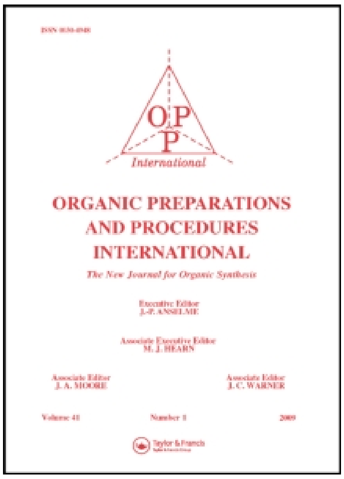

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THE SYNTHESIS OF PEROPYRENE-TYPE POLYCYCLIC AROMATIC HYDROCARBONS

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THE SYNTHESIS OF PEROPYRENE-TYPE POLYCYCLIC AROMATIC HYDROCARBONS

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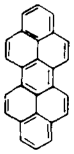
The paucity of research on the health effects and environmental occurrence of the large polycyclic aromatic hydrocarbons (PAHs) is mainly due to a lack of pure compounds to be used as standards. We now report synthesis of several new PAHs (V-X).

The synthesis of peropyrene (I, dibenzo[cd,lm]perylene) through the condensation of perinaphthenone (II, 1-phenalenone) occurs in a melt of zinc powder and zinc chloride and other similar ketones, such as benzanthrone (III, 7H-benz[de]anthracen-7-one) and naphthanthrone (IV, 4H-benzo[de]pyren-4-one) yield several 9- or 11-ring isomeric PAHs, respectively. Since the reaction conditions used are similar for all these condensations, it was thought that using mixtures of two ketones as starting materials would yield PAHs resulting from "cross-reactions" of one ketone with another, in addition to the previously known products. The variable that determines the cross-product yields is the proportion of each ketone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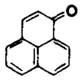
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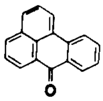
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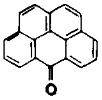
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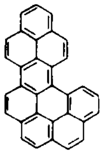
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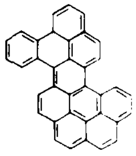
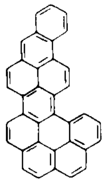

VI

appear to be vigorous enough to cause rearrangements, the reaction has been widely studied and the product PAHs are only combinations of the starting ketones.[5]

Six previously unreported PAHs (V-X) were found from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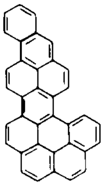
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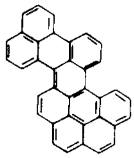
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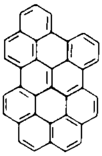
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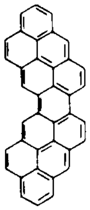
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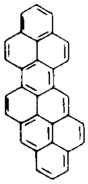

XII

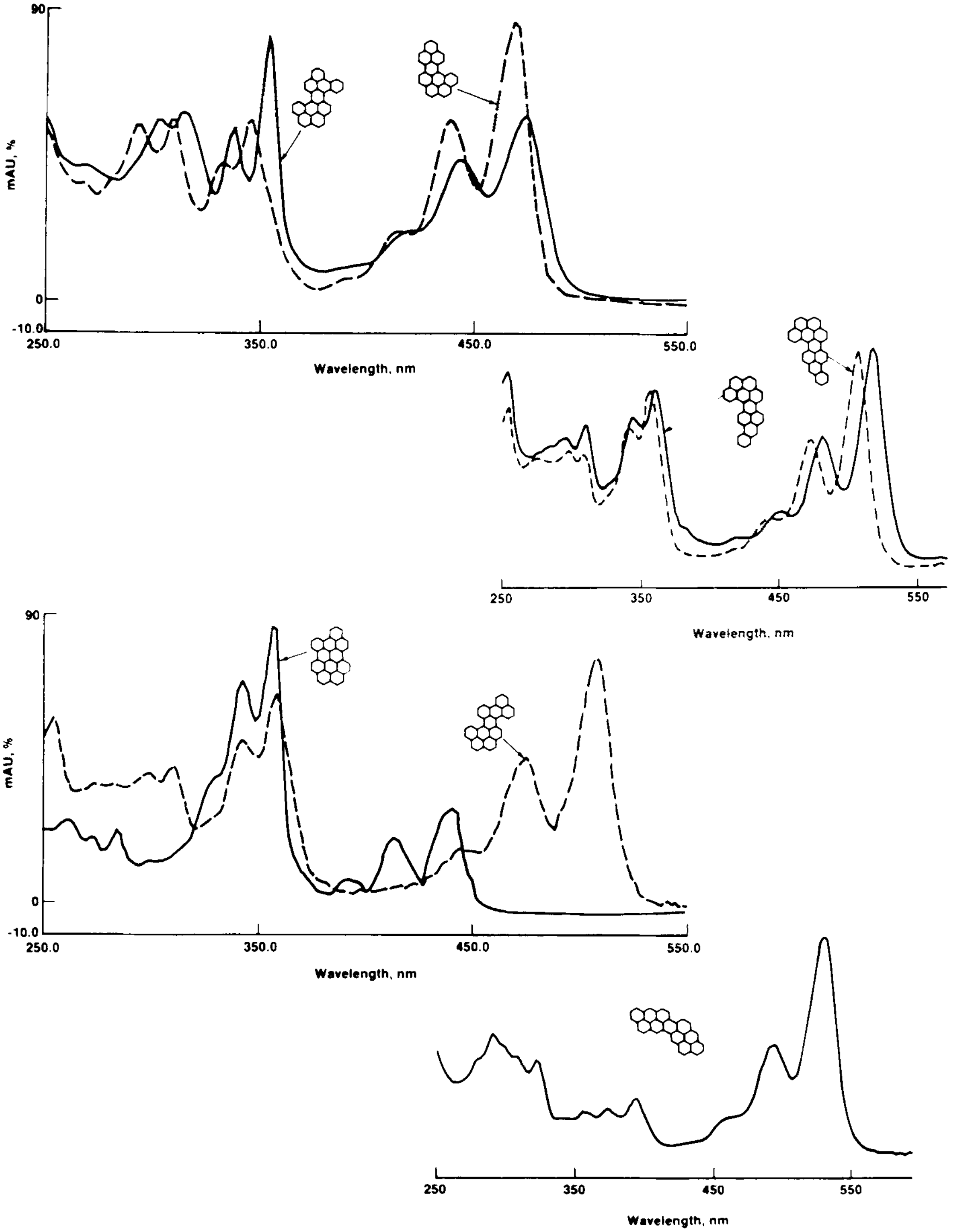
cross-reactions of different ketones. In addition, one previously unknown isomer (XI) from the condensation of two naphthanthrone molecules was identified. Ultraviolet absorbance spectra for V-XI are shown in Figures 1-4. The spectra are shown with linear absorbance scales.

