NEW POLYCYCLIC AROMATIC HYDRO-CARBONS WITH SEVEN FUSED RINGS¹⁻⁸

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Abstract—Four new polycyclic aromatic hydrocarbons containing seven fused rings have been synthesized and their properties described. The spectral data relating to the new compounds are discussed and Clar's principles of annelation have been applied to substantiate the assigned structures.

INTRODUCTION

A GREAT deal of interest is currently being focused on polycyclic aromatic hydrocarbons. These compounds provide interesting models for studies in organic synthesis and physical organic chemistry including spectroscopic studies of various sorts, as well as physiological activity—molecular structure correlations. Although many studies have been made with polycyclic hydrocarbons containing four, five and six fused benzene rings there is a paucity of information regarding the seven fused ring compounds.⁵ This is exemplified in the area of physical-organic chemical studies⁶ as well as in physiological activity studies.⁷ One gets the impression from reading the literature⁷ that few compounds containing seven fused benzene rings have ever been tested for carcinogenic activity and that those which were tested were found to be inactive. Clar's recent two volume treatise on polycyclic hydrocarbons lists thirty-four isomeric hydrocarbons containing seven fused rings with no report regarding carcinogenic activity although these data are given for the four, five and six ring compounds. This is somewhat disturbing since we have learned recently⁸ that naphtho(2,1-a)perylene which we recently synthesized⁹ and which has seven fused benzene rings appear to be a potent carcinogen.

As shown in Chart I, the desired products were first prepared by the dehydrogenation of an appropriate naphthylbenz (a) anthracene.¹⁰

- ¹ The nomenclature used in this paper is that presented in the "Definitive Rules for Nomenclature of Organic Chemistry, J. Amer. Chem. Soc. 82, 5545 (1960).
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- Allied Chemical Corporation Fellow 1963–1964.
- ⁸ E. Clar, Polycyclic Hydrocarbons, 2 Vols., Academic Press, New York (1964).
- A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemistry, J. Wiley, New York (1961).
- ⁷ D. Clayson, *Chemical Carcinogenesis*. Little, Brown and Co., Boston (1962); I. Hieger, *Carcinogenesis*. Academic Press, New York (1961) see also Chapt. 18 in Ref. 5.
- ^e Private communication from Dr. Paul Kotin, Associate Director for Field Studies, National Cancer Institute, National Institutes of Health, Bethesda, Md.
- * F. A. Vingiello, W. W. Zajac Jr. and L. Mahone, J. Org. Chem. 28, 3253 (1963).
- ¹⁰ For the synthesis of these starting compounds see: F. A. Vingiello, A. Borkovec and W. Zajac, Jr., J. Amer. Chem. Soc. 80, 1714 (1958).



* All rings are aromatic unless indicated otherwise.

the influence of $AlCl_3$ or related Friedel-Crafts catalysts is generally known as a Scholl reaction. It appears that $AlCl_3$ produces the same effect at a temperature below or a little above 100° as pyrolysis at much higher temperatures. Although in some cases very complex reaction mixtures are formed and the yields are low, owing to possible side reactions including cracking, the results are usually much better than in the case of pyrolysis.

Naphtho(1,2-a)perylene (III). In view of these facts it seemed useful to attempt the cyclodehydrogenation of 12-(1-naphthyl)benz(a)-anthracene (1) using powdered anhydrous $AlCl_3$ well mixed in acidic alumina and heated under reduced pressure. This reaction was tried at various temperatures, but to no avail. Results were no different when benzene was used as a solvent, as recommended in similar cyclode-hydrogenation reactions by $Clar.^{12}$ Finally, the use of benzene was rejected since in similar instances it has been known to complicate the cyclodehydrogenation reactions with an accompanying phenylation.^{13.14}

Clar and Zandar¹² have reported a successful cyclodehydrogenation of 9,9'-diphenanthryl to dibenzo(b, n)perylene in better than 50% yield. The procedure employed the use of a mixture of anhydrous AlCl₃ and anhydrous SnCl₄ as the catalyst.

