Ultraviolet Absorption Spectra of 9,10-Dihydroanthracenes

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In connection with the recent synthesis of 1′,9-dimethyl-1,2-benzanthracene,[2] it became necessary to differentiate between certain substituted anthracenes and their dihydro derivatives in order to elucidate the structure of an important intermediate in the reaction scheme. The principal criteria used in the past when a similar differentiation was required have been the properties of color and fluorescence. Thus, dihydroanthracenes are generally colorless in the crystalline state and non-fluorescent in solution whereas anthracenes are colored and show a strong fluorescence. The weaknesses in such a generalization have already been mentioned.[3] For this reason, some workers[4] have made use of the difference in ultraviolet absorption characteristics for the identification of certain representatives of these two types of compounds; however the results of Martin[5] led her to state that 9,10-dialkylanthracenes possess the same general spectral characteristics as the dihydro derivatives. Since there is no apparent reason for such an anomaly for this type of anthracene it was considered desirable to reinvestigate the matter. In doing so, we have found that 9,10-dimethyl-9,10-dihydroanthracene (Fig. 1) and 9-methyl-9,10-dihydroanthracene (Fig. 2) bear no resemblance to the fully aromatic parent hydrocarbons in their absorption in the ultraviolet. Furthermore, the dihydro derivatives showed essentially no absorption beyond 290 mμ, whereas Martin[5] reported maxima at wave lengths as long as 386 mμ for several dialkyldihydroanthracenes.

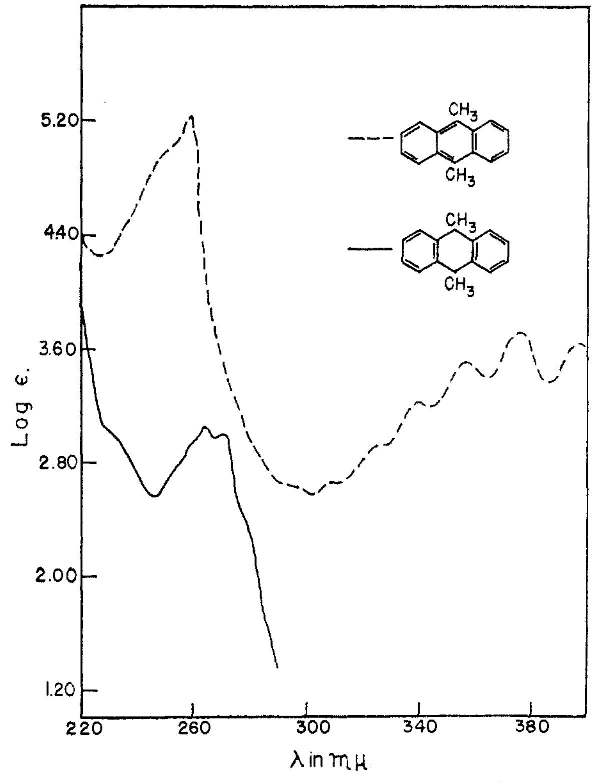

Fig. 1.—Ultraviolet absorption spectra of (a) 9,10-dimethylanthracene, $\lambda_{max.}$ (log ε) *250* (4.99); 260 (5.23); 308 (2.61); 326 (2.91); 340 (3.22); 356 (3.51); 376 (3.70); 396 (3.65); and (b) 9,10-dimethyl-9,10-dihydroanthracene, $\lambda_{max.}$ (log ε) 264 (3.06); 272 (3.00).

