

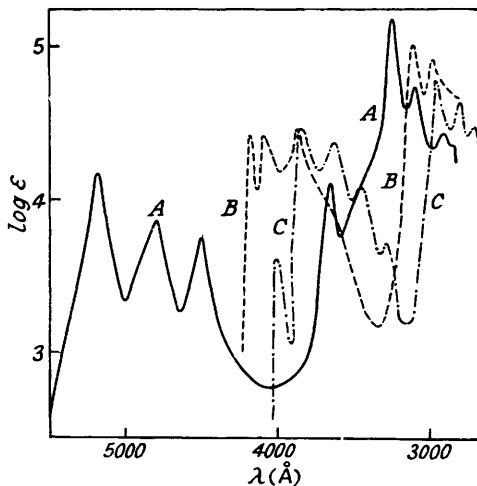
97. 8 : 9-Benzonaphtho(2' : 3'-3 : 4)pyrene.

By JOHN FREDERICK GROVE.

The yellow hydrocarbon, m. p. 320°, obtained by Schroeter (*Ber.*, 1924, 57, 1990) by the action of aluminium chloride on octahydroanthracene, has been dehydrogenated to a red hydrocarbon $C_{28}H_{16}$, shown on spectroscopic evidence to be 9 : 10-benzonaphtho(2' : 3'-4 : 5)pyrene (III). The yellow hydrocarbon is the corresponding terminal octahydro-compound (II).

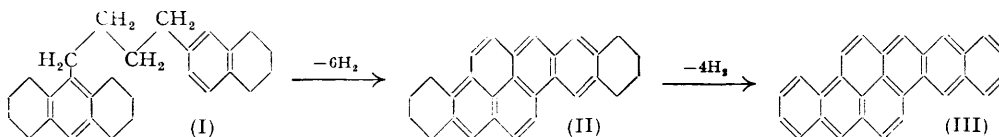
SCHROETER (*Ber.*, 1924, 57, 1990) observed that treatment of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene (octhracene) with 5% anhydrous aluminium chloride for a short time at 80° yielded a mixture of unchanged octahydroanthracene (45%), 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenanthrene (octanthrene) (45%), dodecahydrotriphenylene, a viscous, high-boiling oil, and a yellow hydrocarbon, m. p. 320°. Repetition of this work has confirmed

Ultra-violet absorption spectra.
 A, 8 : 9-Benzonaphtho(2' : 3'-3 : 4)pyrene (III).
 B, The octahydro-derivative (II) of (III).
 C, 3 : 4-Benzopyrene.



Schroeter's results apart from the yields of products, other than octahydrophenanthrene, which were lower.

Dehydrogenation of the yellow hydrocarbon $C_{28}H_{24}$ with palladium-charcoal gave 4 mols. of hydrogen and a red hydrocarbon $C_{28}H_{16}$. The ultra-violet absorption of this



compound (see Figure) was in excellent agreement with that calculated (Table 1) according to Clar's empirical methods (*Ber.*, 1936, 69, 607, 1671; 1940, 73, 81) for the hitherto undescribed 8 : 9-benzonaphtho(2' : 3'-3 : 4)pyrene (III). As might be expected from this correlation, the value (in cm^{-1}) for the lowest-frequency absorption band of the red hydrocarbon also fits correctly into the missing place between 3 : 4-8 : 9-dibenzopyrene and dinaphtho(2' : 3'-3 : 4)(2'' : 3''-8 : 9)pyrene in the scheme drawn up by Cook, Schoental, and Scott (*Proc. Phys. Soc.*, 1950, 63, A, 592).

TABLE I. Calc. for 8 : 9-benzonaphtho(2' : 3'-3 : 4)pyrene according to Clar.

Group	R (cm^{-1})	K (calc.)	$K^2/R = \lambda$ (Å)	Found : λ (Å)
p	1.0865×10^6	7.5	5177	5160
o β	3.208×10^6	10.2 ± 0.1	3180—3308	3250

It follows that the yellow hydrocarbon is the corresponding 1'' : 2'' : 3'' : 4'' : 5'' : 6'' : 7'' : 8''-octahydro-derivative (II) and in confirmation of this the ultra-violet absorption spectrum

(Figure) closely resembles that of 3:4-benzopyrene, the bands being shifted slightly towards longer wave-lengths. The fluorescence spectrum of (II) is also similar to that of 3:4-benzopyrene, the bands being shifted by 1000 cm^{-1} towards the red in quantitative agreement with the available data on pyrene and 1':2':3':4'-tetrahydro-3:4-benzopyrene (Table 2). The spacings between the bands in the fluorescence spectra and between the

TABLE 2.

