*Studies on 3-(Anthraquinon-1-yl)oxazolidin-2-ones. II. 3-(Bromoanthraquinon-1-yl)oxazolidin-2-ones and their Related Compounds**

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It was shown in a previous paper[1] that an introduction of a methyl group into an anthraquinone nucleus of 3-(anthraquinon-1-yl)oxazolidin-2-one decreases the reactivity with an aqueous solution of potassium hydroxide. In other words, the existence of a steric hindrance of the 2-methyl group plays an important part in the hydrolysis process (Scheme I), inhibiting the conversion of the anthraquinon-1-yl-oxazolidin-2-ones into the 1-*N*-2-hydroxyethylamino-anthraquinones to a certain extent.

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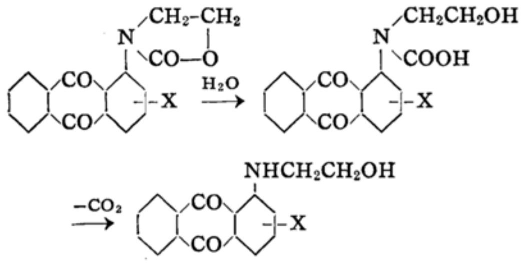
* Presented at the 12th Annual .Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

[1] K. Naiki, This Bulletin, **32**, 361 (1959).



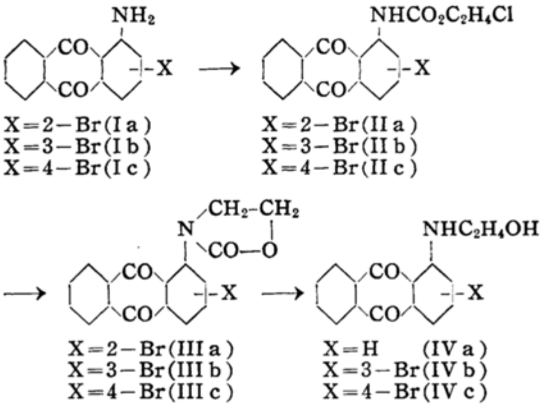
Scheme I

Furthermore, it was shown that in the case of the spectra of 2-chloroethyl methylanthraquinon-1-ylcarbamates the steric inhibition of the $\pi-p$ conjugation, i.e. interaction between an anthraquinone ring and an unshared electron pair of the nitrogen atom, plays an important role. Thus the introduction of the 2-methyl group into the anthraquinone ring results in the lowering of the intensity of the band near 400 mμ ascribed to the Aq-$\ddot{\mathrm{N}}$ chromophore, where Aq represents the anthraquinone ring, and results in the displacement by 43 mμ towards shorter wavelength as compared with 2-chloroethyl 4-methylanthraquinon-1-ylcarbamate. In 3-(methylanthraquinon-1-yl) oxazolidin-2-ones, the steric inhibition of the $\pi-p$ conjugation due to a bulky *N*-substituent, oxazolidin-2-onyl, results in the lowering of the intensity of the band near 400 mμ to a greater extent, and the introduction of the 2-methyl group into the anthraquinone ring weakens the band associated with Aq-$\ddot{\mathrm{N}}$ chromophore.

In the present study, 3-(bromoanthraquinon-1-yl)oxazolidin-2-ones, 2-chloroethyl bromoanthraquinon-1-ylcarbamates and 1-*N*-2-hydroxyethylamino-bromoanthraquinones were synthesized and the effect of the bromine atom according to its position on absorption spectra of 2-chloroethyl bromoanthraquinon-1-ylcarbamates and 3-(bromoanthraquinon-1-yl) oxazolidin-2-ones was discussed in terms of the steric hindrance. None of them has yet been prepared. Furthermore, the effect of the bromine atom according to its position on the reactivity of bromoanthraquinon-1-yloxazolidin-2-ones with potassium hydroxide was investigated.

Preparation and Results

The syntheses of the compounds were carried out according to the following processes (Scheme II).



