Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.40; H, 8.70.

Alternate crystallization of the remainder from acetone and from isooctane furnished III and II, respectively, in over-all amounts of 146 (80%) and 14.7 g (8%).

Condensation of 2-Benzoylbenzoic with 2-Naphthylacetic Acid and Synthesis of Benzo[*a*]pentaphene

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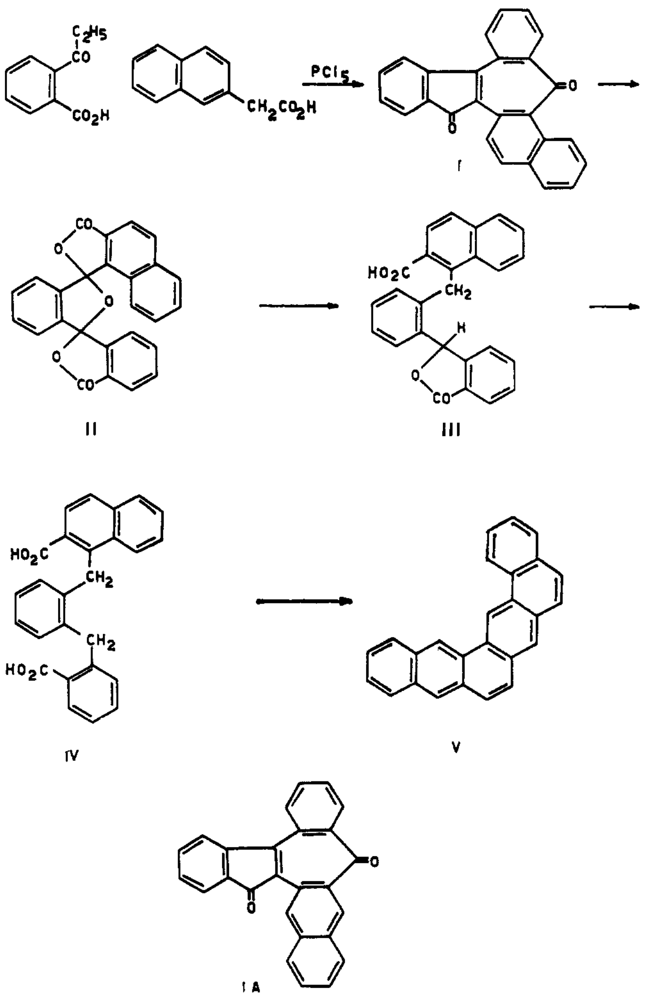
The condensation between 2-benzoylbenzoic and phenylacetic acid to yield a mixture of spiro[3-chloroindene-1,1'-phthalan-3'-one] and 9H,14H-tribenz[*a,e,h*]azulene-9,14-dione, and the easy conversion of the latter compound into pentaphene has previously been reported.[1,2]

When a similar reaction was attempted with 2-naphthylacetic instead of phenylacetic acid as one of the reactants, a single product was isolated for which structure I was assumed on the basis of the infrared absorption spectrum (λ_{CO} 5.88 and 6.00 μ) and of consideration of the greater reactivity of the α with respect to the β position of the naphthalene nucleus toward electrophilic substitutions. Further work has led to the conversion of I, through the intermediates II, III, and IV, into the still unknown polycyclic aromatic hydrocarbon benzo[*a*]pentaphene (V) (see Scheme I).

SCHEME I



Oxidation of I with potassium permanganate in acetone solution gave the dispiro derivative II (only a single carbonyl absorption band at 5.62 μ). This product, on reduction with zinc dust in aqueous sodium hydroxide, afforded a substance whose infrared spectrum pointed to a five-membered lactone ring (λ_{CO} 5.70 μ) and a carboxyl group (λ_{OH} 3.11 μ and λ_{CO} 5.82 μ). Structure III was assigned to this compound on the basis of elemental analysis and of the consideration that *o*-(2-naphthoyl)benzoic acid is readily reduced to *o*-(2-naphthylmethyl)benzoic acid by zinc–sodium hydroxide,[3] whereas reduction of 1,1',3',1''-dispirotriphthalane-3,3''-dione gives only *o*-di(3-phthalidyl)benzene by a similar reaction,[2,4] no reduction taking place beyond this stage. Compound III gave, on protracted reflux with hydriodic acid, the dicarboxylic acid IV and benzo[*a*]pentaphene (V).

