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CODEN: IAASCA **ORIGINAL ARTICLE**

Characterization And Synthesis Of Diazoketone By The Action Of Higher Diazoalkane On Pentanoic Anhydride

Devendra Kumar Gangwar And A.K. Agarwal
Department of Chemistry, Bareilly College, Bareilly U.P.-243005 (India)
Email:gangwardevendra2@gmail.com

ABSTRACT
The diazoketone (1-diazo-1-n-heptyl hexan 2-one) was synthesized by the action of Pentanoic anhydride (1 mol.) on diazo-n-octane (2 mol.) in dry ether at 0^{0}C. Pentanoic anhydride contained only one site of reactivity. The diazoketone so obtained characterized by various physico-chemical reactions.
Key Words : *Pentanoic anhydride, Diazo-n-octane and Diazoketone.*

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INTRODUCTION

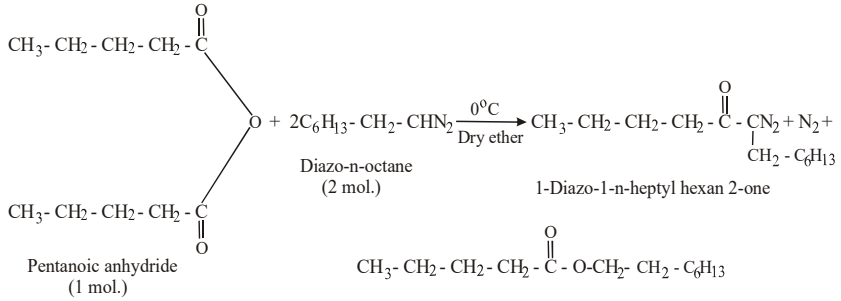
The field of synthetic organic chemistry is too wide. The action of diazoalkanes on carboxylic acid chloride or acid anhydride [1-4] produce diazoketones. A large number of such diazoketones have been synthesized with lower diazolkanes [5-7], such as diazomethane and in few cases diazoethane only by using simple acid anhydride having one site of reactivity. The study of literature also reveals that very little work has been done on the synthesis of diazoketones [8-12] from carboxylic acid chloride, containing one or more sites of reactivity towards diazoalkanes. By using different amounts of a diazoalkane, it is possible to attack one or both the sites present in it. By doing so it is possible to compare the reactivities of these sites. Therefore attempt was made to synthesis the diazoketone by following Robinson and Bradley method [13]. All the diazoketones are yellow viscous liquid but higher diazoketones were less viscous and more stable than lower diazoketones. As diazoketones decomposed on distillation even under vaccum, therefore they could not be purified under the reaction was carried out as such.
In view of the facts attempt have been made to synthesis this dizoketone, which have been characterized by various methods.

EXPERIMENTAL

All the chemical and reagents used in the research work have been of highest purity. The m.p. were determined in the lab whereas elemental analyses and infra red spectral studies were carried out at C.D.R.I. Lucknow.

Synthesis of 1-diazo-1-n-heptyl hexan 2-one:

Pentanoic anhydride (2.8g, 1 mol.) was added installments over a period of half an hour to an etheral solution of pre-estimated diazo-n-actane (4.78g, 2 mol.) at 0^0 C. On removal of ether at low temperature, the diazoketone was obtained as a yellow mobile liquid which contained nitrogen.



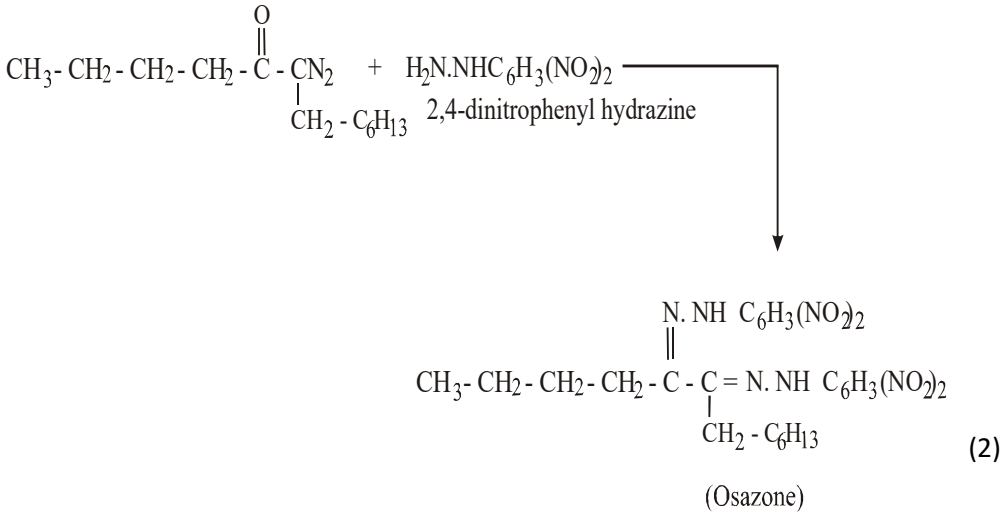
The diazoketone so obtained was characterized by elemental analyses and its reactions with 2,4-dinitrophenyl hydrazine, benzoic acid, phenol, dry hydrochloric acid and silver oxide at 30^0C.

