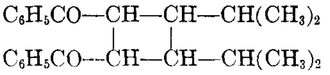
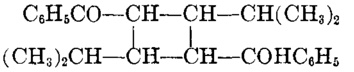


$$\begin{array}{l} C_6H_5CO{-}\underset{|}{C}H{-}\underset{|}{C}H{-}CH(CH_3)_2 \\ C_6H_5CO{-}CH{-}CH{-}CH(CH_3)_2 \end{array}$$



$$\begin{array}{l} C_6H_5CO{-}\underset{|}{C}H{-}\underset{|}{C}H{-}CH(CH_3)_2 \\ (CH_3)_2CH{-}CH{-}CH{-}COHC_6H_5 \end{array}$$

EXPERIMENTAL

All boiling points and melting points are uncorrected.

Dimer of 1-phenyl-4-methyl-2-penten-1-one (I). During 1.5 hr. at a temperature of 50°, 72.1 g. isobutyraldehyde was added to a well agitated solution of 120.7 g. acetophenone, 17 g. potassium hydroxide (reagent grade), 125 ml. methanol, and 125 ml. water. On continuing agitation at 48–50° a white solid formed. After 3.5 hr. the reaction mass was cooled to room temperature neutralized with acetic acid, and filtered on a Buchner funnel. The separated solid was washed with 100 ml. methanol and dried; it weighed 107 g. (61% yield). After 3 recrystallizations from a mixture of 70% methanol and 30% benzene, it gave a constant melting point of 144.5–145°, the dimer of 1-phenyl-4-methyl-2-penten-1-one (I). The liquid organic filtrate combined with the above methanol was fractionated through a 40-cm. Vigreux column yielding 10.5 g. unreacted acetophenone and 38 g. of a liquid boiling 133–134° at 8 mm. n_{D}^{20}: 1.5385, which on redistillation boiled at 130° at 8 mm. n_{D}^{20}: 1.5385. This liquid was identified as the *monomer of 1-phenyl-4-methyl-2-penten-1-one* (II). The distillation residue (12.2 g.) after recrystallization from a methanol-benzene mixture was found to be identical with I having a melting point of: 144.5–145°.

Anal. Calcd. for I: $C_{24}H_{18}O_2$: C, 82.2; H, 8.1. Found: C, 81.6; H, 7.8.

Anal. Calcd. for II: $C_{12}H_{14}O$: C, 82.2; H, 8.1. Found: C, 83; H, 7.86.

Molecular weight determination of I. The modified Rast procedure described by Becker[4] for the semimicro molecular weight determination was applied in principle. When the solution of the organic compound in camphor, prepared as advised by Becker, was used, erroneous and nonreproducible results were obtained, probably due to partial depolymerization of the dimer. The compound to be analyzed was, therefore, thoroughly mixed with the camphor. As five consecutive experiments gave almost identical results, we consider this abbreviation of the procedure to give sufficiently accurate results. Calculated molecular weight: 348, Found: 344 (average).

Determination of the carbonyl content of I *and* II *using hydroxylamine hydrochloride.* The method described by Guenther[5] was employed: Thus 0.5421 g. of I was treated at room temperature with 35 ml. of 0.5*N* hydroxylamine hydrochloride solution, and the liberated hydrochloric acid titrated with 0.5*N* sodium hydroxide solution. The following ketone contents were obtained: After 24 hr.: 32.3%; after 384 hr.: 93.3% and after 480 hr.: 99.9%. In the same way 0.5384 g. of II was treated as I, but gave after 24 hr. a ketone content of 98.2%.

Dioxime of I. The dioxime was prepared according to a procedure described by Vavon and Anziani:[6] Thus 8.9 g. of I, 10 g. hydroxylamine hydrochloride, 70 g. ethanol, 30 g. water, and 3.6 g. sodium hydroxide (reagent grade) were refluxed for 24 hr. The solution was poured into 100 ml. water, the precipitated crystals collected on a Buchner funnel, and recrystallized 4 times from 80% ethanol to a constant m.p. of 184–185°.

Anal. Calcd. for $C_{24}H_{30}N_2O_2$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.13; H, 8.06; N, 7.39.

Oxime of II. The above procedure was followed with the exception that the solution was permitted to stand at room temperature (25–30°) for 24 hr. The oxime, recrystallized 4 times from 80% ethanol, had an m.p. of 57°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.12; H, 8.02; N, 7.41.

Depolymerization of I *to* II. A mixture of 50 g. of I and 1.5 g. anhydrous sodium acetate (reagent grade) was heated in a vacuum of 8 mm. At 185° the mixture became completely liquid, and the depolymerization was considered complete. On distillation without a column, 41 g. were collected, boiling from 130–135° at 8 mm. n_{D}^{20}: 1.5392. On redistillation through a 40-cm. Vigreux column, the ketone (II) boiled at 130° at 8 mm.; n_{D}^{20}: 1.5385.

Dimerization of II *to* I. At a temperature of 50°, 70 g. of I was agitated for 45 min. with a solution of 6 g. potassium hydroxide in 70 g. methanol and 70 g. water. The solid was collected on a Buchner funnel and recrystallized twice from methanol. The resulting white crystals had an m.p. of 143–144°. A mixed melting point with the original ketone (I) showed no depression.

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Synthesis of 2-Phenyltriphenylene and 2,6,10-Trimethyltriphenylene

D. David Lawson and Charles M. Buess

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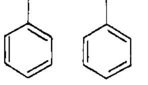
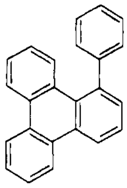
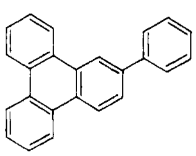
Hansch and Geiger[1] recently prepared a phenyltriphenylene by cyclodehydrogenation of 2,2′-diphenylbiphenyl (I). Although 1-phenyltriphenylene (II) might be expected from this reaction, the authors considered rearrangement to the 2-isomer (III) very likely. In the course of related work in this laboratory, 2-phenyltriphenylene was prepared by an unequivocal method, an adaptation of the Rapson synthesis as improved by Barker, Emmerson, and Periam.[2] The sample was compared with one kindly supplied by Dr. Corwin Hansch and the physical properties including infrared spectra were found to be identical. The melting point of a mixture sample was not depressed. It may therefore be concluded that the phenyl group does migrate under the cyclodehydrogenation conditions employed in ref. 1.



I



II



III

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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 1N 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°).

Acknowledgment. We are indebted to Cyclo Chemical Corporation, Los Angeles, Calif., for partial support of this work.

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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.

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(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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