[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF SCHERING CORPORATION]

REDUCTIONS WITH NICKEL-ALUMINUM ALLOY AND AQUEOUS ALKALI. PART VII. HYDROGENOLYSIS OF SULFUR COMPOUNDS[1]

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Since the remarkable discovery of Bougault, Cattelain, and Chabrier (1) that Raney nickel catalyst brings about hydrogenolysis of sulfur compounds, the reaction has been extensively applied to the elucidation of the structure of several natural products such as biotin (2), penicillin (3), and streptomycin (4). In addition, this hydrogenolysis reaction has found considerable application in synthetic organic chemistry (5).

In a previous publication (6) from this laboratory, it has been reported that sulfonic acid groups and a methylthiol group are readily displaced by hydrogen by the action of nickel-aluminum alloy and aqueous alkali. Under similar conditions, ether linkages as part of heterocyclic ring systems such as the methylenedioxy bridge (7) and furan derivatives (8) are ruptured to phenolic and aliphatic hydroxy compounds respectively. This paper describes the results of studies on this fission reaction with thiophene derivatives as well as other organic sulfur compounds.

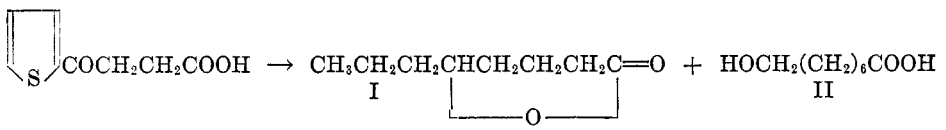
The observation that Raney alloy brings about a rupture of the carbon–sulfur linkage prompted us to investigate the behavior of thiophene derivatives[2] as well as organic sulfides under the conditions of the alloy procedure. β-(α-Thenoyl)-propionic acid[3] (I) on treatment with nickel-aluminum alloy in aqueous alkali solution yielded either a mixture of about equal amounts of γ-ketocaprylic acid (II) and γ-caprylolactone (III) or only the lactone III, the course of the reaction being dependent on the ratio of alloy and I and on the reaction time.

The initial use of insufficient alloy and/or a short reaction time affords only partial conversion of the keto acid (II) to the lactone (III). This result and the

[1] This is part of a paper presented in abstract before the Division of Organic Chemistry at the New York Meeting of the American Chemical Society, September, 1944.

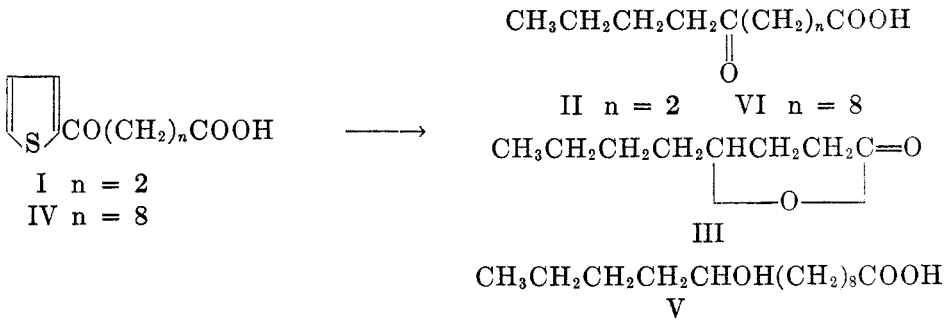
[2] Recently a report of the use of Raney nickel catalyst for the hydrogenolysis of thiophene compounds was published [Blicke and Sheets, *J. Am. Chem. Soc.*, **70**, 3768 (1948)].

[3] In the preliminary announcement of this investigation (Footnote 1) [*Org. Syntheses*, **27**, 70 (1948)] it was reported that β-(α-thenoyl)propionic acid on treatment with nickel-aluminum alloy and aqueous alkali yielded the following two products.:



The analytical data, carbon and hydrogen analyses, and neutral equivalent; the failure to obtain any positive reaction with ketonic reagents, and the known susceptibility of keto groups to the alloy reduction method seemed sufficient preliminary evidence for the formation of products I and II. However, subsequent studies with homologous compounds clearly showed this interpretation of the reaction to be incorrect.

known poisoning effect of sulfur on Raney catalyst are further evidence that the alloy reduction method is essentially a catalytic reaction (*cf.* ref. 10).

