*Studies on 3-(Anthraquinon-1-yl)oxazolidin-2-ones. I. 3-(Methylanthraquinon-1-yl)oxazolidin-2-ones and Their Related Compounds**

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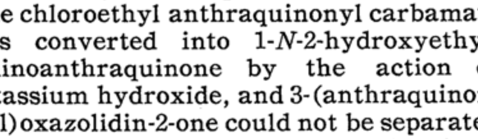
In a previous paper[1], it was reported that 1-aminoanthraquinone reacted with 2-chloroethyl chloroformate and formed 2-chloroethyl anthraquinon-1-yl carbamate. The chloroethyl anthraquinonyl carbamate was converted into 1-*N*-2-hydroxyethylaminoanthraquinone by the action of potassium hydroxide, and 3-(anthraquinon-1-yl)oxazolidin-2-one could not be separated from reaction mixture by fractional recrystallization. The reactions are explained as follows (Scheme I).



Sheme 1

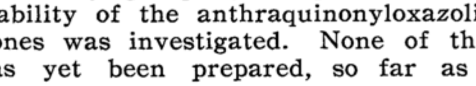
In another paper[2], it was found that 2-chloroethyl anthraquinon-1-yl carbamates which contain 2-substituent in anthraquinone nucleus were converted into 2′-substituted 3-(anthraquinon-1-yl)oxazolidin-2-ones by the action of potassium hydroxide.

The result of these investigations suggests the existence of a steric hindrance of 2′-substituent in the anthraquinonyloxazolidinones which plays an important part in the stability of the anthraquinonyloxazolidinones in aqueous solution of potassium hydroxide. Similarly, an electronic effect of substituent should be considered to be important and this is being investigated in the author's laboratory.

In the present study, 3-(methylanthraquinon-1-yl)-oxazolidin-2-ones, 1-*N*-2-hydroxyethylaminomethylanthraquinones and 2-chloroethyl methylanthraquinon-1-yl carbamates were synthesized and the effect of the methyl group by its position on the stability of the anthraquinonyloxazolidinones was investigated. None of them has yet been prepared, so far as is known.

Preparation and Results

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



Scheme II

2-Chloroethyl 2-methylanthraquinon-1-yl carbamate (Ia), 3-methylanthraquinon-1-yl carbamate (Ib) and 4-methylanthraquinon-1-yl carbamate (Ic) were obtained from the corresponding 1-aminomethylanthraquinones by the action of 2-chloroethyl

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[1] K. Naiki, *J. Soc. Org. Syn. Chem. Japan*, (*Yūki Gōsei Kagaku Kyokaishi*), **12**, 364 (1954).

[2] K. Naiki, ibid., **14**, 84 (1956).

chloroformate in the presence of sodium carbonate in boiling xylene. 1-*N*-2-Hydroxyethylamino-2-methylanthraquinone(IIIa), 1-*N*-2-hydroxyethylamino-3-methylanthraquinone(IIIb) and 1-*N*-2-hydroxyethylamino-4-methylanthraquinone(IIIc) were obtained from the corresponding 2-chloroethyl methylanthraquinonyl carbamates by the action of 20% aqueous solution of potassium hydroxide at 105~107°. Mixtures of the hydroxyethylaminomethylanthraquinones, the 3-(methylanthraquinon-1-yl)-oxazolidin-2-ones(II) (IIa, 2′-methyl; IIb, 3′-methyl; IIc, 4′-methyl) and the unchanged 2-chloroethyl methylanthraquinonyl carbamates were obtained from the corresponding 2-chloroethyl methylanthraquinon-1-yl carbamates by the action of 20% aqueous solution of potassium hydroxide at 98~99° for 1 hour.

