

Reactions of Pyranilydenemethylpyrylium Salts with Ammonia and Amines

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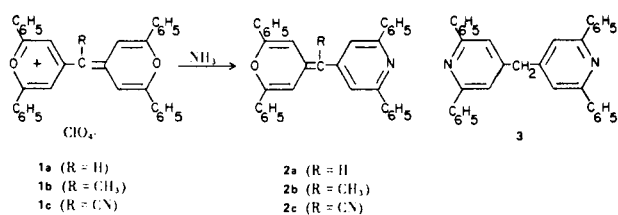
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Pyranilydenemethylpyrylium salts (**1**) react with ammonia to give pyranilydenepyridines as a result of the replacement of one of the oxygen atoms of **1** by nitrogen. Aliphatic primary amines react with **1** by replacing both of the oxygen atoms by nitrogens. Aniline and **1** give the monoreplacement product. Pyranilydenemethylthiopyrylium salts have only the oxygen atom replaced by reaction with primary aliphatic amines.

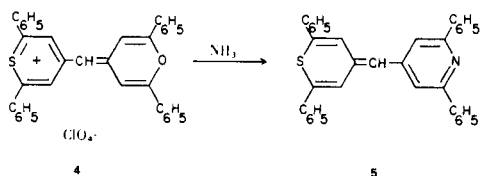
J. Heterocyclic Chem., 13, 577 (1976).

Several years ago we described the reaction of sodium sulfide with pyranilydenemethylpyrylium salts and showed that only one of the oxygen atoms was replaced by sulfur (**1**). We have carried out similar reactions with ammonia and primary amines, and the present paper describes our results.

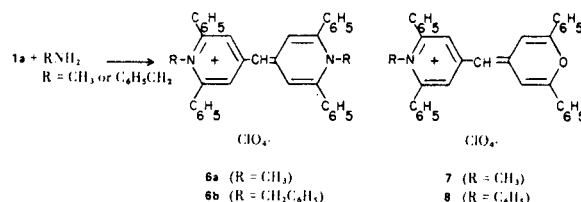
One of the best-known reactions of pyrylium salts is the formation of pyridine or pyridinium derivatives on treatment with ammonia or primary amines (**2**). In the case of pyranilydenemethylpyrylium salts, however, the possibility exists for the replacement of either one or both of the oxygen atoms. We have found that **1a-1c** reacted with ammonium hydroxide in pyridine at steam-bath temperature to give **2a-2c** as the result of replacement of one of the oxygen atoms. At 120° under pressure, **1a** gave the bis pyridine derivative **3**, but under the same conditions **1b** and **1c** gave **2b** and **2c**.



Compound **4** was treated with ammonia in pyridine at 100° to determine whether the oxygen or the sulfur atom is replaced, and it was found that the oxygen was selectively replaced.

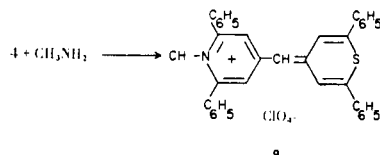


Methylamine and benzylamine reacted with **1a** replacing both oxygen atoms and giving **6a** and **6b**, respectively.



A small amount (about 5%) of **7** was isolated from the reaction with methylamine. Aniline replaced only one of the oxygen atoms of **1a** giving **8**.

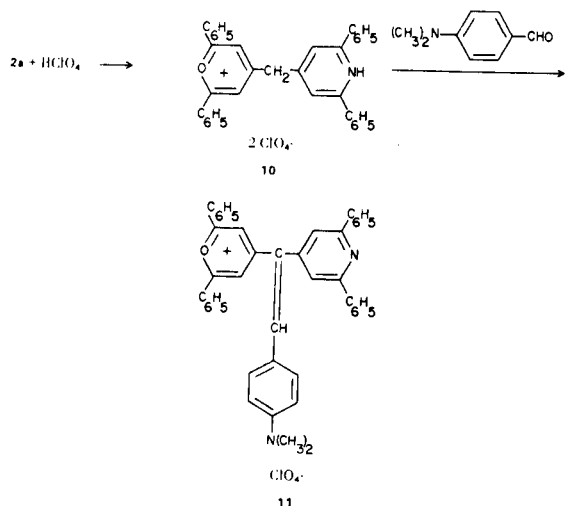
The pyridinium salt **7** on treatment with sodium sulfide in aqueous acetone was recovered unchanged, but **4** and alcoholic methylamine readily gave the pyridinium salt **9**.



Methylation of **2a** and **3** with methyl fluorosulfonate, and subsequent conversion to the perchlorate, gave **7** and **6a**, respectively.

