

The Reactions of Some Pyranylideneiminium Salts with Amines. II.

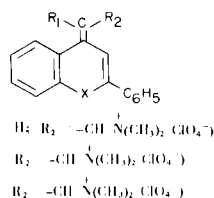
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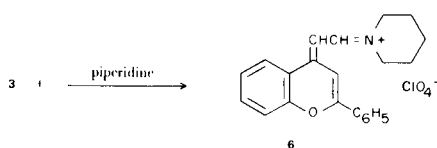
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The iminium salt, *N,N*-dimethyl-*N*-[2-(2-phenyl-4*H*-1-benzopyran-4-ylidene)ethylidene]iminium perchlorate (**3**), reacts with secondary amines by exchanging the dimethylimino group for the added amine. Primary amines also reacted with **3** in the same manner. The bis iminium salts, *N,N,N',N'*-tetramethyl-*N,N'*-[2-(2-phenyl-4*H*-1-benzopyran-4-ylidene)-1,3-propanediylidene]bis(iminium perchlorate) (**4**) and the corresponding thiapyran derivative (**5**), react with ammonia to give 5-dimethylamino-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridine (**10**) and the thia analog **11**. The reactions of **4** and **5** with primary amines give 3-alkyl-5-dimethylamino-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridinium perchlorate salts or the corresponding thiapyrano compounds. Compounds **4** and **5** react with secondary amines by exchanging the dimethylimino groups with the secondary amine and addition of the amine at the 2-position of the pyran or thiapyran ring.

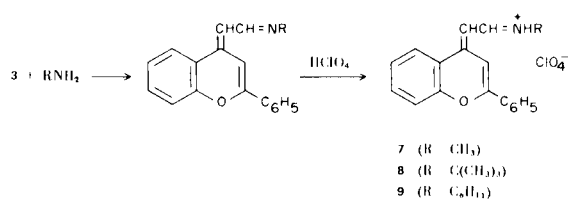
The reactions of *N,N*-dimethyl-*N*-[2-(2,6-diphenyl-4*H*-pyran-4-ylidene)ethylidene]iminium perchlorate (**1**) and *N,N,N',N'*-tetramethyl-*N,N'*-[2-(2,6-diphenyl-4*H*-pyran-4-ylidene)-1,3-propanediylidene]bis(iminium perchlorate) (**2**) with amines have been described (1), and we now report the extension of this study to the iminium salts **3**, **4**, and **5**.



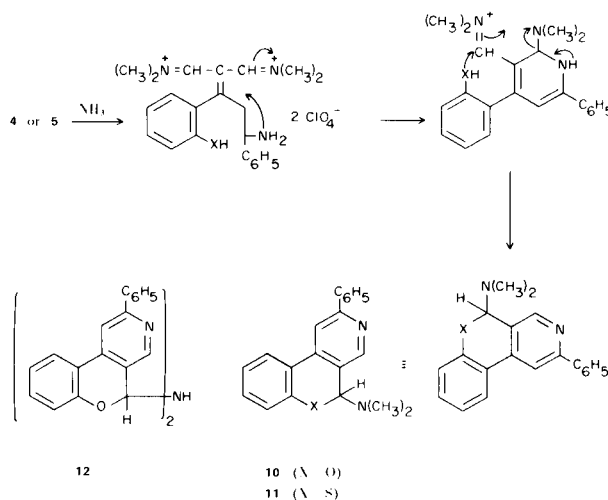
The monoiminium derivative **3** reacted with secondary amines, such as piperidine, to give **6**. This result is completely analogous to our previous results with **1** (1).



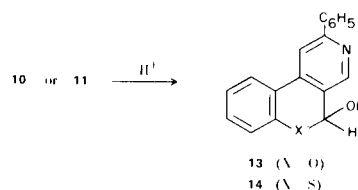
However, primary amines and **3** gave imines (isolated as perchlorate salts, **7-9**) rather than the rearrangement products that were formed with **1** (1).

