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3-Acetyltropolone (**1**) reacted with benzaldehydes in trimethyl orthoformate in the presence of perchloric acid to afford 2-aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates **3a-c** in 25-37% yields. From the filtrates, 3-(3,4-diaryl-3-butenyl)tropolones **4a,b** and 3-(2-methoxycinnamoyl)tropolone (**5**) were also isolated.

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Introduction.

Previously, we reported that 3-acetyltropolone was condensed with benzaldehydes in alkaline condition to afford 3-cinnamoyltropolones, which were converted to 2-aryl-2,3,4,9-tetrahydrocyclohepta[*b*]pyran-4,9-diones by heating in acetic acid containing phosphoric acid and to 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones by selenium dioxide oxidation [1]. When the condensation with benzaldehydes were carried out in boiling trimethyl orthoformate in the presence of perchloric acid, 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones were obtained in one step [2]. Furthermore, the perchloric acid catalyzed reaction with *o*-hydroxybenzaldehydes in triethyl orthoformate gave 2-(3-tropolonyl)-1-benzopyrylium perchlorates [3].

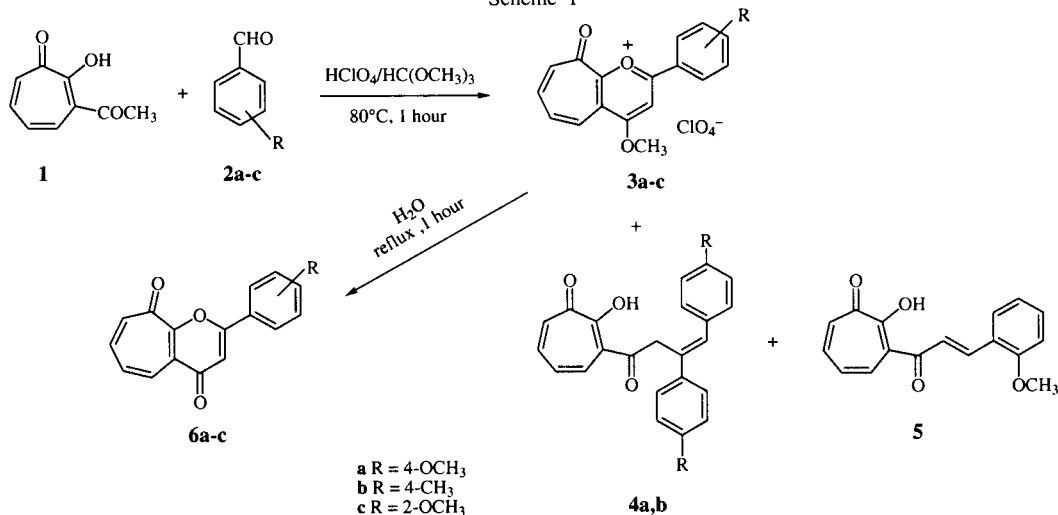
On the other hand, it is known that 2'-hydroxychalcones were treated with perchloric acid in triethyl orthoformate to cyclize to 2-aryl-4-ethoxybenzo[*b*]pyrylium perchlorates [4]. It was also found that the reactions of 2-hydroxyaceto-

phenones with benzaldehydes was carried out in trimethyl orthoformate in the presence of perchloric acid to yield 2-aryl-4-ethoxybenzo[*b*]pyrylium perchlorate [5]. This paper deals with the synthesis of tropone-fused pyrylium salts.

Results and Discussion.