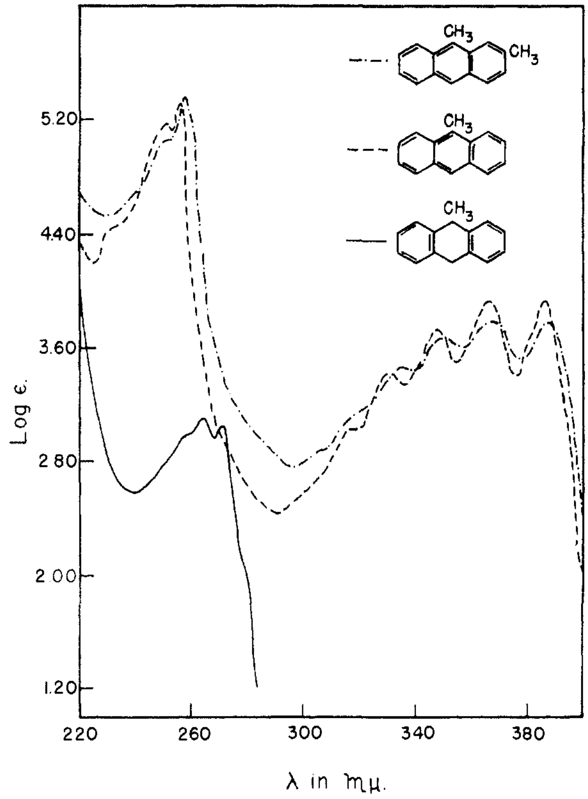

Fig. 2.—Ultraviolet absorption spectra of (a) 2,9-dimethylanthracene, $\lambda_{max.}$ (log ε) 251 (5.05); 258 (5.37); 307 (2.88); *318* (3.13); 334 (3.46); 350 (3.68); 368 (3.80); 386 (3.78); and (b) 9-methylanthracene, $\lambda_{max.}$ (log ε) 252 (5.18); 256 (5.33); 318 (3.04); 331 (3.44); 348 (3.76); 366 (3.96); 386 (3.95); and (c) 9-methyl-9,10-dihydroanthracene, $\lambda_{max.}$ (log ε) 264 (3.11); 271 (3.05).

The compounds reported by Martin[5] were prepared by the Wurtz reaction between the appropriate alkyl halide and the disodium derivative of anthracene. This reaction has recently been shown[6] to give rise to complicated mixtures because of disproportionation and polymerization, and as much as 50% of the anthracene may be recovered. Martin reported[5] the removal of this unreacted material by simple filtration, but treatment with maleic anhydride is necessary for the complete elimination of anthracene from the reaction product.[6] In addition, several of Martin's compounds that were reported as oils have since been prepared in a pure, crystalline condition.[6] The intense ab-

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(1) U. S. Rubber Fellow, 1951-1952.

(2) J. Cason and D. D. Phillips, *J. Org. Chem.*, **17**, 298 (1952).

(3) R. B. Sandin, R. Kitchen and L. F. Fieser, This Journal, **65** 2019 (1943).

(4) E. Clar and J. W. Wright, *Nature*, **163**, 921 (1949); P. L. Julian, W. Cole, G. Diemer and J. G. Schafer, This Journal, **71**, 2058 (1949); E. L. May and E. Mosettig, *ibid.*, **73**, 1301 (1951).

(5) E. Martin, *Ann. combustibles liquides*, **12**, 97 (1937).

(6) B. M. Mikhailov and A. N. Blokhina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 164 (1949); *C. A.*, **44**, 2962 (1950).

sorption shown by anthracene[7] could well account for the qualitative maxima reported[5] beyond 290 mμ, even if anthracene were present to the extent of 10% or less.

The compounds reported herein have been prepared by established methods and the physical properties are in agreement with those reported in the recent literature. Since the absorption spectrum of 2,9-dimethylanthracene has not been previously reported, the curve is given in Fig. 2 although the corresponding 9,10-dihydride was not obtained.

Experimental[8]

9-Methylanthracene.—9-Anthraldehyde (Eastman Kodak Co.) was converted to 9-methylanthracene in 92% yield by means of the modified[9] Wolff–Kishner reduction. The hydrocarbon crystallized from ethanol as pale yellow needles, m.p. 79.2–79.7°, lit.[10] m.p. 81.5°.

9-Methyl-9,10-dihydroanthracene.—9-Methylanthracene was reduced in 85% yield to the dihydro derivative by heating with sodium in amyl alcohol according to the procedure of Schlenk and Bergmann.[11] The dihydride thus obtained crystallized from ethanol as colorless needles, m.p. 58.8–59.8°, lit.[10] m.p. 61.5°.

2,9-Dimethylanthracene.[12]—The preparation of this hydrocarbon was patterned after the following sequence of previously[13] reported reactions: toluene + phthalic anhydride → *o*-(*p*-toluyl)-benzoic acid (I) → *o*-(*p*-methylbenzyl)-benzoic acid (II) → 2-methyl-9-anthrone (III) → 2,9-dimethylanthracene (IV). Improvements in the procedure included the reduction of keto acid I in 92% yield by hydrogenolysis in acetic acid solution in the presence of platinum oxide catalyst,[14] and the conversion in 86% yield of acid II to anthrone III by treatment with anhydrous hydrogen fluoride.[15] The use of concentrated sulfuric acid for this cyclization reportedly[13] gave anthrone III in less than 50% yield. When anthrone III was allowed to react with methylmagnesium bromide, IV was obtained in only 29% yield, whereas the use of methyllithium raised this yield to 50%. 2,9-Dimethylanthracene crystallized from methanol as orange needles, m.p. 83.0–84.0°, lit.[13] m.p. 85°.

Attempted reduction of 2,9-dimethylanthracene with sodium and amyl alcohol[11] gave no dihydro derivative, but there was obtained a low yield of a high-melting yellow solid whose identity was not established.

9,10-Dimethylanthracene.[16]—The hydrocarbon was prepared by the procedure used for the synthesis of 9,10-dimethyl-1,2-benzanthracene.[17] The use of benzene as solvent was a necessary modification to accommodate the low solubility of anthraquinone in ether.

