



Synthesis of Diazoketones by the Action of Diazo-n-octane on 4-n Pentyloxy chloride

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ABSTRACT

The reaction of 4-n Pentyloxy chloride (1 mole) with higher diazoalkane (diazo-n-octane, 2 mole) gives 1-Diazo-3-[4'-n-pentyloxy]-phenyl]-prop -3-one and their characterization are discussed.

Key words: Diazoalkane, 4-n Pentyloxy chloride.

INTRODUCTION

Diazoalkanes in recent years have been found to be susceptible to various systems and functional groups, such as reactive hydrogen¹², olefinic and acetylenic bonds¹³, carbonyl group⁶ (aldehydic and ketonic), hydroxyl³ and carboxylic acid chloride groups⁵ etc, which may be termed as the sites of reactivity towards them.

The action of diazoalkanes on carboxylic acid chlorides or anhydrides produces diazoketones^{1,6,9}. Several workers^{2,4,7,9} have studied the action of only lower diazoalkanes on it. A large number of such diazoketones have been synthesized with lower diazoalkanes namely diazomethane and in few cases diazoethane only^{9,10,14} by using simple acid chlorides having one

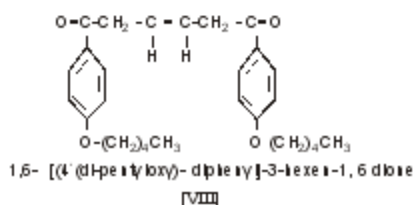
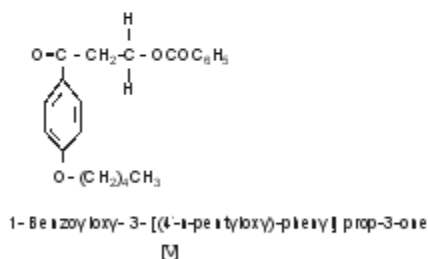
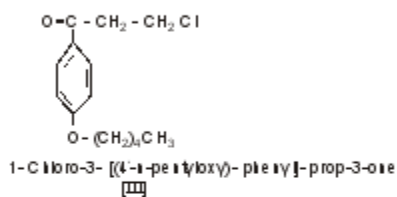
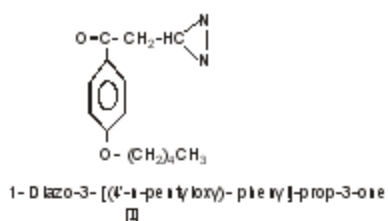
site of reactivity. Some work has also been done in laboratory in the past few years on the synthesis of α -diazoketones from carboxylic acid chloride, containing one or more sites of activity towards diazoalkanes. By using different amounts of a diazoalkane, it is possible to attack one or both the sites present in it. By doing so it is possible to compare the reactivities of these sites¹¹.

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-pentyloxy)-phenyl]-prop-3-one (I)

It was prepared by using a well cooled ethereal solution of 4-n Pentyloxy 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 (3.2 g ,2 mole) at 0Ú C. The reaction mixture was then kept at 0Ú 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 contain nitrogen . As diazoketone, in general decomposed on heating by distillation even under vaccum, hence no attempt was made to purify it.



Characterization

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

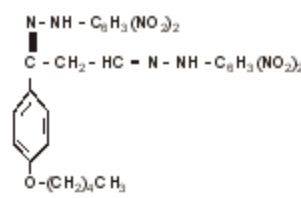
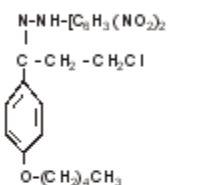
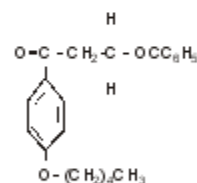
The diazoketone with an aqueous alcoholic sulphuric acid solution of 2,4 dinitro phenyl hydrazine gave a 2,4 dinitro phenyl osazone(II) as an orange solid ,which after crystallization from ethanol, melted at 205°C.

Estimation of elements in the 2,4 dinitrophenylosazone(II)

Found C=48.35 % H=3.71% N=16.95 %
C₂₆H₂₆N₈O₁₂ C=48.59 % H=4.04% N=17.44 %
(Requires)

Absorbed frequencies in IR region (solvent KBr)

3060 (C-H stretching in aromatic) , 1620

**2,4-dinitrophenylhydrazone****2,4-dinitrophenylhydrazide**

(C=N), 1615 (Benzene ring stretching), 1350 (C-NO₂ Stretching), 724 (-CH₂ rocking in -(CH₂)₆ CH₃), 2900 cm⁻¹ (-CH stretching in -CH₂)

Action of dry hydrogen chloride

The diazoketone was dissolved in an ether acetone mixture and the solution was kept at 0°, 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 was extracted with ether, washed and dried. On removal of ether, a reddish liquid containing chlorine but no nitrogen was obtained, it was the expected choroketone (III). This when reacted with 2,4 dinitrophenyl hydrazine forms 2,4 dinitro phenyl hydrazone (IV) which was crystallised with ethanol, M.P 200 °C.

Estimation of elements in the 2,4 dinitrophenylhydrazone (IV)

Found	C=50.68%	H=3.63%	N=10.87%	Cl = 7.02%
C ₂₀ H ₁₉ O ₈ N ₄ Cl (Requires)	C=50.20%	H=3.97%	N=11.71%	Cl =7.32%

Absorbed frequencies in IR region (solvent KBr)

1620 (-C₆H₅), 1620 (C=N), 720 (-CH₂ rock in -(CH₂)₆ CH₃), 675 (C-Cl), 2915 cm⁻¹ (-CH stretching in -CH₂)

Action of phenol and benzoic acid

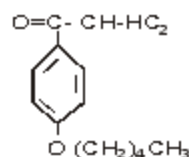
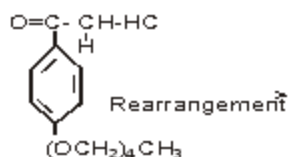
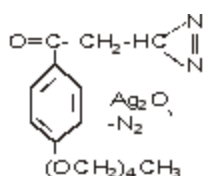
A small amount diazoketone (I) was treated with molten phenol and benzoic acid separately. The reaction mixture was heated till the evolution of nitrogen ceased. Next day, the excess of phenol and benzoic acid were removed with dilute NaOH and Na₂CO₃ solution. Then it was extracted with ether, washed 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.



3- [(4'-pentyloxy)-phenyl] prop-1-en-3-one
[VII]

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