A solution of 3-acetyltropolone (**1**) and three molar equivalents of 4-methoxybenzaldehyde (**2a**) in trimethyl orthoformate (nine molar equivalents) was heated at 80° for 1 hour in the presence of 70% perchloric acid (a half molar equivalent). The precipitate was recrystallized from glacial acetic acid to afford light yellow flakes (mp 206-208°) in 37% yield. Its structure was determined to be 4-methoxy-2-(4-methoxyphenyl)-9-oxocyclohepta[*b*]pyrylium perchlorate (**3a**) on the basis of elemental analysis ($C_{18}H_{15}ClO_8$) and spectral data. The ir spectrum showed absorptions at ν_{\max} 1607 (C=O), 1248 (=O⁺-), and 1085 cm^{-1} (ClO₄⁻). In the ¹H nmr spectrum, two singlet peaks for the methoxyl groups at δ 4.00 (4'-OCH₃) and 4.59

Scheme 1



(4-OCH₃) and a singlet peak for the 3-H proton at δ 7.98 were observed. The filtrate was allowed to stand over a week to give an additional precipitate which was recrystallized from ethanol to yield light yellow needles (mp 179-180°) in 28% yield. Its structure was shown to be 3-[3,4-di(4-methoxyphenyl)-3-butenoyl]tropolone (**4a**) on the basis of elemental analysis (C₂₅H₂₂O₅) and spectral data. In the ir spectrum, two carbonyl absorptions were observed at ν max 1646 (1'-C=O) and 1600 cm⁻¹ (1-C=O). The ¹H nmr spectrum showed two singlet peaks for the methoxyl groups at δ 3.78 and 3.88 and a singlet peak at δ 4.06 for the methylene protons.

In a similar manner, the reactions of 3-acetyltropolone (**1**) with 4-methyl- and 2-methoxybenzaldehyde **2b,c** gave the corresponding 2-aryl-4-methoxy-9-oxocyclohepta[b]pyrylium perchlorates **3b,c**. From the filtrates, 3-[3,4-di(4-methylphenyl)-3-butenoyl]tropolone (**4b**) and 3-(2-methoxycinnamoyl)tropolone (**5**) were isolated, respectively.

EXPERIMENTAL

Measurements.

All melting points were determined with a Yanaco MP JP-3 apparatus and are uncorrected. The ir spectra were taken on a JASCO IRA-1 spectrophotometer. The nmr spectra were recorded with a JEOL JNM-EX 90 spectrometer (90 MHz for ¹H and 22.5 MHz for ¹³C) and partly with a JEOL JNM-PMX60SI (60 MHz for ¹H). The mass spectra were measured on a JEOL JMS-01-SG spectrometer.

Reaction of 3-Acetyltropolone (**1**) with Benzaldehydes **2a-c** in Trimethyl Orthoformate in the Presence of Perchloric Acid.

General Procedure.

To a solution of 3-acetyltropolone (**1**) (328 mg, 2.0 mmoles) and benzaldehyde **2a-c** (6.0 mmoles) in trimethyl orthoformate (2 ml, 18 mmoles) was added 70% perchloric acid (140 mg, 1.0 mmole). This mixture was heated at 80° for 1 hour. After cooling, the precipitate was collected, washed twice with ethyl acetate, and recrystallized from glacial acetic acid to give 2-aryl-4-methoxy-9-oxocyclohepta[b]pyrylium perchlorates **3a-c**. The filtrate was allowed to stand for a week at room temperature to give the precipitate, which was collected, washed twice with ethanol, and recrystallized from ethanol to give 3-(3,4-diaryl-3-butenoyl)tropolones **4a,b** from 4-methoxy- and 4-methylbenzaldehydes **2a,b** and 3-(2-methoxycinnamoyl)tropolone (**5**) from 2-methoxybenzaldehyde (**2c**), respectively.

a) Reaction with 4-Methoxybenzaldehyde (**2a**).

4-Methoxy-2-(4-methoxyphenyl)-9-oxocyclohepta[b]pyrylium Perchlorate (**3a**).

