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Received June 25, 1998

2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates **1a-c** reacted with hydroxylamine hydrochloride and hydrazine sulfate in the presence of triethylamine to afford 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-oximes **3a-c** and 4-hydrazones **4a-c** in good yields, respectively. On the other hand, the reactions with methylhydrazine and phenylhydrazine gave respectively 1-methyl- and 1-phenyl-substituted 5-aryl-3-(3-tropolonyl)pyrazoles **5a-c** and **6a-c** in excellent yields. Treatment with 4-nitrophenylhydrazine gave 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-(4-nitrophenyl)hydrazones **7a-c** in good yields.

J. Heterocyclic Chem., **35**, 1339 (1998).

Introduction.

In a preceding paper, we reported synthesis of 2-aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates by the reactions of 3-acetyltropolone with benzaldehydes in trimethyl orthoformate in the presence of perchloric acid [1].

In the chemistry of six-membered oxygen heterocycles, there are many reports on the reactions of monocyclic pyrylium salts, while the reactions of bicyclic chromylium and flavylium salts are not necessarily numerous except for a few examples [2,3,4]. It is known that pyrylium salts react readily with a variety of nucleophilic reagents and the reactions provide most important and useful routes to products as well as addition products.

In the present paper, we describe the reactions of 2-aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates **1a-c** with nitrogen nucleophiles such as hydroxylamine, hydrazine, methylhydrazine, and phenylhydrazine.

Results and Discussion.

Reactions of 2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium Perchlorates **1a-c** with Hydroxylamine.

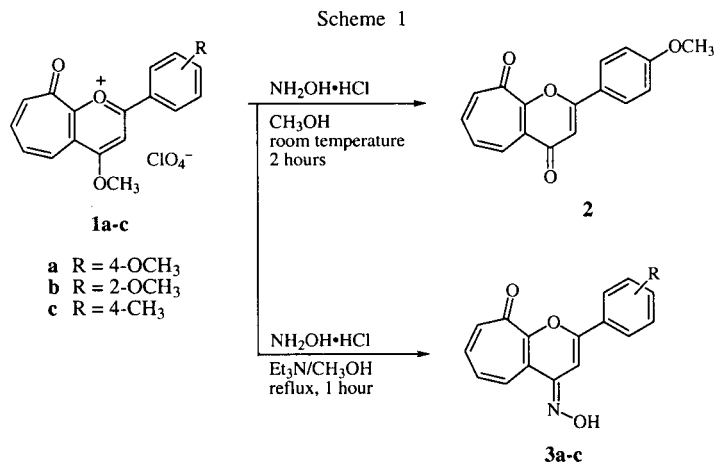
Although the positive charge of the 2-aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates **1a-c** is usually written on the ring oxygen atom, the charge is able to be on the carbon atoms at the 2- and 4-position by resonance. In addition, the pyrylium salts **1a-c** has a methoxyl group at the 4-position as a leaving group. Previously it was reported that 2,4,6-triphenylpyrylium salts reacted with hydroxylamine to yield an acyclic intermediate which cyclized to give an isoxazole [5].

When a mixture of 4-methoxy-2-(4-methoxyphenyl)-9-oxocyclohepta[*b*]pyrylium perchlorate (**1a**) and hydroxylamine hydrochloride in methanol was stirred for 2 hours at room temperature, 2-(4-methoxyphenyl)-4,9-dihydro-

cyclohepta[*b*]pyran-4,9-dione (**2**) was obtained in a quantitative yield. The same reaction at refluxing temperature afforded compound **2** (34%) and its oxime, 2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-oxime (**3a**) as yellow needles (mp 215-216°) in 42% yield. Then, the reaction was carried out at refluxing temperature in the presence of triethylamine to give oxime **3a** (70%). The structure of oxime **3a** was confirmed on the basis of elemental analysis (C₁₇H₁₃NO₄) and spectral data. The ir spectrum showed three typical absorptions at ν 3164 (OH), 1631 (C=N), and 1597 cm⁻¹ (C=O). The ¹H nmr spectrum exhibited a signal at δ 7.51 for the 3-H proton. In a similar manner, pyrylium salts **1b,c** yielded the corresponding 4-oximes **3b,c** in moderate yields.

Reactions of 2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium Perchlorates **1a-c** with Hydrazines.