It was Nenitzescu^{15,16} who first called attention to the fact that anhydrous, freshly sublimed, pure AlCl₃ fails to initiate certain Friedel-Crafts reactions, but these reactions take place if the AlCl₃ is activated by the presence of water or an acidic cocatalyst. Nenitzescu and Cantuniari¹⁵ have shown that cyclohexane, even at reflux temperature, remains completely unchanged if it is in contact with pure freshly sublimed AlCl₃ in the absence of moisture. However, by addition of water reaction takes place. Similar results were obtained by adding HCl or HBr to the reaction mixture. From these results Nenitzescu concluded that the substance added acts in such a way as to activate the AlCl₃. Later Ott and Brugger¹⁷ among many other investigators of Friedel-Crafts reactions concluded that tin, silicon and tellurium tetrachlorides had a similar co-catalyst effect.

When the procedure of Clar was modified in view of the above facts, the results were very successful.

Anhydrous $AlCl_3$ and anhydrous $SnCl_4$ were added to a mixture of 12-(1-naphthyl)benz(a) anthracene (I) and activated acidic alumina. The pressure was reduced to 1 mm and the mixture was heated at 150° for 1 hr. An unusually high yield of 60% of the desired naphtho(1,2-a) perylene (III) was obtained.

Naphtho(2,1-1)benzo(a)pyrene (IV). Heldman¹⁸ has shown that AlCl₃ is activated in reactions with hydrocarbons by substances like NaBr and NaCl. By taking advantage

- ¹² E. Clar and M. Zander, J. Chem. Soc. 1861 (1958).
- ¹⁸ M. Zander, Chem. Ber. 92, 2749 (1959).

¹¹ C. Friedel and J. M. Crafts, Bull. Soc. Chem. Fr. 39, 195 (1883).

¹⁴ F. A. Vingiello and T. J. Delia, J. Org. Chem. 29, 2180 (1964).

¹⁵ C. D. Nenitzescu and E. I. P. Cantuniari, Ber. Dtsch. Chem. Ges. 66, 1097 (1933).

¹⁴ C. D. Nenitzescu, I. Necsain, A. Glatz and M. Zalman, Chem. Ber. 92, 10 (1959).

¹⁷ E. Ott and W. Brugger, Z. Electrochem. 46, 105 (1940).

¹⁸ J. D. Heldman, J. Amer. Chem. Soc. 66, 1789 (1944).

of this fact Clar,¹⁹ and Badger²⁰ and others have effectively applied AlCl_o-NaCl melt cyclization reactions at temperatures slightly over 100°. This method becomes particularly profitable when the use of solvents is restricted or not recommended. Thus, 1-benzoylnaphthalene gives benzanthrone only in a very small yield when heated with powdered anhydrous AlCl_a alone at 140°. The disadvantage of this method is that the reaction mixture is not a homogeneous melt, but a sticky, semi-solid mass, which cannot be stirred effectively. The method becomes technically feasible if the AlCl₂ is replaced with a mixture of one part NaCl and five parts AlCl₃. This forms a melt which can be efficiently stirred. In this way 1-benzoylnaphthalene gives benzanthrone in 76% yield.²¹ 1,5-Dibenzoylnaphthalene yields the important dibenzo(a,h)pyrene-3, 8-quinone, a condensation which could not be achieved by the plain $AlCl_8$ method.²² Clar has shown that CO₂ can be used as a hydrogen acceptor in this type of reaction.¹⁹ For example, if 5-(1-naphthyl)tetracene is treated with a NaCl-AlCl_a melt permeated with CO₂, cyclodehydrogenation is achieved in good yield with the formation of dibenzo(a,f)perylene and a fluoranthene derivative. The success encountered by Clar¹⁹ suggested that this last procedure might prove fruitful in the ring closure of I. When I was added to a melt of five parts of anhydrous AlCl_a and one part of NaCl maintained at 130° and permeated with a strong stream of dry CO₂ naphtho(2,1-1)benzo-(a)pyrene (IV) was isolated in 10% yield after an extensive work-up. The reaction time was nine minutes. Longer reaction times lead to tars, as did an atmosphere of air.

Naphtho(1,2-1)benzo(a) pyrene (V) and naphtho(2,3-1)benzo(a) pyrene(VI). When the procedure just described for the preparation of IV was applied to 12-(2-naphthyl) benz(a)-anthracene (II), there was obtained, after an extensive work-up, 21 % of V and 4% of VI.

