[Contribution from the Chemical Laboratories of the Virginia Polytechnic Institute]

Some New Alkyl 1,2,3,4-Dibenzopyrenes

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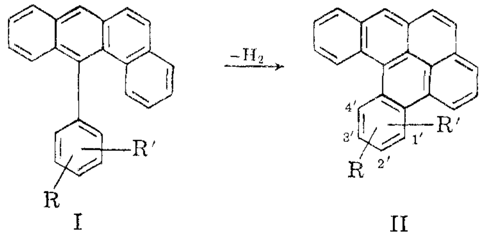
Using a previously described method, 9-mono- and dimethylphenyl-1,2-benzanthracenes were prepared and catalytically cyclodehydrogenated to give a series of new alkyl-substituted 1,2,3,4-dibenzopyrenes.

Recent studies on the environmental and health aspects of air pollution have unveiled the fact that the organic fraction of air pollutants contains polycyclic aromatic hydrocarbons,[4] some of them known carcinogens, others unknown compounds.[5] This discovery has led some workers to associate the presence of polycyclic aromatic compounds in air with the increase in the incidence of lung cancer. Shore and Katz[5] have pointed out the difficulty of identifying small quantities of alkyl substituted polynuclear aromatic hydrocarbons of unknown structure suspected of being present in polluted air. We sought to alleviate this problem by preparing some methyl[6] derivatives of 1,2,3,4-dibenzopyrene, a potent carcinogen discovered over twenty years ago[7] and a likely air pollutant. Only the 7-methyl-[8] and 5-phenyl[7]-1,2,3,4-dibenzopyrenes have been prepared previously.

An observation of Vingiello and Borkovec[9] made during a study of the aromatic cyclodehydration of ketones to 9-aryl-1,2-benzanthracenes (I) suggested the possibility of cyclodehydrogenating these compounds to 1,2,3,4-dibenzopyrenes (II).

The 9-mono- and dimethylphenyl-1,2-benzanthracenes (I) required for this study were synthesized according to the procedure of Vingiello and Borkovec.[9,10] Of all the benzanthracenes (Ia–Ii) in only two cases, namely, Ic and Ih, are the *ortho*-positions in the phenyl ring different, leading to the possibility of two isomeric products being formed by the loss of hydrogen. In Chart I the structures given for IIc and IIh list as the first possibility that structure resulting from loss of a hydrogen atom in the phenyl ring *para* to a methyl group in preference to loss of a hydrogen *ortho* to a methyl group.



I II

I. (a) $R = R' = H$
(b) $R = 2\text{-}CH_3, R' = H$
(c) $R = 3\text{-}CH_3, R' = H$
(d) $R = 4\text{-}CH_3, R' = H$
(e) $R = 2\text{-}CH_3, R' = 3\text{-}CH_3$
(f) $R = 2\text{-}CH_3, R' = 4\text{-}CH_3$
(g) $R = 2\text{-}CH_3, R' = 5\text{-}CH_3$
(h) $R = 3\text{-}CH_3, R' = 4\text{-}CH_3$
(i) $R = 3\text{-}CH_3, R' = 5\text{-}CH_3$
II. (a) $R = R' = H$
(b) $R = 4'\text{-}CH_3, R' = H$
(c) $R = 3'\text{-}$ or $1'\text{-}CH_3, R' = H$
(d) $R = 2'\text{-}CH_3, R' = H$
(e) $R = 4'\text{-}CH_3, R' = 3'\text{-}CH_3$
(f) $R = 4'\text{-}CH_3, R' = 2'\text{-}CH_3$
(g) $R = 4'\text{-}CH_3, R' = 1'\text{-}CH_3$
(h) $R = 3'\text{-}$ or $1'\text{-}CH_3, R' = 2'\text{-}CH_3$
(i) $R = 3'\text{-}CH_3, R' = 1'\text{-}CH_3$

The dehydrogenating activity of aluminum chloride has often been used in the preparation of highly condensed aromatic hydrocarbons. Unfortunately, the reaction suffers because the yields are often low and isolation of the desired product is difficult. However, since Clar and Stewart[11] were able to effect cyclodehydrogenation of 9-phenyl-1,2-benzanthracene (Ia) to 1,2,3,4-dibenzopyrene (IIa) with aluminum chloride in boiling benzene, although in unspecified yield, the use of this reagent appeared to be an attractive approach to the cyclodehydrogenation of the hydrocarbons Ib–Ii. Of the many different reagents

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(2) This paper has been abstracted from the Doctorate thesis presented to the Virginia Polytechnic Institute by Walter W. Zajac in 1959.

