[Contribution from the General Electric Company, Research Laboratory]

Methoxyphthalic Acid Esters

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The di-*n*-octyl, bis(2-ethylhexyl), and dilauryl esters of 4-methoxyisophthalic acid and the mono- and di-allyl esters of methoxyterephthalic acid have been prepared and characterized. The solubilities of isophthalic, 4-methoxyisophthalic, terephthalic, and methoxyterephthalic acids in water and ethylene glycol have been determined.

The only prevously reported esters of the methoxyphthalic acids are diethyl 4-methoxyisophthalate[2] and the dimethyl esters[2,3] of 3-methoxyphthalic, 4- and 5-methoxyisophthalic, and methoxyterephthalic acids. A number of the higher esters of the methoxy derivatives of the phthalic acids have now been prepared and characterized. The ethyl esters of these acids were also prepared and their rates of saponification and acid-catalyzed hydrolysis were determined.[4]

In direct esterification reactions of the methoxyphthalic acids and the corresponding unsubstituted phthalic acids, it was observed that the former acids entered into reaction much more readily than did the latter. This effect was most striking in the case of methoxyterephthalic and terephthalic acids. Either the methoxyl group was enhancing the reactivity of the carboxyl or it was increasing the solubility of the acid in the reaction mixture. In order to better understand this effect, the water and ethylene glycol solubilities of methoxyterephthalic and 4-methoxyisophthalic acids were determined, Table I. These results clearly show that the presence of the methoxyl group does impart greater solubility, especially in the case of the terephthalic acid. These data indicate that the primary effect is one of solubility.

TABLE I

SOLUBILITY OF DIBASIC ACIDS

Acid	Procedure	Temp., °C.	Solubility (g. per 100 g. of sat'd soln.) Ethylene Glycol	Water
Terephthalic	A	100	0.2	
	B	27	0.03	
	B	28		0.002[a]
Methoxyterephthalic	A	100	3.0	0.3
	B	27	0.8	
	B	28		0.2
Isophthalic	B	27	0.7	
	B	28		0.02
4-Methoxyisophthalic	B	27	0.9	
	B	28		0.04

A. Solvent was added to solid acid until solution was complete.

B. A saturated solution with excess acid was filtered and the filtrate was titrated with standard base.

[a] Literature value is 0.0015% in cold water.[5]

The increased ease of esterification of the methoxyterephthalic acid as compared with terephthalic acid is demonstrated by the direct esterification of these two acids with allyl alcohol. It was observed that a 90% conversion of methoxyterephthalic acid to the monoallyl and diallyl esters occurred when it was heated at reflux for 8 hours with an excess of allyl alcohol and *d*-camphorsulfonic acid catalyst. Under the same conditions of temperature and time and catalysis only 7% of the terephthalic acid underwent conversion.

EXPERIMENTAL

The esters of 4-methoxyisophthalic acid were prepared by heating a mixture of 4-methoxyisophthalic acid, the desired alcohol, xylene, and concentrated sulfuric acid catalyst at a gentle reflux to remove the water of reaction by azeotropic distillation. After complete reaction the sulfuric acid was removed by reaction with excess calcium carbonate and a subsequent filtration. Distillation of the sulfuric acid-free ester solution gave the purified ester. The esters and their properties are tabulated in Table II.

Reaction of allyl alcohol with methoxyterephthalic acid. A mixture of 1.96 g. of methoxyterephthalic acid, 50 ml. of allyl alcohol, and 20 mg. of *d*-camphorsulfonic acid was heated at reflux for eight hours in a Soxhlet apparatus containing 25 g. of Drierite in the thimble. The cooled reaction product was filtered to remove 0.20 g. of methoxyterephthalic acid. Allyl alcohol was removed from the filtrate by means of a stream of nitrogen and subsequently by evacuation. The semicrystalline residue, in benzene solution, was extracted with dilute aqueous bicarbonate to separate the monoallyl from the diallyl ester.