The pyridine derivative **2a** was protonated to give **10** and the latter was allowed to react with *p*-dimethylamino-benzaldehyde in acetic anhydride giving the dye **11**.

The electronic spectra of the products formed by the reaction of pyranilydenemethylpyrylium salts with ammonia serve as a convenient guide to the type of product formed. The replacement of one oxygen atom by nitrogen gives a product that absorbs in the region of 380 nm. If two oxygens are replaced with nitrogen, the product absorbs at about 300 nm.



EXPERIMENTAL

The melting points were determined with a Meltemp apparatus and are uncorrected. The absorption spectra were recorded on Cary model 14 and 17 spectrometers and the mass spectra on a Hitachi RMS-4 spectrometer.

Compounds **1a**, **1b**, and **1c** were prepared by the published procedures (3), (4), and (5), respectively.

4-[(2,6-Diphenyl-4H-pyran-4-ylidene)methyl]-2,6-diphenylpyridine (**2a**).

A solution of 6 g. (0.01 mole) of **1a** in 120 ml. of pyridine was heated on a steam bath and 30 ml. of 28% ammonium hydroxide was added in portions over 1 hour. The solution was chilled and the solid was collected and crystallized from ethoxyethanol giving 4.3 g. (87% yield) of **2a**, m.p. 177-178°. The λ max in acetonitrile was 380 nm ($\epsilon = 35,200$). The mass spectrum showed peaks (relative %) at 475 (100), 474 (9.1), 398 (3), and 370 (3).
Anal. Calcd. for $C_{35}H_{25}N_2O$: C, 88.4; H, 5.3; N, 2.9. Found: C, 88.2; H, 5.4; N, 2.9.

4-[1-(2,6-Diphenyl-4H-pyran-4-ylidene)ethyl]-2,6-diphenylpyridine (**2b**).

The procedure described for the preparation of **2a** was repeated with **1b** giving an 83% yield of product; m.p. 187-188° (from pyridine and methanol). The λ max in acetonitrile was 355 nm (19,700). The mass spectrum showed peaks at 489 (100), 488 (14), 412 (0.3), and 384 (2.3).

Anal. Calcd. for $C_{36}H_{27}NO$: C, 88.3; H, 5.5; N, 2.9. Found: C, 88.6; H, 5.6; N, 2.9.

4-[(2,6-Diphenyl-4H-pyran-4-ylidene)cyanomethyl]-2,6-diphenylpyridine (**2c**).

The same procedure was repeated with **1c** giving an 80% yield of **2c**, m.p. 249-250° (from pyridine and methanol). The λ max in acetonitrile was 390 nm ($\epsilon = 21,200$). The mass spectrum showed peaks at 500 (100), 499 (3.8), 423 (3.8), 395 (4.0), and a M^{++} at 250 (3.8).

Anal. Calcd. for $C_{36}H_{24}N_2O$: C, 86.4; H, 4.8; N, 5.6. Found: C, 86.1; H, 4.7; N, 5.3.

4,4'-Methylenebis(2,6-diphenylpyridine) (**3**).

A mixture of 25 g. of **1a**, 200 ml. of 28% ammonium hy-

droxide, and 200 ml. of acetonitrile was heated under pressure at 120° for 5 hours. After cooling, the product was collected and recrystallized from ethoxyethanol giving 17.5 g. (87%) of **3**, m.p. 169-170°.

Anal. Calcd. for $C_{35}H_{26}N_2$: C, 88.6; H, 5.5; N, 5.9. Found: C, 88.5; H, 5.4; N, 6.0.

4-[(2,6-Diphenyl-4H-thiopyran-4-ylidene)methyl]-2,6-diphenylpyridine (**5**).

A solution of 1 g. of **4** (**1**), 20 ml. of pyridine, and 5 ml. of 28% ammonium hydroxide was refluxed for 5 minutes, 50 ml. of methanol was added, and the solution was chilled. The solid was collected and recrystallized from pyridine and methanol yielding 0.51 g. of **5**, m.p. 195-196°. The λ max (acetonitrile) was 392 ($\epsilon = 29,000$), and the mass spectrum showed peaks at 491 (100), 490 (8.0), 414 (4.1), and M^{++} 245 (7.0).

Anal. Calcd. for $C_{35}H_{25}N_2S$: C, 85.5; H, 5.1; S, 6.5; N, 2.8. Found: C, 85.4; H, 4.9; S, 6.3; N, 3.1.

4-[(1-Methyl-2,6-diphenyl-4H-pyrid-4-ylidene)methyl]-1-methyl-2,6-diphenylpyridinium Perchlorate (**6a**).

Method A.