It was found that 2,4,6-triphenylpyrylium reacted with hydrazine to afford a pyrazole via the ring-opening and



recyclization [5]. On the other hand, the reactions of 4-ethoxychromanyl salts with hydrazine and phenylhydrazine to give 4-arylpyrazoles and chromanone phenylhydrazones, respectively [6]. In the present work, the reactions of 2-aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium perchlorates **1a-c** with hydrazine, methylhydrazine, and phenylhydrazine were carried out.

A solution of the pyrylium salt **1a** and hydrazine sulfate in acetonitrile was refluxed for 1 hour in the presence of triethylamine afforded 2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-hydrazone (**4a**) as red needles (mp >300°) in 93% yield. Its structure was established by elemental analysis (C₁₇H₁₄N₂O₃) and spectral data. In the ir spectrum, three typical absorptions were observed at ν 3348 (NH₂), 1627 (C=N), and 1597 cm⁻¹

(C=O). Since product **4a** is less soluble in organic solvent, the nmr spectrum was measured in deuteriochloroform containing 10% deuteriotrifluoroacetic acid. The 3-H protons were observed at δ 7.24 as a singlet peak. The pyrylium perchlorates **1b,c** also reacted with hydrazine to produce the 4-hydrazones **4b,c** in good yields.

Meanwhile, the reactions of the pyrylium salt **1a** with methylhydrazine gave 5-(4-methoxyphenyl)-1-methyl-3-(3-tropolonyl)pyrazole (**5a**) as orange yellow needles (mp 112-113°) in 87% yield. Its structure was determined on the basis of elemental analysis (C₁₈H₁₆N₂O₃) and spectral data. The ir spectrum showed the two characteristic absorptions at ν 3010 (OH) and 1614 cm⁻¹ (C=O). The NH stretching absorption was not appeared. In the ¹H nmr spectrum, the *N*-CH₃ signal was observed at δ 3.92, while the 4'-H proton in the tropolone ring was observed at lower field (δ 8.57) as a doublet peak (*J* = 9.6 Hz). This is perhaps due to the deshielding effect of the ring current of the pyrazole ring. The pyrylium perchlorates **1b,c** also reacted with methylhydrazine to produce the pyrazoles **5b,c** in high yields.