Addition of HCl to the aqueous extract precipitated 0.60 g. of crude monoester. Two crystallizations from cyclohexane produced 0.18 g. of monoallyl methoxyterephthalic in the form of very fine white needles, which melted sharply, m.p. 108.6°. This compound is readily soluble in acetone or ethanol. No attempt was made to determine which carboxyl group had esterified or if indeed a eutectic mixture of the two

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[2] Fosdick and Fancher, *J. Am. Chem. Soc.*, **63**, 1278 (1941).

[3] (A) Baeyer and Tutein, *Ber.*, **22**, 2187 (1889); (B) Bradbury and Weizmann, *J. Chem. Soc.*, **105**, 2751 (1914); (C) Buehler, Powers, and Michels, *J. Am. Chem. Soc.*, **66**, 417 (1944); (D) Calandra and Svarz, *J. Am. Chem. Soc.*, **72**, 1027 (1950); (E) Onnertz, *Ber.*, **34**, 3747 (1901); (F) Tomita and Uyeo, *J. Chem. Soc., Japan*, **64**, 70 (1943); (G) Wessley, Benedikt, and Benger, *Monatsh*, **80**, 201 (1949).

[4] Burkhard and Burnett, in publication.

[5] Baeyer, *Ann.*, **251**, 284 (1889).

TABLE II

ESTERS OF 4-METHOXYISOPHTHALIC ACID

4-Methoxyisophthalate Ester	b.p., °C.	Press., (mm.)	n_D^{20}	Viscosity, Centistokes 100°F	Viscosity, Centistokes 210°F	VTC[a]	Analysis Calc'd C	Analysis Calc'd H	Analysis Calc'd Sap. Eq.	Analysis Found C	Analysis Found H	Analysis Found Sap. Eq.
Di-*n*-octyl	233	1	1.4970	46.7	6.2	0.87	71.39	9.59	210	70.7	9.5	206
Bis(2-ethylhexyl)	225	1	1.4990	82.3	7.6	0.91	71.39	9.59	210	71.5	9.9	201
Dilauryl	297–303	1.5	m.p. 39.5–41°	—	—	—	74.39	10.59	266	74.4	11.1	262

[a] VTC = viscosity temperature coefficient.[6]

isomeric monoallyl methoxyterephthalates had been obtained.

Anal. Calc'd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12; Equiv. weight, 236. Found: C, 61.5; H, 5.4; Equiv. weight, 232.

The presence of a single allyl double bond was established by the addition of bromine vapor to a thin film of monoester on a ground glass slide. The dibromide, 2,3-dibromopropyl carboxymethoxybenzoate, was a solid, m.p. 103–105°.

Anal. Calc'd for $2Br/C_{12}H_{12}Br_2O_5$: 0.404/1.000. Found: 0.426/1.000.

The monoallyl methoxyterephthalate-free benzene solution was evaporated in a stream of nitrogen leaving 1.48 g. of clear, light brown oil. A portion of this crude product, 0.28 g. was fractionated in a still consisting of two concentric test tubes, the inner one being held in place with a ground glass joint and serving as a cold finger (liquid nitrogen coolant). The outer tube contained the sample and was heated at 160° at less than 1 mm. pressure. The fraction collected amounted to 99% of the sample charged and was a water-white odorless oil, n_D^{20} 1.5327; yield 53.5%.

Anal. Calc'd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.83. Found: C, 64.7; H, 6.3.

The presence of two allyl double bonds was established by addition of bromine vapor to a thin film of the compound. The bis(2,3-dibromopropyl) methoxyterephthalate was a viscous oil.

Anal. Calc'd $4Br/C_{15}H_{16}Br_4O_5$: 0.537/1.000. Found: 0.535/1.000.

A comparison of the relative rates of esterification of terephthalic acid and methoxyterephthalic acid with allyl alcohol was made under the heterogeneous reaction conditions described above for the preparation of the allyl esters. Equivalent amounts of reactants were employed and the time and temperature of both reactions were equal. At the end of an eight-hour refluxing period 93% of the originally charged terephthalic acid was recovered unchanged while only 10% of methoxyterephthalic acid remained unaltered.

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(6) Wilcock, *Mech. Eng.*, 67, 739 (1944).