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Synthesis of α-Diazoketone by the Action of Diazoalkanes on Propionic Anhydride

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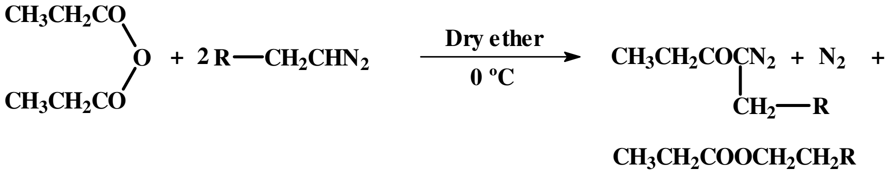
Propionic anhydride reacts with diazo-*n*-alkanes in dry ether at 0 ºC gave 1-diazo-1-*n*-alkyl butanones.

Key Words: α-Diazoketone, Propionic anhydrie, Wolff's and Franzen rearrangement.

INTRODUCTION

A number of methods for the synthesis of α-diazoketones[1-3] are available in literature *e.g.*, Arndt-Eistert method[4], Newmann and Beal method[5], Robinson and Bradley method[6], *etc*. Propionic anhydride was derived from propionic acid by the action of ethyl chloroformate on it. By adopting the method of Robinson and Bradley[6], propionic anhydride (1 mol) was added to diazoalkanes like phenyl diazomethane, diazoethane, diazopropane, diazobutane and diazo-octane (each 2 mol) in dry ether at 0 ºC, after removing of ether, yellow mobile liquid of diazoketones [1-diazo-1-phenyl butanone (I), 1-diazo-1-*n*-methyl butanone (II), 1-diazo-1-*n*-ethyl butanone (III), 1-diazo-1-*n*-propyl butanone (IV), 1-diazo-1-*n*-heptyl butanone (V)] were obtained, as follows:



$$(CH_3CH_2CO)_2O + 2\,R{-}CH_2CHN_2 \xrightarrow[0\ ^\circ C]{\text{Dry ether}} CH_3CH_2COC(N_2)CH_2{-}R + N_2 + CH_3CH_2COOCH_2CH_2R$$

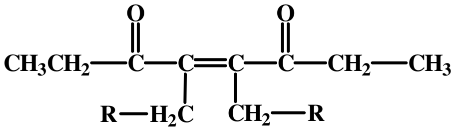
(**I**) R = $-C_6H_5$, (**II**) R = -H, (**III**) R = $-CH_3$, (**IV**) R = $-C_2H_5$, (**V**) R = $-C_6H_{13}$

All the diazoketones are yellow mobile liquid but higher diazoketones were less mobile and more stable than lower diazoketones.

When diazoketones were subjected to the action of benzoic acid, phenol and dry HCl, formed nitrogen free, benzyloxy, phenoxy and chloroketones, respectively. As diazoketones decomposed on distillation even under vaccum, therefore they could not be purified and the reaction was carried out as such. These diazoketones formed hydrazone derivatives with 2,4-dinitrophenyl hydrazine with sharp melting point.

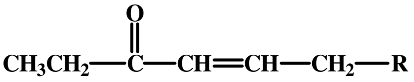
When diazoketones were subjected to the action of a catalyst like silver oxide at different temperatures or photolysis, they gave rise to carbonyl carbenes[8] after elimination of nitrogen. The carbonyl carbenes being highly unstable, then undergo the Franzen rearrangement[9] or the Wolff's rearrangement[10] depending upon their nature and experimental conditions.

Thermolysis of diazoketones in dioxane, in the presence of copper powder, a dimerised product (VI) was obtained free from nitrogen. Irradiation of diazoketones in UV exposure formed a unsaturated ketone (VII) by Franzen rearrangement.



