procedure and work-up were the same as that described for the reduction of 2-pentylpyrrole. From 0.25 g. (0.00185 mole) of 1-(2-pyrryl)pentene in 9.0 ml. of acetic acid and 0.1 g. of 5% rhodium–alumina, there was obtained 0.2 g. (78%) of brown oil with an amine-like odor, b.p. 153° (760 mm.). An infrared spectrum of the crude oil was identical to the one obtained in the previous experiment except for more intense peaks at 1400 and 1545 cm.$^{-1}$. The phenylthiourea derivative melted at 110°. The melting point of a mixture of the phenylthiourea with the phenylthiourea from the previous experiment was 111° with softening at 109°.

10-Azabicyclo[5.2.1]deca-1,3-diene (?).—The 10-azabicyclo[5.2.1]deca-1,3,5-triene (0.25 g., 0.0019 mole), obtained from the pyrolysis of cycloheptano[*a*]pyrrole, was dissolved in ethanol (8 ml.) and hydrogenated using a 5% palladium-on-charcoal catalyst. After the usual work-up, there was obtained 0.25 g. of brown liquid, b.p. 217° (760 mm.), λ_{max} (ethanol) typical pyrrole end absorption at 218 mμ. The product was insoluble in 5% hydrochloric acid solution and gave a negative Ehrlich test.

10-Azabicyclo[5.2.1]decane (?).—From 0.2 g. (0.0015 mole) of 10-azabicyclo[5.2.1]deca-1,3-diene in 5 ml. of acetic acid and 0.1 g. of platinum oxide there was obtained 0.2 g. of yellow oil with an amine-like, camphor-like odor, b.p. 150° (760 mm.). The picrate of the product melted at 216° with darkening at 215°.

Anal. Calcd. for $C_{15}H_{20}N_4O_7$ (picrate): C, 48.91; H, 5.47. Found: C, 49.24; H, 5.20.

Acknowledgment.—This investigation was sponsored by the Office of Ordnance Research, U. S. Army.

Polynuclear Heterocycles. I. 1*H*-Benzo[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one and Related Substances[1a]

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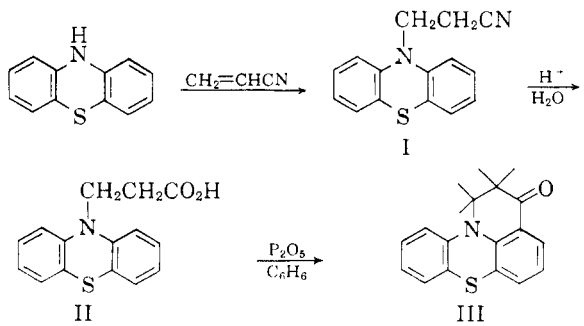
The conditions are described for the conversion of certain cyanoethylated heterocyclic compounds into their corresponding cyclic ketone derivatives. The properties of these ketone derivatives have been investigated. A brief discussion of the spectroscopic data is given.

As an extension of studies of ring closure in heterocyclic systems,[1] the preparation and properties of the interesting compound, 1,2-dihydro-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (III), were investigated. The preparation of III has been reported as indicated by the following equations.[2]



Our attempts to accomplish ring closures of I or II by means of other agents—such as hydrobromic acid in acetic acid, polyphosphoric acid, boron trifluoride, or hydrochloric acid in acetic acid—gave, at best, very poor yields of III. The cyclization of I was not possible owing to rapid reverse cyanoethylation under these conditions.

Compound III may be readily dehydrogenated with palladium–charcoal to 3*H*-pyrido[3,2,1-*kl*]-phenothiazin-3-one (IV).

The condensation product of III with benzaldehyde is believed to be 2-benzyl-3*H*-pyrido[3,2,1-*kl*]-phenothiazin-3-one (V) and not the benzylidene compound suggested by Mackie and Cutler.[3] The structure shown is assigned to V because its ultraviolet spectrum is almost identical with that of IV, indicating that the exocyclic double bond of the intermediate benzylidene compound has migrated into the ring. The tendency toward aromaticity is apparently the driving force in this reaction. It has also been found that III is smoothly reduced to 2,3-dihydro-1*H*-pyrido[3,2,1-*kl*]phenothiazin-3-ol (VI) with sodium borohydride in wet dioxane. The latter material has been made previously by reduction of III with lithium aluminum hydride in ether.[4]

It was of interest to extend this investigation to the benzologs (VII, VIII, and IX) of phenothiazine, phenoxazine, and dihydrophenazine.

The angular compounds VIIIa, VIIIb, and IXb were prepared as described previously.[5–7] The linear derivatives VIIa, VIIb, and VIIc were prepared by the treatment of a 2,3-naphthalenediol with *o*-aminothiophenol, *o*-aminophenol, and *o*-

(1)(a) Contribution No. 2222 from the Kodak Research Laboratories; (b) G. A. Reynolds, J. A. VanAllan, and J. F. Tinker, *J. Org. Chem.*, **24**, 1205 (1959).

