L-*erythro*-2,3-Dihydroxybutanoic Acid and Related Compounds

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THE DL-*erythro*-2,3,-dihydroxybutanoic acid has been described previously (*3, 4*), but the isomers have not been separated nor individual characteristics reported. The procedure followed here is a similar to that used by Ballou (*1*) in synthesizing the monophosphates of the D-*erythro*-isomer.

Table I. Properties of L-*erythro*-2,3-Dihydroxybutanoic Acid (I) and Related Compounds

Compound	M.P., ° C.[a]	$[\alpha]^{25}_D$	Analyses[b]							
			C	H	O	N	C	H	O	N
Methyl 4-*O*-benzyl-α-L-rhamnopyranoside (II)	107–109	−70.0	62.7	7.5	29.8	. . .	62.6	7.6	29.8	. . .
L-*erythro*-2-*O*-benzyl-2,3-dihydroxybutanoic acid (III)	110–112	−76.0	62.8	6.7	30.5	. . .	62.7	6.6	30.5	. . .
Cyclohexylammonium salt of III	162–165	−50.0	66.1	8.8	20.6	4.5	66.0	9.0	20.4	4.3
L-*erythro*-2,3-dihydroxybutanoic acid (I)	70	+10.4	40.0	6.7	53.3	. . .	39.7	6.9	53.3	. . .
Cyclohexylammonium salt of I	117–122	−7.0	54.8	9.7	29.2	6.4	54.6	9.6	29.0	6.6
L-*erythro*-1,2,3-butanetriol tribenzoate	99–101	+25.0	71.7	5.31	22.9	. . .	71.6	5.5	22.7	. . .

[a] Melting points were taken on a melting point block. [b] Analyses by Midwest Microlab, Inc., Indianapolis, Ind.

The starting point for these syntheses was methyl 4-*O*-benzyl-α-1-rhamnopyranoside (II), the D-isomer of which has been described (*1*). Oxidation of II with sodium metaperiodate produced the corresponding dialdehyde in 75% yield. The crude dialdehyde was oxidized with iodine and then hydrolyzed in aqueous acid. Ether extraction of the acid, concentration of the extract, and addition of cyclohexylamine yielded the cyclohexylammonium salt of L-*erythro*-2-*O*-benzyl-2,3-dihydroxybutanoic acid (III). The crystalline acid is obtained from the salt in 79% yield by acidification and extraction with ether.

After treatment of III with hydrogen and palladium, removal of the catalyst, and concentration of the ethanolic solution, addition of cyclohexylamine gave, in 68% yield, the salt of L-*erythro*-2,3-dihydroxybutanoic acid (IV). The free acid was obtained by treating the salt with Dowex 50 (H^+ form). After three recrystallizations from cold acetone, the free acid showed the properties given in Table I.

Reduction of II with $NaBH_4$ and subsequent hydrolysis and catalytic debenzylation produced the hitherto unknown L-*erythro*-1,2,3,-butanetriol, characterized finally as the tribenzoate, the properties of which are given in Table I. The DL-*erythro*-1,2,3,-butanetriol has been characterized previously as its *p*-nitrobenzoate (*2*).

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Symmetrical and Unsymmetrical Fluoroalkoxy- and Fluorophenoxy-*s*-triazines and Related Compounds

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GOOD heat stability is exhibited by tris(1,1,5-tri-*H*-perfluoropentyloxy)-*s*-triazine (*5*); therefore, liquid fluoroalkoxy- and fluorophenoxy-*s*-triazine derivatives are potentially useful as high temperature–stable fluids. A systematic series of these compounds and the required intermediates have been prepared and their properties are reported in Table I. Methods suitable for preparing these compounds will be reported elsewhere (*1*). A discussion of the infrared spectra of these compounds has been published (*3*).

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The properties of 23 simple and mixed fluoroalkoxy- and fluorophenoxy-s-triazine derivatives, $C_3N_3(OR)(OR')(OR'')$, in which R, R′, and R″ are the same or different and include $—CH_2(CF_2)_2H$, $—CH_2(CF_2)_4H$, $—CH_2(CF_2)_6H$, $—CH_2(CF_2)_8H$, $—CH_2(CF_2)_{10}H$, $—CH_2(CF_2)_3F$, $—CH_2(CF_2)_7F$, or $—C_6F_5$, are reported. The properties of 11 intermediate partially substituted fluoroalkoxy derivatives of cyanuric chloride and the chlorination products of two fluoroalkoxy-s-triazines, $C_3N_3(OCCl_2(CF_2)_nCl)_3$ are also described.