The structures of the new polycyclic aromatic hydrocarbons (III-VI) were established by elemental analysis and by UV, visible, and IR absorption spectra. Furthermore, an application of Clar's principles of annelation²³ and the formation of TNF²⁴ molecular compounds further substantiate the assigned structures.

It should be emphasized that the compounds were prepared in a high degree of purity and each showed only one sharp peak upon g.p.c. analysis. Many of the earlier preparations of polycyclic hydrocarbons led to compounds of doubtful purity and this in turn caused difficulties in evaluating the properties of these compounds. For example, pyrene was thought to be a yellow hydrocarbon and a quinonoid structure was held responsible for its colour.²⁵ However it has been shown that the yellow colour originates from a trace of tetracene which can be removed by treatment with maleic anhydride.²⁶ The earlier observations that chrysene was carcinogenic²⁷ are now ascribed to a small amount of 1,2-benzcarbazole in the chrysene. Chrysene purified by chromatography does not exhibit carcinogenic activity.²⁸ Impure dibenz(a,c)anthracene is feebly carcinogenic, but this is not apparently the case for the pure

- ¹⁹ E. Clar and W. Willicks, *Liebigs Ann.* 601, 193 (1956).
- ²⁰ G. M. Badger, J. Chem. Soc. 4417 (1957).
- ²¹ R. Scholl and C. Seer, Liebigs Ann. 394, 111 (1912).
- ²³ R. Scholl and E. Naumann, Ber. Disch. Chem. Ges. 55, 118 (1922).
- ²⁹ E. Clar, Polycyclic Hydrocarbons Vol. I p. 40. Academic Press, New York, N.Y. (1964).
- ²⁴ 2,4,7-Trinitrofluorenone.
- ²⁵ G. Goldschmiedt, Liebigs Ann. 351, 218 (1907).
- 26 E. Clar, Ber. Dtsch. Chem. Ges. 65, 1427 (1932).
- ²⁷ C. C. Twort and J. D. Fulton, J. Path. Bact. 33, 119 (1930).
- ** O. Schürch and A. Winterstein, Hoppe-Seyl. Z. 236, 79 (1935).

hydrocarbon.²⁹ Appropriate samples of III, IV, V and VI were prepared for carcinogenic activity studies. Unfortunately VI decomposed slowly on standing and so only III, IV and V are currently being tested.

Naphtho(1,7,8-efg)anthanthrene (VII). On examination of the structure of naphtho-(1,2-a)perylene (III) and naphtho(2,1-l)benzo(a)pyrene (IV) it is obvious that on further cyclodehydrogenation both of these compounds should yield one and the same product, namely naphtho(1,7,8-efg)-anthanthrene (IV). These cyclizations besides contributing a new and otherwise very difficultly obtainable aromatic compound containing eight fused benzene rings, provide additional support for the structures of III and IV. When III was subjected to the AlCl₃-NaCl melt procedure and when IV was subjected to the AlCl₃-SnCl₄-Al₂O₃ procedure, as described earlier, the expected naphtho(1,7,8-efg)anthanthrene (VII) was obtained as shown in Chart II. The product from both reactions was identical as shown by elemental analysis, UV, visible and IR spectra, m.p. and mixture m.p. and by equivalence of TNF²⁴ adducts.

Other routes to naphtho(1,2-a) perylene (III) and naphtho(1,2-l) benzo(a) pyrene (V). In order to further establish the structures of the perylene III and the pyrene V obtained from the cyclodehydrogenation of 12-(1-naphthyl) benz(a) anthracene (I) and 12-(2-naphthyl) benz(a) anthracene (II) respectively, other routes of synthesis were undertaken.



¹⁹ J. W. Cook, I. Hieger, E. L. Kennaway, and W. V. Mayneord, *Proc. Roy. Soc.* B111, 455 (1942).
²⁰ Ref. 23 p. 47.