RESULTS AND DISCUSSION

Characterisation of 1-diazo-1-n-heptyl hexan 2-one :

(a)Formation of osazone (reaction with 2,4-dinitrophenyl hydrazine) :

The diazoketone with an aquous alcoholic sulphuric acid solution of 2,4-dinitrophenyl hydrazine gave a 2,4-dinitrophenyl osazone.



(2)

Characterization :

Physical State – orange crystalline solid

M.P. - 128^0C

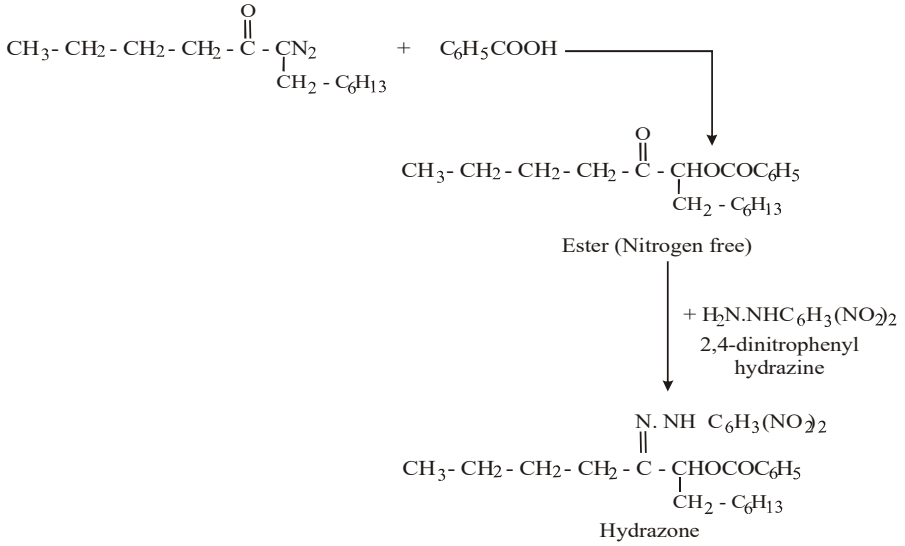
Elemental Analyses :

C=52.44% (obs. 52.54), H=5.39% (obs. 4.89), N = 19.58% (obs. 19.33)

IR (KBr solvent) : 3455 (-NH), 1630 (-C=N), 1610 ($-C_6H_5$), 1332 ($C-NO_2$), 722 cm^{-1} (CH_2 rock in – C_7H_{15})

(b) Action of Benzoic Acid :

The diazoketone on treated with molten benzoic acid gave a nitrogen free brown liquid, which afforded a 2,4-dinitrophenyl hydrazone.



Characterizations

Physical State – orange crystalline solid

M.P. - 225^0C

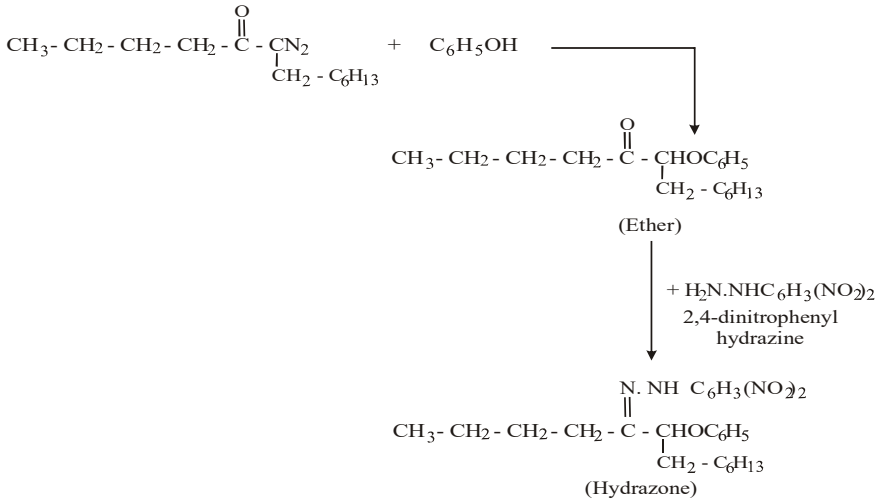
Elemental Analyses :

C = 62.65% (obs. 62.48), H = 6.82% (obs. 5.98), N = 11.24% (obs. 11.84)

IR (KBr solvent) : 2970 (C-Hstr. In – CH_3), 1720 (C=O), 1625 (C=N), 1590 (-C_6H_5), 1330 (C-NO_2), 1310 (C-O-C), 724 cm^{-1} (CH_2 rock in – C_7H_{15}).

(c) Action with Phenol :

The diazoketone on treated with molten phenol, a reddish brown coloured liquid was obtained. It afforded a 2,4-dinitrophenyl hydrazone.