Compound V was the only 8-ring PAH found in the product mixture from condensation of II with III, with no indication that any dinaphtho[8,1,2cde8',1',2',3'pqrst]pentaphene (XII) was formed. If it was formed, the yield would have been at trace levels (less than 0.5%).

The assignment of a specific structure to each of the two very similar 10-ring isomers, VIII and IX, was through parallels between their properties and those of the two similar 9-ring products from benzanthrone condensation.[6] The chromatographic elution orders, wavelengths of highest absorbance, and relative yields in the condensation reactions were all consistent with the suggested assignments. The assignment of the structure of XI was produced by comparison to the four known isomers that have previously been isolated from naphthanthrone condensation.[7] Prior to these syntheses, the since the relative reactivities of the three ketones are different.[1] Since perinaphthenone (II) is the most reactive, if proportionally less of it were used, the yield of peropyrene would be less and that of the cross-products would increase. Equal portions of benzanthrone (III) with naphthanthrone (IV), were used because their reactivities are similar.

Earlier work described the synthesis of three 8-ring isomers that resulted from condensation of II with III.[2] The isolation of the individual compounds in that work relied heavily on advanced separation techniques: shape-sensitive, reversed-phase high performance liquid chromatography with "UV spectrum" photodiode-array detection. In order to characterize the PAH products, both the power of a high efficiency column that separated the PAHs by their shapes and a detector that collected an isomer-specific absorbance spectrum were utilized. This combination allowed isolation of the three similar 8-ring isomers, as well as one previously unreported 9-ring isomer from benzanthrone condensation.

As in the previous work, the UV absorbance spectra of the new PAHs were used to identify specific isomeric structures. The molecular weights (which were used to limit the number of possible structures) were determined by high resolution mass spectrometry. The number of possible structures was further limited by the known reactivities of the ketones.[1] The UV spectral interpretations and structure correlation relied on Clar's annellation theory[3] and Aoki's resonance count theory,[4] as well as on comparisons to spectra of known structures. Although the reaction conditions of a zinc dust melt might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Wavelength, nm

number of PAHs for each of these molecular weights was: 400, 5 isomers; 448, 2 isomers; 450, 7 isomers; and 474, 4 isomers.[8] This work greatly increases the number of known compounds for each isomeric set.

The molar absorption of the trio of 8-ring products of condensation of II with II previously reported[2] is given in the Experimental Section.

EXPERIMENTAL SECTION

All three condensations were performed under almost identical conditions, and the isolation and identification procedures for each product were the same. The relative amounts of each ketone used varied as shown in Table I. The zinc dust mixture was a thoroughly ground and mixed combination of 35.80 g zinc dust, 36.11 g sodium chloride, and 185.66 g zinc chloride (all from J. T. Baker, Phillipsburg, NJ). The materials were mixed in 50-mL beakers which were used as the reaction vessels. The reactions were carried out on a high wattage hot plate, with an initial period of 10-min. heating at 250-275° to activate it by removing any surface zinc oxide from the zinc dust. The temperature was then raised to 330-350°C and kept there for 30-45 min. Constant stirring with a glass rod ensured homogeneous heating of the liquefied mixture, as well as completeness of the reaction. A change in color from yellow to reddish-orange indicated formation of the large PAHs.

