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3-Acetyltropolone (1) reacted with 2-hydroxybenzaldehyde (3a) in the presence of perchloric acid in ethyl orthoformate to afford 2-(3-tropolonyl)-1-benzopyrylium perchlorate (4a). The reactions with 2-hydroxy-5-methylbenzaldehyde (3b), 5-chloro-2-hydroxybenzaldehyde (3c), and 2-hydroxy-1-naphthaldehyde (3d) gave respectively the corresponding products 4b-d. The reactions of 2-acetyl-7-methylamino-tropolone (2) with 3a-d also gave the corresponding products 5a-d, respectively.

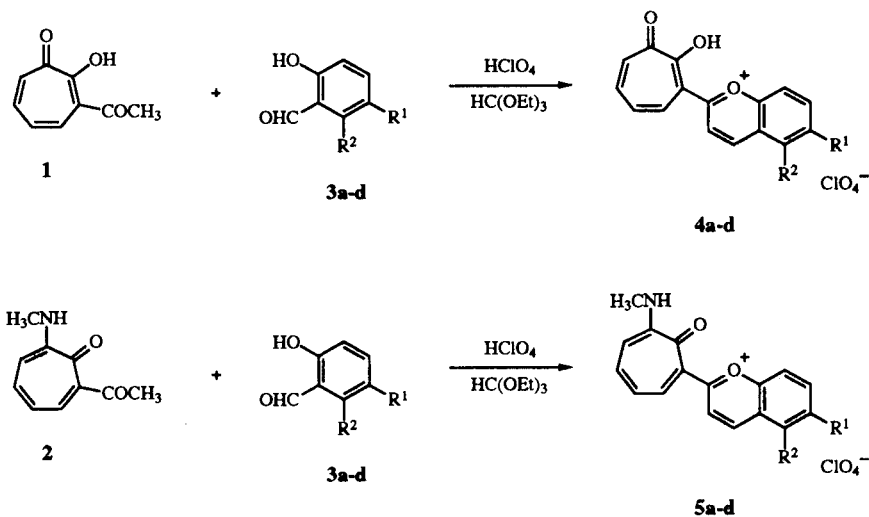
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Six-membered oxygen-heterocycles occur as yellow-colored pigments widely throughout the plant kingdom. One decade ago, we reported that the flavone-like heterocycle-fused troponoid compounds, 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones, were obtained by the oxidative cyclization of 3-cinnamoyltropolones with selenium dioxide [1] and with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [2]. Recently, we also found that 3-acetyltropolone reacted with benzaldehydes in the presence of ethyl orthoformate and perchloric acid to afford 2-aryl-

4,9-dihydrocyclohepta[*b*]pyran-4,9-diones in one step [3]. The reactions of 3-(bromoacetyl)tropolone with benzaldehydes also gave the same compounds [4].

On the other hand, one of the most prominent and attractive colors in nature is brought about by anthocyanins that encompass the entire range of red, violet, and blue pigmentation occurring in plants. These anthocyanins have the 2-phenyl-1-benzopyrylium structure. In general, these ions are called flavylium ions. As one of the synthetic methods, it was reported that acetophenones

Scheme 1



- a $R^1 = R^2 = \text{H}$
 b $R^1 = \text{CH}_3, R^2 = \text{H}$
 c $R^1 = \text{Cl}, R^2 = \text{H}$
 d $R^1, R^2 = -(\text{CH}=\text{CH})_2-$

were treated with 2-hydroxybenzaldehydes in the presence of ethyl orthoformate and perchloric acid to afford flavylum perchlorates [5]. In troponoid chemistry, we preliminarily reported that 3-acetyltropolone (**1**) reacted with 2-hydroxybenzaldehydes in a similar manner to flavylum-like 2-(3-tropolonyl)-1-benzopyrylium perchlorates [6]. This paper deals with the details. In addition, the reactions of 2-acetyl-7-methylaminotropone (**2**) with 2-hydroxybenzaldehydes in the same condition will be described.

Results and Discussion.

