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Synthesis of α-diazoketones by the Action of Diazo-n-octane on 3-methoxy Cinnamoyl Chloride

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ABSTRACT

The reaction of 3-methoxy cinnamoyl chloride (1 mol) with diazo-n-octane (2 mol and 3 mol) gives 1-diazo-1-n-heptyl-4-(3-methoxy) phenyl but 3-ene 2-one and 4-(3-methoxy) phenyl-3-n-heptyl 1-diazoacetyl-5-n-heptyl pyrazoline. The diazoketones were characterised by various physico-chemical techniques.

Keywords: Diazo-n-octane, 3-methoxy cinnamoyl chloride.

INTRODUCTION

A number of methods for synthesis of α-diazo ketones by the reaction of higher diazoalkanes with carboxylic acid chlorides or acid anhydrides[1-4]. The field of synthesis of new α-diazoketones is too wide[5-7]. The study of literature shows that a very little work has been done with higher diazo alkanes[8-10]. By using different amount of diazoalkane, it is possible to attack one or both the sites present in it. By doing so, it is possible to compare the reactivity of these sites[11]. In most cases the acid chloride[12] group is attacked first and the other side afterwards. Thus starting from 3-methoxy cinnamoyl chloride (1 mol) and diazo-n-octane (2 mol and 3 mol) 1-diazo-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one and 4-(3-methoxy) phenyl-3-n-heptyl 1-diazoacetyl-5-n-heptyl pyrazoline were synthesized following the method of Arndt-Eistert.

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

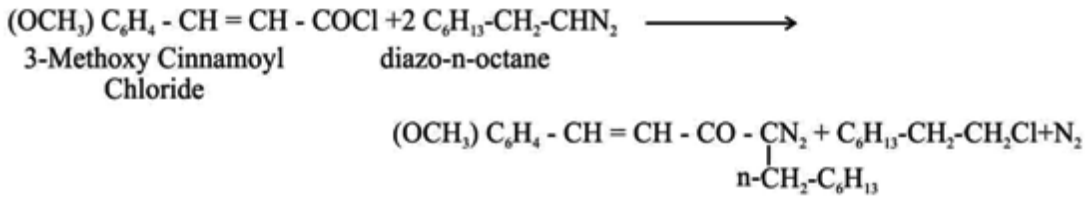
EXPERIMENTAL

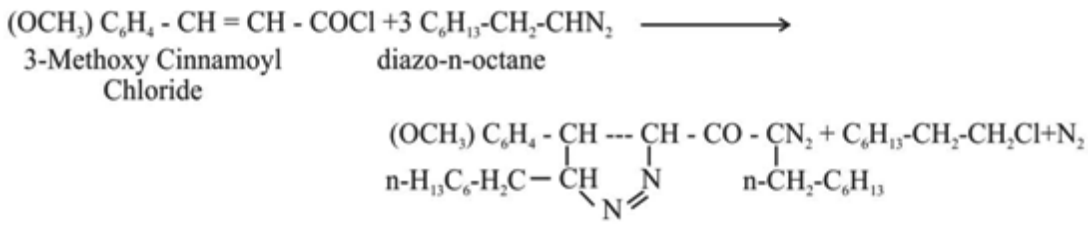
1. Synthesis of 1-diazo-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one : It was prepared by using 3-methoxy cinnamoyl chloride (2.8 g, 1 mol) on pre-estimated diazo-n-octane (3.99 g, 2 mol) at 0^0C. The reaction mixture was then kept at 0^0C overnight. On removal of ether at low temperature the

diazoketone was obtained as yellow mobile liquid which contained nitrogen.

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

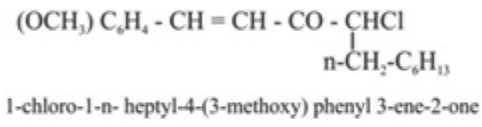
2. Synthesis of 4-(3-methoxy) phenyl-3-n-heptyl 1-diazoacetyl-5-n-heptyl pyrazoline : It was prepared by using 3-methoxy cinnamoyl chloride (2.8 g, 1 mol) on pre-estimated diazo-n-octane (5.98 g, 3 mol) at 0°C. The reaction mixture was then kept at 0°C overnight. On removal of ether at low temperature the diazoketone was obtained as yellow mobile liquid which contained nitrogen.





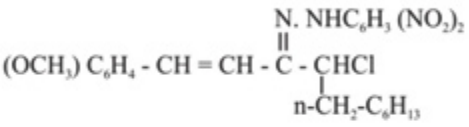
1-diazo-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one

2,4-dinitrophenyl osazone

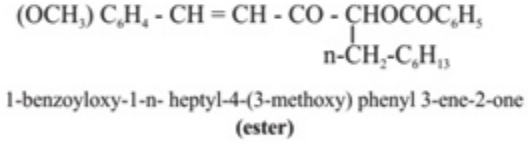


1-chloro-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one

(chloro ketone)

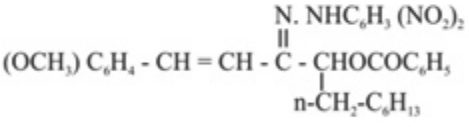


2,4-dinitrophenyl hydrazone

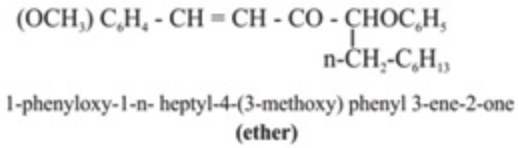


1-benzoyloxy-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one

(ester)

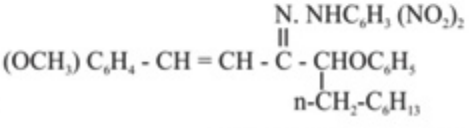


2,4-dinitrophenyl hydrazone



1-phenyloxy-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one

(ether)