After cooling, each reaction beaker and its contents were ground and placed in a 250-mL cellulose thimble (since the amorphous solid product mixture was difficult to break up and remove completely from the beaker). The material was extracted for 75 hrs in a Soxhlet apparatus using 500 mL dichloromethane. For column loading, each extract was concentrated to 50 mL and then diluted with 450 mL toluene to minimize the effect of the dichloromethane on the elution of the first fraction. The extracts were fractionated by adsorption chromatography on basic alumina (125 g, 60-100 mesh, Activity Grade 1 packed in a 75-cm x 1-cm I.D. glass column) using 1 L each of toluene, dichloromethane, ethyl acetate, and 1:1 dichloromethane/methanol. Each fraction was dried under nitrogen on a steam table and redissolved in 50 mL dichloromethane.

Each product PAH was isolated by using reversed-phase high performance liquid chromatography (HPLC). The separation conditions consisted of a Vydac 201TP column with 5-μ particle-size packing, 25 cm x 2.0 cm I.D., with various methanol-dichloromethane solvent gradients. The chromatograph was a Du Pont Model 8800 quaternary solvent HPLC. A Valco C6U injector valve with a 200-μL sample loop was used for sample introduction. A Hewlett-Packard Model 1040A Photodiode Array Detector was used to monitor the effluent and collect UV absorbance (250-600 nm) spectra of each peak. High resolution mass spectrometry (R = 40,000) was used to determine molecular weights. Melting points were determined through differential scanning calorimetry. The crystal forms reported are those from a 80% dichloromethane in methanol solution of the PAH, gently warmed to remove the dichloromethane. Since the pure PAHs were isolated only by HPLC, the total yield for each PAH could not be obtained directly. The yields were determined by weighing the amounts isolated, proportionalizing the amounts injected into the chromatograph to the total volume of each fraction, and adding the amounts found in each fraction (since the alumina adsorption chromatography did not cleanly fractionate the PAHs).

The logarithms of the molar absorptivities, in chloroform: V, 474 nm (4.85) and 346 nm (4.46); VI, 478 nm (4.84) and 354 nm (5.02); VII, 522 nm (4.91) and 363 nm (4.820); VIII, 507 nm (4.86) and 361 nm (4.77); IX, 496 nm (5.08) and 376 nm (4.60); X, 437 nm (5.24) and 360 nm (4.38); and XI, 529 nm (4.82) and 495 nm (4.28). Tribenzo[a,cd,lm]perylene, 437 nm (5.04), 341 nm (5.29), and 266 nm (5.10); phenaleno [1,9,ab]perylene, 469 nm (5.21), 353 nm (4.89), and 267 nm (5.08); and dibenzo[j,lm]naphtho-[1,8ab]perylene, 464 nm (5.12), 354 nm (4.78), and 303 nm (5.20).

TABLE 1. Quantity of Reactants in Grams

Reaction	II	III	IV	Zinc Melt
1	5.73	17.02	-	125.87
2	1.09	-	3.46	33.29
3	-	2.46	2.58	36.77

Benzo[lm]phenanthro[4,5,6abcd]perylene (V), mp. 289-291; orange-yellow platelets, MS: found, 400.14; calc., 400.13, blue-green fluorescence, and 825 mg (estimated yield).

Dibenzo[j,lm]phenanthro[4,5,6abcd]perylene (VI): m.p. 328-332; orange platelets, mass: found, 450.12; calc., 450.14, green fluorescence, and 420 mg (estimated yield).

Dibenzo[rs,vwx]naphtho[2,1,8,7klmn]hexaphene (VII): m.p. 341-344; orange platelets, mass: found, 450.14; calc., 450.14, green fluorescence, and 90 mg (estimated yield).

Benzo[rst]pyreno[3,4,5cde]pentaphene (VIII): m.p. 302-307; orange platelets, mass: found, 450.13; calc., 450.14, green fluorescence, and 15 mg (estimated yield).

Tribenzo[jk,qr,uv]naphtho[2,1,8,7defg]pentacene (IX): m.p. 357-360; orange-red platelets, mass: found, 450.14; calc., 450.14, green fluorescence, and 230 mg (estimated yield).

Benz[2,10]anthra[1,9,8abcd]coronene (X): m.p. 456-461; pale yellow platelets, mass: found 448.14; calc., 448.13, blue fluorescence, and 110 mg (estimated yield).

Naphth[7',8',1',2',3'vwxyz]anthra[2,1,9,8klmno]hexaphene (XI): m.p. 413-416; reddish-purple needles, mass: found 474.16; calc., 474.14, yellow-green fluorescence, and 85 mg (estimated yield) from the condensation of 2.08 g naphthanthrone.

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