation

D. S. TARBELL AND E. J. LONGOSZ[1]

Received November 12, 1958

A number of new mixed benzoic (and mesitoic)-carbonic anhydrides ($C_6H_5COOCOOR$) have been prepared and characterized. They are stable at room temperature, but decompose around 150-170° with carbon dioxide evolution. It has been shown that the thermal decomposition of these anhydrides proceeds by two different paths: A, formation of an ester by loss of carbon dioxide and B, disproportionation to the symmetrical anhydride, alkyl carbonate, and carbon dioxide. Path A is favored when the point of attachment of the alkyl group is a secondary carbon or a primary carbon, with heavy substitution on the β-carbon. Both paths A and B occur about equally when the alkyl group is primary, as ethyl or butyl. Although tertiary amines lower the temperature of decomposition of the anhydrides, they do not alter the course of the decomposition. Rearrangement of the mixed anhydride from (−)-2-octanol proceeds with complete retention of configuration. *N*-Methylpiperidine is a much more effective catalyst than triethylamine in forming the mixed anhydride from a highly branched chlorocarbonate.

It was shown in an earlier paper[2] that mixed carboxylic-carbonic anhydrides, RCOOCOOR,′ were, in general, reasonably stable compounds which could be obtained in pure form. It has been considered[2-4] that the mixed anhydrides decom-

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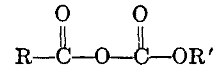
[1] National Science Foundation Fellow, 1958-59.

[2] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958). This paper contains leading references to the literature describing the usefulness of the mixed anhydrides as acylating agents.

[3] J. Herzog, *Ber.*, 42, 2557 (1909); A. Einhorn, *Ber.*, **42**, 2772 (1909); T. Wieland and H. Bernhard, *Ann.*, **572**, 190 (1951).

TABLE I

MIXED CARBOXYLIC-CARBONIC ANHYDRIDES

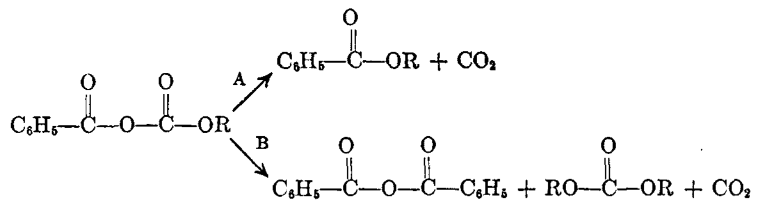


$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OR'$

R	R′	n_D	Formula	Carbon, %		Hydrogen, %		Infrared Bands, Cm.$^{-1}$
				Calcd.	Found	Calcd.	Found	
C_6H_5	CH_2CH_3	n_D^{25} 1.4988	$C_{10}H_{10}O_4$	61.85	62.23	5.19	5.32	1800, 1739
C_6H_5	$CH_2CH_2CH_2CH_3$	n_D^{25} 1.4902	$C_{12}H_{14}O_4$	64.85	64.65	6.35	6.35	1802, 1745
C_6H_5	$CH_2-C(CH_3)_3$	n_D^{25} 1.4849	$C_{13}H_{16}O_4$	66.08	66.44	6.83	7.05	1802, 1745
C_6H_5	$CH_2-C(CH_2CH_3)_3$	n_D^{25} 1.4913	$C_{16}H_{22}O_4$	69.04	69.06	7.97	8.05	1802, 1745
C_6H_5	$CH_2-C_6H_5$			[a]				1800, 1739
C_6H_5	$CH(CH_3)C_6H_{13}$	n_D^{25} 1.4801	$C_{16}H_{22}O_4$	69.04	69.41	7.97	8.17	1795, 1739
C_6H_5	$CH(CH(CH_3)_2)_2$[b]	n_D^{24} 1.4890	$C_{15}H_{20}O_4$	68.16	68.45	7.63	7.73	1795, 1739
2,4,6-$(CH_3)_3-C_6H_2$	CH_2CH_3	n_D^{26} 1.4919	$C_{13}H_{16}O_4$	66.08	65.83	6.83	6.85	1802, 1754
2,4,6-$(CH_3)_3-C_6H_2$	$CH(CH_3)C_6H_{13}$	n_D^{24} 1.4802	$C_{19}H_{28}O_4$	71.22	71.08	8.81	8.85	1802, 1754

[a] Too unstable for valid elemental analysis. [b] Required *N*-methylpiperidine as the tertiary amine during synthesis. Triethylamine gives only 40% conversion of reactants to mixed anhydride.

pose by two routes, path A leading to ester, and path B giving the symmetrical disproportionation products. Thus, for the benzoic-carbonic anhydride:



The present paper gives evidence for this dual mode of decomposition of pure mixed anhydrides, studies the effect of structural changes in R on the proportion of paths A and B, and indicates the stereochemical course of the reaction when the R group is attached to oxygen through an asymmetric carbon.