A 70% perchloric acid was added dropwise to a mixture of 3-acetyltropolone (**1**) [7] and 2-hydroxybenzaldehyde (**3a**) in ethyl orthoformate. When this mixture was stirred at room temperature, the solution deposited 2-(3-tropolonyl)-1-benzopyrylium perchlorate (**4a**) as red crystals in 65% yield. Its structure was confirmed by elemental analysis ($C_{16}H_{11}ClO_7$) and spectral data. The uv spectra shows four absorption bands at λ 217.5, 323, 370, and 505 nm. The former three bands correspond to those (241, 326, and 349 nm) of benzopyrylium perchlorate [8]. The band at λ 505 nm might be the characteristic interaction between benzopyrylium and tropolone ring. The uv band for 4'-hydroxyflavylum perchlorate was observed at λ 438 nm [9]. In the ir spectrum, typical three bands are observed at 3149, 1620, and 1094 cm^{-1} for the hydroxyl, tropolone carbonyl, and perchlorate group, respectively. The 1H nmr spectrum shows signals at very low field, δ 9.0-10.4 (11H, m).

The reactions with 2-hydroxy-5-methylbenzaldehyde (**3b**), 5-chloro-2-hydroxybenzaldehyde (**3c**), and 2-hydroxy-1-naphthaldehyde (**3d**) gave also the corresponding 2-(3-tropolonyl)-1-benzopyrylium perchlorates **4b-d** in 57-80% yields, respectively.

The reactions of 2-acetyl-7-methylaminotropone (**2**) [10] with 2-hydroxybenzaldehydes **3a-d** were also carried out in a similar manner to give the corresponding 2-(7-methylamino-2-troponyl)-1-benzopyrylium perchlorates **5a-d** in 26-44%, respectively. The structures were also confirmed by elemental analyses and spectral data. The 1H nmr spectral signals were observed at higher field, δ 6.8-8.3, than those for the tropolonyl compounds **3a-d**. This may be attributed to strong electron-releasing effect of the methylamino group.

EXPERIMENTAL

Measurements.

The melting points were determined with XRC-1 micromelting point apparatus and are uncorrected. The ir spectra were taken on a Perkin-Elmer FT-IR 1730 spectrophotometer and the uv spectra on a Shimadzu UV-265 spectrophotometer. The 1H

nmr spectra were measured with a JEOL JNM PMX-60SI spectrometer (60 MHz) with tetramethylsilane used as the internal standard.

2-(3-Tropolonyl)-1-benzopyrylium Perchlorates **4a-d**.

General Procedure.

A 70% perchloric acid (0.2 ml, 3.0 mmoles) was added dropwise to a stirred mixture of 3-acetyltropolone (**1**) (164 mg, 1.0 mmole) and 2-hydroxybenzaldehydes **3a-d** (3.0 mmoles) in ethyl orthoformate (5 ml) at room temperature. After stirring for 20 minutes, a precipitate was collected and recrystallized to give 2-(3-tropolonyl)-1-benzopyrylium perchlorates **4a-d**.

2-(3-Tropolonyl)-1-benzopyrylium Perchlorate (**4a**).

This compound was obtained in a yield of 228 mg (65%), mp 198-200° (from acetic acid); uv (methanol): λ max 217.5 (log ϵ 4.46), 323 (3.95), 370 (3.90), 505 nm (3.99); ir (potassium bromide): ν max 3149 (OH), 1620 (C=O), 1098 cm^{-1} (ClO_4^-); 1H nmr (deuteriodimethyl sulfoxide): δ 9.00-10.41 (11H, m).

Anal. Calcd. for $C_{16}H_{11}ClO_7$: C, 54.79; H, 3.16. Found: C, 54.48; H, 3.20.

6-Methyl-2-(3-tropolonyl)-1-benzopyrylium Perchlorate (**4b**).

This compound was obtained in a yield of 292 mg (80%), mp 208-210° (from acetic acid); ir (potassium bromide): ν max 3202 (OH), 1611 (C=O), 1093 cm^{-1} (ClO_4^-); 1H nmr (deuteriodimethyl sulfoxide): δ 2.30 (3H, s, CH_3), 8.82-10.63 (10H, m).

Anal. Calcd. for $C_{17}H_{13}ClO_7$: C, 55.98; H, 3.59. Found: C, 55.66; H, 3.41.

6-Chloro-2-(3-tropolonyl)-1-benzopyrylium Perchlorate (**4c**).

