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Action of Diazo-n-Octane on Carboxylic Acid Chloride Having Two Different Sites of Reactivity

KEYWORDS: Diazo-n-octane, 2-methyl acryloyl chloride and Diazoketone

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ABSTRACT *The reaction of 2-methyl acryloyl chloride (1 mol) with diazo-n-octane (2 and 3 mols) gave a mixture of 1-diazo-1-n-heptyl 3-methyl but 3-en 2-one (I) and 3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline (II) respectively in dry ether at 0°C. 2-methyl acryloyl chloride contained two sites of reactivity, an olefinic bond and an acid chloride group. The reactivity of diazoalkanes towards 2-methyl acryloyl chloride is mainly due to the diazogroup present in them. The diazoketones were charactrized by various physico-chemical techniques.*

INTRODUCTION

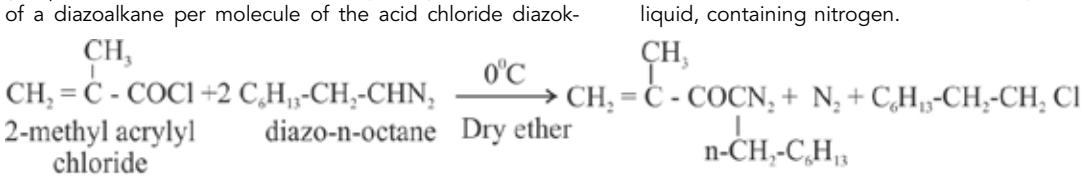
The reaction of diazomethane in recent years has been carried out with various systems and functional groups such as reactive hydrogen, olefinic[1-3] and acetylenic bond, carbonyl group (aldehydic and ketonic) and carboxylic acid chloride or acid anhydride group etc., which may be termed as the sites of reactivity towards it. The action of diazoalkanes on carboxylic acid chlorides or anhydrides[4-6] produce diazoketones. A large number. of diazoketones have been syntesized with lower diazoalkanes by using simple acid chlorides having one site of reactivity[7-10]. Some work has also been done in laboratory in the past few years on the synthesis of diazoketones from carboxylic acid chloride[11-14], containing one or more sites of reactivity towards diazoalkanes. α,β-unsaturated acid chlorides such as 2-methyl acryloyl chloride contained two sites of reactivity towards diazoalkanes, namely an olefinic bond and an acid chloride group. It is possible to attack one or both sites present in them, by using different amounts of diazoalkanes. The acid chloride group is attacked first and therefore by using two molecules of a diazoalkane per molecule of the acid chloride diazoketone, **1-diazo-1-n- hepty-3-methyl but 3-en-2-one (I)** can be synthesized with the olefinic bond intact. By using three molecules of a diazoalkanes the d ouble bond can also be attacked, resulting in the formation of the diazoketones, **3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline (II)** with a pyrazoline ring.

Above diazoketones were light yellow syrupy liquids. The easily removable diazo group present in them, prevented their purification by distillation, even under vaccum.

EXPERIMENTAL

Synthesis of 1-diazo-1-n- heptyl-3-methyl but 3-en-2-one(I) :

2-methyl acryloyl chloride (1.35g, 1 mol) was dissolved in dry ether and cooled under ice. Then it was added in gradually to an etheral solution of pre-estimated diazo-n-octane (3.62g, 2 mols) at 0°C. The reaction mixture was kept overnight. On removing the solvent at room temperature, diazoketone was obtained as a yellow thin syrupy liquid, containing nitrogen.

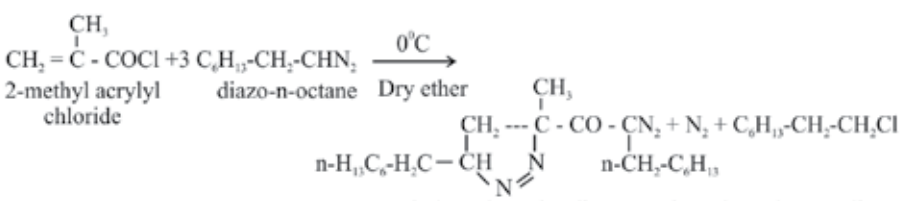


1-diazo-1-n- heptyl-3-methyl but 3-en-2-one

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

Synthesis of 3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline (II) :

2-methyl acryloyl chloride (0.91 g, 1 mol) was dissolved in dry ether and cooled under ice. It was then gradually added to an etheral solution of pre-estimated diazo-n-octane (3.66g, 3 mols) at 0°C. The reaction mixture was kept at low temperature, diazoketone was obtained as a yellow thin syrupy liquid, containing nitrogen.