(2) N. L. Smith, *J. Org. Chem.*, **15**, 1125 (1950).

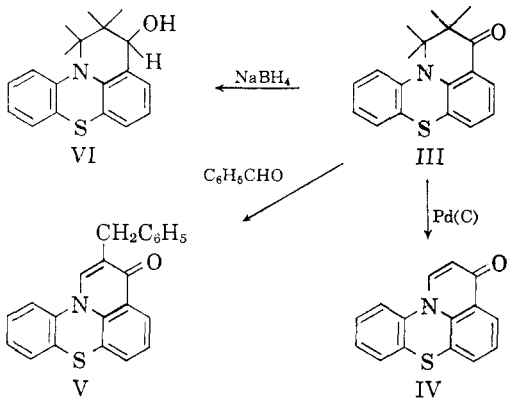
(3) A. Mackie and A. A. Cutler, *J. Chem. Soc.*, 2577 (1954).

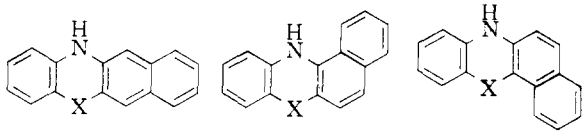
(4) E. F. Godefroi and E. L. Wittle, *J. Org. Chem.*, **21**, 1163 (1956).

(5) F. Kehrmann and J. H. Dardel, *Ber.*, **55**, 2346 (1922).

(6) O. Kym, *Ber.*, **23**, 2458 (1890).

(7) J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 651 (1954).



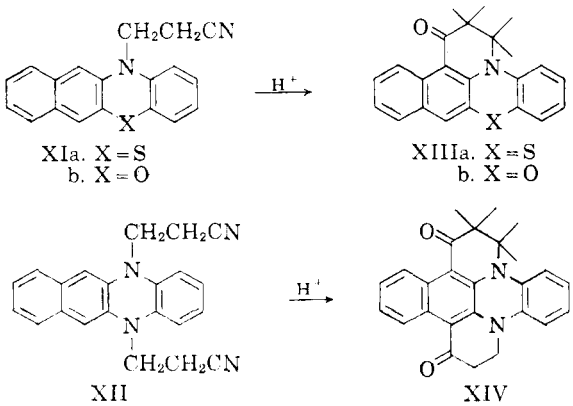


VIIa. (X = S) VIIIa. (X = S) IXa. (X = S)
VIIb. (X = O) VIIIb. (X = O) IXb. (X = O)
VIIc. (X = NH) VIIIc. (X = NH)

phenylenediamine in an inert, high-boiling solvent. Although 12*H*-benzo[*b*]phenothiazine (VIIa) has been prepared previously[8] by the reduction of 12*H*-benzo[*b*]phenothiazine-6,11-dione (X), we were unable to reduce X beyond the dihydroxy stage, and, on working up the reaction mixture, the latter compound was oxidized back to X.

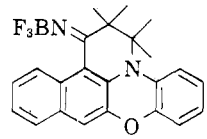
In all cases, cyanoethylation of the linear compounds was carried out without difficulty. Compounds VIIa and VIIb gave XIa and XIb, respectively, and VIIc yielded the dicyanoethylated product (XII). The angular IXa gave 7*H*-benzo[*c*]phenothiazine-7-propionitrile in poor yield (10%–30%); none of the other angular heterocycles gave cyanoethylated products. These results with the angular derivatives may be related to their instability in solution. We have observed marked changes in their ultraviolet absorption spectra on standing for a short time.

The linear cyanoethylated products XIa, XIb,



and XII were cyclized readily by acidic agents such as hydrochloric acid in acetic acid to yield XIIIa, XIIIb, and XIV. That the ring closure proceeds by way of an intermediate imino compound was demonstrated by the isolation of the red complex XV prepared by the ring closure of XIb with boron trifluoride etherate.

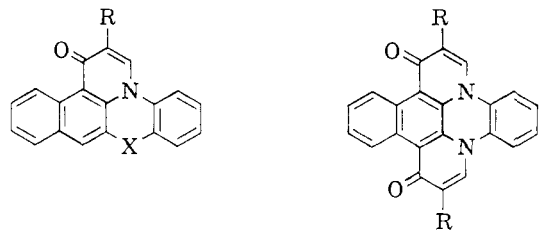
Recrystallization of XV from ethanol resulted in hydrolysis of XV to XIIIb.



XV

The cyanoethylation product of IXa could not be cyclized and attempts to hydrolyze it to the acid were unsuccessful.

