Properties of Polyester Fluids with Desirable Synthetic Lubricant Characteristics

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THE LITERATURE contains numerous references to synthetic fluids that have properties desirable for lubricant use (*2, 4, 6, 8, 9, 11*). During the past 10 years the increasing demand for liquids possessing good lubricity, thermal stability, oxidation-corrosion stability, low pour points, and small temperature viscosity coefficients has shifted emphasis toward the synthesis of various classes of compounds meeting these requirements, such as ethers, esters, alkyl-aryl hydrocarbons, halogenated hydrocarbons, and silicones. The class of compounds that best meets all of the increased requirements for thermal stability to 550° F. is probably the ester, and particularly esters of such polyols as pentaerythritol and trimethylolpropane, and the esters of such readily available polybasic acids as sebacic, "isosebacic" (*11*), adipic and phthalic acids.

Although a considerable amount of work has been done in the development of certain ester-based synthetic lubricants, there is little available information describing the esters of polyols such as pentaerythritol and trimethylolpropane. Information concerning the rheological properties, as affected by structure, of these compounds is particularly lacking. Barnes and Fainman (*1*) describe several nonspecific esters of the previously mentioned polyols, giving viscometric and pour point data. Berlow, Barth, and Snow (*2*) only briefly mention the aliphatic pentaerythritol esters as potential lubricants in their survey of pentaerythritol chemistry. Murphy and Zisman (*10*) and Cohen, Murphy, O'Rear, Ravner, and Zisman (*4*), in their studies of ester lubricants, include several esters of pentaerythritol and trimethylolpropane. Murphy and Zisman (*10*) showed that generalizations derived from a study of the relationship between molecular structure and viscosity-temperature properties of hydrocarbons and monoesters can be successfully extended to predict the properties of a variety of synthetic liquids, including esters.

This study searched for esters of polyols and other alcohols having minimum viscosity-temperature coefficients without sacrificing low pour point and good thermal stability.

EXPERIMENTAL

Synthesis. The simple and mixed esters of low molecular weight were prepared by refluxing stoichiometric quantities of the acids and alcohols in a suitable solvent (benzene, toluene, or xylene) in the presence of a small amount of *p*-toluenesulfonic acid. The water of reaction was removed azeotropically and measured. The esterification was considered complete when the collected water equaled the theoretical expected amount. The reaction mixture was washed with water, dilute aqueous sodium bicarbonate solution and again with water. After drying the neutral ester with anhydrous sodium sulfate, the solvent was removed under reduced pressure. The esters then were distilled in vacuo.

Esters of higher molecular weight were prepared in a similar manner; however, to avoid thermal decomposition they were not distilled. After removal of solvents the crude ester was stirred with a mixture of decolorizing charcoal (1 part) and chromatographic grade alumina (3 parts) at 80° to 100° C. for 1 to 3 hours. Filtration of the mixture through a fritted glass plate gave a final product with a very low neutralization number. Where no boiling point is reported in the tables of data, this purification method was used.

Test Procedures. Commercially available ASTM Fenske-Ostwald-type viscometers were used, and the methods described in ASTM D445-53T were followed. The ASTM slopes were calculated from the viscometric data plotted on ASTM standard viscosity charts.

Pour points were determined as described in ASTM D97-47 and/or by a similar micromethod which agreed with results from the macro ASTM method. When crystallization occurred it is noted in the tables.

The procedures described in Federal Specifications (VV-L-791e method 5103.3) were followed in determining the neutralization number of the purified esters.

The thermal stability of the compounds was determined in an apparatus similar to that described by Blake and others (*3*). The apparatus provides a method for heating the test sample in an inert atmosphere. Any volatile materials produced from thermal decomposition are vaporized from the sample, condensed and trapped in the apparatus, and thus removed from the test sample. A test consisted of heating about 20 ml. of the liquid in a nitrogen atmosphere at 536° F. for 24 hours. After the heating period, the 100° F. viscosity was determined, and the per cent change from the pretest viscosity was calculated. If a large amount of volatile material was collected during the test, the compound tested was considered to have failed.

