X,X,X-Trichlorobenzo[*b*]phenazine (III).—A mixture of 1 g. of 1,4-dihydro-1,1,4,4-tetrachloro-2,3-naphthoquinone hydrate and 0.5 g. of *o*-phenylenediamine in 5 ml. of acetic acid was heated on the steam bath for 15 min., cooled, and the solid collected. The solid was boiled in 100 ml. of toluene, the insoluble material filtered off, and the filtrate diluted with ligroin and chilled. The solid that separated was collected and recrystallized from chloroform to give 0.2 g. of red product, m.p. 235°.

Mononitrobenzo[*b*]phenazine-6,11-quinone (XIV).—Benzo[*b*]phenazine (I) (20 g.) was added, with stirring, to 200 ml. of nitric acid (*d* 1.42). The reaction mixture was then heated on the steam bath for 2 hr. After cooling, 50 ml. of water was added. The bright yellow product was collected by filtration and crystallized twice from cyclohexanone to give 12 g. of XIV, m.p. 312°. If 6,11-dinitrobenzo[*b*]phenazine (XIII) is substituted for I in the above reaction, XIV is again obtained.

Polynuclear Heterocycles. IV. The Synthesis of Some New Heterocyclic Quinones[1]

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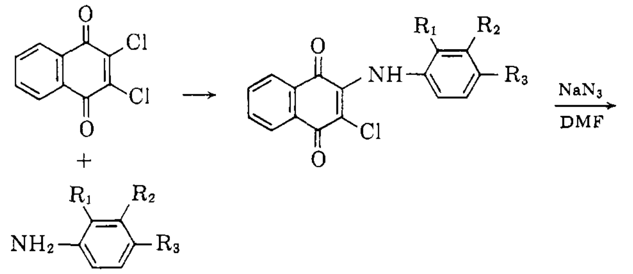
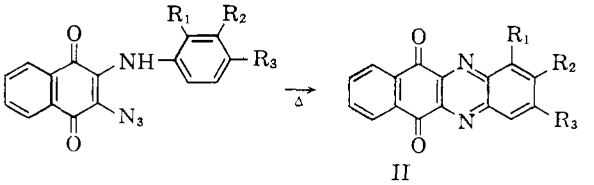
2-Arylamino-3-azido-1,4-naphthoquinones, on heating, undergo a ring closure to give 6,11-benzo[*b*]phenazinequinones. The corresponding 2-cycloalkylamino-3-azido-1,4-naphthoquinones undergo an analogous transformation to yield 5,10-dioxo-4a,11-diazabenzo[*b*]fluorenes. The secondary product obtained in these reactions is a 2-aryl(or cycloalkyl)amino-3-amino-1,4-napthoquinone.

It has been shown[2] that 2-anilino-3-chloro- (Ie), 2-(2-naphthylamino)-3-chloro- (I. R_1 = H; R_2R_3 fused benzo), and 2-(1-naphthylamino)-3-chloro-1,4-naphthoquinone (I. R_1R_2 fused benzo; R_3 = H) react with sodium azide in dimethylformamide at 90–100° to give 6,11-dihydro-6,11-dioxo-5,12-diazanaphthacene (IIe) and 8,13-dihydro-8,13-dioxo-7,14-diazabenzo[*a*]-naphthacene, respectively. The over-all reaction is represented by the following general equations, in which R_1, R_2, and R_3 are hydrogen, a fused benzene ring, or various other substituents.



I

Ia. $R_1 = R_2 = H; R_3 = NO_2$
b. $R_1 = R_2 = H; R_3 = OCH_3$
c. $R_1 = R_2 = H; R_3 = Cl$
d. $R_1 = R_2 = H; R_3 = CH_3$
e. $R_1 = R_2 = R_3 = H$
f. $R_1 = CH_3; R_2 = H; R_3 = N(C_2H_5)_2$

