SYNTHESIS OF ACETYLENE DERIVATIVES OF DIPHENYLOLPROPANE ETHERS

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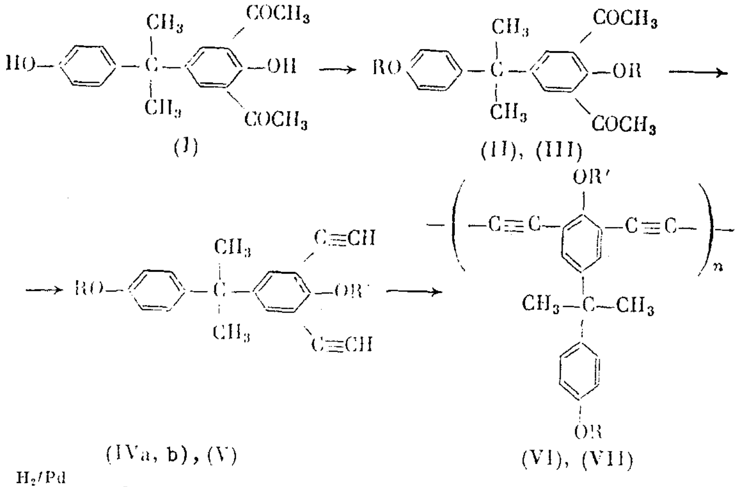
Syntheses are reported for monomers and oligomers of dipropyl and di(propen-1-yl) (cis,cis and cis,trans isomers) ethers of 2-(4′-hydroxy-3′,5′-diethynylphenyl)-2-(4″-hydroxyphenyl)propane.

Oligomers obtained by the oxidative condensation of diethynyl derivatives of ethers of 2,2-bis(4′-hydroxyphenyl)propane (diphenylolpropane, DPP) form heat-resistant films with good adhesion to metal and glass with high electrical resistance [1,2]. The feasibility of forming high-quality films depends significantly on the solubility of the oligomers in organic solvents. The solubility of such oligomers is a function of the structure of the alkoxy groups and the arrangement of the ethynyl substituents in the aromatic rings [2-4]. An asymmetrical arrangement of the substituents in the DPP molecule should presumably impart good solubility to the resultant oligomers.

In the present work, we studied the synthesis of ethynyl derivatives of several DPP ethers starting from diketone (I) [5].



$(II) \xrightarrow{H_2/Pd} (III)$

$R = CH_2CH{=}CH_2$ (II), C_3H_7 (III); $R = R' = CH{=}CHCH_3$-cis (IVa); $R =$ = cis-$CH{=}CHCH_3$, R' = trans-$CH{=}CHCH_3$ (IVb); $R = R' = C_3H_7$ (V).

The direct alkylation of (I) by allyl bromide or propyl iodide in the presence of base gave ethers (II) and (III) in 92 and 71% yields, respectively. Attempts to carry out the exhaustive hydrogenation of (II) on Raney nickel were unsuccessful and led to the products of hydrogenolysis with dealkylation of both ether groups. This side-reaction is virtually eliminated upon the hydrogenation of (II) on $Pd/CaCO_3$ by the theoretical amount of hydrogen. The yield of ether (III) was 83%. Regioselective hydrogenolysis of (III) occurs upon further hydrogenolysis under the same conditions. The ether group in the acylated benzene ring undergoes dealkylation as indicated by thin-layer chromatography and IR and PMR spectroscopy. Indeed, the PMR spectrum of the hydrogenolysis product has a signal for only one CH_2O group 3.82 ppm (triplet). The IR spectrum of this compound has a second carbonyl stretching band, indicating formation of intramolecular hydrogen bonding [4]. This finding suggests location of the hydroxyl group in the same ring as the acetyl substituents.

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Ketoethers (II) and (III) were converted to bisacetylenes (IV) and (V) in 28 and 46% yield by the action of PCl_5 in $POCl_3$ at 100°C with subsequent dehydrohalogenation of the chloride mixture by $NaNH_2$ in liquid ammonia. The final step in the preparation of (IV) features base-catalyzed isomerization of the allyl group with displacement of the double bond to the α,β-position and formation of a 2:1 isomer mixture.