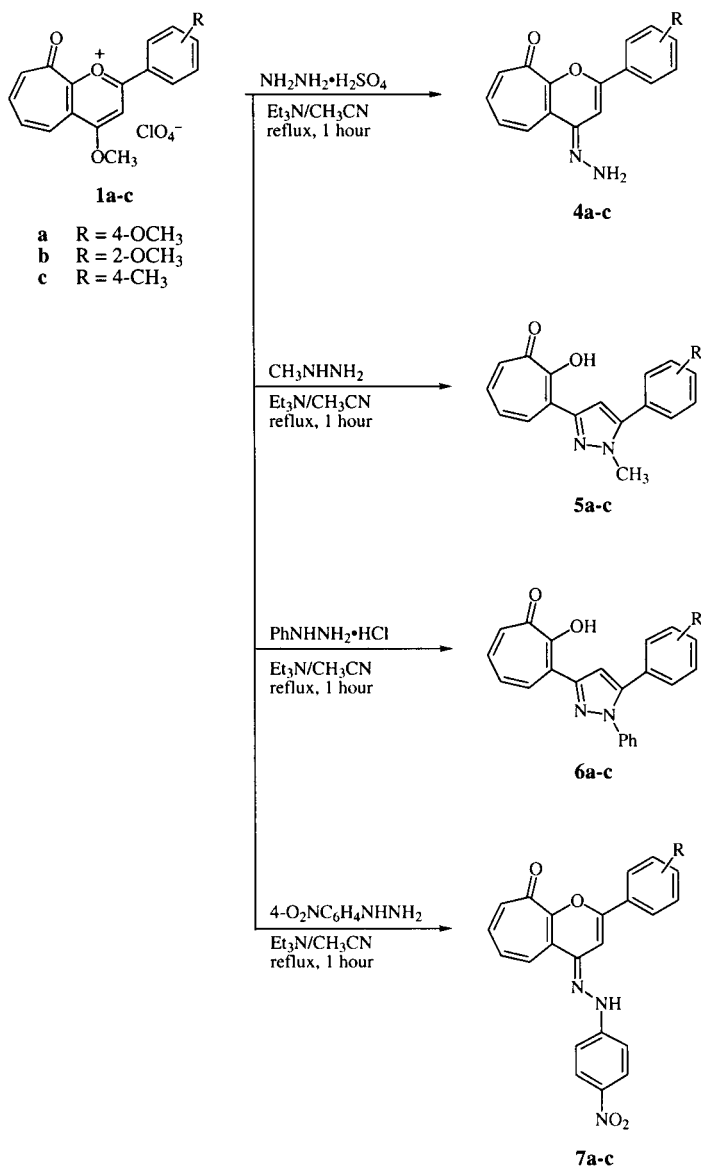
Furthermore, the reaction of the pyrylium salt **1a** with phenylhydrazine was carried out to afford 5-(4-methoxyphenyl)-1-phenyl-3-(3-tropolonyl)pyrazole (**6a**) as pale yellow needles (mp 181-182°) in 94% yield. The structure was established on the basis of elemental analysis (C₂₃H₁₈N₂O₃) and spectral data. The ir spectrum showed the two absorptions at ν 3176 (OH) and 1612 cm⁻¹ (C=O) similar to the 1-methylpyrazole **5a**. In the ¹H nmr spectrum, the 4-H proton in the pyrazole ring was observed at δ 6.88 as a singlet peak. On the other hand, the reaction with 4-nitrophenylhydrazine gave 2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-(4-nitrophenyl)hydrazone (**7a**) as red needles (mp 253-254°) in 96% yield. An elemental analysis (C₂₃H₁₇N₃O₅) and spectral data supported its structure. In the ir spectrum, the three characteristic absorptions were observed at ν 3276 (NH), 1631 (C=N), and 1589 cm⁻¹ (C=O). Since product **7a** is less soluble in an organic solvent, the nmr spectrum was measured in deuteriochloroform containing 10% deuteriotrifluoroacetic acid. The 3-H proton in the pyran-4-one ring was observed at δ 7.92 instead of the 4-H proton (δ 6.88) in the pyrazole ring of the product **6a**. The pyrylium perchlorates **1b,c** also reacted with phenylhydrazine and 4-nitrophenylhydrazine to produce the pyrazoles **6b,c** and the 4-(4-nitrophenyl)hydrazones **7b,c** in excellent yields, 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

Scheme 2



recorded with a JEOL JNM-EX 90 spectrometer (90 MHz for ^1H and 22.5 MHz for ^{13}C).

Reaction of 2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium Perchlorates **1a-c** with Hydroxylamine.

a) A mixture of 4-methoxy-2-(4-methoxyphenyl)-9-oxocyclohepta[*b*]pyrylium perchlorate (**1a**) (99 mg, 0.25 mmole) and hydroxylamine hydrochloride (35 mg, 0.5 mmole) in methanol (2 ml) was stirred for 2 hours at room temperature. The precipitate was collected and recrystallized from glacial acetic acid to give 2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione (**2**) (64 mg, 92%), mp 235-236° (lit [7] 231-233°).

b) A mixed solution of **1a** (99 mg, 0.25 mmole) and hydroxylamine hydrochloride (35 mg, 0.5 mmole) in methanol (2 ml) was refluxed for 1 hour. The precipitate was worked up, as described above to afford **2** (24 mg, 34%). The filtrate was evaporated to dryness and the residue was recrystallized from ethanol to give 2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-oxime (**3a**) (31 mg, 42%), mp 215-216°; ir (potassium bromide): ν max 3164 (OH), 1631 (C=N), 1597 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.94 (3H, s, OCH₃), 7.08 (2H, d, $J = 9.2$ Hz, 2'-, 6'-H), 7.40-7.46 (5H, m), 7.51 (1H, s, 3-H), 8.09 (2H, d, $J = 9.2$ Hz, 3'-, 5'-H); ^{13}C nmr (deuteriodimethyl sulfoxide): δ 55.2 (OCH₃), 93.5 (=C-), 114.2 (=C-), 122.5 (=C<), 123.3 (=C<), 126.9 (=C-), 127.6 (=C-), 130.1 (=C-), 136.8 (=C-), 137.7 (=C-), 144.4 (=C<), 153.3 (=C<), 154.9 (=C<), 161.1 (=C<), 178.2 (C=O).