The properties of this polycyclic hydrocarbon are different from those of hexaphene,[5] which should be formed if the reaction between 2-benzoylbenzoic and 2-naphthylacetic acid had led to compound IA by condensation at the β position of the naphthalene nucleus.

Experimental Section

Melting points were taken on a Kofler hot stage, and are not corrected. Infrared spectra were recorded, as Nujol mulls, on a Perkin-Elmer Infracord, Model 137, spectrophotometer. Ultraviolet-visible spectra were determined in 95% ethanol using a Beckman Model DU apparatus.

Condensation between 2-Naphthylacetic and 2-Benzoylbenzoic Acids.—A mixture of 2-naphthylacetic acid (10 g), 2-benzoylbenzoic acid (12 g), and phosphorus pentachloride (11.3 g) was heated for 1 hr in an oil bath at 140–150°. After addition of benzene (50 ml) the reaction mixture was heated to reflux, then allowed to cool and the solid was filtered to give 5 g of I as red prisms. An analytical sample of the product, after crystallization from xylene, melted at 238–240°.

Anal. Calcd for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found: C, 87.45; H, 4.08.

Oxidation of I with Potassium Permanganate.—A solution of I (4 g) and potassium permanganate (3.5 g) in acetone (200 ml) was refluxed for 1 hr. After addition of methanol to eliminate excess permanganate and evaporation of the solution, the residue was extracted with 2 *N* sodium carbonate (three 50-ml portions). Acidification of the combined extracts afforded crude II (2.8 g), which was purified by crystallization from benzene. The product so obtained contained benzene, and melted with strong gas evolution at 120–125°.

Anal. Calcd for $C_{26}H_{14}O_5 \cdot {}^4/_3\ C_6H_6$: C, 79.99; H, 4.34. Found: C, 80.03; H, 4.26.

Heating *in vacuo* over boiling xylene, caused the substance to lose 21.0% of its weight to yield a vitreous product melting between 140 and 150°.

Anal. Calcd for $C_{26}H_{14}O_5$: C, 76.84; H, 3.47. Found: C, 76.95; H, 3.58.

Reduction of II with Zinc and Alkali.[6]—A solution of the dispiro derivative II (3 g) in boiling 2 *N* sodium hydroxide (90 ml) was treated portionwise over a 2-hr period with zinc dust (7 g). The mixture was then allowed to boil for a further 2 hr, after addition of 30 ml 2 *N* sodium hydroxide. The hot, alkaline solution

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(2) A. Marsili and M. Isola, *Tetrahedron*, in press.

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(4) E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951).

(5) E. Clar, *Ber.*, **73**, 81 (1940).

(6) Modification of the procedure is described by Clar; see ref 4.

was filtered and acidified to give a solid which was crystallized twice from benzene to yield pure III (1.15 g) as colorless blades, mp 218–220°.

Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.81; H, 4.70.

When the filtered, hot, alkaline solution was allowed to cool slowly to room temperature, a sodium salt separated, from which pure III could be obtained on acidification. Product III is readily soluble in 5% sodium carbonate.

Treatment of III with Hydriodic Acid and Red Phosphorus.[6]—A mixture of III (1.15 g), red phosphorus (0.6 g), 55% hydriodic acid (6 ml), and xylene (10 ml) was refluxed for 140 hr. The cooled reaction mixture was then filtered and the residue was washed with benzene and extracted with hot 2 *N* sodium hydroxide. The filtered, alkaline solution, on acidification, afforded the dicarboxylic acid IV (0.7 g). An analytical sample of the product (from acetic acid) had mp 274–276°.

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.51; H, 5.02.

The organic combined layers were washed with 2 *N* sodium hydroxide and evaporated. Crystallization of the residue from benzene–hexane afforded V as yellow needles (80 mg): mp 220–222°; main infrared bands at 6.60, 6.70, 10.41, 10.56, 11.15, 11.35, 12.29, 12.51, 13.49, 14.30 μ; λ_{max} 216, 222, 239, 256, 284, 308, 322, 351, 410, 422 mμ (log ϵ 4.49, 4.49, 4.85, 4.66, 4.37, 4.78, 4.99, 4.50, 2.70, 2.70) (the spectrum of pentaphene[4] has maxima at 245, 257, 289, 302, 314, 329, 345, 356, 379, 399, 412, 423 mμ). The product dissolves in hot, concentrated sulfuric acid giving a pink solution with blue fluorescence. The mass spectrum of this hydrocarbon exhibits an intense molecular peak at *m/e* 328, as expected for $C_{26}H_{16}$. Also the doubly charged molecular ion is very abundant, while fragment peaks are very low.

Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.84; H, 5.16.

Acknowledgments.—This paper is dedicated to Professor Remo de Fazi on his 75th birthday. Thanks are due to Dr. A. Mandelbaum (Technion, Israel Institute of Technology, Haifa) for the mass spectrum, Dr. V. Malaguzzi for the ultraviolet spectrum, and Professor G. Berti for full discussion of these results.

The Meisenheimer Reaction in the 1,5-Naphthyridine Series

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Meisenheimer[1] observed the formation of 4-chloroquinoline when quinoline 1-oxide was refluxed with sulfuryl chloride. Bobranski and co-workers[2] found that pyridine 1-oxide with the same reagent gave a mixture of 2- and 4-chloropyridines. Bobranski[3] showed that both 2- and 4-chloroquinolines are obtained from quinoline 1-oxide and isomers have been found in this reaction by other workers[4,5] in the pyridine series. Since Hart[6] reported the formation of only 2-chloro-1,5-naphthyridine from the action of phosphorus oxychloride on 1,5-naphthyridine 1-oxide, it was of interest to inquire whether this reaction afforded both 2-chloro and 4-chloro as expected. We have now repeated his work and wish to report that 2-chloro- and 4-chloro-1,5-naphthyridines are obtained in roughly equal amounts in this reaction. Gas chromatography confirms the presence of the two compounds. They were separated on a preparative gas chromatograph and comparison with synthetic 2- and 4-chloronaphthyridine using infrared analyses, gas chromatography retention time, and mixture melting points confirms their structures.

Experimental Section

Meisenheimer Reaction.—1,5-Naphthyridine[7] (4.5 g) was oxidized by heating to 70° with a mixture of acetic acid (10 ml) and 40% peracetic acid (5 ml) for 3 hr. The mono- and dioxides were separated by fractional crystallization using methylcyclohexane.[6] The mono-1-oxide (0.77 g) was heated to reflux with phosphorus oxychloride (30 ml) and phosphorus pentachloride for 20 min and the crude mixture was collected. This crude mixture was analyzed on a Beckman G.C. 4 gas chromatograph using a 12-ft aluminum column 0.25 in. in diameter filled with 15% SE-30 on Chromosorb W. The column temperature was 240° and the helium pressure was 40 psi. Two distinct peaks were obtained with retention times of 8.06 and 8.95 min which were subsequently identified as the 2- and 4-chloro-1,5-naphthyridines, respectively. The areas under the two curves assuming equal thermal conductivity indicate 56.8% 2-chloro-1,5-naphthyridine and 43.2% 4-chloro-1,5-naphthyridine.

2-Chloro-1,5-naphthyridine.—2-Hydroxy-1,5-naphthyridine[8] (4.9 g) was refluxed with a mixture of 5 g of phosphorus pentachloride and 100 ml of phosphorus oxychloride for 4 hr. Excess phosphorus oxychloride was removed *in vacuo*, the residue was dissolved in cold water and basified with concentrated ammonium hydroxide, and the precipitate was filtered. There was obtained 4.1 g (70% of the theoretical amount) which was recrystallized from ligroin and melted 114–116° (lit.[6] mp 112°).

4-Chloro-1,5-naphthyridine.—This compound was prepared by the method of Hauser and co-workers[9] and melted at 102–103° (lit.[9] mp 102–102.5°).

Separation and Identification of Isomers.—The crude mixture from the Meisenheimer reaction above was separated using a F & M Model 810 gas chromatograph with a 20-ft, $^3/_8$-in.-o.d. aluminum column filled with 15% SE-30 on Chromosorb W. The sample was dissolved in acetone and injected into the column which was set at 150°. The 2-chloro-1,5-naphthyridine fraction melted at 115–118° and the 4-chloro-1,5-naphthyridine melted at 103–104°. A mixture of the two synthetic isomers behaved exactly as did the crude product of the Meisenheimer reaction when introduced into the gas chromatograph. Infrared spectra of the separate isomers and the synthetic compounds were identical. There was no depression of melting point between synthetic and separated compounds; however, an approximately equal mixture of 2- and 4-chloro compounds melted in the range 72–93°.[10]

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(10) All melting points are corrected.

Oxymercuration of Allenes[1]

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Several inconsistencies have emerged in studies of electrophilic addition to cyclic and straight-chain

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