Reaction of the cyclic ketones XIIIa, XIIIb, and XIV with benzaldehyde gave the products XVIa XVIb, and XVIIa, while dehydrogenation with palladium–charcoal gave XVIc, XVId, and XVIIb. With XVIIb, the yield was poor, owing to solubility difficulties. The ultraviolet spectra of compounds XVI and XVII when R = H and R =

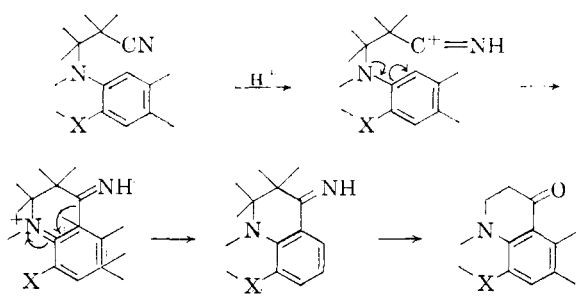


XVIa. X = S; R = $CH_2C_6H_5$
XVIb. X = O; R = $CH_2C_6H_5$
XVIc. X = S; R = H
XVId. X = O; R = H

XVIIa. R = $CH_2C_6H_5$
XVIIb. R = H

$CH_2C_6H_5$ are nearly identical, indicating their close structural relationship. Compounds XIIIa, XIIIb, and XIV were reduced to the corresponding carbinols, XVIIIa, XVIIIb, and XIX, by treatment with sodium borohydride in moist dioxane.

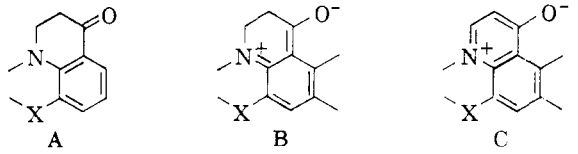
It is interesting to note the greatly enhanced ease of cyclization of the cyanoethylated naphthacene derivatives of type XI compared to the anthracene derivatives of type I. The 11-position of the naphthacene derivatives appears to be particularly reactive in respect to this type of ring closure. The following reaction mechanism is postulated:



(8) K. Fries and K. Kerkow, *Ann.*, **427**, 281 (1922).

The effect of X on the ring closure is noticeable but is not as important as the effect of the fused benzene ring. The following relative rates of cyclization were obtained for compounds of type XI: X = O >; X = NCH_2CH_2CN >; X = S. The first two members are not interchanged, probably because when XII undergoes one ring closure, the position at which the second ring closure takes place has been deactivated. The ring closure of these cyanoethylated derivatives is also complicated by the reverse cyanoethylation which is a competing reaction under the conditions used for ring closure. Only the most favorable cases undergo ring closure.

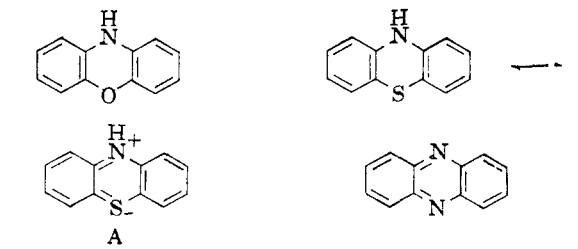
The infrared absorption of the carbonyl group in the dihydro derivatives, XIIIa, XIIIb, and XIV, is at about 6.15 μ, in contrast to III, which has a normal absorption at 5.92 μ for a conjugated ketone. This shift is even more pronounced in the completely aromatic compounds, XVIa, XVIb, and XVIIa, all of which have a strong carbonyl absorption at about 6.34 μ. These data suggest that the keto group in XIIIa, XIIIb, and XIV exists partially in the charge separated form B, whereas, in XVIa, XVIb, and XVIIa, the keto group has lost its double bond character completely and exists exclusively as the charge separated form C.



A B C

This difference in carbonyl character is reflected in the chemical behavior of these compounds. Thus, the dihydro compounds, III, XIIIa, XIIIb, and XIV, readily form the oximes XXI, XXa, XXb, and XXII, respectively, and may be reduced to carbinols with sodium borohydride. In contrast, the completely aromatic compounds XVIa, XVIb, and XVIIIa do not form oximes nor can they be reduced with sodium borohydride.

Discussion of the Ultraviolet Absorption Spectra.—To determine the effect on the ultraviolet spectrum of ring closure of the β-cyanoethyl derivatives, it was necessary to examine the spectra of the parent compounds. Comparison of the ultraviolet absorption spectrum of phenoxazine, with the spectra of phenothiazine and phenazine, revealed a most striking difference in the region 240 to 250 mμ; the extinction coefficients of these compounds are 16,000, 41,000, and 120,000, respectively (see Fig. 1). Examination of the structural formulae of these materials shows that, in the case of phenothiazine, the resonance hybrid A may be of greater importance than in phenoxazine, since the sulfur atom can expand its octet and form a contributor of this type. Phenazine, of course, must exist exclusively in the *ortho*-quinoid form. These considerations indicate that the strong band in the 240–250-mμ region has its origin in the *ortho*-quinoid structure.