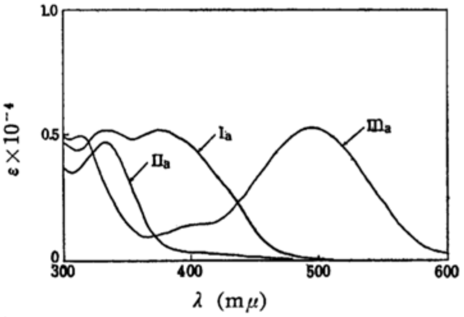


Fig. 1. Absorption spectra of the derivatives of 1-amino-2-methylanthraquinone (in toluene)
Ia: 2-Chloroethyl 2-methylanthraquinon-1-yl carbamate
IIa: 3-(2-Methylanthraquinon-1-yl) oxazolidin-2-one
IIIa: 1-*N*-2-Hydroxyethylamino-2-methyl-anthraquinone

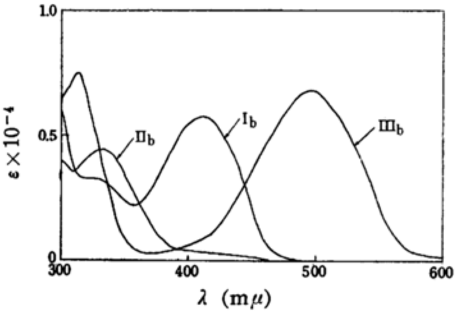


Fig. 2. Absorption spectra of the derivatives of 1-amino-3-methylanthraquinone (in toluene)
Ib: 2-Chloroethyl 3-methylanthraquinon-1-yl carbamate
IIb: 3-(3-Methylanthraquinon-1-yl) oxazolidin-2-one
IIIb: 1-*N*-2-Hydroxyethylamino-3-methyl-anthraquinone

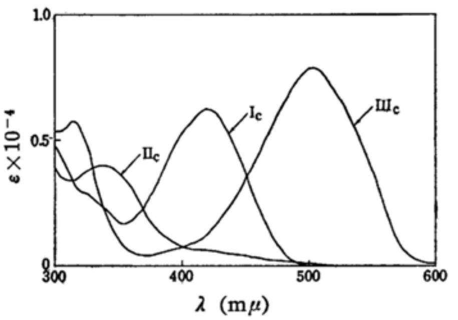


Fig. 3. Absorption spectra of the derivatives of 1-amino-4-methylanthraquinone (in toluene)
Ic: 2-Chloroethyl 4-methylanthraquinon-1-yl carbamate
IIc: 3-(4-Methylanthraquinon-1-yl) oxazolidin-2-one
IIIc: 1-*N*-2-Hydroxyethylamino-4-methyl-anthraquinone

The proportion of the constituents of the reaction mixtures was determined by spectrophotometry. These results are shown in Table I. Each of the constituents was separated from the reaction mixtures by column chromatography from benzene on alumina.

Absorption spectra of the compounds obtained above are shown in Figs. 1, 2 and 3, respectively. Absorption maxima and extinction coefficients are given in Table III.

Discussion

Effects of the Methyl Group According to its Position on the Stability of the Methylanthraquinonyloxazolidinones.— On account of aqueous dispersion of solid materials, various difficulties may be introduced in the discussion when their stabilities are compared with one another. Nevertheless, it may probably be considered that there exists some close relation between the stability and the factors such as electronic and steric effects of groups. Table I shows clearly that the 2′-methyl group increases the stability of

Table I
THE PROPORTION OF THE CONSTITUENTS OF THE REACTION PRODUCT FROM THE 2-CHLOROETHYL METHYLANTHRAQUINON-1-YL CARBAMATES AND 20% AQUEOUS SOLUTION OF POTASSIUM HYDROXIDE*

Position of CH_3	I %	II %	III %
2	7	77	16
3	13	23	64
4	14	51	35

* Determined by the spectrophotometry.

the anthraquinonyloxazolidinone in aqueous solution of potassium hydroxide. In other words, it shows the existence of steric hindrance of the methyl group in the hydrolysis process (cf. Scheme I).