Scheme II

2-Chloroethyl 2-bromoanthraquinon-1-ylcarbamate(IIa), 3-bromoanthraquinon-1-ylcarbamate(IIb) and 4-bromoanthraquinon-1-ylcarbamate(IIc) were obtained from the corresponding 1-amino-bromoanthraquinones (Ia, Ib and Ic, respectively) by the action of 2-chloroethyl chloroformate in the presence of sodium carbonate in boiling xylene.

3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one(IIIa) was prepared from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 98~99°C for 1 hr. The mixture of 1-*N*-2-hydroxyethylaminoanthraquinone(IVa) and 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIa) was obtained from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 105~107°C for 1 hr. Each of the constituents was separated by a column chromatography from benzene on alumina.

The mixture of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone(IVb), 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIb) and 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate was obtained from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate by the action of a 20% aqueous solution of potassium hydroxide at 98~99°C for 1 hr. and each of the constituents was separated by a column chromatography from benzene on alumina. In the same way, 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone(IVc) and 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one(IIIc) were obtained from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate.

The proportion of constituents of the reaction mixture from the corresponding 2-chloroethyl bromoanthraquinon-1-ylcarbamates by the action of a 20% aqueous

TABLE I. THE PROPORTIONS OF THE CONSTITUENTS OF THE REACTION PRODUCTS OBTAINED FROM 2-CHLOROETHYL BROMOANTHRAQUINON-1-YLCARBAMATES AND A 20% AQUEOUS SOLUTION OF POTASSIUM HYDROXIDE

Position of Br	II %	III %	IV %
2	0	100	0
3	29	7	64
4	44	26	30

solution of potassium hydroxide at 98~99°C for 1 hr. was determined.

The results are shown in Table I. The reaction mixture obtained from the chloroethyl bromoanthraquinon-1-ylcarbamate and potassium hydroxide can be separated into the constituents by a column chromatography from benzene on alumina, but it is observed that the 2-chloroethyl bromoanthraquinon-1-ylcarbamate is gradually converted into the corresponding bromoanthraquinon-1-yloxazolidin-2-one on alumina. For this reason, the determination of the proportion of constituents was carried out by a spectrophotometry. Since the absorption bands of the constituents are separated from each other, the determination was carried out exactly. The absorption spectra of 2-chloroethyl bromoanthraquinon-1-ylcarbamates, 3-(bromoanthraquinon-1-yl)oxazolidin-2-ones and 1-*N*-2-hydroxyethylamino-bromoanthraquinones are shown in Figs. 1—3, respectively.

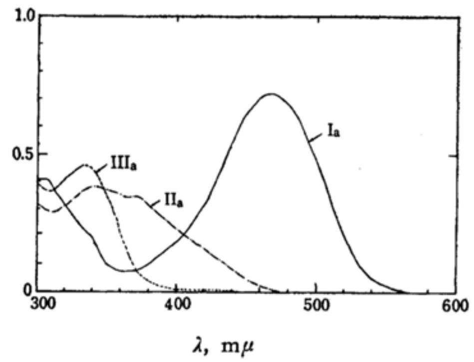


Fig. 1. Absorption spectra of 1-amino-2-bromoanthraquinones.
Ia: 1-Amino-2-bromoanthraquinone (in ethanol)
IIa: 2-Chloroethyl 2-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIa: 3-(2-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)

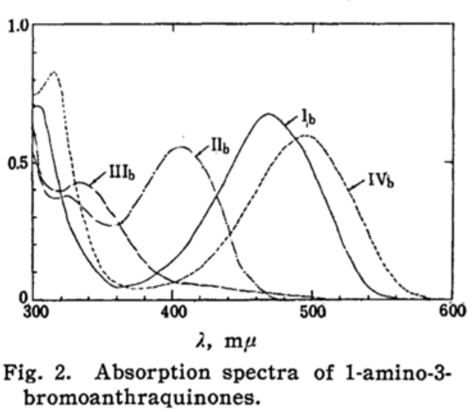


Fig. 2. Absorption spectra of 1-amino-3-bromoanthraquinones.
Ib: 1-Amino-3-bromoanthraquinone (in ethanol)
IIb: 2-Chloroethyl 3-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIb: 3-(3-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)
IVb: 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone (in toluene)

