The ultraviolet spectrum of 2-phenyltriphenylene does not exhibit as much fine structure as that of triphenylene or its alkyl derivatives.[2-4]

In the course of our study a sample of 2,6,10-trimethyltriphenylene was prepared by dehydrogenation of the product obtained by self-condensation of 4-methylcyclohexanone under conditions employed in the Mannich triphenylene synthesis.[5] Although the spectrum of this compound was reported recently,[2] no details of its preparation were given. The procedure employed by us is therefore included here.

EXPERIMENTAL

2-(1'-Cyclohexenyl)-1-p-biphenylylcyclohexanol. To a solution of 0.80 moles of *n*-butyllithium[6] was added in 5 to 10 g. portions 167 g. of 4-bromobiphenyl while the temperature was held below 0°. The mixture was then warmed to 5° and stirred for 30 min. (until all the 4-bromobiphenyl had dissolved). A solution of 133 g. of 2-(1'-cyclohexenyl)-cyclohexanone in 200 ml. of ether was added while the temperature was held just below 5° with external cooling. The mixture was allowed to warm to room temperature and stand overnight. The ethereal solution was treated with 1*N* hydrochloric acid, separated, and dried over anhydrous sodium sulfate. Ether and volatile material was removed by distillation, eventually on a steam bath at water pump pressure. The residual crude oil (170 g.) was used directly in the next step.

2-(1',2'-Epoxycyclohexyl)-1-p-biphenylylcyclohexanol. To a solution of 160 g. of the crude oil above in 400 ml. of ether cooled to −40° was slowly added 1.25 l. of the ether solution of perphthalic acid.[7] After 3 hr. at −40° the mixture was allowed to warm to +5° and was kept at that temperature for 16 hr. The resulting precipitate was separated; it contained only a small amount of desired product which remained after extraction with aqueous sodium bicarbonate. The ethereal solution was dried and the ether was evaporated. The oily residue was extracted with 250 ml. of ethanol at 5° and the residue was collected and washed with more cold ethanol. Yield: 82 g.; 35% based on 4-bromobiphenyl; m.p. 147–148°.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 81.46; H, 8.17.

2-Phenyltriphenylene. A solution of 70 g. of the epoxide in 400 ml. of acetic acid and 350 ml. of 48% hydrobromic acid was refluxed for 20 hr. The reaction mixture was poured into 3 l. of water, the product was extracted with benzene, and the benzene solution was washed with aqueous sodium bicarbonate and dried over sodium sulfate. The crude oil (5,6,7,8,9,10,11,12-octahydro-2-phenyltriphenylene) obtained after evaporation of the benzene was mixed with 15 g. of 5% palladium on charcoal and dehydrogenated at 300° for 6 hr. under nitrogen. The cooled product was extracted with 250 ml. of benzene. The benzene was evaporated and the residue slowly crystallized. Oily products were extracted with 200 ml. of petroleum ether (63–69°). Yield: 6.0 g.; m.p. 180–185°. The sample was further purified by chromatography in benzene on alumina and by recrystallization from 3:1 ethanol-benzene. M.p. 182–185° (lit.[1] 183–184°), small needles.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.82; H, 5.14. Ultraviolet maxima in 95% ethanol: 261.5 mμ (log ε, 4.91); 268.5 mμ (log ε, 4.96); 301 mμ (inflection, log ε, 4.37).

2,6,10-Trimethyltriphenylene. A mixture of 450 g. of 4-methylcyclohexanone with 1.4 l. of methanol containing 246 g. of concentrated sulfuric acid was refluxed for 12 hr. After dilution with 2.5 l. of methanol, crystals of 1,2,3,4,5,-6,7,8,9,10,11,12-dodecahydro-2,6,10-trimethyltriphenylene separated. These were collected and washed with acetone. Yield: 20 g.; 5%; m.p., 194–196° (lit.[3] 195°).

The dodecahydro compound was dehydrogenated like the 2-phenyl analog and the product was recrystallized from ethanol. Yield: 90%; m.p. 188–189° (lit.[3] 190°).

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A Fifth Route to 1,2,3-Triphenylazulene[1a]

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1,2,3-Triphenylazulene was synthesized by Assony and Kharasch,[1b] in one step, in 25% yield, by the reaction of diphenylacetylene with 2,4-dinitrobenzenesulfenylchloride, and also in very low over-all yield by a nine-step synthesis from cycloheptanone. Battiste and Breslow[2] have recently synthesized the azulene by dehydration of a diphenylcyclopropenecarboxylic acid derivative, and Büchi[3] reports its formation by irradiation of solutions of diphenylacetylene.