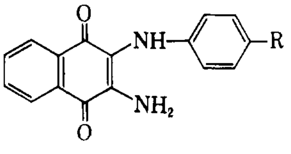


II

IIa. $R_1 = R_2 = H; R_3 = NO_2$
b. $R_1 = R_2 = H; R_3 = OCH_3$
c. $R_1 = R_2 = H; R_3 = Cl$
d. $R_1 = R_2 = H; R_3 = CH_3$
e. $R_1 = R_2 = R_3 = H$
f. $R_1 = CH_3; R_2 = H; R_3 = N(C_2H_5)_2$

In this paper, further work on the scope of this reaction is reported. The effect of electron-withdrawing and electron-attracting substituents in the arylamino moiety of I on ring closure was first examined. During the course of synthesizing such compounds, it was found that the reaction of 2,3-dichloro-1,4-naphthoquinone with aromatic amines was sensitive to steric[3] as well as electronic effects. The preparation of 2-(4-nitroanilino)-3-chloro-1,4-naphthoquinone (Ia) could not be achieved by direct interaction of the components, presumably because of the weak basicity of the amine.[4] Ia was prepared by nitration[5] of 2-anilino-3-chloronaphthoquinone (Ie), and compounds Ib,[6] Ic,[7] and Id[8] as described in the literature.

Treatment of Ia with sodium azide in dimethylformamide at 90–100° gave 2-(4-nitroanilino)-3-amino-1,4-naphthoquinone (IIIa) and none of the heterocyclic quinone (IIa). In contrast, Ib gave the quinone, IIb (in 46% yield), and a 32% yield of IIIb. The ring closure of Ic, Id, and If also proceeded readily to give the quinones IIc, IId, and IIf, respectively. No attempt was made to isolate the secondary product in the latter three reactions.



IIIa. R = NO_2
b. R = OCH_3
e. R = H

The reaction of 2-anilino-3-chloronaphthoquinone (Ie) with sodium azide described previously[2] was repeated and a second product obtained which was identical with the 2-anilino-3-amino-1,4-naphthoquinone (IIIe) prepared according to Fries.[5] A comparison of the ultraviolet spectrum of IIIe with the spectra

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[1] Communication no. 2307 from the Kodak Research Laboratories.

[2] J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 2873 (1962).

[3] Aromatic amines in which there is an *ortho* substituent, such as *o*-chloroaniline and 2,4-dichloroaniline, did not react with 2,3-dichloronaphthoquinone, whereas the reaction proceeded smoothly with 3,4-dichloroaniline.

[4] The reaction of 2,3-dichloro-1,4-naphthoquinone with *p*-nitroaniline in trichloropropane with dimethylaniline as base gave 2-(4-nitroanilino)-naphthoquinone that was identical with the product obtained from 2-hydroxynaphthoquinone and *p*-nitroaniline.

[5] K. Fries and K. Billig, *Ber.*, **58**, 1128 (1925).

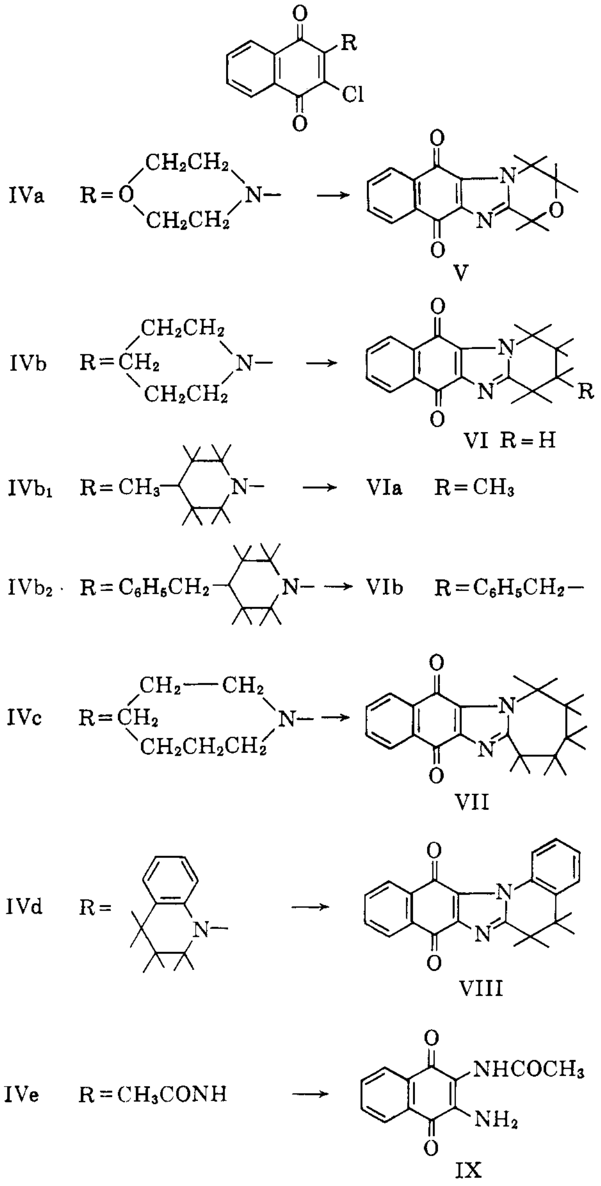
[6] N. G. Buü-Hoi, *Bull. soc. chim. France*, **11**, 578 (1944).