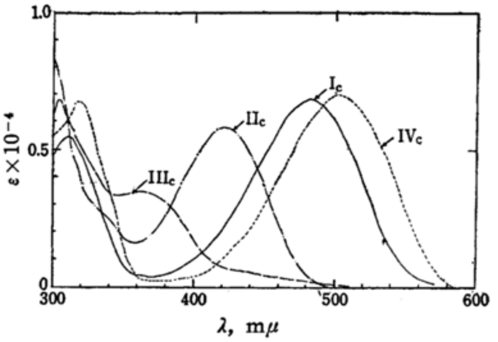


Fig. 3. Absorption spectra of 1-amino-4-bromoanthraquinones.
Ic: 1-Amino-4-bromoanthraquinone (in ethanol)
IIc: 2-Chloroethyl 4-bromoanthraquinon-1-ylcarbamate (in toluene)
IIIc: 3-(4-Bromoanthraquinon-1-yl)-oxazolidin-2-one (in toluene)
IVc: 1-*N*-2-Hydroxyethylamino-4-bromoanthraquinone (in toluene)

TABLE II. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF 1-AMINO-BROMOANTHRAQUINONES

Compound	λ_{max}, mμ		$\varepsilon_{max}\times10^{-4}$	
I a*	308	469	0.436	0.760
I b*	~305	471	(0.732)	0.689
I c*	312	483	0.570	0.701
II a**	342	370	0.386	0.346
II b**	325	406	0.375	0.555
II c**	~335	423	(0.269)	0.580
III a**	334	~395	0.472	(0.031)***
III b**	335	~410	0.417	(0.062)***
III c**	342	~420	0.347	(0.064)***
IV b**	313	496	0.821	0.593
IV c**	318	503	0.683	0.697

Bracketed values are absorption bands of low intensity.
* Solvent: ethanol; concn. 1×10^{-4} mol./l.
** Solvent: toluene; concn. 1×10^{-4} mol./l.
*** Solvent: toluene; concn. 1×10^{-3} mol./l.

Absorption maxima and extinction coefficients are given in Table II.

Discussion

Effect of the Bromine Atom according to its Position on Absorption Spectra.—In the case of the spectra of 2-chloroethyl anthraquinon-1-ylcarbamates, the introduction of the 2-bromine atom into an anthraquinone ring results in the lowering of an intensity of the band near 400 mμ ascribed to Aq-$\ddot{\mathrm{N}}$ chromophore and the displacement by 53 mμ towards a shorter wavelength as compared with 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate. This fact may be explicable in terms of the steric hindrance of the $\pi-p$ conjugation, between the anthraquinone ring and an unshared electron pair of the nitrogen atom, due to a repulsion between the carbonyl group and the 2-bromine atom which arises from the overlapping of the van der Waals radii. It is pointed out that $\varepsilon_2/\varepsilon_4$ is considerably smaller for 2-chloroethyl bromoanthraquinon-1-ylcarbamates than for 2-chloroethyl methylanthraquinon-1-ylcarbamates. Projection diagrams (Fig. 4) of uniplanar structures, employing van der Waals radii, indicate only a slightly larger overlapping for 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate than for 2-chloroethyl 2-methylanthraquinon-1-ylcarbamate. Hence additional effects, i. e. the coulombic interaction of the carbonyl group with the 2-bromine atom and the hydrogen bonding between the carbonyl group and the 2-methyl group, must be considered in an explanation of the spectral diffrence between 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate and 2-methylanthraquinon-1-ylcarbamate (Table III).