The reaction mixture obtained from the chloroethyl methylanthraquinonyl carbamates and potassium hydroxide can be separated into the constituents by the column chromatography from benzene on alumina. It is observed, however, that the unreacted 2-chloroethyl methylanthraquinonyl carbamates are gradually converted into the corresponding methylanthraquinonyloxazolidinones on alumina in the column. For this reason, the use of the column chromatography to determine exactly the proportion of the constituents is not desirable in a strict sense. Thus, the determination of the proportion of the constituents was attempted by the spectrophotometry. Since the principal absorption bands of the constituents are apart from one another as shown in Figs. 1, 2 and 3, the determination of the proportion of the constituents was carried out exactly.

The Effect of the 2-Methyl Group on Absorption Spectra.—A marked difference in intensity of light absorption between mono- and dimethylated 1-aminoanthraquinones was explained by the steric hindrance of the *N*-methyl group with the adjacent carbonyl group[3]. Accordingly, it may be expected that another substituent at 2-position provides a further steric effect. This expectation agrees with the experimental result of the 1-amino-2-methoxyanthraquinones shown in Table II[4].

TABLE II
ABSORPTION SPECTRA OF 1-AMINO-2-METHOXYANTHRAQUINONES

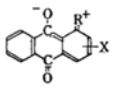
Compound	Principal absorption band (in ethanol)
1-Amino-2-methoxyanthraquinone	478 mμ
1-Methylamino-2-methoxyanthraquinone	520 mμ
1-Dimethylamino-2-methoxyanthraquinone	506 mμ

It is now apparent that the steric hindrance of the methyl group of the compounds discussed here plays an important part. It has been known that the first absorption band of the 1-substituted anthraquinones can be attributed to resonance hybrid of the normal and the extreme ionic form (IV). The explanation of the formation of the ionic form is given by the well-known mechanism (V) which shows a mesomeric shift of the electrons from the 1-substituted group to the carbonyl oxygen atom. Thus, the contribution of the ionic form will be further increased by the 1-substituent with the greater electron-donating ability, resulting in the stronger the donating power, the longer the wave length of absorption maxima. This is illustrated in the case of the hydroxyethylaminoanthraquinones (Table III). However, in the 2-chloroethyl anthraquinonyl carbamates, another electron shift may be introduced in the opposite sense (VI). This alternative effect will counter the shift of the electrons to the anthraquinone ring and lower the wave length of absorption.

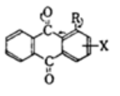
TABLE III
ABSORPTION SPECTRA OF 1-AMINOMETHYLANTHRAQUINONES*

Compound	$\lambda_{max.}$ (mμ)		$\varepsilon_{max.} \times 10^{-4}$	
Ia	336	378	0.518	0.520
Ib	320	414	0.335	0.580
Ic	∼325	421	(0.271)	0.618
IIa	332	∼400	0.469	(0.021)**
IIb	333	∼405	0.443	(0.040)**
IIc	337	∼420	0.388	(0.052)**
IIIa	312	492	0.501	0.518
IIIb	313	497	0.768	0.687
IIIc	315	504	0.580	0.792

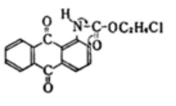
Bracketed values are absorption bands of low intensity.
∼ denotes point of inflexion.
* Measured by a Shimadzu QB-50 Electrophotometer. Solvent: toluene; concn. 1×10^{-4} mol./l.
** Concn. 1×10^{-3} mol./l.



(IV)



(V)



(VI)

The further effect will come into play if such a group as methyl is introduced in the 2-position, for the steric hindrance from both the carbonyl and the methyl group forces atoms attached to the substituting group out of the plane of the anthraquinone nucleus. Consequently, in the case of the spectrum of 2-chloroethyl 2-methylanthraquinon-1-yl carbamate, the intensity of the corresponding absorption band (336 mμ) to that of anthraqinone becomes stronger and the primary band (378 mμ)

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[3] R. H. Peters et al., *J. Chem. Soc.*, **1953**, 2101.
[4] K. Naiki, *J. Org. Syn. Chem. Japan* (*Yûki Gôsei Kagagu Kyokaishi*), **11**, 113 (1953).

becomes weaker than the other methylanthraquinonyl carbamates. If a more bulky group such as the oxazolidinonyl group is at the 1-position of the anthraquinone nucleus, the steric effect inhibits the shift of the electrons from the nitrogen atom to the anthraquinone nucleus, and spectra of the anthraquinonyloxazolidinones are very similar to that of anthraquinone itself.

