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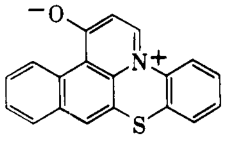
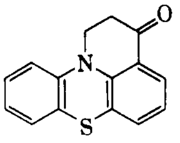
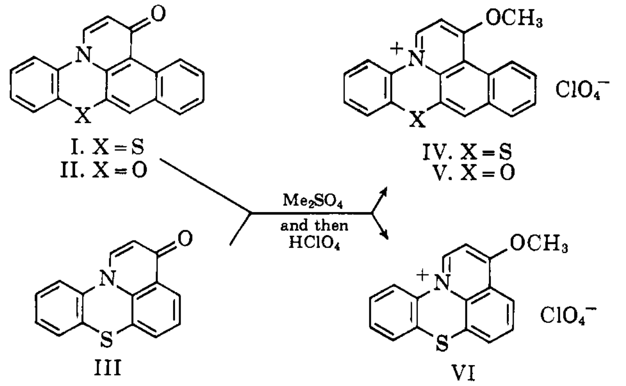
3*H*-Pyrido[3,2,1-*kl*]phenothiazin-3-one and related compounds react with dimethyl sulfate and phosphorus oxychloride to give the corresponding alkoxy or chloro quaternary salts. That these salts are electrophilic is demonstrated by their reaction with piperidine and 2,3-dimethylbenzothiazolium perchlorate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

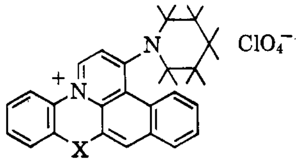

B

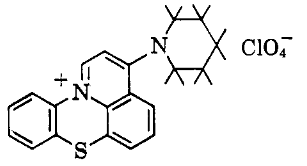
In view of the work of Hünig and Köbruck[3] with N-substituted 4-pyridone, it seemed likely that compounds of type A would undergo oxygen alkylation to yield alkoxy quaternary compounds which, in turn, would react readily with nucleophilic reagents. Accordingly, I, 1*H*-benzo[*b*]pyrido[1,2,3-*m*,*n*]phenoxazin-1-one (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.

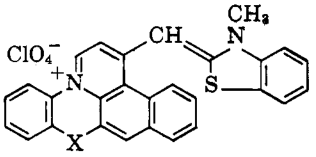


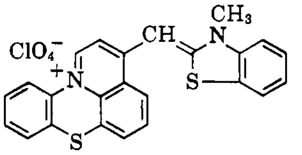
I. X = S
II. X = O
IV. X = S
V. X = O
III
VI

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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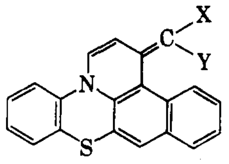
(1) Contribution no. 2308 from the Kodak Research Laboratories.

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

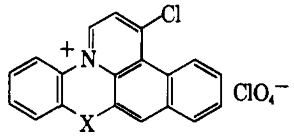
(3) S. Hünig and G. Köbrick, *Ann.*, **317**, 181 (1958).



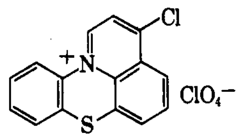
XVI. X = NO_2; Y = H
XVII. X = Y = CN
XVIII. X = CN; Y = CO_2CH_3

temperatures. The yields by either method are between 60–70%.

1 - Chlorobenzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium perchlorate (XIX) and the chloro compounds XX and XXI were prepared by heating I, II, and III with phosphorus oxychloride, followed by conversion of the dichlorophosphite salt to the perchlorate. These chloro quaternary salts are more reactive than the corresponding methoxy compounds, as shown by the fact that

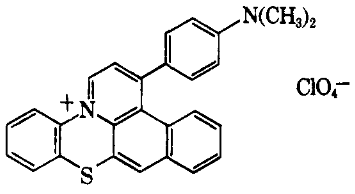


XIX. X=S
XX. X=O



XXI

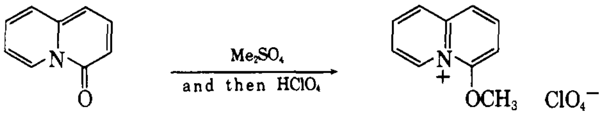
they readily yield the ketones, I, II, and III, on hydrolysis, with an aqueous pyridine solution, while the methoxy derivatives are only hydrolyzed by means of sodium carbonate or alkali solutions, and by the fact that XIX readily alkylated N,N-dimethylaniline to yield the dye XXII, while IV gave very little reaction, as evidenced by the weak color formed. Comparable



XXII

yields of alkylation products were obtained from piperidine with both the chloro and the methoxy quaternary salts when the reaction time was four hours, but the chloro compounds gave superior yields when the reaction time was shortened to fifteen minutes.

