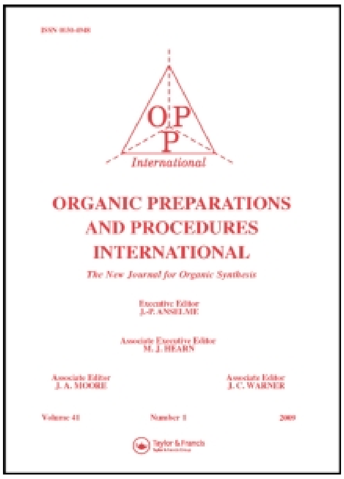

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED SYNTHESIS OF TRIBENZO[a,cd,1m]PERYLENE

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To cite this Article Fetzer, J. C. and Biggs, W. R.(1986) 'AN IMPROVED SYNTHESIS OF TRIBENZO[a,cd,1m]PERYLENE', Organic Preparations and Procedures International, 18: 4, 290 — 295
To link to this Article: DOI: 10.1080/00304948609458159
URL: http://dx.doi.org/10.1080/00304948609458159

AN IMPROVED SYNTHESIS OF TRIBENZO[a,cd,lm]PERYLENE

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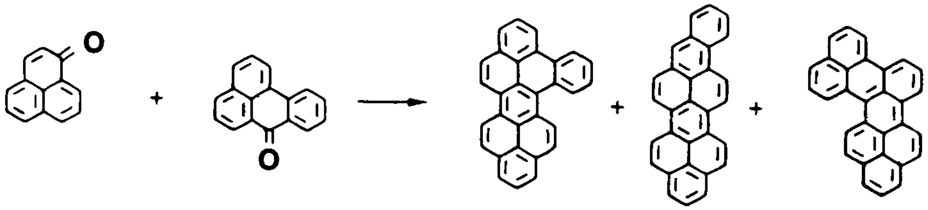
The study of the adverse effects on health and the presence of polycyclic aromatic hydrocarbons (PAHs) in a variety of materials[1] has been hampered by the lack of pure reference materials. Our previous work described a program of synthesis of large PAHs to circumvent this problem.[2,3] The zinc dust condensation of perinaphthenone (I) with 7H-benzo[de]anthracen-7-one [benzanthrone (II)] yielded ten major PAHs of



I II III IV V

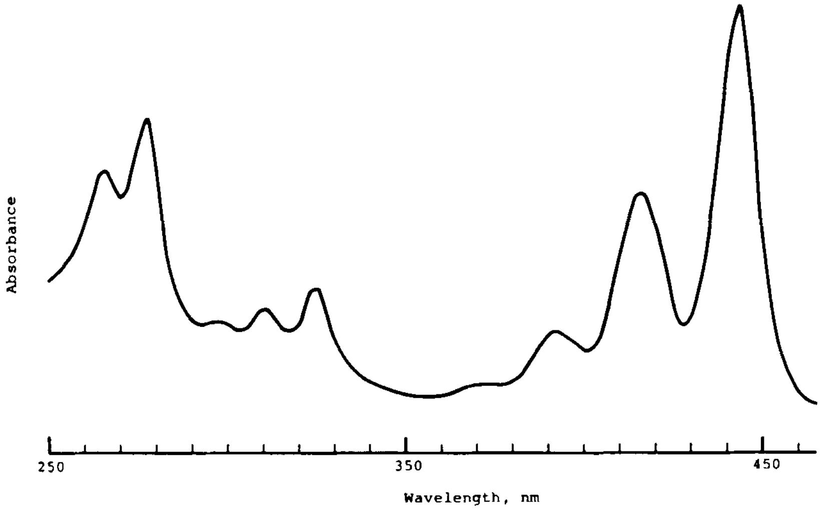
seven through nine rings, four of which had not been previously reported. Three eight-ring isomers, tribenzo[a,cd,lm]perylene (III), benzo[rst]naphtho[2,1,8cde]pentaphene (IV), and phenaleno[1,9ab]perylene (V), were found. Isolation of each PAH from the product mixture was difficult. Preparative-scale, reversed-phase HPLC (after initial purification by extraction and absorption chromatography) was needed since the many PAHs were not separated in the initial steps. We now describe an improved synthesis of III.

The zinc dust fusion procedure used initially[2] was identical to Clar's synthesis of dibenzo[cd,lm]perylene (peropyrene) from perinaphthenone;[4] an alternative, higher yield synthesis of this PAH which involved preliminary formation of an intermediate ketone yielded about three times more dibenzo[cd,lm]perylene than the direct condensation.[5] We thought that a similar initial step in the reaction of I with II would increase the eight ring PAH yield. Benzanthrone was found to be much less reactive to the basic methanolic treatment than perinaphthenone. A large excess of benzanthrone over perinaphthenone would result in condensation of perinaphthenone with the less reactive benzanthrone rather than perinaphthenone with itself. Also, benzanthrone yields the nine-ring PAHs violanthrene and isoviolanthrene[5,6] when the basic methanol step is used. These two compounds are produced as minor products in the direct fusion reaction; benzanthrone has differing favored reaction sites for each reaction. Four other isomers are the major nine-ring PAHs produced by direct condensation. With an excess of benzanthrone over perinaphthenone and an initial basic methanol step, these four would not be produced. The two known nine-ring isomers are much easier to separate.[2,3] In addition, the different reaction sites of benzanthrone would result in the formation of greater amounts of IV than from direct fusion.