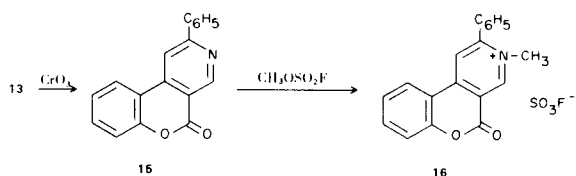


The bis iminium salts **4** and **5** reacted with ammonia to give the pyridine derivatives **10** and **11**, and in the case of **4**, a small amount of the dimer **12** was isolated. The rearrangements to give these products are analogous to those which have been described previously (1,2).

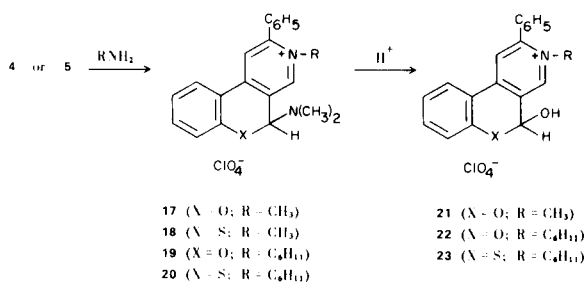


Compounds **10** and **11**, on treatment with acid, gave the carbinols **13** and **14**. Compound **13** was oxidized with chromic oxide to produce the lactone **15**, which, in turn, was methylated with methyl fluorosulfonate giving the pyridinium salt **16**.

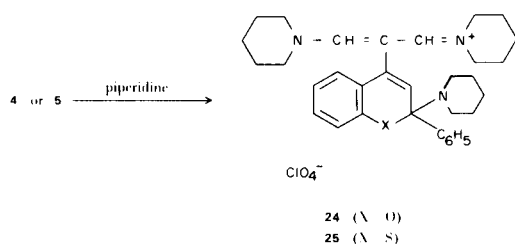




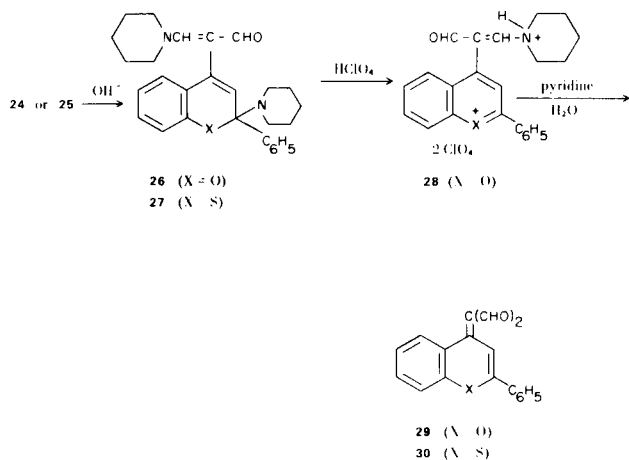
Methylamine and cyclohexylamine reacted with **4** and **5** to give the pyridinium salts **17**, **18**, **19**, and **20**, respectively. Acid hydrolysis of **17**, **19**, and **20** gave the carbinols **21**, **22**, and **23**. Methylation of **13** also gave **21**.



Compounds **4** and **5** reacted with secondary amines in the same manner as described for **2** (1) to give triadducts such as **24** and **25**.



We were able to synthesize the bis aldehyde **30**, which we could not obtain previously (3), by the following series of reactions. The hydrolysis of **27** with refluxing aqueous acetic acid gave **30**.



EXPERIMENTAL

Compounds **3** and **4** were prepared as described previously (3). *N,N,N',N'*-Tetramethyl-*N,N'*-[2-(2-phenyl-4*H*-1-benzothiazopyran-4-ylidene)-1,3-propanediylidene]bis(iminium perchlorate) (**5**).