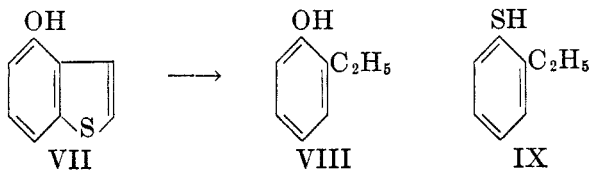


However, the higher homologous acid, ω-(α-thenoyl)pelargonic acid (IV) gave only the 10-hydroxymyristic acid (V). With acid I good yields of the lactone (III) could be secured by the use of approximately a 3:1 ratio of alloy to compound I.

The reaction of Raney catalyst on I and IV also gave III and V respectively. However, a 25:1 ratio of catalyst to compound I and IV was used. In the latter reaction none of the keto compounds II and VI were obtained. The structure of VI was confirmed by independent synthesis using the Grignard reaction between *n*-butyl bromide and ω-carbethoxypelargonyl chloride. The hydroxy acid V on oxidation with chromic acid yielded the keto acid VI which was identical with that prepared by the Grignard reaction.

Several thiophenecarboxylic acids and thienylaliphatic acids gave the normal hydrogenolysis products. With several of these compounds the initial hydrogenolysis did not proceed to completion and a second treatment with Raney alloy was necessary in order to obtain products qualitatively free of sulfur. However, in none of these reactions was the amount of Raney alloy used comparable to the excesses of Raney nickel catalyst required for similar hydrogenolyses.

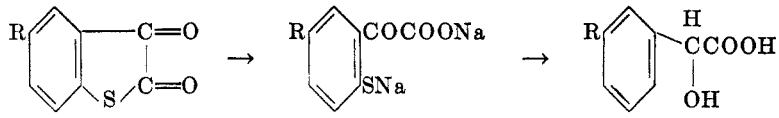
On treatment with Raney alloy, 4-hydroxythianaphthene (VII) gave *o*-ethylphenol (VIII) and viscous gum.



VII VIII IX

Although the latter product gave a positive test for sulfur, no definite crystalline material could be isolated. Thianaphthene has been reduced with sodium and alcohol; and, in addition to the normal reduction product, small amounts of *o*-ethylthiophenol (IX) have been isolated (9). High-pressure hydrogenation of thianaphthene gives a variety of products among which are ethylbenzene and *o*-ethylthiophenol.

The reduction of thianaphthenequinone (X) and the 5-methyl derivative (XII) were studied since these substances possess two carbonyl groups, one of which is adjacent to the ring sulfur atom.



X R = H
XII R = CH_3

XI

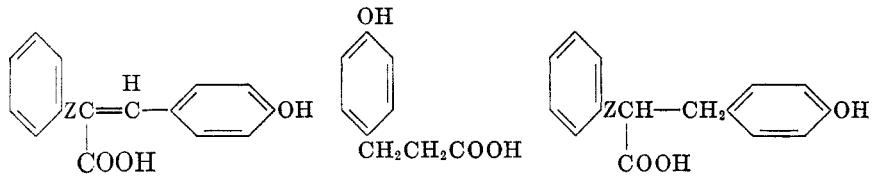
XIII R = H
XIV R = CH_3

However, in alkaline solution, the heterocyclic ring ruptured with the formation of the sodium salt of the glyoxalic acid (XI) prior to any reduction of X and XII. Compound X gave mandelic acid (XIII); and the 5-methyl derivative (XI) gave *m*-methylmandelic acid (XIV).

The failure of the alloy procedure to reduce the α-hydroxy group in the acids XIII and XIV is surprising in view of the ease with which benzyl alcohols (10) may be reduced. Except for the formation of traces of phenylacetic acid, mandelic acid was recovered unchanged after treatment with Raney alloy. It therefore may be assumed that the hydrogenolysis of the sulfhydryl group in XI did not alter the course of the reaction. These results, however, parallel those obtained with the Clemmensen method in that α-keto acids are reduced to the α-hydroxy compounds (11) rather than to the completely reduced compounds.

The hydrogenolysis of organic sulfides and thiophenols with Raney alloy proceeded in good yield, di-*p*-tolyl sulfide and benzyl mercaptan yielding toluene and thiosalicyclic acid and thio-*p*-cresol giving benzoic acid and toluene respectively. With *o*-carboxyphenylthioglycolic acid, it was necessary to repeat the treatment with Raney alloy in order to secure benzoic acid free of any sulfur compound.

