[Contribution from Research and Development Department, Socony Mobil Laboratories]

Moonalkyl *cis*-Δ^4-Tetrahydrophthalates

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Methyl through octadecyl monoesters of *cis*-Δ^4-tetrahydrophthalic acid were prepared by direct esterification of the anhydride. A melting point curve is presented and a comparison made with the corresponding phthalates. Barium and calcium salts of each acid ester were also prepared.

The physical properties of the monoesters of *cis*-Δ^4-tetrahydrophthalic acid are reported for the first time. The melting point curve for this series of tetrahydrophthalates is more regular than the one for the corresponding phthalates.[2] These tetrahydrophthalate derivatives should be useful for the characterization of the normal primary alcohols.

cis-Δ^4-Tetrahydrophthalic anhydride was prepared by a Diels-Alder reaction of butadiene with maleic anhydride.[3] Direct esterification of the anhydride with equimolar amounts of alcohol at 110–116° followed by recrystallization gave the monoesters in good yield. This direct method of preparation eliminated the time consuming purification through the sodium salt.

The compositions and properties of these monoesters are given in Table I while the accompanying Figure 1 shows a melting point comparison of the monoalkyl tetrahydrophthalates and the corresponding monoalkyl phthalates.

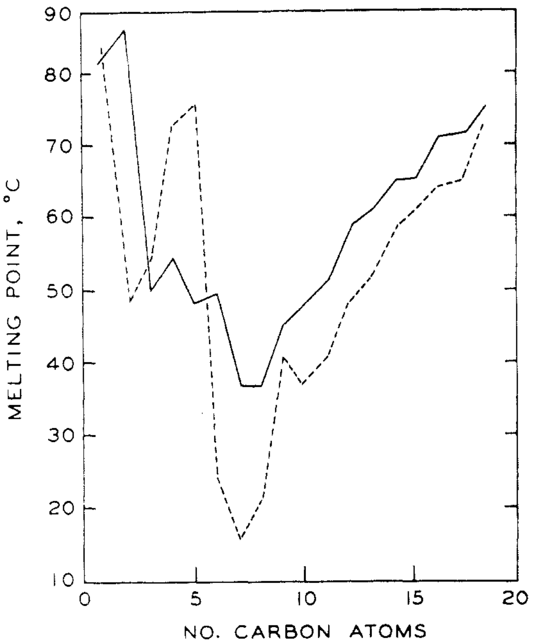

Fig. 1.—Melting Point Comparison of Monoalkyl Tetrahydrophthalates (————) and Monoalkyl Phthalates (– – – –).

All of the monoalkyl tetrahydrophthalates are white crystalline solids, soluble in organic solvents. Melting points in conjunction with acid numbers serve to identify the individual alcohols. It will be noted that the melting point curve is more regular for the tetrahydrophthalates than for the phthalates. From the heptyl through octadecyl esters the tetrahydrophthalates show gradually increasing alternation, both the odd and even members forming smooth curves.

A number of metal salts of monoalkyl tetrahydrophthalic acid have been prepared for medical research.[4] Barium and calcium salts of the entire series were prepared as potential rust inhibitors for certain hydrocarbon systems. All of the calcium salts are high melting white powders. The heptadecyl and octadecyl barium salts are white waxes while the lower molecular weight members are amber colored gums. The actual metal contents of all these salts check closely the calculated values as indicated by the examples in the experimental section.

EXPERIMENTAL

Materials. *cis*-Δ^4-Tetrahydrophthalic anhydride, m.p. 102–103°, was prepared by the method of Diels and Alder[3] and was used after one recrystallization from petroleum ether. The alcohols, methyl to heptyl, were Eastman Kodak white label and were used directly without further purification. The higher-membered alcohols were those prepared by Meyer and Reid.[5]

Preparation of mono-n-alkyl cis-Δ^4-tetrahydrophthalates. The most satisfactory method of preparing the half esters is illustrated by the following example. 1-Heptanol, 5.8 g. (0.05 mole) and *cis*-Δ^4-tetrahydrophthalic anhydride, 7.6 g. (0.05 mole) were weighed into a 50-ml. flask fitted with a stirrer, thermometer, and condenser. The reactants were heated to 90° where complete solution occurred with exothermic reaction. The temperature rose to 116°. This temperature was maintained for 10 minutes after which the product was chilled in an ice-bath. The resulting crystals were recrystallized to constant melting point from acetone. All melting points are corrected.

