FORMATION OF SULPHUR COMPOUNDS IN HYDRODENITROGENATION OF QUINOLINE, 1,2,3,4-TETRAHYDROQUINOLINE, PYRIDINE, PIPERIDINE AND 1-PENT-4-ENYLAMINE ON A NICKEL–TUNGSTEN CATALYST IN THE PRESENCE OF HYDROGEN SULPHIDE

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Hydrodenitrogenation (HDN) of quinoline and 1,2,3,4-tetrahydroquinoline on a sulphided nickel–tungsten catalyst in the presence of hydrogen and of its mixture with hydrogen sulphide has been studied in an autoclave at 350°C. The results show that hydrogen sulphide exhibits rate-accelerating effect on HDN of the above compounds by formation of sulphur compounds. It was found that neutral portion of the reaction mixture contains octahydro-2*H*-1-benzothiopyran, octahydro-1*H*-2-benzothiopyran, octahydro-2-methylbenzo(*b*)thiophene and other sulphur compounds. The reaction scheme for HDN of quinoline that accounts for favourable effect of hydrogen sulphide is proposed. In the neutral portion of the reaction mixture from HDN of piperidine and 1-pent-4-enylamine in the presence of hydrogen sulphide further sulphur-containing compounds were identified.

Hydrogenolysis of quinoline as a model compound on industrial catalysts has been studied not only in the presence of hydrogen[1–8] or hydrogen and hydrogen chloride[9], but especially in recent years also in the presence of hydrogen and hydrogen sulphide[10–15]. It was found that hydrogen sulphide is an important factor in hydrodenitrogenation (HDN) of nitrogen compounds as well as are organic bases in hydrodesulphurization (HDS) of sulphur compounds. Both reactions HDS and HDN, are not advisable to study separately, as their reaction products affect each other. It was found that the presence of hydrogen sulphide or sulphur compounds that evolve hydrogen sulphide during hydrogenolysis *a*) retards hydrogenation of benzene ring in the case of quinoline[10,14] and other aromatic systems[13], *b*) accelerates hydrogenation of the ring containing nitrogen atom[10,12,13], *c*) facilitates the cleavage of C–N bonds in saturated heterocyclic ring and in transiently formed amines. As sulphidation of catalysts does not exert significant effect on the cleavage of C–N bonds, it is assumed that this reaction is not catalysed by metal sulphides and that it proceeds on the support[13]. The mechanism of this reaction corresponds to Hofmann E-2 cleavage[12,16]. Some authors prefer the presumption that the cleavage of C–N bonds takes place on oxidation-reduction sites of catalysts as a result of hydrogenolysis[6].

These three effects mentioned above lead to the increase in the extent of HDN of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline[12–14]. Similarly to HDN of pyridine and

piperidine, hydrogen sulphide *a*) increases the acidity of surface of aluminium oxide used as support[10,13,14], *b*) maintains the catalyst in fully sulphided state[10], *c*) enables migration of Ni or other active metal atoms to the support surface[13] and affects thus the cleavage of C–N bonds, *d*) forms active complex compounds on catalyst surface that are unstable and undergo decomposition in the absence of hydrogen sulphide[13], *e*) reacts with nitrogen-containing compounds[10,12]. In the course of these reactions there can proceed formation of compounds containig-SH group that is then cleaved in further stages of the reaction[12]. A similar reaction leads to formation of 2-(3-chloropropyl)aniline in HDN of quinoline in the presence of hydrogen chloride[17].

As follows from the above discussion, the main reason of the increase in the rate of HDN of quinoline, 1,2,3,4-tetrahydroquinoline and decahydroquinoline caused by hydrogen sulphide is assumed to be above all the increased activity of catalyst. Formation of sulphur compounds as intermediates has not yet been proved.