This note reports the synthesis of this unique hydrocarbon by a fifth route, based on the azulene synthesis which was briefly communicated by Ziegler and Hafner[4,5] and by Hafner and Kaiser.[6]

The essential steps in the synthesis, which involves reaction of 1,2,3-triphenylcyclopentadiene with *N*-methylpyridinium iodide, have been formulated by Ziegler and Hafner[4,5] and Hafner and Kaiser[6] for other cases.

(1) (a) This work was carried out as an assigned project, suggested by Mr. Earl M. Evleth, in the organic synthesis course conducted by Professor Norman Kharasch in the fall of 1958. The interest and assistance of Mr. Evleth and Dr. Kharasch are gratefully acknowledged. (b) S. J. Assony, and N. Kharasch, *J. Am. Chem. Soc.*, **80**, 5978 (1958).

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The triphenylazulene was obtained in 20% overall yield and was shown to be identical with the product of Assony and Kharasch by its melting point, mixture melting point, and infrared spectrum.

EXPERIMENTAL

1,2,3-Triphenylcyclopentadiene (III) was prepared in 55% yield from 1,2,3-triphenylcyclopentadiol, by the method of Paulson.[7]

1,2,3-Triphenylazulene. To 1,2,3-triphenylcyclopentadiene (2 g., 0.007 mol.) was added 20 ml. diphenyl ether and sodium methoxide (0.3 g., 0.007 mol.). The mixture was heated to 70° under nitrogen. Generation of the triphenylcyclopentadienyl anion was indicated by the intense red color of the reaction mixture. Pyridium methiodide (2.0 g., 0.01 mol.) was added to the solution, causing a distinct darkening of the reaction mixture. The solution was refluxed 1 hr., when evolution of methylamine was noted. The reaction mixture was chromatographed on a column of alumina (20 × 2.5 cm.) using low boiling mixed alkanes as solvent and eluting with a 50%, by volume, mixture of benzene and mixed alkanes. A blue band developed, which, after elution and aspiration of the eluate to dryness, yielded a blue solid (0.5 g., 20%). Recrystallization from nitromethane gave the characteristic blue compound melting at 215.5°.

A mixture-melting point of the product and that prepared *via* the sulfenyl chloride–diphenylacetylene route showed no depression and the infrared spectra of the two samples, run consecutively, also exhibited no observable differences.

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A New Route to 2,5-Dimethoxyphenylacetic Acid

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The mechanism of the amination of various halobenzenes in the presence of sodium amide and liquid ammonia has been elucidated by Roberts and co-workers.[1] Such aminations of halobenzenes which are nonactivated for nucleophilic substitution appear to involve a "benzyne" intermediate. With an explanation of the course of these reactions came a renewed interest in the further characterization of similar reactions and in the synthetic possibilities of such reactions. Thus Bunnett and Brotherton prepared a number of dialkylanilines by the reaction of bromobenzene with sodium amide and dialkylamines[2] and studied some reactions of "benzyne" and "α-naphthalyne";[3] Hrutfiord and Bunnett recognized the utility of such reactions in the synthesis of heterocyclic and homocyclic compounds.[4] Scardiglia and Roberts have extended earlier studies from their laboratory to include reactions of nonactivated aryl halides with various nucleophilic agents induced by alkali amides in liquid ammonia.[5] Additionally extensive characterization of similar reactions has been carried out by Huisgen and co-workers.[6] Recently Leake and Levine have reported the phenylation of ketones by reaction with phenyl halides and alkali amides.[7]

It seemed that an improved synthesis of 2,5-dimethoxyphenylacetic acid might be achieved by reactions presumably involving a "benzyne" intermediate. 2,5-Dimethoxyphenylacetic acid may be readily converted to homogentisic acid (2,5-dihydroxyphenylacetic acid), a compound of considerable biochemical interest. Studies of the nature and mode of formation of homogentisic acid in animals have provided many of the fundamental data on the intermediary metabolism of tyrosine and phenylalanine. A strong indication that homogentisic acid is an intermediate in the oxidative degradation of phenylalanine and tyrosine was first obtained from isotopic experiments.[8-11]

An improved synthesis of homogentisic acid was desirable. In the best published synthesis of this compound the synthesis of the intermediate 2,5-dimethoxyphenylacetic acid presents serious limitations to the synthesis of homogentisic acid itself since the over-all yield of the intermediate is 30–40% and reactions and work-up procedures are lengthy.[12] It seemed of considerable interest to attempt the synthesis of this intermediate using 2,5-dimethoxybromobenzene with appropriate nucleophiles under conditions where formation of a "benzyne" intermediate might be expected, *i.e.*, in the presence of a metal amide and liquid ammonia. Attempts to use diethyl malonate as a potential nucleophile with potassium amide and liquid ammonia were unsuccessful. However the

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