A NEW BISTETRACYCLONE. 2,2′-p-PHENYLENEBIS (3,4,5-TRIPHENYLCYCLOPENTADIENONE) AND ITS DIELS-ADLER PRODUCTS

JERRY HIGGINS AND JOE F. JONES
Illinois State University, Normal, Illinois

ABSTRACT.—A new bistetracyclone, 2, 2′-p-phenylenebis (3,4,5-triphenylcyclopentadienone) (3) was synthesized by the basic condensation of benzil and α,α′-bis (phenylacetyl)-p-xylene (2). Compound 3 reacted with phenylacetylene and dimethyl acetylenedicarboxylate to give the Diels-Alder products, 4 and 5, respectively.

In the course of studies aimed at producing a polytetracyclone polymer and some derived aromatic Diels-Alder polymers, it became necessary to prepare compounds 3, 4, and 5 for model compound studies.

The bistetracyclone (3) was prepared by the basic condensation of benzil with α,α′-bis (phenylacetyl)-p-xylene (2) in diethylene glycol solvent (Fig. 1). Compounds 4 and 5 were prepared by the Diels-Alder reaction of 3 with phenylacetylene and dimethyl acetylenedicarboxylate, respectively, in refluxing diglyme (Fig. 2). In the Diels-Alder reactions the products are formed by first giving the 1,4-cycloaddition products followed by the elimination of carbon monoxide to give the aromatic ring structure. These reaction sequences are well known and can be found in the literature in a detailed review by Ogliaruso and coworkers (Ogliaruso, *et al.* 1965). No attempt was made to separate and characterize the different isomers which are probably formed when phenylacetylene reacts with the bistetracyclone (3).

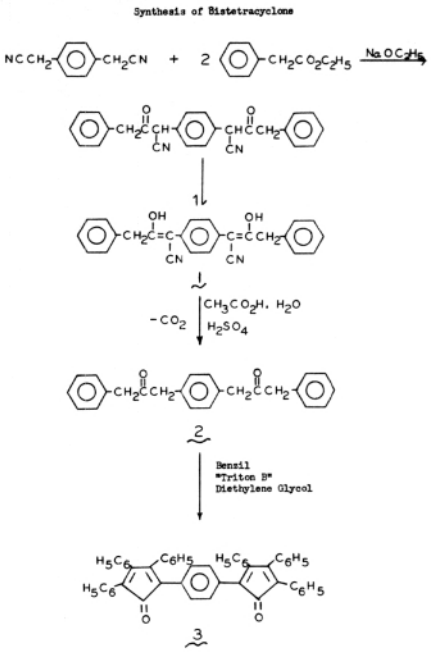

FIGURE 1.—Synthesis of Bistetracyclone.

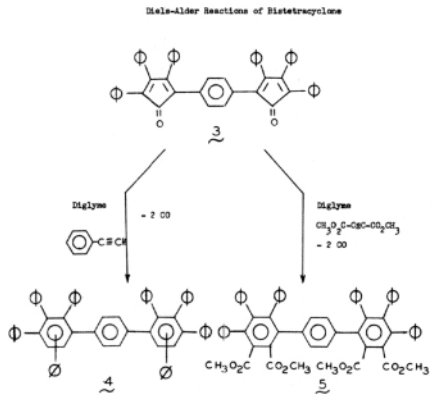

FIGURE 2.—Diels-Alder reactions of Bistetracyclone.

The basic condensation of p-phenylenediacetonitrile with ethyl phenylacetate produces the corresponding product (1) in approximately 60% yield. It is interesting to note that compound 1 exists almost completely in the enol structural form. This is evidenced by the absence of the carbonyl band and the presence of a strong O-H band in the ir spectrum.

EXPERIMENTAL

Preparation of Compound 1. - To a 1l round-bottom flask were added 25 g (0.16 mole) *p*-phenylenediacetonitrile, 164 g (1.0 mole) ethyl phenylacetate, 400 ml of

absolute ethanol, and 68 g (1.0 mole) sodium ethoxide. The solution was refluxed for 5 hr and then allowed to stand overnight. The ethanol solvent was removed with a vacuum evaporator and the residue poured into 1l of ice and stirred until all the ice melted (~1 hr). The solution was then extracted twice with 400 ml portions of ether to remove the excess ethyl phenylacetate. Acetic acid (125 ml) was then added to the aqueous solution and a thick oil separated which partially crystallized upon standing for about 0.5 hr. The crystals were removed by suction filtration and washed with methanol. The remaining oil was then dissolved in 500 ml of methanol and cooled at 0° for 48 hr, and a second crop of crystals was obtained to give a total of 37 g (59%) of product melting at 183-185°. A small portion was recrystallized from methanol for analysis (m.p. 186-187°). The remaining product was used without further purification. *Anal.* Calcd for $C_{26}H_{20}N_2O_2$: C, 79.55; H, 5.15; N, 7.13. Found: C, 79.40; H, 5.18; N, 7.00.

Preparation of Compound 2. - To 300 ml of glacial acetic acid was added 8 g (0.02 mole) of compound 1 and the solution refluxed until all of the compound dissolved. While the solution continued to reflux, 50 ml of 50% aqueous sulfuric acid was added slowly. The solution was then refluxed for 24 hr. The solution was cooled and added to 1l of cool water. The product was filtered and dried to give 6.2 g (90%) of crude product. The product was purified by recrystallization from 95% ethanol (m.p. 80-81°). *Anal.* Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.47. Found: C, 83.99; H, 6.37.

Preparation of Compound 3. - To 50 ml of triethylene glycol were added 1 g of compound 2, 2 g of benzil, and 1 ml of 30% Triton B methanol solution. The temperature of the solution was raised to 130° and kept at this temperature for 30 min. The solution was cooled and filtered to give a quantitative yield of the *bis*-tetracyclone melting at 355-359°. *Anal.* Calcd. for $C_{52}H_{34}O_2$: C, 90.41; H, 5.03. Found: C, 90.29: H, 4.94.

Preparation of Compound 4. - To 50 ml of diglyme were added 0.5 g of compound 3 and 1 g of phenylacetylene. The solution was refluxed until the solution turned from a dark purple to a clear solution (30-45 min.). The solution was then cooled and poured into 200 ml of methanol. The methanol solution was cooled and the product filtered to give a quantitative yield of white product melting at 365-368°. *Anal. Calcd.* for $C_{66}H_{16}$: C, 94.47; H, 5.53. Found: C, 93.85; H, 5.42.

Preparation of Compound 5. - The exact same procedure was used as for the preparation of compound 4. The product melted at 338-339°. *Anal Calcd.* for $C_{62}H_{62}O_{16}C_8$ 81.03; H, 5.05. Found: C, 81.11; H, 4.89.

Literature Cited

Ogliaruso, M. A., Romanelli, M. G., and Becker, E. I. 1965. Bistetracyclones. *Chem. Rev.*, 65, 261.

Manuscript received August 21, 1971.