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SYNTHESIS OF SOME P-PHENYLENE DIACRYLIC ACID ESTERS, A NEW METHOD

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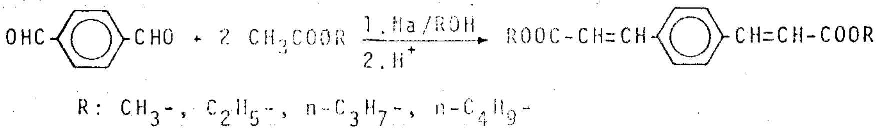
ABSTRACT

In this study methyl-, ethyl-, n-propyl- and n-butyl- esters of p-pehnylene diacrylic acid (p-PDA) were synthesized in a new method.

INTRODUCTION

Esters of p-PDA were prepared by the condensation reaction of p-phenylene diacrylic acid dichloride (Ruggli, 1941; Wiley, 1949) with alcohols (Manecke, 1966; Suzuki, 1969) or from the reaction of terephthalaldehyde with malonic acid mono esters (Metzner, 1970; Vogel, 1977).

In this work, p-phenylene diacrylates were synthesized by means of Claisen aldol condensation reaction of terephthalaldehyde with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate.



The esters of p-PDA are pale yellow, crystalline solid, have pleasant-odour and their melting points are usually low. Since p-PDA and its derivates have two double bonds, they can be easily polymerize under UV-visible light to a lineer high polymers which are contain cyclobutan rings (Hasegawa, 1968; Suzuki, 1969; Nakanishi, 1973).

All chemicals used are commercial and in pure grade. Melting point determination apparatus is Büchi Model: SPM-20. IR Spectrophotometer is Perkin-Elmer Model: 377. NMR Spectrophotometer is Varian Model: T-60.

General Procedure:

In a 100 ml round bottom flask, equipped with a reflux condenser, introduced 0.04 mole (0.92 g) of sodium and 12 ml of xylene was placed in a hot plate having magnetic stirrer. The flask was heated while stirring until sodium metal is melted and divided into small particles (sodium sand). Then was cooled down by stirring strengthly and xylene was decanted. Then 1-2 ml of alcohol with has the same alcohol group of 0.15 mole ester used, was introduced into the flask and it was cooled down immediately at 0 °C. Then 0.015 mole (2.01 g) of terephthalaldehyde (for preventing of the polymerization small of picric acid also added or oxygen gas passed through the reaction mixture) was slowly added. The mixture became dark red about one hour. At the end of the reaction, about 3 ml of glacial acetic acid in 15 ml of water was added into the reaction mixture. The content of the flask was transfered into a separatory-funnel and the organic layer was separated and dried over Na_2SO_4. After, solvents in the medium were removed by a Rotatory Evaporator. Solid material left in the flask which was mostly p-PDA- acrylate was recrystallized from ethanol.

RESULT AND DISCUSSION

In this work, p-phenylene dimethyl acrylate (p-PDA-Me), p-phenylene diethyl acrylate (p-PDA-Et), p-phenylene di-n-propyl acrylate(p-PDA-n-Pr) and p-phenylene di-n-butyl acrylate (p-PDA-n-Bu) were synthesized. The melting point, yields and spectral data (IR and NMR) are given.

p-Phenylene dimethyl acrylate: m.p. 162 °C (lit. 166, 171); yield (%) 22.2; IR (cm^{-1}) 3100 (arom. CH), 2950 (aliph. CH), 1700 (C=O), 1200 (C—O), 1000 (ethylenic C=C); NMR (δ) 4.0 ($—OCH_3$), 4.4-6.65 (-CH=CH-), 7.6—8.0 (arom. CH).

p-Phenylene diethyl acrylate: m.p. 90–91 °C (lit. 93–94); yield (%) 20.5; IR (cm^{-1}) 3070 (arom. CH), 2900 (aliph. CH), 1710 (C=O), 1180 (C—O), 1000 (ethylenic C=C); NMR (δ) 1.3–1.6 ($-CH_3$), 4.2-4.6 ($-OCH_2-$), 6.4–6.65 (-CH=CH-), 7.56—7.95 (ar. CH) p-Phenylene di -n- propyl acrylate: m.p. 70 °C (lit. 73); yield (%) 15; IR (cm^{-1}) 3100 (arom. CH), 2930 (aliph. CH), 1710 (C=O), 1180 (C—O) 1000 (ethylenic C=C); NMR (δ) 1.0—1.3 (-CH$_3$), 1.7-2.1 (-CH$_2$-), 4.3—4.5 (-OCH$_2$-), 6.4—6.75 (-CH=CH-), 7.6—8.0 (arom. CH)

p-Phenylene di-n-butyl acrylate: m.p. 71 °C (lit. 74); yield (%) 13.2; IR (cm^{-1}) 3050 (arom. CH), 2970-2850 (aliph. CH), 1710 (C=O), 1200 (C—O), 1000 (ethylenic C=C); NMR (δ) 1.0—1.2 (-CH$_3$), 1.3—2.0 (-CH=CH-), 4.3—4.6 (-OCH$_2$-), 6.4—6.75 (-CH=CH-) 7.65—8.0 (arom. CH).

The most diffucuties are encountered in this reaction the polymerization of p-PDA-esters in the media. This is partly prevented by addition of proper inhibitors, such as picric acid or oxygen gas stream. It was observed that the increasing carbon chain of the alcohol in the ester, decreasing the yields of p-PDA-esters.

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