In our previous work[18] we reported on HDN of pyridine, piperidine and 1-pent-4-enylamine at 300°C and a pressure of 14–16 MPa on a sulphided nickel–tungsten catalyst with the use of hydrogen and hydrogen sulphide. In the neutral portion of the reaction mixture we found a series of new compounds, of which four compounds containing sulphur have been identified: 1-pentanethiol, di(1-pentyl) sulphide, 2-methylthiacyclopentane, and thiacyclohexane. Although the structure of other compounds was not known and is reported in the present work, the results obtained clearly demonstrated that hydrogen sulphide increased the conversion of above compounds by formation of new sulphur compounds. Based on these results, the reaction mechanism of HDN of pyridine and piperidine in the presence of hydrogen sulphide has been proposed.

These results led us to analyse in more detail the reaction mixture obtained by HDN of quinoline and 1,2,3,4-tetrahydroquinoline by hydrogen in the presence of hydrogen sulphide on the same catalyst. The assumption about formation of new compounds by reaction of reaction intermediates with hydrogen sulphide was fully justified and a series of new sulphur compounds was found in acidic and neutral portion of the reaction mixture. Detailed analysis and proof of the compounds detected were made possible by peerforming HDN in an autoclave with the use of pure compounds. Such an arrangement is, of course, far from modelling industrial conditions under which HDS and HDN are carried out, but the absence of solvent in the reaction mixture allowed to identify also those compounds that were present in low concentrations. On the basis of this study the reaction mechanism of HDN of quinoline in the presence of hydrogen sulphide has been proposed which accounts for the favourable effect of hydrogen sulphide on HDN of compounds of this type.

At the same time, in the present work we continued in the study of neutral and acidic portion obtained by HDN of 1-pent-4-enylamine in the presence of hydrogen sulphide[18]. With the use of preparative gas chromatography we were able to identify a series of other compounds on the basis of their mass spectra. For purposes of reliable identification, some compounds were synthesized as model substances.

EXPERIMENTAL

Compound used. Quinoline was rectified and then converted into sulphate that was crystallized three times from ethanol. The base released was rectified and the fraction boiling at 101—102°C/1·3 kPa used. 1,2,3,4-Tetrahydroquinoline was obtained by hydrogenation of quinoline in aqueous ethanolic NaOH solution by excess Ni–Al alloy powder[19]. The procedure was modified such that after the reduction, ethanol and all the present neutral compounds were removed by steam distillation from acidic solution and then the solution was made alkaline and the product was obtained by steam distillation. The crude product was extracted with ether and dried with KOH pellets to give the pure tetrahydro derivative by rectification.

Model compounds. 1-Pentanethiol, cyclopentanethiol, di(1-pentyl) sulphide, dicyclopentyl sulphide, di(1-pent-4-enyl) sulphide, cyclopentyl 1-pentyl sulphide, and di(1-pentyl) sulphide were obtained by reported procedures. 1-Pent-4-enylmercaptane, prepared by reaction of 1-pent-4-enyl bromide with thiourea[20,21], underwent cyclisation and polymerisation during distillation to give 2-methylthiacyclopentane and thiacyclohexane.

Preparation of catalyst was reported earlier[22]. The analysis of reaction mixtures was made on an instrument equipped with a flame ionisation detector, using 10% methyl phenyl silicone on Chromosorb W (column length 3 m) and 5% OV-17 silicone elastomer on Inerton AW (column length 2·5 m). Preparative gas chromatography was carried out on Chrom 3 instrument equipped with thermal conductivity detector, using 10·3% E 302 silicone elastomer on Chromaton N (column length 2·4 m).

