Registry No.—**5** (R = Me), 62521-48-6; **5** (R = Et), 62521-49-7; **5** (R = Ph), 62521-50-0; **6**, 62521-51-1; hydroperoxide ion, 14691-59-9; 2,3-dimethylbenzo[*b*]thiophene 1,1-dioxide, 16958-01-3.

References and Notes

(1) B. Zwanenburg and J. ter Weil, *Tetrahedron Lett.*, 935 (1970).
(2) (a) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921); (b) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, New York, N.Y. 1965, pp 116–118.
(3) (a) C. Bunton and G. Minkoff, *J. Chem. Soc.*, 665 (1949); (b) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 2428 (1958); (c) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *ibid.* **81**, 108 (1959).
(4) Dioxane may be used, but yields are generally lower. In methanol, 3-methoxy-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide is also formed and complicates the separation procedure. Acetone (see ref 1) is satisfactory if the temperature is maintained at 40–50 °C.
(5) A. W. Weston and C. M. Suter, *J. Am. Chem. Soc.*, **61**, 389 (1939).
(6) (a) T. Durst and K.-C. Tin, *Tetrahedron Lett.*, 2369 (1972); (b) D. F. Tavares, R. E. Estep, and M. Blezard, *ibid.* 2373 (1970); (c) H. O. House, ref 2b, pp 122–123; (d) J. K. Crandall and L.-H. Chang, *J. Org. Chem.*, **32**, 435 (1967).
(7) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **72**, 1985 (1950): **1a** was stirred with 1 N NaOH for 6 days, resulting in the formation of a liquid (no reported boiling point) product.
(8) H. L. Vaughn and M. D. Robbins, *J. Org. Chem.*, **40**, 1187 (1975).
(9) F. G. Bordwell, B. B. Lampert, and W. H. McKellin, *J. Am. Chem. Soc.*, **71**, 1702 (1949).
(10) E. G. G. Werner, *Recl. Trav. Chim., Pays-Bas* **68**, 509 (1949).
(11) J. R. Catch, D. F. Elliott, D. H. Hey, and E. R. H. Jones, *J. Chem. Soc.*, 272 (1948).
(12) Ng. Ph. Buu-Hoi and P. Cagniant, *Ber.*, **B76**, 1269 (1943).
(13) F. G. Bordwell and C. E. Osborne, *J. Am. Chem. Soc.*, **81**, 1995 (1959).
(14) C. F. H. Allen and S. Converse, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 226.
(15) Reversing the order of addition of hydrogen peroxide and sodium hydroxide did not affect the outcome of the reaction.
(16) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).
(17) (a) H. Kloosterziel and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **71**, 361 (1952); (b) F. G. Bordwell and C. J. Albisetti, *J. Am. Chem. Soc.*, **70**, 1558 (1948); (c) F. Arndt, A. Kirsch, and P. Nachtwey, *Ber.*, **B59**, 1074 (1926).
(18) In another run, in which the temperature was maintained at 20–25 °C, compound **2** comprised 15% of the product mixture.

Notes

3,3,5,5- and 3,3,7,7-Tetraphenylpyromellitide and Their Tetrathio Analogues

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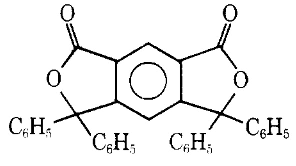
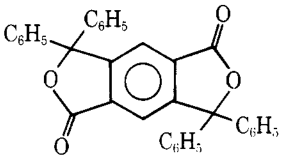
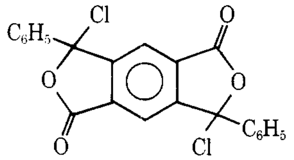
A synthesis of 3,3,7,7-tetraphenylpyromellitide (**2**) from pyromellityl chloride via a Friedel–Crafts reaction has been reported;[2] however, on the basis of the present work it appears that the reported compound was actually the 3,3,5,5-tetraphenylpyromellitide (**1**). Apparently the trans isomer was lost in the purification procedure owing to its greater reactivity. The pseudo acid chloride (**3**) of 2,5-dibenzoylterephthalic acid has also been isolated and identified[3,4] as has the pseudo-4,6-dibenzoylisophthaloyl chloride (**4**).[4] These materials were used to produce polyamides or polyanthrazolines and were not reacted further to the tetraphenylpyromellitides.