The mixed anhydrides synthesized and studied are listed, along with analytical and infrared data, in Table I. They were prepared from benzoic (or mesitoic) acid and the appropriate alkyl chlorocarbonate in the presence of triethylamine or of *N*-methylpiperidine in ether solution. (The latter base proved superior in the case of the chlorocarbonate derived from the highly branched alcohol, 2,4-dimethyl-3-pentanol.) The chlorocarbonates were generated from phosgene and the appropriate alcohol.

With the exception of benzoic-benzylcarbonic mixed anhydride, the mixed anhydrides showed no essential changes in their infrared absorption spectra after standing at room temperature for several months. A temperature greater than 100° was required to effect a marked degree of decomposition. Even at the temperature of boiling toluene, 112°, no change in the infrared spectrum was observed for a sample of the mixed anhydride dissolved in toluene, after a heating period of 8 hr. The temperature range of 150–170° was selected for the rearrangements since it gave total decompositions within a convenient time interval of 2 to 4 hr. As seen from the reaction paths, both modes of decomposition of the mixed anhydride lead to the evolution of carbon dioxide. Assuming both these paths of decomposition to occur simultaneously, the measurement of the total quantity of carbon dioxide evolved should give a reliable indication of the predominant path taken by the reaction, since path A evolves one equivalent of carbon dioxide, and path B evolves one-half equivalent of carbon dioxide.

Hence, the mixed anhydrides were heated in a flask provided with a nitrogen sweep, and the carbon dioxide was trapped in an absorption tube filled with "Ascarite." Isolation of the three expected products from each of the rearrangements and in the yields required by the total quantity of carbon dioxide trapped, within experimental error, indeed proved the validity of the original assumptions. As seen from Table II, the course taken by the rearrangement depends on the type of alkyl group in the mixed anhydride. When the point of attachment of the alkyl component is a secondary carbon atom or a primary carbon atom with heavy substitution on the β-carbon atom, the decomposition is chiefly to the respective ester. When the point of attachment is a primary carbon atom, such as ethyl or butyl, the decomposition proceeds about equally along paths A and B. The mixed anhydride derived from mesitoic acid leads to

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(4) D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1947); E. Schipper and J. Nichols, *J. Am. Chem. Soc.*, **80**, 5714 (1958). A recent communication [T. B. Windholz, *J. Org. Chem.*, **23**, 2044 (1958)] reports observation of paths A and B.

TABLE II

THERMAL REARRANGEMENT OF MIXED CARBOXYLIC-CARBONIC ANHYDRIDES $\left(\mathrm{R{-}\overset{O}{\overset{/\!/}{C}}{-}O{-}\overset{O}{\overset{/\!/}{C}}{-}O{-}R'}\right)$

