



Project Summary

Polynuclear Aromatic Compounds

Synthesis and Purification

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This report reviews and discusses the synthesis and/or purification of polynuclear aromatic (PNA) compounds commonly found as pollutants in the environment. It also presents details of the experimental procedures and techniques as well as the chromatographic and spectroscopic evidence of structure and priority of the compounds supplied to the U.S. Environmental Protection Agency. In addition, it describes the apparatus designed and constructed to meet the synthesis needs together with safety improvements for handling toxic compounds.

Introduction

The final report upon which this summary is based (see box at end of paper for ordering instructions) provides details of synthesis and purification of 10-g samples of 10 hydrocarbons, 6 nitrogen heterocyclics and 2 oxygen heterocyclics for use as instrumental standards and in other studies at the Chemistry and Physics Laboratory of the EPA's North Carolina Environmental Research Center. The compounds are listed in alphabetical order for each category in Table 1

Compounds Obtained Through Purification of Available Materials

Purification Techniques

Since several of the compounds needed by EPA were commercially available (3,6,11,12,13,14, and 16), and purification rather than synthesis was indicated, it became important to examine and utilize any and all purification routes.

An earlier report (EPA-600/2-78-006) described techniques and apparatuses which became important in laboratory practices for safe production of the final pure compounds.

Because some of the products and intermediates were suspected carcinogens, final handling procedures were reviewed. Included were development of an improved Soxhlet apparatus, a modified sublimation apparatus, a solid sample dispenser and apparatus for safe cleaning of laboratory equipment. Zone refinement was also used for purification and the refinement apparatus was redesigned to improve refinement methods.

The improved Soxhlet and sublimation apparatuses became important for achievement of project goals in this study; they should prove

Table 1. Compounds Supplied to the EPA during the Reporting Period

Hydrocarbons

Benzo[ghi]perylene (1), mp 276-277 °C, 10.4 g

Benzo[e]pyrene (2), mp 178-179 °C, 9.96 g

Chrysene (3)^a, mp 251-253 °C, 11.6 g

Coronene (4), mp 437-440 °C, 10.5 g

1,2,3,6,7,8-Hexahdropyrene (5)^{a,b}, mp 133-134 °C, 10.0 g

sym-Octahydroanthracene (6)^{a,b}, mp 72-73 °C, 13.7 g

Perylene (7), mp 275-277 °C, 13.2 g

1,2,3,4-Tetrahydroanthracene (8)^{a,b}, mp 89-90 °C, 10.3 g

4,5,9,10-Tetrahydropyrene (9)^{a,b}, mp 139-140 °C, 10.4 g

1,10-Trimethylenephenanthrene (10), mp 80.5-81.0 °C, 13.2 g

Nitrogen Heterocyclics

Acridine (11)^a, mp 109-110 °C, 12.7 g

Benzo[f]quinoline (12)^a, mp 90-91 °C, 12.9 g

Benzo[h]quinoline (13)^a, mp 50.5-51.5 °C, 11.1 g

Carbazole (14)^{a,b}, mp 243-244 °C, 10.5 g

11H-Indeno[1,2-b]-quinoline (15), mp 167-169 °C, 10.7 g

Phenanthridine (16)^a, mp 106.5-107.5 °C, 12.1 g

Oxygen Heterocyclics

Dinaphtho[2,1-b:1',2'-d]furan (17), mp 156-157 °C, 10.7 g

peri-Xanthenozanthene (18), mp 241-242 °C, 9.7 g

^aCompound available from commercial source and not synthesized.

^bCompound resulted from shared cost and effort.

equally useful to other researchers. Design details are shown below (Figures A-1 and A-2 from the final report).

Generally, the individual samples were contained in about 100 vials and ranged from 9.9 to 13.7g. The redesigned sampling device greatly aided the safe handling of toxic compounds.