A

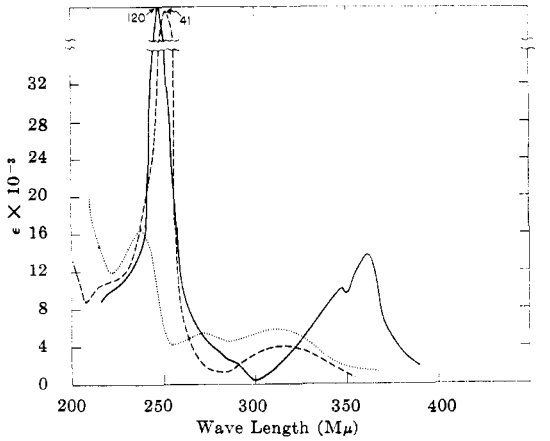


Fig. 1.—(1) Phenazine ——— (in CH_3CN); (2) phenoxazine ..... (in CH_3OH); (3) phenothiazine ——— in CH_3OH)

The linear benzologs of these compounds, 12*H*-benzo[*b*]phenothiazine (VIIa), 12*H*-benzo[*b*]phenoxazine (VIIb), and benzo[*b*] phenazine, show, in general, a bathochromic shift and a splitting of the high intensity bands (Fig. 2). 12*H*-Benzo[*b*]phenothiazine and 12*H*-benzo[*b*]phenazine have very similar spectra, but the latter compound again shows a very high intensity band, as shown in Table I. The absorption curve of benzo[*b*]phenazine is not shown in Fig. 2, since it would be off scale.

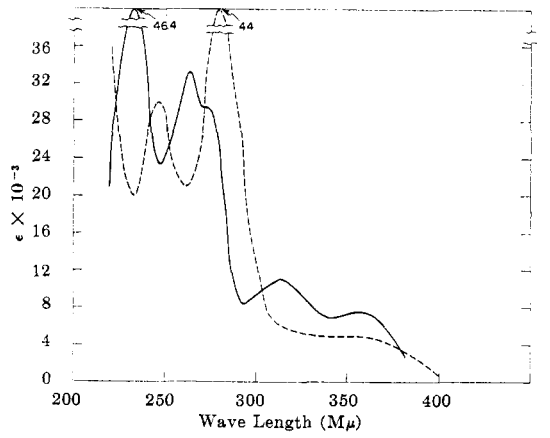


Fig. 2.—(1) 12*H*-Benzo[*b*]phenoxazine (VIIb) ———; (2) 12*H*-benzo[*b*]phenothiazine (VIIa) ———; both in CH_3CN

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA

	λ_{max} (in mμ)	λ_{max} (in mμ)
12*H*-Benzo[*b*]phenoxazine	232 (46,000)	264 (33,000)
12*H*-Benzo[*b*]phenothiazine	247 (30,000)	278 (44,000)
Benzo[*b*]-phenazine	249 (44,000)	278 (123,000)

In Fig. 3, the spectrum of 1,2-dihydro-3*H*-pyrido-

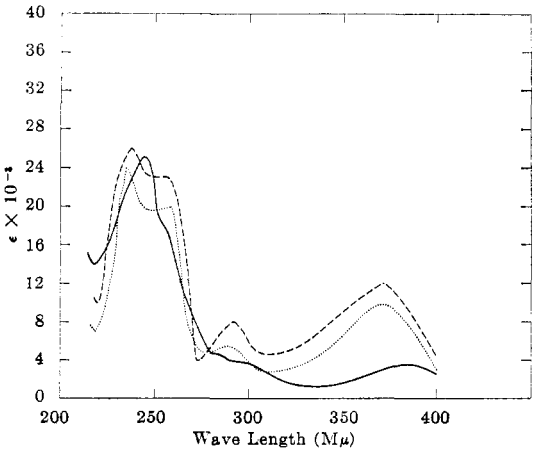


Fig. 3.—(1) 1,2-Dihydro-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (III) ———; (2) 3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (IV) .....; (3) 2-benzyl-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (V) -------- (all in CH_3CN)

[3,2,1-*kl*] phenothiazin-3-one (III) is compared with its dehydrogenated product (IV) and with its condensation product with benzaldehyde (V). The similarity of the spectra of the latter two materials leaves little doubt that the ring has become fully aromatic.

