

## Note

### Reaction of ethyl cyanoacetate with benzal-4-acetylanilines: An unexpected result

Anjali Sidhu & Mangat Rai\*

Department of Biochemistry and Chemistry  
Punjab Agricultural University, Ludhiana 141 004, India

E-mail : anjali\_sidhu\_pau@yahoo.co.in

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Reaction of ethyl cyanoacetate with benzal-4-acetylanilines **1a-10a**, the compounds containing both azomethine and ketone linkages, in equimolar ratio, in the presence of pyridine yields solid products, which have been characterized as ethyl benzalcyanoacetate and its derivatives **1b-10b** on the basis of elemental analysis and spectral studies. The reaction of **1a-10a** with two moles of ethyl cyanoacetate also results in the formation of the same products **1b-10b**, by an unexpected attack of ethyl cyanoacetate on azomethine linkage only rather than on both the reactive centres *i.e.* carbon-nitrogen double bond and carbon-oxygen double bond.

**Keywords:** 4-Aminoacetophenone, ethyl cyanoacetate, benzal-4-acetylanilines, ethyl benzalcyanoacetate, benzaldehydes

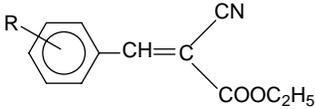
Chemistry of multiple bonds has achieved a dramatic development in the past decades because of their importance in the organic synthesis<sup>1,2</sup>. The carbon-nitrogen double bond is intermediate in its reactivity between carbonyl compounds and alkenes<sup>3</sup>. The present work was aimed at studying the reaction of ethyl cyanoacetate with benzal-4-acetylaniline and its C-phenyl derivatives, the compounds containing both carbon-nitrogen double bond as well as carbon-oxygen double bond and the unexpected results of the present study are being presented in this communication.

The reaction of ethyl cyanoacetate with benzal-4-acetylanilines **1a-10a**, the compounds obtained by condensing 4-aminoacetophenone with benzaldehyde and substituted benzaldehydes **1-10** (ref. 4), in equimolar ratio in the presence of pyridine yielded crude solids which were purified by recrystallization from benzene. The IR spectra of the products contained absorption bands at 2230 and 1725  $\text{cm}^{-1}$  indicating the presence of cyano and ester group respectively. The absorption at 1590 and 850  $\text{cm}^{-1}$  was due to the presence of  $-\text{CH}=\text{C}<$  linkage. In addition to the above bands, absorption bands of functional group of the product were also observed.

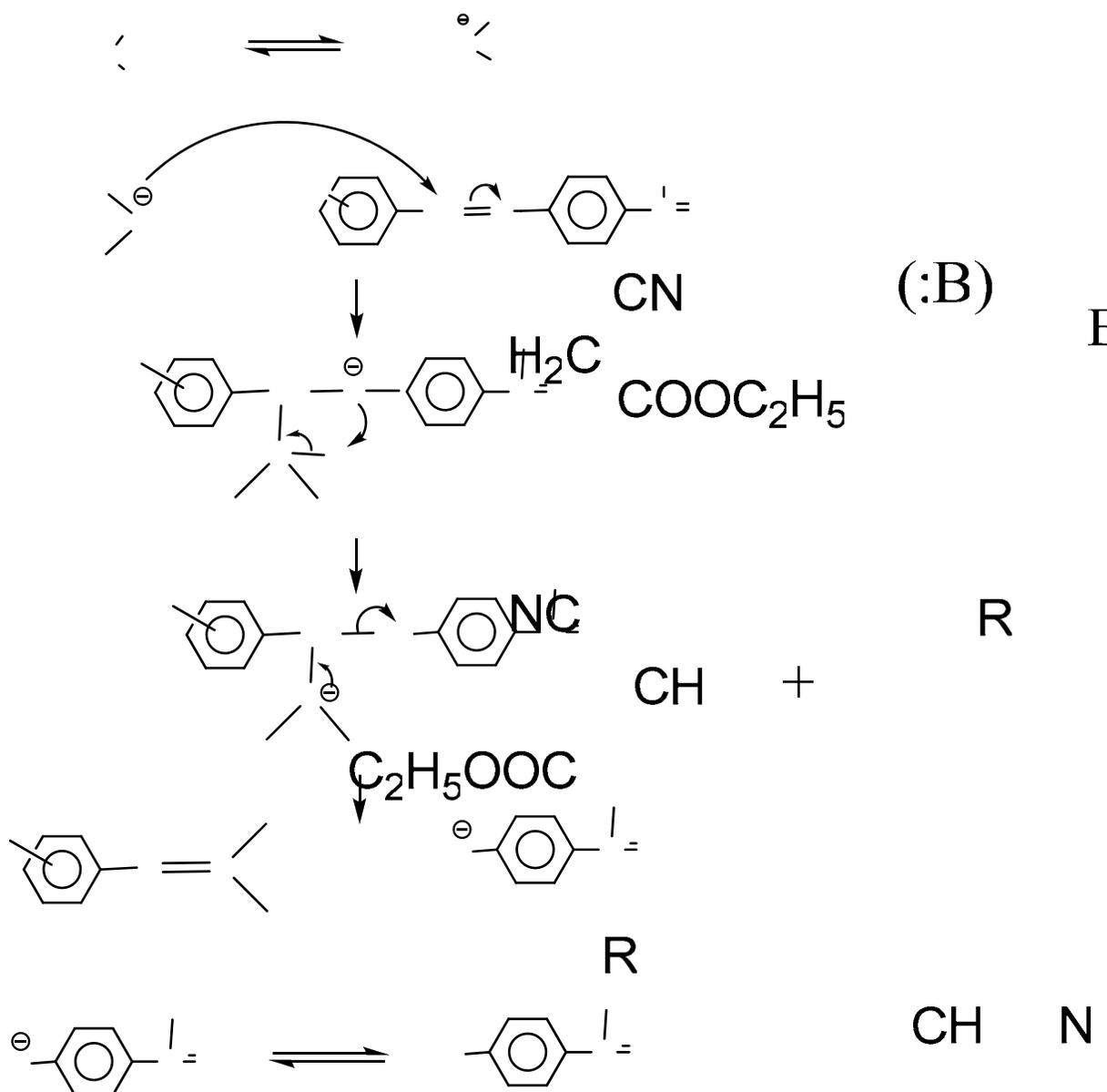
For instance the absorption band between 3400-3300  $\text{cm}^{-1}$  in the compounds **3b**, **7b** and **8b** was indicative of presence of phenolic group in these products. In the IR spectra of **9b** and **10b** the bands between 1540-1500 and 1360-1300  $\text{cm}^{-1}$  were due to nitro group.