Cyclopentyl 1-pent-4-enyl sulphide. 1·02 g of cyclopentanethiol was dissolved in a solution of 0·56 g of KOH in 3 ml of 96% ethanol. After cooling, 1·5 g of 1-pent-4-enyl bromide were added. After the initial reaction had subsided, during which KBr precipitate formed, the reaction mixture was refluxed for 1 h, the cooled mixture was poured into water and extracted with ether. The extracts were combined, dried over calcium chloride and distilled to give 0·85 g of the product boiling at 98—99°C/1·3 kPa. For $C_{10}H_{18}S$ (170·3) calculated: 70·52% C, 10·65% H; found: 70·30% C, 10·56% H. 1-Pent-4-enyl 1-pentyl sulphide was prepared in a similar way, from 1-pentanethiol and 1-pent-4-enyl bromide, in 68% yield. The product boiled at 95—96°C/1·3 kPa. For $C_{10}H_{20}S$ (172·3) calculated: 69·70% C, 11·70% H; found: 69·40% C, 11·49% H.

trans-2-*Allylcyclohexanethiol* was obtained by reaction of 1,2-epithiacyclohexane with allylmagnesium bromide[23,24]. After distillation, the product (b.p. 84—85°C/1·6 kPa) contained *trans*-2-allylcyclohexanethiol as the main component, along with *trans*-octahydro-2*H*-1-benzothiopyran and octahydro-2-methylbenzo(*b*)thiophene, both compounds being in approx. same amounts. The distillate contained also 3-allyl-1-cyclohexene which was formed from the compound to be prepared by elimination of hydrogen sulphide during decomposition of the reaction mixture after Grignard reaction. The amount of both cyclic compounds in the distillate increased slowly on standing the distillate at room temperature. Mass spectrum confirmed the structure of four compounds mentioned above.

Hydrogenolysis of 1,2,3,4-tetrahydroquinoline. The starting compound (20 g) and 0·50 g of the catalyst was heated in an autoclave for 8 h at 300°C. The initial hydrogen pressure was 8·5 MPa, maximal pressure was 14·5 MPa. After cooling, the pressure decreased to 6·5 MPa. The portion of the reaction mixture (14·7 g) was diluted with 15 ml of water and acidified with dilute HCl to weakly acidic reaction. After extraction with 8 ml of ether, the ether layer was separated and concentrated by distillation, yielding *c.* 0·05 g of neutral portion. Treatment of 17·4 g of the reaction mixture from hydrogenolysis at 350°C afforded the ether extract which was distilled to give 0·45 g of the fraction boiling at 80—200°C/1·3 kPa. The distillation residue weighed

0·05 g. The fraction contained propylcyclohexane (90%) as the main component, cyclohexane, methylcyclohexane, ethylcyclohexane, propylbenzene, ethylmethylbenzene, C_9 and C_{10} hydrocarbons (*c.* 9%) and higher boiling substances (*c.* 1%). Nearly the same composition of the neutral portion was obtained also in the case of HDN carried out at 300°C, except that the mixture contained less than 1% of the higher boiling portion and about 25% of propylcyclohexane.

Hydrogenolysis of 1,2,3,4-*tetrahydroquinoline in the presence of hydrogen sulphide.* The tetrahydro derivative (20·0 g) and 0·50 g of the catalyst were placed in an autoclave which was purged with hydrogen and then pressured by hydrogen sulphide from a pressure cylinder to a pressure of 1·85 MPa and then by hydrogen to a pressure of 6 MPa. The autoclave was heated to 350°C for 8 h. Maximum pressure was 14·5 MPa. During heating, hydrogen pressure was increased twice from 11·3 to 13·8 MPa. After cooling, 16·8 g of the reaction mixture was diluted with 17 ml of water, acidified by dilute HCl and extracted with 8 ml of ether. Distillation gave 1·30 g of the fraction boiling at 80—150°C/1·3 kPa and 0·30 g of the distillation residue. The fraction was divided into two portions by preparative gas chromatography, fraction 1 (0·50 g) and fraction 2 (0·12 g). As found by GC/MS analysis, fraction 1 of neutral portion of the reaction mixture after HDN of 1,2,3,4-tetrahydroquinoline contained in addition to propylcyclohexane (95—98% of the fraction) also the following compounds: cyclohexane, methylcyclohexane, propylbenzene, ethylcyclohexane, ethylmethylbenzene (position of substituents could not be determined as all the three isomers show identical mass spectrum), 3-propylcyclohexene, C_9H_{16}, three hydrocarbons C_9H_{18}, and C_9H_{20} and $C_{10}H_{20}$. By using the same method it was found that fraction 2 of neutral portion contains *cis*- and *trans*-octahydro-2*H*-1-benzothiopyran as the main component (90—95%). Further compounds present in this fraction were two stereoisomers of octahydro-2-methyl-benzo(b)thiophene, hexahydroindane (*cis* and *trans*), 2-methylindole, 2-methyl-2,3-dihydrobenzo(*b*)thiophene, 2-ethyl-2,3-dihydrobenzofuran, $C_9H_{16}S$, $C_{10}H_{18}S$, $C_9H_{16}S$, two compounds $C_{11}H_{18}S$, and further compounds of mass 152·, 154, 154, 154, and 168, the structure of which could not be determined unambiguously.