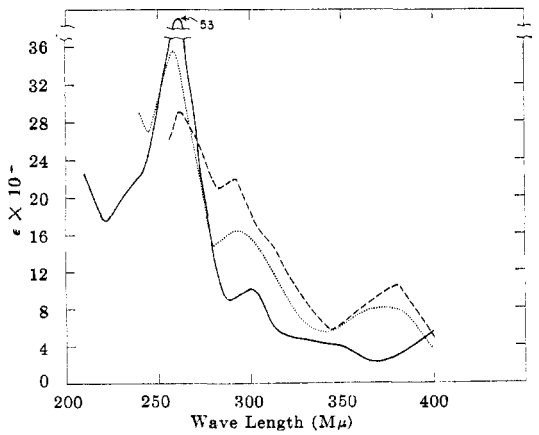


Fig. 4.—(1) 2,3-Dihydro-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]-phenothiazin-1-one (XIIIa) ———; (2) 2-benzyl-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenothiazin-1-one (XVIa) -------; (3) 1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenothiazin-1-one (XVIc) ..... (all in CH_3CN)

In Fig. 4, the spectrum of 2,3-dihydro-1*H*-benzo-[*b*]pyrido[1,2,3-*mn*]phenothiazin-1-one (XIIIa) shows a high intensity band at λ_{max} 262 mμ (83,000) which is suppressed in the dehydrogenated compound and in its benzyl derivative.

In Fig. 5, the spectrum of 2,3-dihydro-1*H*-benzo-[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one (XIIIb) is re-

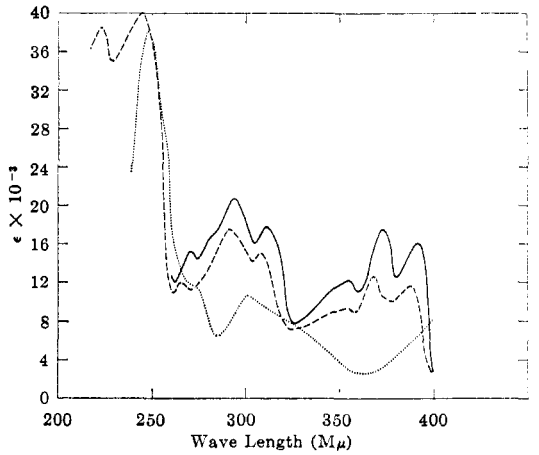


Fig. 5.—(1) 2-Benzyl-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one (XVIb) ——— (in dioxane); (2) 1*H*-benzo-[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one (XVId) ——— (in CH_3CN); (3) 2,3-dihydro-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]-phenoxazin-1-one (XIIb) ..... (in CH_3CN)

markably different from its dehydrogenated derivatives, XVIb and XVId. These latter compounds show considerably more fine structure than any of the materials previously examined.

The spectrum of 2,3,10,11-tetrahydrobenzo[*b*]-dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XIV) is remarkable in that the long wave length has been shifted to the 530–560-mμ region, and all the fine structure in the ultraviolet region has disappeared. On dehydrogenation of XIV to XVIIb, the long wave-length band has returned to the 400-mμ region, and the ultraviolet region has regained its fine structure (Fig. 6). The reasons for these changes are not known.

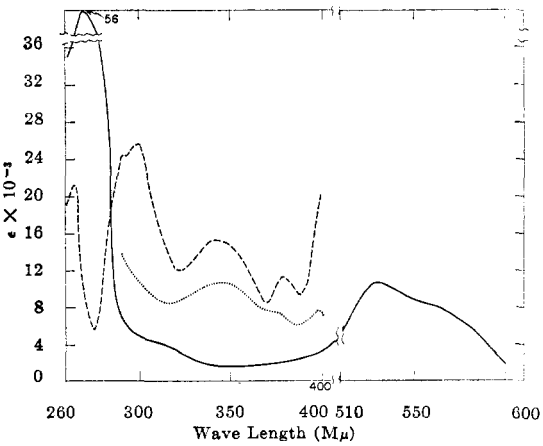


Fig. 6.—(1) 2,3,10,11-Tetrahydrobenzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XIV) ——— (in dioxane); (2) 2,11-Dibenzylbenzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XVIIa) -------- (in dioxane); (3) benzo-[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XVIIb) ..... (in dioxane)

Finally, we have prepared 2,3,5,6-tetrahydro-1*H*, benzo[*ij*]quinolizine-1,7-dione (XXIII) by the method of Braunholtz and Mann[9] for comparison

(9) J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 1817 (1953).

with our compounds. This material was easily dehydrogenated to 1*H*,7*H*-benzo[*ij*]4,9-quinolizine-1,7-dione (XXIV). Condensation of XXIII with benzaldehyde gave 2,6-dibenzyl-1*H*,7*H*-benzo[*ij*]-quinolizine-1,7-dione (XXV) in excellent yield. The spectrum of this latter compound is similar to that of the parent unsubstituted compound, XXIV, which leaves little doubt as to its structure (Fig. 7).