2,4-dinitrophenyl hydrazone

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

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

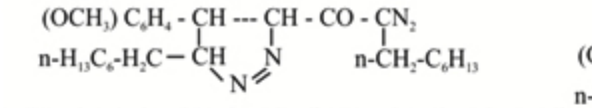
RESULTS AND DISCUSSION

Characterisation of 1-diazo-1-n- heptyl-4-(3-methoxy) phenyl 3-ene-2-one

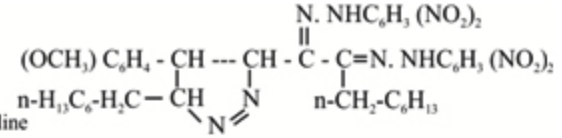
The diazoketone with an aqueous alcoholic sulphuric acid solution of 2, 4- dinitrophenyl hydrazine gave a 2,4-dinitrophenyl osazone as an orange solid, which after crystallisation from ethanol, melted at 158^{0}C (Found C= 55.78%, H = 4.55%, N=17.32%, $C_{30}H_{32}O_9N_8$, required C= 55.55%, H = 4.93%, N=17.28%) absorbed frequencies IR(KBr) : 3435 (-NH), 1632(C=N), 1620 (-C_6H_5), 1355(C-NO_2), 970(-CH=CH-), 724 Cm^{-1} (CH_2 rock in-C_7H_{15}). With dry HCl formed chloroketone afforded 2, 4- dinitrophenyl hydrazone. With benzoic acid gave an ester, afforded 2,4 nitro phenyl hydrazone. (Found C= 63.12%, H = 5.32%, N=9.25%, $C_{31}H_{34}O_7N_4$, required C= 64.80%, H = 5.92%, N=9.75%) absorbed frequencies IR(KBr) : 3350 (-NH), 1720 (C=O), 1615 (C=N), 1580 (-C_6H_5), 1320(C-NO_2), 965(-CH=CH-), 724 Cm^{-1} (CH_2 rock in-C_7H_{15}). With phenol gave an ether, afforded 2,4 nitro phenyl hydrazone.

Characterisation of 4-(3-methoxy) phenyl-3-n-heptyl 1-diazoacetyl-5-n-heptyl pyrazoline

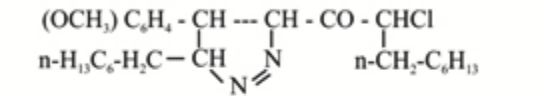
The diazoketone with an aqueous alcoholic sulphuric acid solution of 2, 4- dinitrophenyl hydrazine gave a 2,4-dinitrophenyl osazone as an orange solid, which after crystallisation from ethanol melted at 132^{0}C (Found C= 57.76%, H = 6.20%, N=17.33%, $C_{38}H_{48}O_9N_{10}$, required C= 57.86%, H = 6.09%, N=17.56%) absorbed frequencies IR(KBr) : 3440 (-NH), 1632(C=N), 1620 (-C_6H_5), 1332(C-NO_2), 725 Cm^{-1} (CH_2 rock in-C_7H_{15}). With dry HCl formed chloroketone afforded 2, 4- dinitrophenyl hydrazone. With benzoic acid gave an ester, afforded 2,4 nitro phenyl hydrazone. (Found C= 65.14%, H = 7.25%, N=11.12%, $C_{39}H_{50}O_7N_6$, required C= 65.54%, H = 7.00%, N=11.76%) absorbed frequencies IR(KBr) : 3350 (-NH), 1720 (C=O), 1625 (C=N), 1590 (-C_6H_5), 1320(C-NO_2), 724 Cm^{-1} (CH_2 rock in-C_7H_{15}). With phenol gave an ether, afforded 2,4 nitro phenyl hydrazone.



4-(3-methoxy) phenyl-3-n-heptyl 1-diazoacetyl-5-n-heptyl pyrazoline

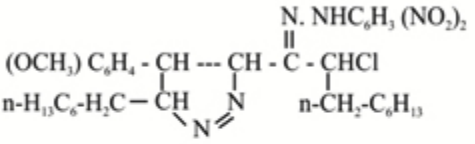


2,4-dinitrophenyl osazone

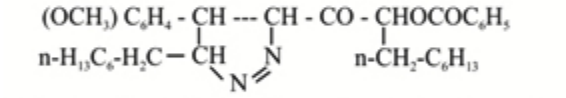


4-(3-methoxy) phenyl-3-n-heptyl 1-chloro-5-n-heptyl pyrazoline

(chloro ketone)

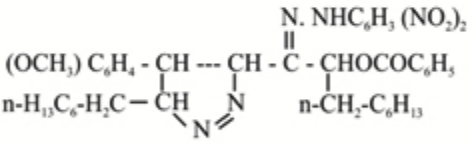


2,4-dinitrophenyl hydrazone

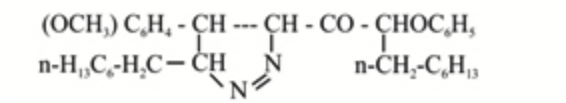


4-(3-methoxy) phenyl-3-n-heptyl 1-benzoyloxy-5-n-heptyl pyrazoline

(ester)

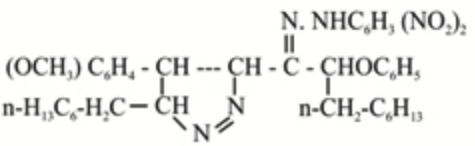


2,4-dinitrophenyl hydrazone



4-(3-methoxy) phenyl-3-n-heptyl 1-phenyloxy-5-n-heptyl pyrazoline

(ether)



2,4-dinitrophenyl hydrazone

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