DISCUSSION

Pentaerythritol Esters. The pentaerythritol esters synthesized in this research include many structural variations. Generalizations can be made, some of which are very similar to those mentioned by Murphy and Zisman (*10*) for hydrocarbons and monoesters.

For esters formed by esterifying completely pentaerythritol with an acid of definite structure: increasing the acid chain length results in increased viscosities, higher pour points and higher freezing points (except for lower members of a series); and acid chain branching results in increased viscosities, lower pour points and increases in the ASTM viscosity slopes.

Other generalizations are made using test data obtained from esterification mixtures formed by the reaction of a polyol with an equimolar amount of more than one kind of an acid. These products are not definite compounds and consequently the properties obtained may be due, in a considerable part, to the multiplicity of products as well as to structural differences. Such generalizations are: alicyclic groups in the acid moiety increase the viscosities, generally lower the pour points, but have very little effect on the ASTM viscosity slopes; mixed open chain acids generally have very little effect on the viscosities and on the ASTM viscosity slopes, but tend to lower the pour points; and mixed open and branched chain acids increase the viscosities and the ASTM viscosity slopes, and greatly lower the pour points when compared with analogous open chain compounds.

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Table I. Properties of Pentaerythritol Esters

Compd. No.	Acids Used to Esterify Polyol	Molar Ratio Acid/Polyol	Viscosity, Cs.		ASTM Slope	Pour P., ° F.	Neut. No.	n_{D}^{25}	B.P., ° C./mm. Hg	Thermal[a] Stability
			100° F.	210° F.						
			Symmetrical Open Chain Esters							
1	Ethanoic	4	. . .	. . .	. . .	180^{b}	0.05	. . .	. . .	. . .
2	Pentanoic	4	17.2	3.66	0.76	−70	0.12	1.4480	176–86/0.15	6
3	Hexanoic	4	21.2	4.23	0.76	−65	0.60	1.4519	231–36/0.3	. . .
4	Heptanoic	4	22.4	4.47	0.74	−25	0.05	1.4530	233/0.1	3
5	Octanoic	4	27.6	5.32	0.70	40^{b}	1.84	1.4542	247–48/0.09	. . .
6	Nonanoic	4	32.7	5.89	0.69	50^{b}	2.0	1.4554	269–74/0.1	17.4
7^{c}	Nonanoic	4	35.3	6.35	0.67	40^{b}	0.05	1.4553	. . .	. . .
8	Undecanoic	4	. . .	. . .	. . .	102^{b}	. . .	. . .	. . .	. . .