A solution of 30 g. of 4-methylthiaflavium perchlorate in 36 ml. of dimethylformamide, 54 ml. of 1,2,3-trichloropropane, and 30 ml. of phosphoryl chloride was heated on a steam bath for 2 hours, cooled, and poured into 250 ml. of methyl alcohol to which 25 ml. of 70% perchloric acid had been added. The blue solid was collected and washed with alcohol giving 27 g. of analytically pure product, m.p. 237-238°. The λ_{\max} ($\epsilon \times 10^{-3}$) are 267 (30.4), 303 (27.4), 400 (17.3), and 520 nm (11.9).

Anal. Calcd. for C₂₂H₂₄Cl₂N₂O₈S: C, 48.3; H, 4.4; N, 5.1. Found: C, 48.0; H, 4.3; N, 4.8.

N-[2-(2-phenyl-4*H*-1-benzopyran-4-ylidene)ethylidene]piperidinium Perchlorate (**6**).

A mixture of 1 g. of **3**, 3 ml. of piperidine, and 15 ml. of methyl alcohol was refluxed for 5 minutes, cooled, and the solid was collected and crystallized from nitromethane giving 0.9 g. of **6**, m.p. 258-259°. The λ_{\max} ($\epsilon \times 10^{-3}$) are 238 (22.7), ~260 (8.6), 316 (18.0), 430 (45.5), and ~450 nm (35.4).

Anal. Calcd. for C₂₂H₂₂ClNO₅: C, 63.5; H, 5.3; N, 3.4. Found: C, 63.8; H, 5.4; N, 3.7.

N-[2-(2-Phenyl-4*H*-1-benzopyran-4-ylidene)ethylidene]methyliminium Perchlorate (**7**).

A mixture of 3 g. of **3**, 50 ml. of ether, and 10 ml. of 40% aqueous methylamine was stirred until the solid dissolved (0.5 hour). The ether phase was separated and the ether was evaporated. The residue was dissolved in methyl alcohol, 2 ml. of 70% perchloric acid was added, and the solid was collected and crystallized from acetic acid, yielding 2.6 g. of **7**, m.p. 204-205°. The λ_{\max} ($\epsilon \times 10^{-3}$) are 240 (22.0), ~268 (9.0), 320 (13.0), 425 (38.0), and ~445 nm (30.1).

Anal. Calcd. for C₁₈H₁₆ClNO₅: C, 59.8; H, 4.5; N, 3.9. Found: C, 59.8; H, 4.7; N, 3.6.

N-[2-(2-Phenyl-4*H*-1-benzopyran-4-ylidene)ethylidene]-*t*-butyliminium Perchlorate (**8**).

A mixture of 3 g. of **3**, 10 ml. of *t*-butylamine and 30 ml. of alcohol was refluxed for 8 hours and evaporated to dryness. The residue was dissolved in alcohol, 2 ml. of 70% perchloric acid was added, and the solid was collected and crystallized from alcohol giving 2.1 g. of **8**, m.p. 239-240°. The λ_{\max} ($\epsilon \times 10^{-3}$) are 236 (21.0), ~260 (8.4), 318 (17.3), 425 (44.0), and ~445 nm (36.4).

Anal. Calcd. for C₂₁H₂₂ClNO₅: C, 62.5; H, 5.5; N, 3.5. Found: C, 62.1; H, 5.5; N, 3.2.

N-[2-(2-Phenyl-4*H*-1-benzopyran-4-ylidene)ethylidene]cyclohexyliminium Perchlorate (**9**).

Compound **9** was prepared by the method described for **8** using cyclohexylamine and refluxing the reaction mixture for 1 hour. The yield of **9** was 60%, m.p. 174-175° (from alcohol). The λ_{\max} ($\epsilon \times 10^{-3}$) are 238 (24.7), ~265 (10.1), 320 (18.0), 425 (42.0), and ~448 nm (36.4).

Anal. Calcd. for C₂₃H₂₄ClNO₅: C, 64.3; H, 5.6; N, 3.3. Found: C, 64.4; H, 5.8; N, 2.9.