This compound was obtained as light yellow flakes in a yield of 292 mg (37%), mp 206-208°; ir (potassium bromide): ν max 1607 (C=O), 1248 (=O⁺-), 1085 cm⁻¹ (ClO₄⁻); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 4.00 (3H, s, 4'-OCH₃), 4.59 (3H, s, 4-OCH₃), 7.17 (2H, d, J = 9.2 Hz), 7.54-7.74 (3H, m), 7.98 (1H, s, 3-H), 8.29 (1H, d, J = 9.2 Hz), 8.43 (2H, d, J = 9.2 Hz); δ (deuteriotrifluoroacetic acid, 60 MHz)

4.2 (3H, s, 4'-OCH₃), 4.6 (3H 4-OCH₃), 7.2-8.6 (8H, m), 8.7 (1H, s, 3-H).

Anal. Calcd. for C₁₈H₁₅ClO₈: C, 54.76; H, 3.83. Found: C, 54.49; H, 3.78.

3-[3,4-Di(4-methoxyphenyl)-3-butenoyl]tropolone (**4a**).

This compound was obtained as light yellow needles in a yield of 224 mg (28%), mp 179-180°; ir (potassium bromide): ν max 3188 (OH), 1646 (1'-C=O), 1600 cm⁻¹ (1-C=O); ¹H nmr (deuteriochloroform): δ 3.78 (3H, s, OCH₃), 3.88 (3H, s, OCH₃), 4.06 (2H, s, CH₂), 6.81 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.8 Hz), 7.05-7.48 (10H, m); ¹³C nmr (deuteriochloroform): δ 30.9 (CH₂), 55.2 (OCH₃), 55.3 (OCH₃), 114.0 (=C-), 114.1 (=C<), 123.0 (=C-), 127.3 (=C<), 127.7 (=C-), 128.9 (=C-), 130.9 (=C<), 131.8 (=C-), 136.4 (=C-), 136.7 (=C<), 137.0 (=C<), 138.3 (=C-), 146.2 (=C-), 157.9 (=C<), 160.8 (=C<), 169.5 (=C<), 171.2 (=C<), 197.2 (1'-C=O); ms: m/z (%) 402 (M⁺, 86), 281 (100), 121 (41).

Anal. Calcd. for C₂₅H₂₂O₅: C, 74.61; H, 5.51. Found: C, 74.37; H, 5.43.

b) Reaction with 4-Methylbenzaldehyde (**2b**).

4-Methoxy-2-(4-methylphenyl)-9-oxocyclohepta[b]pyrylium Perchlorate (**3b**).

This compound was obtained as yellow needles in a yield of 189 mg (25%), mp 205-207°; ir (potassium bromide): ν max 1598 (C=O), 1223 (=O⁺-), 1085 cm⁻¹ (ClO₄⁻); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.49 (3H, s, CH₃), 4.63 (3H, s, OCH₃), 7.40-7.72 (5H, m), 7.96 (1H, s, 3-H), 8.13 (2H, d, J = 8.1 Hz), 8.30 (1H, d, J = 8.5 Hz); δ (deuteriotrifluoroacetic acid, 60 MHz) 2.6 (3H, s, CH₃), 4.8 (3H, s, OCH₃), 7.6-8.6 (9H, m).

Anal. Calcd. for C₁₈H₁₅ClO₇: C, 57.08; H, 3.99. Found: C, 57.07; H, 4.06.

3-[3,4-Di(4-methylphenyl)-3-butenoyl]tropolone (**4b**).

This compound was obtained as yellow needles in a yield of 111 mg (15%), mp 213-215°; ir (potassium bromide): ν max 3188 (OH), 1648 (1'-C=O), 1600 cm⁻¹ (1-C=O); ¹H nmr (deuteriochloroform): δ 2.31 (6H, s, 2 x CH₃), 4.07 (2H, s, CH₂), 7.04-7.40 (14H, m); ¹³C nmr (deuteriochloroform): δ 21.0 (CH₃), 21.3 (CH₃), 31.5 (CH₂), 123.1 (=C-), 127.7 (=C-), 128.0 (=C-), 129.3 (=C-), 129.4 (=C-), 129.5 (=C<), 129.8 (=C-), 132.0 (=C<), 135.5 (=C<), 136.0 (=C<), 136.5 (=C-), 138.0 (=C<), 138.4 (=C-), 139.9 (=C<), 146.3 (=C-), 169.5 (=C<), 171.4 (=C<), 197.3 (1'-C=O).