9	Tetradecanoic	4	. . .	. . .	. . .	140^{b}	0.2	. . .	. . .	. . .
10	Heptadecanoic	4	. . .	. . .	. . .	158^{b}	0.35	. . .	. . .	. . .
			Symmetrical Branched Chain Esters							
11	Isobutanoic	4	7.3^{d}	3.42	0.77	113^{b}	. . .	. . .	181/0.6	. . .
12	Trimethylethanoic	4	. . .	12.19	. . .	178^{b}	. . .	. . .	145–7/0.08	. . .
13	2-Ethylbutanoic	4	61.4	6.46	0.83	−30	0.01	1.4526	. . .	^{e}
14^{c}	Isooctanoic	4	75.9	8.44	0.76	−55	0.05	1.4571	. . .	. . .
			Mixed Open-Chain Esters							
15	Pentanoic	2	19.6	4.08	0.75	−65	1.0	1.4500	216–33/0.45	. . .
	Heptanoic	2								
16	Ethanoic	2	38.6	5.80	0.75	10^{b}	0.05	1.4528	. . .	3.1
	Decanoic	2								
17	Octanoic	2	28.4	4.87	0.76	−65	0.07	1.4530	. . .	. . .
	Ethanoic	1								
	Hexanoic	1								
18	Pentanoic	2	19.5	4.23	0.71	−45	0.05	1.4530	. . .	22.3
	Nonanoic	2								
19	Hexanoic	3	36.4	6.35	0.69	45	0.05	1.4573	. . .	. . .
	Tetradecanoic	1								
20	Heptanoic	2	28.7	5.23	0.70	−5	0.02	1.4538	228–9/0.12	2.9
	Nonanoic	2								
21	Butanoic	1	35.5	6.37	0.67	60	0.07	1.4559	. . .	. . .
	Hexanoic	1								
	Octanoic	1								
	Tetradecanoic	1								
22	Hexanoic	2	36.0	6.20	0.70	30	0.04	1.4579	. . .	. . .
	Undecanoic	2								
23	Hexanoic	3	43.5	7.31	0.67	70–80^{b}	0.02	. . .	. . .	. . .
	Heptadecanoic	1								
24	Nonanoic	2	36.0	6.42	0.68	40	0.04	. . .	. . .	. . .
	Octanoic	1								
	Decanoic	1								
25	Hexanoic	2	41.8	7.00	0.67	50	0.03	1.4583	. . .	. . .
	Undecanoic	1								
	Tetradecanoic	1								
26	Pentanoic	2	46.9	7.89	0.66	70–80^{b}	0.08	. . .	. . .	−3.4
	Tetradecanoic	2								
			Mixed Branched and Open-Chain Esters							
27^{c}	Butanoic	2	62.6	7.81	0.74	−45	0.06	1.4586	. . .	. . .
	Isodecanoic	2								
28	Hexanoic	2	45.6	6.58	0.75	−65	0.03	1.4561	. . .	1.9
	Isodecanoic	2								
29	2-Ethylbutanoic	2	98.5	9.19	0.77	−30	0.16	. . .	. . .	^{e}
	Isodecanoic	2								
30	Octanoic	2	46.1	6.66	0.74	−50	0.04	1.4559	. . .	. . .
	2-Ethylhexanoic	2								
31	Nonanoic	2	45.4	6.81	0.71	−40	0.03	1.4565	. . .	. . .
	Isooctanoic	2								
32	Nonanoic	2	43.6	6.41	0.74	−60	0.04	. . .	235–75/0.45	. . .
	2-Ethylhexanoic	2								
33	Heptanoic	2	46.1	6.78	0.70	−50	0.01	1.4564	. . .	3.3
	Isodecanoic	2								
34	Nonanoic	2	58.0	6.96	0.77	−45	0.63	1.4561	. . .	. . .
	2-Ethyl-4-methyl-pentanoic	2								
35	Hexanoic	1	42.9	6.49	0.72	−60	0.50	1.4559	. . .	. . .
	Decanoic	1								
	Isodecanoic	1								
	2-Ethylhexanoic	1								