5-Dimethylamino-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridine (**10**).

A mixture of 9 g. of **4**, 20 ml. of concentrated ammonium hydroxide, and 100 ml. of methyl alcohol was refluxed for 15

minutes, evaporated to dryness, and the residue was crystallized from petroleum ether yielding 5.4 g. of **10**, m.p. 83-83.5°. The λ max ($\epsilon \times 10^{-3}$) are 258 (37.0) and 312 nm (8.9). The mass spectrum shows 302 (6.2%) [M^+]; 258 (100%) [$M-(CH_3)_2N$]; other fragments less than 2%. The nmr in dimethyl sulfoxide d_6 shows $N(CH_3)_2$ at δ 2.38 (S, 6H); proton at 5-position δ 6.12 (S, 1H); aromatic protons at δ 6.93-8.39 (M, 9H); proton at 1-position δ 8.44 (S, 1H); and proton at 4-position δ 8.60 ppm (S, 1H).

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.4; H, 6.0; N, 9.3. Found: C, 79.5; H, 6.1; N, 9.0.

5-Dimethylamino-2-phenyl-5H-1-benzothiopyrano[3,4-c]pyridine (**11**).

Compound **11** was prepared by the method described for **10** using **5**; yield 70% of product, m.p. 136-137° (from aqueous alcohol). The λ max ($\epsilon \times 10^{-3}$) are 247 (43.8) and 327 nm (7.2). The mass spectrum shows 318 (4.1%) [M^+]; 275 (23%) [$M-CH_3(CH_2)N$]; 274 (100%) [$M-(CH_3)_2N$]; 242 (3%) [274-S].

Anal. Calcd. for $C_{20}H_{18}N_2S$: C, 75.4; H, 5.7; N, 8.8. Found: C, 75.8; H, 6.0; N, 8.8.

5,5'-Aminobis(2-phenyl-5H-1-benzopyrano[3,4-c]pyridine (**12**)).

The method described for the preparation of **10** was repeated using 100 ml. of acetonitrile as the solvent. The reaction mixture was chilled and 0.4 g. of **12** was collected and crystallized from water, m.p. 251-252°. The mass spectrum shows 531 (2%) [M^+]; 273 (3%); and 258 (100%), which are the result of cleavage of the aminoheterocyclic bond.

Anal. Calcd. for $C_{36}H_{25}N_3O_2$: C, 81.3; H, 4.7; N, 7.9. Found: C, 81.2; H, 4.9; N, 7.8.

5-Hydroxy-2-phenyl-5H-1-benzopyrano[3,4-c]pyridine (**13**).

A solution of 10 g. of **10** in 50 ml. of warm acetic acid was treated with 10 ml. of 70% perchloric acid, diluted with water until cloudy, and after chilling, the solid was collected and crystallized from ethyl acetate giving 7 g. of **13**, m.p. 194-195°. The λ max ($\epsilon \times 10^{-3}$) are 255 (38.0) and 305 nm (12.4). The mass spectrum shows 275 (100%) [M^+]; 274 (7%) [M-1]; 258 (100%) [M-OH]; 246 (39%) [M-HCO]; and 103 (5%) [C_6H_5CN]. The nmr spectrum (dimethyl sulfoxide d_6) shows the protons at the 5-position δ 6.41 (S, 1H), at the 1-position δ 8.33 (S, 1H), at the 4-position δ 8.6 (S, 1H), and aromatic δ 6.92-8.28 ppm (M, 9H).

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.5; H, 4.8; N, 5.1. Found: C, 78.8; H, 4.9; N, 5.0.

5-Hydroxy-2-phenyl-5H-1-benzothiopyrano[3,4-c]pyridine (**14**).