The PMR spectra permit unequivocal selection of the cis,cis (IVa) and cis,trans isomers (IVb) of the four possible geometrical isomers. Thus, for example, isomer (IVa) displays a multiplet at 6.22-6.28 ppm (J 6.7 Hz) in the region for the α-ethylenic protons. This indicates that the ethylenic protons of both propenoxyl groups are in cis arrangement to each other and, thus, (IVa) is the cis,cis isomer. Groups of signals are observed for (IVb) in the same region at 6.22-6.28 (J 6.7 Hz) and 6.38 ppm (br.d, J 12.6 Hz). This finding indicates that one of the propenoxy group has cis configuration, while the other has trans configuration. Comparison of the spectra of (IVa) and (IVb) and of the dipropen-1-yl ether of DPP, specially prepared by the isomerization of the diallyl ether of DPP in ammonia in the presence of $NaNH_2$ and found to be the cis,cis isomer (J = 6.7 Hz), shows that the chemical shifts, signal multiplicity, and coupling constants of the analogous protons are identical for the ether groups in dipropen-1-yl ether of DPP, one of the groups in (IVa), and group with cis configuration in (IVb). This result suggests that the trans configuration in ether (IVb) has a propenoxy group in the ethynylated aromatic ring.

The oxidative polycondensation of (V) and (IV) was carried out in pyridine in the presence of CuCl with O_2 as the oxidizing agent [2]. Products (VI) and (VII) are light grayish powders with very high solubility in chloroform, cyclohexanone, and ethyl acetate and moderate solubility in CCl_4, benzene, and toluene. Molecular weight determinations showed that the polymeric chain in (VI) and (VII) consists of about 10 monomer units.

EXPERIMENTAL

The PMR spectra were carried out on Tesla BS-487C and Varian XL-200 spectrometers. The IR spectra were carried out on a UR-20 spectrometer.

2-(4′-Allyloxy-3,5-diacetylphenyl)-2-(4″-allyloxyphenyl)propane (II). A mixture of 34 g allyl bromide and 26.8 g K_2CO_3 in 100 ml acetone was stirred at reflux for 6 h, diluted with 50 ml ether, and filtered. Chromatography on silica gel with benzene as the eluent gave 23 g (92%) (II) as a viscous, light yellow liquid. Found: C, 76.54; H, 7.22%. Calculated for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19%. PMR spectrum in CCl_4 (δ, ppm): 1.66 (6H, $C(CH_3)_2$), 2.50 (6H, $COCH_3$), 4.30 d and 4.38 d (4H, OCH_2), 5.05-5.50 m (4H, $=CH_2$), 5.75-6.30 m (2H, $-CH=$), 6.70 d and 7.05 d (4H, arom), 7.48 (2H, arom). IR spectrum in CCl_4 (ν, cm^{-1}): 1700 (C=O).

2-(3′,5′-Diacetyl-4′-propoxyphenyl)-2-(4″-propoxyphenyl)propane (III). a. A sample of 0.7 g (II) and 0.1 g $Pd/CaCO_3$ in 5 ml methanol was agitated in a hydrogen atmosphere for 2 h at 20°C. The catalyst was filtered off. Methanol was distilled off in vacuum and the residue was dissolved in ether. The solution was washed with 5% aq. KOH and water to give 0.6 g (83%) (III), mp 53-54°C (ethanol). Found: C, 75.50; H, 8.28%. Calculated for $C_{25}H_{32}O_4$: C, 75.72; H, 8.13%. PMR spectrum in CCl_4 (δ, ppm): 0.80-1.90 m (10H, CH_2-CH_3), 1.59 (6H, $C(CH_3)_2$), 2.48 (6H, $COCH_3$), 3.75 t and 3.83 t (4H, OCH_2), 6.65 d and 6.97 d (4H, arom), 7.42 (2H, arom). IR spectrum in CCl_4 (ν, cm^{-1}): 1.705 (C=O).

b. A mixture of 8.6 g (I), 3.7 g powdered KOH, and 52.5 g iodopropane in 80 ml propanol was stirred for 24 h at 60°C, poured into water, and extracted with ether. The extract was washed with 10% aq. NaOH and water to give 7.8 g (71%) (III).

