80. *Synthetical Applications of Activated Metal Catalysts. Part VI.* Desulphurisations with Raney Cobalt.*

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Raney cobalt has been used to desulphurise dibenzothiophen and a number of acylthiophens, thiophencarboxylic acids, thiazoles, and thioamides. In general it is less effective than Raney nickel, but some differences have been noted.

Raney nickel has been extensively used in the desulphurisation of organosulphur compounds,[1,2] but other related catalysts have not been systematically investigated. A less active catalyst might have some advantages, especially if it could effect desulphurisation without the complete reduction of all unsaturated groups. Raney cobalt is a weak hydrogenation catalyst,[3,4] and its activity has now been compared with that of nickel in desulphurisation. An example of such use of Raney cobalt has been reported.[4]

Desulphurisation of 2-acetylthiophen with W-7 Raney nickel gives [2,5] hexan-2-one, and a little dodecane-2 : 11-dione. Under similar conditions, 2-benzoylthiophen gave some 1 : 8-dibenzoyloctane in addition to the expected valerophenone, and various thiophencarboxylic acids likewise also gave small amounts of dimeric products.[2,5] 2-Acetylthiophen, 2-benzoylthiophen, 3-acetylthionaphthen, thiophen-2-carboxylic acid, γ-2-thienylbutyric acid, and β-2-thenoylpropionic acid have now been desulphurised with Raney cobalt. However, on the basis of the extent of desulphurisation under similar conditions, W-7 Raney cobalt is much less effective than W-7 Raney nickel; in the desulphurisation of 3-acetylthionaphthen, for example, Raney cobalt was about one-tenth as active as Raney nickel.[5] Again small yields of dimer were generally obtained in addition to the expected monomeric products; but the ratio of dimer to monomer was not identical with that observed in experiments with Raney nickel. The desulphurisation of 2-benzoylthiophen with W-7 Raney cobalt, for example, gave no dibenzoyloctane, and with " Aller " Raney cobalt the ratio of dibenzoyloctane to valerophenone was 1 : 7·3. With W-7 Raney nickel, however, the ratio was 1 : 18·6, that is less than half the number of dimerisations for the number of molecules attacked. However, with γ-2-thienylbutyric acid, and in

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* Part V, *J.*, 1957, 4417.

[1] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013; Venkataraman, *J. Indian Chem. Soc.*, 1958, **35**, 1.

[2] Badger, Rodda, and Sasse, *J.*, 1954, 4162.

[3] Reeve and Christian, *J. Amer. Chem. Soc.*, 1956, **78**, 860; Ried and Schiller, *Chem. Ber.*, 1953, **86**, 730.

[4] Aller, *J. Appl. Chem.*, 1957, **7**, 130; 1958, **8**, 163.

[5] Badger and Sasse, *J.*, 1957, 3862.

agreement with the results obtained with nickel,[7] the proportion of dimer increased with the concentration of the reaction mixture. Such a result is, of course, expected if the dimer results from a recombination of free radicals.

Desulphurisations with Raney cobalt without simultaneous reduction of unsaturated groups could not be achieved. In the desulphurisation of β-2-thenoylpropionic acid there was some simultaneous reduction of the keto-group, for 4-hydroxyoctanolactone and 4 : 13-dihydroxyhexadecanedioic dilactone were obtained in addition to 4-oxo-octanoic acid and 4 : 13-dioxohexadecanedioic acid. Moreover, in the desulphurisation of 3-acetylthionaphthen 3-phenylbut-3-en-2-one could not be detected although this material was specially searched for, by using infrared spectroscopy.

The effect of W-7 Raney cobalt on thiazoles was similar to that of a rather weak nickel catalyst.[6] Some deamination of 2-amino-4-phenylthiazole occurred, and acetophenone was isolated. The thiol group of 2-mercaptobenzothiazole was removed, but no product resulting from the desulphurisation of the benzothiazole ring system could be detected.

Dibenzothiophen was also desulphurised by W-7 Raney cobalt, but here again the catalyst was less effective than nickel.[5] This experiment was carried out in ethanol as solvent, and a small amount of acetaldehyde was detected. However, the dehydrogenation was slower than with Raney nickel, and only after prolonged heating was sufficient aldehyde formed to permit identification.