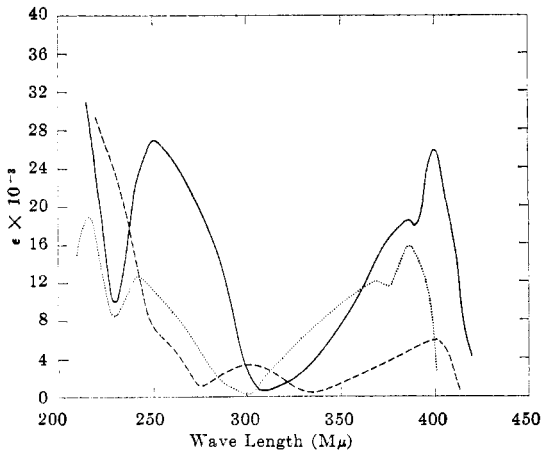
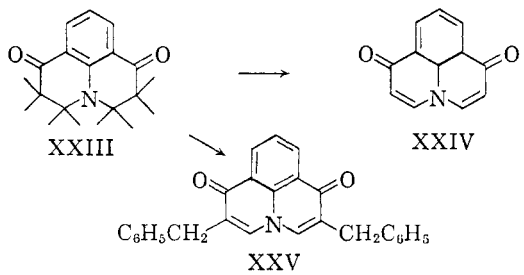


Fig. 7.—(1) 2,6-Dibenzyl-1*H*,7*H*-benzo[*ij*]quinolizine-1,7-dione (XXV) ——— (in CH_3CN); (2) 1*H*,7*H*-benzo[*ij*]quinolizine-1,7-dione (XXIV) ..... (in CH_3CN); (3) 2,3,5,6-tetrahydro-1*H*,7*H*-benzo[*ij*]quinolizine-1,7-dione (XXIII) ------- (in CH_3CN)

The infrared spectra of these compounds again show the carbonyl absorption shifted to 6.2 mμ, indicative of the charge separation existing in these compounds.



Thus, the dehydrogenation of dihydro-4-quinolones and their condensation with aromatic aldehydes appear to be general reactions and afford a large variety of compounds which were previously inaccessible.

Experimental

12*H*-Benzo[*a*]phenothiazine (VIIIa),[6] 7*H*-benzo[*c*]phenothiazine (IXa),[5] 12-*H*-benzo[*a*]phenoxazine (VIIIb),[7] and 7*H*-benzo[*c*]phenoxazine (IXb)[7] were prepared according to the methods given in the literature. The linear isomers were made by a modification of Hinsberg's method,[10] as illustrated by the preparation of 12*H*-benzo[*b*]phenothiazine (VIIa).

12*H*-Benzo[*b*]phenothiazine (VIIa).—A mixture of 32 g. (0.2 mole) of 2,3-naphthalenediol and 22 g. of *o*-aminothiophenol in 200 ml. of trichlorobenzene was refluxed for 20 hr. After cooling, the product was collected by filtration, washed with benzene, and crystallized from trichlorobenzene to give 30 g. of VIIa, m.p. 278°; yield, 65%.[11]

12*H*-Benzo[*b*]phenoxazine (VIIb).[8]—Melting point, 298° (from ethoxyethanol); yield, 68%.

5,12-Dihydrobenz[*b*]phenazine (VIIc).[10]—Melting point, >400° (from trichlorobenzene); yield, 93%.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.7; H, 5.2; N, 12.1. Found: C, 82.4; H, 4.9; N, 11.7.

Phenothiazine-10-propionitrile (I), phenothiazine-10-propionic acid (II), and 1,2-dihydro-3*H*-pyrido[3,2,1-*kl*]-phenothiazin-3-one (III) were prepared according to Smith's[2] method and 2-benzyl-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one (V) according to that of Mackie and Cutler.[3]

12*H*-Benzo[*b*]phenothiazine-12-propionitrile (XIa).—A mixture of 30 g. of VIIa, 60 ml. of acrylonitrile, 250 ml. of acetonitrile, and 2.5 ml. of Triton B was heated on the steam bath for 2 hr. After cooling, the product was collected by filtration and crystallized from chlorobenzene to give 22 g. of XIa, m.p. 190°.

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.6; H, 4.7; N, 9.3. Found: C, 75.9; H, 4.8; N, 9.1.

Similarly prepared were the following:

12*H*-Benzo[*b*]phenoxazine-12-propionitrile (XIb), m.p., 153° (from aqueous acetone); yield, 86%.

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 79.7; H, 4.9; N, 9.8. Found: C, 79.6; H, 5.3; N, 9.5.

5,12-Dihydrobenzo[*b*]phenazine-5,12-dipropionitrile (XII), m.p., 220° (from *o*-dichlorobenzene); yield, 91%.

Anal. Calcd. for $C_{22}H_{18}N_4$: C, 78.2; H, 5.3; N, 16.5. Found: C, 77.9; H, 5.6; N, 16.8.

7*H*-Benzo[*c*]phenothiazine-7-propionitrile, m.p., 212° (from acetonitrile); yield, 10–30%.

Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.6; H, 4.6; N, 9.3. Found: C, 75.2; H, 4.7; N, 9.4.

2,3-Dihydro-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenoxazine-1-one (XIIIb).—A suspension of 18 g. of XIb in 100 ml. of acetic acid was brought to reflux and 50 ml. of hydrochloric acid (d = 1.18) was added during 10 min. The mixture turned dark red and then light yellow. After 2-hr. reflux, the mixture was chilled. The bright yellow product was collected by filtration and crystallized from chlorobenzene to give 12 g. of XIIIb; m.p., 227°.