In the case of the methylanthraquinonyloxazolidinones, it seems that the 2-methyl group in the anthraquinone nucleus increases the steric inhibition and the absorption intensity at about 400 mμ becomes weaker than the other methylanthraquinonyloxazolidinones.

Experimental

2-Chloroethyl 2-Methylanthraquinon-1-yl carbamate (Ia).—The synthesis of the compound was reported in the previous paper2). The product was recrystallized from ethanol, giving yellow needles, m. p. 173∼174°.

2-Chloroethyl 3-Methlanthraquinon-1-yl carbamate (Ib). — A mixture of 1.08 g. of 1-amino-3-methylanthraquinone (m. p. 185∼189°), 0.76 g. of 2-chloroethyl chloroformate, 0.54 g. of sodium carbonate and 70 ml. of xylene was refluxed with stirring for 2 hours. Insoluble substance was removed by hot filtration and the filtrate was evaporated to a volume of about 20 ml. for crystallization. Yield, 1.27 g. (83% of the theory) of yellow needles, m. p. 198∼200°. The product was recrytallized from ethanol, giving yellow needles, m. p. 201∼202°. *Anal.* Found: N, 4.34. Calcd. for $C_{18}H_{14}O_4NCl$: N, 4.07%.

2-Chloroethyl 4-Methylanthraquinon-1-yl carbamate (Ic). — A mixture of 1.88 g. of 1-amino-4-methylanthraquinone (m. p. 180∼182°), 1.24 g. of 2-chloroethyl chloroformate, 0.95 g. of sodium carbonate and 18 ml. of xylene was refluxed with stirring for 6 hours. The insoluble substance was removed by hot filtration and the filtrate was cooled. The crystal formed was collected and dried. Yield, 2.45 g. (90% of the theory) of yellow needles, m. p. 187∼188°. It was recrystallized from ethanol, giving yellow needles, m. p. 190∼191°. *Anal.* Found: N, 4.25. Calcd. for $C_{18}H_{14}O_4NCl$: N, 4.07%.

Behavior of 2-Chloroethylmethylanthraquinon-1-yl carbamates on Alumina.—2-Chloroethyl 3-methylanthraquinon-1-yl carbamate (0.40g., m. p. 198∼199°) was dissolved in benzene, then adsorbed on alumina, stood overnight and eluted by the use of ethanol. The substance (0.30 g., m. p. 213∼215°), consisting of 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one and unchanged 2-chloroethyl 3-methylanthraquinon-1-yl carbamate, was obtained. It was separated into the constituents by means of chromatography on alumina from benzene. 2-Chloroethyl 3-methylanthraquinon-1-yl carbamate passed through the column; 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one was eluted by the use of ethanol. Pure 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one was obtained.

Similar treatment of 2-chloroethyl 2-methylanthraquinon-1-yl carbamate and 4-methylanthraquinon-1-yl carbamate gave 3-(2-methylanthraquinon-1-yl) oxazolidin-2-one and 3-(4-methylanthraquinon-1-yl) oxazolidin-2-one, respectively.

3-(2-Methylanthraquinon-1-yl)oxazolidin-2-one (IIa).—The synthesis was reported in the previous paper2). Pale yellow needles, m. p. 226∼227°.