The desulphurisation of phenanthridinethione offers a useful route to phenanthridine.[7] With active Raney nickel catalysts, however, the reaction is complicated by reduction to dihydrophenanthridine, necessitating a final dehydrogenation. With W-7 Raney cobalt, however, the desulphurisation smoothly gives phenanthridine in high yield. 2-Mercaptoquinoline with Raney cobalt gives quinoline, 2 : 2′-diquinolyl, and 2 : 2′-diquinolyl sulphide, together with a cobalt complex. Acridinethione was very resistant to desulphurisation by Raney cobalt, but some acridine and 9 : 9′-diacridyl were isolated. Imidazolidinethione did not yield imidazolidine, but gave ethylenediamine, presumably by hydrolysis of the parent base. Some *NN*-diformylethylenediamine was also isolated. It seems likely that the formylation of the ethylenediamine results from the action of the cobalt on the methanol solvent. In this respect Raney cobalt differs from Raney nickel, which does not formylate primary amines in methanol.[8]

2 : 2′-Dipyridyl could not be isolated following the refluxing of pyridine with either W-7 Raney cobalt or with a " degassed " cobalt. This behaviour is in marked contrast to that with Raney nickel.[9] Pyridine can therefore be used as a solvent for desulphurisations with Raney cobalt.

EXPERIMENTAL

Preparation of Raney Cobalt.—W-7 Raney cobalt was prepared from cobalt–aluminium alloy (30% Co, 70% Al; Lights) by the same method as for W-7 Raney nickel.[10] The more active " Aller " Raney cobalt was prepared at 15—20°.

Desulphurisation of 2-*Acetylthiophen.*—(1) A mixture of 2-acetylthiophen (30 g.), W-7 Raney cobalt catalyst (prepared from 125 g. of cobalt–aluminium alloy), and methanol (to 200 c.c.) was refluxed for 5 hr. The filtrate and methanol extracts of the catalyst were combined, methanol removed, and the residue distilled; three fractions were collected: (*a*) hexan-2-one, b. p. 60°/30 mm. (2·77 g.), identified as the dinitrophenylhydrazone; (*b*) 2-acetylthiophen, b. p. 102°/20 mm. (26·3 g.), identified as the dinitrophenylhydrazone; and (*c*) an oil, b. p. 80—90°/0·5 mm. (0·5 g.). Redistillation of fraction (*c*) and recrystallisation from light petroleum (b. p. <40°) gave dodecane-2 : 11-dione (10 mg.), m. p. and mixed m. p. 54—56°.

(ii) A mixture of 2-acetylthiophen (60 g.), W-7 Raney cobalt (from 250 g. of alloy), and methanol (to 250 c.c.) was refluxed for 24 hr. Distillation gave the following fractions: (*a*) a non-ketonic forerun, b. p. 100°/22 mm. (1·0 g.); (*b*) 2-acetylthiophen, b. p. 104—105°/22 mm.

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[6] Badger and Kowanko, *J.*, 1957, 1652.

[7] Taylor and Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 6295.

[8] Ainsworth, *J. Amer. Chem. Soc.*, 1956, **78**, 1635.

[9] Badger and Sasse, *J.*, 1956, 616.

[10] Billica and Adkins, *Org. Synth.*, 1949, **29**, 24.

(50·75 g.); (*c*) an oil, b. p. 90—120°/0·03 mm. (0·996 g.); and (*d*) a small amount of solid removed from the neck of the flask. Fraction (*c*) was extracted seven times with light petroleum (b. p. <40°). Purification of the extracts by chromatography on alumina, and recrystallisation of the product from light petroleum gave dodecane-2 : 11-dione, plates, m. p. and mixed m. p. 54—56° (identity confirmed by infrared spectra). The petroleum-insoluble portion was identical with fraction (*d*) (by infrared spectra). Recrystallisation from benzene–light petroleum gave a *compound* as needles (30 mg.), m. p. 88·5—89° (Found: C, 58·1; H, 4·75; S, 24·3; O, 12·4%), whose spectrum in carbon tetrachloride (sodium chloride prism) showed a carbonyl band at 5·94 μ (suggesting a CO·C:C system), and a CH_2 absorption at 6·99 μ, but had little similarity to that of diacetyldithienyl.