Anal. Calcd. for C₁₇H₁₃NO₄; C, 69.14; H, 4.44; N, 4.74. Found: C, 68.96; H, 4.51; N, 4.68.

c) To a solution of **1a-c** (0.5 mmole) and hydroxylamine hydrochloride (70 mg, 1.0 mmole) in methanol (5 ml) was added triethylamine (0.2 ml, 1.5 mmoles). After refluxing for 1 hour, the precipitate was collected and recrystallized from ethanol to afford 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-oximes **3a-c**.

2-(4-Methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-Oxime (**3a**).

This compound was obtained in a yield of 103 mg (70%).

2-(2-Methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-Oxime (**3b**).

This compound was obtained as yellow needles in a yield of 100 mg (68%), mp 220-221°; ir (potassium bromide): ν max 3264 (OH), 1624 (C=N), 1567 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.95 (3H, s, OCH₃), 7.03-7.42 (7H, m), 7.52 (1H, s, 3-H), 7.83-8.04 (2H, m); ^{13}C nmr (deuteriodimethyl sulfoxide): δ 55.8 (OCH₃), 100.1 (=C-), 112.1 (=C-), 119.4 (=C<), 120.5 (=C-), 122.3 (=C<), 127.7 (=C-), 128.1 (=C-), 130.0 (=C-), 131.6 (=C-), 136.8 (=C-), 137.7 (=C-), 144.3 (=C<), 150.3 (=C<), 155.1 (=C<), 157.4 (=C<), 178.3 (C=O).

Anal. Calcd. for C₁₇H₁₃NO₄; C, 69.14; H, 4.44; N, 4.74. Found: C, 69.31; H, 4.62; N, 4.95.

2-(4-Methylphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-Oxime (**3c**).

This compound was obtained as yellow needles in a yield of 75 mg (54%), mp 225-226°; ir (potassium bromide): ν max 3216 (OH), 1632 (C=N), 1598 cm^{-1} (C=O); ^1H nmr (deuteriodimethyl sulfoxide): δ 2.35 (3H, s, CH₃), 6.94-7.15 (4H, m), 7.15 (1H, s, 3-H), 7.29 (2H, d, $J = 8.1$ Hz, 3'-, 5'-H), 7.81 (2H, d, $J = 8.1$ Hz, 2'-, 6'-H), 7.88 (1H, s, $J = 11.1$ Hz, 5-H); ^{13}C nmr (deuterio-

dimethyl sulfoxide): δ 20.8 (CH₃), 94.3 (=C-), 122.5 (=C<), 125.1 (=C-), 127.5 (=C-), 128.2 (=C<), 129.3 (=C-), 130.0 (=C-), 136.7 (=C-), 137.7 (=C-), 140.4 (=C<), 144.0 (=C<), 153.3 (=C<), 154.8 (=C<), 154.8 (=C<), 178.1 (C=O).

Anal. Calcd. for C₁₇H₁₃NO₃; C, 73.11; H, 4.69; N, 5.02. Found: C, 73.09; H, 4.69; N, 4.93.

Reaction of 2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium Perchlorates **1a-c** with Hydrazine.

To a solution of **1a-c** (0.5 mmole) and hydrazine sulfate (130 mg, 1.0 mmole) in acetonitrile (5 ml) was added triethylamine (0.2 ml, 1.5 mmoles). After refluxing for 1 hour, the precipitate was collected and recrystallized from glacial acetic acid to afford 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione 4-hydrazones **4a-c**.

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

This compound was obtained as red needles in a yield of 137 mg (93%), mp >300°; ir: ν max 3348 (NH₂), 1627 (C=N), 1597 cm^{-1} (C=O); ^1H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 3.91 (3H, s, OCH₃), 7.05 (2H, d, $J = 9.0$ Hz, 3'-, 5'-H), 7.24 (1H, s, 3-H), 7.26-7.75 (3H, m), 7.76 (2H, d, $J = 9.0$ Hz, 2'-, 6'-H), 8.30 (1H, d, $J = 9.2$ Hz, 8-H).

Anal. Calcd. for C₁₇H₁₄N₂O₃; C, 69.37; H, 4.79; N, 9.52. Found: C, 69.37; H, 4.91; N, 9.52.