A solution of 1 g. of **11** in 15 ml. of acetic acid was refluxed for 2 hours, diluted with water, chilled, and the solid was collected and crystallized from alcohol yielding 0.6 g. of **14**, m.p. 157-158°. The λ max ($\epsilon \times 10^{-3}$) are 246 (42.5) and 326 nm (7.3). The mass spectrum shows 291 (29%) [M^+]; 290 (7%) [M-1]; 275 (31%); 274 (58%) [M-OH]; 262 (16%) [M-HCO]; 258 (100%) [M-SH]; 158 (9%); and 31 (13%). The nmr spectrum (dimethyl sulfoxide d_6) shows the aromatic protons at δ 7.3-8.4 (M, 9H), proton at the 1-position δ 8.35 (S, 1H), proton at the 4-position δ 8.78 ppm (S, 1H), and the proton at the 5-position, which will be described in more detail. The spectrum shows a peculiar triplet for H-5 at δ 6.19 which appears to consist of a doublet ($J = 5$ Hz) and a small peak which is not quite centered between the doublet peaks. The hydroxy absorbs at δ 6.57 ($J = 5$ Hz) and exchanges with deuterium oxide as the H-5 becomes a singlet. The integrals

for H-5 and the OH were exactly the same. Heating the sample to 60° causes the H-5 and OH absorptions to change to broad overlapping doublets and raising the temperature to 90° results in two singlets which do not integrate quite the same. The addition of one drop of water to the sample causes the internal peak of the H-5 absorption to disappear. A tentative explanation of this behavior is that the sample consists of two isomers which do not readily interchange and the isomer present in the smaller amount is undergoing rapid exchange of the hydroxyl group. It is assumed that the OH absorption of this isomer is under that of the other isomer, which is quite possible on the basis of the shape of this absorption. It also must be assumed that addition of a drop of water causes a shift of the H-5 absorption of the minor isomer so that it overlaps a peak of the other isomer.

Anal. Calcd. for $C_{18}H_{13}NOS$: C, 74.2; H, 4.5; N, 4.8. Found: C, 74.0; H, 4.4; N, 4.7.

2-Phenyl-5H-1-benzopyrano[3,4-c]pyridin-5-one (**15**).

A solution of 2 g. of **13** in 10 ml. of pyridine was added to 3 g. of chromium trioxide in 15 ml. of pyridine. The mixture was stirred for 2 hours, poured into water, and the solid was collected and crystallized from alcohol giving 1.5 g., m.p. 195-196°. The λ max ($\epsilon \times 10^{-3}$) are 267 (34.6) and 327 nm (13.5). The mass spectrum shows 273 (100%) [M^+]; 245 (12%) [M-CO]; and 244 (8%) [M-HCO]. The nmr in deuteriochloroform shows aromatic protons including the proton in position one at δ 7.3-8.2 (M, 10H), proton at 4-position δ 9.52 ppm (S, 1H). In DMSO the aromatics are at δ 7.32-8.23, 1-H at δ 8.65, and 4-H at δ 9.25 ppm.

Anal. Calcd. for $C_{18}H_{11}NO_2$: C, 79.1; H, 4.0; N, 5.1. Found: C, 79.0; H, 4.2; N, 5.2.

3-Methyl-5-oxo-2-phenyl-5H-1-benzopyrano[3,4-c]pyridinium Fluorosulfonate (**16**).

To a solution of 1 g. of **15** in 25 ml. of methylene chloride was added 0.5 g. of methyl fluorosulfonate, and after 3 hours, the solid was collected and crystallized from alcohol giving 1.2 g. of **16**, m.p. 257-259°. The λ max ($\epsilon \times 10^{-3}$) are 231 (16.2), 236 (16.6), 298 (19.8), and \sim 335 nm (12.5). The nmr (DMSO) shows CH_3 δ 4.17 (S, 3H), aromatics δ 7.33-7.67 (M, 8H), 10-H two doublets at δ 8.78 and 8.92 ($J = 2$ Hz, 1H), 1-H δ 9.17 (S, 1H), and 4-H δ 10.1 ppm (S, 1H).