Desulphurisation of 2-*Benzoylthiophen.*—(i) 2-Benzoylthiophen (30 g.), W-7 Raney cobalt (from 125 g. of alloy), and methanol (to 200 c.c.) were refluxed for 5 hr. Distillation of the product gave: (*a*) *n*-valerophenone, b. p. 80°/0·05 mm. (1·83 g.), identified as the dinitrophenylhydrazone; (*b*) 2-benzoylthiophen, b. p. 100—102°/0·05 mm. (24·75 g.); and (*c*) a residue from which 1 : 8-dibenzoyloctane could not be obtained.

(ii) In this experiment desulphurisation was effected as above except that Aller Raney cobalt was used. Distillation of the product gave (*a*) *n*-valerophenone, b. p. 80—100°/0·04 mm. (2·2 g.); (*b*) 2-benzoylthiophen, b. p. 110—120°/0·04 mm. (25·5 g.); and (*c*) a residue (0·5 g.), 1 : 8-dibenzoyloctane (30 mg., from ethanol), m. p. and mixed m. p. 92—93°.

Desulphurisation of 3-*Acetylthionaphthen.*—3-Acetylthionaphthen (30 g.), W-7 Raney cobalt (from 125 g. of alloy), and methanol (to 200 c.c.) were refluxed for 5 hr. Distillation gave: (*a*) a mixture (4·44 g.) from which 3-phenylbutan-2-one (1·4 g.; b. p. 110—112°/24 mm.; identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 171—172°) and 3-acetylthionaphthen (3·04 g.) were obtained; (*b*) 3-acetylthionaphthen, b. p. 96—102°/0·1 mm. (24·16 g.); and (*c*) a small intractable residue.

Desulphurisations of Acidic Derivatives of Thiophen.—(i) A stirred mixture of thiophen-2-carboxylic acid (5 g.), W-7 Raney cobalt (from 65 g. alloy), and 10% aqueous sodium carbonate (to 100 c.c.) was heated at 80—90° for 2 hr. The catalyst was removed and washed with hot sodium carbonate solution, and the aqueous solutions acidified. The precipitate of thiophen-2-carboxylic acid (3·75 g.) was removed and the liquors extracted with ether to give valeric acid (isolated as the *p*-bromobenzyl*iso*thiuronium salt, m. p. and mixed m. p. 162°; 3·3 g. equivalent to 0·97 g. of acid).

(ii) γ-2-Thienylbutyric acid (8·0 g.) was heated (steam-bath) and stirred with W-7 Raney cobalt (from 125 g. of alloy) in 10% aqueous sodium carbonate (to 900 c.c.) for 1·75 hr. Distillation of the acidic product gave: (*a*) *n*-octanoic acid, b. p. 72—73°/0·05 mm. (2·57 g.); (*b*) γ-2-thienylbutyric acid, b. p. 104°/0·05 mm. (4·90 g.), and (*c*) a residue (0·2 g.), which gave impure hexadecane-1 : 16-dicarboxylic acid (*ca.* 8 mg.), identified by its infrared spectrum.

(iii) γ-2-Thienylbutyric acid (30 g.), W-7 Raney cobalt (from 250 g. of alloy), and 10% aqueous sodium carbonate (300 c.c.) were heated for 5 hr. Distillation gave (*a*) a forerun (mainly octanoic acid), b. p. 60—80°/0·1 mm. (1·68 g.); (*b*) *n*-octanoic acid, b. p. 80°/0·1 mm. (6·25 g.); (*c*) γ-2-thienylbutyric acid, b. p. 115°/0·1 mm. (18·9 g.), and (*d*) a residue (1·2 g.). The residue (*d*) was extracted with sodium carbonate (charcoal), and the extract acidified. Recrystallisation from ether and then from concentrated nitric acid yielded hexadecane-1 : 16-dicarboxylic acid, m. p. and mixed m. p. 123—124°.