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

This compound was obtained as red needles in a yield of 85 mg (58%), mp >300°; ν max 3350 (NH₂), 1627 (C=N), 1598 cm^{-1} (C=O); ^1H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 3.98 (3H, s, OCH₃), 6.89-7.88 (7H, m), 7.26 (1H, s, 3-H), 8.07 (1H, d, $J = 11.3$ Hz, 5-H).

Anal. Calcd. for C₁₇H₁₄N₂O₃; C, 69.37; H, 4.79; N, 9.52. Found: C, 69.46; H, 4.82; N, 9.61.

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

This compound was obtained as red needles in a yield of 107 mg (77%), mp >300°; ir: ν max 3340 (NH₂), 1625 (C=N), 1592 cm^{-1} (C=O); ^1H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.43 (3H, s, CH₃), 7.32 (2H, d, $J = 9.8$ Hz, 3'-, 5'-H), 7.51-7.79 (4H, m), 7.95 (1H, d, $J = 8.4$ Hz, 8-H), 8.29 (2H, d, $J = 9.8$ Hz, 2'-, 6'-H).

Anal. Calcd. for C₁₇H₁₄N₂O₂; C, 73.36; H, 5.07; N, 10.07. Found: C, 73.78; H, 5.05; N, 9.98.

Reaction of 2-Aryl-4-methoxy-9-oxocyclohepta[*b*]pyrylium Perchlorates **1a-c** with Methylhydrazine.

To a solution of **1a-c** (0.5 mmole) and methylhydrazine (46 mg, 1.0 mmole) in acetonitrile (5 ml) was added triethylamine (0.2 ml, 1.5 mmoles). The mixture was heated for 1 hour under refluxing. After removal of the solvent, the residue was recrystallized from ethanol to give 5-aryl-1-methyl-3-(3-tropolonyl)pyrazoles **5a-c**.

5-(4-Methoxyphenyl)-1-methyl-3-(3-tropolonyl)pyrazole (**5a**).

This compound was obtained as orange yellow needles in a yield of 134 mg (87%), mp 112-113°; ir (potassium bromide): ν max 3010 (OH), 1613 cm^{-1} (C=O); ^1H nmr (deuteriochloroform): δ 3.83 (3H, s, OCH₃), 3.92 (3H, s, NCH₃), 6.97

(2H, d, J = 8.9 Hz, 3"-, 5"-H), 7.09-7.38 (4H, m), 7.40 (2H, d, J = 8.9 Hz, 2"-, 6"-H), 8.57 (1H, d, J = 9.6 Hz, 4-H), 9.40 (1H, br, OH); ¹³C nmr (deuteriochloroform): δ 37.5 (NCH₃), 55.1 (OCH₃), 108.9 (=C-), 113.9 (=C-), 121.9 (=C-), 122.6 (=C<), 127.0 (=C-), 129.4 (=C<), 129.9 (=C-), 136.9 (=C-), 137.7 (=C-), 144.2 (=C<), 147.4 (=C<), 159.7 (=C<), 169.6 (1'- or 2'-C), 170.8 (1'- or 2'-C).

Anal. Calcd. for C₁₈H₁₆N₂O₃: C, 70.11; H, 5.23; N, 9.09. Found: C, 70.09; H, 5.32; N, 9.26.

5-(2-Methoxyphenyl)-1-methyl-3-(3-tropolonyl)pyrazole (**5b**).

This compound was obtained as orange yellow needles in a yield of 120 mg (78%), mp 127-128°; ir (potassium bromide): ν max 3148 (OH), 1619 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform): δ 3.79 (3H, s, OCH₃), 3.81 (3H, s, NCH₃), 6.94-7.37 (9H, m), 8.61 (1H, d, J = 9.6 Hz, 4'-H); ¹³C nmr (deuteriochloroform): δ 37.4 (NCH₃), 55.3 (OCH₃), 110.1 (=C-), 110.9 (=C-), 119.3 (=C-), 120.5 (=C-), 122.2 (=C<), 127.0 (=C-), 129.3 (=C<), 130.5 (=C-), 131.6 (=C-), 136.8 (=C-), 137.6 (=C-), 141.2 (=C<), 147.2 (=C<), 156.8 (=C<), 169.3 (1'- or 2'-C), 171.0 (1'- or 2'-C).

Anal. Calcd. for C₁₈H₁₆N₂O₃: C, 70.11; H, 5.23; N, 9.09. Found: C, 70.37; H, 5.27; N, 8.87.