[a] Per cent change in 100° F. viscosity after heating 24 hours at 536° F. in nitrogen atmosphere.
[b] Crystalline at indicated temperature.

Table I. Properties of Pentaerythritol Esters (*Continued*)

Compd. No.	Acids Used to Esterify Polyol	Molar Ratio Acid/Polyol	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope	Pour P., ° F.	Neut. No.	n_{D}^{25}	B.P., ° C./mm. Hg	Thermal[a] Stability
36	Nonanoic	3	42.6	6.66	0.71	−10	0.04	1.4562	...	...
	2-Ethyl-4-methyl pentanoic	1								
37	Decanoic	2	57.1	8.19	0.69	−40	0.01	1.4588	...	...
	Isooctanoic	2								
38	Hexanoic	1	44.2	6.84	0.71	40	0.03	1.4570	...	...
	Nonanoic	1								
	Tetradecanoic	1								
	2-Ethylhexanoic	1								
39	Nonanoic	2	49.3	7.40	0.70	−60	0.14	...	...	...
	Isodecanoic	2								
40	Pentanoic	1	47.8	7.63	0.67	30	0.03	1.4590	...	...
	2-Ethylhexanoic	1								
	Undecanoic	1								
	Tetradecanoic	1								
41	Hexanoic	2	58.6	8.41	0.68	70–80[b]	0.19	...	...	...
	Heptadecanoic	1								
	2-Ethylhexanoic	1								
42	Hexanoic	1	49.0	7.79	0.66	40	0.02	...	...	...
	2-Ethylhexanoic	1								
	Undecanoic	1								
	Tetradecanoic	1								
43	Nonanoic	1	66.6	9.30	0.67	60	0.10	...	...	...
	Pentadecanoic	1								
	2-Ethylhexanoic	2								
44	Decanoic	1	74.8	10.37	0.65	65	0.02	1.4562	...	...
	Heptadecanoic	1								
	Isooctanoic	2								
45	Tetradecanoic	2	63.7	8.61	0.70	70–80[b]	0.08	...	...	...
	2-Ethylhexanoic	2								
		Esters Containing Aromatic or Alicyclic Structures								
46	Hexanoic	3	36.7	5.99	0.73	−65	0.05	1.4602	...	4.9
	Cyclohexanecarboxylic	1								
47	Hexanoic	2	99.9	10.10	0.73	−30	0.03	1.4706	...	5.9
	Cyclohexanecarboxylic	2								
48	Butanoic	2	79.3	9.15	0.73	−45	0.40	1.4702	...	6.8
	4-Cyclohexylbutanoic	2								
49	Heptanoic	3	52.2	7.59	0.70	−55	0.06	1.4633	...	...
	Cyclohexanecarboxylic	1								
50	Heptanoic	3	45.0	6.99	0.70	−60	0.02	...	...	...
	4-Cyclohexylbutanoic	1								
51	Heptanoic	3	49.2	7.32	0.70	−60	0.33	1.4632	...	...
	4-Cyclohexylbutanoic	1								
52	Nonanoic	2	108	10.70	0.73	−35	0.03	1.4760	...	...
	Benzoic	1								
	Cyclohexanecarboxylic	1								
53	Hexanoic	2	58.3	8.49	0.67	40	0.02	1.4630	...	...
	Tetradecanoic	1								
	Cyclohexanecarboxylic	1								
54	Nonanoic	3	51.7	7.77	0.68	−5[b]	0.13	...	...	4.4
	Cyclohexanecarboxylic	1								
55	Nonanoic	3	39.2	6.36	0.71	−10	0.20	1.4728	267–8/0.15	...
	Phenylethanoic	1								
56	Nonanoic	3	62.6	8.46	0.70	−35	0.03	1.4619	...	...
	4-Cyclohexylbutanoic	1								
57	Heptanoic	2	60.5	8.81	0.67	10	0.06	1.4640	...	...
	Tetradecanoic	1								
	4-Cyclohexylbutanoic	1								
58	Heptanoic	1	54.8	8.42	0.65	10	0.02	1.4641	...	...
	Undecanoic	2								
	4-Cyclohexylbutanoic	1								
59	Isodecanoic	2	103.4	11.45	0.68	−5	0.01	1.4667	...	...
	Tetradecanoic	1								
	4-Cyclohexylbutanoic	1								
60	Isodecanoic	2	114.3	12.79	0.66	65	0.02	1.4670	...	...
	Heptadecanoic	1								
	4-Cyclohexylbutanoic	1								

[c] Prepared from technical pentaerythritol; contains some polypentaerythritols.
[d] Supercooled. [e] Thermal stability test failure due to formation of volatile materials

Table II. Properties of Polypentaerythritol Esters

Compd. No.	Acids Used to Esterify Polyol	Molar Ratio Acid/Polyol	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope	Pour P., ° F.	Neut. No.	n_D^{25}	Thermal Stability[a]
			Dipentaerythritol Esters						
1	Butanoic	6	65.0	8.84	0.68	55[b]	0.03	1.4529	−1.5
2	Hexanoic	6	52.0	8.21	0.67	70–80[b]	0.06	. . .	. . .
3	Butanoic	3	71.6	9.69	0.67	−40	0.06	1.4569	4.1
	Nonanoic	3							
4	2-Ethylhexanoic	6	360	21.0	0.72	10	0.61	1.4688	. . .
5	Isodecanoic	6	288	20.4	0.67	−5	. . .	1.4647	. . .
			Tripentaerythritol Esters						
6	Butanoic	8	115	15.4	0.64	−20	0.04	1.4572	14.9
7	Pentanoic	8	112	13.6	0.64	−50	0.05	1.4580	. . .
8	Hexanoic	8	107	13.9	0.61	20	0.02	1.4588	. . .
9	Heptanoic	8	115	14.3	0.61	10	0.03	1.4598	. . .
10	Hexanoic	4	234	21.4	0.64	. . .	0.05	1.4633	. . .
	Isodecanoic	4							
11	Nonanoic	8	154	17.2	0.63	70–80[b]	. . .	. . .	. . .

