Table III. Observed Molar Polarizations, Molar Refractions, and Dipole Moments for Substituted Cinnamonitriles

X	$_\infty P_2$	R_D	μ	σ_μ
F	212.9	43.3	2.88	0.01
Cl	201.4	49.1	2.73	0.08
Br	210.4	52.0	2.80	0.02
I	238.6	54.5	3.00	0.04
CN	73.9	52.2	1.01	. . .

deviation of the dipole moment, σ_μ, according to the expression

$$\sigma_\mu = \left[\sum_i \left(\frac{\partial\mu}{\partial x_i}\right)^2 \sigma^2 x_i\right]^{\frac{1}{2}}$$

where μ is the dipole moment and x_i is the ith slope (or intercept).

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RECEIVED for review October 14, 1968. Accepted August 8, 1969. Work was supported by the National Science Foundation Undergraduate Research Participation Program.

Diesters from Trialkylacetic Acids and Glycols

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Diesters from trialkylacetic acids and the following glycols were prepared: straight-chain α,ω-glycols, β,β-disubstituted propanediols, lower molecular weight polyethylene glycols, and 2,2,3,3,4,4-hexafluoropentanediol. Viscosities at 212°, 100°, and −40° F., ASTM viscosity slopes, and pour points were determined and compared.

TRIALKYLACETIC ("neo") acids have recently become commercially available, and their structures have been described (*6*). Their esterification requires more rigorous conditions than those employed for conventional acids. The esters are much more resistant toward both acid and base hydrolysis than conventional esters (*1*), and the preparation and physical properties of several types of monoesters have been described (*3*). The synthesis of diesters from straight-chain α,ω-glycols, β,β-disubstituted propanediols, polyethylene glycols, and 2,2,3,3,4,4-hexafluoropentanediol is reported here. Viscosities, ASTM viscosity slopes between 212° and 100° F., and pour points were determined and compared.

EXPERIMENTAL

Starting materials were used as received. In general, the method of Coopersmith *et al.* (*1*) was used for the esterifications. Products of Type III and IV could be prepared by using toluene in place of xylene as azeotroping agent. Instead of *p*-tolenesulfonic acid, products of Type III were prepared with sulfuric acid catalyst. When this was the case, the catalyst was neutralized with an excess of solid calcium hydroxide, followed by filtration. This avoided contact with aqueous bases, which might have resulted in losses due to water solubility.

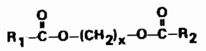
Products of Type II were especially difficult to prepare. Water formation usually stopped before the theoretical amount had azeotroped. When this occurred, the reaction mixture was cooled, additional catalyst was added, and azeotroping was resumed. If necessary, this procedure was repeated until the theoretical amount of water was obtained. Most products were obtained in analytical purity by vacuum distillation through a vacuum-jacketed Vigreux column, 5.5 inches long. Products of Type III were usually slightly yellow after one distillation and were redistilled. Most yields could be improved.

Physical properties were determined by ASTM methods: kinetic viscosity by method D 445-65, ASTM slope between 212° and 100° F. by method D 341-43, and pour point by method D 97-57. Only one cooling bath, dry ice–acetone, was used for the pour points. The approximate densities of Table IV were determined by weighing 10 ml. of the product in a graduated cylinder at room temperature.

DISCUSSION

Diesters from Straight-Chain α,ω-Glycols (I, Table I). The first six products contained identical acyl groups ($R_1 = R_2$). At constant $R_1 = R_2$, increasing the glycol chain length from $x = 4$ to $x = 8$ increased the viscosities, but gave lower ASTM slopes (runs 1 to 4). Increasing the glycol chain length from $x = 4$ to $x = 10$, while simultaneously decreasing the acid chain length, gave lower viscosities at −40° F. and lower ASTM

Table I. Diesters from Trialkylacetic Acids and Straight Chain α,ω-Glycols

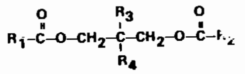


$R_1-\overset{O}{\overset{\|}{C}}-O-(CH_2)_x-O-\overset{O}{\overset{\|}{C}}-R_2$ I