Anal. Calcd. for $C_{19}H_{12}NO_2$: C, 79.4; H, 4.5; N, 4.7. Found: C, 79.4; H, 4.7; N, 4.7.

This compound has also been prepared by hydrolysis of the nitrile to the carboxylic acid which was then ring-closed with phosphorus pentoxide.

12*H*-Benzo[*b*]phenoxazine-12-propionic Acid.—A mixture of 30 g. of the nitrile (XIb), 30 g. of potassium hydroxide, and 275 ml. of methanol was refluxed 16 hr., poured into ice water, acidified with hydrochloric acid, and the solid collected. The solid was stirred 0.5 hr. with 500 ml. of warm potassium carbonate solution, filtered, and the filtrate acidified with hydrochloric acid. The solid was collected and crystallized from aqueous ethanol to yield 12 g. of product; m.p., 141°.

Anal. Calcd. for $C_{19}H_{15}NO_3$: C, 74.8; H, 4.9; N, 4.6. Found: C, 74.8; H, 5.0; N, 4.5.

A mixture of 5 g. of this acid, 25 ml. of phosphorus pentoxide, and 200 ml. of dry benzene was refluxed 4 hr., poured onto ice and the benzene layer washed with sodium carbonate solution. The benzene layer was separated and evaporated. The residue was crystallized from alcohol to give 2.2 g. of XIIIb; m.p., 228°.

2,3-Dihydro-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenothizin-1-one (XIIIa), m.p. 155° (from butanol); yield, 81%.

Anal. Calcd. for $C_{19}H_{13}NOS$: C, 75.2; H, 4.3; N, 4.6. Found: C, 75.1; H, 4.2; N, 4.6.

2,3,10,11-Tetrahydrobenzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]-

(10) O. Hinsberg, *Ann.*, **319**, 257 (1901).

(11) We were unable to obtain VIIa by the procedure described by Fries and Kerkow.[8]

phenazine-1,12-dione (XIV), blue crystals, melting at 344° (from trichlorobenzene); yield, 84%.

Anal. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.8; H, 4.7; N, 8.3. Found: C, 77.8; H, 4.8; N, 8.3.

1*H*-Benzo[*b*]pyrido[1,2,3-*mn*]phenothiazin-1-one (XVIc).—A mixture of 2 g. of XIIIa, 0.3 g. of palladium on charcoal, and 100 ml. of *p*-cymene was refluxed 4 hr., filtered hot, and the filtrate cooled to room temperature to yield 1.3 g. of XVIc; m.p., 225°.

Anal. Calcd. for $C_{19}H_{11}NOS$: C, 75.8; H, 3.7; N, 4.6. Found: C, 75.8; H, 3.9; N, 4.5.

Similarly prepared were: **3*H*-Pyrido[3,2,1-*kl*]phenothiazin-3-one (IV)**, m. p. 204° (from toluene); yield, 89%.

Anal. Calcd. for $C_{18}H_9NOS$: C, 71.7; H, 3.6; N, 5.6. Found: C, 71.5; H, 3.5; N, 5.4.

1*H*-Benzo[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one (XVId), m. p. 273° (from *p*-cymene); yield, 90%.

Anal. Calcd. for $C_{19}H_{11}NO_2$: C, 80.0; H, 3.9; N, 4.9. Found: C, 79.8; H, 4.1; N, 4.6.

Benzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XVII), m. p. >400°; yield, 40%.

Anal. Calcd. for $C_{22}H_{12}N_2O_2$: C, 78.5; H, 3.5; N, 8.3. Found: C, 78.6; H, 3.8; N, 8.0.

1*H*,7*H*-Benzo[*ij*]quinolizine-1,7-dione (XXIV), m.p. 245°; yield, 50%.

Anal. Calcd. for $C_{12}H_7O_2N$: C, 73.0; H, 3.6; N, 7.1. Found: C, 72.6; H, 4.0; N, 7.2.

2,11-Dibenzylbenzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazine-1,12-dione (XVIIa).—To a suspension of 3 g. of XIV in 50 ml. of hot pyridine containing 6 ml. of benzaldehyde was added 3 ml. of 10% potassium hydroxide in methanol. In 5 min., yellow crystals of the product began to separate. After 15 min., the reaction mixture had solidified. Pyridine (50 ml.) was added and heating was continued for 1 hr. The yellow crystals were filtered off and the residue was crystallized from trichlorobenzene to give 3.5 g. of XVIIa; m.p., 338°.

Anal. Calcd. for $C_{36}H_{24}N_2O_2$: C, 83.9; H, 4.7; N, 5.4. Found: C, 83.7; H, 5.0; N, 5.4.

