

## SEPARATION OF PYRENEDIONES BY COLUMN CHROMATOGRAPHY\*

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Pure 1,6-, 1,8- and 4,5-pyrenediones were needed as reference compounds in connection with studies conducted in this laboratory on the photochemical oxidation of pyrene<sup>1</sup>. The procedure reported by VOLLMANN and co-workers<sup>2</sup> for the preparation and separation of 1,6- and 1,8-pyrenediones involves a laborious series of processes, namely reduction of the crude mixture of diones to a mixture of the corresponding dihydroxy derivatives, acetylation, fractional recrystallization of the acetates, separate hydrolysis of each acetate, and oxidation of each pyrenediol to the corresponding dione. From 250 g of the crude oxidation mixture, they obtained 15 g of 1,8-pyrenediol diacetate, from which they isolated an unstated amount of 1,8-pyrenedione.

After tests with a variety of adsorbents and solvents, we have found that 1,6- and 1,8-pyrenediones are readily separated on a column of silica gel by use of glacial acetic acid as the solvent. Acetic acid apparently acts as a stabilizer for the somewhat sensitive 1,8-pyrenedione; in addition, it produces sharper bands than do the other solvents tested. The final purification of 1,6-pyrenedione was accomplished on a column of activated alumina, with benzene as the solvent.

The composition of each fraction eluted from the column was checked by thin-layer chromatography; this proved to be a convenient method for ascertaining where overlapping of bands occurred.

## EXPERIMENTAL

*Apparatus and reagents*

Standard chromatographic columns (50 × 5 cm, 45 × 4 cm, 35 × 3 cm and 25 × 2 cm) were used. Each had a round-bottomed flask of the appropriate size sealed on top for use as an eluant reservoir. Commercial silica gel, 200 or 100 mesh, was used as received from the supplier. Commercial alumina for chromatography was rendered neutral either by soaking it overnight in 10 % acetic acid at room temperature, or by digesting it at 60° with 2.5 N HCl for 6 h. The filtered alumina, after thorough washing with water, was then activated by being heated at 120–140° for 24 h. Thin-layer chromatography was performed with a silica gel by use of microscope slides, with ethyl acetate as the solvent.

IR spectra were measured in KCl pellets, and UV and visible spectra in meth-

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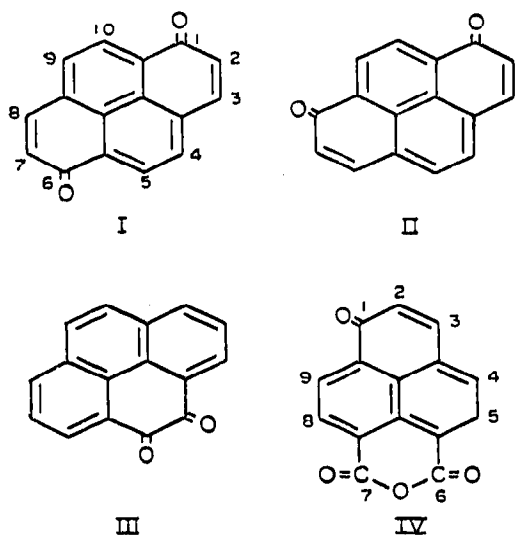
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anol solution, by means of commercial recording spectrophotometers (Perkin-Elmer "Infracord", Model 137\*, and Beckman DK-2\*, respectively).

### Materials

*Crude mixture containing 1,6-pyrenedione (I) and 1,8-pyrenedione (II).* This was prepared by following, approximately, the procedure of GOLDSCHMIEDT<sup>3</sup>. A mixture of finely ground pyrene (10 g) and  $K_2Cr_2O_7$  (15 g) in 100 ml of *ca.* 4 N  $H_2SO_4$  was heated at 90° for one hour and then refluxed for one hour. The reaction mixture was diluted with cold water and filtered, and the insoluble material was washed and dried; yield, 10.6 g.

*4,5-Pyrenedione (III).* This dione was prepared by oxidation of pyrene in aqueous acetone with  $NaIO_4$  and  $OsO_4$  according to the published procedure<sup>4</sup>. The crude dione was purified on a column of alumina, with benzene as the developing



solvent. A sample was recrystallized from chlorobenzene and then from glacial acetic acid, yielding yellow-orange needles, m.p. 303–305°; lit. m.p. 304.5–306.5°<sup>4</sup>; 310°<sup>2</sup>. The dione produces a blue color in concentrated  $H_2SO_4$ .