1-Methyl-5-(4-methylphenyl)-3-(3-tropolonyl)pyrazole (**5c**).

This compound was obtained as orange yellow needles in a yield of 133 mg (91%), mp 142-143°; ir (potassium bromide): ν max 3200 (OH), 1605 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform): δ 2.38 (3H, s, CH₃), 3.92 (3H, s, NCH₃), 7.07-7.37 (9H, m), 8.57 (1H, d, J = 9.5 Hz, 4'-H); ¹³C nmr (deuteriochloroform): δ 21.1 (4"-CH₃), 37.6 (NCH₃), 109.0 (=C-), 121.9 (=C-), 127.0 (=C-), 127.3 (=C<), 128.4 (=C-), 129.2 (=C-), 129.4 (=C<), 136.8 (=C-), 137.6 (=C-), 138.3 (=C<), 144.3 (=C<), 147.4 (=C<), 169.6 (1'- or 2'-C), 170.7 (1'- or 2'-C).

Anal. Calcd. for C₁₈H₁₆N₂O₂: C, 73.95; H, 5.52; N, 9.59. Found: C, 74.14; H, 5.55; N, 9.60.

Reaction of 2-Aryl-4-methoxy-9-oxocyclohepta[b]pyrylium Perchlorates **1a-c** with Phenylhydrazines.

a) To a solution of **1a-c** (0.5 mmole) and phenylhydrazine hydrochloride (72 mg, 0.5 mmole) in acetonitrile (5 ml) was added triethylamine (0.2 ml, 1.5 mmoles). The mixture was heated for 1 hour under refluxing. After removal of the solvent, the residue was recrystallized from ethanol to give 5-aryl-1-phenyl-3-(3-tropolonyl)pyrazoles **6a-c**.

5-(4-Methoxyphenyl)-1-phenyl-3-(3-tropolonyl)pyrazole (**6a**).

This compound was obtained as light yellow needles in a yield of 174 mg (94%), mp 181-182°; ir (potassium bromide): ν max 3176 (OH), 1612 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform): δ 3.85 (3H, s, OCH₃), 6.88 (1H, s, 4-H), 6.99 (2H, d, J = 8.9 Hz, 3"-, 5"-H), 7.25-7.63 (10H, m), 7.75 (2H, d, J = 8.9 Hz, 2"-, 6"-H); ¹³C nmr (deuteriochloroform): δ 55.3 (OCH₃), 106.6 (=C-), 114.6 (=C-), 121.5 (=C<), 122.6 (=C-), 125.0 (=C-), 126.7 (=C<), 127.6 (=C-), 128.1 (=C-), 129.3 (=C-), 129.6 (=C-), 136.8 (=C<), 139.8 (=C-), 141.0 (=C-), 143.7 (=C<), 151.0 (=C<), 161.0 (=C<), 170.2 (1'- or 2'-C), 170.5 (1'- or 2'-C).

Anal. Calcd. for C₂₃H₁₈N₂O₃: C, 74.58; H, 4.90; N, 7.56. Found: C, 74.54; H, 4.71; N, 7.36.

5-(2-Methoxyphenyl)-1-phenyl-3-(3-tropolonyl)pyrazole (**6b**).

This compound was obtained as light yellow needles in a yield of 163 mg (88%), mp 169-170°; ir (potassium bromide): ν max

3185 (OH), 1610 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform): δ 3.89 (3H, s, OCH₃), 6.91-7.60 (14H, m), 8.12 (1H, d, J = 7.5 Hz); ¹³C nmr (deuteriochloroform): δ 55.3 (OCH₃), 111.1 (=C-), 111.2 (=C<), 120.7 (=C-), 121.6 (=C<), 121.8 (=C-), 123.6 (=C-), 126.8 (=C-), 127.1 (=C-), 128.4 (=C<), 128.7 (=C-), 128.8 (=C-), 129.0 (=C-), 137.8 (=C-), 140.4 (=C-), 148.8 (=C<), 156.8 (=C<), 170.1 (1'- or 2'-C), 170.4 (1'- or 2'-C).

Anal. Calcd. for C₂₃H₁₈N₂O₃: C, 74.58; H, 4.90; N, 7.56. Found: C, 74.44; H, 5.03; N, 7.42.

5-(4-Methylphenyl)-1-phenyl-3-(3-tropolonyl)pyrazole (**6c**).