Methylation of 4-quinolizone[4] (XXIII) with dimethyl sulfate, followed by treatment with perchloric acid, gave 4-methoxyquinolizinium perchlorate (XXIV).



XXIII XXIV

In contrast to the 4-methoxy quaternary salts, nucleophilic reagents do not react with XXIV in the manner expected; either unidentified products or 4-quinolizone were isolated from the reaction mixture.

Experimental

1-Methoxybenzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (IV).—A mixture of 0.03 mole of 1*H*-benzo[*b*]pyrido-[1,2,3-*m,n*]phenothiazin-1-one (I) and 4 volumes of dimethyl sulfate was heated for 4 hr. on the steam bath, cooled to room temperature, and diluted with 100 ml. of ether. The yellow solid was collected, suspended in 50 ml. of methanol, and 5 ml. of 70% perchloric acid was added to the suspension. After chilling, the crude product was collected and recrystallized from acetonitrile; yield, 90%, m.p. 220°.

Anal. Calcd. for $C_{20}H_{14}ClNO_5S$: C, 57.7; H, 3.4; N, 3.4. Found: C, 57.4; H, 3.5; N, 3.2.

The following three compounds were prepared by this procedure.

1-Methoxybenzo[*b*]pyrido[1,2,3-*m,n*]phenoxazinium Perchlorate (V).—Yield, 88%; m.p. 224° (from acetonitrile).

Anal. Calcd. for $C_{20}H_{14}ClNO_6$: C, 60.2; H, 3.5; N, 3.5. Found: C, 59.9; H, 3.5; N, 3.5.

3-Methoxypyrido[3,2,1-*kl*]phenothiazinium Perchlorate (VI).—Yield, 93%; m.p. 227° (from acetonitrile).

Anal. Calcd. for $C_{16}H_{12}ClNO_5$: C, 52.6; H, 3.3; N, 3.8. Found: C, 52.2; H, 3.5; N, 4.0.

4-Methoxyquinolizinium Perchlorate (XXIV).—Yield, 91%; m.p. 160° (from acetonitrile).

Anal. Calcd. for $C_{10}H_{10}ClNO_5$: C, 46.3; H, 3.9; N, 5.4. Found: C, 46.0; H, 3.8; N, 5.5.

1-(1-Piperidyl)benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (VII).—A mixture of 0.005 mole of IV and 0.006 mole of piperidine in 5 ml. of tetrahydrofuran was refluxed for 3 hr. and cooled to room temperature. The yellow solid was collected and crystallized from acetonitrile to give a yield of 50% of VII, m.p. 208°.

Anal. Calcd. for $C_{24}H_{21}ClN_2O_4S$: C, 61.5; H, 4.5; N, 6.0. Found: C, 61.8; H, 4.3; N, 5.8.

The mother liquors were flooded with ether and the solid that separated was identified as I (0.4 g.).

The following compounds were prepared in a similar manner.

1-(1-Piperidyl)benzo[*b*]pyrido[1,2,3-*m,n*]phenoxazinium Perchlorate (VIII).—Yield, 85%; m.p. 265° (from ethanol).

Anal. Calcd. for $C_{24}H_{21}ClN_2O_5$: C, 63.7; H, 4.6; N, 6.2. Found: C, 63.2; H, 4.4; N, 5.8.

3-(1-Piperidyl)pyrido[3,2,1-*kl*]phenothiazinium Perchlorate (IX).—Yield, 45%; m.p. 178° (from alcohol).

Anal. Calcd. for $C_{20}H_{19}ClN_2O_4S$: C, 57.4; H, 4.5; N, 6.7. Found: C, 57.2; H, 4.8; N, 7.0.

1 - (3 - Methyl - 2(3) - benzothiazolylidenemethyl)benzo[*b*]-pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (X).—A mixture of 1 g. of IV and 0.66 g. of 2,3-dimethylbenzothiazolium perchlorate in 20 ml. of pyridine was refluxed for 2 hr. The purple solution was diluted with ethanol, chilled, and the solid collected and recrystallized from ethoxyethanol. The yield of product melting at 175° was 0.5 g.

Anal. Calcd. for $C_{28}H_{19}ClN_2O_4S_2$: C, 61.3; H, 3.5; N, 5.1. Found: C, 61.2; H, 3.5; N, 4.8.

Absorption in the visible region at 541 mμ (ϵ 28 × 10^3).

Compounds XI and XII were also prepared by this procedure.