Hydrogenolysis of quinoline. Quinoline (20 g) and the catalyst (0·50 g) were heated at 300°C and 10—15 MPa for 6 h. In the absence of hydrogen sulphide, 0·2 g of the neutral portion was obtained by the above described treatment; in the presence of hydrogen sulphide this portion increased to 0·50 g. During the reaction, the consumed hydrogen was substituted for fresh one, maintaining the required pressure. Composition of both fractions was very similar to those obtained by HDN of 1,2,3,4-tetrahydroquinoline.

Hydrogenolysis of 1-*pent*-4-*enylamine.* Neutral portion from HDN of 1-pent-4-enylamine in the presence of hydrogen sulphide, obtained by the reported procedure[18], was divided into two fractions by preparative gas chromatography: fraction 1 (1·22 g) that contained 1-pentanethiol, 2-methylthiacyclopentane and thiacyclohexane as the main components, and fraction 2 (0·12 g). By this way, the concentration of studied higher boiling compounds could be increased and some of them could be identified. The following compounds were found in both portions: 2-methyl-1-butene, pentane, 2-methylbutane, 2-methylthiacyclopentane, thiacyclohexane, 1-pentanethiol, 1-butyl-1-propyl sulphide, ethyl 1-pentyl sulphide, 2,3-benzothiophene, $C_5H_{10}S_2$, $C_8H_{16}S$, 2-methylbutyl 2-propyl sulphide, 1-pentyl 2-propyl sulphide, 1-pentyl 1-propyl sulphide, $C_9H_{14}S$, 1-butyl 1-pent-4-enyl sulphide, $C_9H_{18}S$, ethyl 1-heptyl sulphide, $C_9H_{20}S$, two isomers $C_{10}H_{18}S$, 2-(1-pentyl)thiacyclohexane, 2-(1-hexyl)thiacyclopentane, three isomers $C_{10}H_{20}S$, di(1-pentyl) sulphide, 2-methylbutyl 3-methylbutyl sulphide, 1-heptyl 1-propyl sulphide, $C_8H_{18}S_2$, $C_9H_{20}S_2$, $C_{10}H_{20}S_2$, 5-mercapto-1-pentyl 1-pentyl sulphide, di(1-pentyl) disulphide, $C_{10}H_{15}N$, 2-methyl-1-(1-pentyl)pyrrole, two isomers $C_{10}H_{17}N$, $C_{11}H_{19}N$, $C_{12}H_{21}$. .N, and $C_{15}H_{27}N$. Fraction 2 showed positive test on pyrrole with spruce chip moistened with hydrochloric acid.