Anal. Calcd. for $C_{19}H_{14}FNO_5S$: C, 58.9; H, 3.6; N, 3.6. Found: C, 58.8; H, 3.8; N, 3.8.

3-Methyl-5-dimethylamino-2-phenyl-5H-1-benzopyrano[3,4-c]pyridinium Perchlorate (**17**).

A mixture of 9 g. of **4**, 15 ml. of 40% aqueous methylamine, and 150 ml. of methyl alcohol was heated until a clear solution was obtained, and after chilling, the solid was collected and crystallized from water to give 7.3 g. of **17**, m.p. 226-227°. The λ max ($\epsilon \times 10^{-3}$) are 224 (17.5), 300 (20.9), and 370 nm (8.0).

Anal. Calcd. for $C_{21}H_{21}ClN_2O_5S$: C, 60.5; H, 5.1; N, 6.7. Found: C, 60.2; H, 5.1; N, 6.4.

3-Methyl-5-dimethylamino-2-phenyl-5H-1-benzothiopyrano[3,4-c]pyridinium Perchlorate (**18**).

The procedure described for the preparation of **17** was followed using **5**. A 95% yield of **18** was obtained, m.p. 193-194° (from methyl alcohol). The λ max ($\epsilon \times 10^{-3}$) are 248 (20.0), 304 (18.7), and 398 nm (4.8). The nmr (trifluoroacetic acid) shows $N(CH_3)_2$ at δ 2.82 (S, 6H), NCH_3 at δ 4.33 (S, 3H), 5-H at δ

6.17 (S, 1H), aromatics δ 7.5-7.8 (M, 9H), 8.46 (S-1H), and 4-H δ 9.27 ppm (S, 1H).

Anal. Calcd. for $C_{21}H_{21}ClN_2O_4S$: C, 58.3; H, 4.9; N, 6.5. Found: C, 58.5; H, 4.8; N, 6.4.

3-Cyclohexyl-5-dimethylamino-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridinium Perchlorate (**19**).

Compound **19** was prepared by the procedure described for **17** using cyclohexylamine. The yield was 85%, m.p. 224-225° (from acetic acid). The λ max ($\epsilon \times 10^{-3}$) are 303 (20.8) and 375 nm (8.0). The nmr (deuteriochloroform) shows cyclohexyl protons δ 2.17 (M, 10H), $N(CH_3)_2$ at δ 2.67 (S, 6H), 5-H δ 6.68 (S, 1H), aromatics δ 8.07-8.25 (M, 9H), 1-H δ 8.3 (S, 1H), and 4-H δ 9.32 ppm (S, 1H).

Anal. Calcd. for $C_{26}H_{29}ClN_2O_5$: C, 64.4; H, 6.0; N, 5.8. Found: C, 64.8; H, 5.9; N, 5.7.

3-Cyclohexyl-5-dimethylamino-2-phenyl-5*H*-1-benzothiapyrano[3,4-*c*]pyridinium Perchlorate (**20**).

The procedure used for the preparation of **18** was repeated using cyclohexylamine to give **20** in 67% yield, m.p. 167-168° (from methanol). The λ max ($\epsilon \times 10^{-3}$) are 248 (16.0), 305 (18.5), and 400 nm (4.7).

Anal. Calcd. for $C_{26}H_{29}ClN_2O_4S$: C, 62.3; H, 5.8; N, 5.6. Found: C, 62.1; H, 5.7; N, 5.4.

5-Hydroxy-3-methyl-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridinium Perchlorate (**21**).

To a solution of 1 g. of **17** in 5 ml. of boiling water was added 1 ml. of 70% perchloric acid, and after cooling, the solid was collected and crystallized from water; yield 78%, m.p. 130-131°.

