

Synthesis of α -Diazoketone by The Action of Diazoalkane On Carboxylic Acid Chloride

KEYWORDS

Diazoalkane, Azelaoyl Chloride and iso-phthaloyl chloride.

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ABSTRACT The diazoketone, 1,11-bis-(diazo 1,11-diamyl) undecan-2, 10-di-one was synthesised by the action of Azelaoyl Chloride on diazo-n-hexane and 1,3-bis- α -diazo-n-heptanoyl benzene on diazo-n-hexane. The diazoketones were characterized by various physico-chemical techniques.

1. Introduction :

The action of diazo-alkanes on acid chlorides give rise to diazoketones¹⁻⁴. The survey of chemical literature reveals that a large number of diazoketones have been synthesized, But the field is quite open in the case higher honeologues⁵⁻¹². A member of methods for the synthesis of diazoketones are available in the literature, Arndt-Eistest method¹³ (or modified)¹⁴, Newmann and Bear method¹⁵, Robinson and Bear method¹⁶ etc. A variety of acid chlorides¹⁷ have been used for the synthesis of diazoketones.

Keeping these facts in view, we have selected Azelaoyl chloride and Iso-phthaloyl chloride for these diazoketones.

2. Experimental :

1. Synthesis of 1,11-bis(diazo 1,11-diamyl undecan-2,10di-one :

It was prepared by the action of Azelaoyl Chloride (2.25g, 1 mol.) on diazo-n-hexane (5.6g, 5 mol.) using Arndt-Eistest method.

The diazoketone so obtained is a light yellow oily liquid. The easily removable diazogroup, prevented its purification by distillation even under vacuum.

 $\rm HOOC$ – $\rm (CH_2)_7$ – COOH + 2SOCl_ CIOC – $\rm (CH_2)_7$ COCl + 2SO_ + 2HCl

$$4C_{5}H_{11} - CH N_{2} + ClOC - (CH_{2})_{7} - COCl \rightarrow N_{2}C - C - (CH_{2})_{7} - C - CN_{2}$$

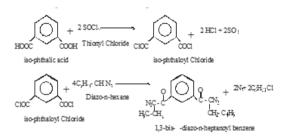
Diazo-n-hexane
$$Azelaoyl Chloride H_{9}C_{4} - CH_{2} CH_{2}C_{4}H_{9}$$

 $+ 2C_6H_{13}Cl + 2N_2$

The diazoketone so obtained was characterized by elemental analyses and its reactions with 2,4-dinitrophenyl hydrazine, benzoic acid, phenol and dry hydrochloric acid.

2. Synthesis of 1,3-bis- -diazo-n-heptanoyl benzene :

It was prepared by adding dry etheral solution of isolphthaloyl (1.65g, 1 mol.) chloride to a cold etheral solution of diazo-n-hexane (6.48g, 4 mol.) at 0°C. The reaction mixture was kept overnight. On removal of ether, a yellow viscous liquid was obtained.



The diazoketone so obtained was characterised by elemental analyses and its reactions with 2,4-dinitro-phenyl hydrazine, benzoic acid, phenol and dry hydrochloric acid.

The elemental analyses and IR spectral studies were carried out at CDRI Lucknow.

3. Results and Discussion:

1. Characterization of 1, 11-bis-(diazo 1,11-diamyl) undecan-2,10-dione :

(a) Formation of osazone (reaction with 2,4-dinitrophenylhydrazine) - It was treated with an aqueous sulphuric acid solution of 2, 4-dinitrophenyl hydrazine then an osazone was obtained. This on crystallisation from ethanol gave orange product.

$$(NO_{2})_{2}H_{3}C_{6}HN.N = C-C-(C+C_{1})_{7}C-C-N. NH C_{6}H_{3} (NO_{2})_{2}$$

$$(NO_{2})_{2}H_{3}C_{6}HN.N=C-C-(C+C_{1})_{7}C-C-N. NH C_{6}H_{3} (NO_{2})_{2}$$

$$H_{9}C_{4}-H_{2}C = C_{4}H_{9}$$

(Osazone) Physical State - orange crystalline solid

M.P. - 164°C

Elemental Analyses :