Run No.	R_1[a]	R_2[a]	x	B. P., ° C./Mm.	Refractive Index, n_D^{25}	Yield, %	Kinematic Viscosity, Cs. 212° F.	100° F.	−40° F.	ASTM Slope	Pour Point, ° F.	Mol. Wt.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1	C_9H_{19}	C_9H_{19}	4	163–6/0.08	1.4484	18.1	3.09	14.66	9,833	0.81	−75	398.6	72.31	71.99	11.63	11.23
2	C_9H_{19}	C_9H_{19}	5	177–8/0.17	1.4499	11.3	3.42	16.96	12,650	0.79	−65	412.6	72.76	72.82	11.72	11.58
3	C_9H_{19}	C_9H_{19}	6	180–6/0.14	1.4507	61.5	3.71	19.25	14,251	0.78	−70	426.7	73.19	73.03	11.81	11.47
4	C_9H_{19}	C_9H_{19}	8	198–203/0.17	1.4530	63.8	4.34	23.52	16,254	0.76	−70	454.7	73.95	73.76	11.97	11.61
5	C_6H_{13}	C_6H_{13}	10	181/0.08	1.4444	78.0	3.50	11.76	1,621	0.63	−85[b]	398.6	72.31	72.28	11.63	11.48
6	C_6H_{13}	C_6H_{13}	12	196–7/0.07	1.4464	75.0	3.63	14.70	not det.	0.69	−30[c]	426.7	73.19	73.03	11.81	11.88
7	C_4H_9	$C_{12}H_{25}$	6	163–73/0.07	1.4466	26.0	3.73	19.86	15,970	0.80	−70	398.6	72.31	72.21	11.63	11.39
8	C_6H_{13}	$C_{12}H_{25}$	6	174–7/0.05	1.4504	31.3	3.98	21.09	16,661	0.77	−70	426.7	73.58	73.80	11.81	11.54
9	C_6H_{13}	C_9H_{19}	8	173–86/0.08	1.4465	23.4	3.18	13.30	3,159	0.69	−85	412.6	72.76	72.56	11.72	11.41
10	C_4H_9	$C_{12}H_{25}$	8	178–85/0.07	1.4480	27.0	4.29	23.48	15,621	0.75	−75	426.7	73.19	72.94	11.81	11.58
11	C_4H_9	C_9H_{19}	10	164–74/0.06	1.4462	16.5	3.73	17.05	4,750	0.74	−90	412.6	72.76	72.83	11.72	11.53
12	C_6H_{13}	C_9H_{19}	10	186–97/0.05	1.4493	26.3	4.03	18.00	5,763	0.70	−85	440.7	73.58	73.80	11.89	11.61
13	C_4H_9	$C_{12}H_{25}$	10	204–7/0.1	1.4510	25.2	5.24	30.99	22,214	0.73	−65	454.7	73.95	73.48	11.97	11.63
14	C_4H_9	C_6H_{13}	12	178–82/0.07	1.4420	32.7	3.50	14.17	not det.	0.71	−25	398.6	72.31	72.48	11.63	11.59
15	C_4H_9	C_9H_{19}	12	186–205/0.12	1.4488	19.5	4.39	21.72	7,095	0.71	−85	440.7	73.58	73.80	11.89	11.97

[a] Contains α,α – dialkyl groups.
[b] Started to crystallize at −85° F.
[c] Started to crystallize at −5° F.