This compound was obtained as light yellow needles in a yield of 161 mg (91%), mp 160-162°; ir (potassium bromide): ν max 3165 (OH), 1697 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform): δ 2.35 (3H, s, CH₃), 6.84 (1H, s, 4-H), 7.15-7.52 (13H, m), 7.79 (1H, d, J = 8.1 Hz); ¹³C nmr (deuteriochloroform): δ 21.1 (CH₃), 106.7 (=C-), 121.6 (=C-), 123.6 (=C-), 125.6 (=C-), 126.7 (=C-), 127.2 (=C-), 128.3 (=C<), 128.7 (=C-), 129.1 (=C-), 129.9 (=C<), 137.6 (=C<), 137.8 (=C-), 140.3 (=C-), 140.4 (=C<), 141.3 (=C<), 151.9 (=C<), 169.8 (1'- or 2'-C), 170.6 (1'- or 2'-C).

Anal. Calcd. for C₂₃H₁₈N₂O₂: C, 77.95; H, 5.12; N, 7.91. Found: C, 77.66; H, 4.99; N, 7.71.

b) To a solution of **1a-c** (0.5 mmole) and 4-nitrophenylhydrazine (72 mg, 0.5 mmole) in acetonitrile (5 ml) was added triethylamine (0.2 ml, 1.5 mmoles). After refluxing for 1 hour, the precipitate was collected and recrystallized from glacial acetic acid to afford 2-aryl-4,9-dihydrocyclohepta[b]pyran-4,9-dione 4-(4-nitrophenyl)hydrazones **7a-c**.

2-(4-Methoxyphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione 4-(4-Nitrophenyl)hydrazone (**7a**).

This compound was obtained as red needles in a yield of 199 mg (96%), mp 253-254°; ir (potassium bromide): ν max 3276 (NH), 1631 (C=N), 1589 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 3.97 (3H, s, OCH₃), 6.96 (2H, d, J = 9.2 Hz, 3'-, 5'-H), 7.13 (2H, d, J = 9.2 Hz, 2'-, 6'-H), 7.63-7.74 (4H, m), 7.92 (1H, s, 3-H), 8.19 (2H, d, J = 9.2 Hz, 2"-, 6"-H), 8.21 (2H, d, J = 9.2 Hz, 3"-, 5"-H).

Anal. Calcd. for C₂₃H₁₇N₃O₅: C, 66.50; H, 4.13; N, 10.12. Found: C, 66.35; H, 4.18; N, 10.31.

2-(2-Methoxyphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione 4-(4-Nitrophenyl)hydrazone (**7b**).

This compound was obtained as red needles in a yield of 129 mg (62%), mp 240-241°; ir (potassium bromide): ν max 3185 (NH), 1618 (C=N), 1594 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 3.85 (3H, s, OCH₃), 6.96 (2H, d, J = 9.8 Hz), 7.09-7.73 (6H, m), 7.28 (1H, s, 3-H), 8.19 (1H, d, J = 9.1 Hz), 8.28 (1H, d, J = 8.9 Hz), 8.54 (2H, d, J = 8.9 Hz, 3"-, 5"-H).

Anal. Calcd. for C₂₃H₁₇N₃O₅: C, 66.50; H, 4.13; N, 10.12. Found: C, 66.52; H, 4.11; N, 9.93.

2-(4-Methylphenyl)-4,9-dihydrocyclohepta[b]pyran-4,9-dione 4-(4-Nitrophenyl)hydrazone (**7c**).

This compound was obtained as red needles in a yield of 188 mg (94%), mp 217-218°; ir (potassium bromide): ν max 3420 (NH), 1631 (C=N), 1590 cm⁻¹ (C=O); ¹H nmr (deuteriochloroform + deuteriotrifluoroacetic acid): δ 2.50 (3H, s, CH₃), 6.98 (2H, d, J = 9.1 Hz, 3'-, 5'-H), 7.03 (1H, s, 3-H), 7.39-7.72 (7H, m), 7.92 (1H, d, J = 9.9 Hz), 8.18 (2H, d, J = 9.1 Hz, 3"-, 5"-H).

Anal. Calcd. for $C_{23}H_{17}N_3O_4$: C, 69.16; H, 4.29; N, 10.52.
Found: C, 69.35; H, 4.29; N, 20.42.

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