Analytical and preparative high-pressure liquid chromatography which became available during EPA support of this project were valuable for determining purity of samples. A description of the technique used in purifying a sample of sym-octahydro-

anthracene is described in the final report.

Nitrogen heterocyclic PNA compounds were purified using one or more of the techniques listed above. Attempts to purify acridine (11) failed until complexation with catechol proved successful. Since acridine (11) was one of the later compounds used, no experience was available to indicate whether its usage would be practical with other nitrogen heterocyclics.

Compounds Synthesized

The compounds shown in Table 1, excluding the seven exceptions, were synthesized. In each case, the final report provides the synthesis route and experimental details.

Coronene (4) is difficult to synthesize on an increased scale because starting

material at an advanced stage of synthesis is scarce; also, the higher temperatures required, especially in the sublimation of 4 and its intermediates, adds to the difficulty.

A heater, which operates at 500+ °C, was developed. This heater is essential to the scale-up preparation of 1,4, and 7. An improvement in preparation of perylene and development of an alternate route which does not require perylene were major factors in the synthesis scheme.

The following reactions provided an increased yield of 1 and eliminated a step in the synthesis of coronene (4). Preparation of 24 (scheme 1 of the final report) is shown by the following partial scheme.

Selective reduction through catalytic hydrogenation, dissolving metal reactions, and HI-P4 reductions proved to be important in the synthesis of several PNA compounds (2,8,9,10). The direct conversion of 1-tetralone to naphthalene by heating in the presence of a mixture of NaOH·KOH has been extended to the preparation of 1,2,3,4-tetrahydroanthracene (8) as shown in the final report (scheme 3).

This reaction shows promise for the synthesis of specific hydroaromatics. In

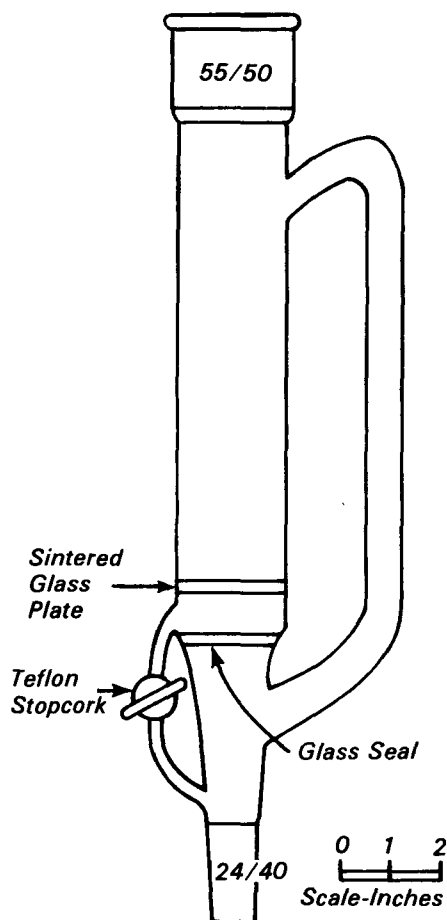


Figure A-1. An improved soxhlet apparatus.