Methylation of **13** with methyl fluorosulfonate in methylene chloride also gave **21**, m.p. 130-131°. The λ max ($\epsilon \times 10^{-3}$) are 304 (23.0), and 355 nm (12.5). The nmr spectrum (DMSO) shows $\overset{+}{N}CH_3$ δ 4.17 (S, 3H), 5-H δ 6.73 (S, 1H), aromatics δ 7.8-8.5 (M, 9H), 1-H δ 8.59 (S, 1H), 4-H δ 9.7 ppm (S, 1H).

Anal. Calcd. for $C_{19}H_{16}ClNO_6$: C, 58.5; H, 4.1; N, 3.6. Found: C, 58.8; H, 4.3; N, 3.3.

3-Cyclohexyl-5-hydroxy-2-phenyl-5*H*-1-benzopyrano[3,4-*c*]pyridinium Perchlorate (**22**).

A solution of 3 g. of **19** in 25 ml. of acetic acid and 6 ml. of concentrated hydrochloric acid was boiled for 5 minutes, diluted with water until turbid, and after chilling, the solid was collected and crystallized from ethoxyethanol giving 1.9 g. of **22**, m.p. 235-236°. The λ max ($\epsilon \times 10^{-3}$) are 301 (23.4) and 350 nm (13.0).

Anal. Calcd. for $C_{24}H_{24}ClNO_6$: C, 63.0; H, 5.3; N, 3.1. Found: C, 63.3; H, 5.4; N, 2.8.

3-Cyclohexyl-5-hydroxy-2-phenyl-5*H*-1-benzothiapyrano[3,4-*c*]pyridinium Perchlorate (**23**).

A solution of 1 g. of **20** in 20 ml. of acetic acid was refluxed and four 1-ml. portions of water were added at hourly intervals. The solution was chilled and the solid was collected and crystallized from aqueous alcohol giving 0.6 g. of **23**, m.p. 210-212°. The λ max ($\epsilon \times 10^{-3}$) are 305 (21.3) and 380 nm (5.5).

Anal. Calcd. for $C_{24}H_{24}ClNO_5S$: C, 60.8; H, 5.1; N, 3.0. Found: C, 60.9; H, 5.1; N, 2.7.

N-[3-Piperidino-2-(2-phenyl-2-piperidino-2*H*-1-benzopyran-4-yl)-1-propen-3-ylidene]piperidinium Perchlorate (**24**).

A mixture of 4 g. of **4**, 10 ml. of piperidine, and 50 ml. of ethyl acetate was heated until a solution was obtained, and after

chilling, the solid was collected and crystallized from butyl alcohol giving 4.1 g. of **24**, m.p. 211-212°. The λ max ($\epsilon \times 10^{-3}$) are 228 (27.0), and 315 nm (49.0).

Anal. Calcd. for $C_{33}H_{42}ClN_3O_5$: C, 66.4; H, 7.1; N, 7.1. Found: C, 66.6; H, 7.1; N, 7.0.

N-[3-Piperidino-2-(2-phenyl-2-piperidino-2*H*-1-benzothiapyran-4-yl)-1-propen-3-ylidene]piperidinium Perchlorate (**25**).

Compound **25** was prepared from **5** by the procedure described for the preparation of **24**; yield 51% m.p. 197-198°. The λ max ($\epsilon \times 10^{-3}$) are 248 (22.0) and 319 nm (40.8).

Anal. Calcd. for $C_{33}H_{42}ClN_3O_4S$: C, 64.7; H, 6.9; S, 5.2. Found: C, 64.5; H, 6.9; S, 5.1.

2-(2-Phenyl-2-piperidino-2*H*-1-benzopyran-4-yl)-3-piperidinoacrolein (**26**).

A mixture of 2 g. of **24**, 100 ml. of 5% aqueous sodium hydroxide and 100 ml. of ether was stirred for 40 hours, the ether layer was separated and the ether evaporated, and the residue was crystallized from isopropyl alcohol giving 1 g. of **26**, m.p. 195-196°. The λ max ($\epsilon \times 10^{-3}$) are 225 (24.7), 282 (26.0), and 380-390 nm (5.2). The mass spectrum shows 428 (3%) [M^+]; 399 (4%) [M-CHO]; 344 (100%) [M-C₅H₁₀N]; 316 (4%) [344-CHO]; and peaks at 314, 261, 233, 231, 207, 202, 159, and 98.