C= 50.37% (obs. 50.25), H=4.85% (obs. 4.79), N=20.89% (20.78)

I.R. (KBr) : 3455 (-NH), 1620(C=N), 1350 (C-NO₂), 720 cm $^{\text{-1}}$ (CH $_{2}$ rock in – C $_{5}\text{H}_{11}$)

(b) Action of Benzoic Acid :

On treatment with molten benzoic acid, a nitrogen free brown liquid was obtained which on treatment with 2,4-di-

nitropheneyl hydrazine gave hydrazone. It was crystallised from ethanol as orange solid.

$$\begin{array}{cccc} & O & O \\ H_5 C_6 & COOHC - C - (CH_{2)_7} - C - CHOOC C_6 H_5 \\ & & & \\ H_9 C_4 - H_2 C & & CH_2 - C_4 H_9 \end{array}$$

Nitrogen free compound (ester)

$$\begin{array}{ccccccccc} (O_2 N)_2 H_3 C_6 HN. N & N. \ NH \ C_6 H_3 \ (NO_2)_2 \\ & \parallel & \parallel \\ H_5 \ C_6 \ \ COOHC \ - C \ (CH_2)_7 \ - C \ - CHOOC \ C_6 H_5 \\ & \mid \\ H_9 C_4 \ - H_2 C & CH_2 \ - C_4 H_9 \end{array}$$

(Hydrazone)

Physical State - orange crystalline solid

M.P. - 222°C

Elemental Analyses :

C= 61.03% (obs. 60.92), H= 6.06% (obs. 5.96), N=12.12% (obs. 11.98)

I.R. (KBr) : 3360 (-NH), 1622(C=N), 1580 (C_{_{0}}H_{_{5}}), 1335 (C-NO_{_{2}}), 745 cm^{-1} (CH_{_{2}} rock in - C_{_{5}}H_{_{1}})

(c) Action of Phenol :

With phenol, it gave a reddish brown liquid. This on treatment with 2,4-dinitrophenyl hydrazine yielded an orange solid hydrazone.

$$\begin{array}{ccccc} & & & & & O \\ H_5 C_6 & OHC - C - (CH_2)_7 & - & C - CHO C_6 H_5 \\ H_9 C_4 CH_2 & & & CH_2 C_4 - H_6 \end{array}$$

Nitrogen free compound (Ether)

(Hydrazone)

Physical State - orange crystalline solid

M.P. - 222°C

Elemental Analyses :

C= 61.03% (obs. 60.92), H= 6.06% (obs. 5.96), N=12.12% (obs. 11.98)

I.R. (KBr) : 3360 (-NH), 1622(C=N), 1580 (-C₄H₂), 1335 (C-NO₂), 745 cm⁻¹ (CH₂ rock in $-C_{e}H_{1,1}$)

Physical State–orange crystalline solid M.P. - $254^{\circ}C$

Elemental Analyses :

C= 62.21% (obs. 62.10), H= 6.45% (obs. 6.41), N=12.90%

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(12.87)

I.R. (KBr) : 3352 (-NH), 1625(C=N), 1590 (C_6H_5), 1335(C-NO_1), 1273(C-O-C), 725 cm^{-1} (CH_2 rock in $-C_6H_{-1}$)

(d) Action of dry HCl gas :

A red liquid was obtained, which possesses chlorine but no nitrogen. It was extracted as chloroketone. This on treatment with 2,4-dinitrophenyl hydrazine gave hydrazone.

$$\begin{array}{cccc} & & & & O & & \\ & & & & \\ & & & \\ CI & H & C & -C & -(CH_2)_7 & -C & -CH & CI \\ & & & & & \\ H_9 & C_4 & -H_2 & C & & CH_2 & -C_4 & H_9 \end{array}$$