3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline

The diazoketone so obtained was characterised by elemental analyses and its reactions with 2,4-dinitrophenyl hydrazine, benzoic acid, phenol, and knorr's test.

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

RESULTS AND DISCUSSION

Characterisation of 1-diazo-1-n- heptyl-3-methyl but 3-en-2-one(I) :

a) Formation of 2,4-dinitrophenyl osazone :

The diazoketone with an aqueous alcoholic sulphuric acid solution of 2, 4- dinitrophenyl hydrazine gave a **2,4-dinitrophenyl osazone** as an orange solid, which after crystallisation from ethanol, melted at 125^0**.**

Elemental analyses:

Found(%) : C= 52.01, H = 5.22, N=20.31, $\mathbf{C_{24}H_{28}O_8N_8}$, requires (%) : C= 51.79, H = 5.03, N=21.14).

IR(KBr): 3435 (-NH), 1610(C=N), 1315(C-NO_2), 970(C=C), 734 Cm^{-1} (CH_2 rock in-C_7H_{15}.

b) Action of dry HCl :

With dry HCl gas in ether-acetone mixture at 0^0, formed a red liquid, **chloroketone** containing chlorine**.** It afforded 2, 4- dinitrophenyl hydrazone, crytallised from ethanol melted at 170^0.

Elemental analyses:

Found(%) : C= 54.95, H = 6.38, N=14.31, Cl=8.48, $\mathbf{C_{18}H_{25}O_4N_4Cl}$, requires (%) : C= 54.47, H = 6.30, N=14.12, Cl=8.95).

IR(KBr) : 1612(C=N), 1590(-C_6H_5), 970(C=C), 672(C-Cl), 732 Cm^{-1} (CH_2 rock in-C_7H_{15}.

c) Action of benzoic acid :

The diazoketone on treatment with molten benzoic acid gave a dark brown liquid, an **ester** free from nitrogen**.** It afforded 2,4-dinitrophenyl hydrazone, crytallised from ethanol melted at 171^0.

Elemental analyses:

Found(%): C= 62.38, H = 6.32, N=11.79, $\mathbf{C_{25}H_{30}O_6N_4}$, requires (%) :

C= 62.24, H = 6.22, N=11.6

IR(KBr) : 3350 (-NH), 1730 (C=O), 1605 (C=N), 1580 (-C_6H_5), 1270(C-O-C) 1320(C-NO_2), 965(C=C), 730 Cm^{-1} (CH_2 rock in-C_7H_{15}).

d) Action of phenol :

With phenol gave a nitrogen free red liquid, an **ether.** It afforded 2,4 nitro phenyl hydrazone, crytallised from ethanol melted at 185^0.

Elemental analyses:

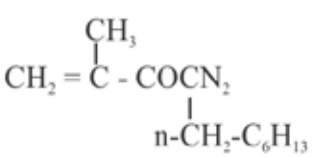
Found(%): C= 63.68, H = 6.71, N=12.42, $C_{24}H_{30}O_5N_4$, requires (%) :

C= 63.43, H = 6.60, N=12.33

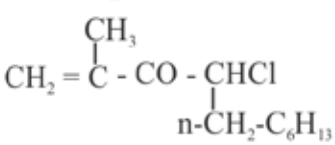
IR(KBr) : 1615 (C=N), 1720 (C=O), 1595 (-C_6H_5), 1272(C-O-C), 970(C=C), 740 Cm^{-1} (CH_2 rock in-C_7H_{15}).

e) Action of silver oxide at 30^0.

