

Fluorinated Esters Derived from Terpenes**

by

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Abstract

Fluorinated acid chlorides in the C₃ to C₉ range were reacted with diols prepared from terpene diacids to give good yields of potentially useful esters. These esters were shown to be of greater stability and low temperature properties than those prepared from fluorinated alcohols and corresponding terpene diacids by direct esterification.

Introduction

During the investigation of terpene derived materials as temperature stable fluids, our attention turned to the preparation of various esters containing fluorine.

Fluorocarbons because of their great stability have been suggested for use as temperature stable fluids, but due to their large temperature coefficients of viscosity and high freezing points, their utility in this respect is limited.⁵

Hydrocarbon esters of pinic acid, a 2,2-dimethyl-3-(carboxy)-cyclobutaneacetic acid, have been shown to possess extremely low freezing points and have been the subject of a previous investigation.⁴

In 1956, a variety of partially fluorinated esters were prepared.¹ These compounds were characterized by high thermal stability and low freezing points. The properties of one of these compounds, a bis 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7-dodecafluoroheptyl ester of pinic acid, indicated that the fluorinated esters of these terpene acids would be attractive.

In this connection, six new diesters containing fluorine were prepared from terpene acids or diols and it is the purpose of this work to describe their

synthesis and their properties.

The terpene acids utilized in this work were pinic and *sym*-homopinic (2,2-dimethyl-1,3-bis-cyclobutaneacetic acid) prepared from *cis*-*dl*-pinonic acid. The *cis*-*dl*-pinonic acid used was prepared by potassium permanganate oxidation of α -pinene.⁸

The terpene diols were those prepared by the metal hydride reduction of the diethyl esters of pinic and *sym*-homopinic acid.

1,1-Dihydro-heptafluorobutanol was prepared by the metal hydride reduction of ethyl heptafluorobutyrate.

The diesters described were prepared either by reaction of the perfluorinated acid chloride with the appropriate terpene diol or by direct Fisher type esterification of the terpene acid with the 1,1-dihydro-heptafluorobutanol using a sulfuric acid catalyst. The identity of the esters was established by saponification to the original terpene material and by infrared spectrometry. All esters reported were shown to be free of contamination by vapor phase chromatography. Preliminary experiments indicate that the esters of the terpene diols were considerably more stable than those from the terpene acids and in general their freezing points were lower.

The analytical results for the fluorinated ester are tabulated in Table I.

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Table 1

Ester	Freezing Point (Glass) C°	% Yield	B. P. °C/mm.	n _D ²⁰	d ₄ ²⁵	Calc.		Found	
						C	H	C	H
	-55	95	82-83°/0.05	1.3775	1.2197	40.90	3.58	41.06	4.12
	-45	99	94-95°/0.02	1.3678	1.3484	37.10	2.93	37.01	2.58
	-25	63	142-143°/0.05	1.3514	1.4265	31.59	1.70	31.90	1.90
	-55	99	91-92°/0.05	1.3655	1.3303	38.31	3.21	38.57	3.37
	-45	58	101-102°/0.01	1.3750	1.3186	38.31	3.21	38.66	3.42
	-40	75	103-104°/0.05	1.3785	1.3197	37.10	2.93	37.24	2.86

Experimental

2, 2-Dimethyl-3-(carboxy)-cyclobutaneacetic Acid (Pinic Acid). Crude pinic acid was prepared by hypochlorite oxidation of *dl-cis*-pinonic acid (m. p. 100-101°). Esterification of this crude product according to the procedure of Wielicki, *et al.*⁹ and distillation yielded diethyl pinate b. p. 107-108°/1mm. Yield 65%. Analysis by infrared spectrometry and vapor phase chromatography showed this to be pure diethyl pinate.

1-Hydroxymethyl-2, 2-dimethyl-3-(1-hydroxyethyl)-cyclobutane. Diethyl pinate, 157g. (0.69 moles), was dissolved in an equal volume of anhydrous ether. The resulting solution was added dropwise to a well-stirred cold mixture of 50g. of lithium aluminum hydride in one liter of anhydrous ether. The addition was so regulated that a gentle reflux was maintained during addition (two hours). The excess hydride was decomposed with careful addition of water, then dilute sulfuric acid and the diol was extracted from the aqueous layer with three 100 cc. portions of ether. The combined ether extracts were washed with sodium bicarbonate, water, and dried over anhydrous sodium sulfate. After removal of the solvent at reduced pressure, the residual oil was distilled to

yield 91.6g. (84%) of pure colorless diol⁵ b. p. 105-107°/0.05mm²⁰ 1.4731.

2, 2-Dimethyl-bis-1, 3-cyclobutaneacetic Acid (Sym-homopinic Acid).⁷ *Sym*-homopinic acid was prepared by the Willgerodt reaction on *cis-dl*-pinonic acid (m. p. 100-101°) according to the procedure of Stinson and Lawrence.⁷ Isolation of the crude diacid was difficult and purification of this product by recrystallization was tedious due to formation of oils. Esterification of the crude acid with ethanol in toluene using a sulfuric acid catalyst and distillation of the crude diester yielded 90% of pure diethyl *sym*-homopinate, b. p. 120°, 1.6mm. n_D²⁰ 1.4486 (Lit. 119-120°/1.6mm., n_D²⁰ 1.4479).⁷ Saponification of this diester with 25% sodium hydroxide yielded crystalline *sym*-homopinic acid, m. p. 118-119.5°. This material was utilized in the preparation of fluorinated diesters.

