



Action of Higher Diazoalkanes on 4-n Pentyl Benzoyl Chloride

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ABSTRACT

The reaction of 4-n Pentyl Benzoyl chloride (1 mole) with higher diazoalkane (diazo-n-octane, 2 mole) gives 1-Diazo-3-[4-n-pentyl]-phenyl]-prop-3-one and there characterization are discussed.

Key words: diazoalkane, 4-n Pentyl Benzoyl chloride

INTRODUCTION

The action of diazoalkanes on carboxylic acid chlorides or anhydrides produces diazoketones^{1, 8, 12}. Several workers^{2,4,10,13} have studied the action of only lower diazoalkanes on it. Quite a large number of α -diazoketones, as the survey of literature indicates, have been synthesized elsewhere from simple carboxylic acid chloride, containing only one site reactivity towards diazomethane and in few cases diazoethane also^{6,9,13,14,15,18}. Some work has also been done in laboratory in the past few years on the synthesis of α -diazoketones from carboxylic acid chloride, containing one or more sites of activity 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 sites¹⁷.

The synthesis and reaction of α -diazoketones are well known^{3,7,16}. Therefore attempt was made to synthesise the diazoketones by following the Arndt and Eistert's method⁵ by using two molecules of the diazoalkanes per molecule of carboxylic acid chloride. After working out the reactions mixtures, as before the diazoketones (I) was obtained as light yellow thin syrupy liquid. As the diazoketones decomposed on distillation even under vacuum, therefore they could not be obtained in a pure state.

EXPERIMENTAL

Synthesis of 1-Diazo-3-[(4ⁿ-n-pentyl) -phenyl]-prop-3-one (I)

It was prepared by using a well cooled ethereal solution of 4-n Pentyl benzoyl chloride (1 mol) was added in small installment, over a period of half an hour to an ethereal solution of pre-

estimated diazo-n-octane (3.2g, 2 mole) at 0°C. The reaction mixture was then kept at 0°C overnight. On removal of ether at low temperature, the diazoketone (I) was obtained as a light yellow thin syrupy liquid (yield 2.4 g) with characteristic odour. It contains nitrogen. As diazoketone, in general, decomposed on heating by distillation even under vacuum, hence no attempt was made to purify it.

Characterization

Formation of 2, 4 dinitrophenyl osazone (II) of the diazoketone

The diazoketone with an aqueous alcoholic sulphuric acid solution of 2,4 dinitrophenyl

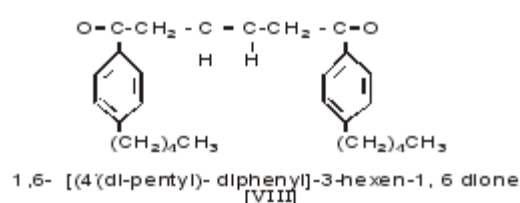
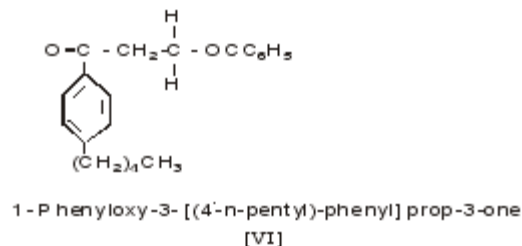
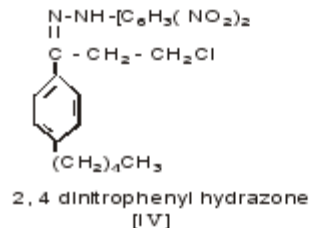
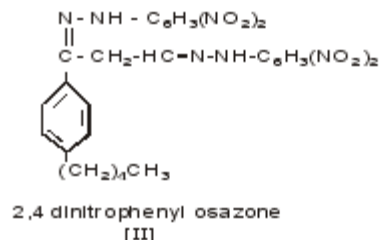
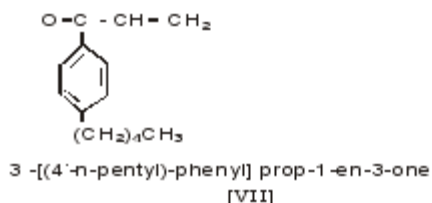
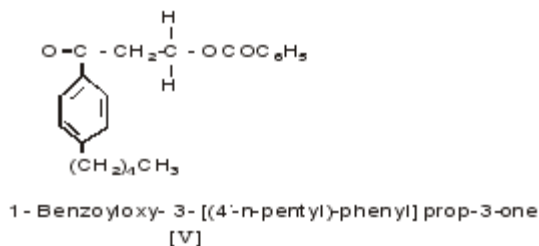
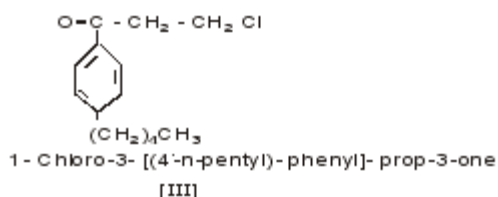
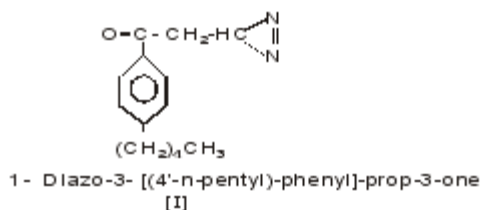
hydrozone gave a 2,4 dinitrophenyl osazone as an orange solid, which after crystallization from ethanol, melted at 123°C.