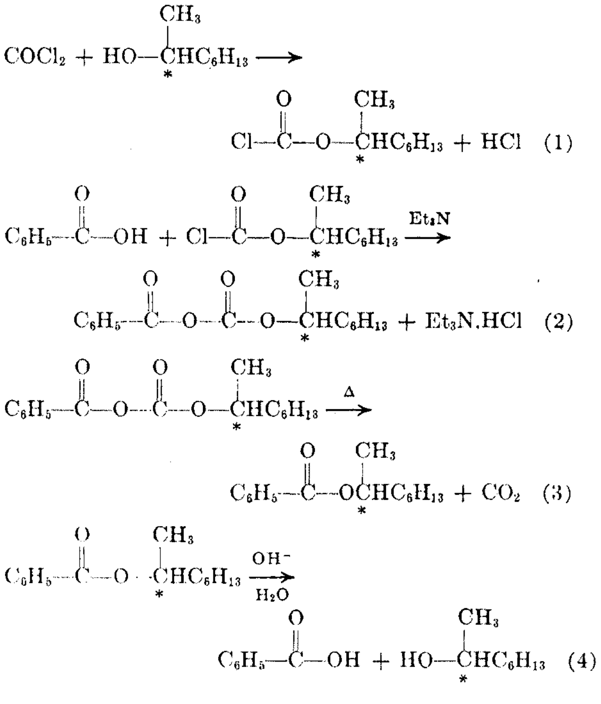
R	R′	Temp.	Catalyst (Mole %)	CO_2 Evolved % of Theory	% Ester Predicted	% Ester Recovered
C_6H_5	CH_2CH_3	150°	None	69	38	41
C_6H_5	CH_2CH_3	155°	None	70	40	—
C_6H_5	CH_2CH_3	130°	$C_6H_5N(CH_3)_2$(4)	69	38	42
C_6H_5	CH_2CH_3	70°	$C_5H_{10}NCH_3$(4)	68	36	35
C_6H_5	CH_2CH_3	125°	$C_5H_{10}NCH_3$(1)	75[a]	50	—
C_6H_5	$CH_2CH_2CH_2CH_3$	150°	None	78	56	50
C_6H_5	$CH_2CH_2CH_2CH_3$	115°	Et_3N(3)	75	50	—
C_6H_5	$CH_2C(CH_3)_3$	150°	None	79	58	48
C_6H_5	$CH_2C(CH_2CH_3)_3$	150°	None	89	78	85
C_6H_5	1-$CH(CH_3)C_6H_{13}$	170°	None	84	68	65
C_6H_5	$CH(CH_3)C_6H_{13}$	170°	None	84	68	—
C_6H_5	$CH(CH_3)C_6H_{13}$	115°	$C_5H_{10}NCH_3$(4)	84	68	—
C_6H_5	$CH(CH(CH_3)_2)_2$	*Ca.* 170°	None	—	—	71[b]
2,4,6-$(CH_3)_3C_6H_2$	CH_2CH_3	170°	None	56	12	10
2,4,6-$(CH_3)_3C_6H_2$	$CH(CH_3)C_6H_{13}$	170°	None	90	80	77

[a] This rearrangement in 1.9 molar excess of ethyl carbonate. [b] Benzoate ester of 2,4-dimethyl-3-pentanol formed during attempted acylation of ethanol by mixed anhydride. This ester formed during distillation of reaction mixture, which contained unreacted mixed anhydride.

substantially the same result when the alkyl component is 2-octyl, but gives almost exclusively disproportionation when the alkyl component is ethyl. The presence of tertiary amines, such as triethylamine, *N*-methylpiperidine, or *N,N*-dimethylaniline during the rearrangement process evidently has a catalytic effect, since the elimination of carbon dioxide takes place at a much lower temperature. A significant fact is that the ratio of the two reaction paths is not altered. Neither does the presence of excess diethyl carbonate during the decomposition of benzoic-ethylcarbonic anhydride shift the reaction path markedly.

Ester formation (path A) occurs directly from the mixed anhydride, and not through prior disproportionation to symmetrical products (path B) followed by esterification of the anhydride by the organic carbonate.[4a] Equivalent amounts of diethyl carbonate and benzoic anhydride were heated under the conditions of the decomposition, but no carbon dioxide was eliminated. The same results were obtained with di-2-octyl carbonate and benzoic anhydride. The addition of tertiary amines had no effect in promoting this reaction; only starting materials were isolated in each case.

Some insight into the mechanism of the reaction was gained by the rearrangement of benzoic-2-octylcarbonic anhydride, where a center of asymmetry was introduced into the alkyl portion of the anhydride. It was found that the configuration at this center of asymmetry was completely retained in the resulting 2-octyl benzoate. This rules out the formation of an easily racemizable carbonium ion, resulting from an alkyl oxygen cleavage as a step in the rearrangement process. Also ruled out is a prior dissociation to a benzoate ion and a rearward attack by this ion on the center of asymmetry, to invert the configuration. The path leading to disproportionation products must also lead to retention of configuration, since the sample of optically active 2-octyl benzoate was contaminated with di-2-octyl carbonate, because of identity of boiling points of the two compounds. Hydrolysis of the mixture, however, yielded 2-octanol with a rotation identical to that of the starting alcohol. The following sequence of reactions was carried out with (−)-2-octanol:



$$\mathrm{COCl_2 + HO{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} \longrightarrow Cl{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} + HCl} \qquad (1)$$

$$\mathrm{C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}OH + Cl{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} \xrightarrow{Et_3N} C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} + Et_3N.HCl} \qquad (2)$$

$$\mathrm{C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} \xrightarrow{\Delta} C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}O\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} + CO_2} \qquad (3)$$

$$\mathrm{C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13} \xrightarrow[H_2O]{OH^-} C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}OH + HO{-}\underset{*}{\overset{CH_3}{\overset{|}{C}}}HC_6H_{13}} \qquad (4)$$

(4a) *Cf.* T. B. Windholz, ref. 4.