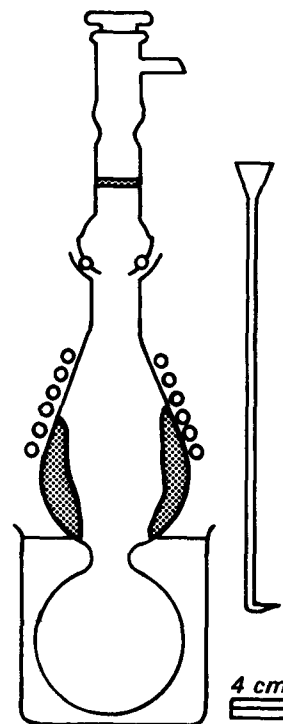
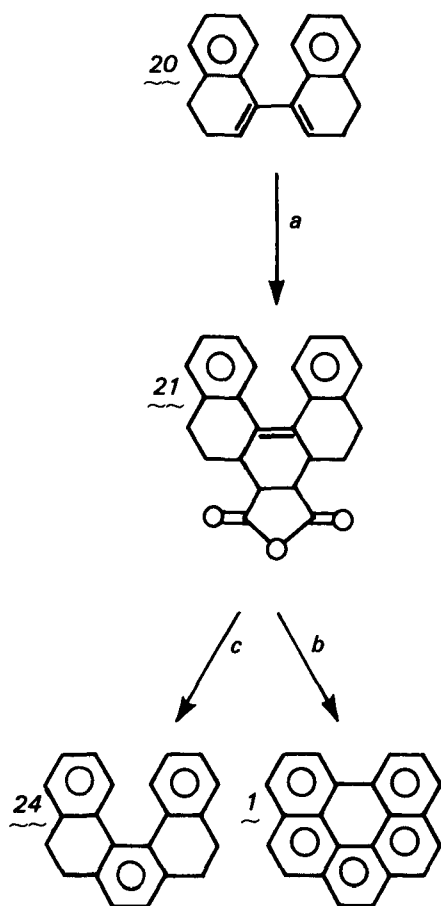


Figure A-2. An improved sublimation apparatus.



^aMaleic anhydride, Δ . ^bPt/C, Δ . ^cCu₂ quinoline, Δ .

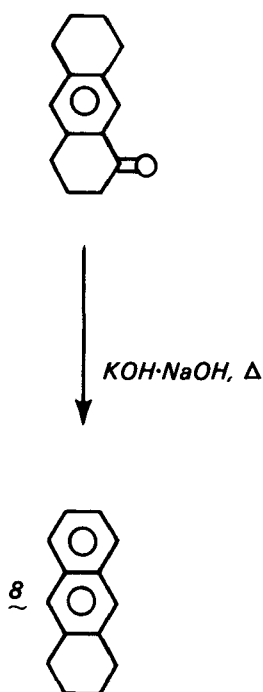
contrast, very selective hydrogenation conditions are required to produce 8 from anthracene.

Instrumental Studies

Gas liquid chromatography and high-pressure liquid chromatography were used to determine priority of the intermediate and final PNA compounds. The identity of each was established through the synthesis route and use of spectroscopy studies (IR, UV, ¹HNMR, and ¹³CNMR) as well as mass spectrometry. From these data, HNMR was the most definitive. With the exception of coronene (mass spectrum supplied as substitute), a photoreduced ¹HNMR trace was included in the final report.

Conclusions

The synthesis and chemistry of PNA compounds are of interest to a broad spectrum of industrial and governmental laboratories because these



compounds are an integral part of petroleum, petroleum products, coal liquids, and shale oil. While there is a current diminished interest in the synthesis of pure aromatic compounds

in air pollution studies, other environmental problems requiring high purity standards which involve PNA compounds are bound to emerge as the uses of coal and petroleum products, which are rich in polynuclear aromatics and their hydrogenative derivatives, continue to increase.

Recommendations

In an earlier report (EPA-600/2-78-006) the use of stable isotopes as labels was suggested in PNA aromatics. Their partially hydrogenated derivatives will become more important and systematic synthesis of representative labelled compounds should be initiated. The pure standard samples (labelled and unlabelled) would then be available as advances in instrumentation and pressures for controlling pollution occur. Large-scale synthesis of ¹³C labelled compounds is a reality; for example, in another project, this laboratory produced 100g samples of two different aromatic hydrocarbons containing a single specific ¹³C label with a 95% + ¹³C.

Given the rapidly escalating costs of synthesis, some attention should be directed to consolidating inter- and intra-governmental agencies to support future synthesis projects.

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James E. Meeker is the EPA Project Officer (see below).

The complete report, entitled "Polynuclear Aromatic Compounds—Synthesis and Purification," (Order No. PB 81-125 015; Cost: \$9.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:
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