[7] K. Fries and P. Ochwat, *Ber.*, **56**, 1291 (1923).

[8] A. Plagemann, *ibid.*, **15**, 484 (1882).

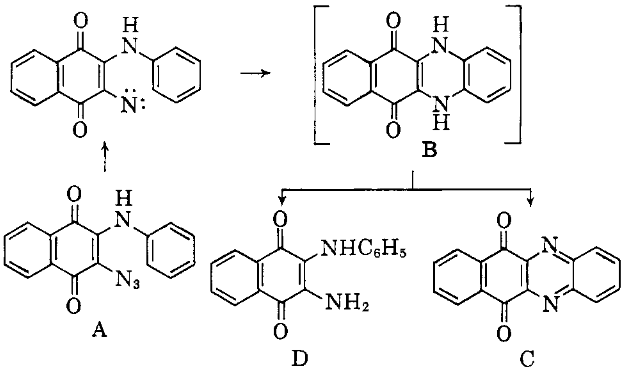
of IIIa and IIIb confirms the similarity of structure of these three materials. The ultraviolet absorption spectra of IIb, IIc, and IId are closely similar to the absorption spectrum of 6,11-dihydro-6,11-dioxo-5,12-diazanaphthacene,[2] thus supporting the structures assigned.

Smolinsky[9] reported that pyrolysis of properly constituted aromatic azides resulted in attack of the azene intermediate upon the C—H bond of a saturated carbon atom with insertion of the nitrogen atom into the bond. In order to see if this same type of reaction occurs in this series, the compounds IVa–IVe were prepared and treated with sodium azide in dimethylformamide. Unexpectedly, it was found that these compounds gave higher yields of the heterocyclic quinones than the arylamino derivatives. Thus, 2-morpholino-3-chloro-1,4-naphthoquinone (IVa) gave 1,2,3,4,5,10-hexahydro-5,10-dioxo-2-oxa-4a,11-diazabenzo[*b*]fluorene (V), in 49% yield, and 2-piperidino-3-chloro-1,4-naphthoquinone (IVb), under the same conditions, gave 1,2,3,4,5,10-hexahydro-5,10-dioxo-4a,11-diazabenzo[*b*]fluorene (VI) in about 47% yield. Introduction of a methyl or a benzyl group, as in IVb_1 and IVb_2, into the piperidino moiety of IVb did not appreciably affect the yield of quinones VIa and VIb. The 2-(hexamethyleniminyl)-3-chloro-1,4-naphthoquinone (IVc) and 2-(tetrahydroquinolyl)-3-chloro-1,4-naphthoquinone (IVd) gave the corresponding quinones, 6,11-dihydro-6,11-dioxo-5a,12-diazabenzo[*f*]cycloheptano[*a*]indene (VII) and 5,6,8,13-tetrahydro-8,13-dioxo-7,13b-diazadibenzo[*a,i*] fluorene (VIII), in somewhat lower yields. 2-Acetamido-3-chloro-1,4-naphthoquinone (IVe) gave the known 2-acetamido-3-amino-1,4-naphthoquinone (IX) as the sole identifiable product.