(iv) A stirred mixture of β-2-thenoylpropionic acid (7 g.), W-7 Raney cobalt (from 250 g. of alloy), and aqueous sodium carbonate (to 300 c.c.) was heated (steam-bath) for 5 hr. The catalyst was extracted with sodium carbonate, and the combined filtrates were acidified. On cooling, 4 : 13-dioxohexadecanedioic acid (0·27 g.), m. p. and mixed m. p. 152—153°, separated. Concentration of the mother liquors and cooling gave β-2-thenoylpropionic acid (1·415 g.), and the liquors were then extracted with ether, the ether evaporated, and the product distilled. Four fractions were collected: (*a*) 4-hydroxyoctanolactone, b. p. 114—118°/22 mm. (0·89 g.), n 1·4456 (lit. n_D^{19} 1·4451); (*b*) b. p. 152—166°/22 mm. (0·62 g.); (*c*) b. p. 180°/22 mm. (0·54 g.); and (*d*) a residue (0·5 g.). Recrystallisation of fractions (*b*) and (*c*) gave 4-oxo-octanoic acid, m. p. and mixed m. p. 50—52°. The residue was separated into an acidic and a neutral fraction. Repeated recrystallisation of the latter from benzene–light petroleum gave impure 4 : 13-dihydroxyhexadecane-1 : 16-dioic dilactone, m. p. 76—78° (3·7 mg.), identified by its infrared spectrum.

Desulphurisation of Thiazoles.—(i) A mixture of 2-amino-4-phenylthiazole (5 g.), W-7 Raney cobalt (from 65 g. of alloy), and methanol (250 c.c.) was refluxed in a slow stream of nitrogen for 4 hr. The exit gases were passed into dilute hydrochloric acid (later evaporation of which gave ammonium chloride, 0·15 g.). The mixture furnished 2-amino-4-phenylthiazole (4·4 g.) and acetophenone (0·55 g.), identified and weighed as the dinitrophenylhydrazone.

(ii) 2-Mercaptobenzothiazole (10 g.) and W-7 Raney cobalt (from 65 g. of alloy) in methanol (250 c.c.) were refluxed for 4·5 hr. The catalyst was removed and well washed with boiling methanol, and the combined filtrates were acidified with dilute hydrochloric acid (100 c.c.), and distilled from the steam-bath. On cooling 2-mercaptobenzothiazole (3·0 g.) was deposited, and the liquors were treated with toluene-*p*-sulphonyl chloride (9·0 g.) and aqueous alkali. Steam distillation gave benzothiazole (2·74 g.), but amines could not be detected. A similar attempt to desulphurise benzothiazole (10 g.) gave unchanged material (6·08 g.) and a tar from which amines could not be obtained.

Desulphurisation of Dibenzothiophen.—A mixture of dibenzothiophen (5 g.), W-7 Raney cobalt (from 40 g. of alloy), and ethanol (200 c.c.) was refluxed for 14 hr. (A very faint reaction for acetaldehyde was obtained by passing a stream of nitrogen through the flask into a dimedone solution.) The filtrate was evaporated and the residue extracted with benzene (a little insoluble material being discarded), the benzene evaporated, and the product recrystallised from ethanol. The first crop on chromatography gave dibenzothiophen (1·8 g.), m. p. and mixed m. p. 98—99°, identified by formation of the picrate, m. p. and mixed m. p. 123—124°. The liquors were evaporated and the residue recrystallised from benzene–light petroleum (b. p. 40—60°) to give diphenyl (1·2 g.), m. p. and mixed m. p. 69—70°, also identified by formation of 4 : 4′-dibromodiphenyl, m. p. and mixed m. p. 169°.

Desulphurisation of Thioamides.—(i) A mixture of phenanthridinethione (1 g.), dimethylformamide (10 c.c.), ethanol (10 c.c.), and W-7 Raney cobalt (from 10 g. of alloy) was refluxed for 1·5 hr. The catalyst was removed from the hot solution and well washed with hot solvent, and the combined filtrates were evaporated under reduced pressure. After recrystallisation from acetone–water the crude phenanthridine (0·61 g., 72%) had m. p. 105—106°. Similar desulphurisation in pyridine gave less-pure phenanthridine.