[a] Per cent change in 100° F. viscosity after heating 24 hours at 536° F. in nitrogen atmosphere. [b] Crystalline at indicated temperature.

Table III. Properties of Trimethylolpropane Esters

Compd. No.	Acids Used to Esterify Polyol	Molar Ratio Acid/Polyol	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope	Pour P., ° F.	Neut. No.	n_D^{25}	B.P., ° C./mm. Hg	Thermal Stability[a]
1	Nonanoic	1	29.5	4.63	0.71	. . .	0.20	1.4428	174–196/0.6	1.1
	Trimethylethanoic	2								
2	Decanoic	2	23.0	4.40	0.75	−35[b]	0.05	1.4520	. . .	2.3
	Ethanoic	1								
3	Nonanoic	2	23.1	4.33	0.74	−70	0.07	1.4483	174–202/0.4	. . .
	Trimethylethanoic	1								
4	Nonanoic	1	45.5	6.25	0.75	−60	0.02	1.4624	187–227/0.35	−8.1
	2-Ethylhexanoic	1								
	Cyclohexanecarboxylic	1								
5	2-Ethylhexanoic	3	30.2	4.42	0.85	−60	0.05	1.4509	. . .	[c]
6	Nonanoic	1	25.5	4.64	0.75	−40[b]	0.13	1.4838	234–248/0.45	−0.2
	2-Ethylhexanoic	1								
	Phenylethanoic	1								
7	Nonanoic	2	42.4	5.89	0.78	−40	0.11	1.4791	255–260/0.8	. . .
	Benzoic	1								
8	Nonanoic	3	22.5	4.63	0.71	−40	0.14	1.4531	204–211/0.1	−3.8
9	Heptanoic	1	22.8	4.66	0.79	−50	0.02	1.4530	. . .	. . .
	Decanoic	2								
10	Tetradecanoic	1	33.2	5.83	0.70	20	0.10	. . .	. . .	. . .
	Pentanoic	1								
	2-Ethylhexanoic	1								
11	Nonanoic	2	37.2	6.25	0.70	−60	0.04	1.4629	234–245/0.45	. . .
	4-Cyclohexylbutanoic	1								
12	Undecanoic	2	45.7	7.84	0.67	−45	0.02	1.4641	. . .	. . .
	4-Cyclohexylbutanoic	1								
13	Nonanoic	1	41.9	6.25	0.75	−50	0.04	1.4582	. . .	−25.6
	Isodecanoic	2								
14	Pentanoic	1	36.9	6.74	0.66	−70	0.10	1.4608	. . .	. . .
	Isodecanoic	1								
	9-Octadecenoic	1								
15	Pentanoic	1	43.2	7.35	0.67	70–80[b]	0.15	. . .	. . .	. . .
	Isodecanoic	1								
	Heptadecanoic	1								
16	Pentanoic	1	36.4	6.89	0.65	70–80[b]	0.04	. . .	. . .	0.4
	Decanoic	1								
	Heptadecanoic	1								
17	Tetradecanoic	2	56.2	8.66	0.65	40	0.04	1.4658	. . .	. . .
	4-Cyclohexylbutanoic	1								
18	Tetradecanoic	2	44.1	7.37	0.67	50	0.03	1.4590	. . .	. . .
	Isodecanoic	1								

[a] Per cent change in 100° F. viscosity after heating 24 hours at 536° F. in nitrogen atmosphere. [b] Crystalline at indicated temperature. [c] Thermal stability test failure due to formation of volatile materials.