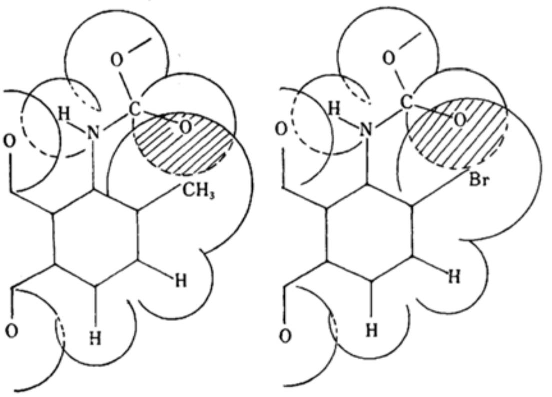


Fig. 4. Projection diagrams of 2-chloroethyl 2-bromo- and 2-methyl-anthraquinon-1-ylcarbamates.

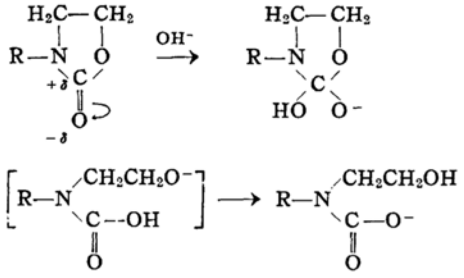
TABLE III. ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS OF THE PRIMARY BANDS OF 2-CHLOROETHYL ANTHRAQUINON-1-YLCARBAMATES

Substituent of anthraquinone nucleus	$\lambda_{\max}$ mμ	$\varepsilon\times10^{-4}$	$\varepsilon_2/\varepsilon_4$
2-Methyl	378	0.520(ε_2)	0.84
4-Methyl	421	0.618(ε_4)	
2-Bromo	370	0.346(ε_2)	0.60
4-Bromo	423	0.580(ε_4)	

In the spectra of 3-(anthraquinon-1-yl)-oxazolidin-2-ones, it is expected that an absence of intermolecular hydrogen bonding possibility results in the lowering of the intensity of the band near 400 mμ as compared with the compounds which have intermolecular hydrogen bonding possibility, 2-chloroethyl anthraquinon-1-ylcarbamates. It is further expected that the introduction of a bulky group, such as oxazolin-2-onyl, into the 1-position of the anthraquinone ring increases the extent of steric inhibition of the $\pi-p$ conjugation, between the anthraquinone ring and the unshared electron pair of the nitrogen atom, and results in the lowering of the intensity of the band near 400 mμ ascribed to Aq-$\ddot{\mathrm{N}}$ chromophore. If the 2-bromine atom is introduced into the anthraquinone ring, the steric hindrance inhibits the $\pi-p$ conjugation between the ring and the unshared electron pair of the nitrogen atom to a greater extent. This is illustrated in Table II.

The Effect of the 2-Bromine Atom on the Reactivity of 3-(Bromoanthraquinon-1-yl)-oxazolidin-2-ones with the Hydroxide Ion.—On account of an aqueous dispersion of solid material, various difficulties may be introduced in the discussion when the reactivities are compared with each other. Nevertheless, it may be probable that some close relation exists between the reactivity and factors such as electronic and steric effects of groups in the anthraquinone nucleus. Table I shows clearly that the 2-bromine atom decreases the reactivity of the 3-(bromoanthraquinon-1-yl)-oxazolidin-2-ones with potassium hydroxide to a considerable extent. In other words, it shows the existence of a steric hindrance of the 2-bromine atom in the hydrolysis, this effect inhibiting the conversion of 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one into 1-*N*-2-hydroxyethylamino-2-bromoanthraquinone.

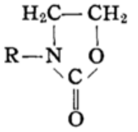
In the basic hydrolysis of 3-substituted oxazolidin-2-ones, there is a carbonyl carbon atom at which attack would be expected to occur. A mechanism of the hydrolysis reaction may be illustrated as follows (Scheme III).



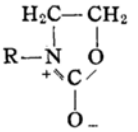
Scheme III

The addition complex has a more or less tetrahedral configuration at the site of substitution. Its formation controls the rate of the reaction. It may be probable, therefore, that the steric hindrance to the formation of the addition complex, due to overlapping of the van der Waals radii and the coulombic interaction of the 2-bromine atom with the hydroxide ion, inhibits the conversion of 3-(2-bromoanthraquinon-1-yl)-oxazolidin-2-one into 1-*N*-2-hydroxyethylamino-2-bromoanthraquinone. Further effects must, however, be considered in an explanation of the experimental results.