It is unreasonable to suppose that the asymmetric center is disturbed in reactions (1) and (2) and it is well known that Reaction 4 proceeds with retention of configuration.[5] Hence two inversions of configuration in the sequence, one in Reaction 3 and another in one of the other three reactions, leading to apparent retention during the sequence, can be ruled out. Houssa and Phillips[6] obtained the same stereochemical result when they heated potassium benzoate and (−)-2-octyl chlorocarbonate. However, this procedure was attended by low yields of the optically active ester, the formation of large quantities of (−)-2-octanol, and a poor overall material balance; furthermore, threre was no evidence that the mixed anhydride was actually an intermediate.

Further evidence for the lack of formation of a carbonium ion during the decomposition of the mixed benzoic-carbonic anhydride is that no rearrangement of the neopentyl skeleton took, place. Under certain conditions, the neopentyl system undergoes a skeletal rearrangement, presumably through a carbonium ion.[7] In the light of this evidence, it is difficult to explain the ready decomposition of the benzyl mixed anhydride, which eliminated carbon dioxide even at room temperature. The major path followed in this decomposition could not be determined because of similarity of the boiling points of all three products. However, the three expected products are present in more than trace amounts, because of strong absorption at the expected frequencies in the infrared.

A procedure for making esters reported by Newman,[8] in which the sodium salt of an acid is heated with an alkyl chlorosulfite, is undoubtedly similar to the one discussed in this paper.

Work is currently in progress in these laboratories to elucidate the mechanism of these rearrangements and to establish their relationship to various 1,3-rearrangements, such as the decomposition of chlorocarbonates[9] and chlorosulfites,[10] and the rearrangement of thione carbonates.[11]

EXPERIMENTAL[12]

2,4-Dimethyl-3-pentanol,[4] *2,2-diethyl-1-butanol,*[13] *and neopentyl alcohol*[14] were prepared following the references indicated, and had physical properties in agreement with those reported.

Preparation of alkyl chlorocarbonates. Except for ethyl chlorocarbonate, which was commercially available, all the chlorocarbonates used in this study were prepared by the action of phosgene on the respective alcohol. Following is the general method used: In a 250-ml., three necked flask set in a Dry Ice-acetone bath, was condensed approximately 100 g. (1 mole) of phosgene. The flask was transferred to an ice bath and fitted with a stirrer, a condenser, and a dropping funnel. Over a period of one hour, 0.7 mole of the alcohol was added. The ice bath was removed after the addition and the mixture allowed to stand at room temperature overnight. The excess phosgene was removed by means of an aspirator for *ca.* 2 hr., and the residue fractionally distilled. The chlorocarbonates synthesized in this manner are listed in Table III.

Di-2-octyl carbonate was made by the action of 2-octanol on 2-octyl chlorocarbonate. Our sample had b.p. 118–123° (0.7–1 mm.), n_D^{25} 1.4280; the reported[15] b.p. is 168° (13 mm.).

Preparation of carboxylic-carbonic anhydrides. In a 250-ml. three-necked flask were placed benzoic acid, an equimolar quantity of pure triethylamine and dry ether (100 ml. for every 0.04 mole of reagent used). The flask was equipped with a stirrer, addition funnel, and reflux condenser. The mixture was cooled to 0 to 5° and an equimolar quantity of the alkyl chlorocarbonate was added at such a rate as to keep the temperature of the mixture between 0 and 5°. After the addition, the reaction was allowed to continue for an additional 0.5 hr. at the temperature of the ice bath, then slowly warmed to room temperature. The triethylamine hydrochloride was recovered by filtration in better than 95% yield in all cases. The filtrate was washed thoroughly with dilute hydrochloric acid, saturated sodium bicarbonate solution, and water, then dried over anhydrous magnesium sulfate. After thorough drying, the ether was removed under reduced pressure at room temperature, leaving behind a clear, mobile liquid. The mixed anhydrides thus prepared are listed in Table I. Little or no change in the infrared absorption spectra of the samples was noticed after standing at room temperature for several months.