Table II. Diesters from Trialkylacetic Acids and β,β-Disubstituted Propanediols

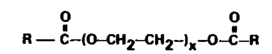


$R_1-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{R_4}{\overset{R_3}{C}}-CH_2-O-\overset{O}{\overset{\|}{C}}-R_2$ II

Run No.	R_1[a]	R_2[a]	R_3	R_4	B. P., ° C./Mm.	Refractive Index, n_D^{25}	Yield, %	Kinematic Viscosity, Cs. 212 ° F.	100 ° F.	−40 ° F.	ASTM Slope	Pour Point, ° F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mol. Wt.
16	C_9H_{19}	C_9H_{19}	CH_3	CH_3	156–8/0.13	1.4490	59	3.96	27.62	not det.	0.85	−35	72.76	72.85	11.72	11.74	412.6
17	C_6H_{13}	C_6H_{13}	C_2H_5	nC_4H_9	123–32/0.06	1.4453	25[b]	3.58	24.73	15,900	0.89	−65	71.83	71.80	11.53	11.40	384.6
18	C_6H_{13}	C_6H_{13}	CH_3	C_2H_5	133–5/0.03	1.4002	68	2.20	8.31	3,143	0.85	−80	70.13	69.94	11.18	10.90	342.5
19	C_4H_9	C_9H_{19}	C_2H_5	nC_4H_9	116–47/0.1	1.4470	50[b]	3.48	23.90	not det.	0.89	−35	72.31	72.09	11.63	11.59	398.6

[a] Contains the α,α-dialkyl structure.
[b] Required two distillations for analytical purity.

Table III. Diesters from Trialkylacetic Acids and Polyethylene Glycols



$$R-\overset{O}{\overset{\|}{C}}-(O-CH_2-CH_2-)_x-O-\overset{O}{\overset{\|}{C}}-R$$

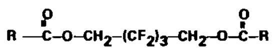
III

Run No.	R[a]	x	B. P., °C./Mm.	Refractive Index, n_D^{25}	Yield, %	Kinematic Viscosity, Cs. 212 °F.	100 °F.	−40 °F.	ASTM Slope	Pour Point, °F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mol. Wt.
20	C_4H_9	4	174–9/1.2	1.4364	37[b]	2.47	8.83	1,258	0.75	−80	59.64	59.46	9.45	9.23	362.4
21	C_6H_{13}	2	126–39/0.23	1.4370	63	1.81	5.55	620	0.78	< −85	65.42	65.10	10.37	10.17	330.4
22	C_6H_{13}	4	180–8/0.09	1.4438	35[b]	2.70	9.54	2,192	0.71	−80	63.13	62.97	10.12	10.16	418.6
23	C_9H_{19}	2	163–72/0.11	1.4489	39	3.14	16.48	> 40,000	0.82	−60	69.52	69.65	11.18	11.30	414.6
24	C_9H_{19}	3	170–7/0.05	1.4505	41	3.62	18.26	22,000	0.77	−60	68.08	68.14	10.99	10.91	458.7
25	C_9H_{19}	4	202–6/0.06	1.4520	50	4.45	19.42	> 40,000	0.67	−55	66.89	66.82	10.83	10.82	502.7
26	$C_{12}H_{25}$	2	199–201/0.05	1.4545	48	5.42	39.85	not det.	0.78	−35	72.24	72.27	11.72	11.79	498.8

[a] Contains the α,α-dialkyl structure.

[b] Losses during isolation.

Table IV. Diesters from Trialkylacetic Acids and Hexafluoropentanediol



$$R-\overset{O}{\overset{\|}{C}}-O-CH_2-(CF_2)_3-CH_2-O-\overset{O}{\overset{\|}{C}}-R$$

IV

Run No.	R[a]	B. P., °C./Mm.	Refractive Index, n_D^{25}	Density	Yield, %	Kinematic Viscosity, Cs. 212 °F.	100 °F.	−40 °F.	ASTM Slope	Pour Point, °F.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found	Mol. Wt.
27	C_6H_{13}	133–6/0.02	1.4042	1.11	87	2.00	5.02	2,650	0.88	Below −85	52.29	52.05	6.93	6.66	26.12	26.18	436.2
28	C_9H_{19}	158–65/0.08	1.4220	1.08	66	3.87	26.7	85,000	0.86	−50	57.57	57.90	8.13	8.07	21.90	21.60	520.6
29	$C_{12}H_{25}$	181–200/0.10	1.4310	1.05	33	6.68	77.8	not det.	0.89	−15	61.55	61.83	9.00	9.03	18.85	18.90	604.7