1-(3-Methyl-2(3)-benzothiazolylidenemethyl)benzo[*b*]pyrido-[1,2,3-*m,n*]phenoxazinium Perchlorate (XI).—Yield, 60%; m.p. 224° dec. (from ethoxyethanol).

Anal. Calcd. for $C_{28}H_{19}ClN_2O_5S$: C, 63.3; H, 3.6; N, 5.3. Found: C, 62.9; H, 3.7; N, 5.0.

3-(3-Methyl-2(3)-benzothiazolylidenemethyl)pyrido[3,2,1-*kl*]phenothiazinium Perchlorate (XII).—Yield, 40%; m.p. 245° (from a mixture of pyridine and ethanol).

Anal. Calcd. for $C_{24}H_{17}ClN_2O_4S_2$: C, 58.2; H, 3.4; N, 5.6. Found: C, 58.5; H, 3.4; N, 5.2.

1-Cyanomethylene-1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazine (XVI).—A mixture of 1 g. of IV, 0.25 g. of potassium *t*-butoxide, 5 ml. of nitromethane, and 5 ml. of *t*-butyl alcohol was refluxed for 1 hr., cooled to room temperature, and poured into dilute hydrochloric acid. The red solid was collected, washed with a small amount of cold alcohol, and recrystallized from acetonitrile to yield 0.8 g. of product, m.p. 187°.

Anal. Calcd. for $C_{10}H_{12}N_2O_2S$: C, 69.8; H, 3.5; N, 8.1. Found: C, 70.3; H, 3.8; N, 7.9.

1-Dicyanomethylene-1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazine (XVII). Method A.—A mixture of 0.8 g. of IV, 0.2 g. of potassium *t*-butoxide, 5 ml. of malononitrile, and 5 ml. of *t*-butyl alcohol was refluxed for 1 hr. and then poured into dilute

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[4] V. Boekelheide and J. P. Lodge, Jr., *J. Am. Chem. Soc.*, **73**, 3681 (1951).

hydrochloric acid. The red solid was collected and recrystallized from acetic anhydride to yield 0.8 g. of XVII, m.p. 315°. The material was identical with a sample prepared by method B, as shown by the infrared absorption curve.

Method B.—A solution of 1.5 g. of the ketone I, 0.5 g. of malononitrile, and 35 ml. of acetic anhydride was refluxed for 1 hr. and then chilled. The solid was recrystallized from acetic anhydride to give 0.9 g. of XVII, m.p. 315°.

Anal. Calcd. for $C_{22}H_{11}N_3S$: C, 75.8; H, 3.2; N, 12.0. Found: C, 75.7; H, 3.0; N, 12.1.

1-Carbomethoxycyanomethylene-1*H*-benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazine (XVIII). Method A.—The reaction was carried out as just described in procedure A, but using 5 ml. of methyl cyanoacetate in place of the malononitrile. The yield of product was 0.7 g., m.p. 255°.

Anal. Calcd. for $C_{23}H_{14}N_2O_2S$: C, 72.2; H, 3.7; N, 7.3. Found: C, 71.8; H, 3.9; N, 7.0.

Method B.—The ketone I (1 g.) and 1 ml. of methyl cyanoacetate in 10 ml. of acetic anhydride was refluxed for 3 hr. and, after cooling, the solid was collected and recrystallized from *p*-cymene; yield, 0.8 g., m.p. 256°.

Anal. Found: C, 72.1; H, 3.7; N, 6.8.

1-Chlorobenzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (XIX).—A mixture of 2 g. of I and 25 ml. of phosphorus oxychloride was refluxed for 2 hr., cooled to room temperature, and diluted with 100 ml. of ether. The red solid was collected and washed with ether; m.p. 193°. The dichlorophosphite salt in this case was not hygroscopic and proved to be pure, but in the following examples they were hygroscopic.

Anal. Calcd. for $C_{19}H_{11}Cl_3NO_2SP$: C, 50.4; H, 2.4; Cl, 23.1. Found: C, 50.8; H, 2.5; Cl, 23.5.

A sample of the dichlorophosphite salt was added to a mixture of 70% perchloric acid in ethanol. After the mixture had been warmed for a few minutes on the steam bath and chilled in a deep freeze, the solid XIX was collected, m.p. 222°.

Anal. Calcd. for $C_{19}H_{11}Cl_2NO_4S$: Cl, 16.7. Found: Cl, 16.9.

The following compounds were prepared by this procedure.

1-Chlorobenzo[*b*]pyrido[1,2,3-*m,n*]phenoxazinium Perchlorate (XX).—An orange solid was obtained; yield, 65%, m.p. 240°.