From these data it is concluded that cyclization of 2-arylamino-3-azidonaphthoquinones is adversely affected by an electron-withdrawing group in the arylamino moiety. Thus, the nitro group in Ia completely inhibits ring closure, and the azide is reduced to the amine IIIa by hydrogen that presumably is acquired from the solvent. The cyclization of 2-cycloalkylamino-3-azidonaphthoquinones proceeds more readily than in the case of the corresponding arylamino derivatives.

In all the foregoing examples it will be noted that the initial cyclization product (B), presumably obtained by an insertion reaction, has undergone dehydrogenation. This point has been proved unequivocally in the case of the 6,11-dihydro-6,11-dioxo-5,12-diazanaphthacenes which were synthesized by another route.[2] The infrared spectra of the heterocyclic quinones V through VIII showed no NH absorption. This fact, together with the elemental analyses which fit the dehydrogenated, better than the dihydro, empirical formula, leaves little doubt that the original cyclization product has undergone partial dehydrogenation. It is believed that this dehydrogenation may have occurred at the expense of the azide group of the reaction intermediate. A portion of the azide A undergoes cyclization to B which, in turn, is oxidized to C by the nitrene generated from azide A; the by-product is D (*cf.* ref. 9). The yield of quinone never exceeded 50%, a fact that could be explained by this mechanism.



Attempts to isolate the azide intermediate were unsuccessful, with the single exception of 2-azido-3-morpholino-1,4-naphthoquinone (X). Temperatures which are high enough to bring about replacement of the chlorine atom with an azido group are also high enough to cause elimination of nitrogen. Thermal decomposition of X proceeded smoothly to give V in 47% yield. As Smolinsky has pointed out, the isoelectronic species >C:, Ö:, and Ṅ: all have a tendency to enter the C—H bond of a saturated carbon. The

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(9) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).

TABLE I

ALKYLAMINES PREPARED FROM 2,3-DICHLORONAPHTHOQUINONE

Compound no.	Empirical formula	Solvent of recrystal-lization	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Calcd. Cl	Found C	Found H	Found N	Found Cl
IVa[9]	$C_{14}H_{12}ClNO_3$		152								
IVb[9]	$C_{15}H_{14}ClNO_2$		87								
IVc	$C_{16}H_{16}ClNO_2$	Ethanol	77	66.5	5.6	4.9	12.3	65.7	5.3	4.8	12.1
IVd	$C_{19}H_{14}ClNO_2$		Impure purple gum								
IVe[4]	$C_{12}H_8ClNO_3$		219								
IVb$_1$	$C_{16}H_{16}ClNO_2$	Ethanol/H_2O	79	66.3	5.6	4.8	12.2	66.0	5.3	4.5	12.2
IVb$_2$	$C_{22}H_{20}ClNO_2$	Acetonitrile	110	72.4	5.5	3.8	9.7	72.2	5.8	3.8	9.8

TABLE II

DIAZANAPHTHACENEQUINONES

Compound no.	Empirical formula	Solvent of recrystal-lization	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIb	$C_{17}H_{10}N_2O_3$	Dimethylformamide	322	70.4	3.5	9.6	70.3	3.4	9.6
IIc	$C_{16}H_7ClN_2O_2$	Dichlorobenzene	290	65.4	3.6	9.4	65.3	3.5	9.2
IId	$C_{17}H_{10}N_2O_2$	Trichlorobenzene	326	74.4	3.7	10.4	74.3	3.6	10.2
IIf	$C_{21}H_{19}N_3O_2$	Alcohol	225	73.0	5.5	12.2	72.7	5.8	12.4