³¹ R. N. Jones and C. Sandorfy, in A. Weissberger, *Technique of Organic Chemistry*, Vol. IX, Interscience Publishers, Inc., New York, N.Y., 1956, pp. 247-580. It was felt that if 11-(1-naphthyl)benz(a)anthracene (XI) could be prepared it might be readily converted to III (see chart III). Therefore, the method of Burger and Mosettig³⁴ was used to prepare 11-keto-5,6,8,9,10,11-hexahydrobenz(a)anthracene (VIII). Vingiello *et al.*⁹ prepared 8-(1-naphthyl)benz(a)anthracene by allowing the appropriate Grignard reagent to react with 8-keto-8,9,10,11-tetrahydrobenz(a)anthacene, followed by dehydration and aromatization. Essentially following their procedure, 11-hydroxy-11-(1-naphthyl)-5,6,8,9,10,11,-hexahydrobenz(a)anthracene (IX) was prepared by allowing 1-naphthylmagnesium bromide to react with the ketone VIII. When the crude carbinol IX was distilled under reduced pressure dehydration occurred and 11-(1-naphthyl)-5,6,8,9-tetrahydrobenz(a)anthracene (X) was obtained. Aromatization of the tetrahydro compound X with Pd-C gave 11-(1-naphthyl)benz(a)anthracene (XI).

The procedure of Burger and Mosettig³⁴ was used to prepare 11-keto-8,9,10,11tetrahydrobenz(a)anthracene (XII). From this, 11-(1-naphthyl)benz(a)anthracene (XI) was prepared using procedures analogous to those just described (see Chart III). When XI was dehydrogenated III was produced. This product was identical in m.p. mixture m.p. and UV, visible and IR spectra to that obtained from I.

Another synthetic route to naphtho(1,2-1)benz(a)pyrene (V) is outlined in Chart IV. The method of Fieser and Heymann³⁵ was used to prepare 1-keto-1,2,3,4-tetrahydrobenz(a)anthracene (XV). This was allowed to react with 1-naphthylmagnesium bromide. Since alcohols of the type XVI are known to be relatively unstable, no attempt was made to isolate XVI in pure form. However, the crude product did show an OH peak in its IR spectrum. When XVI was distilled XVIII was isolated and not XVII. If XVII was formed at all, it apparently underwent a hydrogenation reaction under the conditions of the reaction. Similar observations have been reported.^{36,37} Aromatization of the tetrahydro compound XVIII with Pd–C yielded a yellow oil which had an UV spectrum typical of a fully aromatic benz(a)anthracene but resisted attempts at crystallization. Besides this yellow oil the reaction produced V. This product was identical in m.p. mixture m.p., and UV, visible and IR spectra to that obtained from II. Some physical properties of the new hydrocarbons and their TNF²⁴ adducts are shown in Table 1.

Clar's principles of annelation²³ as applied to the correlation of the color with the structure of polynuclear hydrocarbons, may be usefully applied to compounds III-VII (Table 1). These principles are especially useful in differentiating between the structures V and VI where these isomeric compounds arise as products of a single reaction. It is an easy task to assign the structure V to the purple compound since the number of sextets is not increased by linear annelation and big shifts of β -bands to longer wavelengths are observed. Angular annelation, as in the case of structure VI, brings in a new sextet and a shift to shorter wavelengths and, therefore, no particular deepening of the colour follows.

- ¹⁵ L. F. Fieser and H. Heymann, J. Amer. Chem. Soc. 63, 2333 (1941).
- ³⁸ E. Clar, Ber. Disch. Chem. bis. 63, 512 (1930).
- ³⁷ E. Clar, W. Kelly, and J. W. Wright, J. Chem. Soc. 1108 (1954).

³³ M. P. Groenwege, Colloquim Spectroscopicum Internationale VI Amsterdam p. 579. Pergamon Press, London (1956).

³⁸ Ref. 13. p. 2744.

⁴⁴ A. Burger and E. Mosettig, J. Amer. Chem. Soc. 59, 1302 (1937).



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Spectral interpretations

1. Ultraviolet spectra. In 1936 Clar introduced the comparative method in the study of the absorption spectra of polycyclic aromatic hydrocarbons and called it the annelation method, which attributes bands of similar intensity and general character to similar origin.³⁰ He showed that the condensed polycyclic hydrocarbons generally exhibit three main band systems in the near UV and visible regions of the spectrum which he classified as β , ρ and α systems. When the UV and visible absorption spectra of the hydrocarbons III-VII were measured, they were found to be similar to the spectra of their parent compounds as far as general shape and intensity are concerned. When the peak frequencies are compared (Tables 2-4) it is found that the values and positions of the peaks follow the principles of the annelation method.

