Synthesis and Identification of the Three Isomers of Bis(3,3-diphenylphthalidyl) Ketone

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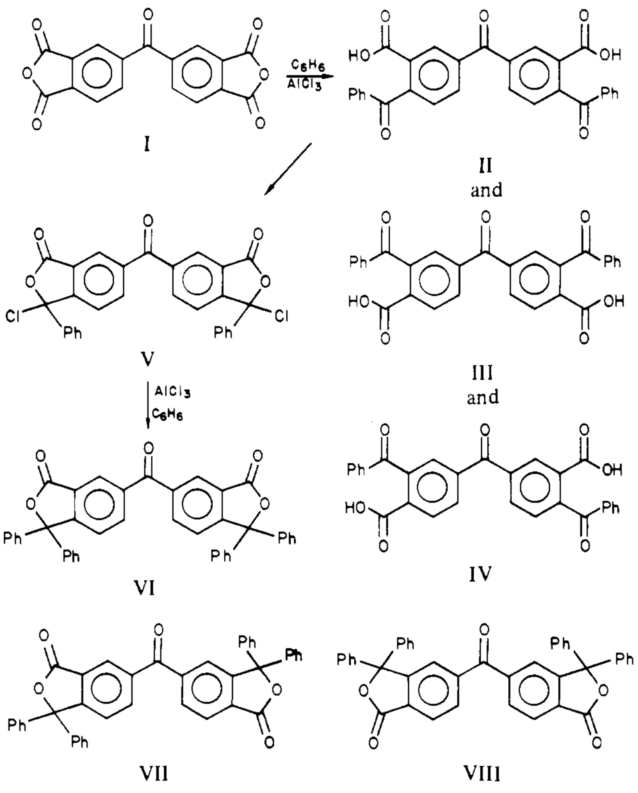
The three isomers of bis(3,3-diphenylphthalidyl) ketone have been synthesized and identified. The starting material 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) was subjected to a Friedel–Crafts reaction with benzene to produce the three isomers of benzophenonedibenzoyldicarboxylic acid. One of these was separated owing to its insolubility in chloroform. This isomer and the mixture of the other two isomers were then treated with thionyl chloride to yield the pseudoacid chlorides which were subsequently treated again with Friedel–Crafts conditions with benzene to yield the desired products. The mixture of the two isomers was separated by elution chromatography on silica gel. The overall yields for the isomers ranged from 13 to 19% for a total product yield of 45%. Properties and NMR spectral data are given.

Scheme I



Discussion

In the investigation of polyimidines as high-temperature polymers,[1,2] a synthetic method for bis(diphenylphthalidyl) monomers was developed.[3] This three-step synthesis was extended to a ketone-containing monomer as shown in the reaction sequence (Scheme I).

The NMR spectrum (100 MHz) of the bis(3,3-diphenyl-6-phthalidyl) ketone (VI) shows only four types of aromatic protons, which indicates that the molecule is symmetrical about the carbonyl. The four pendent phenyl groups appear as a singlet at 7.37 ppm. Upon expansion, the six downfield aromatic protons appear as three quartets. The NMR spectrum (100 MHz) of the 3,3-diphenyl-5-phthalidyl 3′,3′-diphenyl-6′-phthalidyl ketone (VII) shows that the four pendent phenyl groups now appear as two closely spaced singlets at 7.24 and 7.28 ppm, and the six downfield aromatic protons no longer give symmetrical adsorption. The bis(3,3-diphenyl-5-phthalidyl) ketone (VIII) gives a non-first-order NMR spectrum (100 MHz) which resembles the spectrum of benzophenone. The four pendent phenyl groups adsorb between 7.28 and 7.37 ppm, and the six downfield aromatic protons appear between 7.60 and 7.66 ppm.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and compared favorably to theoretical values. The NMR spectra were obtained on a Varian HA-100 spectrometer using deuterated chloroform and Me_4Si as an internal standard. The infrared spectra were obtained on a Beckman IR 10 spectrophotometer using KBr disks. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

All solvents and reagents were commercial grade and were used without further purification unless otherwise noted.