TABLE III

4a,11-DIAZABENZO[*b*]FLUORENEQUINONES

Compound no.	Empirical formula	Solvent of recrystal-lization	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
V	$C_{14}H_{10}N_2O_3$	Trichlorobenzene	342	66.3	3.9	11.0	66.3	3.9	10.7
VI	$C_{15}H_{12}N_2O_2$	Ethanol	253	71.3	4.8	11.1	71.1	5.1	10.6
VII	$C_{16}H_{14}N_2O_2$	Ethanol	218	72.2	5.3	10.5	72.0	5.6	10.5
VIII	$C_{19}H_{12}N_2O_2$	Trichlorobenzene	320	75.9	4.0	9.3	75.4	3.4	9.0
VIa	$C_{16}H_{14}N_2O_2$	Methanol	214	72.3	5.3	10.5	71.4	5.2	10.4
VIb	$C_{22}H_{18}N_2O_2$	Ethanol	180	77.3	5.3	8.2	77.4	5.6	7.9

results reported in this paper again emphasize this similarity.

Experimental

The 2-N-alkyl(and N-aryl)amino-3-chloro-1,4-naphthoquinones, Ib–Ie, were prepared by the method of Acharya and Tilak.[10] A solution of the amine (2.5 moles) in ethyl alcohol was added to a boiling solution of 2,3-dichloro-1,4-naphthoquinone in ethyl alcohol and the mixture refluxed for 4–5 hr. After cooling, the crystalline product which separated was washed with alcohol and crystallized from a suitable solvent. The melting points and analytical data are collected in Table I.

2-(3,4-Dichloroanilino)-3-chloro-1,4-naphthoquinone.—A mixture of 22.7 g. (0.1 mole) of 2,3-dichloro-1,4-naphthoquinone, 16.2 g. (0.1 mole) of 3,4-dichloroaniline, 25 ml. of N,N-dimethylaniline, and 100 ml. of acetic acid was refluxed for 4.5 hr., cooled, and the solid was collected and washed with methanol; yield, 24.3 g., m.p. 240° (from dichlorobenzene).

Anal. Calcd. for $C_{16}H_8Cl_3NO_2$: C, 54.5; H, 2.3; N, 4.0; Cl, 30.0. Found: C, 54.5; H, 2.1; N, 4.2; Cl, 29.7.

2-Chloro-, 2,4- and 2,5-dichloroaniline failed to react under these conditions.

2-(4-Diethylamino-2-methylanilino)-3-chloro-1,4-naphthoquinone (If) was prepared in a similar manner; light brown crystals, m.p. 188° (from butanol).

Anal. Calcd. for $C_{21}H_{21}ClN_2O_2$: C, 68.5; H, 5.9; N, 7.6; Cl, 9.5. Found: C, 68.1; H, 5.7; N, 7.7; Cl, 9.9.

The quinones IIb–IIf and V through VIII were prepared by a procedure similar to that described below. The melting points and analytical data are collected in Tables II and III.

1,2,3,4,5,10-Hexahydro-5,10-dioxo-2-oxa-4a,11-diazabenzo-[*b*]fluorene (V).—A mixture of 6.1 g. (0.022 mole) of 2-chloro-3-morpholino-1,4-naphthoquinone, 30 ml. of dimethylformamide, and 3 g. (0.046 mole) of sodium azide, dissolved in the minimum amount of water, was heated on the steam bath for 16–20 hr. The reaction mixture was chilled, filtered, washed with alcohol, and the solid crystallized from trichlorobenzene (m.p. 342°). The 2-aminoaryl(and alkyl)aminonaphthoquinones obtained as a secondary product in this reaction were isolated by adding methanol to the filtrate and chilling it until a crystalline product separated.

Other amines isolated in this manner were: 2-amino-3-[4-methoxyanilino]-1,4-naphthoquinone (IIIb), m.p. 162° (from ethanol); yield, 30%.

Anal. Calcd. for $C_{17}H_{14}N_2O_3$: C, 69.4; H, 4.1; N, 9.5. Found: C, 69.1; H, 4.6; N, 9.2. λ_{max} 242 (17,700) λ_{max} 300 (21,200) in acetonitrile.

2-Amino-3-[4-benzylpiperidino-1]-1,4-naphthoquinone, m.p. 143° (from ethanol); yield, 25%.

Anal. Calcd. for $C_{22}H_{22}N_2O_2$: C, 76.4; H, 6.4; N, 8.1. Found: C, 76.5; H, 6.8; N, 8.2.