(3) This investigation was supported in part by a research grant (S-73) from the Bureau of State Services (Division of Sanitary Engineering Services and Division of Special Health Services) of the National Institutes of Health, Public Health Service.

(4) J. Thomas, B. Tebbens, M. Mukai, and E. Sanborn, *Anal. Chem.*, 29, 1835 (1957).

(5) V. Shore and M. Katz, *Anal. Chem.*, **28**, 1399 (1956).

(6) It is known that methyl groups may greatly enhance the carcinogenic activity of aromatic polynuclear hydrocarbons.

(7) E. Clar, *Ber.*, **63**, 112 (1930).

(8) J. Cook and E. Kennaway, *Am. J. Cancer*, **33**, 50 (1938).

(9) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **77**, 4823 (1955). During the purification of the 9-aryl-1,2-benzanthracenes *via* column chromatography on alumina the following was reported. "The occurrence of a yellow band on the chromatography column, when the cyclization product was chromatographed, suggests that a small amount of the dibenzopyrene is formed. Presumably the initial cyclodehydration reaction is followed by a small amount of cyclodehydrogenation."

(10) F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **78**, 1240 (1956).

(11) E. Clar and D. Stewart, *J. Chem. Soc.*, 687 (1951).

studied we found aluminum chloride to be the most successful; therefore, its use is described in some detail in the experimental section of this paper.

With the exception of 9-(3,4-dimethylphenyl)-1,2-benzanthracene (Ih), all the 9-(monomethyl- and dimethylphenyl)-1,2-benzanthracenes (Ib–Ii) can be cyclodehydrogenated to the corresponding monomethyl- and dimethyl-1,2,3,4-dibenzopyrenes (IIb–IIi) with aluminum chloride in boiling benzene. The yields are low, ranging from 23% to 2% (see Table I), but typical of those obtained from cyclodehydrogenation reactions.

TABLE I

9-(Phenyl)-1,2-benzanthracenes (I)	Yield of the 1,2,3,4-Dibenzopyrenes (II)
Ib. R = 2-CH_3, R′ = H	19% IIb (R = 4′-CH_3, R′ = H)
Ic. R = 3-CH_3, R′ = H	13% IIc (R = 3′-CH_3, or 1′-CH_3, R′ = H)
Id. R = 4-CH_3, R′ = H	17% IId (R = 2′-CH_3, R′ = H)
Ie. R = 2-CH_3, R′ = 3-CH_3	23% IIe (R = 4′-CH_3, R′ = 3′-CH_3)
If. R = 2-CH_3, R′ = 4-CH_3	2% IIf (R = 4′-CH_3, R′ = 2′-CH_3)
Ig. R = 2-CH_3, R′ = 5-CH_3	3% IIg (R = 4′-CH_3, R′ = 1′-CH_3)
Ih. R = 3-CH_3, R′ = 4-CH_3	No dibenzopyrene could be isolated
Ii. R = 3-CH_3, R′ = 5-CH_3	2% IIi (R = 3′-CH_3, R′ = 1′-CH_3)

A rather large variety of reagents and reaction conditions were tried in an attempt to improve the yields, but to no avail. The following known reagents and reaction conditions were tried: aluminum chloride in boiling carbon disulfide,[12] aluminum chloride in boiling *p*-cymene,[13] aluminum chloride-sodium chloride melt,[14] anhydrous ferric chloride in boiling benzene, anhydrous stannic chloride in boiling benzene, anhydrous aluminum chloride-anhydrous stannic chloride in boiling benzene,[15] phosphorus oxychloride in boiling benzene, palladium-charcoal at 350°, palladium-charcoal in boiling *p*-cymene, and sulfur at 325° (5 mm.).

All the mono- and dimethyl-1,2,3,4-dibenzopyrenes (IIb–IIi) prepared in this investigation crystallize as tiny yellow needles with melting points around 200°. They all can be readily sublimed at low pressures (0.10 mm.). The 1,2,3,4-dibenzopyrenes are slightly soluble in ethanol and in acetic acid, readily soluble in benzene, in toluene, and in xylene, and very soluble in nitrobenzene. In solution the dibenzopyrenes possess a brilliant yellow-green fluorescence. The dibenzopyrenes dissolve in concentrated sulfuric acid imparting a claret color to the solution which changes to an olive green color within a minute. Picrates of IIa–IId were prepared and melted as follows: IIa, 231–232°; IIb, 226–227°; IIc, 220–221°; IId, 217–218°.

