TABLE II

ISOLATION OF 3-NITRODURENE BY PRODUCT ANALYSIS

Fraction	Eluant	Volume, ml.	Weight, g.	M.p., °C.	Product
1	Petroleum ether	40	0.1005	79.5–80.5	Durene
2	Petroleum ether	10	.0785	78.5–80	Durene
3	Pet. ether–ethanol, 95:5	25	.1232	77–79	Durene (impure)
4	Pet. ether–ethanol, 95:5	25	.0637	113–114	3-Nitrodurene
5	Pet. ether–ethanol, 95:5	15	.0596	99–105	3-Nitrodurene (impure)
6	Chloroform	25	.0514	203–207	3,6-Dinitrodurene

troleum ether fraction or in the petroleum ether–ethanol fraction, whereas 3,6-dinitrodurene was contained in the chloroform fraction. Also in this case, a very small amount of a reddish pigment remained adsorbed on the alumina.

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ROME, ITALY

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Esters of γ-(Tetrahydro-2-furyl)-alkanols

BY C. R. RUSSELL, L. S. HAFNER, H. E. SMITH AND L. E. SCHNIEPP

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The preparation and properties of esters derived from 3-(tetrahydro-2-furyl)-1-propanol, 4-(tetrahydro-2-furyl)-2-butanol and 1,5-bis-(tetrahydro-2-furyl)-3-pentanol with fat acids from C_2 to C_{18} and with aliphatic dicarboxylic acids from C_6 to C_{10} are described.

Further studies relative to a program of developing new chemicals from furfural have led to the preparation of a series of esters derived from 3-(tetrahydro-2-furyl)-1-propanol, 4-(tetrahydro-2-furyl)-2-butanol and 1,5-bis-(tetrahydro-2-furyl)-3-pentanol with the fat acids from C_2 to C_{18}, and with adipic, azelaic and sebacic acids. The properties of these esters are described in this paper.

The γ-(tetrahydro-2-furyl)-alkanols employed in this investigation were obtained as by-products in the synthesis of a number of polyhydroxyalkanes previously reported.[2] Few derivatives of these ether-alcohols have been described, although the parent compounds have been known for some time.[3,4,5] A number of esters of 1,5-bis-(tetrahydro-2-furyl)-3-pentanol, including the azelate, have been previously reported.[6] Little information about the properties of these esters, most of which were derived from alkoxy acids, was given other than that they were effective plasticizers for vinyl, acrylic and cellulose type polymers. No esters of 4-(tetrahydro-2-furyl)-2-butanol have been reported, and only the acetate of 3-(tetrahydro-2-furyl)-1-propanol has been prepared.[7]

The esters of the present series were prepared by heating the reactants and a catalytic amount of *p*-toluenesulfonic acid dissolved in benzene to reflux, and removing the water of reaction. Purification of the esters was accomplished by distillation. The more volatile esters were fractionated by distillation through conventional columns, whereas the higher boiling esters were distilled from falling-film and alembic flask type molecular stills previously described.[8] Most of the once-distilled esters contained impurities in amounts varying from 1 to 5%, and were reprocessed until analytically pure samples having constant physical properties were obtained. In a few cases it was necessary to remove free acid, which co-distilled with the ester, by passing the ester dissolved in *n*-heptane through a column of adsorptive alumina. The methods of purification and the order in which they were applied are given in Table I.

No attempts were made to obtain maximum yields of purified products. The yields recorded in Table I are based on those fractions of the once-distilled esters having a degree of purity in excess of 95%, as determined by the saponification equivalent and the free acid content.

All of the esters except the stearates were clear liquids. A few of the higher members of the series were slightly straw-colored. The stearates were white solids. A number of the more volatile esters possessed pleasant fruity odors characteristic of low molecular weight esters in general.

Experimental

Preparation of Esters, General Procedure.—To 200 ml. of benzene containing 2 g. of *p*-toluenesulfonic acid were

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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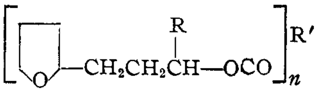
TABLE I