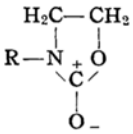
3-Substituted oxazolidin-2-ones may be described as a resonance hybrid of structures V—VII.



(V)

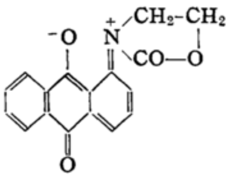


(VI)



(VII)

If the $-\ddot{N}-C=O$ system is planar, there will be a flow of a charge away from the nitrogen atom into the carbonyl oxygen atom; in other words, structure VI is much more important than structure VII, in which the positive charge is on the carbonyl carbon atom. In 3-anthraquinon-1-yloxazolidin-2-ones, an additional structure VIII contributes to the resonance hybrid. This means that if the $Aq-\ddot{N}$ system is planar, there will be a flow of a charge away from the nitrogen atom into the anthraquinone ring, this resulting in a decrease of the contribution of structure VI to the resonance hybrid. The steric hindrance of the 2-bromine atom to the planar configuration of the $Aq-\ddot{N}$ system decreases the contribution of structure VIII, increasing the contribution of structure VI to the resonance hybrid.



(VIII)

On the other hand, a nucleophilic attack occurs readily at the position at which an open sextet of electrons can be provided readily. It is therefore reasonable to suppose that the contribution of structure VI is unfavorable for the formation of an addition complex in the reaction of 3-(anthraquinon-1-yl)oxazolidin-2-ones with the hydroxide ion. The steric hindrance of the 2-bromine atom to the planar configuration of the $Aq-\ddot{N}$ system inhibits the conversion of 3-(2-bromoantraquinon-1-yl)-oxazolidin-2-one into 1-*N*-2-hydroxyethylamino-2-bromoanthraquinone.

It is also expected that the introduction of electron attracting groups into the anthraquinone ring results in the decrease of contribution of strueture VI to the resonance hybrid and the formation of the addition complex will be facilitated, increasing the rate of conversion of 3-(anthraquinon-1-yl)oxazolidin-2-ones into 1-*N*-2-hydroxyethylaminoanthraquinones. This is illustrated by the comparison of reactivities of 3-(bromoanthraquinon-1-yl)-oxazolidin-2-ones with those of 3-(methylanthraquinon-1-yl)oxazolidin-2-ones (Table IV).

TABLE IV. CONVERSION OF 3-(ANTHRAQUINON-1-YL)OXAZOLIDIN-2-ONES INTO 1-*N*-2-HYDROXYETHYLAMINOANTHRAQUINONES*

Compound	Conversion, %
3-(2-Methylanthraquinon-1-yl)oxazolidin-2-one	17
3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one	0
3-(3-Methylanthraquinon-1-yl)oxazolidin-2-one	73
3-(3-Bromoanthraquinon-1-yl)oxazolidin-2-one	90
3-(4-Methylanthraquinon-1-yl)oxazolidin-2-one	41
3-(4-Bromoanthraquinon-1-yl)oxazolidin-2-one	54

* KOH, 20%; Temp., 98~99°C; Reaction time, 1 hr.

Experimental

1-Amino-2-bromoanthraquinone (**Ia**).—Red plates (glacial acetic acid), m. p. 179~180°C.

Anal. Found: N, 4.62. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

1-Amino-3-bromoanthraquinone (**Ib**)[2]. — Red prisms (glacial acetic acid), m. p. 242~243°C.

Anal. Found: N, 4.70. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

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[2] F. Ullmann and O. Fisher, *Ber.*, **49**, 2154 (1956).

1-Amino-4-bromoanthraquinone (Ic)(3).—The compound was separated by a column chromatography from benzene on alumina and recrystallized from ligroin, giving red needles, m. p. 179~180°C.

Anal. Found: N, 4.69. Calcd. for $C_{14}H_8O_2NBr$: N, 4.64%.