The diazoketone, when stirred with freshly prepared silver oxide in dioxin solution at 30^0 gave yellow liquid. It formed a 2,4- dinitrophenyl hydrazone derivative, crystalised from ethanol, melted at 125^0, identical with original osazone. Hence the diazoketone remains unaffected.

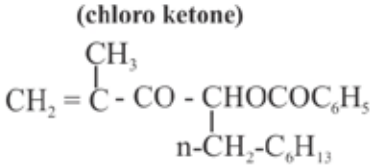


1-diazo-1-n- heptyl-3-methyl but 3-en-2-one



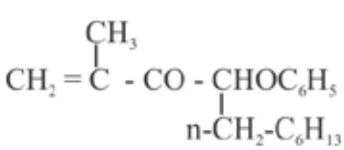
1-chloro-1-n- heptyl-3-methyl but 3-en-2-one

(chloro ketone)



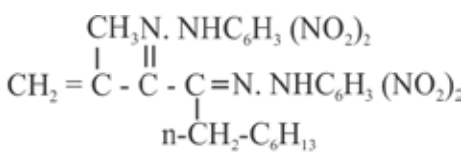
1-benzoyloxy-1-n- heptyl-3-methyl but 3-en-2-one

(ester)

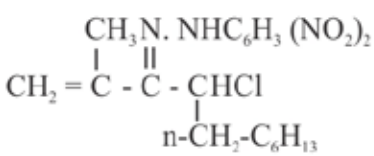


1-phenyloxy-1-n- heptyl-3-methyl but 3-en-2-one

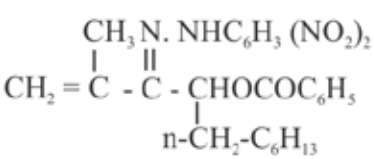
(ether)



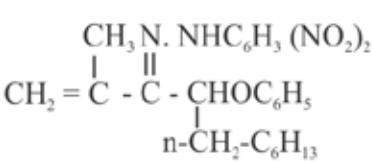
2,4-dinitrophenyl osazone



2,4-dinitrophenyl hydrazone



2,4-dinitrophenyl hydrazone



2,4-dinitrophenyl hydrazone

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Characterisation of 3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline (II) :

a) Formation of 2,4-dinitrophenyl osazone :

The diazoketone with an aqueous alcoholic sulphuric acid solution of 2, 4- dinitrophenyl hydrazine gave a **2,4-dinitrophenyl osazone** as an orange solid, which after crystallisation from ethanol melted at 171^0**.**

Elemental analyses:

Found(%) : C= 55.32, H = 6.41, N=20.39, $\mathbf{C_{32}H_{44}O_8N_{10}}$, requires (%) : C= 55.17, H = 6.32, N=20.11

IR(KBr) : 3440 (-NH), 1622(C=N), 1342(C-NO_2), 745 Cm^{-1} (CH_2 rock in-C_7H_{15}).

b) Knorr's test for Pyrazoline ring :

The diazoketonw when treated with 2 ml. of moderately concentrated sulphuric acid and few drops of sodium dichromate solution, gave a bluish colouration.

c) Action of benzoic acid :

The diazoketone on treatment with molten benzoic acid gave a red liquid, an **ester**, containing nitrogen. It afforded 2,4 nitro phenyl hydrazon,. crytallised from ethanol melted at 202^0.

Elemental analyses:

Found (%) C= 63.66, H = 7.39, N=13.50, $\mathbf{C_{33}H_{46}O_6N_6}$, requires (%) : C= 63.82, H = 7.51, N=13.74

IR(KBr) : 3350 (-NH), 1720 (C=O), 1615 (C=N), 1590 (-C_6H_5), 1320(C-NO_2), 1265 (C-O-C) 734 Cm^{-1} (CH_2 rock in-C_7H_{15}).

d) Action of phenol :

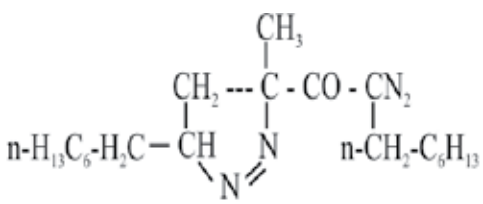
With phenol gave an **ether**, containing nitrogen. It afforded 2,4 nitro phenyl hydrazone, crytallised from ethanol melted at 182^0.