3-(3-Methylanthraquinon-1-yl) oxazolidin-2-one (IIb).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 3-methylanthraquinon-1-yl carbamate (m. p. 198∼199°) and 30 g. of 20% aqueous solution of potassium hydroxide was heated in a boiling water bath with vigorous stirring for 1 hour. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.82 g. of reddish powder. The product, consisting of unchanged 2-chloroethyl 3-methylanthraquinon-1-yl carbamate, 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one and 1-*N*-2-hydroxyethylamino-3-methylanthraquinone, was dissolved in benzene and chromatographed on alumina. 1-*N*-2-Hydroxyethylamino-3-methylanthraquinone is most strongly adsorbed and 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one is more strongly adsorbed than 2-chloroethyl 3-methylanthraquinon-1-yl carbamate. The red band, containing 1-*N*-2-hydroxyethylamino-3-methylanthraquinone, was eluted by the use of ethanol. Yield, 0.38 g. of red needles, m. p. 234∼235°. The pale orange band, containing 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one, was eluted by the use of ethanol. Yield, 0.18 g. of pale orange needles, m. p. 235∼236°. It was recrystallized from ethanol, giving pale orange needles, m. p. 235∼236°. *Anal.* Found: N, 4.50. Calcd. for $C_{18}H_{13}O_4N$: N, 4.56%. The yellow eluate, containing 2-chloroethyl 3-methylanthraquinon-1-yl carbamate, was evaporated for crystallization. Yield, 0.14 g. of yellow needles, m. p. 198∼199°

3-(4-Methylanthraquinon-1-yl) oxazolidin-2-one (IIc).—A mixture of 0.50 g. of finely powdered 2-chloroethyl 4-methylanthraquinon-1-yl carbamate (m. p. 187∼188°) and 15 g. of 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hour. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.33 g. of reddish brown powder. It was fractionally recrystallized from ethanol, giving pale brown needles, m. p. 201∼202°. *Anal.* Found: N, 4.58. Calcd. for $C_{18}H_{13}O_4N$: N, 4.56%.

The chromatographic separation of the reaction product obtained above, consisting of 1-*N*-2-hydroxyethylamino-4-methylanthraquinone, 3-(4-methylanthraquinon-1-yl) oxazolidin-2-one and unchanged 2-chloroethyl 4-methylanthraquinon-1-yl carbamate, was carried out in the same with the 3-methyl derivative. Yield, 0.100 g. of 1-*N*-2-hydroxyethylamino-4-methylanthraquinone, m. p. 153∼154°, 0.130 g. of 3-(4-methylanthraquinon-1-yl) oxazolidin-2-one, m. p. 201∼202°, and 0.060 g. of

2-chloroethyl 4-methylanthraquinon-1-yl carbamate, m. p. 189∼190°.

Determination of the Proportion of the Constituents of the Reaction Product Obtained from the 2-Chloroethyl Methylanthraquinon-1-yl Carbamates and 20% Aqueous Solution of Potassium Hydroxide.—A mixture of 0.20 g. of finely powdered 2-chloroethyl methylanthraquinon-1-yl carbamate and 6.00 g. of 20% aqueous solution of potassium hydroxide was heated with vigorous stirring in a boiling water bath for 1 hour. After being diluted with water, the precipitate was collected, washed with water and dried. Yield, 0.16 g. of pale red powder, m. p. 192∼201°, from 2-chloroethyl 2-methylanthraquinon-1-yl carbamate; 0.15 g. of brownish red powder, m. p. 139∼149°, from 2-chloroethyl 3-methylanthraquinon-1-yl carbamate; 0.16 g. of reddish brown powder, m. p. 148∼167°, from 2-chloroethyl 4-methylanthraquinon-1-yl carbamate.

The proportion of the constituents of the products obtained above were determined by the use of a Shimadzu QB-50 Electrophotometer. Optical densities (D) of the benzene solutions of the products are shown in Tables IV, V and VI. It was found by simple caluculation that the reaction product obtained from 2-chloroethyl 2-methylanthraquinon-1-yl carbamate contains 21 mg. of 1-*N*-2-hydroxyethylamino-2-methylanthraquinone, 124 mg. of 3-(2-methylanthraquinon-1-yl) oxazolidin-2-one and 12 mg. of 2-chloroethyl 2-methylanthraquinon-1-yl carbamate; the product obtained from 2-chloroethyl 3-methylanthraquinon-1-yl carbamate contains 91 mg. of 1-*N*-2-hydroxyethylamino-3-methylanthraquinone, 33 mg. of 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one and 26 mg. of 2-chloroethyl 3-methylanthraquinon-1-yl carbamate; the product obtained from 2-chloroethyl 4-methylanthraquinon-1-yl carbamate contains 51 mg. of 1-*N*-2-hydroxyethylamino-4-methylanthraquinone, 82mg. of 3-(4-methylanthraquinon-1-yl) oxazolidin-2-one and 27 mg. of 2-chloroethyl 4-methylanthraquinon-1-yl carbamate.