The ultraviolet absorption spectra and the visible absorption spectra of the dibenzopyrenes were obtained using a Perkin-Elmer model 3000 Spectracord (1-cm., quartz cell) at a concentration of 5 mg. per liter for the ultraviolet spectra and 10 mg. per liter as the concentration for the visible spectra. The solvent was 95% ethanol. It is well established that a bathochromic shift is observed most characteristically in the spectra of alkyl derivatives of polynuclear aromatic hydrocarbons.[16] The wave-length maxima of the dibenzopyrenes (II) are recorded in Table II. It can be seen from these data that the expected bathochromic shift was observed.

TABLE II

ABSORPTION MAXIMA OF THE 1,2,3,4-DIBENZOPYRENES (II)

Wave Length in mμ

IIa	IIb	IIc	IId	IIe	IIf	IIg	IIi
240	243	244	244	244	243	243	244
253	254	253	256	256	255	254	253
261	263	263	263	264	263	263	264
271	272	273	272	273	271	271	272
289	288	289	288	288	287	289	287
301	298	298	297	300	298	301	299
315	315	314	315	318	312	314	317
330	330	329	329	333	328	329	332
359	360	361	362	358	358	356	356
379	378	378	379	380	379	375	378
401	399	400	399	401	400	399	399

Although incomplete at this time, the carcinogenic activity tests being conducted by Dr. W. F. Dunning, Prof. Exper. Pathology, Cancer Research Laboratory, University of Miami, on 2′-methyl-1,2,3,4-dibenzopyrene (IId) reveal that this compound is a potent carcinogen.

EXPERIMENTAL[17,18,19]

Cyclodehydrogenation of 9-(4-methylphenyl)-1,2-benzanthracene (Id). A. *Aluminum chloride and benzene.* Six grams of

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(12) L. Ruzicka and H. Hosli, *Helv. Chem. Acta*, **17**, 470 (1934); L. Ruzicka and K. Hoffman, *Helv. Chem. Acta*, **20**, 1155 (1937); L. Ruzicka and E. Morgeli, *Helv. Chem. Acta*, **19**, 377 (1936); L. Ruzicka and K. Hoffman, *Helv Chem. Acta*, **22**, 126 (1939); L. Ruzicka and R. Markus, *Helv. Chem. Acta*, **23**, 385 (1940); J. Cook, C. Hewett, W. Mayeord, and E. Roe, *J. Chem. Soc.*, 1727 (1934); J. Cook and C. Hewett, *J. Chem. Soc.*, 365 (1934); J. Cook and C. Hewett, *J. Chem. Soc.*, 1098 (1933); Ng. Buu-Hoi, Ng. Hoan, and P. Jacquignon, *J. Chem. Soc.*, 1381 (1951).

(13) R. Linstead and K. Michaelis, *J. Chem. Soc.*, 1134 (1940).

(14) R. Weitzenbock and C. Seer, *Ber.*, **46**, 1994 (1913); H. Reimlinger and A. van Overstraeten, *Chem. Ber.*, **91**, 2151 (1958).

(15) E. Clar and M. Zander, *Chem. Ber.*, 1861 (1958).

(16) R. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

(17) All melting points are corrected.

(18) All analyses were carried out by Geller Microanalytical Laboratories, Bardonia, N. Y.

anhydrous aluminum chloride was added to a solution of 1.0 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) in 60 ml. of anhydrous benzene. The mixture was heated on a steam bath for 2 hr. The mixture was allowed to cool to room temperature and then decomposed with 100 ml. of a 10% hydrochloric acid solution. The orange organic layer which possessed a brilliant yellow-green fluorescence was separated. The aqueous layer was extracted with five 25-ml. portions of fresh benzene and the combined benzene extracts were washed twice with water and dried over anhyd. magnesium sulfate. The solvent was removed until only an oil remained. This oil was dissolved in 5 ml. of benzene and chromatographed on a column packed with Fisher's Alumina (80–200 mesh). The first fraction was eluted with petroleum ether (b.p. 30–60°) and possessed a blue fluorescence under ultraviolet radiation (3660 Å). Unfortunately the time required to remove this band was about 1 week. After this fraction was removed, the yellow band which remained on the column was eluted with benzene (500 ml. of benzene was required to remove this band). Concentration of the benzene solution yielded a red oil which was triturated with *ca.* 20 drops of ethyl acetate. The expected 2′-methyl-1,2,3,4-dibenzopyrene (IId) crystallized as a yellow solid, m.p. 208–209°; yield, 0.17 g. (17%). The hydrocarbon was recrystallized from a benzene-ethanol mixture as tiny yellow needles, m.p. 210–211°.