Thermal rearrangement of mixed carboxylic-carbonic anhydrides. The mixed anhydride (about 0.05 mole) prepared and isolated as described above, was accurately weighed into a 50 ml. round bottomed flask, equipped with a gas inlet tube, thermometer, and a reflux condenser. The reflux condenser was attached to a U-trap filled with "Anhydrite," which in turn was attached to an absorption bulb filled with "Ascarite." Heating of the flask containing the mixed anhydride was accomplished by means of an oil bath. The carbon dioxide evolved was swept by a continuous stream of nitrogen. The absorption bulb was periodically weighed and the heating stopped when it reached constant weight. After dissolving the rearrangement product in ether and washing it with dilute hydrochloric acid, saturated sodium bicarbonate solution and water, it was dried over anhydrous magnesium sulfate. The products of the rearrangement were isolated by means of fractional distillation through a vacuum-jacketed Vigreux column (100 × 10 mm.). The experiments with ethyl, butyl, and neopentyl mixed anhydrides are not described in detail because their decomposition products represent known products. The yield of benzoate ester reported in Table II represents a corrected yield, that is, it includes benzoate ester obtained in a pure form and also that contaminated with organic carbonate in

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[5] B. Holmberg, *Ber.*, **45**, 2997 (1912).

[6] A. Houssa and H. Phillips, *J. Chem. Soc.*, 2510 (1929).

[7] F. C. Whitmore and G. H. Fleming, *J. Chem. Soc.*, 1269 (1934). F. C. Whitmore, E. L. Wittle, and A. H. Popkin, *J. Am. Chem. Soc.*, **61**, 1586 (1939). I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 169 (1946).

[8] M. S. Newman and W. S. Fones, *J. Am. Chem. Soc.*, **69**, 1046 (1947).

[9] K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955).

[10] C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

[11] H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *J. Am. Chem. Soc.*, **78**, 70 (1956).

[12] Melting points are uncorrected. Microanalyses are by Miss Annette Smith and Dr. Franz Pascher.

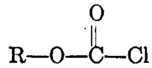
[13] S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, **78**, 5416 (1956).

[14] D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.*, **74**, 4052 (1952).

[15] H. Hunter, *J. Chem. Soc.*, 1389 (1924).

TABLE III

PROPERTIES OF ALKYL CHLOROCARBONATES



$R-O-C(=O)-Cl$

R	B.P.	n_D	Literature, B.P.	Literature, n_D^{20}
n-C_4H_9	45–46° (18 mm.)	1.4095 (24°)	138°[a]	1.4128
$CH_2C(CH_3)_3$	39° (15 mm.)	1.4085 (23°)	52° (27 mm.)[b]	1.4091
$CH_2-C_6H_5$	73–74° (3 mm.)	1.5146 (25°)	103° (19–20 mm.)[c]	—
$CH(CH(CH_3)_2)_2$	95–97° (69–70 mm.)	1.4220 (20°)	90–100° (60–70 mm.)[d]	1.4225
$CH(CH_3)C_6H_{13}$	92–93° (12 mm.)	1.4252 (25°)	92° (13 mm.)[e]	1.4282
$CH_2-C(C_2H_5)_3$[f]	133° (85 mm.)	1.4381 (24°)	—	—

[a] A. N. Kost, Russian Doctoral Dissertation, *Chem. Abstr.*, **47**, 9907 (1953). [b] F. Strain *et al.*, *J. Am. Chem. Soc.*, **72**, 1254 (1950). [c] J. Thiele and F. Dent, *Ann.*, **302**, 257 (1898). [d] D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957). [e] H. Hunter, *J. Chem. Soc.*, 1389 (1924). [f] Calcd. for $C_9H_{17}O_2Cl$: C, 56.10; H, 8.90. Found: C, 56.63; H, 9.14. The carbamate, made by the action of concentrated aqueous ammonia on this chlorocarbonate had m.p. 93.5–94.5° after purification by sublimation. Calcd. for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 61.91; H, 10.98; N, 8.36.

intermediate fractions. These corrections were made by application of ultraviolet and hydrolysis experiments. The experiments with the optically active mixed anhydride, and cases in which new compounds were formed, are described in detail below.