[a] Contains the α,α-dialkyl structure.

slopes (run 5 *vs.* run 1). However, when the glycol chain length became too long ($x = 12$, run 6), the ester crystallized at low temperatures. In runs 7 to 15, the acyl groups were different. The long-chain glycol with $x = 12$ again gave a relatively high pour point, but this could be overcome by increasing the difference in the acyl chain length (runs 14 and 15).

Diesters from β,β-Disubstituted Propanediols (II, Table II). Durr and coworkers (*2*) reported high thermal stabilities for similar esters. Based on pour points and viscosities at −40° F., Type II has relatively poor low-temperature fluidity. ASTM slopes are relatively high. This probably results from lack of free rotation and chain flexibility caused by bunching of the alkyl substituents near the carboxyl groups. One product, run 18, had a low pour point, but this was achieved only because its molecular weight was lower than the other products of Type II.

Diesters from Polyethylene Glycols (III, Table III). Where comparisons between compounds of similar molecular weights are available (runs 22, 23, 25, and 26), the ester from the longer-chain polyethylene glycols had lower ASTM slopes and pour points. The ether oxygens apparently contribute increased chain flexibility. MacPhail (*4*) has recently described several closely related esters.

Diesters from 2,2,3,3,4,4-Hexafluoropentanediol (IV, Table IV). Viscosities increase as the acyl groups become larger. While run 27 still had good low-temperature fluidity, runs 28 and 29 became progressively worse. ASTM slopes were relatively high. The approximate densities increased with increasing fluorine content. Snead and Gisser (*5*) have demonstrated superior thermal and oxidative stability for related esters.

Comparison of Types I to IV. If one considers diethylene glycol as a pentanediol in which the center methylene group has been replaced by an ether oxygen, a comparison between the various pentanediol esters of neodecanoic acid ($R = C_9H_{19}$) can be made. Based on pour points and viscosities at −40° F., the best low-temperature fluidity was obtained by Type I, followed by Types III, IV, and II (runs 2, 23, 28, and 16).

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RECEIVED for review March 10, 1969. Accepted November 4, 1969.

Selective Hydrogenation of the Double Bond in Unsaturated Aliphatic Isocyanates

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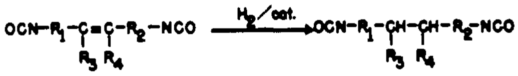
Unsaturated aliphatic isocyanates were hydrogenated selectively in high yields to their saturated counterparts over palladium or platinum catalysts at ambient temperatures and low pressures (10 to 40 p.s.i.). Continued reduction beyond the point of theoretical hydrogen uptake resulted in a gradual loss of isocyanate content with concomitant formation of the appropriately substituted formamide and symmetrical urea. Catalyst activity apparently was destroyed during this sluggish secondary reaction, because hydrogen uptake ceased at relatively low levels of conversion of the isocyanate function.

AS PART of a program directed toward utilizing the double bond in olefinic isocyanates as a selective reaction site, we decided to explore the possibility of catalytically hydrogenating various unsaturated aliphatic mono- and diisocyanates to their saturated counterparts, as illustrated for the diisocyanate case by Equation 1. This transformation was of interest to us academically as an example of a novel selective reaction of olefinic isocyanates and commercially as a potential route to certain polymer-forming diisocyanates whose olefinic precursors were more readily accessible.



$$OCN{-}R_1{-}\underset{R_3}{\underset{|}{C}}{=}\underset{R_4}{\underset{|}{C}}{-}R_2{-}NCO \xrightarrow{H_2/\text{cat.}} OCN{-}R_1{-}\underset{R_3}{\underset{|}{CH}}{-}\underset{R_4}{\underset{|}{CH}}{-}R_2{-}NCO \quad (1)$$