Table IV. Properties of Dibasic Acid Esters

Compd. No.	Acid	Alcohol	Molar Ratio Alcohol/Acid	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope	Pour P., ° F.	Neut. No.	n_D^{25}	Thermal Stability[a]
1	Butyladipic	1-Methylcyclohexylmethanol	2	232	11.77	0.86	0	. . .	1.4753	. . .
2	Isopropyladipic	1-Methylcyclohexylmethanol	2	74.3	7.58	0.79	−25	0.3	1.4754	. . .
3	Sebacic	1-Methylcyclohexylmethanol	2	46.9	7.19	0.70	−70	0.02	1.4735	2.1
4	Azelaic	1-Methylcyclohexylmethanol	2	44.6	7.00	0.69	−50	0.01	1.4737	−4.2
5	Isosebacic	1-Methylcyclohexylmethanol	2	54.3	7.00	0.75	−50	0.07	1.4753	0.2
6	Azelaic	1-Methylcyclohexylmethanol Nonanol	1 1	20.4	4.53	0.70	30[b]	1.7	1.4603	. . .
7	Sebacic	1-Methylcyclohexylmethanol Isodecanol	1 1	29.2	5.60	0.70	−60	2.0	1.4628	. . .
8	Sebacic	1-Methylcyclohexylmethanol Decanol	1 1	23.9	5.30	0.65	70[b]	0.02	1.4609	4.5
9	Sebacic	1-Methylcyclohexylmethanol Isotridecanol	1 1	40.1	6.77	0.68	−60	0.04	1.4638	−5.1
10	Sebacic	1-Methylcyclohexylmethanol Octadecanol	1 1	38.8	7.39	0.63	70–80[b]	0.05	1.4652	. . .
11	Azelaic	1-Methylcyclohexylmethanol 2,2-Dimethyl-1-pentanol	1 1	21.4	4.37	0.73	−60	0.02	1.4588	. . .
12	Isosebacic[c]	2-Ethyl-1-hexanol	2	11.2	3.06	0.70	−80	0.07	1.4482	4.5
13	Isosebacic[c]	Octanol	2	11.7	3.15	0.71	25	0.03	1.4472	. . .
14	Isosebacic[c]	Dodecanol	2	20.5	5.20	0.62	70–80[b]	. . .	1.4532	. . .
15	Isosebacic[c]	Isotridecanol	2	40.0	6.51	0.70	−60	0.15	1.4568	. . .
16	Sebacic	Isotridecanol	2	39.9	6.89	0.67	−60	0.05	1.4580	−10.3
17	Sebacic	4-Methylcyclohexanol	2	34.5	5.95	0.70	70 80[b]	. . .	1.4660	. . .
18	Sebacic	Isotridecanol 4-Methylcyclohexanol	1 1	35.7	6.29	0.69	−60	0.09	1.4609	[d]
19	Isosebacic[c]	Isotridecanol Octadecanol	1 1	39.2	7.24	0.64	40[b]	0.11	1.4573	. . .
20	Sebacic	Isotridecanol Isodecanol	1 1	28.9	5.79	0.66	−65	0.07	1.4560	−7.7
21	Sebacic	Isotridecanol Benzyl alcohol	1 1	23.6	5.04	0.67	−50[b]	0.02	. . .	. . .
22	Sebacic	Isotridecanol 2-Propyl-1-heptanol	1 1	26.0	5.30	0.67	−60	0.02	. . .	. . .
23	Sebacic	Isodecanol Tetradecanol	1 1	26.6	4.98	0.72	. . .	. . .	1.4530	. . .

[a] Per cent change in 100° F. viscosity after heating 24 hours at 536° F. in nitrogen atmosphere.

[b] Crystalline at indicated temperature.

[c] Product of U. S. Industrial Chemicals Co., New York, N. Y. is a physical mixture of 2-ethylsuberic acid (72–80%); 2,5-diethyladipic acid (12–18%); and sebacic acid (6–10%).

[d] Thermal stability test failure due to formation of volatile materials.