In the  $^1\text{H}$  NMR spectra of the compounds, the protons resonated in the expected region. The  $^1\text{H}$  NMR spectra of the products contained a two proton quartet at  $\delta$  4.4 and a three proton triplet at 1.5 indicating the presence of ethyl group. Multiplet signals of integration corresponding to six protons in compound **1b**, five protons in compounds **2b**, **3b**, **4b**, **9b** and **10b**, four protons in compounds **5b**, **7b** and **8b** and three protons in compound **6b** observed between  $\delta$  6.8-8.1 accounted for aromatic protons along with one olefinic proton. A singlet at about  $\delta$  4.0 corresponding to three protons in compounds **4b** and **7b**, six protons in compound **5b** and nine protons in compound **6b** indicated the presence of methoxy protons in these products. A one proton singlet at about  $\delta$  9.4 in compounds **3b**, **7b** and **8b** showed the presence of the phenolic proton. Mass spectra of the compounds revealed that the molecular ion peak also constituted the base peak. On the basis of elemental analysis and spectral data, the compounds have been characterized as ethyl benzalcyanoacetate and its derivatives **1b-10b**. The ethyl benzalcyanoacetates along with their physical characteristics and molecular ion peaks ( $m/z$ ) are recorded in **Table I**.

**Table I** — Characteristics and molecular ion peaks of ethyl benzalcyanoacetates



Compd	R	m.p. °C	Yield %	M <sup>+</sup> m/z	Mol. formula
<b>1b</b>	H	48	55	201	C <sub>12</sub> H <sub>11</sub> NO <sub>2</sub>
<b>2b</b>	4-Cl	154	60	235	C <sub>12</sub> H <sub>10</sub> NO <sub>2</sub> Cl
<b>3b</b>	4-OH	146	44	217	C <sub>12</sub> H <sub>11</sub> NO <sub>3</sub>
<b>4b</b>	4-OCH <sub>3</sub>	130	42	231	C <sub>13</sub> H <sub>13</sub> NO <sub>3</sub>
<b>5b</b>	3-OCH <sub>3</sub> , 4-OCH <sub>3</sub>	125	75	261	C <sub>14</sub> H <sub>15</sub> NO <sub>4</sub>
<b>6b</b>	3-OCH <sub>3</sub> , 4-OCH <sub>3</sub> , 5-OCH <sub>3</sub>	47	68	291	C <sub>15</sub> H <sub>17</sub> NO <sub>5</sub>
<b>7b</b>	3-OCH <sub>3</sub> , 4-OH	74	79	247	C <sub>13</sub> H <sub>13</sub> NO <sub>4</sub>
<b>8b</b>	3-OC <sub>2</sub> H <sub>5</sub> , 4-OH	200	80	261	C <sub>14</sub> H <sub>15</sub> NO <sub>5</sub>
<b>9b</b>	2-NO <sub>2</sub>	97	56	246	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>
<b>10b</b>	3-NO <sub>2</sub>	75	58	246	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>



Scheme I

The reaction of ethyl cyanoacetate with benzal-4-acetylaniline and its C-phenyl derivatives **1a-10a** in 2:1 molar ratio also yielded the same products **1b-10b** respectively. The formation of ethyl benzalcyanoacetates **1b-10b** can be explained by the attack of the carbanion formed from ethyl cyanoacetate 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).

Ethyl cyanoacetate reacted unexpectedly with azomethine linkage only leaving the ketonic moiety intact under the reaction conditions, leading to the

formation of mono addition-elimination products rather than bis addition at two reactive centres, even when the reaction was carried out with two moles of ethyl cyanoacetate.

#### Experimental Section

The melting points were determined on electric melting point apparatus and are uncorrected. Homogeneity of the compounds was checked by TLC. The compounds gave satisfactory elemental analysis. The IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using KBr disc. The <sup>1</sup>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 reaction of ethyl cyanoacetate with benzal-4-acetylanilines.** Benzal-4-acetylaniline/its derivative **1a-10a** (0.01 mol) was taken in dry benzene (20 mL) in a conical flask (100 mL). Then ethyl cyanoacetate (0.01 mol) and a few drops of pyridine were added to the above solution. The reaction mixture was heated and shaken briskly for 15 min. The flask was then cooled, stoppered and allowed to stand at RT for 24 hr when a crude solid separated out which was filtered and purified by recrystallization from benzene to get pure ethyl benzalcyanoacetate/its derivative **1b-10b**. Evaporation of solvent from filtrate yielded gelly like mass,

TLC of which indicated the presence of 4-aminoacetophenone and unreacted starting materials.

Condensation of ethyl cyanoacetate with benzal-4-acetylanilines **1a-10a** in 2:1 molar ratio was also carried out by following the above procedure.

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