Ultra-violet spectra (in benzene).							
Compound	$\nu \times 10^{-2}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\log \epsilon$	Compound	$\nu \times 10^{-2}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\log \epsilon$
(III)	193.8		4.15	(II)	240.4		4.40
	208.0	1420	3.87		245.0	1390	4.42
	222.2	1420	3.75		258.9		4.50
	273.2		4.10		320.8		5.00
	307.7		5.17		334.7	1390	4.90
	322.2	1450	4.74				
	344.2		4.43				
	351.8		4.34				

Fluorescence spectra.

Compound	$\nu \times 10^{-2}$ (cm^{-1})	Compound	$\nu \times 10^{-2}$ (cm^{-1})	Shift due to $-\text{[CH}_2\text{]}_4-$ (cm^{-1})
Pyrene ^a	268.5	1':2':3':4'-Tetrahydro-3:4-benzopyrene ^a	263	550
	264		250	—
	261		—	—
	258		—	—
3:4-Benzopyrene ^a	248	(II)	237.8	2 × 510
	234		224.2	2 × 490
	220.5		210.5	2 × 500
(III) ^b	190.5		—	—
	177.0		—	—
	163.1		—	—

^a Schoental and Scott (*J.*, 1949, 1683); solution in light petroleum. ^b Solution in benzene.

bands in each group in the absorption spectra are constant within the limits of experimental error for both (II) and (III) and are close to the expected value of 1400 cm^{-1} .

Cook and Hewett (*J.*, 1933, 398) suggested that the formation of 3:4-benzopyrene by the action of aluminium chloride on tetrahydronaphthalene arose by dehydrogenation of 1-phenyl-4-1'-tetralylbutane. By a similar process (I) (from 2 mols. of octahydroanthracene) could give rise to the octahydrobenzonaphthopyrene (II).

EXPERIMENTAL

M. p.s are uncorrected. Microanalyses are by Weiler and Strauss, Oxford.

Ultra-violet Absorption Spectra.—These were obtained by using a Hilger medium quartz spectrograph in conjunction with a Spekker spectrophotometer.

Fluorescence Spectra.—Light from a mercury arc, after passing through a filter and lens system, entered the quartz cell containing the solution to be examined at right angles to the slit of the spectrograph and a few mm. from it. Exposures varied from 5 min. to 1½ hr. Solutions were approx. 10^{-5}M in benzene: excitation radiation 3650 Å.

1'':2'':3'':4'':5':6':7':8'-Octahydro-8:9-benzonaphtho(2':3'-3:4)pyrene (II). The brown gummy residue, b. p. $>160^\circ/1.5$ mm. (approx. 10 g.), from the treatment of 1:2:3:4:5:6:7:8-octahydroanthracene (70 g.) with anhydrous aluminium chloride (3.82 g.) for 3 hours at 90° (cf. Schroeter, *loc. cit.*) was digested with ether (100 ml.) and set aside for some hours. The yellow insoluble residue (3.7 g.) was sublimed at $280^\circ/1$ mm. The sublimate, colourless prisms (1.0 g.), m. p. 232° , from benzene-acetic acid, was identified as dodecahydrotriphenylene by dehydrogenation (5.8 mols. of hydrogen evolved) to triphenylene, identical with an authentic specimen. The unsublimed residue (2.7 g.) crystallised from benzene in yellow plates, m. p. 320° (1.0 g.), of 1'':2'':3'':4'':5':6':7':8'-octahydro-8:9-benzonaphtho(2':3'-3:4)pyrene [Found: C, 93.2; H, 6.8%; *M* (Rast), 393. $\text{C}_{28}\text{H}_{24}$ requires C, 93.3; H, 6.7%; *M*, 360]. It showed an intense violet fluorescence in benzene.

8:9-Benzonaphtho(2':3'-3:4)pyrene (III).—The above yellow hydrocarbon (0.16 g.), when heated at 320 — 350° in the presence of palladised charcoal (0.03 g.) in carbon dioxide, evolved 3.8 mols. of hydrogen. The dark red residue crystallised from a large volume of hot toluene in red plates (0.10 g.) of 8:9-benzonaphtho(2':3'-3:4)pyrene, m. p. 338 — 339° (Found: C, 95.1;

H, 4.9. $C_{23}H_{18}$ requires C, 95.4; H, 4.6%). It showed an intense green fluorescence in benzene.

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