

A STUDY OF THE OXIDATION OF SECONDARY ALCOHOLS WITH RANEY NICKEL

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Studies were conducted to determine the comparative efficacy of some potential hydrogen acceptors such as ethyl acetoacetate, benzal acetone and benzaldehyde to effect the oxidation of secondary alcohols to the corresponding ketones with Raney nickel. All experiments were carried out at reflux temperature and ordinary Raney nickel was employed. Ethyl acetoacetate and benzal acetone were found more effective than benzaldehyde.

INTRODUCTION

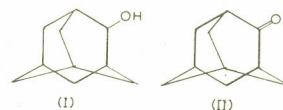
The oxidation of primary and secondary alcohols to aldehydes and ketones can be done by heating the alcohols with an excess of suitable ketone in presence of aluminium ter-butoxide [1]. The use of Raney nickel as a catalyst in effecting various reductive transformations of organic compounds is quite well known [2-4]. It is also known that the carbonyl group of an aldehyde and ketone may be converted to the hydrocarbon by the reduction of their thioacetals with Raney nickel in dilute ethanol solutions [5]. It has been reported that certain secondary alcohols may be dehydrogenated catalytically with Raney nickel to the corresponding ketones at higher temperatures, i.e. up to 250° and even then the yield is very low [6]. Chakravarti and Robinson [7] carried out a conversion of the strychnine into an isomeric product neostrychnine by refluxing the former in xylene solution in the presence of Raney nickel catalyst. Kleiderer and Kornfield [8] reported that the attempted oxidation of cholesterol to cholestenone by using cyclohexanone as hydrogen acceptor and special aerated Raney nickel catalyst gave lower yields as compared to the usual Raney nickel kept under toluene. Chakravarti *et al.* [9-10] observed that when cholesterol was heated under reflux with large excess of Raney nickel in a solvent like *p*-cymene, having a boiling point 177°; a dimer was formed having a molecular formula C₅₄H₉₀O.

RESULTS AND DISCUSSIONS

This work records the comparative efficacy of the following hydrogen acceptors to effect the oxidation with Raney nickel: (i) Ethyl acetoacetate. (ii) Benzal acetone.

(iii) Benzaldehyde.

The experimental procedure involved merely refluxing a mixture of the compound to be oxidised with Raney nickel and hydrogen acceptor in toluene. The results of the oxidation of various secondary alcohols with Raney nickel and ethyl acetoacetate are given in Table 1. It was observed during the oxidation of 2-adamantanol(I) [11] to 2-adamantanone (II) [12] that the special aerated Raney nickel was not better than the ordinary Raney nickel kept under toluene. For this reason ordinary Raney nickel was employed in all the subsequent reactions.



The oxidation of secondary alcohols was also effected with benzal acetone and the results are given in Table 2. The results of oxidation with ethyl acetoacetate and benzal acetone as hydrogen acceptors are promising. The oxidation of 1, 4-cyclohexanediol to 1, 4-cyclohexanedion with ethyl acetoacetate and benzal acetone gave low yield (Tables 1 and 2) probably due to the fact that when enough 1,4-cyclohexanedion is formed, a state of oxidation-reduction equilibrium is reached because 1,4-cyclohexanedion is a potential hydrogen acceptor. Similarly the oxidation of 1,4-cyclohexanediol with Raney nickel and benzaldehyde also gave poor yield.

The choice of benzaldehyde as a hydrogen acceptor was made due to two main reasons. Firstly, it has a favourable oxidation potential [13] and secondly, on reduction it is converted to toluene [8] which is already present in the reaction mixture and no other side product is formed.

Table-1. Oxidation with ethyl acetoacetate and Raney nickel. (refluxed for 20 hr).

Compound oxidised	Product isolated	Yield (%)
2-Adamantanol	2-Adamantanone	76
Cholestanol	Cholestanone	85
9-Fluorenol	Fluorenone	80
Diundecylcarbinol	Laurone	64
1,4-Cyclohexanediol	1,4-Cyclohexanedione	47

Table 2. Oxidation with benzal acetone and Raney nickel (refluxed for 20 hr).