The reduction of α-phenylmercapto-*p*-hydroxycinnamic acid (XV) (12) and its oxygen analog (XVI) (12) was investigated since these acids were included in a study of the action of Raney alloy on α,β-diarylacrylic acid. The thio ether XV and ether XVI underwent rupture to yield β-(*p*-hydroxyphenyl)propionic acid (XVII). The dihydro derivative XVIII also gave XVII, whereas XIX was recovered in 60% yield and only a small amount of XVII was obtained.



XV Z = O
XVI Z = S

XVII

XVIII Z = O
XIX Z = S

EXPERIMENTAL

The reductions were carried out as previously described (10). It was necessary to modify the procedure for several compounds and the reduction for these compounds is described in

detail. The yields are calculated to the purified reduction product. Alkali-insoluble compounds were reduced in a 2000-cc. flask equipped with an adapter and efficient reflux condenser. All melting points are corrected.

1. *Reduction of γ-(α-thenoyl)propionic acid.* Twenty grams of this acid (13) in 1000 cc. of 10% sodium hydroxide was reduced with 50 g. of Raney alloy. The acidified solution was extracted with three 250-cc. portions of ether. The combined ether extracts were then extracted with 2% sodium carbonate solution. From the ether solution was obtained 4.6 g. of γ-caprylolactone, b.p. 116–117° (10 mm.), 84–85° (2 mm.), n_D^{25} 1.4420 [literature, b.p. 127° (16 mm.), n_D^{19} 1.4451 (14)].

Anal. Calc'd for $C_8H_{14}O_2$: C, 67.56; H, 9.92.
Found: C, 67.41; H, 10.06.

The *phenylhydrazide* melted at 108–108.5° after recrystallization from chloroform-petroleum ether.

Anal. Calc'd for $C_{14}H_{22}N_2O_2$: N, 11.19. Found: N, 11.25.

The combined sodium carbonate extracts were acidified and extracted with ether. The ether residue amounted to 6.6 g., and distilled at 156–157° (10 mm.). The distillate solidified, and after recrystallization from petroleum ether melted at 54–54.5°; literature m.p. for *γ-ketocaprylic acid*, 53° (15).

Anal. Calc'd for $C_8H_{14}O_3$: C, 60.74; H, 8.87; N.E., 158.
Found: C, 60.47, 60.80; H, 8.91, 9.04; N.E., 158.7.

The *semicarbazone* prepared in the usual manner melted at 155–156° after recrystallization from ethyl alcohol; literature m.p. 153° (16).

The above described reduction was repeated except that the alloy was added over a period of 5–6 hours. The reaction mixture was heated at 70–80° overnight and then filtered. From the acidified filtrate 11.8 g. of γ-caprylolactone, b.p. 83–85° (2 mm.), n_D^{25} 1.4421, was obtained. None of the γ-ketocaprylic acid was obtained in this reaction.

With Raney nickel catalyst (75–80 g.), 5 g. of the β(α-thenoyl)propionic acid in 200 cc. of ethanol at reflux temperature for 5 hours (17) gave 3.5 g. of the γ-caprylolactone, b.p. 80–82° (1 mm.), n_D^{25} 1.4428. The *phenylhydrazide* melted at 107–108°, mixed m.p. with product from Raney alloy reduction 107–108°.

2. *Reduction of ω-(α-thenoyl)pelargonic acid.* Twenty grams (18) of this acid was reduced as described for the corresponding propionic acid compound. The only product isolated was soluble in sodium carbonate solution, crude yield 16 g., m.p. 49.5–52.5°. Recrystallized from a mixture of benzene–petroleum ether the *10-hydroxymyristic acid* melted at 56–57°.

Anal. Calc'd for $C_{14}H_{28}O_4$: C, 68.79; H, 11.56.
Found: C, 68.60, 68.90; H, 11.49, 11.57.

The hydroxy acid (5 g.) was oxidized with 5 g. of chromic acid in 150 cc. of acetic acid at 50–60° essentially as described (19). The keto product was isolated in a crude yield of 4.6 g., m.p. 67–69°. The *semicarbazone* was prepared in the usual manner, and melted at 159–160° after recrystallization from methanol.

Anal. Calc'd for $C_{15}H_{29}N_3O_3$: N, 14.04. Found: N, 13.91.