2-Amino-3-[4-nitroanilino]-1,4-naphthoquinone (IIIa).—A mixture of 7.3 g. (0.22 mole) of 2-chloro-3-[4-nitroanilino]-1,4-naphthoquinone, 30 ml. of dimethylformamide, and 3 g. (0.046 mole) of sodium azide, suspended in 5 ml. of water, was heated on the steam bath overnight. The reaction mixture was chilled, the crystals which separated were filtered, washed with 20 ml. of alcohol, and crystallized from trichlorobenzene to give 4.6 g. of IIIa; m.p. 286–288°.

Anal. Calcd. for $C_{16}H_{11}N_3O_4$: C, 62.2; H, 3.6; N, 13.6. Found: C, 62.2; H, 3.4; N, 13.2.

3-Acetamido-2-amino-1,4-naphthoquinone (IX).—A mixture of 4 g. of 2-acetamido-3-chloro-1,4-naphthoquinone (IVe) and 2 g. of sodium azide in 4 ml. of water was heated on the steam bath for 4 hr. Alcohol (25 ml.) was added and the mixture chilled. The product was filtered off and crystallized from ethoxyethanol to give 1.8 g. of bright red crystals of 3-amino-2-acetamido-1,4-naphthoquinone (m.p. 237°) identical with that prepared by Fieser and Martin.[11]

2-Azido-3-morpholino-1,4-naphthoquinone (X).—A solution of 3 g. of sodium azide in 10 ml. of water was added to 6 g. of 2-chloro-3-morpholinonaphthoquinone in 200 ml. of acetone.

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[10] R. V. Acharya and B. D. Tilak, *J. Sci. Ind. Res.* (India), **14B**, 221 (1955).

[11] L. F. Fieser and E. L. Martin, *J. Am. Chem. Soc.*, **57**, 1844 (1935).

After standing overnight at room temperature, the mixture was heated for 5–10 min. on the steam bath. Water was added to the mixture until crystallization began. On chilling, the product which separated was collected by filtration and again recrystallized from acetone–water to give 2.8 g. of 2-azido-3-morpholino-1,4-naphthoquinone, m.p. 85°.

Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.9; H, 5.0; N, 19.2. Found: C, 63.8; H, 4.8; N, 19.2.

2-(4-Nitroanilino)-1,4-naphthoquinone.—A mixture of 2,3-dichloro-1,4-naphthoquinone (11.3 g.), *p*-nitroaniline (7.0 g.), and 14 ml. of dimethylaniline in 100 ml. of trichloropropane was refluxed for 3 hr. The blue solution was cooled and the bright red crystals of 2-(4-nitroanilino)-1,4-naphthoquinone were collected (yield, 7.3 g.; m.p., 346°) (from trichlorobenzene). The infrared spectrum of this compound is identical to that of a specimen prepared according to Baltzar.[12]

In all cases in which a substance was prepared by alternate routes, identity was established by comparison of the infrared absorption spectra.

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[12] C. Baltzar, *Ber.*, **14**, 1899 (1881).

Polynuclear Heterocycles. V. Preparation and Reactions of Some Alkoxy and Chloro Quaternary Heterocyclic Compounds[1]

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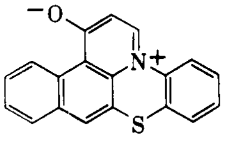
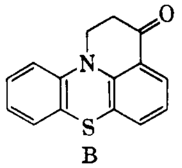
Received July 26, 1962

