

## Note

### Condensation of dimethyl malonate with benzal-4-acetylanilines: A chemoselective reaction

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Dimethyl malonate has reacted chemoselectively with carbon-nitrogen double bond of benzal-4-acetylanilines (**1-8**) leaving the carbon-oxygen double bond, considered to be more reactive, intact under reaction conditions, leading to the formation of mono addition-elimination products rather than *bis* attack at both the double bonds, even when the reaction has been carried out with two moles of dimethyl malonate.

**Keywords:** Benzal-4-acetylanilines, dimethyl malonate, dimethyl benzalmalonates, 4-aminoacetophenone, benzaldehydes

Dimethyl malonate undergoes condensation reaction with carbonyl compounds<sup>1</sup>. Reaction of dimethyl malonate with imines either gives addition products<sup>1</sup> or addition-elimination products<sup>2</sup>. The carbon-nitrogen double bond is intermediate in its reactivity<sup>3</sup> between carbonyl compounds and alkenes. In continuation of earlier work<sup>4</sup> on benzal-4-acetylaniline and its C-phenyl derivatives<sup>5</sup>, the compounds containing carbon-nitrogen as well as carbon-oxygen double

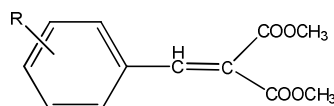
bonds, this communication describes the chemo-selective reaction of dimethyl malonate with benzal-4-acetylanilines.

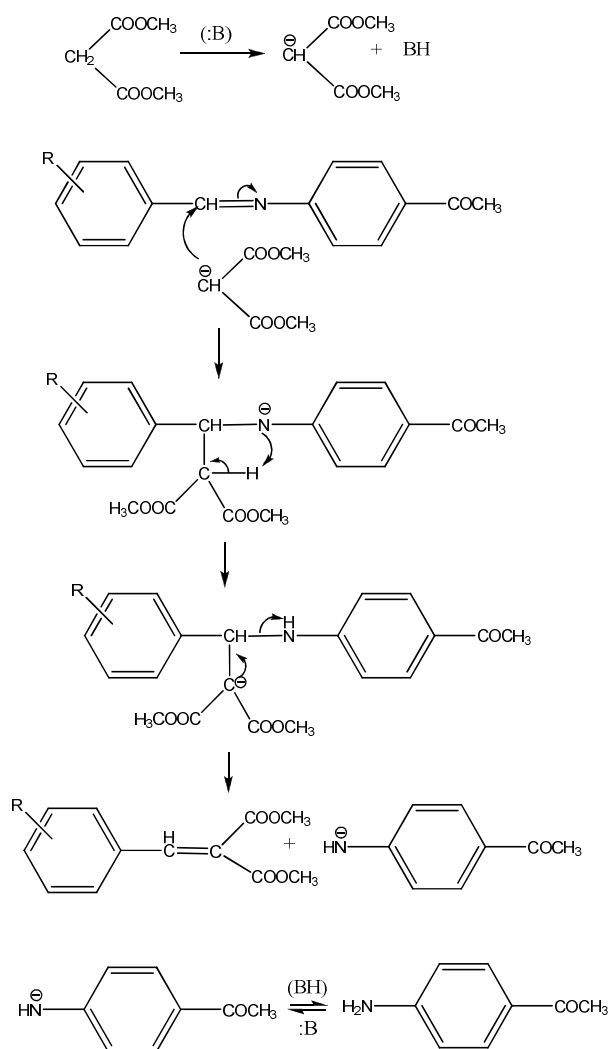
Condensation of dimethyl malonate with benzal-4-acetylanilines (**1-8**) in equimolar ratio in the presence of pyridine resulted in the formation of crude solids (**1-8a**). The products were characterized as dimethyl benzalmalonate and its derivatives on the basis of elemental analysis and spectral data. The Infrared spectra of the products contained absorption bands  $\sim 1720\text{ cm}^{-1}$  exhibiting the presence of ester group. The absorption at about  $1590$  and  $800\text{ cm}^{-1}$  depicted the presence of  $-\text{CH}=\text{C}-$  linkage. In addition to the above bands the absorption bands due to functional groups of the products were also observed.  $^1\text{H}$  NMR spectra of the products in  $\text{CDCl}_3$  contained multiplet signals between  $\delta 7.0 - 8.1$  for aromatic protons along with one olefinic proton. A singlet for six protons in the  $^1\text{H}$  NMR spectra of the products at about  $\delta 4.4$  was assigned to methyl protons of two ester groups. The protons of the functional groups of the products **3-8a** resonated in the expected field. The mass spectra of the compounds revealed that the molecular ion peak also constituted the base peak. The products along with their physical characteristics and spectral data are recorded in **Table I**.