2-Chloroethyl 2-Bromoanthraquinon-1-ylcarbamate (IIa)(4).—Yellow needles (ethyl alcohol), m. p. 188~189°C.

Anal. Found: N, 3.48. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

2-Chloroethyl 3-Bromoanthraquinon-1-ylcarbamate (IIb).—A mixture of 2.00 g. of 1-amino-3-bromoanthraquinone (m. p. 240~241°C), 1.20 g. of 2-chloroethyl chloroformate (b. p. 150~151°C), 0.90 g. of sodium carbonate and 30 ml. of xylene was refluxed with stirring for 8 hr. The insoluble material was removed by hot filtration and the filtrate was evaporated to a volume of about 15 ml. for crystallization. Yield, 2.65 g. (99% of the theory) of yellow needles, m. p. 215~216°C. It was recrystallized from ethanol, giving yellow needles, m. p. 220~221°C.

Anal. Found: N, 3.53. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

2-Chloroethyl 4-Bromoanthraquinon-1-ylcarbamate (IIc).—A mixture of 2.00 g. of 1-amino-4-bromoanthraquinone (m. p. 175~176°C) 1.20 g. of 2-chloroethyl chloroformate (b. p. 150~151°C), 0.90 g. of sodium carbonate and 20 ml. of xylene was refluxed with stirring for 2 hr. The insoluble material was removed by hot filtration and the filtrate was evaporated to a volume of about 10 ml. for crystallization. Yield, 2.55 g. (94% of the theory) of yellow needles, m. p. 201~202°C. It was recrystallized from ethanol, giving yellow needles, m. p. 203~204°C.

Anal. Found: N, 3.67. Calcd. for $C_{17}H_{11}O_4NBrCl$: N, 3.42%.

3-(2-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIa)(4).—Pale brown plates (toluene), m. p. 284°C (decomp.).

Anal. Found: N, 4.09. Calcd. for $C_{17}H_{10}O_4NBr$: N, 4.11%.

3-(3-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIb) and 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone (IVb).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate and 30 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was collected, washed with water, and dried. Yield, 0.92 g. of reddish brown powder. The product, consisting of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone, 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one and 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, was dissolved in benzene and chromatographed on alumina. 1-*N*-2-Hydroxyethylamino-3-bromoanthraquinone is most strongly adsorbed and 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one is more strongly adsorbed than 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, which is gradually converted into 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one on alumina in the column. The red band, containing 1-*N*-2-hydroxylamino-3-bromoanthraquinone, was eluted by the use of ethanol. Yield, 0.15 g. of red needles, m. p. 213~214°C. It was recrystallized from toluene, giving red needles, m. p. 213~214°C.

Anal. Found: N, 4.08. Calcd. for $C_{16}H_{12}O_3NBr$: N, 4.11%.

The pale brown band, containing 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.07 g. of pale brown crystalline powder, m. p. 215~229°C. It was recrystallized from ethanol, giving pale brown needles, m. p. 243~244°C.

Anal. Found: N, 3.73. Calcd. for $C_{17}H_{10}O_4NBr$: N, 3.76%.

The yellow elute, containing 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate, was evaporated for crystallization. Yield, 0.70 g. of yellow needles, m. p. 212~215°C.

3-(4-Bromoanthraquinon-1-yl)oxazolidin-2-one (IIIc) and 1-*N*-2-Hydroxyethylamino-4-bromoanthraquinone (IVc).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate (m. p. 201~202°C) and 30 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.88 g. of reddish brown powder. The product was treated as in the foregoing experiment. The red band, containing 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone, was eluted by the use of ethanol. Yield, 0.45 g. of red needles, m. p. 176~177°C. It was recrystallized from ethanol, giving red needles, m. p. 181~182°C.

Anal. Found: N, 4.09. Calcd. for $C_{16}H_{12}O_3NBr$: N, 4.11%.

The pale brown band, containing 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.20 g. of pale brown needles, m. p. 197~202°C. It was recrystallized from ethanol, giving pale brown needles, m. p. 208~209°C.