A systematic study has shown that in uniplanar aromatic hydrocarbons, the ratio of the frequencies of the α - and β -bands is a constant, 1:1.35. This rule applies only if the hydrocarbons are uniplanar and there is no overlapping of hydrogen atoms, as in anthracene and pyrene. In diphenyl and in perylene there is some degree of overlapping and the loss of resonance energy in the case of perylene can be detected by the decrease ratio $\nu\alpha$: $\nu\beta = 1:1.30$. Owing to increased overlapping a higher degree of twisting or another type of strain can be assumed in naphtho(1,2-a)perylene (III) and the resulting loss of resonance energy becomes apparent in the ratio $\nu\alpha$: $\nu\beta$ which decreases to 1:1.28. This is a much higher degree of overlapping of hydrogen atoms in naphtho(2,1-1)benzo(a)pyrene (IV) and the ratio decreases accordingly to 1:1.27. A similar observation can be made with naphtho(1,2-1)benzo(a)pyrene. The loss of intensity and vibrational structure of these last curves as compared with the curve of the parent compound is striking. The degree of overlapping of hydrogen atoms is lower in naphtho(2,3-1)benzo(a)pyrene (VI) and the ratio rises accordingly to 1:1.31.

2. Infrared spectra. According to Jones³¹ the general characteristics of the IR absorption spectra of polycyclic aromatic hydrocarbons are the aromatic carbon-hydrogen stretching frequencies between 3090-3000 cm⁻¹, a number of bands centered around the 1600 cm⁻¹ and 1500 cm⁻¹ regions indicating the presence of aromatic rings, and a number of strong bands between 900 and 650 cm⁻¹. The IR spectra of hydro-carbons III-VII were consistent with these features. The γ -vibrations giving rise to the intense bands at 900-735 cm⁻¹ include the out of plane deformations of carbon-hydrogen bonds in the substituted aromatic rings. Groenwege³² has shown that this can be used to establish the structure of polycyclic hydrocarbons. Zander³³ recently applied this method to the identification of a tetrabenzopentacene, the synthesis of which from two molecules of triphenylene in an AlCl₃-ZnCl₂ melt was not unambiguous. Table 5 shows that compounds III-VI exhibit peaks at all four, "solo," "duo," "trio" and "quartet" carbon-hydrogen vibration regions, but as expected hydrocarbon VII had the "quartet" carbon-hydrogen vibration peak missing between 770 cm⁻¹ and 755 cm⁻¹.

Gas chromatographic analysis. Although the application of high-temperature gas chromatography with ionization detectors to polycyclic hydrocarbons has been described by several authors,³⁸⁻⁴⁰ most of this research deals with compounds having less than seven fused benzene rings and so it became necessary to extend the research in

³⁸ F. Duperi, Nat. Cancer Inst. Monogr. 9, 183 (1962).

³⁰ B. J. Gudzinowicz and W. R. Smith, Analyt. Chem. 32, 1767 (1960).

⁴⁰ E. Sawacki, Chemist-analyst. 53, No. 2, 60 (1964).

Table 4	E	IIV	nu	244	254	286	300	312		326	337	382	403	407		430	460			
			nm	240	257	287	297	310		350	367	385	402	408	424	433	466			
Table 3		IV	nu	240	254	264	274	281)	293/	307	323	336	352	384	4 04	440	470	•	-	1:31
		>	шu	243	253			282)	291)	311	327	337	352	370	406	430	460	•	-	1.27
	6 8	١٧	na	244	254			286)	293/	312	327	337		383	4 04	430	460	•	-	1.27
	43		nu	241	253	262	273	293		306	318	330	353	372	401	446			-	1:35
Table 2		III	nu		252	266	277	295		308	335	349		380	400	430			1	1:28
	878		nm	245	251	264	279	291		323	337	352	369	392	414	439			I	<u>1-30</u>

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		C—H Vibrations (cm ⁻¹)									
		Solo	Duo	Trio	Quartet						
		H	H H	H H							
		900860	860800	810-750	770–735						
	III	883	848	793 807	763						
	IV	869	849 830	808	755						
	v	868	854	800	769						
	VI	865	855	802	770						
	VII	895 865	849	802	_						
CH ₈	•	878	840	805 770	747						
CH ₃	•	878	840	805 770	747						
CH ₃	*	878	839	805 770	745						