Benzophenonedibenzoyldicarboxylic Acids (II, III, and IV). To a mixture of 100 g (0.31 mol) of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (I) (Gulf Oil Chemical Co.) in 850 mL of benzene (dried by azeotropic distillation) was added 190 g (1.43 mol) of anhydrous aluminum chloride. The mixture was heated at reflux for 4 h. After cooling of the mixture, the aluminum chloride complex was destroyed by the addition of 500 g of ice and 100 mL of 12 M hydrochloric acid. The benzene layer was extracted three times with 500 mL of 3 N sodium hydroxide. The sodium hydroxide extract was acidified with hydrochloric acid, and the isomeric acids were filtered, washed with water, and dried in a vacuum desiccator. This yield was 87 g (57%).

This mixture of isomers was washed with chloroform to give 35 g of diacid II, mp 255–257 °C.

Bis(3,3-diphenyl-6-phthalidyl) Ketone (VI). A mixture of 48 g (0.10 mol) of benzophenone-4,4′-dibenzoyl-3,3′-dicarboxylic acid (II) and 140 mL of thionyl chloride was heated at reflux for 4 h. The excess thionyl chloride was removed by distillation, and the residue was dried under vacuum to give 51 g of the pseudoacid chloride.

Dry benzene (260 mL) was added to the pseudoacid chloride followed by 56 g (0.42 mol) of aluminum chloride. The mixture was heated at reflux until the evolution of hydrogen chloride ceased. After being cooled, the aluminum chloride complex was destroyed with 6 N hydrochloric acid. The benzene layer was extracted with 5% sodium bicarbonate and dried over sodium sulfate. The benzene was removed under vacuum, and the residue was recrystallized from acetone and water to give 32 g (13% based on tetracarboxylic dianhydride) of bis(3,3-diphenyl-6-phthalidyl) ketone (VI), mp 238–239 °C.

3,3-Diphenyl-5-phthalidyl 3′,3′-Diphenyl-6′-phthalidyl Ketone (VII) and Bis(3,3-diphenyl-5-phthalidyl) Ketone

0021-9568/79/1724-0156$01.00/0

(*VIII*). A mixture of 19 g (0.04 mol) of the unseparated isomers of benzophenone-3,3′-dibenzoyl-4,4′-dicarboxylic acid (III) and benzophenone-3,4′-dibenzoyl-4,3′-dicarboxylic acid (IV) and 55 mL of thionyl chloride was heated at reflux for 4 h. The excess thionyl chloride was removed by distillation, and the pseudoacid chlorides were dried under vacuum.

Dry benzene (150 mL) was added to the mixture followed by 21.3 g (0.16 mol) of aluminum chloride. The mixture was heated at reflux until the evolution of hydrogen chloride ceased. After being cooled, the aluminum chloride complex was destroyed by pouring it over 200 g of ice and 50 mL of 12 M hydrochloric acid. The benzene layer was extracted with 5% sodium bicarbonate and dried over sodium sulfate. The benzene was removed under vacuum to give 23.5 g of a mixture of lactone isomers VII and VIII.

The isomers were separated on a silica gel (J. T. Baker 60–200 mesh) column. The lactone isomers (1.5 g) were dissolved in a minimum amount of benzene, and the solution was placed on a 2.5 × 30 cm silica gel column slurry-packed with hexane. Elution with successive benzene in hexane solutions [hexane (150 mL), 10% (200 mL), 25% (200 mL), 50% (200 mL), and benzene (150 mL)] gave fractions which upon workup yielded TLC-pure isomers. The 3,3-diphenyl-5-phthalidyl 3′,3′-diphenyl-6′-phthalidyl ketone (VII) eluted first followed by the bis(3,3-diphenyl-5-phthalidyl) ketone (VIII). Isomer VII melted at 163–166 °C and the yield was 19% (based on tetracarboxylic dianhydride).