An analytical sample was prepared by sublimation (0.1 mm.) followed by recrystallization of the sublimate from a mixture of benzene and ethanol. The melting point remained unchanged.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.09. Found: C, 95.21; H, 5.02.

The other cyclodehydrogenations using aluminum chloride were carried out in a similar fashion. The new dibenzopyrenes are listed in Table III together with their respective melting points and analytical data.

TABLE III

NEW DIBENZOPYRENES

Hydrocarbon	M.P.	Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
IIb	206–207	94.90	94.90	5.09	4.86
IIc	213–214	94.90	94.84	5.09	4.90
IId	210–211	94.90	95.21	5.09	5.02
IIe	201–202	94.50	94.40	5.49	5.77
IIf	198–199	94.50	94.78	5.49	4.88
IIg	207–209	94.50	94.75	5.49	4.82
IIi	215–216	94.50	94.85	5.49	4.79

Of the great number of experiments using various reagents and reaction conditions which were tried in unsuccessful attempts to cyclodehydrogenate the benzanthracenes (I) only the following appear worthy of mention.

B. *Stannic chloride and benzene.* Ten grams of anhydrous fuming stannic chloride was added to a solution of 1.5 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) in 150 ml. of anhydrous benzene. The mixture was heated on a steam bath for 2 hr. and then worked-up in the usual manner. There was obtained 1.47 g. of the original hydrocarbon, m.p. 115–117°, (lit.,[9] m.p. 116.5–117.5°).

C. *Aluminum chloride–stannic chloride and benzene.* A mixture of 1.0 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id), 1.0 g. of anhydrous powdered aluminum chloride, 1.0 g. of anhydrous fuming stannic chloride, and 10 ml. of anhydrous benzene was heated for 1 hr. The mixture was allowed to cool to room temperature and then decomposed with 100 ml. of a 10% hydrochloric acid solution and worked-up in usual manner. The only material which could be isolated from the chromatographic separation was an unpurifiable red solid, m.p. 129–240°. This red solid could not be purified by sublimation under reduced pressure (0.1 mm.). Its ultraviolet absorption spectrum indicated an untractable mixture of compounds.

D. *Palladium-charcoal and p-cymene.* In a three-neck flask equipped with a stirrer and a water cooled condenser, a mixture of 1.0 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id), 3.0 g. of 10% palladium on charcoal, and 50 ml. of *p*-cymene was heated for 39 hr. The mixture was cooled to room temperature and then worked-up in the usual manner. There were obtained white plates, yield 0.95 g., m.p. 114–116° of the starting hydrocarbon.

E. *Aluminum chloride and carbon disulfide.* Five grams of anhydrous powdered aluminum chloride was added to a solution of 0.75 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) in 75 ml. of carbon disulfide. The mixture was heated on a steam bath for 3 hr. The mixture was cooled to room temperature and then decomposed with 100 ml. of a 10% hydrochloric acid solution and worked-up in the usual manner. Only 0.15 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) could be isolated and identified.

F. *Palladium-charcoal at 350°.* In a 100-ml. round bottom flask, 2.0 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) and 3.0 g. of 10% palladium on charcoal were intimately mixed. The mixture was then heated in a nitrogen atmosphere for 6 hr. at 350° (±10°). The mixture was then allowed to cool to room temperature and the mixture was extracted with 100 ml. of hot benzene and worked-up in the usual manner. There was obtained 9-(4-methylphenyl)-1,2-benzanthracene (Id) 1.19 g. (60%). No other material could be isolated and no yellow band corresponding to a 1,2,3,4-dibenzopyrene was observed on the chromatographic column.

G. *Sodium chloride and aluminum chloride.* An intimate mixture of 15.0 g. of powdered anhydrous aluminum chloride, 3.0 g. of sodium chloride, and 1.2 g. of 9-(4-methylphenyl)-1,2-benzanthracene (Id) was placed in a 100-ml. round-bottom flask and placed in an oil bath preheated to 100°. The temperature of the bath was raised to 145° and the mixture was heated at that temperature for 2 hr. The melt was poured onto ice water and the resulting gummy mass was extracted with 200 ml. of benzene and worked-up in the usual manner. There was obtained 0.11 g. (10%) of the expected cyclodehydrogenation product, 2′-methyl-1,2,3,4-dibenzopyrene (IId), m.p. 205–206°.

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(19) The chromatographic separations were all done on a column 18 mm. × 370 mm. wet packed (30–60° petroleum ether) with Fisher's adsorption alumina, 80–200 mesh.