2-(4′-Propoxy-3′,5′-diethynylphenyl)-2-(4″-propoxyphenyl)propane(V). A mixture of 10.0 g (III) and 14.8 g PCl_5 in 30 ml $POCl_3$ was heated for 5 h at 100°C and carefully poured into a mixture of ice and ether. The aqueous layer was extracted with ether. The combined ethereal solution was washed with aqueous $NaHCO_3$ and water, dried over $CaCl_2$, and concentrated to a volume of about 150 ml. The solution of chlorides obtained was slowly added to $NaNH_2$ prepared from 12 g sodium in 800 ml liquid ammonia and stirred for 2.5 h. Then, 27 g NH_4Cl was added. The mixture was diluted with ether and ammonia was removed. Chromatography on alumina with benzene as the eluent gave 4.2 g (46%) (V) as a viscous, yellowish liquid. Found: C, 83.25; H, 7.78%. $C_{25}H_{28}O_2$: C, 83.29; H, 7.83%. PMR spectrum in CCl_4 (δ, ppm): 0.80-1.90 m (10H, CH_2CH_3), 1.52 (6H, $C(CH_3)_2$), 2.97 (2H, $\equiv CH$), 3.78 t and 4.08 t (4H, OCH_2), 6.70 d and 6.95 d (4H, arom) 7.20 (2H, arom). IR spectrum in CCl_4 (ν, cm^{-1}): 2115 ($C\equiv C$), 3325 ($\equiv CH$).

2-(4′-Propenyloxy-3′,5′-diethynylphenyl)-2-(4″-propenoxyphenyl)propane(IV) was obtained by analogy to (V) in 28% yield. The (IVa)/(IVb) ratio was 2:1. The mixture of (IVa) and (IVb) was obtained by analogy and separated by preparative thin-layer chromatography on alumina with 2:1 hexane–benzene as the eluent. (IVa): mp 73-74°C (hexane). Found: C, 84.21; H, 6.88%. Calculated for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%. PMR spectrum in $CDCl_3$ (δ, ppm): 1.57 (6H, $C(CH_3)_2$), 1.64 d.d and 1.71 d.d (6H, CH_3), 3.09 (2H, $\equiv CH$), 4.59 q and 4.75 q (2H, $=C\underline{H}CH_3$), 6.22-6.28 m (2H, $OCH=$), 6.81 d and 7.03 d (4H, arom), 7.22 (2H, arom). IR spectrum in CCl_4 (ν, cm^{-1}): 1675 ($O-C=C$), 2115 ($C\equiv C$), 3325 ($\equiv CH$). (IVb): mp 62.5-63.5°C (hexane). Found: C, 84.47; H, 6.92%. Calculated for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79%. PMR spectrum in $CDCl_3$ (δ, ppm): 1.53 d.d and 1.64 d.d (6H, CH_3), 1.56 (6H, $C(CH_3)_2$), 3.08 (2H, $\equiv CH$), 4.74 q (H, $C\underline{H}CH_3$), 4.91 m (H, $=C\underline{H}CH_3$), 6.22-6.28 m (H, $OCH=$), 6.38 br.d (H, $OCH=$) 6.81 d and 7.02 d (4H, arom), 7.21 (2H, arom). IR spectrum in CCl_4 (ν, cm^{-1}): 1675 ($O-C=C$), 2115 ($C\equiv C$), 3325 ($\equiv CH$).

Oxidative Polycondensation. A mixture of 1.56 g (V) and 0.15 g CuCl in 40 ml pyridine was shaken in a long-necked hydrogenation flask in an oxygen atmosphere. After no further oxygen evolution was observed (63 ml), the reaction mixture was poured into distilled water. The precipitate was filtered off and washed with dilute aq. ammonium hydroxide, water, and ethanol to give 1.47 g (94%) (VI). Found: C, 83.86; H, 7.22%. Calculated for $(C_{25}H_{26}O_2)_n$: C, 83.76; H, 7.31%.

Analogously, (VII) was obtained in 95% yield from a mixture of (IVa) and (IVb). Found: C, 84.46; H, 6.34%. Calculated for $(C_{25}H_{22}O_2)_n$: C, 84.71; H, 6.26%.

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