[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Carcinogenic Hydrocarbons. V. A Comparison of the Fluorescence Intensity of Cholanthrene and Certain of its Homologs[1]

BY WILLIAM F. BRUCE

A preliminary study of the relative fluorescence intensities of some of the homologs of cholanthrene has shown a diminution of fluorescence intensity as the series is ascended.[2] In that study numerically equal concentrations of the hydrocarbons were fortuitously employed. By using equimolecular concentrations, we now find that the higher members of the series are nearly alike in fluorescence intensity, although a slight diminution with increasing molecular weight is still apparent. As a result, the apparent connection between fluorescence intensity and carcinogenic activity which resulted from comparison of numerically equal concentrations has nearly disappeared now that equimolecular concentrations are used. The slight decline in fluorescence intensity is not at all comparable with the rapid diminution of carcinogenic activity.

In addition to re-examining the fluorescence intensity of these cholanthrene homologs, we have also included in the present study the parent hydrocarbon cholanthrene. The fluorescence intensity of this hydrocarbon is distinctly less than that of 20-methylcholanthrene. Although the fluorescence intensity and carcinogenic activity change in the same direction and approximately to the same extent in a comparison of these two substances, the assumption of any real connection between these two properties does not at present appear justified in view of the relation found for the other homologs.

In order to examine more closely the connection between structure and fluorescence intensity, the result of altering some of the numerous variables was tested. The light admitted to the photocell, the solvent and the concentration appeared to be the most significant, and the effect of altering these variables in turn is shown in Table I. Variation of the filters by which the fluorescent light reaching the photocell was controlled showed a wide variation in the intensity of response, but no difference in the relative positions of the homologs in the intensity series. Variation of solvent showed that the fluorescence in benzene was more intense than in absolute alcohol; but in carbon disulfide, a solution of cholanthrene in one instance fluoresced much less than did the pure solvent alone. Variation of the concentration showed a rapidly diminishing fluorescence intensity as the concentration was decreased. The concentration giving maximum fluorescence was not determined.

A detailed study of the fluorescence of the more complex aromatic hydrocarbons does not appear to have been made. Sambursky[3] has reported that pure phenanthrene does not fluoresce in the visible, but that anthracene shows some blue fluorescence in the region 4500–4600 Å., which includes the more intense region of the cholanthrene visible fluorescence. Both substances show more fluorescence of lower frequency in benzene than in methanol. The maximum fluorescence intensity for anthracene occurred at a concentration of 2×10^{-4} mole per liter, which is comparable with the stock solution used for the cholanthrene series, namely, 4×10^{-4} mole per liter. Cholanthrene can be considered either as a phenanthrene or anthracene derivative; some resemblance in fluorescence to either or both of these might therefore be expected.

Experimental

In determining the data shown in Table I, the apparatus described by Hand[4] was used. The incident light from the capillary mercury arc was filtered by Corning filter 585. The fluorescent light was filtered in turn by the four different filters indicated in the table: Corning 038, Noviol A, a light yellow; Corning G584J, a blue-green; Corning G38H, Noviol C, a deep yellow; and Corning G371R, a fluorescent greenish yellow. Stock solutions of the hydrocarbons were freshly prepared in dark bottles with the following amounts for 50 cc. of solvent: cholanthrene, 5.0 mg.; 20-methylcholanthrene, 5.4 mg.; 20-ethylcholanthrene, 5.6 mg.; 20-*i*-propylcholanthrene, 5.9 mg. The more dilute solutions were prepared by diluting 5 ml. of stock solution with 45 ml. of solvent and similar dilution from this solution. The glass container was carefully rinsed with solvent between determinations. The solvents used were thiophene-free benzene, absolute ethanol and reagent grade carbon bisulfide. Each reading of the photronic cell was repeated twice, but no deviations of more than 0.05 unit were found.

An examination of the bluish fluorescent light by a spectroscope showed that it consisted of a faint continuous

(1) Previous paper, Bruce, THIS JOURNAL, **63**, 301 (1941).
(2) Bruce and Todd, *ibid.*, **61**, 157 (1939).
(3) Sambursky, *Trans. Faraday Soc.*, **36**, 427–432 (1940).
(4) Hand, *Ind. Eng. Chem., Anal. Ed.*, **11**, 306 (1939).