Chloroketone

Physical State - orange crystalline solid

M.P. - 210°C

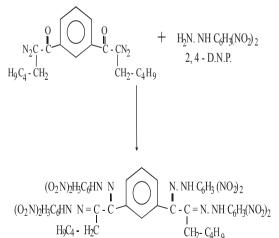
Elemental Analyses :

C= 52.58% (obs. 52.29), H= 6.10% (obs. 5.98), N=14.87% (14.80), Cl = 9.42% (obs. 9.39)

I.R. (KBr) : 3320 (-NH), 1633 (C=N), 1620 (C₆H₅), 1385 (C-NO₂), 720 cm⁻¹ (CH₂ rock in – C₅H₁₁), 645 Cm⁻¹ (C-Cl)

Characterization of 1,3-bis- -diazo-n-heptanoyl benzene .

(a) Formation of Osazone (Reaction with 2,4-dinitrophenyl Hydrazine :



It was treated with an aqueous alcoholic sulphuric acid solution of 2,4-dinitrophenyl hydrazine, then an osazone was obtained. This on crystallization from ethanol gave red product.

The osazone, so obtained was characterized by elemental analyses and IR spectra.

Physical State - red crystalline solid

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M.P. - 198°C

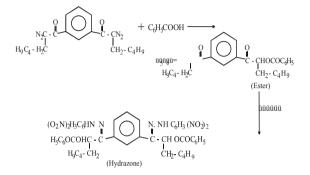
Elemental Analyses :

C= 50.28% (obs. 50.10), H= 4.00% (obs. 3.86), N=21.33% (Obs.21.12)

I.R. (KBr) : 3085 (C-H aromatic), 1620(C=N), 1340 (C-NO₂), 740 cm⁻¹ (CH₂ rock in– C₅H₁₁)

(b) Action of Benzoic Acid :

On treatment molten benzoic acid, a nitrogen free product was obtained, which on treatment with 2,4-dinitrophenyl hydrazine gave hydrazone.



Physical State - Reddish Yellow crystalline solid.

 $M.P. = 199^{\circ}C$

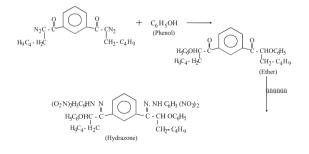
Elemental Analyses :

C= 61.20% (obs. 60.87), H= 5.10% (obs. 4.79), N=12.41% (Obs.12.76)

I.R. (kBr) : 1730 (C=O), 1620(C=N), 1275 (-E-O-C), 735 $\rm cm^{-1}$ (-CH_2 rock in – $\rm C_5H_{11}$

(c) Action of phenol :

It produced nitrogen free red liquid, which reacted with 2,4-dinitrophenyl hydrazine to give hydrazone.



Characterisation :

Physical State - Orange crystalline solid

M.P. - 175°C

Elemental Analyses :

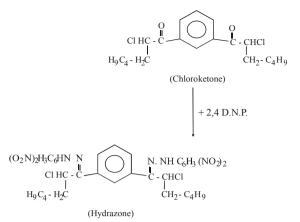
C= 62.41% (obs. 62.10), H= 5.46% (obs. 5.16), N=13.24% (Obs.12.95)

I.R. (KBr) : 1625 (C=N), 1260(C-O-C), 735 Cm 1 (CH $_{\rm 2}$ rock in – C $_{\rm 5}{\rm H}_{11}$)

(d) Action of dry HCl :

When treated with dry HCl gas it gave a nitrogen free

chloro-derivative, which on subsequent treatment with 2,4-dinitrophenyl hydrazine gave hydrazone.



Characterisation :

Physical State - Orange crystalline solid

$M.P. = 175^{\circ}C$

Elemental Analyses :

C= **5**2.53% (obs. 52.20), H= 4.92% (obs. 4.54), N=15.32% (Obs.15.64)

Cl = 9.71(obs. 9.36)

I.R. (KBr) : 1635 (C=N), 1610 (C_6H_5), 1255 (C-O-C), 746 $\rm Cm^{-1}$ (CH_2 rock in – C_6H_1)

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