Short Communication

Synthesis of novel esters of 4-(2'-phenyl-isopropyl)phenol used as column packings for gas liquid chromatography

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Five esters have been prepared from 4-(2'-phenyl-isopropyl)phenol which is one of the by-products in the manufacture of phenol with a view to characterize their resolving abilities when used as stationary phases in gas liquid chromatography. The spectral data and physical characteristics of these esters have been described.

One of the by-products in the manufacture of phenol by cumene hydroperoxide route is 4-(2'-phenyl-isopropyl)phenol (PIP). A few PIP esters have been synthesized with a view to characterize their resolving abilities when used as stationary phases in gas liquid chromatography. The synthesis and chromatographic characteristics of 4-(2'-phenylisopropyl)phenyl terephthalate (PIPT) has already been reported. Chromatographic characteristics of the PIP esters have also been reported. This communication describes the preparation and physical characteristics of these esters.

Preparation of diphenylisopropylphenylmalonate (DPIPM) - This ester was prepared by the reaction of excess of PIP with maleic acid dichloride at low temperature. Maleic acid dichloride was prepared from maleic acid (5.8 g, 0.05 mol) and phosphorous pentachloride (20.85 g, 0.1 mol) by stirring at 120-25°C for 4 h. To the mixture of 21.2 g (0.1 mol) of PIP, 200 mL benzene, and 20.2 g (0.2 mol) of triethylamine taken in a 500 mL round bottom flask, was slowly added the maleic acid dichloride solution (0.05 mol, 7.65 g in 50 mL benzene) for 30 min at 30-35°C, with stirring maintaining the temperature (also with external cooling). After stirring for one hour, it was refluxed for two hours, cooled and washed with water, then concentrated and dried over sodium sulphate to yield 18.5 g DPIPM (73.4% yield).

Further purification was done by column chromatography using benzene: pet ether (50:50) as eluent. BP (observed) 220-230°C at 1 mm.

IR (neat) 1740, 1755 cm⁻¹. ¹H NMR (90 MHz, CDCl₃): δ 1.66 (12H, s, -CH₃), 6.55 (2H, s, H H)-C=C'), 7.2 (18H, m, Ar-H). MS: M⁺ 504, base 119.

Anal. Calcld. for C₃₄H₂₅O₄: C, 80.95; H, 6.34.
Found: C, 80.55; H, 6.38.

Preparation of n-butyli[(phenylisopropyl)phenyl]maleate (BPPIPM) - Monobutyl ester of maleic acid was prepared by reaction of n-butanol (1 mol) and maleic anhydride (1.02 mol) at 80-90°C giving 62.6% yield in 2 h and its acid chloride was prepared from maleic acid (5.8 g, 0.05 mol) and phosphorous pentachloride (20.85 g, 0.1 mol) by stirring at 120-25°C for 4 h. To the mixture of 21.2 g (0.1 mol) of PIP, 200 mL benzene, and 20.2 g (0.2 mol) of triethylamine taken in a 500 mL round bottom flask, was slowly added the maleic acid dichloride solution (0.05 mol, 7.65 g in 50 mL benzene) for 30 min at 30-35°C, with stirring maintaining the temperature (also with external cooling). After stirring for one hour, it was refluxed for two hours, cooled and washed with water, then concentrated and dried over sodium sulphate to yield 18.5 g DPIPM (73.4% yield).

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In order to ascertain that the synthesised ester is maleate only and not the fumarate, di(PIP) fumarate was prepared and the NMR of di(PIP) fumarate and di(PIP) maleate were compared. The NMR clearly shows that in the case of maleate, maleic acid protons show a singlet which is upfield from aromatic protons while in case of fumarate, fumaric acid protons merge with the aromatic protons to give multiplet. Preparation of di(PIP) fumarate was similar to that of the maleate ester except that fumaryl chloride was added instead of maleic acid dichloride and the solvent used was toluene. The yield was 77.58%. Further purification was done by column chromatography using pet ether: ethyl acetate (95:5) as eluent. MP (observed) 134°C.

IR (neat) 1740 cm⁻¹. ¹H NMR (90 MHz, CDCl₃): δ 1.66 (12H, s, -CH₃), 7.25 (20H, m, Ar-H). MS: M⁺ 504, base 197.

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Found: C, 80.55; H, 6.38.
prepared by interaction with PCl₅ (20.85 g, 0.1 mol). The solid acid chloride obtained was taken in 50 mL of dry benzene. In a 500 mL round bottom flask, 21.2 g (0.1 mol) of PIP, 200 mL benzene, and 20.2 g (0.2 mol) of triethylamine were taken and the acid chloride was slowly added to it under stirring at 30-35°C. Further procedure was similar to that of DPIPM. The crude product (33.5 g) was distilled under vacuum at 180-190°C at 2 mm to yield the pure product (26.35 g, 72% yield).

IR (neat): 1740, 1760 cm⁻¹ IH NMR (90 MHz, CDCl₃): δ 0.9 (3H, t, J = 7 Hz, -CH₂), 1.4 (4H, m, -CH₂), 1.66 (6H, s, C-CH₃), 4.2 (2H, t, J=6 Hz, -COOCH₂), 6.55 (2H, s, -C=C-), 7.1 (9H, m, Ar-H). MS: M⁺ 366, base 197.

Preparation of [(phenyl/isopropyl)phenylacetate (PIPA)] - The title compound was prepared by acetylation of PIP (0.1 mol, 25.61 g) with acetic anhydride (60 ml.), acetic acid (5 mL) and a drop of concentrated sulphuric acid giving 23.05 g of the product (90% yield). (b.p. 120°C at 0.05 mm, b.p. 170-173° at 3 mm)
IR (neat): 1750 cm⁻¹ IH NMR (60 MHz, CCl₄): δ 1.6 (6H, s, cumyl CH₃), 2.2 (3H, s, O-C-CH₃), 7.0-7.5 (9H, m, Ar-H). MS: M⁺ 258, base 197.
Anal. Calcd. for C₁₇H₁₁O₂: C, 80.31; H, 7.08. Found: C, 80.28; H, 7.17.

Preparation of [(4,4’-isopropylidenedibiphenyldiacetate (IPBPDA)] - The title compound was prepared from 4,4’-isopropylidene bisphenol (Biphenol A, 22.8 g, 0.1 mol), acetic anhydride (60 mL) and acetic acid (5 mL) in presence of catalytic amount of concentrated sulphuric acid in 86% yield by reported method⁵. (m.p. 76°C, m.p. 79.5-81.5°C and 80-82°C (refs. 4,5)).
IR (nujol): 1750 cm⁻¹ IH NMR (60 MHz, CCl₄): δ 1.6 (6H, s, cumyl CH₃), 2.2 (6H, s, O-C-CH₃), 6.9-7.3 (8H, d of quartet, Ar-H). MS: M⁺ 312.

Conclusions - Maleate, fumarate, acetate, diacetate and phosphate esters of (phenyl isopropyl)phenol have been prepared and analyzed by elemental microanalysis IR, NMR and mass spectrometry. The yields are in the range of 70-80% in the case of maleate, fumarate and phosphate and 85-90% in the case of acetate and diacetate esters. Observed and reported melting and boiling points of the respective esters are matching.

References