A mixture of 1 g. of **1a**, 25 ml. of alcohol, and 4 ml. of aqueous methylamine was heated on a steam bath for 1 hour and filtered hot to remove 0.1 g. of **7**. The filtrate was cooled giving 0.4 g. of **6a**, m.p. 95-96°.

Method B.

A suspension of 1 g. of **3** in 2.5 ml. of methylene chloride was treated with 3 ml. of methyl fluorosulfonate, and after being refluxed overnight, the yellow crystals were collected. The solid was dissolved in 7 ml. of acetic acid and 2 ml. of 70% perchloric acid was added. The precipitate was collected and dissolved in hot pyridine and water was added until the solution was turbid. After chilling, the solid was collected, 0.6 g. m.p. 94-95°. The λ max (acetonitrile) was 515 (92,000).

Anal. Calcd. for $C_{37}H_{31}ClN_2O_4$: C, 73.7; H, 5.2; N, 4.6. Found: C, 73.4; H, 5.4; N, 4.7.

4-[(1-Benzyl-2,6-diphenyl-4H-pyrid-4-ylidene)methyl]-1-benzyl-2,6-diphenylpyridinium Perchlorate (**6b**).

A solution of 2.9 g. of **1a**, 4 ml. of benzylamine, and 8 ml. of pyridine was heated on a steam bath for 10 minutes, cooled, and diluted with 50 ml. of ether. The solid was collected and crystallized from alcohol yielding 2.1 g. (56%) of **6b**, m.p. 146-147°.

Anal. Calcd. for $C_{49}H_{39}ClN_2O_4$: C, 77.9; H, 5.2; N, 3.7. Found: C, 77.6; H, 5.5; N, 3.5.

4-[(2,6-Diphenyl-4H-pyran-4-ylidene)methyl]-1-methyl-2,6-diphenylpyridinium perchlorate (**7**).

Method A.

A solution of 1 g. of **2a**, 3 ml. of methyl fluorosulfonate, and 20 ml. of methylenechloride was refluxed 1 hour, cooled, and the solid collected and crystallized from pyridine and methanol, yield 0.7 g., m.p. 279-280°.

Method B.

The small amount of **7** that was obtained during the preparation of **6a** (Method A) was recrystallized, m.p. 279-280°.

Anal. Calcd. for $C_{36}H_{28}ClNO_5$: C, 73.3; H, 4.8; N, 2.4. Found: C, 73.6; H, 4.8; N, 2.3.

4-[(2,6-Diphenyl-4H-pyran-4-ylidene)methyl]-1,2,6-triphenylpyridinium Perchlorate (**8**).

A solution of 6 g. of **1a**, 7 ml. of aniline, and 30 ml. of pyridine was refluxed for 0.5 hour, diluted with methanol, and the solid was collected; yield 4.6 g. (from pyridine and methanol), m.p. 262-263°. The λ max in acetonitrile was 505 nm ($\epsilon = 72,000$).

Anal. Calcd. for $C_{41}H_{30}ClNO_5$: C, 75.5; H, 4.6; N, 2.1. Found: C, 75.2; H, 5.0; N, 2.1.

4-[(2,6-Diphenyl-4*H*-thiopyran-4-ylidene)methyl]-1-methyl-2,6-diphenylpyridinium Perchlorate (**9**).

A mixture of 4 g. of **4**, 3 ml. of 25% aqueous methylamine, and 125 ml. of alcohol was refluxed for 0.5 hour and cooled. The solid was recrystallized from alcohol; yield 1 g., m.p. 145-147°. The λ max (acetonitrile) was 485 nm ($\epsilon = 37,000$).

Anal. Calcd. for $C_{36}H_{28}ClNO_4S$: C, 71.3; H, 4.7; N, 2.3, S, 5.3. Found: C, 71.0; H, 4.6; N, 2.5; S, 5.2.

4-[1-(2,6-Diphenyl-4-pyridyl)-2-(4-dimethylaminophenyl)vinyl]-2,6-diphenylpyrylium Perchlorate (**11**).

A mixture of 1 g. of **2a**, 20 ml. of methanol, and 1 ml. of 70% perchloric acid was heated until the solid dissolved, and after chilling **10** (m.p. 148-150°) was collected. A solution of 1 g. of **10**, 1 g. of *p*-dimethylaminobenzaldehyde, and 20 ml. of acetic

anhydride was refluxed for 20 minutes, chilled, and the solid was collected, yield 0.8 g., m.p. 223-224°. The λ max (acetonitrile) was 635 ($\epsilon = 73,000$).

Anal. Calcd. for $C_{44}H_{35}ClN_2O_5$: C, 74.7; H, 5.0; N, 4.0; Cl, 5.0. Found: C, 74.5; H, 5.0; N, 4.3; Cl, 5.1.

Acknowledgment.

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