GC–MS *analysis* was made on AEI MS 902 mass spectrometer (Associated Electric Industries, Manchester, G.B.) connected to Pye Unicam 104 gas chromatograph *via* stainless steel capillary tube and Biemann separator. Glass chromatographic column (4 mm i.d. and 1·8 m length) was filled with 3% OV-17 silicone elastomer on Gas Chrom Q and heated to 50–150°C. In the course of analysis of the samples containing thiols it was observed that at higher temperatures thiols undergo dehydrogenative dimerisation to the corresponding symmetrical disulphides (due to the catalytic action of metallic capillary tube). This reaction takes place around 100°C, and at 150°C the conversion is nearly quantitative, as demonstrated by obtained mass spectra. For that reason, the samples containing thiols were analysed at temperatures as low as possible (around 50°C).

Mass spectra were recorded at electron energy 70 eV and resolution 1 000. Further presented are the spectra of some sulphur compounds detected in analysed reaction mixtures (*m/e* with the corresponding relative intensity in parentheses): Cyclopentyl 1-pent-4-enyl sulphide: 39 (41), 41 (100), 45 (17), 47 (21), 53 (16), 55 (15), 59 (12), 60 (9), 61 (20), 67 (97), 68 (80), 69 (89), 81 (28), 87 (28), 115 (53), 112 (49), 113 (21), 115 (77), M^+ 170 (10·6).

(1-Pent-4-enyl) 1-pentyl sulphide: 39 (24), 41 (83), 45 (11), 47 (15), 53 (12), 55 (11), 59 (8), 60 (11), 61 (100), 67 (41), 68 (61), 69 (90), 87 (20), 101 (37), 102 (54), 115 (14), 117 (48), 129 (5), M^+ (172(5)

trans-2-Allylcyclohexanethiol: 39 (11), 41 (21), 53 (10), 54 (7), 55 (10), 67 (32), 68 (13), 79 (32), 80 (19), 81 (100), 93 (24), 107 (13), 113 (5), 114 (8), 122 (24), 123 (10), 141 (6), 155 (9), M^+ 156(24).

Octahydro-2-methyl-benzo(*b*)thiophene: 39 (16), 41 (31), 45 (3), 53 (11·6), 54 (8·3), 55 (18·5), 59 (10), 60 (8), 61 (21), 67 (31), 68 (8·3), 74 (18·5), 75 (9·2), 77 (11), 79 (29), 80 (10·6), 81 (89), 93 (13·5), 94 (10), 95 (29), 96 (48), 107 (20), 113 (20), 114 (36), 122 (25), 123 (12·5), 141 (81·5), M^+ 156 (100).

Octahydro-2*H*-1-benzothiopyran: 39 (11·5), 41 (23), 45 (11), 47 (5), 53 (8·3), 54 (5·5), 55 (12·5), 59 (3·8), 60 (6), 61 (4·2), 67 (30), 77 (6·2), 79 (18), 80 (8·3), 81 (40), 87 (72), 93 (10·4), 94 (9), 95 (7·6), 96 (12), 97 (11), 100 (28), 109 (14), 113 (77), 114 (13), 122 (7), 123 (5), 127 (7), 128 (11·5), M^+ 156 (100).

Cyclopentanethiol: 39 (42·4), 41 (86), 42 (19·5), 45 (23), 53 (11), 55 (12·7), 59 (12·4), 60 (36·5), 67 (57), 68 (59), 69 (100), 70 (17), 73 (17), 74 (9), M^+ 102 (76·3), 104 (10·8).

1-Pentanethiol: 39 (27·5), 41 (67), 42 (100), 43 (42·5), 45 (14·2), 46 (14·8), 47 (35), 55 (81), 56 (6·7), 57 (6), 61 (24), 70 (78), 71 (9), M^+ (104 (75), 105 (4·8), 106 (3·3).

2-Methylthiacyclopentane: 39 (54), 41 (50), 45 (58), 46 (16·5), 47 (15·5), 53 (16·5), 55 (12·6) 58 (19·4), 59 (47), 60 (25), 61 (10), 74 (22·3), 85 (9·3), 87 (100), 88 (7), 89 (6·2), M^+ 102 (33), 103 (2·7), 104 (1·7).

