

Action of higher diazoalkanes on 4-nitrocinnamoyl chloride

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ABSTRACT

The reaction of 4-Nitro cinnamoyl chloride (1 mol) with higher diazoalkanes (2 and 4) give a 1-diazo-1-n-alkyl-4-nitro phenyl-3-butenone and 4-nitrophenyl-3-n-alkyl-diazoacetyl-5-n-alkyl-pyrazoline are discussed.

Key words: Diazolkanes, 4-nitrocinnamoyl chloride.

INTRODUCTION

The synthesis and reaction of alpha-diazoketones are well known¹⁻⁴, as the survey of literature indicates, carboxylic acid chloride like 4-nitrocinnamoyl chloride contains two sites of reactivity-susceptible to the action of diazo-alkanes. Several workers⁵⁻⁸, have studied the action of only lower diazoalkanes on it. 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. In most cases the acid chloride groups is attacked first and the other site afterwards. When the other site is also attacked, then in the case of 4-nitrocinnamoyl chloride, a diazoketone containing a pyrazoline ring is formed. Thus starting from 4-nitrocinnamoyl chloride (1 mol) and diazo-n-hexane (2 and 4 mol), 1-diazo-1-n-amylyl-4-nitrophenyl-3-butenone (1) and 4-nitrophenyl-3-n-amylyl-diazoacetyl-5-n-amylyl-pyrazoline (2) were synthesised and with diazo-n-octane (2 and 4 mol), 1-diazo-1-n-heptylyl-4-nitrophenyl-3-butenone (3) and 4-nitrophenyl-3-n-nitrophenyl-diazoacetyl-5-n-heptylyl-pyrazoline (4) were synthesised following the method of Arndt and Eistert.

All the above diazoketones were light yellow mobile liquids. The easily removable diazo group present in them, prevented their purification

by distillation even under vacuum. The diazoketones (1&3) were characterised by the formation of 2,4-dinitrophenylsazone and 4-nitrocinnamoyl chloride by the action of ethanolic KOH but it failed to Arndt and Eistert synthesis and Franzen rearrangement¹⁰. As the diazoketones (2&4) failed to give a 2,4-dinitrophenylsazone, it was characterised by the preparation of a benzoate¹¹ by the action of molten benzoic acid on it. The pyrazoline ring in the diazoketone as well as in the benzoate was indicated by Knorr's test¹².

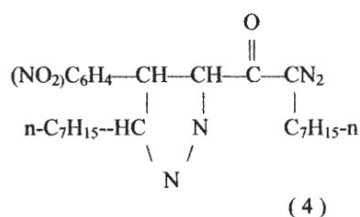
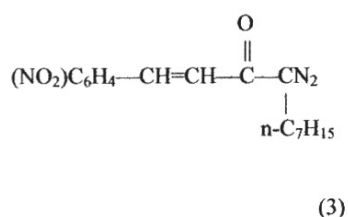
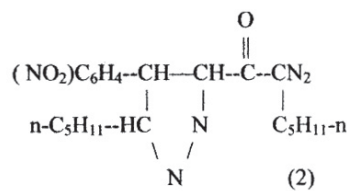
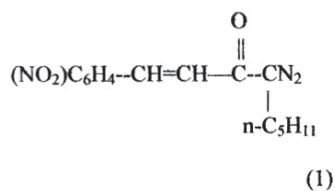
EXPERIMENTAL

1-Diazo-1-n-amylyl-4-nitrophenyl-3-butenon (1)

It was prepared by using 4-nitrocinnamoyl chloride (1 mol, 2.2g) and pre-estimated diazo-n-hexane (2 mol., 2.64g) as a mobile liquid. It formed at 2,4-dinitrophenylsazone, crystallised from ethanol, m.p. 225° (Found C = 51.6%, H = 3.86%, N = 19.6%; C₂₉H₂₉O₁₀N₉ requires C = 51.02%, H = 3.93%, N = 19.84%: absorbed frequencies (-C=N-) 1675, (-CH=VH-) 985, (-CH₂ in n-amylyl group) 740 cm⁻¹. The diazoketone on treatment with ethanolic KOH, gave 4-nitrocinnamic acid, m.p. 290°.

4-Nitrophenyl-3-n-amylyl-diazoacetyl-5-n-amylyl-pyrazoline

Obtained by using 4-nitrocinnamoyl chloride (1 mol., 2.8g) pre-estimated diazo-n-



hexane (4 mol., 5.88g) as a yellow mobile liquid. On treatment with molten benzoic acid, it gave a benzoate which afforded a 2,4-dinitrophenylhydrazone in cold, which was crystallised from chloroform, m.p. 235° (Found C = 60.23%, H = 5.47%, N = 14.25%: C₃₄H₃₉O₈N₇ requires C = 60.62%, H = 5.79%, N = 14.56%; absorbed frequencies (-C=N-) 1620, (C₆H₅COO-) 1720, (-N-N-) 1415, (-CH₂ in amyl group) 722 cm⁻¹.

1-Diazo-1-n-heptyl-4-nitrophenyl-3-butenone(3)

Obtained by using 4-nitrocinnamoyl chloride (1 mol., 2.8g) pre-estimated diazo-n-hexane (4 mol., 3.68g) as a light yellow mobile liquid. It formed a 2,4-dinitrophenylhydrazone, crystallised from ethanol, m.p. 165°C (Found C = 51.1%, H = 3.8%, N = 19.75%, C₂₉H₂₉H₁₀N₉ requires C = 52.48%, H = 4.37%, N = 19%; absorbed frequencies (-C=N-) 1670, (-CH=CH-) 990, (-CH₂ in a n-heptyl group) 740 cm⁻¹. The diazoketone on treatment with ethanolic KOH, gave 4-nitrocinnamic acid, m.p. 289°C.

4-Nitrophenyl-3-n-heptyl-diazoacetyl-5-n-heptyl-pyrazoline (4)

Prepared by using 4-nitrocinnamoyl chloride (1 mol., 2.9g) and diazo-n-octane (4 mol., 7.64g) as a yellow mobile liquid. On treatment with molten benzoic acid, it gave a benzoate which afforded a 2,4-dinitrophenylhydrazone in cold, which was crystallised from chloroform, m.p. 260°C (Found C = 62.18%, H = 6.54%, N = 13.56%, C₃₈H₅₀O₈N₇ requires C=62.29%, H = 6.83%, N = 13.38%, absorbed frequencies (-C=N-) 1625, (C₆H₅COO-) 1715, (-N=N-) 1410, (-CH₂ in n-heptyl group) 720 cm⁻¹.

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