Similarly prepared were:

2-Benzyl-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenothiazin-1-one (XVIa), m. p. 193° (from butanol); yield, 81%.

Anal. Calcd. for $C_{26}H_{16}NOS$: C, 80.1; H, 4.1; N, 3.6. Found: C, 79.9; H, 4.4; N, 3.4.

2-Benzyl-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenoxazin-1-one (XVIb), m. p., 240° (from dichlorobenzene); yield, 86%.

Anal. Calcd. for $C_{26}H_{17}NO_2$: C, 83.2; H, 4.5; N, 3.75. Found: C, 83.1; H, 4.4; N, 3.9.

2,6-Dibenzyl-1*H*,7*H*-benzo[*ij*]quinolizine-1,7-dione (XXV), m.p. 183° (from butanol); yield, 85%.

Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.9; H, 5.0; N, 3.7. Found: C, 82.7; H, 5.2; N, 3.6.

2,3-Dihydro-1*H*-pyrido[3,2,1-*kl*]phenothiazin-3-ol (VI).—To a solution of 2.53 g. (0.01 mole) of III in 50 ml. of dioxane was added 0.2 g. (0.005 mole) of sodium borohydride in 10 ml. of 25% aqueous dioxane. The mixture was heated 0.5 hr. on the steam bath, cooled, diluted with cold, dilute hydrochloric acid, and the solid collected and crystallized from a mixture of benzene and petroleum ether to yield 2.2 g. of VI; m.p., 124°.[4]

Similarly prepared were: **2,3-Dihydro-1*H*-benzo[*b*]pyrido-[1,2,3-*mn*]phenothiazin-1-ol (XVIII)**, m.p. 95° (from benzene–petroleum ether); yield, 62%.

Anal. Calcd. for $C_{19}H_{15}NOS$: C, 75.0; H, 4.6; N, 4.6. Found: C, 74.8; H, 4.8; N, 4.4.

1,2,3,10,11,12-Hexahydrobenzo[*b*]dipyrido[3,2,1-*de*:1,2,3-*mn*]phenazin-1,12-diol (XIX), m.p. 226° (from aqueous dioxane); yield, 55%.

Anal. Calcd. for $C_{22}H_2N_{20}O_2$: C, 76.7; H, 5.8; N, 8.14. Found: C, 76.2; H, 6.0; N, 7.7.

2,3-Dihydro-1-isonitroso-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]-phenothiazine (XXa).—A mixture of 6.0 g. of XIIIa, 3.0 g. of hydroxylamine hydrochloride, and 30 ml. of pyridine was heated on the steam bath for 1 hr., cooled, and diluted with water. The solid was collected by filtration, washed with water, dried, and crystallized from ethoxyethanol to give 5.5 g. of XXa; m.p., 230°.

Anal. Calcd. for $C_{19}H_{14}N_2OS$: C, 71.8; H, 4.4; N, 8.8. Found: C, 71.0; H, 4.4; N, 8.4.

Similarly prepared were:

2,3-Dihydro-1-isonitroso-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]phenoxazine (XXb), m.p. 234° (from acetic acid); yield, 95%.

Anal. Calcd. for $C_{19}H_{14}N_2O_2$: C, 75.5; H, 4.6; N, 9.3. Found: C, 75.7; H, 5.0; N, 9.1.

2,3-Dihydro-3-isonitroso-1*H*-pyrido-[3,2,1-*kl*]phenothiazine (XXI), m.p. 225° (from toluene); yield, 67%.

Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.2; H, 4.5; N, 10.4. Found: C, 66.6; H, 4.5; N, 10.5.

1,2,3,10,11,12-hexahydro-1,2-diisonitrosobenzo[*b*]-dipyrido-[3,2,1-*de*:1,2,3-*mn*]phenazine (XXII) (ten times the quantity of pyridine was needed for this preparation), m.p., 255° (from trichlorobenzene); yield, 81%.

Anal. Calcd. for $C_{22}H_{18}N_4O_2$: C, 71.4; H, 4.9; N, 15.1. Found: C, 70.8; H, 4.7; N, 14.5.

2,3-Dihydro-1-imino-1*H*-benzo[*b*]pyrido[1,2,3-*mn*]-phenoxazine (XV).—A mixture of 5 g. of the cyanoethyl compound Xb and 50 ml. of boron trifluoride etherate was heated on the steam bath for 2 hr., cooled to room temperature, diluted with 100 ml. of ether, and the red solid collected. Recrystallization from acetic acid yielded 4.5 g. of product (m.p. 248°–249°) with an analysis indicating the boron trifluoride complex plus 0.5 mole of acetic acid.

Anal. Calcd. for $C_{20}H_{16}BF_3N_2O_3$: C, 62.5; H, 4.2; N, 7.3. Found: C, 62.9; H, 4.1; N, 7.4.

Recrystallization from ethanol resulted in hydrolysis of the amino group to give the ketone (XIIIb).