TABLE 5

* The synthesis of these compounds has been reported, F. A. Vingiello and W. W. Zajac, J. Org. Chem., 26, 2228 (1961), but the infrared data were just taken and are included here for the sake of completeness.

this field. It is of prime importance to find conditions for detecting the two isomeric pairs of compounds III and IV and V and VI since each pair comes from the same starting material, namely I and II respectively. After many experiments the following satisfactory conditions were found.⁴¹

For detecting III and IV: Column $2' \times \frac{1}{4}$ " Cu containing 2.5% SE-30 on Chromosorb P, sample volume: 3 ul., carrier gas (He) flow at 40 p.s.i.g.: 60 ml/min, column temperature: 290°, detector temperature: 325°, sensitivity: 16×10^2 . Using these conditions a single peak was obtained with a retention time of 2 min 30 sec for IV and a single peak with a retention time of 5 min 20 sec for III. For detecting V and VI: column 6' $\times \frac{1}{4}$ " Cu containing 3.5% SE-30 on Gas-Chrom Z, sample volume: 10 ul., carrier gas (He), flow at 40 p.s.i.g.: 45 ml/min, column temperature: 310°, detector temperature: 368°, sensitivity: 16×10^2 . Using these conditions a single peak was obtained with a retention time of 5 min 10 sec for VI and a single peak with a retention time of 6 min 24 sec for V.

EXPERIMENTAL^{43,43}

Naphtho(1,2-a)perylene (III). A mixture of 0.5 g (0.0014 mole) of I, 0.5 g powdered anhydrous AlCl₂, 0.5 g anhydrous fuming SnCl₄ and 25 g of alumina was heated at 150° (1 mm) for 1 hr. The mixture was cooled to room temp. decomposed with 100 ml 10% HCl(aq) and then extracted with ether. The ether extract was washed with water, then with 3N NH₄OH₄, again with water, and dried over MgSO₄. The ether was replaced with benzene and upon addition of a small amount of EtOH, the hydrocarbon crystallized. The solid was filtered and the filtrate concentrated to yield additional product. The total yield was 0.30 g (60%).

An analytical sample was prepared by recrystallizing the hydrocarbon from 10% benzene-EtOH three times, yielding III as brick red microcrystals, m.p. 248-249°. (Found: C, 95.1; H, 4.9. $C_{18}H_{16}$ requires: C, 95.4; H, 4.6%.)

The 2,4,7-trinitrofluorenone adduct was prepared by mixing hot saturated solutions of III in benzene and TNF in EtOH. The yield was quantitative. The product on recrystallization from 10% benzene-EtOH gave fine brown needles, m.p. 298-299°. (Found: C, 73.8; H, 3.7; N, 6.3. $C_{e1}H_{21}N_{2}O_{7}$ requires: C, 73.8; H, 3.2; N, 6.3%.)

Naphtho(2,1-1)benzo(a)pyrene (IV). To a stirred melt of 10 g of anhydrous AlCl₂ and 2 g NaCl at 110° and under a strong stream of pre-heated, bone dry CO₃, 1·0 g (0·0028 mole) of I was added in one portion. The temp of the mixture was allowed to increase to 130° over a period of 9 min. Longer times led to tars, as did an atmosphere of air. The hot mixture was decomposed with an ice-cold 10% HClaq. The resulting dark solid, which fluoresced⁴⁴ greenish red, was filtered, washed with 3N NH₄OH, then water, and dried. The solid was then chromatographed using a 12 in coupled column.⁴⁶ A mixture of pet. ether⁴⁶ and benzene (1:1) was used to elute the first band which was colourless and fluoresced blue.⁴⁴ Benzene was used to elute the second band which was yellow and possessed a brilliant red fluorescene.⁴⁴ The benzene solution was concentrated and when EtOH was added, a red solid formed which was sublimed (0·1 mm). The crystalline sublimate was recrystallized from 10%