Thiacyclohexane: 39 (46), 41 (55), 45 (48), 46 (46), 47 (26·5), 53 (14·5), 54 (10), 55 (36), 56 (12), 58 (10), 59 (24), 60 (37), 61 (54), 67 (47), 68 (58), 69 (15), 73 (9·6), 74 (20·5), 87 (100), M^+ 102 (84), 103 (6·7), 104 (4·1).

Di(1-pentyl) sulphide: 39 (13), 41 (52), 42 (36), 43 (55), 45 (7·5), 46 (5·5), 47 (11), 55 (29), 60 (8), 61 (59), 69 (57), 70 (100), 71 (17), 103 (72·5), 104 (26), 105 (11·6), 117 (16·5), 131 (5·2), M^+ 174 (46·4), 175 (5·8), 176 (2·6).

Di(1-pentyl)disulphide: 39 (15), 41 (45), 42 (36), 43 (100), 45 (6·6), 47 (9), 55 (28·3), 59 (3·7), 60 (3·8), 61 (5·7), 69 (9·7), 70 (19), 71 (47), 79 (3·6), 87 (2·6), 101 (3·4), 102 (3·6), 103 (9·3), 104 (8·4), 136 (24·7), 138 (2·2), M^+ 206 (25), 207 (3·3), 208 (2·5).

2-(1-Pentyl)thiacyclohexane: 39 (11), 41 (32·6), 43 (13·5), 45 (6·7), 53 (6·7), 55 (24), 59 (11·3), 61 (18), 67 (16·3), 69 (19·6), 81 (7·6), 87 (7·4), 101 (100), 102 (10), 103 (7·2), 115 (15), 143 (4·8), 157 (3), M^+ 172 (19), 173 (2), 174 (1·8).

RESULTS AND DISCUSSION

As reported already in the previous work[18], the composition of neutral portions from HDN of pyridine, piperidine, and of 1-pent-4-enylamine is very similar. According to the proposed reaction scheme, 1-pent-4-enylamine can be regarded as intermediate formed in the cleavage of piperidine ring. Neutral portion of the reaction mixture after HDN of 1-pent-4-enylamine in the presence of hydrogen sulphide was cut into two fractions by preparative gas chromatography. This made it possible to increase the concentration of studied compounds in the mixture and to determine some of them by gas chromatography combined with mass spectrometry. In addition to the already reported compounds found earlier, such as 1-pentanethiol, 2-methylthiacyclopentane and thiacyclohexane that formed *c.* 95% of the total neutral portion, the following substances were detected which are listed according to their relative proportion in the reaction mixture: (2-methylbutyl) (3-methylbutyl) sulphide, di(1-pentyl) sulphide, di(1-pentyl) disulphide, 1-heptyl 1-propyl sulphide, ethyl 1-heptyl sulphide, 2-(1-pentyl)thiacyclohexane, 2-(1-hexyl)thiacyclopentane, 1-pentyl 1-propyl sulphide, 1-butyl 1-propyl sulphide, ethyl 1-pentyl sulphide, (2-methylbutyl) 2-propyl sulphide, 1-pentyl 2-propyl sulphide, (5-mercapto-1-pentyl) 1-pentyl sulphide, 1-butyl 1-pent-4-enyl sulphide, and 2,3-benzothiophene.

The mixture contained also further compounds, the structure of which could not be determined unambigously: $C_5H_{10}S_2$, $C_8H_{16}S$, $C_8H_{18}S_2$, $C_9H_{14}S$, $C_9H_{18}S$, $C_9H_{20}S$, $C_9H_{20}S_2$ two isomers $C_{10}H_{18}S$, three isomers $C_{10}H_{20}S$ and $C_{10}H_{20}S_2$.