Five grams of the pelargonic acid was refluxed for 5 hours with 80 g. of Raney nickel catalyst (17) in 100 cc. of ethanol. The reaction mixture was worked up as described, and a crude yield of 3.5 g. of the 10-hydroxymyristic acid was obtained. Recrystallized from benzene-petroleum ether, m.p. 54–55°; mixed m.p. with product from the Raney alloy reduction, 54.5–56°.

The *10-ketomyristic acid* was also prepared by the Grignard reaction of ω-carbethoxypelargonyl chloride and *n*-butyl bromide (20). The crude keto acid was separated from sebacic acid by formation of the *semicarbazone*. The latter after recrystallization from methanol melted at 158–159°; mixed m.p. with the product from the chromic acid oxidation 159–160°.

3. *Reduction of γ-(α-thienyl)butyric acid.* To 30 g. of the butyric acid (13a) dissolved in 750 cc. of 10% sodium hydroxide there was added 60 g. of Raney alloy. The reduction was carried out in the usual manner and after acidification of the alkaline solution the reduction

product was extracted with ether. After removing the ether, the residue (26 g.) was fractionated. Fraction I was obtained in a yield of 10 g. and was identified as *caprylic acid;* b.p. 100° (1 mm.), n_D^{24} 1.4352 [literature, b.p. 240°, n_D^{20} 1.4268 (21)]. The *amide* was prepared in the usual manner and melted at 105–105.5° [literature m.p. 106°, 105.5° (21)].

The second fraction amounted to 13 g., b.p. 130–133° (1 mm.), n_D^{21} 1.4982. It was identified by its boiling point, refractive index, and analysis as starting material.

Anal. Calc'd for $C_8H_{10}O_2S$: C, 56.44; H, 5.92.

Found: C, 56.13; H, 5.75.

The *p-bromophenacyl ester* was prepared in the known manner and recrystallized from aqueous alcohol, m.p. 58–59°; mixed m.p. with *p*-bromophenacyl ester of γ-(α-thienyl)-butyric acid, 58–59°.

Anal. Calc'd for $C_{16}H_{15}BrO_3S$: C, 52.32; H, 4.12.

Found: C, 52.13; H, 4.33.

4. *Reduction of β-(α-thienyl)acrylic acid.* This acid was prepared from thiophene aldehyde (22), potassium acetate, and acetic anhydride (23). Twenty grams of the acrylic acid was dissolved in 750 cc. of 10% sodium hydroxide and 50 g. of alloy added. The product isolated from the reaction mixture gave a qualitative test for sulfur and was, therefore, reduced with an additional 25 g. of alloy. The reaction mixture, after filtration and acidification, was extracted with ether. The ether was evaporated and the residue distilled. The first fraction, yield 6 g., b.p. 106–110° (5 mm.), n_D^{26} 1.4215, was identified as *heptylic acid.* The *amide* prepared in the usual manner melted at 95–96° [literature b.p. 223°, n_D^{20} 1.4234; amide m.p. 96°, 96.5° (24)].

5. *Reduction of thiophene-2-carboxylic acid.* Twenty grams of thiophene-2-carboxylic acid was dissolved in 750 cc. of 10% sodium hydroxide and treated with 60 g. of Raney alloy. The reduction product gave a qualitative test for sulfur and the reduction was repeated with the same amounts of alkali and alloy. After filtration of the nickel, the alkaline solution was worked up by the usual method. The oily residue, which amounted to 11 g., was identified as *valeric acid,* b.p. 90–95° (3 mm.), n_D^{26} 1.4088; *p-bromophenacyl ester,* m.p. 64–65° [literature n_D^{20} 1.4086, *p*-bromophenacyl ester, 63° (25)]; mixed m.p. with an authentic sample of valeric acid *p*-bromophenacyl ester, 63–64°.

6. *Reduction of 4-methylthiophene-2-carboxylic acid.* The reduction of 25 g. of this compound was carried out as described for the thiophene-2-carboxylic acid. The reduction product was identified as *4-methylpentanoic acid,* yield 12 g.; b.p. 86–88° (11 mm.), n_D^{24} 1.4133; *p-bromophenacyl ester,* m.p. 78–80° [literature n_D^{20} 1.4144; *p*-bromophenacyl ester 77.3° (26)].