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-\underset{R-H_2C}{\underset{|}{C}}=\underset{CH_2-R}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

(VI)



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH=CH-CH_2-R$$

(VII)

EXPERIMENTAL

1-Diazo-1-phenyl butanone (I) (R= -C_6H_5): Prepared by using propionic anhydride (2.5 g, 1 mol) and pre-estimated phenyl diazomethane (4.52 g, 2 mol) as a yellow mobile liquid. With 2,4-dinitrophenyl hydrazine, it afforded a 2,4-dinitrophenyl osazone as an orange solid, crystallized from ethanol, m.p.: 226 ºC. (Found C = 51.2 %, H = 3.34 %, N= 21.3 %; $C_{22}H_{18}O_8N_8$ requires C = 50.57 %, H = 3.44 %, N= 21.45 %; absorbed frequencies: 3450 (-NH), 1675 (C=N), 1610 (-C_6H_5), 1332 (C-NO_2), 724 cm^{-1} (C-H def. in-CH_3). With HCl formed chloroketone, afforded a 2,4-dinitrophenyl hydrazone. With benzoic acid gave an ester, afforded a 2,4-dinitrophenyl hydrazone (Found C = 61.3 %, H = 4.67 %, N = 11.76 %; $C_{23}H_{20}O_6N_4$ required C = 61.6 %, H = 4.46 %, N = 12.5 %. IR (KBr, ν_{max}, cm^{-1}): 1724 (C=O), 1620 (C=N), 1300 (C-O-C). With phenol formed an ether, afforded a 2,4-dinitrophenyl hydrazone.

1-Diazo-1-*n*-methyl butanone (II) (R=-H): Prepared by using propionic anhydride (2.5 g, 1 mol) and pre-estimated diazo-*n*-ethane (2.14 g, 2 mol) as a yellow mobile liquid. With 2,4-dinitrophenyl hydrazine, it afforded a 2,4-dinitrophenyl osazone as an orange solid, crystallised from ethanol, m.p.: 136 ºC. (Found C = 44.2 %, H = 3.44 %, N = 24.3 %; $C_{17}H_{16}O_8N_8$ required C = 44.34 %, H = 3.47 %, N = 24.34 %; absorbed frequencies 3450 (-NH), 1675 (C=N), 1610 (-C_6H_5), 1332 (C-NO_2), 724 cm^{-1} (C-H def. in -CH_3). With HCl formed chloroketone, afforded a 2,4-dinitrophenyl hydrazone. With benzoic acid, gave an ester, afforded a 2,4-dinitrophenyl hydrazone (Found C = 55.3 %, H = 4.67 %, N = 14.76 %; $C_{18}H_{18}O_6N_4$ required C = 55.95 %, H = 4.66 %, N = 14.5 %; IR (KBr, ν_{max}, cm^{-1}): 1720 (C=O), 1640 (C=N), 1310 (C-O-C). With phenol formed an ether, afforded a 2,4-dinitrophenyl hydrazone.

1-Diazo-1-*n*-ethyl butanone (III) (R=-CH_3): Prepared by using propionic anhydride (2.5 g, 1 mol) and pre-estimated diazo-*n*-propane (2.68 g, 2 mol) as a yellow mobile liquid. With 2,4-dinitrophenyl hydrazine, it afforded a 2,4-dinitrophenyl osazone as an orange solid, crystallised from ethanol, m.p.: 136 ºC. (Found C = 45.34 %, H = 3.13 %, N = 23.33 %; $C_{18}H_{18}O_8N_8$ required C = 45.56 %, H = 3.79 %, N = 23.62 %; absorbed frequencies 3455 (-NH), 1670 (C=N), 1620 (-C_6H_5), 1332 (C-NO_2), 724 cm^{-1} (C-H def. in -CH_3). With HCl formed chloroketone, afforded a 2,4-dinitrophenyl hydrazone. With benzoic acid, gave an ester, afforded a 2,4-dinitrophenyl hydrazone (Found C = 57.3 %, H = 4.67 %, N = 14.76 %; $C_{19}H_{20}O_6N_4$ required C = 57 %, H = 5 %, N = 14 %; IR (KBr, ν_{max}, cm^{-1}): 1722 (C=O), 1645 (C=N), 1320 (C-O-C). With phenol formed an ether, afforded a 2,4-dinitrophenyl hydrazone.