Preparation of calcium salts. Mono-*n*-tridecyl tetrahydrophthalate, 5 g. (0.014 mole) was dissolved in 100 ml. of a 50% by volume of an acetone-distilled water mixture and

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[2] Goggans and Copenhaver, *J. Am. Chem. Soc.*, **61**, 2909 (1939).

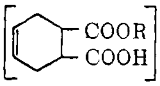
[3] Diels and Alder, *Ber.*, **62**, 2087 (1929); *Ann.*, **460**, 113 (1928).

[4] Rice, Rubin, Scholler, and Reid, *J. Org. Chem.*, **16**, 501 (1951).

[5] Meyer and Reid, *J. Am. Chem. Soc.*, **55**, 1574 (1933).

TABLE 1

MONOESTERS OF *cis*-Δ^4-TETRAHYDROPHTHALIC ACID



R	M.P., °C.	Carbon		Hydrogen		Acid Number	
		Calc'd	Found	Calc'd	Found	Calc'd	Found
Methyl	81.2–83.1	58.67	58.49	6.57	6.80	304.6	306.8
Ethyl	86.0–86.9	60.59	60.51	7.12	7.29	283.0	283.0
n-Propyl	48.2–50.5	62.25	62.16	7.60	7.65	264.4	266.9
n-Butyl	52.2–54.2	63.70	63.54	8.02	8.11	248.0	247.7
n-Amyl	47.1–49.0	64.98	64.80	8.39	8.51	233.6	230.9
n-Hexyl	48.5–49.5	66.13	66.35	8.72	8.78	220.6	220.0
n-Heptyl	36.0–37.9	67.13	67.35	9.02	9.08	209.1	210.3
n-Octyl	36.5–37.1	68.05	67.77	9.28	9.35	198.7	197.6
n-Nonyl	42.9–44.5	68.88	68.61	9.52	9.77	189.3	191.8
n-Decyl	51.2–52.1	69.64	69.40	9.74	9.76	180.7	182.0
n-Undecyl	50.8–52.0	70.33	70.31	9.94	10.21	172.9	174.4
n-Dodecyl	58.0–59.0	70.97	70.85	10.13	10.18	165.7	167.2
n-Tridecyl	61.0–61.8	71.55	71.39	10.29	10.56	159.2	159.7
n-Tetradecyl	65.3–66.0	72.09	72.25	10.45	10.59	153.1	153.3
n-Pentadecyl	66.1–66.8	72.59	72.46	10.60	10.75	147.4	147.6
n-Hexadecyl	70.1–70.7	73.05	73.12	10.73	10.94	142.9	142.7
n-Heptadecyl	70.0–71.0	73.48	73.40	10.85	10.90	137.3	137.2
n-Octadecyl	73.5–74.9	73.88	73.93	10.97	11.24	132.8	132.6

the solution was heated to boiling. The soluble ammonium salt was formed by the addition of 1.5 ml. of aqueous ammonia. To this hot stirred solution there was added 25 ml. of a hot solution of 2.0 g. $CaCl_2$ in distilled water. The resulting heavy white precipitate was suction-filtered, washed thoroughly with distilled water, and dried in a vacuum pistol.

Anal. Calc'd for $C_{42}H_{70}CaO_8$: Ca, 5.39. Found: Ca, 5.53.

Barium salts. The lower members of the series of barium half esters (methyl to butyl) were prepared in the following manner. The monomethyl ester, 5 g., (0.027 mole) was dissolved in 100 ml. of a 50% by volume acetone-distilled water mixture and placed in a 250-ml. flask fitted with a stirrer and a dropping funnel. One drop of phenolphthalein solution was added and the solution was "titrated" with a solution of 6.2 g. of $Ba(OH)_2 \cdot 8H_2O$ in 150 ml. of water. The solution was evaporated to dryness under a vacuum leaving the clear, glassy barium salt.

Anal. Calc'd for $C_{18}H_{22}BaO_8$: Ba, 27.3. Found: Ba, 27.4.

Barium salts of the higher members of the series were prepared by neutralization of the half ester with NaOH and converting the soluble sodium salt to the barium salt with $BaCl_2$. Thus, 20 g. (0.055 mole) of the mono-*n*-tetradecyl ester was dissolved in 50 ml. of 50% by volume of acetone-water. This solution was neutralized with dilute NaOH. The addition of 7 g. $BaCl_2 \cdot 2H_2O$ caused separation of the barium salt as a heavy oil which was taken up in petroleum ether, washed several times with water, and evaporated to dryness. Yield of glassy barium salt was 16 g.

Anal. Calc'd for $C_{44}H_{74}BaO_8$: Ba, 15.8. Found: Ba, 16.0.

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