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Received December 5, 1990

3-(2-Bromoacetyl)tropolone (**1**) reacted with benzaldehydes **2a-g** in the pressence of alkali at low temperature to give 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-g** in good yields.

J. Heterocyclic Chem., **28**, 817 (1991).

Previously, we reported the preparation of 2-aryl-2,3,4,-9-tetrahydro- and 4,9-dihydrocyclohepta[*b*]pyran-4,9-diones [1] and 2-arylidene-3,8-dihydrocyclohepta[*b*]furan-3,8-diones [2,3] by cyclization of 3-cinnamoyltropolones. The latter compounds were also obtained by the reaction of 3-acetyltropolone with benzaldehydes in the presence of ethyl orthoformate and perchloric acid [4].

On the other hand, oxidation of 2'-hydroxychalcones with alkaline hydrogen peroxide is well-known as Algar-Flynn-Oyamada reaction [5,6]. Depending on the substitution of the chalcone and the reaction conditions, this reaction gives flavonols or aurones. However, the oxidation of 3-cinnamoyltropolones gave exclusively 2-arylidene-3,8-dihydrocyclohepta[*b*]furan-3,8-diones and did not give flavonol-like compounds, 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones [2].

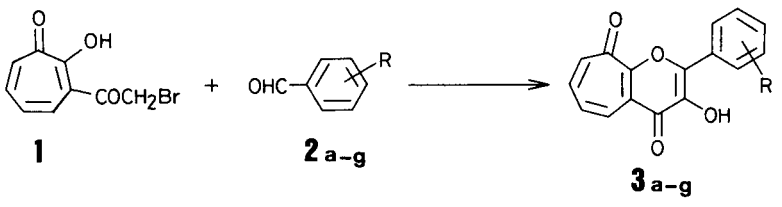
Recently, we found that a mixture of 3-(2-bromoacetyl)-tropolone and benzaldehydes in methanol was refluxed to give 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones [7]. Now, this reaction was carried out in the presence of alkali at low temperature to afford 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones as a series of new compounds. This paper deals with these results.

A sodium hydroxide solution (3.5 molar equivalents) was added dropwise to an ice-cooled mixture of 3-(2-bromoacetyl)tropolone (**1**) and 4-methoxybenzaldehyde (**2a**) in methanol. When this mixture was stirred at the same temperature, the solution deposited 3-hydroxy-2-(4-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione (**3a**) as yellow crystals in good yield (94%). Its structure was confirmed by the elemental analysis ($C_{17}H_{12}O_5$) and spectral data. In the ir spectrum, typical three absorption bands are observed at 3401, 1694, and 1638 cm^{-1} for the hydroxyl group, pyran-carbonyl group, and tropone-carbonyl group, respectively. The ^1H nmr spectrum shows a signal for the methoxyl group at δ 3.90.

The reactions with 3,4-dimethoxy- **2b**, 4-hydroxy-3-methoxy- **2c** , 2-hydroxy- **2d**, 2-hydroxy-4-methyl- **2e**, 3,4-methylenedioxy- **2f**, and 4-dimethylaminobenzaldehyde (**2g**) gave also the corresponding 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3b-g**, respectively, in good yields (82-91%) except for **3c** (31%) and **3g** (45%).

It was found that the reaction of 3-(2-bromoacetyl)tropolone (**1**) with benzaldehydes gave 2-arylidene-3,8-dihydrocyclohepta[*b*]furan-3,8-diones in the absence of alkali at high temperature [7] and, in this work, gave 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones in the presence of alkali at low temperature. These results are similar to those of the reactions of 2'-hydroxy-2-chloroacetophenone with benzaldehydes [8].

Scheme 1



1 **2 a-g** **3 a-g**

a R = 4-OCH_3
b R = 3,4-$(OCH_3)_2$
c R = 3-OCH_3-4-OH
d R = 2-OH
e R = 2-OH-4-CH_3
f R = 3,4-(OCH_2O)
g R = 4-$N(CH_3)_2$

EXPERIMENTAL

Measurements.

The melting points were uncorrected. The ir spectra were taken on a Perkin-Elmer FT-IR 1730 spectrophotometer. The uv spectra were obtained on a Shimadzu UV-265 spectrophotometer. The ^{1}H nmr spectra were measured with a Bruker AC-80 spectrometer.

2-Aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-g**.

General Procedure.

A solution of sodium hydroxide (140 mg, 3.5 mmoles) in water (5 ml) was stepwise added to a stirred mixture of 3-(2-bromoacetyl)tropolone (**1**) (243 mg, 1.0 mmole) and benzaldehydes, **2a-g**, (2.0 mmoles) in methanol (10 ml) at ice-cooled temperature. After stirring for 3 hours a precipitate was collected and recrystallized to give 2-aryl-3-hydroxy-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-g**.

