

# A Convenient Synthesis of 2-Arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones

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3-(2-Bromoacetyl)tropolone (**1**) reacted with several benzaldehydes **2a-e** to afford 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones **3a-e** in very good yields.

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3-Acetyltropolone has similar structure and properties to 2-hydroxyacetophenone and reacted with benzaldehydes to give 3-cinnamoyltropolones [1]. These 3-cinnamoyltropolones were oxidized with alkaline hydrogen peroxide [2], manganese(III) and lead(IV) acetate [3], or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [4] to afford 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones. However, their yields were not good (yields: 17-40% with H<sub>2</sub>O<sub>2</sub>/OH<sup>-</sup>, trace-12% with M(OAc)<sub>n</sub>, and 39-53% with DDQ). On the other hand, it was reported that the treatment of 2-chloro-2'-hydroxyacetophenone with benzaldehydes gave aurones (2-arylidene coumaran-2-ones) in one step [5]. This reaction was applied to synthesis of 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones. Thus, the reactions of 3-(2-bromoacetyl)tropolone [6], prepared from 3-acetyltropolone, with several benzaldehydes were carried out.

Similarly, the reactions with 4-methoxy-, 3,4-dimethoxy-, 3,4-methylenedioxy-, and 4-dimethylaminobenzaldehyde gave the corresponding 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones (**3b-e**) in 80-85% yields. Compound **3e** is a new compound. Its structure was confirmed by elemental analysis and spectral data. All the yields were improved in comparison with those of oxidation of 3-cinnamoyltropolones. It is found that this method was very simple and effective for synthesis of 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones.

## EXPERIMENTAL

### Measurements.

The melting points are 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 <sup>1</sup>H NMR spectra were measured with a Bruker AC-80 spectrometer.

### 2-Arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-dione **8a-e**.

#### General Procedure.

A mixed solution of 3-(2-bromoacetyl)tropolone (**1**) (243 mg, 1.0 mmole) and the benzaldehydes **2a-e** (2.0 mmoles) in methanol (5 ml) was heated for 2 hours on a water bath. After cooling, the resulting reddish precipitate was collected and recrystallized from ethanol to give 2-arylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-diones **3a-e**.

### 2-Benzylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-dione (**3a**).

This compound was obtained in a yield of 220 mg (89%), mp 200-202° (lit [2], 201-203°).

### 2-(4-Methoxybenzylidene)-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-dione (**3b**).

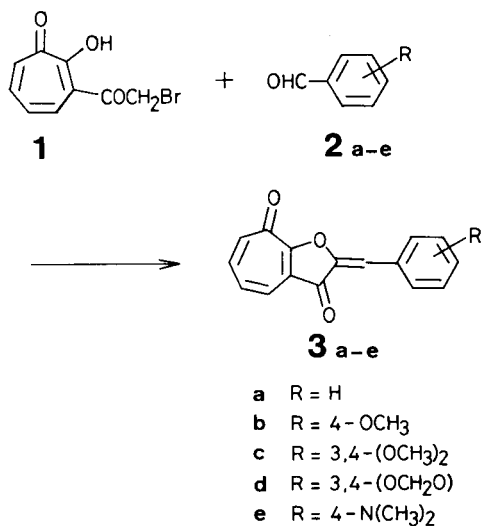
This compound was obtained in a yield of 225 mg (80%), mp 225-226° (lit [2], 227-228°).

### 2-(3,4-Dimethoxybenzylidene)-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-dione (**3c**).

This compound was obtained in a yield of 263 mg (85%), mp 285-286° (lit [2], 285-286°).

### 2-(3,4-Methylenedioxybenzylidene)-3,8-dihydro-2*H*-cyclohepta[*b*]-

Scheme 1



When a solution of 3-(2-bromoacetyl)tropolone (**1**) and 2 equivalents of benzaldehyde (**2a**) was heated for 2 hours on a water bath, 2-benzylidene-3,8-dihydro-2*H*-cyclohepta[*b*]furan-3,8-dione (**3a**) was isolated in a very good yield (89%). The product was identified by comparison with an

furan-3,8-dione (**3d**).

This compound was obtained in a yield of 245 mg (83%), mp 278-279° (lit [2] 279.5-280°).

2-(4-Dimethylaminobenzylidene)-3,8-dihydro-2H-cyclohepta[b]furan-3,8-dione (**3e**).

This compound was obtained as purple red needles in a yield of 238 mg (81%), mp 253-255°; ir (potassium bromide):  $\nu$  max 1718 (C=O), 1638 (C=O), 1597  $\text{cm}^{-1}$  (C=C); uv (methanol):  $\lambda$  max 224 (log  $\epsilon$  4.42), 265 (4.14), 307 (4.01), 535 nm (4.30);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  3.00 (6H, s,  $\text{CH}_3$  x 2), 6.6-8.0 (9H, m).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{15}\text{NO}_3$ : C, 73.70; H, 5.15; N, 4.78. Found: C, 73.52; H, 4.85; N, 4.67.

#### REFERENCES AND NOTES

- [1] K. Imafuku, A. Yamane and H. Matsumura, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 308 (1980).
- [2] K. Yamaguchi, K. Imafuku and H. Matsumura, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 998 (1980).
- [3] K. Imafuku, K. Suezaki and H. Matsumura, *Heterocycles*, **16**, 637 (1981).
- [4] K. Imafuku and K. Yamaguchi, *Bull. Chem. Soc. Japan*, **54**, 2855 (1981).
- [5] J. E. Gowan, P. M. Hayden and T. S. Wheeler, *J. Chem. Soc.*, 862 (1955).
- [6] C.-Y. Qian, Z.-T. Jin, B.-Z. Yin and K. Imafuku, *J. Heterocyclic Chem.*, **26**, 601 (1989).