Table V. Properties of Miscellaneous Esters

Compd. No.	Acid	Alcohol	Molar Ratio Acid/Alcohol	Viscosity, Cs. 100° F.	Viscosity, Cs. 210° F.	ASTM Slope	Pour P., ° F.	Neut. No.	n_D^{25}
1	2-Ethyl-4-methylpentanoic	2,2,4-Trimethyl-1,3-pentanediol	2	3.60	1.27	0.93	-60	0.04	1.4419
2	Cyclohexanecarboxylic	1-Methylcyclohexylmethanol	1	11.4	2.67	0.80	-25	0.05	1.4752
3	Nonanoic	2,2-Diethyl-1,3-pentanediol	2	11.5	3.10	0.74	-80	1.0	1.4491
4	Nonanoic	1-Phenyl-1,2-dihydroxyethane	2	19.2	3.52	0.84	-20[a]	0.06	1.4813
5	Octadecanoic Cyclohexanecarboxylic	2,2,4-Trimethyl-1,3-pentanediol	1 1	22.3	4.76	0.69	60	0.05	1.4604
6	4-Cyclohexylbutyric	1,4-Butanediol	2	26.7	5.10	0.71	65	0.05	...
7	Butanoic	1,2,3,4,5,6-Hexanehexol	6	32.4	4.61	0.83	-50	0.06	1.4542
8	Butanoic	1,2,3,4,5,6-Cyclohexanehexol	6	35.1	17.8	0.77	70-80[a]	0.02	...
9	1,2-Cyclohexanedicarboxylic	2,2-Dimethyl-1-pentanol	0.5	38.6	4.34	0.92	-50	0.02	1.4590
10	Hexanoic	3,3,5,5-Tetrakis(hydroxymethyl)-4-pyranol	5	96.9	10.2	0.72	-15	0.02	1.4660
11	Chlorendic[b]	1-Butanol	1	104	7.54	0.88	10	0.01	1.5128
12	Hexanoic	Dowanol-122[c]	2	138	10.6	0.80	-5	0.05	1.5179

[a] Crystalline at indicated temperature.

[b] 1,4,5,6,7,7-Hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid.

[c] 2,2′-[Isopropylidenebis(*p*-phenyleneoxy)]diethanol.

Pentaerythritol esters generally have high boiling points, good thermal stability, and low pour points, when the compounds have an ASTM viscosity slope greater than 0.7. When structural changes were made to lower the value of this slope, the pour point increased and the esters tended to crystallize. The ester formed from pentaerythritol using an equimolar mixture of pentanoic and tetradecanoic acids (no. 26, Table I) has properties typical of this class of esters. The ASTM viscosity slope of this compound was the lowest attained in the simple or mixed pentaerythritol esters; however, the ester was a solid at room temperature.

With very few exceptions, these esters are thermally stable to temperatures of 536° F. for 24 hours, the notable exceptions being esters containing the 2-ethylbutyrate moiety.

Those esters which became crystalline during the pour point determinations also crystallized at about the same temperature when blended with materials (other esters, ethers, or hydrocarbons) having much lower pour points.

Esters prepared from a technical grade of pentaerythritol had the same general characteristics as those prepared from a pure grade of pentaerythritol. The viscosities were somewhat higher and the pour points somewhat lower, due to the presence of polypentaerythritols in the technical pentaerythritol.

Polypentaerythritol Esters. Esters prepared from di- and tripentaerythritol were expected to be extremely viscous; however, some of these, Nos. 3, 6, and 7 in Table II, had surprisingly low pour points. Perhaps this property can be attributed to small amounts of mono and tripentaerythritol reported to be present in dipentaerythritol and to the mono- and di- compounds in tripentaerythritol (*5*). Pour points of the simple esters of tripentaerythritol pass through a minimum with the octapentanoate ester. The flattest viscosity slopes, however, were found with the octahexanoate and octaheptanoate esters. Only three of these esters were tested individually in the thermal stability apparatus. Nos. 1 and 3 exhibited very good thermal stability. No explanation can be made for the greater viscosity change of No. 6.

Trimethylolpropane Esters. Table III gives the data for the trimethylolpropane esters. They had very low pour points and relatively flat ASTM viscosity slopes. Their viscosities were lower than both the analogous pentaerythritol or polypentaerythritol esters.

