Dehydrocyclization of Aromatics: A Convenient Synthesis of Triphenylene

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The synthesis of triphenylene in good yields (up to 60%) by treatment of o-terphenyl over 0.6% platinum-on-silica gel in the gas phase (600° C.) in an atmosphere of hydrogen has been accomplished. The effect of temperature and contact time on the yield was also determined.

DURING INVESTIGATIONS of the catalytic hydrocracking of polyphenyls (*5*), it was found that 0.6% platinum-silica gel catalyzed the abstraction of ortho hydrogens in aromatic systems leading to the formation of fused ring systems. This observation led to a study of the synthesis of triphenylene from *o*-terphenyl and of other dehydrocyclization reactions (*6*).

Although a few syntheses of triphenylene from *o*-terphenyl are reported (*1*, *3*, *4*), these are characterized either by low yields, involved isolation procedures, or lengthy reaction time for small quantities of product.

Triphenylene can be prepared in good yields (up to 60%) by treatment of *o*-terphenyl over 0.6% platinum-on-silica gel at 600° C. in an atmosphere of hydrogen over comparatively short time periods. In addition, the crude product is easily purified by crystallization from benzene-alcohol. Variation of temperature and contact time (Table I) show that maximum yields are obtained at about 600° C. and eight seconds contact time. When nitrogen was used as the carrier gas, virtually no reaction occurred.

Other catalysts such as nickel-chromia-alumina, molybdena-alumina, nickel-silica-alumina, cobalt-alumina, and iron-silica-alumina were also tested for their ability to promote dehydrocyclization of *o*-terphenyl. Gas chromatograms of the crude products from these runs showed that they contained varying amounts of triphenylene but isolated yields would only have been from 10 to 25%.

EXPERIMENTAL

Materials and Equipment. Davison 0.6% platinum-silica gel (6–12 mesh) catalyst and *o*-terphenyl (Eastman Grade, or Monsanto Co.'s Santowax-O) were used. A vertical Vycor reactor tube (30 mm. × 470 mm.) was charged with approximately 120 ml. of catalyst. The lower and upper portions of the tube were filled with porcelain electrical insulators (¼ inch). A sample of *o*-terphenyl (15–20 grams) was placed in a pressure-equalized addition funnel attached to the upper portion of the reactor, and hydrogen or nitrogen was introduced into the system through a side arm of the funnel. The sample was melted by a heating tape wrapped around the funnel, and the reactor was heated by a furnace (Hoskins, type FH303A). The temperature was measured by a thermocouple inserted into a thermowell located in the center of the reactor tube. The product receiver (125 ml. Erlenmeyer flask) was adapted with inlet and outlet side arms and heated with a heating tape to prevent blockages. The system also included inlet and outlet gas flowmeters.

Triphenylene. Molten *o*-terphenyl or Santowax-O (15 grams, 0.65 mole) was added dropwise to the catalyst bed (the system was previously flushed out with nitrogen) in a stream of hydrogen (100 ml. per minute) at 600° during a period of 57 minutes. The crude orange condensate (13.8 grams) was dissolved in hot benzene and the solution was treated with charcoal and then evaporated to a yellow crystalline solid. The solid was crystallized from 480 ml. of benzene-alcohol (1:1) to yield 8.7 grams (58%) of crystalline triphenylene, m.p. 200–200.5° (lit. (*2*), m.p. 198°). An authentic sample mixed with an sample prepared as above caused no depression in the melting point. Melting points were taken on a Fischer-Johns melting point apparatus and are uncorrected. The product was also identified by ultraviolet spectroscopy. The same catalyst was used for several runs before the activity diminished.

Table I. Effect of Temperature and Contact Time on Triphenylene Yield

Temp., ° C.	Contact Time, Sec.	Quantity o-Ph$_3$ Reacted, g.	Total Run Time, Min.	%[a], Yield
450	7.9	10	21	15
560	7.8	20	80	43
600	7.9	15	57	58[b]
650	7.1	10	37	50
650	2.8	15	17	33
650	0.7	15	9	11
650[c]	4.6	15	25	1.3

[a] Yield after one recrystallization of the crude product from benzene-alcohol. [b] Repeated runs at this temperature and contact time gave yields that varied from 43 to 58%. [c] Nitrogen carrier gas used in place of hydrogen.

LITERATURE CITED

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