(ii) A mixture of 2-mercaptoquinoline (3 g.), W-7 Raney cobalt (from 30 g. of alloy) and methanol (60 c.c.) was refluxed for 5 hr., a brown solid separating. The solid was washed well with boiling methanol, and the combined filtrates were evaporated to give 2 : 2′-diquinolyl (0·026 g.), m. p. and mixed m. p. 193—194°, and quinoline [isolated as the picrate (4·10 g.), m. p. and mixed m. p. 203°]. The mixed catalyst and brown solid were continuously extracted with hot dimethylformamide for 12 hr. Concentration to 10 c.c. gave *tris-(2-mercaptoquinoline)cobalt* (?) (0·455 g.), which formed shining black needles (from dimethylformamide) (Found: C, 60·3; H, 3·4; N, 7·4; S, 18·0; Co, 11·8. $C_{27}H_{6}N_{3}S_{3}Co$ requires C, 60·1; H, 3·4; N, 7·8; S, 17·8; Co, 10·9%). The dimethylformamide extracts after removal of the complex were diluted to 100 c.c. with water. The resulting solid was dried and chromatographed in benzene on alumina to give 2 : 2′-diquinolyl (0·295 g.), m. p. and mixed m. p. 193° (also red complex with Cu^+), and *di-2-quinolyl sulphide* (0·045 g.), which [from light petroleum (b. p. 100—120°)] had m. p. 188° (Found: C, 75·3; H, 4·4; N, 9·25; S, 11·1. $C_{18}H_{12}N_{2}S$ requires C, 75·0; H, 4·2; N, 9·7; S, 11·1%). Its m. p. was not depressed by admixture with a specimen prepared by fusing 2-chloroquinoline and sodium sulphide for 20 hr.

The complex was not affected by dilute hydrochloric acid. It was heated withc oncentrated hydrochloric acid at 140—160°, and the mixture poured into concentrated sodium hydroxide. Ether extraction gave 2-mercaptoquinoline (identified by paper chromatography) and diquinolyl sulphide (identified by paper chromatography and by its isolation as the picrate, m. p. and mixed m. p. 197°).

(iii) A mixture of acridinethione (3 g.), dimethylformamide (30 c.c.), ethanol (30 c.c.), and W-7 Raney cobalt (from 30 g. of alloy) was refluxed for 13 hr. The catalyst was separated, washed with hot dimethylformamide and with boiling ethanol, the combined filtrates evaporated, and the residue extracted with boiling 0·5N-sodium hydroxide (2 × 250 c.c.). The extracts on cooling and saturation with carbon dioxide gave acridinethione (0·92 g.). The alkali-insoluble portion was continuously extracted with light petroleum (b. p. 65—69°) for 2 hr. to give acridine [identified as the picrate (0·10 g.), m. p. and mixed m. p. 261—262°]. The petroleum-insoluble fraction (0·85 g.) was chromatographed in chlorobenzene on alumina to give 9 : 9′-diacridyl (0·43 g.), m. p. and mixed m. p. 393°. The chlorobenzene-insoluble fraction was not identified.

(iv) A mixture of imidazolidinethione (10 g.), W-7 Raney cobalt (from 125 g. of alloy), and methanol (to 250 c.c.) was refluxed for 5 hr. The catalyst was washed with hot methanol, and the combined filtrates were concentrated to 75 c.c. Cooling gave imidazolidinethione (3·02 g.; m. p. and mixed m. p. 197—198°). Evaporation of the filtrate and distillation gave ethylenediamine [identified as the picrate (6·0 g.), m. p. and mixed m. p. 231—233°]. The residue (b. p. 100°/760 mm.) was treated with a little methanol and gave imidazolidinethione (1·61 g.) and a yellow, viscous oil (3·28 g.), b. p. 190°/0·01 mm., which partly solidified. Trituration with ethanol, and recrystallisation from ethanol and from ethyl acetate gave NN-*diformylethylenediamine* (2·68 g.), m. p. 109—110° not depressed by admixture with a specimen prepared by formylation of ethylenediamine (Found: C, 41·7; H, 7·1; N, 23·9; O, 27·5. $C_4H_8O_2N_2$ requires C, 41·4; H, 6·9; N, 24·1; O, 27·6%).

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