Dibasic Acid Esters. The physical properties of a number of dibasic acid esters are listed in Table IV. Molecular structural changes affect the properties of these esters in ways very similar to those described by Cohen and others (*4*). A few further effects of molecular structure on the physical properties can be seen from the data in Table IV. An alicyclic structure in a terminal position of the molecule greatly increases the viscosity and lowers the pour point when compared with an open-chain compound of similar molecular weight (compare No. 3, Table IV with the octyl sebacates such as Nos. 12 and 13). The effect on viscosity of an aromatic ring in a similar position is only intermediate. Chain branching in the dibasic acid molecule greatly increases the viscosity and moderately increases the ASTM viscosity slope.

As a class the dibasic acid esters are thermally stable to temperatures of at least 536° F. when in an inert atmosphere. The only compound of this class that was considered a failure (Table IV, No. 18) was an ester from a secondary alcohol. This failure was expected.

Miscellaneous Esters. Table V lists the properties of various esters synthesized and studied that do not fall directly into the above classes. Generally, these compounds possess temperature-viscosity relationships that are less desirable than those of previously mentioned ester types. Their thermal stabilities are also lower than those of the other esters.

ACKNOWLEDGMENT

The authors express gratitude to Texaco, Inc. for sponsoring this work and for permission to publish this article. They also thank Susan Pyle and C.D. Smith for their assistance in this work.

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RECEIVED for review September 2, 1960. Accepted May 28, 1962.

Preparation and Properties of Some *N*-Aryl Hydroxamic Acids

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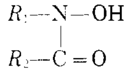
N-Phenylbenzohydroxamic acid, introduced by Shome (*13*) as reagent superior to cupferron, has found extensive analytical applications (*2, 10–12*). A recent search (*15*) for analogous reagents with more desirable analytical characteristics produced several hydroxamic acids



$$\begin{matrix} R_1\text{—N—OH} \\ | \\ R_2\text{—C}=\text{O} \end{matrix}$$

in which R_1 and R_2 are substituted by aryl, furyl, thienyl, etc. Preparation and properties of these substituted hydroxamic acids are presented here. Spectral properties in ultraviolet and visible regions, solubility in water and organic solvents, and storage qualities important for characterization and analytical application of hydroxamic acids are described. Of the 22 hydroxamic acids described here eight were previously prepared by other workers, but some of their properties are recorded for the first time.

The general methods employed in the synthesis of hydroxamic acids are outlined by Yale (*17*) in a well documented review article. We prepared these by reacting *N*-aryl hydroxylamines with acid chlorides at low temperatures in an ether solution buffered with pyridine (*15*). Both mono- and di-substituted derivatives are formed showing, thereby, that both of the hydrogen atoms of *N*-aryl hydroxylamine are attacked. Mono-derivatives are soluble in ammonia and are separated from the di-derivatives by taking advantage of this property.

EXPERIMENTAL

Materials and Apparatus. All hydroxamic acids were recrystallized from mixtures of benzene and petroleum ether at least two times and were vacuum dried. For preparing standard solutions, a small quantity of each hydroxamic acid was weighed on a Mettler microbalance and was dissolved in spectroscopic grade of 95% ethyl alcohol or glass-distilled water. Graduated apparatus of standard calibration was used for measurements.

Ultraviolet and visible absorption spectra of the hydroxamic acids were scanned on a Beckman Model DK-2 ratio recording spectrophotometer using two 10-mm. matched silica cells. The absorption measurements, made at constant wavelength for the calculation of molar absorptivity, ϵ, were performed on an Unicam SP 500 spectrophotometer. Molar absorptivity is expressed in units of liters per mole cm.

Preparation. *N*-Phenylhydroxylamine (*5*), *N*-1-naphthylhydroxylamine (*14*), and *N*-*p*-tolylhydroxylamine (*15*) were freshly prepared and crystallized from a mixture of benzene and petroleum ether before use.

All acid chlorides used in this study were prepared by the action of thionyl chloride on the corresponding acids. An excess of thionyl chloride was employed and the reaction mixture heated on the steam bath for 1 to 2 hours, after which the excess of thionyl chloride was distilled off and the acid chloride obtained by distillation under reduced pressure. The boiling points and the yields of these acid chlorides were in agreement with literature values (*16*).

Procedure for Synthesis. One molar proportion of *N*-arylhydroxylamine was dissolved in liberal excess of cold diethyl ether and the solution stirred mechanically with external

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