

A New and Simple Synthesis of 2-Aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones

Dao-Lin Wang and Zhong-Tian Jin*

Department of Chemistry, Yanbian University,
Yanji, Jilin Province, People's Republic of China

Kimiaki Imafuku*

Department of Chemistry, Faculty of Science, Kumamoto University,
Kurokami, Kumamoto 860, Japan

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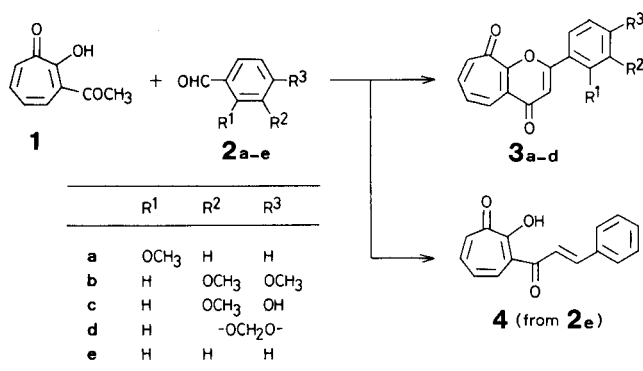
3-Acetyltropolone (**1**) reacted with 2-methoxybenzaldehyde (**2a**) in the presence of ethyl orthoformate and perchloric acid to afford 2-(2-methoxyphenyl)-4,9-dihydrocyclohepta[*b*]pyran-4,9-dione (**3a**). The reactions with 3,4-dimethoxybenzaldehyde (**2b**), vanillin (**2c**), and piperonal (**2d**) gave respectively the corresponding products **3b-d**. The reaction with benzaldehyde (**2e**) gave uncyclized 3-cinnamoyltropolone (**4**).

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Previously, we reported that flavone-like heterocycle-fused troponoid compounds, 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones were obtained by oxidative cyclization of 3-cinnamoyltropolones with selenium dioxide [1,2] and with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [3]. The reaction of 3-cinnamoyltropolone with bromine also gave 5,7-dibrominated cyclized product [4]. On the other hand, it was found that 2-hydroxyacetophenones were treated with benzaldehydes in the presence of orthoformate and perchloric acid to afford flavones at one-step [5].

A mixture of 3-acetyltropolone (**1**) and each of benzaldehydes **2a-d** in ethyl orthoformate was refluxed for 10 minutes in the presence of 70% perchloric acid to give 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-d**. The products **3a** was obtained in 20% yield and the products **3b-d** in 64-78% yields. The former and the latter have respectively one and two oxygen-substituents in the aldehyde. However, the reaction with unsubstituted benzaldehyde (**2e**) gave only 3-cinnamoyltropolone (**4**). In a similar manner, the reactions with *p*-nitro- and *p*-dimethylamino-benzaldehyde gave no isolated product.

Scheme 1



From the results, the reaction mechanism is considered as follows, according to Dorofeenko [5]. The aldehydes

reacted with orthoester in acidic condition to form benzylic carbocations *via* acetals. The carbocations reacted with the acetyl group of the tropolone **1** and cyclized to give 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-d**. In this process, the methoxy and/or hydroxy group stabilize the carbocation but the nitro group destabilizes. The dimethylamino group was protonated to form ammonium ion and destabilized the carbocation as electron-withdrawing group.

Thus, this reaction provides a convenient one-step process to 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones by using alkoxy- and/or hydroxy-substituted benzaldehydes.

EXPERIMENTAL

Measurements.

The melting points are uncorrected. The ir and uv spectra were taken on a Tiansin WFD-7G spectrophotometer and a Shimadzu UV-650 spectrophotometer, respectively. The ¹H nmr spectra were measured with a JEOL JNM-FX100 spectrometer (100 MHz).

Reactions of 3-Acetyltropolone (**1**) with Benzaldehydes **2a-e**.

To a mixture of 3-acetyltropolone (**1**) (328 mg, 2.0 mmoles) and benzaldehydes **2a-e** (6.0 mmoles) in ethyl orthoformate (3.0 ml) was added 70% perchloric acid (0.2 ml). This mixture was refluxed for 10 minutes. After cooling, the precipitate was collected, washed twice with ethyl acetate, and recrystallized from glacial acetic acid to give 2-aryl-4,9-dihydrocyclohepta[*b*]pyran-4,9-diones **3a-d** (by using benzaldehydes **2a-d**) or 3-cinnamoyltropolone **4** (by using benzaldehyde **2e**).

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

This compound was obtained from the reaction with 2-methoxybenzaldehyde (**2a**) as pale yellow needles in a yield of 110 mg (20%), mp 216-217° (lit [1], mp 218-220°).

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

This compound was obtained from the reaction with 3,4-di-

methoxybenzaldehyde (**2b**) as pale yellow needles in a yield of 397 mg (64%), mp 264-265°; ir (potassium bromide): ν max 1634 (C=O), 1591 cm^{-1} (C=O); uv (methanol): λ max 234 (log ϵ 4.14), 270 (3.98), 337 nm (4.20); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.90 (6H, s, CH_3 x 2), 7.05-7.9 (7H, m), 7.20 (1H, s, H-3).

Anal. Calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_5$: C, 69.67; H, 4.55. Found: C, 70.01; H, 4.33.

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

This compound was obtained from the reaction with vanillin (**2c**) as pale yellow needles in a yield of 462 mg (78%), mp 286-287°; ir (potassium bromide): ν max 3234 (OH), 1642 (C=O), 1603 cm^{-1} (C=O); uv (methanol): λ max 268 (log ϵ 3.98), 334 nm (4.02); ^1H nmr (deuteriodimethyl sulfoxide): δ 3.89 (3H, s, OCH_3), 7.10 (1H, s, H-3), 7.03-7.9 (7H, m).

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_5$: C, 68.91; H, 4.08. Found: C, 69.17; H, 4.10.

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

This compound was obtained from the reaction with piperonal (**2d**) as pale yellow needles in a yield of 435 mg (74%), mp

278-279°; ir (potassium bromide): ν max 1641 (C=O), 1596 cm^{-1} (C=O); uv (methanol): λ max 246 (log ϵ 4.26), 267 (4.00), 338 nm (4.30); ^1H nmr (deuteriodimethyl sulfoxide): δ 6.11 (2H, s, CH_2), 7.05-7.9 (7H, m), 7.09 (1H, s, H-3).

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{O}_5$: C, 69.29; H, 3.23. Found: C, 68.99; H, 2.98.

3-Cinnamoyltropolone (**4**).

This compound was obtained from the reaction with benzaldehyde (**2e**) as yellow needles in a yield of 485 mg (95%), mp 145-146° (lit [1], mp 144-145°).

REFERENCES AND NOTES

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