Evaporation of the solvent from the filtrate yielded a jelly like mass, TLC of which indicated the presence

**Table I** — Physical characteristics and spectral data of dimethyl benzalmalonates

Compd	R	m.p. °C	Yield (%)	$^1\text{H}$ NMR spectrum ( $\delta$ ) functional group	$\text{M}^{+\bullet}$ $m/z$	Mol. Formula
<b>1a</b>	H	140	72	—	220	$\text{C}_{12}\text{H}_{12}\text{O}_4$
<b>2a</b>	4-Cl	39	81	—	254	$\text{C}_{12}\text{H}_{11}\text{O}_4\text{Cl}$
<b>3a</b>	4-OH	56	89	9.8 (s, 1H, OH)	236	$\text{C}_{12}\text{H}_{12}\text{O}_5$
<b>4a</b>	4-OCH <sub>3</sub>	45	80	4.1 (s, 3H, OCH <sub>3</sub> )	250	$\text{C}_{13}\text{H}_{14}\text{O}_5$
<b>5a</b>	3-OCH <sub>3</sub> , 4-OCH <sub>3</sub>	89	79	4.0 (s, 6H, 2 $\times$ OCH <sub>3</sub> )	280	$\text{C}_{14}\text{H}_{16}\text{O}_6$
<b>6a</b>	3-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 5-OCH <sub>3</sub>	40	77	4.0 (s, 9H, 3 $\times$ OCH <sub>3</sub> )	310	$\text{C}_{15}\text{H}_{18}\text{O}_7$
<b>7a</b>	3-OCH <sub>3</sub> , 4-OH	65	80	4.1 (s, 3H, OCH <sub>3</sub> ), 9.7 (s, 1H, OH)	266	$\text{C}_{13}\text{H}_{14}\text{O}_6$
<b>8a</b>	3-OC <sub>2</sub> H <sub>5</sub> , 4-OH	60	85	4.4 (q, 2H, OCH <sub>2</sub> CH <sub>3</sub> ) 1.5 (t, 3H, OCH <sub>2</sub> CH <sub>3</sub> ), 9.7 (s, 1H, OH)	280	$\text{C}_{14}\text{H}_{16}\text{O}_6$





Scheme I

of 4-aminoacetophenone and unreacted starting materials. Condensation of dimethyl malonate with benzal-4-acetylanilines (**1-8**) in 2:1 molar ratio also yielded the same products **1-8a** respectively. The formation of dimethyl benzylmalonate and its derivatives can be explained by the attack of the carbanion, formed by abstraction of a proton from the active methylene moiety of dimethyl malonate, on carbon-nitrogen double bond of benzal-4-acetylanilines, to give unstable addition products which lose 4-aminoacetophenone to yield the stable addition-elimination products (Scheme I).

Thus, dimethyl malonate reacted chemoselectively with carbon-nitrogen double bond leaving the carbon-oxygen double bond, considered to be more

reactive, intact under reaction conditions, resulting in the formation of mono addition-elimination products rather than *bis* attack at both the reactive centres, even when the condensation was carried out with two moles of dimethyl malonate.

### Experimental Section

The purity of the products was checked by TLC. The compounds gave satisfactory elemental analysis. The melting points were determined on electric melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr disc. The  $^1\text{H}$  NMR spectra were recorded on a Bruker Spectrospin 300 MHz spectrometer in  $\text{CDCl}_3$  with TMS as internal standard. Mass spectra were recorded on Perkin-Elmer Clarus 500 mass spectrometer.

**General procedure for the condensation of dimethyl malonate with benzal-4-acetylanilines:** Dimethyl malonate (0.01 mole) was added to benzal-4-acetylaniline/its derivative (**1-8**, 0.01 mole) taken in dry benzene (25 mL) in a conical flask (100 mL). After adding a few drops of pyridine, the contents were heated and shaken briskly for 20-30 min. The flask was then cooled, stoppered and allowed to stand at RT for 24 hr. The crude solid which separated out was filtered and purified by recrystallization from benzene to get respective dimethyl benzylmalonate (**1-8a**). Removal of the solvent from the filtrate gave a jelly like mass, TLC of which indicated the presence of 4-aminoacetophenone and unreacted starting materials.

Reaction of dimethyl malonate with benzal-4-acetylanilines **1-8** in 2:1 molar ratio was carried out in the same manner.

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