

**NOTE****Action of Higher Diazoalkanes on Carboxylic Acid Chloride**

SHALINI GUPTA\*, POONAM GARG and A.K. AGARWAL

Department of Chemistry, Bareilly College, Bareilly-243 001, India

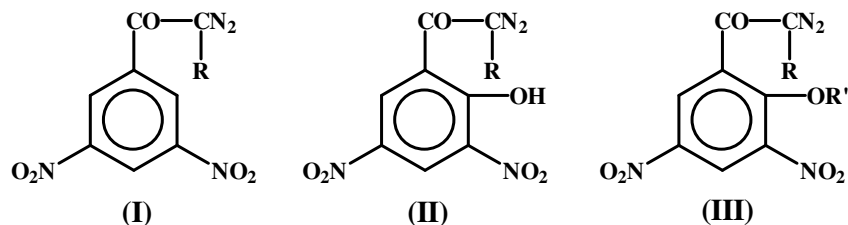
E-mail: dr\_himanshu1975@yahoo.co.in

3,5-Dinitrobenzoyl chloride with diazoalkane gave a  $\omega$ -diazo- $\omega$ -*n*-alkyl 3,5-dinitroacetophenone and 3,5-dinitrosalicyl chloride with diazoalkane gave a mixture of  $\omega$ -diazo- $\omega$ -*n*-alkyl-*o*-hydroxy-3,5-dinitroacetophenone and  $\omega$ -diazo- $\omega$ -*n*-alkyl-*o*-alkoxy-3,5-dinitroacetophenone respectively.

**Key Words:** Diazoalkane, 3,5-Dinitrosalicyl chloride.

The synthesis and reaction of  $\alpha$ -diazoketones are well known<sup>1-3</sup>. The literature survey indicates, 3,5-dinitrobenzoyl chloride (1 mol) in dry ether at 0 °C with higher diazoalkane (1 mol) in presence of triethylamine (1 mol) gave a diazo- $\omega$ -*n*-alkyl-3,5-dinitroacetophenone (I) by following the method of Newman and Beal<sup>4</sup>.

Carboxylic acid chloride like 3,5-dinitrosalicyl chloride contains two sites of reactivity, the phenolic hydroxy group and an acid chloride group, both of which are susceptible to the action of diazoalkane. By adopting the method of Arndt Eistert and Partale<sup>5</sup>, Robinson and Bradley<sup>6</sup> and several other workers<sup>7,8</sup>, 3,5-dinitrosalicyl chloride (1 mol) with diazoalkane (2 and 4 mol) gave a mixture of  $\omega$ -diazo- $\omega$ -*n*-alkyl-*o*-hydroxy 3,5-dinitroacetophenone (II) and  $\omega$ -diazo- $\omega$ -*n*-alkyl-*o*-alkoxy-3,5-dinitroacetophenone (III). The separation of mixture of diazoketones II and III could be possible by treating with 1 % NaOH solution.



R = -*n*-propyl  
 -*n*-amyl  
 -*n*-heptyl

R' = -*n*-butoxy  
 -*n*-hexoxy  
 -*n*-octoxy

**$\omega$ -Diazo- $\omega$ -*n*-propyl-3,5-dinitroacetophenone (I, R = -*n*-propyl):** It was synthesized by mixing 3,5-dinitrobenzoyl chloride (1 mol, 4.6 g), triethyl amine (1 mol, 2.02 g) and pre-estimated diazo-*n*-butane (1 mol, 1.68 g). The yellow mobile liquid diazoketone afforded a 2,4-dinitrophenylosazone, crystallized from ethanol, m.p. 210 °C. (Found (%): C = 44.09, H = 2.2, N = 23.36; C<sub>23</sub>H<sub>18</sub>N<sub>10</sub>O<sub>12</sub> requires (%): C = 44.08, H = 2.87, N = 22.36. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): (-C=N-) 1620, (-C-NO<sub>2</sub>) 1220, (CH<sub>2</sub> in *n*-propyl group) 720. With benzoic acid it forms benzoate which afforded a 2,4-dinitrophenylhydrazone, crystallized from ethanol, m.p. 195 °C. (Found (%): C = 52.17, H = 3.62, N = 15.21 requires (%): C = 52.16; H = 3.62; N = 15.20. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1625 (-C=N-), 1724 (>C=O in benzoate).

**$\omega$ -Diazo- $\omega$ -*n*-amyl-3,5-dinitroacetophenone (I, R = -*n*-amyl):** It was synthesized by mixing 3,5-dinitrobenzoyl chloride (1 mol, 2.6 g), triethyl amine (1 mol, 1.58 g) and diazo-*n*-hexane (1 mol, 1.74 g). The yellow mobile liquid diazoketone afforded a 2,4-dinitrophenylosazone, crystallized from ethanol, m.p. 215 °C. (Found (%): C = 45.76, H = 3.30, N = 21.05; C<sub>25</sub>H<sub>22</sub>N<sub>10</sub>O<sub>12</sub> requires (%): C = 45.87, H = 3.36, N = 21.4. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1619 (-C=N-), 1221 (-C-NO<sub>2</sub>), 740 (-CH<sub>2</sub> in *n*-amyl group).