Anal. Calcd. for $C_{28}H_{32}N_2O_2$: C, 78.5; H, 7.5; N, 6.5. Found: C, 78.2; H, 7.4; N, 6.4.

2-(2-Phenyl-2-piperidino-2*H*-1-benzothiapyran-4-yl)-3-piperidinoacrolein (**27**).

A mixture of 1 g. of **25** and 25 ml. of 5% methanolic potassium hydroxide was refluxed for 15 minutes, cooled, and the solid was collected and crystallized from isopropyl alcohol, yielding 0.6 g. of **27**, m.p. 168-170°. The mass spectrum shows 444 (8%) [M^+]; 415 (15%) [M-CHO]; 361 (100%) [M-C₅H₉N]; 360 (75%) [M-C₅H₁₀N]; 332 (30%).

Anal. Calcd. for $C_{28}H_{32}N_2OS$: C, 75.7; H, 7.2; N, 6.3; S, 7.2. Found: C, 75.3; H, 7.0; N, 6.1; S, 7.3.

4-(1-Formyl-2-piperidiniumvinyl)flavylium Bisperchlorate (**28**).

To a solution of 1 g. of **26** in 10 ml. of toluene was added 0.5 ml. of 70% perchloric acid. A red oil separated which eventually crystallized. The solid was crystallized from acetic acid giving 0.5 g. of **28**, m.p. 170-172°.

Anal. Calcd. for $C_{23}H_{23}Cl_2NO_{10}$: C, 50.8; H, 4.3; N, 2.6; Cl, 13.0. Found: C, 50.4; H, 4.5; N, 2.6; Cl, 13.2.

4-Diformylmethylene-2-phenyl-4*H*-1-benzopyran (**29**).

A solution of 2 g. of crude **28** in 10 ml. of pyridine was diluted with water and the red solid that separated was collected, washed with methyl alcohol, and crystallized from isopropyl alcohol, giving 0.6 g. of **29**, m.p. 175-177°. The λ max ($\epsilon \times 10^{-3}$) are 240 (18.8), 325 (14.4), and 415-425 nm (19.0). The mass spectrum shows 276 (23%) [M^+]; 248 (98%) [M-CO]; 247 (100%) [M-HCO]; 231 (92%) [248-OH]; 220 (9%) [248-CO]; 219, 217, 202, 189, 171, 165, 115, 105 (10%) [C₆H₅CO]; 102 (5%) [C₆H₅≡CH]; 77 (19%) [C₆H₅].

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.3; H, 4.4. Found: C, 77.9; H, 4.5.

4-Diformylmethylene-2-phenyl-4*H*-1-benzothiapyran (**30**).

A solution of 1 g. of **27** in 20 ml. of acetic acid plus 5 ml. of water was refluxed for 5 minutes, cooled, and the purple solid was collected and crystallized from acetic acid, yielding 0.4 g. of

30, m.p. 157-158°. The λ max ($\epsilon \times 10^{-3}$) are 250 (22.1), 305 (10.9), and 410-450 nm (12.4). The nmr spectrum (deuteriochloroform) shows the aromatic protons at δ 7.42-7.92 (M, 9H), the proton in the 3-position at δ 9.67 (S, 1H), and the aldehyde protons at δ 10.3 ppm (S, 2H). The mass spectrum shows 292 (30%) [M^+]; 264 (100%); 247 (92%) [264-OH]; 236, 235, 234, and 202.

Anal. Calcd. for $C_{18}H_{12}O_2S$: C, 74.0; H, 4.1; S, 11.0. Found: C, 74.3; H, 3.9; S, 10.7.

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