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

This compound was obtained as yellow needles in a yield of 280 mg (94%); mp 204-205° (from methanol); ir (potassium bromide): ν max 3401 (OH), 1694 (C=O), 1638 cm^{-1} (C=O); uv (methanol): λ max 229 (log ϵ 3.19), 288 nm (3.48); ^{1}H nmr (deuteriochloroform): δ 3.90 (3H, s, OCH_3), 6.65-8.4 (8H, m).

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08. Found: C, 68.76; H, 4.27.

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

This compound was obtained as yellow needles in a yield of 290 mg (89%), mp 271-273° (from methanol); ir (potassium bromide): ν max 3436 (OH), 1687 (C=O), 1637 cm^{-1} (C=O); uv (methanol): λ max 227 (log ϵ 3.48), 281 nm (3.80); ^{1}H nmr (deuteriochloroform): δ 3.92 (6H, s, OCH_3 x 2), 6.8-8.1 (7H, m).

Anal. Calcd. for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32. Found: C, 66.29; H, 4.43.

3-Hydroxy-2-(4-hydroxy-3-methoxyphenyl)-4,9-dihydrocyclohepta-[*b*]pyran-4,9-dione (**3c**).

This compound was obtained as yellow needles in a yield of 95 mg (31%), mp 189-190° (from ethyl acetate); ir (potassium bromide): ν max 3375 (OH), 1686 (C=O), 1636 cm^{-1} (C=O); uv (methanol): λ max 230 (log ϵ 3.43), 294 nm (3.61); ^{1}H nmr (deuteriochloroform): δ 3.90 (3H, s, OCH_3), 6.7-8.2 (7H, m).

Anal. Calcd. for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87. Found: C, 65.08; H, 3.85.

3-Hydroxy-2-(2-hydroxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione (**3d**).

This compound was obtained as orange needles in a yield of 240 mg (85%), mp 277-278° (from methanol); ir (potassium bromide): ν max 3463 (OH), 3393 (OH), 1685 (C=O), 1632 cm^{-1} (C=O); uv (methanol): λ max 228 (log ϵ 2.62), 283 nm (3.39); ^{1}H nmr (deuteriochloroform):δ 6.85-7.9 (m).

Anal. Calcd. for $C_{16}H_{10}O_5$: C, 68.08; H, 3.57. Found: C, 68.21; H, 3.40.

3-Hydroxy-2-(2-hydroxy-4-methylphenyl)-4,9-dihydrocyclohepta-[*b*]pyran-4,9-dione (**3e**).

This compound was obtained as reddish orange needles in a yield of 243 mg (82%), mp 335-337° (from ethyl acetate); ir (potassium bromide): ν max 3397 (OH), 1697 (C=O), 1639 cm^{-1} (C=O); uv (methanol): λ max 229 (log ϵ 2.34), 287 nm (3.16); ^{1}H nmr (deuteriochloroform): δ 2.35 (3H, s, CH_3), 6.8-8.0 (7H, m).

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08. Found: C, 68.67; H, 4.02.

3-Hydroxy-2-(3,4-methylenedioxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione (**3f**).

This compound was obtained as yellow needles in a yield of 282 mg (91%), mp 224-225° (from methanol); ir (potassium bromide): ν max 3420 (OH), 1693 (C=O), 1641 cm^{-1} (C=O); uv (methanol): λ max 225 (log ϵ 4.06), 289 nm (4.28); ^{1}H nmr (deuteriochloroform): δ 6.10 (2H, s, CH_2), 6.6-8.1 (7H, m).

Anal. Calcd. for $C_{17}H_{10}O_6$: C, 65.88; H, 3.25. Found: C, 65.84; H, 3.35.

3-Hydroxy-2-(4-dimethylaminophenyl)-4,9-dihydrocyclohepta[*b*]-pyran-4,9-dione (**3g**).

This compound was obtained as deep purple needles in a yield of 440 mg (45%), mp 237-239° (from methanol-water); ir (potassium bromide): ν max 3421 (OH), 1685 (C=O), 1613 cm^{-1} (C=O); uv (methanol): λ max 229 (log ϵ 3.54), 306 nm (3.88); ^{1}H nmr (deuteriochloroform): δ 2.85 [6H, s, $N(CH_3)_2$], 6.1-7.95 (8H, m).

Anal. Calcd. for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.69; H, 4.66; N, 4.40.

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