Compound oxidised	Product isolated	Yield (%)
2-Adamantanol	2-Adamantanone	80
Cholestanol	Cholestanone	78
9-Fluorenol	Fluorenone	75
Diundecylcarbinol	Laurone	58
1,4-Cyclohexanediol	1,4-Cyclohexanedione	52

Table 3. Oxidation with benzaldehyde and Raney nickel. (refluxed for 24 hr.)

Compound oxidised	Product isolated	Yield (%)
2-Adamantanol	2-Adamantanone	60
Cholestanol	Cholestanone	62
9-Fluorenol	Fluorenone	50
Diundecylcarbinol	Laurone	56
1,4-Cyclohexanediol	1,4-Cyclohexanedione	40

The results of the oxidation of some secondary alcohols with Raney nickel and benzaldehyde are given in Table 3.

When cholestanol was refluxed with an excess of Raney nickel and any one of the hydrogen acceptors such as ethyl acetoacetate, benzal acetone and benzaldehyde, no dimer [9] was formed and the only product obtained was identified as cholestanone.

Of all the three reagents employed for oxidation of secondary alcohols with Raney nickel; ethyl acetoacetate and benzal acetone were found more effective than benzaldehyde. The superiority consists in that both produce corresponding ketones in better yields.

EXPERIMENTAL

The identity of the final products formed in the oxidation was established by mixed m. ps. determinations with authentic samples and comparison of IR spectra with the

standard.

Preparation of Raney Nickel Catalyst [14] The nickel aluminium alloy powder (300 mg) was added in the course of half-hour to a stirred solution of NaOH (400 g) in water (1.5 l) and temperature maintained at 75°. Digestion at a gradually decreasing temperature was continued for an additional ½ hr. The supernatant liquid was decanted and the catalyst was thoroughly washed with distilled water until the washings were found to be neutral by pH hydron paper. The water was decanted and replaced with toluene. The traces of water were completely removed with Dean and Stork apparatus. The catalyst was refluxed for 4 hr with toluene and finally stored under toluene.

Action of Raney Nickel on 2-Adamantanol. (a) With Ethyl Acetoacetate: 2-Adamantanol (3.8 g, 0.025 mole) ethyl acetoacetate (32.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux at 114° for 20 hr. After the reaction, the mixture was filtered and the filtrate distilled under reduced pressure. The residue obtained was crystallised from cyclohexane to furnish 2-adamantanone as colourless needles (2.88 g; yield 76%). M.P. and mixed m.p. with authentic sample of 2-adamantanone, 285–86°. The identity was confirmed by comparison of IR spectra.

The identity of 2-adamantanone was further established by converting the isolated product to oxime by refluxing with hydroxylamine in ethanol; 2-adamantanone oxime, m.p. 163° [11].

(b) With Benzal Acetone: 2-Adamantanol (3.8 g, 0.025 mole), benzal acetone (36.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were refluxed at 115° for 20 hr. The catalyst was removed by filtration and the filtrate was distilled under reduced pressure and the residue obtained was crystallised from cyclohexane to furnish 2-adamantanone (3.04 g, yield 80%).

(c) With Benzaldehyde: 2-Adamantanol (3.8 g, 0.025 mole) in toluene (100 ml) and Raney nickel (10 g) were refluxed with efficient stirring, while benzaldehyde (31.8 g, 0.3 mole) was added gradually in 4 hr. The contents were refluxed at 113–115° for another 20 hr. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. This gave 2-adamantanone (2.28 g, 60%).

Action of Raney Nickel on Cholestanol. With ethyl acetoacetate: Cholestanol (3.88 g, 0.01 mole), ethyl acetoacetate (32.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux at 114° for 20 hr. A pale yellow gummy residue was obtained. This on crystallisation from ethanol-acetone furnished cholestanone (3.30 g, yield 85%), m.p. and mixed m.p. with authentic sample of cholestanone, 129°. The identity was confirmed

by comparison of the IR spectra.

The above experiment was repeated by employing three time excess of Raney nickel. It gave only cholestanone (80–84% yield) and no dimer [9] could be isolated.

With Benzal Acetone: Cholestanol (3.88 g, 0.01 mole), benzal acetone (36.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux at 115° for 20 hr. This yielded cholestanone (3.03 g, 78%).