- ⁴¹ A Micro-Tek instrument Model GC-2500R equipped with a flame detector was used throughout this work.
- ⁴² All m.p. were taken on a Thomas-Hoover capillary m.p. apparatus and are corrected. All b.p. are uncorrected. IR data was obtained with a Beckman Model IR-5A spectrophotometer using KBr disks, UV and visible spectra were obtained with a Beckman model DK-2A spectrophotometer using solutions of 5 mg of compound in 95% EtOH in 1-cm quartz cells.
- 49 Analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.
- ⁴⁴ Under UV radiation from a Black-ray UV Long Wave (3660A) Lamp as the source. The lamp was manufactured by UV Products, Inc., San Gabriel, California.
- ⁴⁵ The coupled column was 1" × 9" (bottom) and 2" × 3" (top) and was packed with neutral alumina, Brockman Activity I, 80–200 mesh.
- ⁴⁰ Boiling range, 30–60°.

benzene-EtOH yielding IV as yellow neeedles, m.p. 321-322°, 0.103 g (10%). (Found: C, 95.2; H, 4.3. C₃₉H₁₆ requires: C, 95.4; H, 4.6%.)

The 2,4,7-trinitrofluorenone adduct was prepared as has been described above for III and was obtained as black needles m.p. 196–198°. (Found: C, 73.6; H, 3.1; N, 6.6. $C_{41}H_{31}N_3O_7$ requires: C, 73.8; H, 3.2; N, 6.3%.)

Naphtho(1,2-1)benzo(a)pyrene (V) and naphtho(2,3-1)benzo(a)pyrene (VI). The procedure just described above for the cyclodehydrogenation of I was applied to 1.0 g of II. On chromatography⁴⁵ three bands developed. The first band which was colourless and fluoresced blue was removed with pet. ether⁴⁶-benzene (1:1). The yellow and purple bands were separated with benzene. The yellow band which came off the column first gave a yellow solid when the benzene solution was concentrated. This solid was sublimed (0.1 mm) and the sublimate was recrystallized from 10% benzene-EtOH giving VI as small yellow needles, 0.04 g (4%), m.p. 221-222°. (Found: C, 95.4; H, 4.6. C₂₈H₁₆ requires: C, 95.4; H, 4.6%.)

The 2,4,7-trinitrofluorenone adduct was prepared as has been described for III and was obtained as brown crystals, m.p. 204–205°. (Found: C, 73.7; H, 3.4; N, 6.3. $C_{41}H_{21}N_3O_7$ requires: C, 73.8; H, 3.2; N, 6.3%.)

Compound V was obtained as small dark purple needles, 0.21 g (21%), m.p. 315-316°. (Found: C, 95.5; H, 4.6. $C_{18}H_{16}$ requires: C, 95.4; H, 4.6%.)

The 2,4,7-trinitrofluorenone adduct was prepared as has been described for III and was obtained as black needles, m.p. 215-216°. (Found: C, 73.9; H, 3.4; N, 5.8. $C_{41}H_{21}N_3O_7$ requires: 73.8; H, 3.2; N, 6.3%.)

Naphtho(1,7,8-efg)anthanthrene (VII). When the AlCl₃-NaCl melt procedure which was used to give IV was applied to 0.1 g (0.00024 mole) of III and the product hydrolyzed, a dark solid resulted which was chromatographed twice through a 12" column of neutral alumina using benzene as the eluant. Concentration of the benzene solution gave a dark solid which was sublimed (0.1 mm) and when the sublimate was recrystallized from 10% dimethylformamide-EtOH, VII was obtained as small, brown, shiny platelets, 0.0464 g (46%). m.p. 318-319°. (Found: C, 95.9; H, 4.1. C₁₈H₄₁ requires: C, 96.0; H, 4.0%.)

The 2,4,7-trinitrofluorenone adduct was prepared as has been described for III and was obtained as green crystals, m.p. 262–264°. (Found: C, 74·1; H, 3·2; N, 5·9. $C_{41}H_{19}N_{4}O_{7}$ requires: C, 74·0; H, 2·9; N, 6·3%.)

When the AlCl_s-SnCl₄-Al₅O₂ procedure which was used to give III was applied to 0.1 g (0.00024 mole) of IV, 0.0149 g (15%) of VII was obtained.