Table 1. Comparison of Yields of the Two Reactions

Product PAHs	Direct Reaction	MeOH/KOH Reaction
Total PAHs	725 mg	855 mg
Dibenzo[cd,lm]perylene	155	450
III	140	315
IV	<0.5	35
V	95	<0.5
Total Nine-Ring PAHs	330	45
Violanthrene and Isoviolanthrene	20	40
Larger PAHs	5	5

Two reaction yields are shown in Table 1 and the amount of each component is given in milligrams. The mixture from the zinc dust reduction with a basic methanol step did not contain large amounts of the nine-ring PAHs that were difficult to separate, nor was the third eight-ring isomer V formed. By contrast, IV was produced in sufficient quantities for a UV spectrum and a melting range to be determine (not possible in our earlier work). Its spectrum is shown in Fig. 1; the molar absorbtivity of the 438 nm maximum is approximately 78,000. A melting range of 279-283° was observed, which compares to 297-301° for compound II and 353-356° for compound V.[3] The wide melting ranges are most likely due to inaccuracy inherent to the apparatus at elevated temperatures. The UV spectral absorbance bands of IV are broad with shallow minima, indicating that the molecule probably assumes a slightly nonplanar configuration in solution, also suggested by its earlier-than-expected chromatographic elution. Proton and C_{13} NMR spectra could not be obtained because the solubilities of the PAHs were too low.



The structural assignments were based on Clar's annellation principles for the UV/visible spectra of PAHs,[7] a set of "rules" that predicts the wavelength of the absorbance maxima of a PAH of particular structure. The assignments were also based on the reported[8] ability of this type of HPLC column to separate isomeric PAHs by their three-dimensional shape. The various isomers discussed here also follow the spectral trends seen for nine-ring isomers resulting from benzanthrone condensation. X-ray diffraction and photoelectron spectroscopy studies of the isomers discussed here produce structural assignments consistent with those found for the known nine-ring systems. Proton and C_{13} NMR spectra are not definitive, even with very long spectral acquisition times (days) because of low solubilities.

EXPERIMENTAL SECTION

In order to compare the yields of each reaction, 2.1 g of perinaphthenone (I) and 8.2 g of benzanthrone (II) were dissolved in 50 ml of 1:1 acetone/methylene chloride, split into two equal portions, dried at 50° in a 10-torr vacuum, and used in each reaction.

Procedure.- The direct zinc dust fusion used a melted mixture of 5.15 g of ketones, 15.7 g zinc, 19.4 g of sodium chloride and 32.8 g of zinc chloride. The mixture was heated at 250° for 5 min. to activate the zinc dust, and then the temperature was raised to and kept at 330-340° for 30 min.

The second portion of mixed ketones (5.15 g) was added to 100 ml of a 65° saturated methanolic potassium hydroxide solution. The aquamarine color which resulted rapidly changed to brownish purple. The solution was heated at 125° for 10 min. (with most of the methanol boiling off), cooled, neutralized with 1.0 N hydrochloric acid (phenolphthalein end point) and dried in a nitrogen stream at 75°. This product was then reduced with zinc, sodium chloride, and zinc chloride as in the direct procedure.

Each solidified melt was ground into a powder and was exhaustively extracted in a Soxhlet apparatus with 500 ml boiling *o*-xylene. The completeness of extraction was determined by observing the decrease in greenish fluorescence when the thimble contents were exposed to UV light. The extracts were concentrated by boiling away the o-xylene. PAHs were then chromatographically separated (Davidson Grade 81 silica, activated overnight at 150°/10 torr vacuum, 100 g in 2-cm I.D. x 50-cm collumn) from both the unreacted and intermediate ketones. One liter of toluene eluted the small PAHs resulting from reduction of the starting ketones without condensation. A liter of a 1:1 mixture of methylene chloride and ethyl acetate eluted the larger PAHs, and finally 500 ml methanol was used to elute the unreduced ketones. The fraction containing the larger PAHs was dried, redissolved in 50 ml of toluene and separated on basic alumina (150 g, Brockman activity Grade 1) on an identical column as the silica separation. Compounds III and IV were eluted with methylene chloride. Dibenzo[cd,lm]perylene and V were obtained with ethyl acetate as the eluent. Each one liter fraction was dried, redissolved in methylene chloride, and analyzed by reversed-phase HPLC as described in our earlier work.[2,3] Each PAH was characterized by its retention time and unique UV spectrum. Chromatographic peaks were collected and direct-insertion probe mass spectrometry was used to determine molecular weights.

Acknowledgments.- We thank Dr. R. M. Teeter for mass spectra of the compounds and Chevron Research Company for permission to publish this work.

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3-METHYLSUCCINIMIDE AND 3-METHYLPYRROLIDINE

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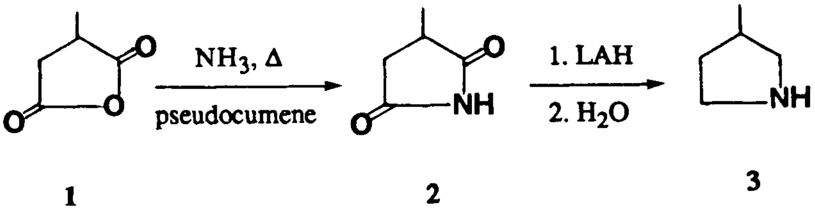
3-Methylpyrrolidine (3) which serves as a model coal liquid constituent is not commercially available and a substantial sized sample of pure material was needed for the study of its thermochemical and thermophysical properties.[1] We have developed procedures for the preparation of 2 and 3 from methylsuccinic anhydride (1). The preparation of 3 has been reported but the experimental details were meager.[2,3]



1 2 3

The use of anhydrous ammonia in refluxing hydrocarbon is superior to ammonium hydroxide[4] in converting 1 to 2 in that tarry residue and decomposition products are avoided and a higher yield (95% vs. 85% reported for succinimide) is obtained. The