Besides the above sulphur-containing compounds, the neutral portion contained also compounds containing nitrogen. With respect to the procedure used for isolation from the reaction mixture after HDN of 1-pent-4-enylamine it was obvious that they should be neutral or weakly acidic. The substance $C_{10}H_{17}N$, that of this group was present in the greatest amount, was identified as 2-methyl-1-(1-pentyl)pyrrole. Further present were two isomers $C_{10}H_{17}N$, $C_{10}H_{15}N$ and three compounds forming homologue series, $C_{11}H_{19}N$, $C_{12}H_{21}N$ and $C_{15}H_{27}N$, most likely the derivatives of 1-(1-pentyl)pyrrole, alkylated on pyrrole ring.

Of hydrocarbons, the neutral portion contained 2-methyl-1-butene, pentane and 2-methylbutane. While in the case of HDN of piperidine in the absence of hydrogen sulphide[18] the neutral portion contained 1-methyl-*Z*-4-isopropylcyclohexane, 1-methyl-*E*-4-isopropylcyclohexane, two isomers of methylisopropylhexene and 4-methylnonane, these compounds were not detected in HDN of 1-pent-4-enylamine in the presence of hydrogen sulphide. One can assume that also here the above compounds are formed but that they react further with hydrogen sulphide to form compounds $C_{10}H_{20}S$.

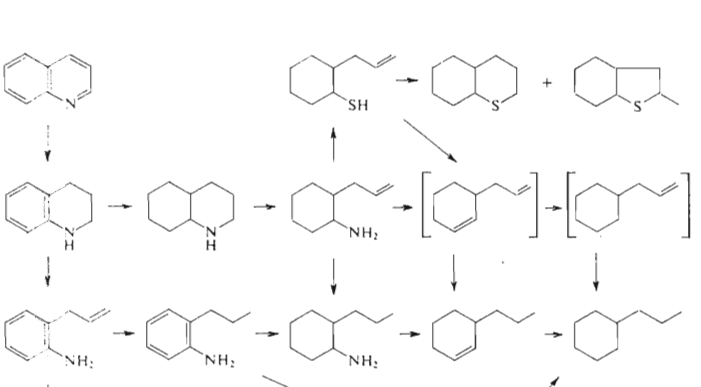
As mentioned already in connection with the proposed reaction mechanism of HDN of piperidine in the presence of hydrogen sulphide[18], intermediate product is 1-pent--4-enylmercaptane that undergoes cyclisation to 1-methylthiacyclopentane and thiacyclohexane and is hydrogenated to 1-pentanethiol. Further reaction of this compound could be its dimerisation to (5-mercapto-1-pentyl) 1-pent-4-enyl sulphide, followed by hydrogenation of the latter compound to give (5-mercapto-1-pentyl) 1-pentyl sulphide. In the present work this sulphide was found in the reaction mixture, which provides another evidence for formation of 1-pent-4-enylmercaptane as intermediate product.

For purposes of the study of HDN of quinoline in the presence of hydrogen sulphide we have followed HDN of 1,2,3,4-tetrahydroquinoline that is primary intermediate in HDN of quinoline. In the reaction mixture we identified compounds that were found earlier by other authors and the presence of which was expected, *e.g.* cyclohexane, methylcyclohexane, ethylcyclohexane, propylcyclohexane, propylbenzene, ethylmethylbenzene, 3-propylcyclohexane, *cis* + *trans* hexahydroindane, 2-methylindole and further compounds such as C_9H_{16}, C_9H_{18}, *etc.* In the reaction mixture hydrocarbons C_9H_{20} and $C_{10}H_{20}$ were not earlier detected. Similarly, also sulphur--containing compounds formed by reaction of hydrogen sulphide with reaction products have not been reported. We have been able to prove the presence of the following compounds: *cis* + *trans*-octahydro-2*H*-1-benzothiopyrane, two isomers of octahydro-2-methylbenzo(*b*)thiophene, 2-methyl-2,3-dihydro-benzo(*b*)thiophene, octahydro-1*H*-2-benzothiopyrane, two compounds $C_9H_{16}S$, $C_{10}H_{18}S$ and two compounds $C_{11}H_{18}S$.