Characterization :

Physical State – orange crystalline solid

M.P. - 205^{0}C

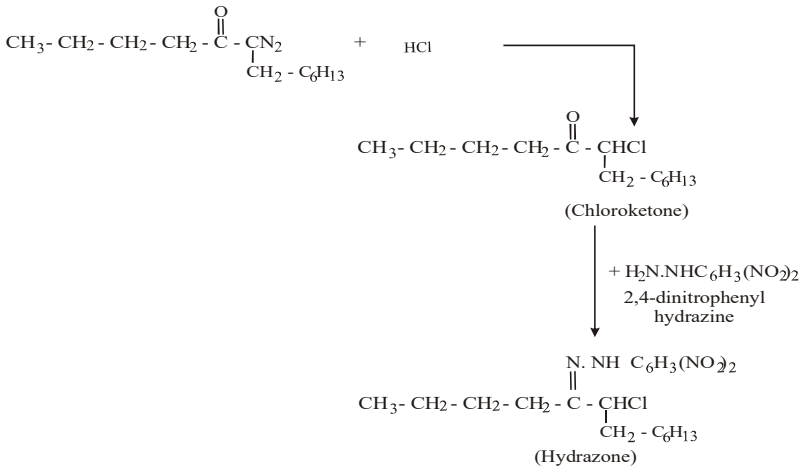
Elemental Analyses :

C=63.82% (obs. 63.52), H =7.23% (obs. 6.88), N = 11.91% (obs. 11.35)

IR (KBr solvent) : 2925 (C-Hstr. In – CH_3), 1630 (C=N), 1615 (-C_6H_5), 1332 (C-NO_2), 1275 (C-O-C), 724 cm^{-1} (CH_2 rock in – C_7H_{15})

(d) Action of dry HCl :

The diazoketone when treated with dry HCl gas, a red liquid was obtained containing chlorine but no nitrogen. It was the extracted chloroketone, which afforded a 2,4-dinitrophenyl hydrazone.



Characterization :

Physical State – Orange Crystalline solid,

M.P. – 226^{0}C

Elemental Analyses :

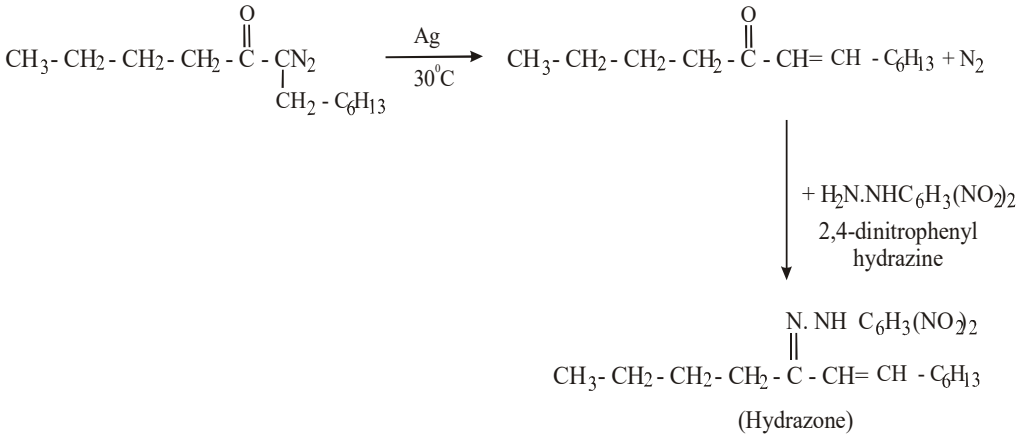
C=55.27% (obs. 55.86), H=7.03% (obs. 7.34),

N=13.57% (obs. 13.07), Cl=8.60% (obs. 8.94)

IR (KBr solvent) : 2950 (C-Hstr. In – CH_3), 1630 (C=N), 1620 (-C_6H_5), 1333 (C-NO_2), 688 (C-Cl), 725 cm^{-1}, (CH_2 rock in – C_7H_{15})

(e) Action of silver oxide :

The diazoketone in dioxan was stirred for two hours at 30^0C in the presence of freshly prepared silver oxide. After filteration, the organic phase was extracted with ether and dried. On removal of ether, nitrogen free yellow liquid was obtained, it formed a 2,4-dinitrophenyl hydrazone.



Characterization :

Physical state - Crystalline solid.
M.P. - 93^0C
Elemental Analyses :
C=60.63% (obs. 60.35), H=7.44% (obs. 7.41), N =14.89% (obs. 14.98)
IR (KBr solvent) : 2955 (C-Hstr. In – CH_3), 1620 (C=N), 1330 (C-NO_2), 945 (CH= CH) 736 cm^{-1} (CH_2 rock in – C_7H_{15}).

CONCLUSION

The characterisation by various physico-chemical techniques suggested the formation of desired products i.e. 1-diazo-1-n-heptyl hexan 2-one.

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