2, 2-Dimethyl-bis-1, 3-(1-hydroxyethyl)-cyclobutane. Diethyl *sym*-homopinate, 95g. (0.37 mole), was reduced with 29g. of lithium aluminum hydride in a similar manner as diethyl pinate above. Distillation of the residual oil left after solvent removal at reduced pressure yielded 57g. (90%) of the diol, b. p. 126-127°/0.3mm²⁰ 1.4741.

General Procedure for Preparation of Fluorinated Acid Chlorides.^{2,3} Phosphorous pentachloride, 42g. (0.2 mole), was placed in a three-neck flask fitted with a dropping funnel, stopper, and gas delivery tube connected to a dry ice acetone trap. To this there was added 0.1 mole of the desired fluorinated acid and the rate of reaction adjusted so that the product could condense in the cold trap. After addition, the flask was warmed to insure reaction completion and this acid chloride was used in the preparation of the esters. Table 2 below lists the acid chlorides prepared.

Table 2

Acid Chloride	B. p. °C./mm.	Yield
$C_2F_5C \begin{array}{l} \diagup O \\ \diagdown Cl \end{array}$	9.0	90%
$C_3F_7C \begin{array}{l} \diagup O \\ \diagdown Cl \end{array}$	38-39°	94%
$C_7F_{15}C \begin{array}{l} \diagup O \\ \diagdown Cl \end{array}$	129°-130°/744mm.	76%

Reaction of Heptafluoro Butyl Chloride with 2, 2-Dimethyl-1, 3- (1-hydroxyethyl) -cyclobutane.

(General procedure for preparation of fluorinated esters of terpene diols). 2, 2-Dimethyl-1-hydroxyethyl-cyclobutane, 10g. (0.057 moles), 50 mls. of pyridine and 200 mls. of benzene were placed in a 600ml. beaker. To this, with stirring, there was slowly added 30g. (0.13 mole) of heptafluorobutyl chloride at such a rate as to prevent boiling. A precipitate of pyridine hydrochloride formed immediately and this mixture was stirred for twenty minutes. Removal of the salt by filtration and distillation of benzene at reduced pressure yielded 32g., 99%, of diester. Distillation of this oil yielded the pure diester, b. p. 90-91°/.05mm. Analytical data and physical properties are tabulated in Table 1.

Preparation of bis-1, 1-Dihydroheptafluorobutyl Ester of Sym-homopinic Acid. (Direct esterification procedure). The bis-1, 1-dihydroheptafluorobutyl ester of sym-homopinic acid and of pinic acid was prepared by refluxing 0.05 mole of the acid with an excess of 1, 1-dihydroheptafluorobutanol in 200 cc. of toluene using 1 ml. of sulfuric acid as catalyst. The physical properties are tabulated in Table 1.

Results and Discussion

The results of this investigation have shown that fluorinated esters, derived from terpenes and containing a gem dimethyl substituent on a cyclobutane ring, have extremely good low temperature viscosities coupled with high temperature stability.

The most probable explanation for this behavior is the presence of the cyclobutane ring containing a gem dimethyl group. This prevents the close alignment of molecules and in this manner lowers freezing points of these type compounds. Along with this effect, the presence of fluorine in the ester portion of these molecules decreases intermolecular hydrogen bonding such that esters of molecular weights approaching 1000 can be prepared with fluidity comparable to water.

Those esters prepared from terpene diols and fluorinated acid chlorides appeared to have slightly better low temperature properties and significantly greater stability. This can be attributed to the close proximity of fluorine to the ester carbonyl group. This tends to deactivate this carbonyl thus increasing the stability of the ester linkage and decreasing its ability to undergo reactions.

The low temperature fluidity and thermal stability of these materials suggest a variety of commercial uses as severe condition lubricants.

Literature

- 1) Faurote, P.D., *et. al.*, *Ind. Eng. Chem.*, **48**, 445(1956).
- 2) Hauptschein, M., *et. al.*, *J. Am. Chem. Soc.*, **74**, 4005(1952).
- 3) Hauptschein, M.; O'Brien, J.F.; Stokes, C.F., and Filler, R.; *Ibid.*, **75**, 87(1953).
- 4) Murphy, C.M.; O'Rear, J.G.; Zisman, W.A.; *NRL Report*, 3995(1952); *Ind. Eng. Chem.*, **45**, 119(1953).
- 5) Murphy, C.M.; Romans, F.B.; Zisman, W.A.; *Trans. Am. Soc. Mech. Engrs.*, **71**, 561(1949).
- 6) Simonsen, J.L., "The Terpenes", Vol. II, p. 153.
- 7) Stinson, J.S. and Lawrence, R.V., *J. Org. Chem.*, **19**, 1047(1954).
- 8) Summers, H.B., *et. al.*, *Ind. Eng. Chem.*, **51**, 549(1959); Samples obtained from the Naval Stores Laboratory, Olustee, Florida.
- 9) Wielicki, E.H., *et. al.*, *J. Polymer Sci.*, XXXVIII, 307(1959).