TABLE I

FLUORESCENCE INTENSITIES OF CHOLANTHRENE AND CERTAIN OF ITS HOMOLOGS (IN MILLIVOLTS)

Concn., mg./ml.	Filters: 038 Alc.	038 Benzene	G 584 J Alc	G 584 J Benzene	G 38 H Alc.	G 38 H Benzene	G 371 R Alc.	G 371 R Benzene
				Cholanthrene				
0.100	4.8	5.6	15.5	16.5+	0.8	0.7	6.6	7.2
.0100	2.7	3.6	13.9	16.5+	0.2	0.2	...	6.1
.00100	0.6	1.3	4.3	8.6	0	0.05	1.5	2.7
	...	0.5	....	4.4	..	0.1	...	...
				20-Methylcholanthrene				
.108	7.1	7.0	16.5+	16.5+	1.0	0.9	9.2	10.2
.0108	4.0	5.2	16.5+	16.5+	0.3	0.4	6.2	7.8
.00108	1.0	1.4	5.6	8.7	0.1	0.1	1.9	2.8
				20-Ethylcholanthrene				
.112	6.0	7.0	16.5+	16.5+	0.8	0.75	7.8	8.75
.0112	3.9	5.0	16.5+	16.5+	0.3	0.3	6.0	7.50
.00112	0.9	1.3	5.4	8.3	0.05	0.1	1.8	2.6
				20-*i*-Propylcholanthrene				
.118	5.8	7.0	16.5+	16.5+	0.8	0.65	7.6	8.8
.0118	4.0	5.0	16.5+	16.5+	0.3	0.3	6.0	7.6
.00118	0.9	1.4	5.3	8.8	0	0.05	1.7	2.8
				Cholanthrene				
.100 in CS_2	0.8		2.4		0.1		1.0	
CS_2	0.3		3.5		0		0.9	

band between about 5200 and 4500 Å., with the greatest intensity between 4750–4510 Å. A photograph of the spectrum showed that the fluorescence continued to the near ultraviolet. The photograph was made using a solution in benzene containing 0.2, 0.22, 0.23, and 0.24 mg. per ml. for the respective homologs. The solution was put in a bent Pyrex tube similar to that described by Wood[5] and illuminated through a 587 Pyrex filter by a 1.5-amp. mercury arc for one hour. The relative intensities were not determined by this method because of the time required and difficulties in maintaining comparable conditions of illumination for each run. The slit width was 1 mm. (0.1 mm. for the reference mercury arc).

(5) R. W. Wood, "Physical Optics," The Macmillan Co., New York, N. Y., 1934, p. 447.

Summary

A study of fluorescence intensities in some homologous 20-substituted cholanthrenes has shown that the fluorescence intensity increases as does the carcinogenic activity in a comparison of cholanthrene and methylcholanthrene. In the higher homologs, however, the rapid decline in carcinogenic activity is not accompanied by a corresponding decline of fluorescence intensity, which remains nearly the same for these substances when equimolecular concentrations are used.

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β-Dialkylaminoethyl Bromide Hydrobromides and β-Dialkylaminoethylamines[1]

BY LAWRENCE H. AMUNDSEN AND KARL W. KRANTZ[2]

β-Diethylaminoethylamine has been prepared by treating β-bromoethylphthalimide with diethylamine and hydrolyzing the product.[3] Because of certain difficulties in the preparation of β-bromoethylphthalimide and in its separation from the by-product, diphthalimidoethane, it has seemed to us desirable to investigate other methods of preparing β-dialkylaminoethylamines. Our investigation has shown that β-dialkylaminoethylamines may be prepared by the addition of

(1) Abstracted from a thesis presented by Karl W. Krantz in partial fulfillment of the requirements for the degree of Master of Science at the University of Connecticut, June, 1940. Presented at the Detroit Meeting of the American Chemical Society, September, 1940. For complete thesis order Document 1458 from American Documentation Institute, Offices of Science Service, 2101 Constitution Avenue, Washington, D. C., remitting $0.61 for microfilm form or $4.30 for photocopies readable without optical aid.

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(3) Ristenpart, *Ber.*, **29**, 2526 (1896).