Elemental analyses:

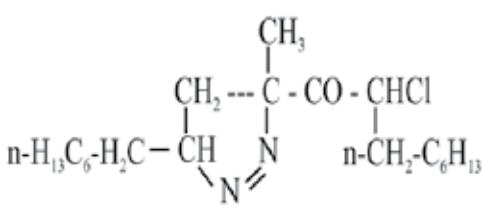
Found(%): C= 64.83, H = 7.99, N=14.41, $\mathbf{C_{32}H_{46}O_5N_6}$, requires (%) :

C= 64.64, H = 7.74, N=14.14

IR(KBr) : 1615 (C=N), 1722 (C=O), 1590 (-C_6H_5), 1265(C-O-C), 935(C=C), 740 Cm^{-1} (CH_2 rock in-C_7H_{15}).

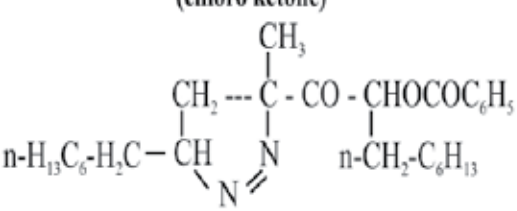


3-methyl 3-n-heptyl 1-diazoacetyl 5-n-heptyl pyrazoline



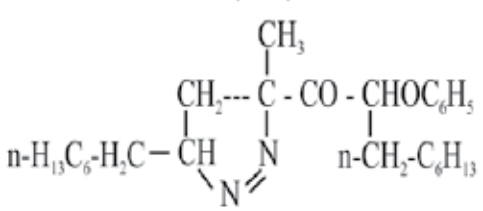
3-methyl 3-n-heptyl 1-chloro 5-n-heptyl pyrazoline

(chloro ketone)



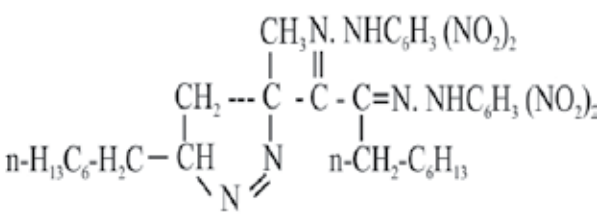
3-methyl 3-n-heptyl 1-benzoyloxy 5-n-heptyl pyrazoline

(ester)

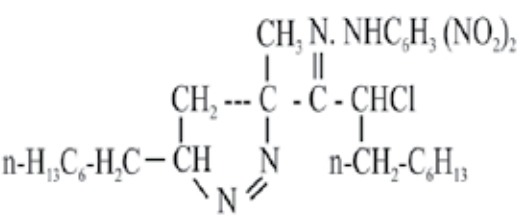


3-methyl 3-n-heptyl 1-phenyloxy 5-n-heptyl pyrazoline

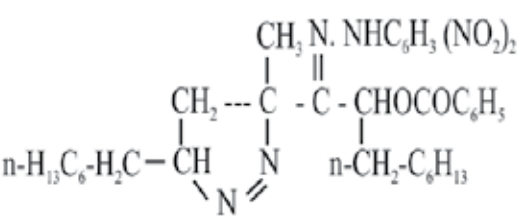
(ether)



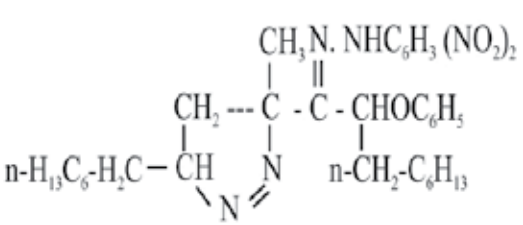
2,4-dinitrophenyl osazone



2,4-dinitrophenyl hydrazone



2,4-dinitrophenyl hydrazone



2,4-dinitrophenyl hydrazone

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