*1-Oxo-6,7-phenalenedicarboxylic acid anhydride ("pyrenic acid anhydride") (IV).* A solution of a crude mixture of 1,6- and 1,8-pyrenediones (550 mg) in glacial acetic acid (65 ml) was oxidized with chromic acid (2.5 g of  $CrO_3$ ) in 3 ml of water by heating the mixture under reflux for 30 min. The dark solution was concentrated to about 10 ml and poured into an excess of cold water. The crude, precipitated acid was separated by filtration, thoroughly washed on the funnel with cold water, and stirred with 500 ml of 5% aqueous  $NaHCO_3$  at 40° for one hour. The suspension was filtered, the insoluble portion was discarded, and the filtrate was neutralized with HCl and kept overnight at room temperature. The resulting light-yellow crystals, on recrystallization from acetic anhydride, yielded the anhydride of "pyrenic acid" (250 mg);

\* Certain commercial instruments are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment identified is necessarily the best available for the purpose.

lustrous light-yellow plates, m.p. 274–276° (darkening at 260°); lit. m.p. above 250°<sup>5</sup>; 174°<sup>2</sup> (printer's error?).

#### *Chromatographic separations*

*Packing of the column.* A column provided with a suitable plug (thick filter paper on a perforated disc above the stopcock) was partially filled with glacial acetic acid; silica gel was gradually added (exothermic reaction!), and the solvent was allowed to drip from the column during the packing. By means of a glass rod sealed to a glass disc, the adsorbent was frequently mixed and packed, to minimize irregularities in the column. The solid column of silica was gradually built up, with alternate additions of acetic acid and dry adsorbent. The column was finally topped with a layer, 2-cm thick, of small glass beads.

*Separation of 1,6- from 1,8-pyrenedione.* A mixture of crude 1,6- and 1,8-pyrenediones (4 g) was dissolved in 150 ml of hot, glacial acetic acid with stirring; the dark solution was cooled to 35–40° and filtered through glass wool. (The dark residue, about 250 mg, was discarded.) The filtrate was poured onto a silica gel column (5 × 50 cm), and this was eluted with glacial acetic acid (2 to 2.2 l; rate, 1.5 ml per min). Four bands were produced on the column, and each was collected as the elution proceeded:

(1) Light-brown band (about 800 mg; unreacted pyrene; green-blue fluorescence).

(2) Dark-brown band (about 250 mg; unreacted pyrene, hydroxylated pyrene impurities, and some "pyrenic acid"; dark-brown and yellow-green spots on a thin-layer chromatogram).

(3) Yellow-brown band (about 650 mg; primarily "pyrenic acid"; brown and yellow-green spots on a thin-layer chromatogram).

(4) Orange-red band (1.6 to 1.8 g; a mixture of 1,6- and 1,8-pyrenediones; a yellow spot and an orange spot on a thin-layer chromatogram).

The orange-red eluate from band 4 was concentrated to about 100 ml, and was then re-chromatographed on a silica gel column. Elution with glacial acetic acid afforded three bands: (a) yellow (about 300 mg; one yellow spot on a thin-layer chromatogram, corresponding to 1,6-pyrenedione); (b) yellow-orange (about 300 mg; a yellow and a red spot on a thin-layer chromatogram, corresponding to a mixture of 1,6- and 1,8-pyrenediones); and (c) a red band (about 1000 mg; a red spot on a thin-layer chromatogram, corresponding to 1,8-pyrenedione).

For analytical purposes, a sample of 1,6-pyrenedione was dissolved in a 1:1 mixture of *p*-dioxane and benzene, purified on an alumina column (benzene eluant), and recrystallized from glacial acetic acid, yielding yellow or slightly orange needles, m.p. 324–326°; lit. m.p. 309°<sup>2</sup>; 310–312°<sup>6</sup>. When dissolved in conc. H<sub>2</sub>SO<sub>4</sub>, it produced an orange-red color. An analytical sample of 1,8-pyrenedione was purified on a silica gel column (HOAc eluant), and was recrystallized from glacial acetic acid; red, lustrous plates, m.p. 272–273°; lit. m.p. 270°<sup>2</sup>; 270–272°<sup>6</sup>; it produced an olive-green color in conc. H<sub>2</sub>SO<sub>4</sub>.