1



2



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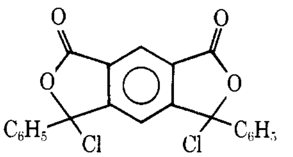
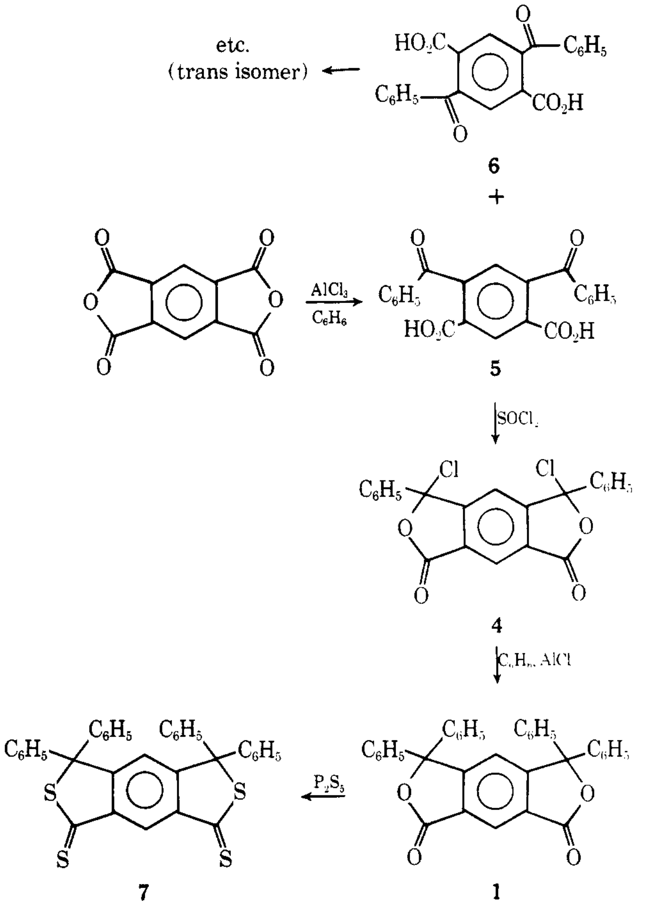


4

It is the purpose of this paper to report the novel, high-yield, unequivocal syntheses of the cis and trans isomers, **1** and **2**, of tetraphenylpyromellitide. Further the tetrathio analogue of each was prepared.

The cis oxo- and thiotetraphenylpyromellitides have been used as monomers for a new type of heterocyclic polymer, polyimidines.[7,8]

The salient features of this reaction scheme are twofold. First, the isomeric dibenzoylphthalic acids, **5** and **6**, can be separated as their potassium salts. The potassium salt of the terephthalic acid isomer crystallizes from aqueous KOH whereas the sodium salts of both isomers are soluble in NaOH solutions. Previous investigators also have used KOH solutions but apparently neutralized them soon after dissolution without waiting for a crystalline precipitate to form. In earlier work[4,5] the isomer separation was performed with more difficulty and lower yields by crystallizing the acids from acetic acid or aqueous ethanol or methanol.



The second important finding is the fact that the pseudo acid chloride (4) will undergo a Friedel–Crafts reaction to result in the cyclic phenylated pyromellitides (1). This could be predicted on the basis of work reported by Bhatt et al.[6]

All reactions occur readily to result in overall yields of the pyromellitides of 23% for the cis and 27% for the trans isomers from the dianhydride. For all compounds the cis form is more soluble but the trans isomers are more reactive.