Anal. Calcd. for $C_{19}H_{11}Cl_2NO_5$: C, 56.6; H, 2.7; N, 3.5. Found: C, 56.9; H, 3.3; N, 3.7.

3-Chloro[3,2,1-*kl*]phenothiazinium Perchlorate (XXI).—Yield, 70%, m.p. 245°.

Anal. Calcd. for $C_{15}H_9Cl_2NO_4S$: C, 48.8; H, 2.4; N, 3.8. Found: C, 49.0; H, 2.5; N, 3.7.

Compounds VII, VIII, and IX from the Chloro Quaternary Compounds XIX, XX, and XXI.—A mixture of 0.005 mole of the chloro quaternary compound and 0.007 mole of piperidine in 25 ml. of tetrahydrofuran was refluxed for 3 hr. and cooled to room temperature. The yields of XIX, XX, and XXI were 59, 90, and 55%, respectively. The products were identified by melting point and the comparison of their infrared absorption curves with the samples prepared from the methoxy quaternary compounds.

When the reaction time was shortened to 15 min., the yields of XIX, XX, and XXI were 40, 53, and 33% from the chloro quaternary salts and 16, 28, and 11% from the methoxy quaternary salts.

1-(4-Dimethylaminophenyl)benzo[*b*]pyrido[1,2,3-*m,n*]phenothiazinium Perchlorate (XXII).—A mixture of 1 g. of I, 1 ml. of N,N-dimethylaniline, and 7 ml. of phosphorus oxychloride was refluxed for 2 hr., chilled, and diluted with ether. The liquid was decanted from the sticky, purple solid and the solid dissolved in hot acetone. To the solution, 2 ml. of 70% perchloric acid was added, and the solution was then diluted with water, chilled, and the solid collected; yield, 0.8 g., m.p. 250°.

Anal. Calcd. for $C_{27}H_{21}ClN_2O_4S$: N, 5.6. Found: N, 5.9.

The 1,2-Dithiolium Cation. A New Pseudoaromatic System. III.[1] Conversion of Dithiolium Salts to Quaternary Pyrazolium Salts and Dithiolethiones

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Received July 25, 1962

4-Phenyl- and 4-*p*-nitrophenyl-1,2-dithiolium salts react with *N,N'*-disubstituted hydrazines to give *N,N'*-disubstituted pyrazolium salts, and with sulfur to give 1,2-dithiole-3-thiones.

In the first paper in this series[2] we reported the reaction of 1,2-dithiolium salts with hydrazine and monosubstituted hydrazines to give pyrazoles. We have now found that *N,N'*-disubstituted hydrazines react analogously with 4-phenyldithiolium salts at −20 to −40°, giving the *N,N'*-disubstituted pyrazolium salts directly in one step. This reaction, formally a simple extension of the pyrazole synthesis, presents several features of interest: (1) It is a new example of the interconversion of cationoid heteroaromatic systems, recalling the formation of quaternary pyridinium compounds from pyrylium[3] and thiapyrylium[4] salts; (2) It is the first known synthesis of quaternary pyrazolium compounds by a route other than the alkylation of a pyrazole; (3) It is the first synthesis of an *N,N'*-diarylpyrazolium compound by any route.

The corresponding reaction between *sym*-dimethylhydrazine and 4-(*p*-nitrophenyl)-1,2-dithiolium hydrogen sulfate[2] (II) gave the nitrophenylpyrazolium salt (V); this was reduced with hydrazine and palladium catalyst to the amine (VI), which was diazotized and coupled with dimethylaniline to give the azo dye (VII).

Only about half the starting material is converted in this reaction to pyrazolium salt (50–65% yield). The rest is sulfurated to give 1,2-dithiole-3-thione (VIII) by a curious disproportionation reaction in which the breakdown of some of the dithiolium compound provides sulfur for the thiocarbonyl group. This reaction tends to predominate at temperatures above −20°; dithiolethione was in fact the only identifiable product given by 3-phenyldithiolium salts under all conditions that we tried. It is not clear how the hydrazine derivative that is present participates in this reaction. Its participation is not necessary, since even in its absence dithiolium salts in refluxing pyridine solution rapidly disproportionate to dithiolethiones. If an equivalent of sulfur is added, the yield is much higher. This reaction was used to prepare IX, the *p*-nitro derivative of VIII, which seems to be the first known nitro compound in the dithiolethione series. Presumably a nitro group

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[1] For the previous paper in this series see E. Klingsberg and A. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

[2] E. Klingsberg, *ibid.*, **83**, 2934 (1961).

[3] E. Shaw, in "Pyridine and Its Derivatives," Part Two, E. Klingsberg, ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 21.

[4] R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).