#### DISCUSSION AND RESULTS

Although the yield of the mixed 1,6- and 1,8-pyrenediones in the oxidation mixture obtained from pyrene had been reported to be 90%<sup>2</sup>, a repetition of that

oxidation procedure, followed by column chromatography, gave only about a 50 % yield of the above mixed diones. Also, the ratio of 1,6-pyrenedione to 1,8-pyrenedione, as isolated by column chromatography, was approximately 1:2; that previously reported<sup>2</sup> was 1:3. By the chromatographic procedure reported here, 4 g of the crude mixture yielded about 400 mg (10 %) of pure 1,6-pyrenedione and 900 mg (22 %) of pure 1,8-pyrenedione.

1-Oxo-6,7-phenalenedicarboxylic acid anhydride ("pyrenic acid anhydride") was prepared and analyzed, in order to permit distinguishing between the desired products and the main impurity (that was always present in the mixture resulting from the oxidation of pyrene with chromic acid or other oxidizing agents).

The required reference compound, 4,5-pyrenedione, was isolated in somewhat lower yield than that reported<sup>4</sup>; recrystallization of the dione from chlorobenzene was found to be important in elimination of an impurity absorbing in the infrared at 5.8  $\mu$ .

The product of oxidation of pyrene with 30 %  $H_2O_2$ , reported to be a mixture of 1,6- and 1,8-pyrenediones<sup>7</sup>, was found to be a complex mixture which could not be separated by column chromatography.

For identification purposes, the complete infrared spectra of 1,6-, 1,8-, and 4,5-pyrenediones and of 1-oxo-6,7-phenalenedicarboxylic acid anhydride ("pyrenic acid anhydride") are reproduced in Fig. 1. The spectra of all three diones show no absorption, due to  $-C=O$  stretching, below 6  $\mu$ , but show such absorption in the region (6.0 to 6.2  $\mu$ ) typical of polycyclic, aromatic quinones<sup>8</sup>. The absorption bands are in agreement with those previously reported (1,6- and 1,8-pyrenediones, 6.1  $\mu$ <sup>9</sup>; 4,5-pyrenedione, 6.0  $\mu$ <sup>4</sup>). Any contamination of the diones by "pyrenic acid" or its anhydride was indicated by absorption in the region below 6  $\mu$ . Fig. 1, IV shows a doublet at 5.6 and 5.7  $\mu$ , in agreement with that reported for other acid anhydrides<sup>10</sup>. A transparent region is found between 9.0 and 11.0  $\mu$  for both 1,6- and 1,8-pyrenediones, whereas strong absorption bands in this region are observed for 4,5-pyrenedione. The above diones show characteristic absorption bands in the "finger print" region between 11.0 and 13.0  $\mu$ .

The absorption bands of the pyrenediones and of "pyrenic acid anhydride" in

TABLE I

U.V. AND VISIBLE SPECTRA OF PYRENEDIONES IN METHANOL \*

1,6-Pyrenedione		1,8-Pyrenedione		4,5-Pyrenedione		"Pyrenic acid anhydride"	
$\lambda_{max}$	$\epsilon$	$\lambda_{max}$	$\epsilon$	$\lambda_{max}$	$\epsilon$	$\lambda_{max}$	$\epsilon$
237	23300	238	30000	238	64900	256	16500
243 (sh)	20400	241 (sh)	29300	254	24600	260 (sh)	15900
251 (sh)	8700	248 (sh)	24400	280	11300	367	13100
265	6900	268 (sh)	9300	291	15300	396 (sh)	13100
277	3300	282 (sh)	6700	308	8600	408 (sh)	9900
351 (sh)	3600	291 (sh)	4100	322	7600		
379 (sh)	9300	306 (sh)	3200	368 (sh)	1400		
400	15600	351	9900	420	2500		
428	16700	366 (sh)	8800				
448	15600	395	5800				
		458	9400				

\* Spectra were recorded 30 min after dissolution of the sample.