This compound was obtained in a yield of 219 mg (57%), mp 220-222° (from acetic acid); ir (potassium bromide): ν max 3144 (OH), 1618 (C=O), 1093 cm^{-1} (ClO_4^-); 1H nmr (deuteriodimethyl sulfoxide): δ 8.64-10.72 (10H, m).

Anal. Calcd. for $C_{16}H_{10}Cl_2O_7$: C, 49.89; H, 2.62. Found: C, 49.72; H, 2.41.

2-(3-Tropolonyl)naphtho[2,1-*b*]pyrylium Perchlorate (**4d**).

This compound was obtained in a yield of 240 mg (60%), mp 270-272° (from acetic acid); ir (potassium bromide): ν max 3147 (OH), 1610 (C=O), 1093 cm^{-1} (ClO_4^-); 1H nmr (deuteriodimethyl sulfoxide): δ 8.93-10.64 (13H, m).

Anal. Calcd. for $C_{20}H_{13}ClO_7$: C, 59.94; H, 3.27. Found: C, 59.56; H, 3.04.

2-(7-Methylamino-2-troponyl)-1-benzopyrylium Perchlorates **5a-d**.

General Procedure.

A 70% perchloric acid (0.2 ml, 3.0 mmoles) was added dropwise to a stirred mixture of 2-acetyl-7-methylaminotropone (**2**) (177 mg, 1.0 mmole) and 2-hydroxybenzaldehydes **3a-d** (3.0 mmoles) in ethyl orthoformate (5 ml) at room temperature. The mixture was stirred for 30 minutes at 45° to deposit 2-(7-methylamino-2-troponyl)-1-benzopyrylium perchlorates **5a-d**.

2-(7-Methylamino-2-troponyl)-1-benzopyrylium Perchlorate (**5a**).

This compound was obtained in a yield of 127 mg (35%), mp 190-192° (from acetic acid); ir (potassium bromide): ν max 3279 (NH), 1616 (C=O), 1089 cm^{-1} (ClO_4^-); 1H nmr (deuteriodimethyl sulfoxide): δ 3.05 (3H, s, CH_3), 6.80-7.75 (10H, m).

Anal. Calcd. for $C_{17}H_{14}ClNO_6$: C, 56.13; H, 3.88; N, 3.85. Found: C, 55.86; H, 3.72; N, 3.63.

6-Methyl-2-(7-methylamino-2-troponyl)-1-benzopyrylium Perchlorate (**5b**).

This compound was obtained in a yield of 166 mg (44%), mp 224-226° (from acetic acid); ir (potassium bromide): ν max 3259 (NH), 1618 (C=O), 1094 cm^{-1} (ClO_4^-); 1H nmr (deuterio-dimethyl sulfoxide): δ 2.20 (3H, s, 6- CH_3), 3.03 (N CH_3), 6.80-7.75 (10H, m).

Anal. Calcd. for $C_{18}H_{16}ClNO_6$: C, 57.23; H, 4.27; N, 3.71. Found: C, 57.14; H, 4.05; N, 3.41.

6-Chloro-2-(7-methylamino-2-troponyl)-1-benzopyrylium Perchlorate (**5c**).

This compound was obtained in a yield of 127 mg (32%), mp 185-187° (from acetic acid); ir (potassium bromide): ν max 3258 (NH), 1611 (C=O), 1098 cm^{-1} (ClO_4^-); 1H nmr (deuterio-dimethyl sulfoxide): δ 3.03 (3H, s, CH_3), 6.81-7.57 (10H, m).

Anal. Calcd. for $C_{17}H_{13}Cl_2NO_6$: C, 51.27; H, 3.29; N, 3.52. Found: C, 51.02; H, 3.34; N, 3.45.

2-(7-Methylamino-2-troponyl)naphtho[2,1-*b*]pyrylium Perchlorate (**5d**).

This compound was obtained in a yield of 107 mg (26%), mp 256-258° (from acetic acid); ir (potassium bromide): ν max 3263 (NH), 1612 (C=O), 1084 cm^{-1} (ClO_4^-); 1H nmr (deuterio-dimethyl sulfoxide): δ 3.06 (3H, s, CH_3), 6.78-8.28 (13H, m).

Anal. Calcd. for $C_{21}H_{16}ClNO_6$: C, 60.95; H, 3.90; N, 3.38. Found: C, 60.57; H, 3.83; N, 3.17.

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