TABLE IV

OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 2-METHYLANTHRAQUINON-1-YL CARBAMATE* AND EXTINCTION COEFFICIENTS OF THE CONSTITUENTS

λ (mμ)	D	$\varepsilon\times10^{-4}$		
		Ia	IIa	IIIa
330	0.670	0.511	0.469	0.346
380	0.086	0.511	0.037	0.109
490	0.128	0.004	0.003	0.518

* Solvent: toluene; conc. 47 mg./l.

TABLE V

OPTICAL DENSITIES OF THF PRODUCT OBTAINED FROM 2-CHLOROETHYL 3-METHYLANTHRAQUINON-1-YL CARBAMATE*AND EXTINCTION COEFFICIENTS OF THE CONSTITUENTS

λ (mμ)	D	$\varepsilon\times10^{-4}$		
		Ib	IIb	IIIb
340	0.475	0.318	0.401	0.685
420	0.147	0.538	0.036	0.124
500	0.357	0.005	0.007	0.672

* Solvent: toluene; concn. 48 mg./l.

TABLE VI

OPTICAL DENSITIES OF THE PRODUCT OBTAINED FROM 2-CHLOROETHYL 4-METHYLANTHRAQUINON-1-YL CARBAMATE* AND EXTINCTION COEFFICIENTS OF THE CONSTITUENTS

λ (mμ)	D	$\varepsilon\times10^{-4}$		
		Ic	IIc	IIIc
340	0.472	0.206	0.378	0.197
420	0.254	0.618	0.051	0.119
500	0.438	0.002	0.015	0.778

* Solvent: toluene; concn. 48 mg./l.

1-*N*-2-Hydroxyethylamino-2-methylnathraquinone (IIIa).—The synthesis was reported in the previous paper[2]. It was purified by means of chromatography from benzene on alumina and recrystallized from toluene, giving red needles, m. p. 141∼142°.

1-*N*-2-Hydroxyethylamino-3-methylanthraquinone (IIIb).—A mixture of 1.00 g. of finely powdered 2-chloroethyl 3-methylanthraquinon-1-yl carbamate (m. p. 198∼199°) and 30 g. of 20% aqueous solution of potassium hydroxide was refluxed with stirring in an oil bath for 1 hour. After being diluted with water, the precipitate was collected, washed with water, dried and recrystallized from toluene. Yield, 0.67 g. (83% of the theory) of red needles, m. p. 180∼181°. It was recrystallized from toluene, giving red needles, m. p. 180.5∼181.0°. *Anal.* Found: N, 5.21. Calcd. for $C_{17}H_{15}O_3N$: N, 5.02%.

1-*N*-2-Hydroxyethylamino-4-methylanthraquinone (IIIc).—A mixture of 0.50 g. of finely powdered 2-chloroethyl 4-methylanthraquinon-1-yl carbamate (m. p. 187∼188°) and 15 g. of 20% aqueous solution of potassium hydroxide was refluxed with stirring in an oil bath for 1 hour. After being diluted with water, the precipitate was collected, washed with water, dried and recrysatllized from toluene. Yield, 0.30 g. (73% of the theory) of brownish red needles, m. p. 163∼164°. It was recrystallized from toluene, giving brownish red needles, m. p. 164∼165°. *Anal.* Found: N, 5.04. Calcd. for $C_{17}H_{15}O_3N$: N, 5.02%.

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