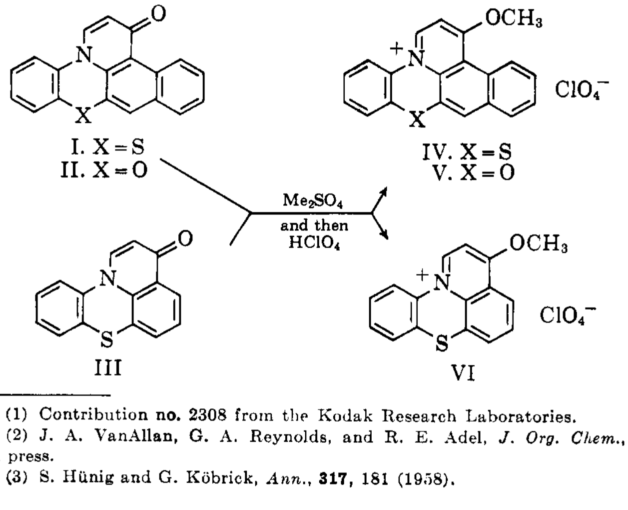
3*H*-Pyrido[3,2,1-*kl*]phenothiazin-3-one and related compounds react with dimethyl sulfate and phosphorus oxychloride to give the corresponding alkoxy or chloro quaternary salts. That these salts are electrophilic is demonstrated by their reaction with piperidine and 2,3-dimethylbenzothiazolium perchlorate to give alkylated piperidine and benzothiazolium salts.

In a previous communication,[2] it was shown that 1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazin-1-one (I) and related compounds exist in the ground state primarily as the charge-separated species A. This conclusion was based on the observation that these compounds absorb in the 1580–1620-cm.$^{-1}$ range of the infrared region of the spectrum, whereas related compounds, such as 1,2-dihydro-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (B), absorb in the usual amide region (1720–1680 cm.$^{-1}$). Structure A also accounts for the fact that I does not form an oxime nor is it reduced with sodium borohydride, while the dihydro derivative readily undergoes both these reactions.

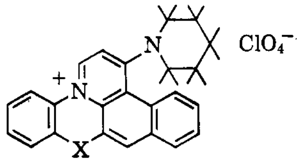

A

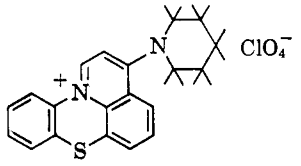

B

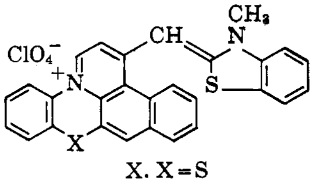
In view of the work of Hünig and Köbruck[3] with N-substituted 4-pyridone, it seemed likely that compounds of type A would undergo oxygen alkylation to yield alkoxy quaternary compounds which, in turn, would react readily with nucleophilic reagents. Accordingly, I, 1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenoxazin-1-one (II), and 3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (III) were heated on the steam bath with dimethyl sulfate to give 1-methoxybenzo[*b*]pyrido[1,2,3-*m,n*]-phenothiazinium perchlorate (IV), 1-methoxybenzo-[*b*]pyrido[1,2,3-*m,n*]phenoxazinium perchlorate (V) and 3-methoxypyrido[3,2,1-*kl*]phenothiazinium perchlorate (VI) in excellent yield. The hygroscopic methosulfate salts were converted to perchlorates by means of 70% perchloric acid in methanol.

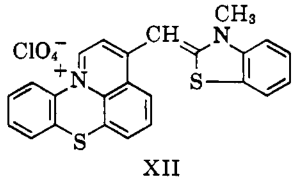


The electrophilic character of IV, V, and VI was demonstrated by their reaction with piperidine and with 2,3-dimethylbenzothiazolium perchlorate to give the piperidine derivatives, VII, VIII, IX, and the benzothiazole derivatives, X, XI, and XII, respectively. Since all three of the methoxy salts reacted in a similar manner with these two nucleophilic reagents, compound IV was chosen to represent this class of compounds in a further study of their reactions with nucleophilic reagents. Nitromethane (XIII), malononitrile (XIV), and methyl cyanoacetate (XV) react with IV in *t*-butyl alcohol in the presence of potassium *t*-butylate to give XVI, XVII, and XVIII. Alternatively, these same products may be obtained by the reaction of I, with XIII, XIV, and XV in acetic anhydride at reflux


VII. X = S
VIII. X = O


IX


X. X = S
XI. X = O


XII

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[1] Contribution no. 2308 from the Kodak Research Laboratories.

[2] J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, in press.

[3] S. Hünig and G. Köbrick, *Ann.*, **317**, 181 (1958).