11-(1-Naphthyl)- $\overline{5}$,6,8,9-tetrahydrobenz(a)anthracene (X). A Grignard reagent was prepared from 2.74 g (0.113 g atom) Mg and 23.4 g (0.113 mole) 1-bromonaphthalene in 75 ml dry ether. When the reaction was complete the ether was replaced with 200 ml dry benzene. To the cooled solution, there was added 20.5 g (0.0826 mole) of VIII in a minimum amount of dry benzene over a period of 10 min. The clear solution which resulted was stirred for 21 hr at room temp and then cooled and decomposed with a solution of 20% NH₄Cl. The benzene layer was separated, washed with water, dried, and concentrated. The residual oil was distilled and the fraction boiling between 240-243° (0.2 mm) was collected. The product, X, was crystallized from benzene-MeOH (1:1) to give 9.55 g (32%) of colourless needles, m.p. 137-138°. (Found: C, 93.6; H, 6.4. C₁₈H₁₁ requires: C, 93.8; H, 6.2%.)

11-(1-Naphthyl)-8,9-dihydrobenz(a)anthracene (XIV). This compound was prepared essentially as was X. A Grignard reagent prepared from 0.247 g (0.0113 g atom) Mg and 2.34 g (0.0113 mole) 1-bromonaphthalene was allowed to react with 2.05 g (0.00833 mole) of XII. The product, XIV distilled between 152–160° (0.4 mm) and was crystallized from acetic acid to yield 0.58 g (19%) of colorless needles, m.p. 122–123°. (Found: C, 94.0; H, 5.8. $C_{18}H_{10}$ requires: C, 94.3; H, 5.7%.)

11-(1-Naphthyl)benz(a)anthracene (XI). A mixture of 0.5 g (0.0014 mole) of X, 0.44 g 10% Pd-C and 55 ml p-cymene was heated under reflux for 3 hr. The hot mixture was filtered free of catalyst and the solvent was removed under red. press. The light viscous oil which resulted was crystallized from ether.

An analytical sample was prepared via elution chromatography on 6 in of neutral aluminia using benzene as the eluant. The benzene solution was concentrated to ca. 25 ml and a small amount of EtOH was added which caused the product, XI, to crystallize as white needles, 0.42 g (84%), m.p. 165-166°. (Found: C, 94.7; H, 5.2. $C_{18}H_{18}$ requires: C, 94.9; H, 5.1%.)

In an analogous manner the dehydrogenation of 0.5 g (0.00141 mole) of XIV gave 0.41 g (82%) of XI.

Cyclodehydrogenation of 11-(1-naphthyl)benz(a)anthracene (XI). When the NaCl-AlCl₃ melt procedure, which has been described earlier, was applied to 0.5 g (0.0014 mole) of XI, there was obtained 55.2 mg (11%) of III, m.p. 248-249°.

When the AlCl_a-SnCl₄-Al₂O₈ procedure, which has been described earlier, was applied to 0.5 g (0.0014 mole) of XI, there was obtained 51 mg (10%) of III, m.p. 248-249°.

1-(1-Naphthyl)-1,2,3,4-tetrahydrobenz(a)anthracene (XVIII). This compound was prepared essentially as was X. A Grignard reagent prepared from 0.365 g (0.015 g atom) Mg and 2.53 g (0.0122 mole) 1-bromonaphthalene was allowed to react with 3.0 g (0.0122 mole) of XV. The product, XVIII distilled between 225-230° (0.35 mm) and was crystallized from EtOH to yield 1.05 g (24%) of colourless crystals, m.p. 177-178°. (Found: C, 93.5; H, 6.2. C₁₉H₁₂ requires: C, 93.8; H, 6.2%).

Cyclodehydrogenation of 1-(1-naphthyl)-1,2,3,4-tetrahydrobenz(a)-anthracene (XVIII). This reaction was conducted essentially as was the cyclodehydrogenation of XI. A mixture of 1.0 g (0.00279 mole) of XVIII, 0.88 g 10% Pd-C and 115 ml p-cymene gave 2.85 mg (3%) dark purple feathery needles which was identified as the previously described V, m.p. 315-316°; visible, UV and IR spectra were superimposable with authentic spectra. The residual oil resisted attempts at crystallization but the UV spectrum showed a typical benz(a)anthracene curve and is presumed to be XIX.

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