With Benzaldehyde: Cholestanol (3.88 g, 0.01 mole), Raney nickel (10 g) and toluene (100 ml) were heated under reflux, while benzaldehyde (31.8 g, 0.3 mole) was added slowly in 4 hr. The contents were refluxed at 113–115° for another 20 hr. This yielded cholestanone (2.41 g, 62%).

Action of Raney Nickel on Fluorenol. With Ethyl Acetoacetate: Fluorenol (4.5 g, 0.025 mole), ethyl acetoacetate (32.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux at 114° for 20 hr. After the reaction, the mixture was filtered and the filtrate was washed with 5% solution of NaOH (3 X 75 ml), then with water (2 X 50 ml). The solvent was evaporated under reduced pressure. The residue obtained was crystallised from ethanol to furnish fluorenone (3.62 g, yield 80%), m.p. and mixed m.p. with authentic sample of fluorenone, 83.0°. The identity was confirmed by comparison of IR spectra.

With Benzal Acetone: Fluorenol (4.5 g, 0.025 mole), benzal acetone (36.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were refluxed at 115° for 20 hr. After the reaction, the mixture was worked up in the usual way. This gave fluorenone (3.39 g, yield 75%).

With Benzaldehyde: Fluorenol (4.5 g, 0.025 mole), Raney nickel (10 g) and toluene (100 ml) were heated under reflux, while benzaldehyde (31.8 g, 0.3 mole) was added slowly in 4 hr. The contents were refluxed at 113–115° for another 20 hr. The reaction mixture was worked up in the usual way and yielded fluorenone (2.26 g, 50%).

Action of Raney Nickel on Diundecylcarbinol. With Ethyl acetoacetate: Diundecylcarbinol (3.4 g, 0.01 mole), ethyl acetoacetate (32.5 g, 0.25 mole), Raney nickel (10.0 g) and toluene (150 ml) were heated under reflux at 114° for 20 hr. Proceeding in the usual way a crystalline residue was obtained which on crystallisation from acetone afforded laurone (2.18 g, yield 64%) m.p. and mixed m.p. with authentic specimen, 69.0°. The identity was confirmed by comparison of spectra.

With Benzal Acetone: Diundecylcarbinol (3.4 g, 0.01 mole), benzal acetone (36.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux with efficient stirring at 115° for 20 hr. After the reaction the mixture was worked up in the usual way. This yielded laurone (1.97 g, 58%).

With Benzaldehyde: Diundecylcarbinol (3.4 g, 0.01 mole), Raney nickel (10 g) and toluene (100 ml) were refluxed with efficient stirring, while benzaldehyde (31.8 g, 0.3 mole) was added slowly in 4 hr. The reaction mixture was refluxed at 113–115° for another 20 hr. The reaction mixture was worked up in a usual way. This yielded laurone (1.90 g, 56%).

Action of Raney Nickel on 1,4-Cyclohexanediol. With Ethyl Acetoacetate: 1,4-Cyclohexanediol (5.8 g, 0.05 mole), ethyl acetoacetate (32.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were heated under reflux with efficient stirring at 114° for 20 hr. The reaction mixture was filtered and the filtrate was removed under reduced pressure. The residue obtained was crystallised from water to give 1,4-cyclohexanedion (2.73 g, yield 47%), m.p. and mixed m.p. with authentic specimen, 78.0°. The identity of 1,4-cyclohexanedion was established by converting the isolated product solution to *p*-benzoquinone m.p. 115° by refluxing with ferric chloride.

With Benzal Acetone: 1,4-Cyclohexanediol (5.8 g, 0.05 mole), benzal acetone (36.5 g, 0.25 mole), Raney nickel (10 g) and toluene (150 ml) were refluxed at 115° for 30 hr. The reaction mixture was worked up as described above. This afforded 1,4-cyclohexanedion (3.02 g, yield 52%).

With Benzaldehyde: 1,4-Cyclohexanediol (5.8 g, 0.05 mole), Raney nickel (10 g) and toluene (100 ml) were heated under reflux while benzaldehyde (31.8 g, 0.3 mole) was added slowly in 4 hr. The reaction mixture was refluxed at 113°–115° for another 20 hr. The reaction mixture was worked up in the usual way and yielded 1,4-cyclohexanedion (2.32 g, 40%).

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