Table I. Fluoroalkoxy- and Fluorophenoxy-s-triazines and Related Compounds

s-Triazine Substituents					
2	4	6	M.P., °C.	B.P., °C./Mm.	N_D^{25}
Cl	Cl	$H(CF_2)_2CH_2O$	...	118/9	1.4621
Cl	Cl	$H(CF_2)_4CH_2O$	...	89–92 /0.4	1.4274
Cl	Cl	$H(CF_2)_6CH_2O$	...	95–97 /0.2	1.4074
Cl	Cl	$H(CF_2)_8CH_2O$	45.5–46.5	109–11 /0.08	...
Cl	$H(CF_2)_4CH_2O$	$H(CF_2)_4CH_2O$	...	128–130/0.06	1.3877
Cl	$H(CF_2)_6CH_2O$	$H(CF_2)_6CH_2O$	...	153–157/0.08	1.3744
Cl	$H(CF_2)_8CH_2O$	$H(CF_2)_8CH_2O$	57.5–60	162–166/0.06	...
Cl	$H(CF_2)_4CH_2O$	$H(CF_2)_6CH_2O$	...	142–144/0.14	1.3792
Cl	$H(CF_2)_4CH_2O$	$H(CF_2)_8CH_2O$	...	143–145/0.04	1.3704
Cl	$H(CF_2)_4CH_2O$	$H(CF_2)_{10}CH_2O$	...	156–166/0.2	1.3663
Cl	$H(CF_2)_6CH_2O$	$H(CF_2)_8CH_2O$	...	154–160/0.03	1.3664
$F(CF_2)_3CH_2O$	$F(CF_2)_3CH_2O$	$F(CF_2)_3CH_2O$	108–109.5^{a,b}	...	...
$H(CF_2)_4CH_2O$	$H(CF_2)_4CH_2O$	$F(CF_2)_4CH_2O$	31–33^{c}	169–174/0.3^{c}	...
$H(CF_2)_6CH_2O$	$H(CF_2)_6CH_2O$	$H(CF_2)_6CH_2O$	54–55.5^{c,f}	172–182/0.04	...
$F(CF_2)_7CH_2O$	$F(CF_2)_7CH_2O$	$F(CF_2)_7CH_2O$	78.5–80.5	...	...
$H(CF_2)_8CH_2O$	$H(CF_2)_8CH_2O$	$H(CF_2)_8CH_2O$	95.5–96.5^{e}	205–215/0.04	...
$H(CF_2)_2CH_2O$	$H(CF_2)_8CH_2O$	$H(CF_2)_8CH_2O$	44–46.5	183–188/0.1	...
$H(CF_2)_4CH_2O$	$H(CF_2)_4CH_2O$	$H(CF_2)_6CH_2O$	...	160–162/0.1	1.3652
$H(CF_2)_4CH_2O$	$H(CF_2)_4CH_2O$	$H(CF_2)_8CH_2O$	...	175–180/0.2	1.3587
$H(CF_2)_4CH_2O$	$H(CF_2)_7CH_2O$	$H(CF_2)_7CH_2O$	...	182–187/0.3	1.3603
$H(CF_2)_4CH_2O$	$H(CF_2)_9CH_2O$	$H(CF_2)_9CH_2O$	40–44^{c}	197–210/0.2	...
$H(CF_2)_7CH_2O$	$H(CF_2)_7CH_2O$	$H(CF_2)_9CH_2O$	23–25.5	181–184/0.03	1.3523
$H(CF_2)_7CH_2O$	$H(CF_2)_9CH_2O$	$H(CF_2)_9CH_2O$	69–70.5^{e}	...	...
$H(CF_2)_4CH_2O$	$H(CF_2)_6CH_2O$	$H(CF_2)_8CH_2O$	...	175–179/0.08	1.3566
$H(CF_2)_4CH_2O$	$H(CF_2)_6CH_2O$	$H(CF_2)_{10}CH_2O$	...	180–187/0.06	1.3565
F_5C_6O	$H(CF_2)_4CH_2O$	$H(CF_2)_4CH_2O$	...	149–152/0.07	1.4024
F_5C_6O	$H(CF_2)_6CH_2O$	$H(CF_2)_6CH_2O$	...	175–177/0.1	1.3851
F_5C_6O	$H(CF_2)_8CH_2O$	$H(CF_2)_8CH_2O$	51–54	182/0.02	...
F_5C_6O	F_5C_6O	$H(CF_2)_4CH_2O$	69–70.5	142–146/0.03	...
F_5C_6O	F_5C_6O	$H(CF_2)_6CH_2O$	...	161–162/0.07	1.4248
F_5C_6O	F_5C_6O	$H(CF_2)_8CH_2O$	55.5–59.5	163–166/0.02	1.4132
F_5C_6O	$H(CF_2)_4CH_2O$	$H(CF_2)_6CH_2O$	...	161–162/0.02	1.3926
F_5C_6O	$H(CF_2)_4CH_2O$	$H(CF_2)_8CH_2O$	...	168–171/0.02	1.3861
F_5C_6O	$H(CF_2)_6CH_2O$	$H(CF_2)_8CH_2O$	...	188–191/0.01	1.3793
$Cl(CF_2)_6CCl_2O$	$Cl(CF_2)_6CCl_2O$	$Cl(CF_2)_6CCl_2O$	105–106	...	...
$Cl(CF_2)_8CCl_2O$	$Cl(CF_2)_8CCl_2O$	$Cl(CF_2)_8CCl_2O$	130.3–132.5	...	...

[a] From carbon tetrachloride. [b] Reported, 103–104° (*4*). [c] Fisher-Johns apparatus. [d] Reported, about 160°/0.1 mm. (*5*). [e] From petroleum ether-toluene. [f] Reported, 46–48° (*4*).

EXPERIMENTAL

Unless otherwise specified, uncorrected capillary melting points are reported. Boiling points were taken as the distillation range of each compound. Refractive indexes were obtained on an Abbe refractometer. The identity of all compounds was verified by elemental analyses for carbon, hydrogen, and fluorine, and for chlorine where applicable.

The compounds in Table I were derived from telomer fluoroalcohols which were redistilled before use. The minimum purity of the telomer alcohols used in the preparations was determined by Felton's (*2*) procedure: 1,1,3-tri-*H*-perfluoropropanol, 100,0%; 1,1,5-tri-*H*-perfluoropentanol, 99.1%; 1,1,7-tri-*H*-perfluoroheptanol, 95.3%; 1,1,9-tri-*H*-perfluorononanol, 92.2%; and 1,1,11-tri-*H*-perfluoroundecanol, 91.3%. No significant quantities of homologous alcohols were present, the impurities being chiefly the isomeric secondary alcohols. Cyanuric chloride free of cyanuric acid was also used in preparing the compounds.

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