Reaction mechanism of HDN of quinoline in the presence and absence of hydrogen sulphide to give propylcyclohexane as the main product was already studied[13-15]. Hydrogenation of benzene ring to cyclohexane one takes place *a*) in hydrogenation of 1,2,3,4-tetrahydroquinoline to decahydroquinoline, *b*) in hydrogenation of 2-propylaniline to 2-propylcyclohexylamine and *c*) in hydrogenation of propylbenzene to propylcyclohexane. These reactions proceed simultaneously and are strongly affected by reaction conditions.

Based on the identification of compounds present in the reaction mixture, the reaction scheme for HDN of quinoline in the presence of hydrogen sulphide on a sulphided Ni–W catalyst can be proposed (Scheme 1). According to this scheme, HDN of quinoline proceeds mainly *via* decahydroquinoline that is further cleaved to give 2-allylcyclohexylamine. The latter can undergo hydrogenation to 2-propylcyclohexylamine. However, the preferred pathway is its substitution reaction with hydrogen sulphide to form 2-allylcyclohexanethiol that affords immediately octahydro-2*H*--1-benzothiopyrane and octahydro-2-methyl-benzo(*b*)thiophene by cyclisation. 2-Allylcyclohexanethiol can also release hydrogen sulphide, yielding 3-allyl-1-cyclohexane. The latter compound can be formed also from 2-allylcyclohexylamine by elimination

of ammonia and can undergo further hydrogenation to give propylcyclohexane. The presence of 2-propylcyclohexanethiol that would be formed by hydrogenation of 2-allylcyclohexanethiol has not been proved. The reaction mixture did not contain also allylcyclohexane. For that reason it seems likely that hydrogenation of 3-allyl--1-cyclohexene to propylcyclohexane proceeds *via* 3-propyl-1-cyclohexene and not *via* allylcyclohexane.



SCHEME 1

Of other compounds, the presence of 2-ethyl-2,3-dihydrobenzofuran in the reaction mixture is surprising, as this compounds contains oxygen. Its presence is likely due to the presence of moisture in the reaction mixture or rather this compound could be formed during treatment of the reaction mixture in acidic medium. Formation of 2-methylindole in HDN of quinoline was already reported[1].

The cleavage of C–N bonds and formation of new C–S bonds in HDN of quinoline in the presence of hydrogen sulphide takes place to a small extent also in the case of compounds with unhydrogenated benzene ring. This idea is supported by the presence of 2-methyl-2,3-dihydro-benzo(*b*)-thiophene, the formation of which can be accounted for by similar reaction from 2-allylaniline in which case substitution reac-

tion with hydrogen sulphide results in formation of 2-allylbenzenethiol that undergoes further cyclisation.

Differences in the amount of neutral portion and in its composition in HDN of 1,2,3,4-tetrahydroquinoline in the presence and absence of hydrogen sulphide are following. The amount of neutral portion obtained by distillation is 7·7 and 2·6% respectively. In the presence of hydrogen, the main product is propylcyclohexane, in the presence of hydrogen sulphide, main products are propylcyclohexane and octahydro-2*H*-1-benzothiopyrane. The amount of some hydrocarbons such as cyclohexane, methylcyclohexane, ethylcyclohexane, propylbenzene, 3-propyl-1-cyclohexene and ethylmethylbenzene remains the same in both cases. In the presence of hydrogen sulphide hydrocarbons C_9H_{16}, C_9H_{18}, and $C_{10}H_{20}$ are formed in smaller amounts; however, the amount of propylcyclohexane increases.

Besides the reactions given in Scheme I, polymerisation and condensation reactions yield further higher boiling compounds which are present mainly in distillation residue. Their amount also increases in the presence of hydrogen sulphide.

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