ESTERS OF γ-(TETRAHYDRO-2-FURYL) ALKANOLS



R	R′	n	Yield[a] %	Method of purifcn.	Dist. °C.[b]	Dist. μ	$n^{25}D$	d^{20}_4[c]	Sapn. equiv. Calcd.	Sapn. equiv. Found	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	C_2H_5	1	88	*d*	57	110	1.4416	0.982	186.3	187.6	$C_{10}H_{18}O_3$	64.48	64.1	9.74	9.8
H	C_3H_7	1	76	*d*	75	50	1.4425	.964	200.3	199.5	$C_{11}H_{20}O_3$	65.95	65.4	10.06	10.1
H	C_5H_{11}	1	82	*d*	86	50	1.4457	.947	228.3	226.0	$C_{13}H_{24}O_3$	68.38	68.0	10.59	10.5
H	C_7H_{15}	1	83	*d*	106	50	1.4484	.930	256.4	255.4	$C_{15}H_{28}O_3$	70.26	69.6	11.00	10.6
H	$(C_2H_5)_2CH$	1	75	*d*	75	50	1.4439	.954	228.3	226.0	$C_{13}H_{24}O_3$	68.38	68.5	10.59	10.4
H	$\left.\begin{matrix}C_4H_9\\C_2H_5\end{matrix}\right>CH$	1	69	*d*	108	200	1.4464	.930	256.4	257.8	$C_{15}H_{28}O_3$	70.26	70.1	11.00	10.8
H	C_8H_{17}	1	68	*d,d,e*	122	90	1.4493	.927	270.4	269.2	$C_{16}H_{30}O_3$	71.06	71.1	11.18	11.2
H	C_9H_{19}	1	63	*f,e,g*	139	330	1.4503	.919	284.4	286.6	$C_{17}H_{32}O_3$	71.78	71.3	11.34	11.1
H	$C_{11}H_{23}$	1	69	*h,g*	142	70	1.4524	.906	312.5	312.1	$C_{19}H_{36}O_3$	73.02	72.5	11.61	11.5
H	$C_{13}H_{27}$	1	71	*h,g*	162	50	1.4540	.902	340.6	338.0	$C_{21}H_{40}O_3$	74.06	74.4	11.84	11.9
H	$C_{17}H_{35}$	1	62	*g*	192	90	1.4570	[i]	396.6	396.8	$C_{25}H_{48}O_3$	75.70	75.5	12.19	12.0
CH_3	CH_3	1	63	*d,d*	71	400	1.4390	.974	186.2	184.0	$C_{10}H_{18}O_3$	64.48	64.3	9.74	9.7
CH_3	C_2H_5	1	77	*d,d*	61	110	1.4392	.963	200.3	199.0	$C_{11}H_{20}O_3$	65.96	65.7	10.06	10.0
CH_3	C_3H_7	1	78	*g,h,d*	70	40	1.4399	.950	214.3	210.5	$C_{12}H_{22}O_3$	67.25	66.7	10.34	10.3
CH_3	C_5H_{11}	1	60	*d,e,d*	86	70	1.4434	.924	242.3	238.0	$C_{14}H_{26}O_3$	69.37	69.3	10.80	10.7
CH_3	C_7H_{15}	1	63	*d,e,d*	100	30	1.4463	.912	270.4	272.1	$C_{16}H_{30}O_3$	71.06	70.9	11.18	11.4
CH_3	$(C_2H_5)_2CH$	1	33	*d,g,d*	72	50	1.4410	.926	242.3	241.0	$C_{14}H_{26}O_3$	69.37	68.9	10.81	10.7
CH_3	$\left.\begin{matrix}C_4H_9\\C_2H_5\end{matrix}\right>CH$	1	38	*d,g,d*	97	100	1.4437	.912	270.4	275.3	$C_{16}H_{30}O_3$	71.06	71.2	11.18	11.2
CH_3	C_8H_{17}	1	64	*h,e*	101	20	1.4480	.912	284.4	282.3	$C_{17}H_{32}O_3$	71.78	71.3	11.34	11.2
CH_3	C_9H_{19}	1	72	*h,e*	109	20	1.4487	.904	298.4	297.0	$C_{18}H_{34}O_3$	72.43	72.7	11.48	11.2
CH_3	$C_{11}H_{23}$	1	26	*f,e,h*	138	100	1.4511	.900	326.5	323.1	$C_{20}H_{38}O_3$	73.56	73.6	11.73	11.2
CH_3	$C_{13}H_{27}$	1	54	*f,f*	105	1.4	1.4529	.885	354.6	353.6	$C_{22}H_{42}O_3$	74.52	74.6	11.94	11.8
CH_3	$C_{15}H_{31}$	1	67	*f,f,j*	140	1.8	1.4541	.882	382.6	383.0	$C_{24}H_{46}O_3$	75.33	75.3	12.11	12.1
CH_3	$C_{17}H_{35}$	1	59	*f,j,k*	130	3.8	1.4552	[l]	410.6	415.0	$C_{26}H_{50}O_3$	76.03	75.9	12.27	12.3
THFE[m]	C_2H_5	1	60	*h*	112	10	1.4633	1.000	284.3	286.5	$C_{16}H_{28}O_4$	67.56	68.0	9.92	9.9
THFE	C_3H_7	1	47	*h,g,h*	123	80	1.4631	0.992	298.4	293.0	$C_{17}H_{30}O_4$	68.42	68.2	10.13	10.0
THFE	C_5H_{11}	1	56	*h,f,h*	140	110	1.4633	.971	326.3	322.7	$C_{19}H_{34}O_4$	69.89	69.5	10.49	10.0
THFE	C_7H_{15}	1	55	*f,f,j*	100	2.6	1.4640	.956	354.4	349.0	$C_{21}H_{38}O_4$	71.14	70.9	10.80	10.8
THFE	C_8H_{17}	1	58	*f,f,f,j*	100	0.4	1.4641	.953	368.5	366.8	$C_{22}H_{40}O_4$	71.70	71.5	10.94	10.8
THFE	C_9H_{19}	1	48	*f*	130	2.8	1.4650	.951	382.4	379.8	$C_{23}H_{42}O_4$	72.17	72.0	11.10	10.8
THFE	$C_{11}H_{23}$	1	56	*f,f*	130	1.0	1.4654	.936	410.5	408.9	$C_{25}H_{46}O_4$	73.12	72.6	11.29	11.2
THFE	$C_{13}H_{27}$	1	46	*f,f*	150	0.6	1.4660	.932	438.6	435.5	$C_{27}H_{50}O_4$	73.92	73.7	11.49	11.6
H	$(CH_2)_4$	2	69	*f*	150	7	1.4687	1.066	185.2	183.0	$C_{20}H_{34}O_6$	64.83	64.5	.9.25	9.2
H	$(CH_2)_7$	2	74	*g,f*	160	2	1.4680	1.031	206.3	204.0	$C_{22}H_{40}O_6$	66.95	66.4	9.77	9.8
H	$(CH_2)_8$	2	69	*f*	165	5	1.4680	1.024	213.3	214.0	$C_{24}H_{42}O_6$	67.56	67.5	9.92	9.9
CH_3	$(CH_2)_4$	2	58	*f*	140	7	1.4627	1.025	199.2	204.0	$C_{22}H_{38}O_6$	66.30	66.2	9.61	9.7
CH_3	$(CH_2)_7$	2	36	*f*	160	5	1.4638	1.011	220.3	217.0	$C_{25}H_{44}O_6$	68.14	67.4	10.06	10.1
CH_3	$(CH_2)_8$	2	63	*f,f*	180	5	1.4631	0.997	227.3	228.3	$C_{26}H_{46}O_6$	68.69	68.4	10.20	10.3
THFE	$(CH_2)_4$	2	67	*f,f*	200	0.3	1.4822	1.077	283.3	279.2	$C_{32}H_{54}O_8$	67.81	67.5	9.60	9.6
THFE	$(CH_2)_7$	2	45	*f*	215	5	1.4805	1.064	304.4	305.5	$C_{35}H_{60}O_8$	69.04	68.8	9.93	9.7
THFE	$(CH_2)_8$	2	23	*f*	260	10	1.4799	1.054	311.4	309.0	$C_{36}H_{62}O_8$	69.42	69.7	10.03	10.0