NMR spectra serve to distinguish between the cis and trans structures, 1 and 2. The central aromatic hydrogens in the trans structure are in identical environments and therefore give rise to just one singlet at δ 8.08, whereas two singlets are observed for the nonidentical, central hydrogens in the cis structure: one at δ 7.58, the other at δ 8.29.

Experimental Section

Dibenzoyliso-(and tere-) phthalic Acids (5 and 6). The Friedel–Crafts addition of benzene to pyromellitic dianhydride was carried out as described previously[4,5] with the exception of the procedure used for purification of the products. The 71.2 g of crude mixture of dibenzoylphthalic acids from reaction of 73 g (0.333 mol) of pyromellitic dianhydride was dissolved in 2500 mL of boiling 6 M aqueous KOH, filtered hot, and cooled overnight in a refrigerator to precipitate the potassium salt of 2,5-dibenzoylterephthalic acid. The precipitate was collected by suction filtration and dissolved in water, and the solution was filtered again. The filtrate was acidified with dilute HCl to precipitate the diacid which was recrystallized from glacial acetic acid, mp 324 °C (lit.[5] 319–320 °C), yield 39.2 g (31.5% based on pyromellitic dianhydride).

The aqueous basic solution from which the above salt precipitated was then acidified with 600 mL of dilute HCl. To this, 500 mL of water was added and the solution was cooled in ice to precipitate 36.2 g of crude 4,6-dibenzoylisophthalic acid. The acid was dissolved in a minimum amount of 6 M aqueous NaOH and dilute HCl was added to lower the pH to less than 1. The precipitate was isolated by filtration, washed briefly with cold water, and dried to yield 31.2 g (25% based on pyromellitic dianhydride), mp 278–280 °C (lit.[5] 277–278 °C).

3,3,5,5-Tetraphenylpyromellitide (1). A solution of 24.0 g (0.07 mol) of 4,6-dibenzoylisophthalic acid and 120 mL of thionyl chloride was heated to reflux for 3 h to give a clear yellow solution. A vacuum line was attached to the flask, and the excess thionyl chloride was removed with the aid of an aspirator until the pseudo acid chloride was left as an off-white paste in the bottom of the flask. Radiant heat from an infrared lamp was useful in this last step. The last vestiges of thionyl chloride need not be removed. To the paste of pseudo acid chloride was added 1 L of dry benzene followed by slow addition with stirring of 70.09 g (0.52 mol) of aluminum chloride. The resulting heterogeneous mixture was refluxed for 16 h, and then the benzene layer was concentrated to about 500 mL by distillation. After cooling, the aluminum chloride complex was destroyed by addition of 500 g of ice and 200 mL of 6 M HCl. The benzene layer was separated from the resulting mixture, filtered, and dried over Na_2SO_4. After filtering again, the benzene solution was concentrated to 200 mL and 800 mL of absolute alcohol was added. Upon cooling 3,3,5,5-tetraphenylpyromellitide precipitated. The precipitate was collected, dried, and dissolved in a minimum amount of boiling benzene. To this was added an equal amount of absolute alcohol and the solution was cooled to yield white platelets: mp 280–282 °C (lit.[2] 275–276 °C); yield 14.9 g (47.0%); NMR ($CDCl_3$) δ 7.16 (20 H), 7.58 (1 H), and 8.29 (1 H). Anal. Calcd for $C_{34}H_{22}O_4$: C, 80.57; H, 4.45. Found: C, 80.02; H, 4.44.

3,3,7,7-Tetraphenylpyromellitide (2). The process described above was repeated except that 2,5-dibenzoylterephthalic acid was used. The reaction mixture workup was changed as described below.