Estimation of elements in the 2,4 dinitrophenyl osazone (II)

Found C=53.73 % H=4.16% N=18.83 %
 $C_{26}H_{26}O_8N_8$ C=53.97 % H=4.49% N=19.37 %
 (Requires)

Absorbed frequencies in IR region (solvent KBr)

3066 (C-H stretching in aromatic), 1626 (C=N), 1615 (Benzene ring stretching), 1356 (C-NO₂ Stretching), 723 (-CH₂ rocking in -(CH₂)₆CH₃), 2906 cm⁻¹ (-CH stretching in -CH₂)



The diazoketone was dissolved in an ether acetone mixture and the solution was kept at 0°C, dry HCl gas then bubbled through this solution for about an hour, till the evolution of nitrogen ceased. After keeping as such overnight, the reaction mixture was poured in water. This organic

phase extracted with ether, washed and dried. On removal of ether, a reddish liquid containing chlorine but no nitrogen was obtained, it was the expected chloroketone (III). This when reacted with 2,4 dinitro phenyl hydrazine forms 2,4 dinitro phenyl hydrazone (IV), which was crystallised with ethanol, M.P 96 °C.

Estimation of elements in the 2,4 dinitro phenyl hydrazone (IV)

Found	C=57.89%	H=5.16%	N=12.55%	Cl = 8.19%
C ₂₀ H ₂₃ O ₄ N ₄ Cl (Requires)	C=57.41%	H=5.50%	N=13.39%	Cl =8.37%

Absorbed frequencies in IR region (solvent KBr)

1624 (C₆H₅), 1616 (C=N), 724 (-CH₂ rock in (-CH₂)₆ CH₃), 669 (C-Cl), 2918 cm⁻¹ (-CH stretching in -CH₂)

Action of phenol and benzoic acid

A small amount diazoketone (I) was treated with molten phenol and benzoic acid separately. The reaction mixture was heated till the evolution of nitrogen ceased. Next day, the excess of phenol and benzoic acid were removed with dilute NaOH and Na₂CO₃ solution. Then it was extracted with ether washed and dried. On removal of ether, gummy masses were obtained (V, VI), which failed to give any derivative.

Action of silver oxide at 30°C

A small amount of the diazoketone (I) in dioxin was treated with a freshly prepared silver oxide suspended in water. The reaction mixture was stirred at room temperature for four hours. Next day it was filtered and concentrated until two layers separated. The organic phase was extracted with ether, washed and dried. On removal of ether, a yellow coloured liquid (VII) free nitrogen was obtained, it failed to give any derivative.

Action of Cu powder or UV rays

In the presence of Cu powder or UV rays the diazoketone (I) dimerises after loss of nitrogen and form (VIII) namely.

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