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.

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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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