[a] Calculated on the basis of the once-distilled product having an analytical purity of 95$^+$%. [b] Observed on final distillation; temperature of hot finger in the falling-film still; vapor temperature in all other distillations. Pressure measured by McLeod and calibrated thermocouple gages attached between the still head and solid CO_2 cooled trap. [c] Measured by Fisher–Davidson Gravitometer. [d] Fractionated through a jacket-heated 3-foot packed column. [e] Low boiling impurities removed on alembic flask still by protracted heating just under the boiling point at low pressures. [f] Distilled on falling-film still. [g] Fractionated through jacket-heated 14-inch packed column. [h] Distilled from alembic flask still. [i] Solid, m.p. 25–27°. [j] Acid removed by passing the ester dissolved in n-heptane through a column of activated Al_2O_3. [k] Recrystallized from acetone. [l] Solid, m.p. 20–21°. [m] Tetrahydrofurylethyl = $\underbrace{(CH_2)_3CH}_{O}(CH_2)_2$.

added the tetrahydrofuryl alkanols and acids as indicated in the table. The reaction mixture was heated at reflux until water ceased to collect in the separating device attached between the flask and reflux condenser, after which period, the reaction mixture was cooled and 400 ml. of benzene added. The benzene solution was extracted with cold 5% sodium hydroxide in an amount slightly less than that calculated as necessary for the removal of excess acid and catalyst. The remaining acid was removed with 5% sodium bicarbonate solution, the benzene layer washed with water until neutral, and dried over anhydrous magnesium sulfate.

Butanol was added during the extraction of a number of the higher molecular weight esters to break up the emulsions which formed.

The dry benzene solutions of the esters were filtered and the solvent removed on a steam-bath under reduced pressure. The crude esters were then purified by the methods indicated in the table. All of the esters which were distilled on the falling-film still were degassed for 1 to 2 hours at 125° at 0.01 to 0.05 mm. before placing them on the still.

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PEORIA 5, ILLINOIS