**$\omega$ -Diazo- $\omega$ -*n*-heptyl-3,5-dinitroacetophenone (I, R = -*n*-C<sub>7</sub>H<sub>15</sub>):** It was synthesized by mixing 3,5-dinitrobenzoyl chloride (1 mol, 1.8 g), triethyl amine (1 mol, 0.79 g) and diazo-*n*-octane (1 mol, 1.09 g). The yellow mobile liquid diazoketone afforded a 2,4-dinitrophenylosazone, crystallized from ethanol, m.p. 160 °C. (Found (%): C = 46.92, H = 3.72, N = 20.5; C<sub>27</sub>H<sub>26</sub>N<sub>10</sub>O<sub>12</sub> requires (%): C = 47.5, H = 3.81, N = 20.52. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1620 (-C=N-), 1225 (-C-NO<sub>2</sub>), 720 (CH<sub>2</sub> in *n*-amyl group).

**$\omega$ -Diazo- $\omega$ -*n*-propyl-*o*-hydroxy-3,5-dinitroacetophenone (II, R = -*n*-propyl) and  $\omega$ -Diazo- $\omega$ -*n*-propyl-*o*-butoxy-3,5-dinitroacetophenone (III, R = -*n*-propyl, R' = -*n*-butyl):** 3,5-Dinitrosalicyl chloride (1 mol, 3.2 g) and pre-estimated diazo-*n*-butane (2.5 mol, 2.72 g) were treated in dry ether at 0 °C, after keeping overnight, the reaction mixture was extracted with 1 % NaOH solution several times till the ether layer ceased to give a violet colouration. The sodium compound was kept overnight which on acidification gave 3,5-dinitrosalicylic acid, m.p. 170 °C. On removal of ether it gave a pale yellow liquid diazoketone containing nitrogen, which produced no colouration with FeCl<sub>3</sub>. It formed a 2,4-dinitrophenylosazone, crystallized from alcohol, m.p. 146 °C. (Found (%): C = 46.33, H = 3.68, N = 20.12; C<sub>27</sub>H<sub>26</sub>N<sub>10</sub>O<sub>13</sub> requires (%): C = 46.41, H = 3.72, N = 20.05. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1620 (-C=N-), 1250 (>C=O in benzoate), 1215 (*o*-substitution), 720 (-CH<sub>2</sub> in *n*-propyl group), 710 (-CH<sub>2</sub> in *n*-hexyl group).

**$\omega$ -Diazo- $\omega$ -*n*-amyl-*o*-hydroxy-3,5-dinitroacetophenone (II, R = -*n*-amyl) and  $\omega$ -Diazo- $\omega$ -*n*-amyl-*o*-hexoxy-3,5-dinitroacetophenone (II, R = -*n*-amyl, R' = -*n*-C<sub>6</sub>H<sub>13</sub>):** The diazoketones were prepared as above, the ether layer on removal of solvent gave a pale yellow diazoketone (II, R = -*n*-C<sub>6</sub>H<sub>13</sub>) which afforded a 2,4-dinitrophenyl osazone, crystallized from ethanol, m.p. 140 °C (Found (%): C =

49.23, H = 4.4, N = 18.6, C<sub>31</sub>H<sub>34</sub>N<sub>10</sub>O<sub>13</sub> requires (%): C = 49.33, H = 4.5, N = 18.56. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1620 (-C=N-), 722 (-CH<sub>2</sub> in *n*-amyl group), 710 (CH<sub>2</sub> in *n*-hexyl group).

**$\omega$ -Diazo- $\omega$ -*n*-heptyl-*o*-hydroxy-3,5-dinitroacetophenone (II, R = *n*-C<sub>7</sub>H<sub>15</sub>) and  $\omega$ -Diazo- $\omega$ -*n*-heptyl-*o*-octoxy-3,5-dinitroacetophenone (II, R = *n*-heptyl, R' = *n*-C<sub>8</sub>H<sub>17</sub>):** The diazoketones were synthesized exactly as above. The pale yellow diazoketone (II, R = *n*-heptyl) afforded a 2,4-dinitrophenylosazone, crystallized from ethanol, m.p. 160 °C (Found (%)) C = 51.6, H = 4.9, N = 17.2; C<sub>35</sub>H<sub>42</sub>N<sub>10</sub>O<sub>13</sub> requires (%): C = 51.85, H = 5.18, N = 17.28. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 1624 (-C=N-), 740 (CH<sub>2</sub> in *n*-heptyl group), 720 (CH<sub>2</sub> in *n*-octyl group).

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