5,7-Diaryl-3,4,6-trihydronaphthalen-2-ones의 One-pot 합성

M. Gopalakrishnan*, H. Manikandan, P. Sureshkumar, J. Thanusu, and V. Kanagarajan
Department of Chemistry, Annamalai University, Annamalai Nagar-608 002, Tamil Nadu, India
(Received April 3, 2007)

ABSTRACT. 5,7-Diaryl-3,4,6-trihydronaphthalen-2-ones have been synthesized from 3,5-diarylcyclohex-2-en-1-ones and methyl vinyl ketone in the presence of sodium ethoxide. The products were characterized by IR, UV-Visible, $^1$H-NMR, $^1^3$C-NMR and mass spectral techniques. To confirm $^1$H and $^1^3$C signals, HSQC spectrum was recorded and analyzed.

Keywords: 3,5-Diarylcyclohex-2-en-1-ones, Methyl Vinyl Ketone, Sodium Ethoxide, One-pot, 5,7-Diaryl-3,4,6-trihydronaphthalen-2-ones

INTRODUCTION

Michael reaction is the nucleophilic addition of a carbanion, formed from compounds containing active methylene group to an alpha-beta unsaturated ketone, ester, nitrile, etc. There is a general interest in the synthesis of bicyclic ketones because this structural unit is the main function of various natural fragments. It is a versatile intermediate in the synthesis of various steroids and hormones. A tandem reaction comprising a Michael addition step followed by an aldol condensation to produce a cyclic compound is Robinson annulation. It is an useful method for the synthesis of natural products consisting of fused ring systems such as terpenes and alkaloids. Robinson annulation can be performed under catalytic conditions using La(OiPr)$_2$-MS 4Al, Al$_2$O$_3$, S-proline, and AB385C. Moreover, solvent-free Robinson annulation with sodium ethoxide was also performed. It can also be effected in one-pot using acid catalysts. In this paper, we report synthesis of some 5,7-diaryl-3,4,6-trihydronaphthalen-2-ones.

RESULTS AND DISCUSSION

Some 5,7-diaryl-3,4,6-trihydronaphthalen-2-ones were synthesized from 3,5-diarylcyclohex-2-en-1-ones and methyl vinyl ketone in the presence of sodium ethoxide. The products were characterized on the basis of their IR, UV-visible, $^1$H NMR, $^1^3$C NMR and Mass spectral studies. To confirm the $^1$H...
and $^{13}$C NMR spectral assignments, HSQC spectrum was recorded for 5a and analyzed. All the spectral studies along with TLC indication bear evidence that the formed products are 5a-e. The compounds were isolated by column chromatography using petroleum ether-benzene (1:4) mixture as an eluent system. Attempts to isolate 3a-e and 4a-e were unsuccessful. The schematic representation describing the route of synthesis is furnished in Scheme 1.

The IR-spectrum of 5a showed one strong carbonyl absorption at 1638 cm$^{-1}$ assignable to a cyclic α,β-unsaturated ketone stretching frequency. The IR spectrum of 1a showed carbonyl absorption at 1653 cm$^{-1}$. 5a is also a α,β-unsaturated ketone but it has a frequency of 1638 cm$^{-1}$, which is lower than the stretching frequency of 1a, is due to extended conjugation.

In the GC-MS spectrum of 5a, the observed single peak confirms its formation as a single product. In the mass spectrum the molecular ion peak observed at 298 is also an additional evidence for the formation of 5a. The other important fragment peaks are 270, 229, 144, 116, 115, 91, 76 and 54, which agree with the fragment pattern of 2-naphthol. The plausible fragmentation pattern is given in Chart 1.

The UV-visible spectrum of 5a shows two major absorptions at 248 nm and 288 nm. The $\lambda_{\max}$ at 248 nm is due to π-π* transition of phenyl substituent. The other $\lambda_{\max}$ at 288 nm may be due to the unsaturated ketone. The calculated $\lambda_{\max}$ value 297 nm is almost equivalent to the observed $\lambda_{\max}$ value. If the compound 5a is a saturated one, then the $\lambda_{\max}$ value should be around 250 nm. But in the case under study $\lambda_{\max}$ is 288 nm which is adequate confirmation of the fact that 5a is unsaturated.

The complete $^1$H and $^{13}$C NMR spectral assignments for the products 5a-e are given in the experimental section.

**Analysis of HSQC Spectrum**

To confirm the $^1$H-NMR and $^{13}$C-NMR signals of 5a, HSQC spectrum was recorded and is given in Plate 1. It shows eight cross peaks, which are analyzed as follows: The cross peaks 1 and 2 reveal that the protons are connected to carbon signal at 36 ppm. The signal for the C-4 carbon appears as two signals at 3 and 2.9 ppm. The third cross peak is connected to a carbon signal at 41.5 ppm. C-3 carbon, which appeared at 41.5 ppm, is connected...
to proton at 3.4 ppm. Hence the signal at 3.4 ppm is conveniently assigned to H-3 proton.

The fourth cross peak is connected to a carbon signal at 44.3 ppm, which is connected to C-6 carbon and two proton signals at 2.9 and 2.7 ppm. Hence the signals at 2.9 and 2.7 ppm are assigned to two H-6 protons.