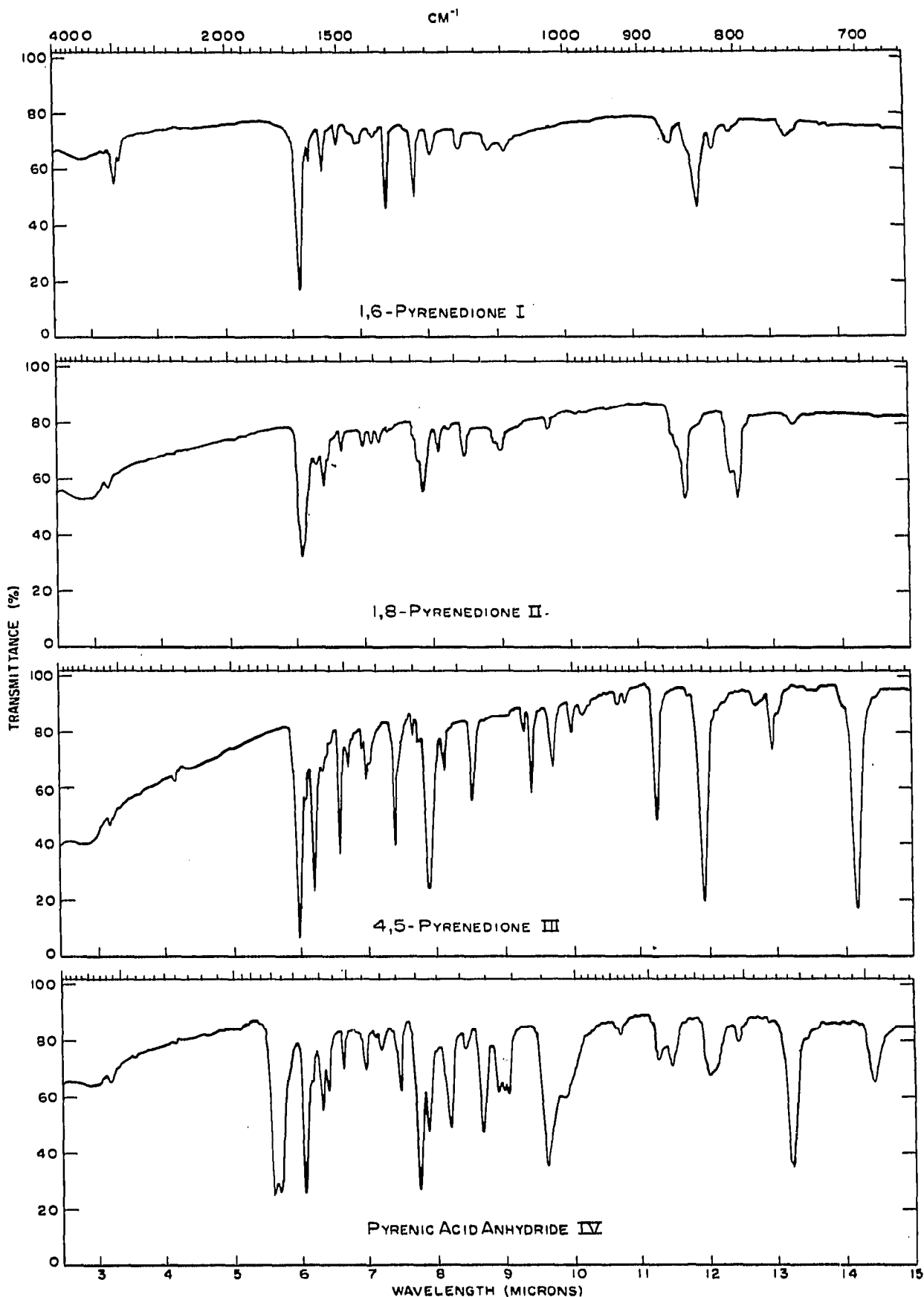


Fig. 1. Spectrograms of materials in potassium chloride pellets. I = 1,6-pyrenedione; II = 1,8-pyrenedione; III = 4,5-pyrenedione; IV = 1-oxo-6,7-phenalenedicarboxylic acid anhydride.

the U.V. and visible regions are listed in Table I. The U.V. spectra for 1,6- and 1,8-pyrenedione differ somewhat from those already published<sup>6</sup>. This is the first report on the complete U.V. and visible spectra for 4,5-pyrenedione and "pyrenic acid anhydride". 4,5-Pyrenedione shows sharp bands at 308 and 322  $m\mu$ , not exhibited by the two other diones.

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#### SUMMARY

The 1,6- and 1,8-pyrenediones were separated directly on a column of silica gel by means of glacial acetic acid as the eluant. The final purification of 1,6-pyrenedione was accomplished on a column of activated alumina by use of benzene as the solvent. The infrared and ultraviolet spectra of purified 1,6-, 1,8-, and 4,5-pyrenediones and of 1-oxo-6,7-phenalenedicarboxylic acid anhydride were recorded.

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