The bis(3,3-diphenyl-5-phthalidyl) ketone (VIII) yielded 13% (based on tetracarboxylic dianhydride) and had a melting point of 194–197 °C.

Acknowledgment

The authors wish to express their appreciation to Dr. B. A. Shoulders, University of Texas at Austin, for his assistance in obtaining NMR data.

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Received for review May 30, 1978. Accepted December 20, 1978. The work was made possible by grants from the Robert A. Welch Foundation and Southwest Texas State University to which the authors extend their gratitude. The supply of BTDA by Gulf Oil Chemicals Corp. is also appreciated.

Synthesis of Esters of 2,4-Pentadienoic Acid

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Nine alkyl 2,4-pentadienoates were synthesized from the corresponding acid chloride and the appropriate alcohol and were characterized by IR and NMR. Improved procedures were developed and are reported for the preparation of 2,4-pentadienoic acid and its acid chloride.

As part of a research program aimed at the evaluation of new flame retardant chemicals, we wished to prepare a series of halogenated derivatives of a 1,3-conjugated system. The system of choice was bromo derivatives of alkyl 2,4-pentadienoates ($BrCH_2CHBrCHBrCHBrCOOR$). We wish to report here the syntheses of the precursor alkyl 2,4-pentadienoates ($CH_2{=}CHCH{=}CHCOOR$) as well as improved yield procedures for preparation of 2,4-pentadienoic acid and its acid chloride.

A number of procedures have been reported previously (*1–8*) for the preparation of 2,4-pentadienoic acid. While the properties of the acid product obtained from these procedures agree with those of the product acid obtained in this report, the reported yields have generally been quite low. The procedure reported here typically gives yields of 60% or better.

Previous reports (*9*) of the preparation of the acid chloride of 2,4-pentadienoic acid (from the acid and $SOCl_2$) have generally led to low yields (50% or less) due to concomitant polymerization of the acid chloride product and/or polymerization of unreacted starting material. Apparently, byproduct HCl enhances polymerization of the acid and the acid chloride. Use of triethylamine as an internal trapping base led to increases in yield of only 4–5% as the triethylamine hydrochloride was extremely difficult to separate completely from the product acid chloride. As suggested by Banks et al. (*10*), we have used powdered molecular sieves as an internal trapping agent for byproduct HCl. Absorption of the HCl by the molecular sieves is more efficient than with the chemical trapping agents and polymerization of the product acid chloride was thus considerably diminished. Yields of acid chloride by the procedure reported here were typically 70–75%.

The methyl (*5*, *6*) and ethyl (*2*) esters of 2,4-pentadienoic acid and alkyl esters (*11*, *12*) of other related systems have been reported previously. The method reported here (from the acid chloride) involves simpler or more readily available materials and generally leads to improved yields. As in the case of the preparation of the acid chloride, powdered molecular sieves were used to trap byproduct HCl from the esterification reaction.

Experimental Section

All boiling and melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 457 spectrometer. NMR spectra were recorded on a Varian T-60 spectrometer using Me_4Si as an internal standard.

2,4-Pentadienoic Acid. Malonic acid (240 g, 2.31 mol) was dissolved in 250 mL of pyridine at 30–40 °C in a 1-L, three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. A 100-mL (1.50 mol) portion of acrolein was then added dropwise to the stirring solution. After the addition of this portion of acrolein, during which time the temperature rose to between 65 and 75 °C, the reaction mixture was stirred an additional 15 min. Second and third portions of acrolein (75 and 25 mL, respectively) were then added in a similar manner. When the addition of the acrolein was complete, the reaction mixture was cooled to room temperature and poured into 1500 g of ice, 500 mL of CCl_4 was added, and the reaction mixture was acidified by dropwise addition of 175 mL of concentrated H_2SO_4. The original 500 mL of CCl_4 was separated and the aqueous portion extracted with an additional 150 mL of CCl_4. Hydroquinone (1.5

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