The fifth cross peak is connected to 7.01 ppm of $^1$H signal and 113.6 ppm of $^{13}$C signal. The seventh cross peak is connected to 6.47 ppm of $^1$H signal and 125.4 ppm of $^{13}$C signal. The fifth and seventh cross peaks may be due to C-8 and C-1 carbons and...
its protons respectively. The proton signals at 7.01 and 6.47 ppm are assigned to II-1 and II-8, respectively. The eighth cross peak appears as a cluster that is connecting the carbon signals at aromatic region and its protons.

Experimental Section

Melting points of the compounds were recorded on an electro-thermal apparatus and are uncorrected. IR-spectra in KBr were recorded in NICOLET AVATAR-330-FT-IR spectrophotometer. UV-visible spectrum was recorded on Hitachi-U-2001 double beam spectrophotometer. 1H NMR spectra were recorded on Bruker AMX-400 spectrometer operating at 400 MHz. 13C NMR spectra were recorded on Bruker AMX-400 spectrometer at operating frequency 100 MHz. The mass spectra were recorded on VG-MICROMASS-7070F double mass spectrometer. The HSQC was recorded on Bruker AMX-400 spectrometer. The purity of the compounds was checked on TLC.

The chalcones were prepared according to the literature, 3,5-Diaryl-cyclohex-2-en-1-ones [la-e] were prepared by adopting the literature procedure.

Preparation of 5,7-Diaryl-3,4,6-trihydronaphthalen-2-one 5a:
A solution of sodium ethoxide was prepared from 0.01 g of freshly cut sodium and 10 ml ethanol in a round-bottomed flask. To this, 3,5-Diphenylcyclohex-2-en-1-one (0.248 g) 1a in absolute ethanol (20 ml) was added and stirred for one hour at room temperature. To this mixture methyl vinyl ketone (0.1 ml) in absolute alcohol (10 ml) was added and the stirring was continued for over night. To the reaction mixture, 100 ml of CHCl3, followed by ice water were added. The organic phase was separated, washed with brine and dried over anhydrous sodium sulphate. The residue, obtained after evaporation of the solvent was subjected to column chromatography using petroleum ether-benzene (1:4) as an eluent mixture to afford 5a. Yield: 55%; m.p. 96-98°C; MS: C29H20O; m/z: 298 (M+), 270, 229, 144, 116, 115, 102, 91, 76, 52; IR cm-1: 3052, 1638, 1590, 1573, 1495, 1446, 761, 697; UV nm: 248, 288; 1H NMR, CDCl3, δ ppm: 2.60-2.78 (m, 2H, H1); 2.83-2.91 (m, 1H, H2); 3.01 (dd, 1H, H8); 3.36-3.44 (m, 2H, H2); 4.43 (m, 2H, H1); 6.47 (s, 3H, II), 7.60-7.56 (m, 10H, Ar-H's); 13C-NMR, CDCl3, δ ppm: 200.2 (C-2); 159.7 (C-7), 157.2 (C-5); 113.6 (C-8); 125.4 (C-1); 44.3 (C-6); 41.5 (C-3); 36.7 (C-4); 138.7-143.7 (C-9, C-10 and two ipso carbons); 125.4-130.7 Ar-C's.

Compounds 5b and 5c were synthesized similarly.

5-(4'-Methoxyphenyl)-7-phenyl-3,4,6-trihydronaphthalen-2-one 5b:
Yield: 50%; m.p.: 102-104°C; MS: C29H20O; m/z: 312 (M+), 284, 243, 144, 116, 115, 102, 91, 76, 52; IR cm-1: 3059, 2973, 1630, 1585, 1570, 1440, 1400, 1375, 756, 693; 1H NMR, CDCl3, δ ppm: 2.62-2.88 (m, 2H, H1), 3.02 (dd, 1H, H2), 2.86-2.99 (m, 2H, H2), 3.38-3.49 (m, 2H, H2), 2.40 (s, 3H, CH3 at phenyl ring), 6.52 (s, 3H, II), 7.08 (s, 3H, II), 7.06-7.24 (m, 10H, Ar-H's); 13C-NMR, CDCl3, δ ppm: 124.5 (C-1); 201.4 (C-2); 42.1 (C-3); 37.3 (C-4); 160.3 (C-5); 44.5 (C-6); 157.8 (C-7); 141.1 (C-8); 21.5 (CH3 at Phenyl ring); 137.6 (C-CH3); 139.2-144.2 (C-9, C-10 and two ipso carbons); 129.7-125.9 (Ar-C's).

5-(4'-Methoxyphenyl)-7-phenyl-3,4,6-trihydronaphthalen-2-one 5c:
Yield: 52%; m.p.: 106-108°C; MS: C29H20O; m/z: 328 (M+), 300, 259, 144, 116, 115, 102, 91, 76, 52; IR cm-1: 3042, 1632, 1587, 1572, 1492, 1446, 1265,
Acknowledgement. We wish to thank NMR Research Centre, Sophisticated Instruments Facility, IISc, Bangalore, India for recording NMR spectra.

REFERENCES