TABLE I

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

	Filters							
Concn., mg./ml.	038		G 584 J		G 38 H		G 371 R	
	Alc.	Benzene	Alc	Benzene	Alc.	Benzene	Alc.	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).

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.

ITHACA, N. Y. RECEIVED SEPTEMBER 23, 1940

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CONNECTICUT]

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

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[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).

ammonia to β-dialkylaminoethyl bromide hydrobromides, followed by treatment of the product with a strong base. Apparently because of the known strong tendency for dimerization leading to the formation of piperazonium dihalides, the yields are unsatisfactory for the lower homologs. Assuming this dimerization of the halide to be the chief cause of the unsatisfactory yields of the lower homologs, various modifications of our method may be proposed whereby these yields might be increased. Reducing the concentration of β-dialkylaminoethyl bromide hydrobromide, the use of a larger excess of ammonia and the use of solvents other than alcohol, or of liquid ammonia without a solvent, are suggested as logical modifications. The lower yields obtained when the alkyl groups were smaller indicate clearly the undesirability of the possible preparation of β-dialkylaminoethylamines from β-aminoethyl bromide hydrobromide and dialkylamines. The unsubstituted β-aminoethyl bromide would probably dimerize even more readily than would its N,N-dimethyl derivative.

TABLE I

β-DIALKYLAMINOETHYL BROMIDE HYDROBROMIDES, $BrR_2HNCH_2CH_2Br$

R	M. p., °C., cor.[a]	Yield, %	Formula	Br, % Calcd.	Br, % Found[b]	
Me	188.5–189.9[c]	83	$C_4H_{11}Br_2N$	68.61	68.46	68.47
Et	208.1–208.4[d]	80	$C_6H_{15}Br_2N$	61.24	60.73	60.89
n-Pr	159.6–160.1[e]	55	$C_8H_{19}Br_2N$	55.30	55.09	54.95
n-Bu	85.7– 85.9	59	$C_{10}H_{23}Br_2N$	50.42	49.95	50.34

[a] All of the corrected melting points given were taken in sealed capillary tubes in a motor stirred oil-bath, the temperatures being read on totally immersed thermometers calibrated by the National Bureau of Standards. [b] Boiling the sample with a strong aqueous solution of a weighed quantity of silver nitrate and titrating the excess with thiocyanate (Volhard method) gave quantitative precipitation of the bromine with all except the dimethyl compound. In this instance, the sample was first decomposed with sodium in liquid ammonia by the method of Vaughn and Nieuwland (*Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931)). [c] Discolors at 185°. [d] Discolors at m. p. Previously reported 209°.[9] [e] Slight discoloration at m. p.

β-Dialkylaminoethyl bromide hydrobromides were prepared from β-dialkylaminoethanols[4] and hydrobromic acid, using the procedure published by Cortese[5] for the preparation of β-aminoethyl bromide hydrobromide. The results are given in Table I. The extraction of these compounds requires variation in the quantity of acetone specified by Cortese; the solubilities in dry acetone vary from very slight to extreme as the molecular weight increases. Acetone was useful for recrystallization of the ethyl homolog only. The propyl and butyl derivatives were purified by recrystallization from ethyl acetate; the ethyl from a 9 to 1 mixture of ethyl acetate and 95% ethanol; the methyl from an 8 to 5 mixture. It will be noted (Table I) that the percentage yields obtained by this procedure decrease with increasing size of the N-alkyl groups. Judging from the varying amounts of tarry by-products, this variation in yields is due at least in part to the greater stability of the smaller molecules at the temperature of the reaction. While rigid adherence to the empirical distillation scheme of Cortese gave acceptable results in all cases, modifications of the scheme to fit the individual reaction rates undoubtedly would have improved the yields. This belief is substantiated by the preparation of β-di-*n*-butylaminoethyl bromide hydrobromide, in which a shortening of the reflux periods from one hour to one-half hour increased the yield from 20% to 59% of the theoretical.

β-Dialkylaminoethylamines were obtained by the addition of ammonia to β-dialkylaminoethyl bromide hydrobromides in alcohol solution, with the results given in Table II. The method is illustrated by the following typical preparation.

β-Di-*n*-butylaminoethylamine.—Liquid ammonia was added to 90% ethanol until a gain in weight of 125 g. per liter was observed. A solution of 49.0 g. of β-di-*n*-butylaminoethyl bromide hydrobromide in 325 cc. of this alcoholic ammonia was allowed to stand for six days and evaporated to a thick paste. This was shaken with a solution of 16 g. of sodium hydroxide in 18 cc. of water, giving two liquid phases. The whole was extracted with three 50-cc. portions of benzene, and the combined extracts dried over anhydrous potassium carbonate. After fractionating off most of the benzene through an efficient column at atmospheric pressure, the residue was distilled at reduced pressure, giving 12.2 g. of colorless liquid.

TABLE II

β-DIALKYLAMINOETHYLAMINES AND N-β-DIALKYLAMINOETHYL-N′-α-NAPHTHYLUREAS

Amines				Ureas				
	B. p., °C.	Pressure, mm.	Yield, %	Formula	M. p., °C. cor.[a]	Nitrogen, % Calcd.	Nitrogen, % Found	
$Me_2NCH_2CH_2NH_2$	....	..	> 5	$C_{15}H_{19}N_3O$	148.6–148.8	16.34	16.07	16.30
$Et_2NCH_2CH_2NH_2$	79– 82	85	28	$C_{17}H_{23}N_3O$	103.7–103.9	14.73	14.39	14.50
n-$Pr_2NCH_2CH_2NH_2$	87– 88	30	34	$C_{19}H_{27}N_3O$	115.7–116.2	13.42	13.02	13.06
n-$Bu_2NCH_2CH_2NH_2$	98–101	13	46	$C_{21}H_{31}N_3O$	101.1–101.6[b]	12.31	12.22	12.11

[a] Footnote (*a*), Table I. [b] Marked discoloration above 93°.