1-Diazo-1-*n*-propyl butanone (IV) (R=-C_2H_5): Prepared by using propionic anhydride (2.5 g, 1 mol) and pre-estimated diazo-*n*-butane (3.22 g, 1 mol) as a yellow mobile liquid. With 2,4-dinitrophenyl hydrazine, it afforded a 2,4-dinitrophenyl osazone as an orange solid, crystallized from ethanol, m.p.: 135 ºC. (Found C = 46.2 %, H = 4.44 %, N = 22.3 %; $C_{19}H_{20}O_8N_8$ requires C = 46.72 %, H = 4.09 %, N = 22.95 %; IR (KBr, ν_{max}, cm^{-1}): 3450 (-NH), 1675 (C=N), 1610 (-C_6H_5), 1332 (C-NO_2), 724 (C-H def. in -CH_3). The diazoketone on treatment with benzoic acid gave an ester, afforded a 2,4-dinitrophenyl hydrazone (Found C = 57.3 %, H = 5.67 %, N = 13.76 %; $C_{20}H_{22}O_6N_4$ required C = 57.97 %, H = 5.31 %, N = 13.52 %; absorbed frequencies 1724 (C=O), 1620 (C=N), 1300 cm^{-1} (C-O-C). With phenol formed an ether, afforded a 2,4-dinitriphenyl hydrazone. In the presence of copper powder in dioxane gave a brown viscous liquid, afforded a 2,4-dinitrophenyl hydrazone. (Found C = 51.98 %, H = 5.56 %, N= 19.21 %; $C_{26}H_{32}O_8N_8$ required C = 53.42 %, H = 5.47 %, N = 19.17 %; IR (KBr, ν_{max}, cm^{-1}): 1685 (C=C), 740 (CH_2 rock in -C_3H_7).

1-Diazo-1-*n*-heptyl butanone (V) (R=-C_6H_{13}): Prepared by using propionic anhydride (2.5 g, 1 mol) and pre-estimated l diazo-*n*-octane (5.38 g, 1 mol) as a yellow mobile liquid. With 2,4-dinitrophenyl hydrazine, it afforded a 2,4-dinitrophenyl osazone as an orange solid, crystallised from ethanol, m.p.: 170 ºC. (Found C = 50.2 %, H = 5.44 %, N = 20.3 %; $C_{23}H_{28}O_8N_8$ required C = 50.73 %, H = 5.14 %, N = 20.58 %; IR (KBr, ν_{max}, cm^{-1}): 3450 (-NH), 1675 (C=N), 1610 (-C_6H_5), 1332 (C-NO_2), 724 cm^{-1} (C-H def. in -CH_3). The diazoketone on treatment with benzoic acid gave an ester, afforded a 2,4-dinitrophenyl hydrazone. (Found C = 61.3 %, H = 6.67 %, N = 11.76 %; $C_{24}H_{30}O_6N_4$ required C = 61.01 %, H = 6.77 %, N = 11.86 %; IR (KBr, ν_{max}, cm^{-1}): 1724 (C=O), 1620 (C=N), 1300 (C-O-C). With phenol formed an ether, afforded a 24-dinitrophenyl hydrazone. With siver oxide at 30 ºC in dioxane gave a nitrogen free brown liquid, afforded a 2,4-dinitrophenyl hydrazone. (Found C = 58.44 %, H = 6.87 %, N = 15.67 %; $C_{17}H_{24}O_4N_4$ required C = 58.62 %, H = 6.89 %, N = 16.09 %; IR (KBr, ν_{max}, cm^{-1}): 1683 (C=C), 722 cm^{-1} (CH_2 rock in C_7H_{15}).

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