Anal. Calcd. for C₂₅H₂₂O₃: C, 81.05; H, 5.99. Found: C, 81.12; H, 5.94.

c) Reaction with 2-Methoxybenzaldehyde (**2c**).

4-Methoxy-2-(2-methoxyphenyl)-9-oxocyclohepta[b]pyrylium Perchlorate (**3c**).

This compound was obtained as yellow needles in a yield of 237 mg (30%), mp 210-212°; ir (potassium bromide): ν max 1612 (C=O), 1224 (=O⁺-), 1085 cm⁻¹ (ClO₄⁻); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 4.12 (3H, s, 2'-OCH₃), 4.20 (1H, d, J = 8.8 Hz), 4.56 (3H, s, 4-OCH₃), 7.34-8.05 (6H, m), 8.40 (1H, d, J = 8.2 Hz), 8.58 (1H, s, 3-H); δ (deuteriotrifluoroacetic acid, 60 MHz) 4.3 (3H, s, 2'-OCH₃), 4.7 (3H, s, 4-OCH₃), 7.2-8.6 (8H, m), 8.8 (1H, s, 3-H).

Anal. Calcd. for C₁₈H₁₅ClO₈: C, 54.76; H, 3.83. Found: C, 54.49; H, 3.80.

3-(2-Methoxycinnamoyl)tropolone (**5**).

This compound was obtained in a yield of 180 mg (32%), mp 126-127° (lit [1] 126-127°).

Hydrolysis of 2-Aryl-4-methoxy-9-oxocyclohepta[b]pyrylium Perchlorates **3a-c**.

General Procedure.

a) A suspended solution of 9-oxocyclohepta[b]pyrylium perchlorate **3a-c** (0.5 mmole) in water (5 ml) was refluxed for 1 hour. The precipitate was collected and recrystallized from glacial acetic acid to give 2-aryl-4,9-dihydrocyclohepta[b]pyran-4,9-diones **6a-c**.

2-(4-Methoxyphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione (**6a**).

This compound was obtained from **3a** in a yield of 133 mg (95%), mp 235-236° (lit [1] 231-233°).

2-(4-Methylphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione (**6b**).

This compound was obtained from **3b** as orange-yellow needles in a yield of 127 mg (96%), mp 202-203°; ir (potassium bromide): ν max 1648 (4-C=O), 1600 cm^{-1} (9-C=O); ^1H nmr (deuteriochloroform): δ 2.40 (3H, s, CH_3), 6.91 (1H, s, 3-H), 7.05-7.33 (5H, m), 7.88 (2H, d, $J = 8.3$ Hz, 3',5'-H), 8.02 (1H, d, $J = 11.0$ Hz, 5-H); ^{13}C nmr (deuteriochloroform): δ 21.4 (CH_3),

108.4 (=C-), 126.3 (=C-), 127.3 (=C<), 129.0 (=C-), 129.7 (=C-), 130.0 (=C-), 137.6 (=C-), 137.8 (=C-), 142.9 (=C<), 164.1 (=C<), 178.5 (C=O), 179.7 (C=O).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_3$: C, 77.26; H, 4.58. Found: C, 77.55; H, 4.61.

2-(2-Methoxyphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione (**6c**).

This compound was obtained from **3c** in a yield of 129 mg (92%), mp 216-217° (lit [1] 216-217°).

b) A solution of **3a** (99 mg, 0.25 mmole) in ethanol (5 ml) was refluxed for 30 minutes in the presence of sodium hydroxide (20 mg, 0.5 mmole) to afford **6a** in 62 mg (88%).

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