Rearrangement of optically active benzoic-2-octylcarbonic anhydride. Optically active 2-octyl chlorocarbonate was made in the manner discussed above using 2-octanol having α_D^{26} −6.82 ± 0.03° (neat, l = 1) and b.p. 81–83° (14 mm.), n_D^{20} 1.4250. Having generated the benzoic mixed anhydride (16.3 g., 0.059 mole) and decomposed it in the standard manner, an 84% yield of carbon dioxide was collected. Upon fractionation of the rearrangement product, there was obtained 11.1 g. of liquid, b.p. 117–119° (0.7–1 mm.), n_D^{26} 1.4680 to 1.4799; reported[6] for 2-octyl benzoate, b.p. 171° (20 mm.), n_D^{25} 1.4840. An authentic sample had b.p. 113–116° (0.5 mm.), n_D^{20} 1.4885. An authentic sample of di-2-octyl carbonate had b.p. 118–123° (0.7–1 mm.), n_D^{25} 1.4280. All fractions, besides showing a strong infrared absorption band at 5.80μ, typical for aromatic esters, showed weaker absorption at 5.75μ, apparently due to the presence of di-2-octyl carbonate. The residue from the distillation yielded benzoic anhydride, 1.8 g. (27%). Saponification of the above distillate in alcoholic potassium hydroxide gave an 80% yield of benzoic acid, indicating that only 80% of the liquid product obtained from the rearrangement was 2-octyl benzoate. From the infrared spectrum and boiling point, the remaining 20% is di-2-octyl carbonate. On this basis, the yield of 2-octyl benzoate from the rearrangement is 65%, reasonably close to the predicted 68%. The 2-octanol obtained from the saponification had α_D^{26} −6.87 ± 0.03° (neat, l = 1) and b.p. 77° (10 mm.), n_D^{20} 1.4250.

Rearrangement of benzoic-2,2-diethyl-1-butylcarbonic anhydride. Fractionation of the rearrangement product resulting from this mixed anhydride (12.3 g., 0.044 mole) yielded two fractions, the first, 1.2 g., with b.p. 109–113° (1 mm.) was contaminated with a white solid (approx. 0.2 g.) which was benzoic acid. The second, b.p. 113–114° (1 mm.) n_D^{26} 1.4942, amounted to 7.8 g. The residue from the distillation amounted to 0.5 g. and yielded 0.2 g. (4%) of benzoic anhydride. An infrared spectrum of the remaining material indicated the presence of organic carbonate and benzoic anhydride. A sample of the second fraction, redistilled before submitting for analysis, had b.p. 110° (0.7 mm.) $n_D^{25.5}$ 1.4945.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.44; H, 9.75.

A similar sample of this material had a maximum in the ultraviolet at 228 mμ (log ε, 4.03) in 95% ethanol. The ultraviolet absorption spectrum[16] of alkyl benzoates has a maximum at 228 mμ (log ε, 4.02 to 4.09) in 95% ethanol. Saponification of this material yielded benzoic acid and an alcohol whose 1-naphthylurethan had m.p. 135–136°, undepressed by the 1-naphthylurethan of authentic 2,2-diethyl-1-butanol. The reported[17] m.p. for this derivative is 135–136°.

Rearrangement of mesitoic-2-octylcarbonic anhydride. Fractionation of the rearrangement product resulting from this mixed anhydride (12.9 g., 0.0403 m.) yielded 8.9 g. of liquid b.p. 137–148° (1 mm.), n_D^{26} 1.4561–1.4871. The first two fractions, 1.3 g., b.p. 137–141°, contained an aromatic ester and an organic carbonate, as evidenced by peaks in the infrared at 5.80μ, and 5.75μ, respectively. The latter three fractions, 7.6 g., b.p. 141–148°, were redistilled, and a middle cut having b.p. 145–147° (1 mm.) n_D^{25} 1.4835 submitted for analysis.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.03; H, 10.26.

In addition, an authentic sample of 2-octyl mesitoate made from mesitoyl chloride and 2-octanol had the same properties and infrared spectrum as the above sample. The residue from the above distillation yielded 1.2 g. (19%) of mesitoic anhydride, m.p. 104°, undepressed by an authentic sample. The reported[18] m.p. for mesitoic anhydride is 106–107°.

Attempted reaction of di-2-octyl carbonate and benzoic anhydride. Di-2-octyl carbonate (4.1 g., 0.014 m.) and benzoic anhydride (3.2 g., 0.014 m.) were heated at 177° in the manner used for the decomposition of the mixed anhydrides. No carbon dioxide was trapped after 3 hr. of heating. The addition of *N*,*N*-dimethylaniline (0.10 g., 0.0008 m.) and continued heating likewise produced no carbon dioxide. Fractionation of the mixture yielded only starting materials. Repetition of the experiment with ethyl carbonate and benzoic anhydride yielded similar results.

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