To a large excess of methylmagnesium iodide in 200 ml. of ether was added a suspension of 21.0 g. (0.1 mole) of anthraquinone in 300 ml. of dry benzene. Approximately 100 ml. of ether was removed from the green solution by rapid distillation and was replaced by 100 ml. of benzene. The solution was heated under reflux for one hour, allowed to stand overnight, and then poured slowly into a cold (0°) mixture of 240 ml. of hydriodic acid (sp. gr. 1.7) and 800 ml. of methanol. After the vigorous reaction had subsided 800 ml. of glacial acetic acid was added. The iodomethyl intermediate, which separated as bright yellow needles, was rapidly filtered and dried without heating, in the absence of light. The yield of crude material was quantitative.

The iodomethyl intermediate was then dissolved in a mixture of 2 l. of dioxane and 100 ml. of concentrated hydrochloric acid and added to a solution of 330 g. of stannous chloride in 1.5 l. of dioxane. The resultant red solution was heated under gentle reflux for 10 minutes during which time the color changed to a pale yellow. After 45 minutes at room temperature, this solution was diluted with water to yield 22 g. (99%) of crude 9,10-dimethylanthracene. Two recrystallizations from benzene gave brilliant yellow needles, m.p. 182.0–183.8°, lit.[18] m.p. 183.5–184.5°.

9,10-Dimethyl-9,10-dihydroanthracene.[19]—To a refluxing solution of 0.80 g. of 9,10-dimethylanthracene in 200 ml. of absolute ethanol was added 6 g. of sodium. The yellow solution was heated under reflux for 16 hours, filtered and poured into 500 ml. of water. There was collected 0.45 g. (55%) of yellow powdery crystals, m.p. 100–140°. These were dissolved in 30 ml. of benzene containing 2.0 g. of maleic anhydride and the mixture was heated under reflux for 8 hours. The adduct was filtered and the filtrate washed with dilute sodium hydroxide solution and water, and finally dried over anhydrous magnesium sulfate. The benzene solution was then passed through a small column of alumina and the eluate concentrated and sublimed at 140° (0.5 mm.) to remove traces of high-melting material. The sublimate crystallized from methanol to give 0.2 g. of 9,10-dimethyl-9,10-dihydroanthracene as colorless plates, m.p. 126.2–128.0°, lit.[19] m.p. 130°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.55.

When 9,10-dimethylanthracene was reduced by heating with sodium and amyl alcohol,[11] there was obtained, in 50% yield, a compound which crystallized from methanol in fine needles, m.p. 270–273°. Analysis (C, 88.98; H, 6.52) indicated that oxygen had been introduced into the molecule.

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[7] R. N. Jones, THIS JOURNAL, **67**, 2127 (1945).

[8] All melting points are corrected. Analyses are by the Microanalytical Division of the Department of Chemistry, University of California. The ultraviolet absorption spectra were measured in 95% ethanol using a Beckman model DU quartz spectrophotometer. Concentrations were adjusted so that all optical density readings were in the range 0.1–1.5.

[9] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[10] F. Krollpfeiffer, *Ber.*, **56**, 1619 (1923).

[11] W. Schlenk and E. Bergmann, *Ann.*, **463**, 153 (1928).

[12] The technical assistance of Mrs. Gloria B. Robbers is gratefully acknowledged.

[13] E. DeB. Barnett and N. F. Goodway, *J. Chem. Soc.*, 1754 (1929).

[14] E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

[15] L. F. Fieser and E. B. Hershberg, *ibid.*, **61**, 1272 (1939).

[16] The technical assistance of Ronald D. Smith is gratefully acknowledged.

[17] R. B. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940).

[18] B. M. Mikhailov and T. K. Kozminskaya, *Doklady Akad. Nauk S.S.S.R.*, **58**, 811 (1947); *C. A.*, **45**, 9522 (1951).

[19] K. Sisido and T. Isida, THIS JOURNAL, **70**, 1289 (1948).

The Synthesis of 2-Thianaphthaldehyde and Some of its Derivatives

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In spite of considerable research activity in the field of thianaphthene chemistry in recent years, no one has reported the 2-aldehyde derived from thianaphthene. 3-Thianaphthaldehyde has been prepared by Komppa and Weckman[1] from the 3-thianaphthylmagnesium bromide and ethyl orthoformate or ethoxymethyleneaniline in yields of 17 and 25%, respectively.

We have prepared the 2-aldehyde from 2-thianaphthyllithium, from the metalation of thianaphthene with *n*-butyllithium,[2] and N-methylformanilide in 62% yield based on starting thianaphthene.

2-Thianaphthaldehyde was carried through several typical aromatic aldehyde reactions such as benzoin condensation, thiosemicarbazone formation, anil formation, and condensation with benzyl cyanide.

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[1] G. Komppa and S. Weckman, *J. prakt. Chem.*, **138**, 109 (1933).

[2] D. A. Shirley and M. D. Cameron, THIS JOURNAL, **74**, 664 (1952).