Anal. Found: N, 3.98. Calcd. for $C_{17}H_{10}O_4NBr$: N, 3.76%.

The yellow elute, containing 2-chloroethyl 4-bromoanthraquinon-1-yl-carbamate, was evaporated for crystallization. Yield, 0.10 g. of yellow needles, m. p. 184~190°C.

1-*N*-2-Hydroxyethylaminoanthraquinone (IVa).—A mixture of 0.50 g. of 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate (m. p. 191~192°C) and 15 g. of a 20% aqueous solution of potassium hydroxide was refluxed with vigorous stirring for 1 hr. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.40 g. of brownish red powder. It was treated as in the foregoing experiment. The red band, containing 1-*N*-2-hydroxyethylaminoanthraquinone, was eluted by the use of ethanol. Yield, 0.05 g. of red needles, m. p. 169~171°C. A mixed m. p. with authentic 1-*N*-2-hydroxyethylaminoanthraquinone(5) (m.p. 172°C) was 170~171°C.

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3) Ger. Pat., 266,563 (1913).

4) K. Naiki, *J. Soc. Org. Syn. Chem., Japan* (*Yūki Gōsei Kagaku Kyōkaishi*), **14**, 84 (1954).

5) K. Naiki, ibid., **12**, 401 (1954).

The pale brown band, containing 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.30 g. of pale brown plates, m. p. 265°C (decomp.).

Determination of the Proportion of the Constituents of the Reaction Product Obtained from 2-Chloroethyl Bromoanthraquinon-1-ylcarbamate and a 20% Aqueous Solution of Potassium Hydroxide.—A mixture of 0.20 g. of finely powdered 2-chloroethyl bromoanthraquinon-1-ylcarbamate and 6.0 g. of a 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hr. After being diluted with water, the precipitate was colleted, washed with water and dried. Yield, 0.18 g. of brownish red powder from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate; 0.18 g. of brownish red powder from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate; 0.18 g. of brownish red powder from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate. The proportion of the constituents of the products obtained above was determined by a Shimadzu QB-50 electrophotometer. Optical densities (*D*) of the toluene solution of the products are shown in Tables V—VII. It was found by simple calculation that the reaction product obtained from 2-chloroethyl 2-bromoanthraquinon-1-ylcarbamate contains 174 mg. of 3-(2-bromoanthraquinon-1-yl)oxazolidin-2-one; the product obtained from 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate contains 10 mg. of 3-(3-bromoanthraquinon-1-yl)oxazolidin-2-one, 106 mg. of 1-*N*-2-hydroxyethylamino-3-bromoanthraquinone and 57 mg. of 2-chloroethyl 3-bromoanthraquinon-1-ylcarbamate; the product obtained from 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate contains 46 mg. of 3-(4-bromoanthraquinon-1-yl)oxazolidin-2-one, 49 mg. of 1-*N*-2-hydroxyethylamino-4-bromoanthraquinone and 86 mg. of 2-chloroethyl 4-bromoanthraquinon-1-ylcarbamate.

TABLE V. OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 2-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ	D	$\varepsilon\times10^{-4}$	
mμ		IIa	IIIa
330	0.480	0.370	0.466
370	0.125	0.346	0.124

* Solvent: toluene; concn. 38 mg./l.

TABLE VI. OPTICAL DENSITIES OE THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 3-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ	D	$\varepsilon\times10^{-4}$		
mμ		IIb	IIIb	IVb
330	0.528	0.372	0.417	0.432
410	0.281	0.556	0.064	0.076
500	0.446	0.020	0.007	0.590

* Solvent: toluene; concn. 43 mg./l.

TABLE VII. OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 4-BROMOANTHRAQUINON-1-YLCARBAMATE*

λ	D	$\varepsilon\times10^{-4}$		
mμ		IIc	IIIc	IVc
340	0.336	0.240	0.347	0.353
420	0.324	0.560	0.054	0.098
500	0.255	0.051	0.007	0.696

* Solvent: toluene; concn. 42 mg./l.

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