The final reaction mixture (after $AlCl_3$ addition) was steam distilled to remove the benzene and the solid residue was isolated by filtration and dried. The filtrate was extracted twice with 100-mL portions of benzene and twice with 100-mL portions of chloroform. The extracts were evaporated on a steam bath and the residue was added to that solid removed directly from the steam distillation residue. The combined solids were subjected to Soxhlet extraction by benzene for 3 days. The benzene solution was reduced in volume to 200–300 mL and an equal amount of absolute alcohol was added to precipitate the tetraphenylpyromellitide. The solid was recrystallized from benzene or benzene–ethanol to yield 15.4 g (48.6%): mp 354–356 °C; NMR ($CDCl_3$) δ 7.31 (20 H, s), 8.08 (2 H, s).

Anal. Calcd for $C_{34}H_{22}O_4$: C, 80.57; H, 4.45. Found: C, 80.50; H, 4.64.

3,3,5,5-Tetraphenyltetrathiopyromellitide (7). A solution of 3.0 g (0.006 mol) of 3,3,5,5-tetraphenylpyromellitide and 0.80 g (0.012 mol) of phosphorus pentasulfide in 50 mL of xylene was heated at reflux for 36 h. The resulting clear red solution was filtered hot and steam distilled until a red residue precipitated in the still pot. After the residue was cooled to room temperature it was collected by vacuum filtration and dissolved in a minimum amount of hot chloroform, filtered, and cooled. The yellow precipitate, probably the dithio derivative, was removed by filtration and the filtrate was concentrated to one-half of its original volume. An equal amount of alcohol was then added and the solution was cooled to 0 °C to facilitate precipitation of the tetrathio compound. The fine, red precipitate that forms was collected by vacuum filtration and dried in a vacuum desiccator overnight to yield 3.1 g (90%) of 3,3,5,5-tetraphenyltetrathiopyromellitide, mp 338–340 °C.

Anal. Calcd for $C_{34}H_{22}S_4$: C, 73.11; H, 3.94; S, 22.94. Found: C, 73.13; H, 3.88; S, 22.89.

3,3,7,7-Tetraphenyltetrathiopyromellitide. The reaction as described above was carried out on the trans isomer except that the reaction was complete in less than 12 h. The crude product was obtained in 90% yield and was extracted with boiling $CHCl_3$. The solution was concentrated and cooled to yield beautiful, deep-maroon crystals, mp 357 ± 2 °C. (Slow heating results in polymerization and no melting point. The value reported was obtained by inserting capillaries into a preheated block.)

Anal. Calcd for $C_{34}H_{22}S_4$: C, 73.11; H, 3.94; S, 22.94. Found: C, 72.95; H, 4.05; S, 22.68.

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Registry No.—**1,** 59914-21-5; **2,** 3886-00-8; **4,** 52496-56-7; **5,** 52497-38-8; **6,** 52497-37-7; **7,** 60095-15-0; phosphorus pentasulfide, 1314-80-3; 3,3,7,7-tetraphenyltetrathiopyromellitide, 62586-46-3.

References and Notes

(1) To whom correspondence should be addressed.
(2) V. G. Drechsler and S. Heidenreich, *J. Prakt. Chem.*, **27,** 52 (1965).
(3) M. Ueda, M. Ohkura, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 719 (1974).
(4) Y. Imai, E. F. Johnson, T. Katto, M. Kurihara, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13,** 2233 (1975).
(5) W. H. Mills and M. Mills, *J. Chem. Soc.*, **101,** 2194 (1912).
(6) M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc. C*, 1772 (1971).
(7) P. E. Cassidy and A. R. Syrinek, *J. Polym. Sci., Polym. Chem. Ed.*, **14,** 1485 (1976).
(8) P. E. Cassidy and F. W. C. Lee, *J. Polym. Sci., Polym. Chem. Ed.*, **14,** 1519 (1976).

Diels–Alder Synthesis of Hindered Aromatic Amines

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Recent interest in this laboratory in highly functionalized butadienes for use as synthons for natural product synthesis has led us to a simple preparation of symmetrical and unsymmetrical, highly hindered aromatic amines. Studies with butadiene 1[1] have shown that it will undergo a variety of ad-

Scheme I