The benzoyl derivative and the phenylurea derived from β-diethylaminoethylamine could not be obtained readily in crystalline form, so the amines were characterized and analyzed as the α-naphthylureas. The ureas were prepared from calculated quantities of α-naphthyl isocyanate

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(4) Samdahl and Weider, *Bull. soc. chim.*, (5) **2**, 2008 (1935).

(5) Cortese, THIS JOURNAL, **58**, 191 (1936); "Organic Syntheses," edited by Fuson, John Wiley and Sons, Inc., New York, N. Y., 1938, Vol. 18, p. 13.

and the amine in benzene and were precipitated with hexane, from which they were subsequently recrystallized.

Summary

Three new dialkylaminoethyl bromide hydrobromides have been prepared by a previously known method. The corresponding dialkylaminoethylamines have been prepared by a new method in which the yield was unsatisfactory with the methyl derivative. These amines have been converted into α-naphthylureas.

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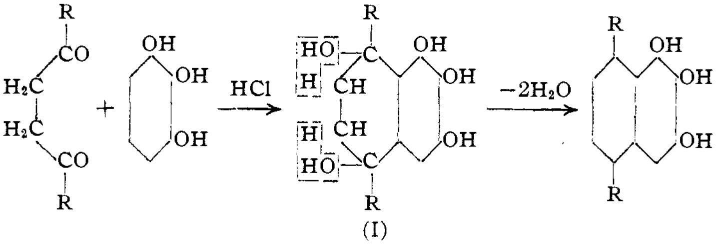
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Syntheses in the Naphthalene and Anthracene Series[1]

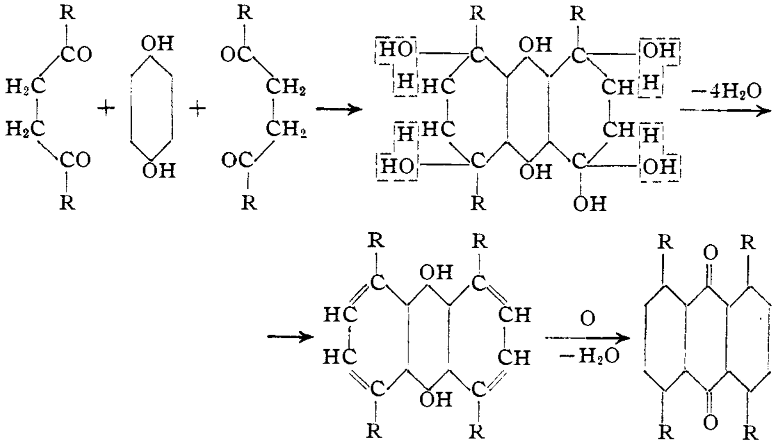
BY JOSEPH B. NIEDERL AND RICHARD H. NAGEL[2]

When the systematic investigations of the condensations of mono- and di- carbonyl compounds with phenols[3] were extended to include the condensations of γ-di-ketones with pyrogallol and hydroquinone, cyclizations followed by aromatizations were encountered. Di-acetone and pyrogallol underwent a single, but the same ketone and hydroquinone underwent double, cyclization–aromatization. In the first case (Reaction "A"), a new naphthalene compound, the 1,2,3-tri-hydroxy-5,8-dimethylnaphthalene was produced, while in the second case (Reaction "B") an anthracene compound, the 1,4,5,8-tetramethylanthraquinone was formed, the latter involving, aside from double cyclization and aromatization of the two outer rings, de-aromatization of the center ring through oxidation.



(I)

REACTION "A"



(II)

REACTION "B"

For the formation of both types of compounds two reaction mechanisms are applicable. One would involve the conventional di-enolization of the γ-di-ketone. This reaction mechanism, which would be the simplest, has however the drawback that it would be inapplicable to condensation systems in which the same type of di-ketone and a mono-hydroxyphenol is used and where condensation products are formed which do not permit interpretation of formation through di-enolization of the reacting γ-di-ketone. The more general reaction mechanism would involve the assumption of the formation of intermediate "phenolhydrin" types of compounds[4] found thus far applicable without exception to all carbonyl compound–phenol condensations, and illustrated above

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[1] Presented before the Division of Organic Chemistry at the recent Cincinnati (Naphthalene Compound Synthesis) and the Detroit (Anthracene Compound Synthesis) meetings of the American Chemical Society.

[2] Abstracted from a portion of the thesis submitted by Richard H. Nagel to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

[3] J. B. Niederl and co-workers, THIS JOURNAL, **50**, 2230 (1928); **51**, 2426 (1929); **58**, 657 (1936); **59**, 1113 (1937); **61**, 345, 348, 1005, 1785 (1939); **62**, 320, 322, 324, 1157, 3070 (1940).

[4] M. E. McGreal and J. B. Niederl, "Abstracts of Papers, 97th meeting Am. Chem. Soc.," Baltimore, Md., 1939, M, pp. 5–7.