7. *Reduction of 5-methylthiophene-2-carboxylic acid.* Twenty-five grams of this acid was reduced in exactly the same manner as described for the 4-isomer. The reduction product amounted to 13.6 g., and was identified as *caproic acid,* b.p. 90–95° (5 mm.), n_D^{24} 1.4150; *amide* m.p. 98.5–99.5° [For caproic acid, n_D^{20} 1.4163; amide m.p. 100° (27)].

8. *Reduction of 4-hydroxythianaphthene.* Twenty grams of 4-hydroxythianaphthene (13a) was reduced in 750 cc. of 10% sodium hydroxide with 50 g. of nickel-aluminum alloy. After the reduction was completed, the acidified solution was extracted with ether, the ether evaporated, and the residue distilled. Fraction I was obtained in a yield of 7.6 g., b.p. 68–70° (6 mm.). This substance was identified as *o-ethylphenol,* the aryloxy derivative melting at 141–142° [literature m.p. 137–138° (28)]; N.E., 180; Found: 179.8. Fraction II (8.2 g.) boiled over a wide range, partially solidified on cooling and gave a positive test for sulfur. This fraction after treatment with 25 g. of alloy yielded 3.9 g. of *o*-ethylphenol. A considerable residue remained after both distillations and on cooling appeared as a viscous, black gum, giving a positive test for sulfur. This residue was not further investigated.

9. *Reduction of 5-methylthianaphthenequinone.* The preparation of this compound has been previously described (29) and the following, which is a modification of the published procedure, gave substantially better yields. Forty-eight grams of oxalyl chloride in 200 cc. of dry ether was added dropwise to 31 g. of *p*-thiocresol in 250 cc. of dry ether. The mixture

was warmed on the steam-bath, the ether evaporated, and the residue freed from excess oxalyl chloride in a vacuum desiccator over potassium hydroxide. The resulting yellow solid was dissolved in 450 cc. of carbon disulfide, cooled to 0°, and 40 g. of aluminum chloride added. The temperature was allowed to rise to room temperature and after refluxing for one-half hour, the reaction mixture was cooled and decomposed with ice and HCl. The carbon disulfide was steam-distilled off, and the residue recrystallized from methyl alcohol, yield 30 g., m.p. 146–147°. From the methyl alcohol mother liquor an additional 5 g. was obtained, melting at 144–146° [literature m.p. 144° (29)].

Fifteen grams of 5-methylthianaphthenequinone was dissolved in 500 cc. of 10% sodium hydroxide, 40 g. of Raney alloy was added, and the reduction carried out as described. The acidified filtrate was cooled, extracted with ether, and the ether evaporated. The residue (11 g.), which did not couple with nitrodiazobenzene, was recrystallized from a mixture of benzene-petroleum ether, yield 9.8 g.; m.p. 93–94°. This compound was identified as *m-methylmandelic acid*. The literature value for this compound is 84° (30).

Anal. Calc'd for $C_9H_{10}O_3$: C, 65.03; H, 6.07; N.E., 166.

Found: C, 64.95; H, 6.42; N.E., 167.

10. *Preparation and reduction of thianapthenequinone.* Thianaphthenequinone was prepared from thiophenol and oxalyl chloride in accordance with the procedure described for the 5-methyl derivative. The compound, after recrystallization from methyl alcohol, melted at 120–121° (31).

Ten grams of the thianaphthenequinone was reduced in the known manner with 15 g. of alloy and 250 cc. of 10% sodium hydroxide. The alkaline solution after filtration was acidified, thoroughly cooled, and extracted with ether. The residue, on recrystallization from a mixture of benzene and petroleum ether, was obtained in a yield of 5 g., m.p. 117–120°. Recrystallized from chloroform, m.p. 120–121°; mixed melting point with mandelic acid, 120–121°. N.E., 152.6.

11. *Reduction of mandelic acid.* Twenty-five grams of mandelic acid was dissolved in 600 cc. of 10% sodium hydroxide solution, 40 g. of Raney alloy was added, and the reduction completed in the usual manner. After filtration of the nickel, the alkaline solution was acidified, thoroughly cooled, and exhaustively extracted with ether. From the evaporation of the ether, a residue of 21 g. was obtained which melted at 114–116°. Recrystallization from chloroform gave a product melting at 119–120°; mixed melting point with mandelic acid showed no depression; N.E., 153; Found: 152.5. The cooled, acidified solution yielded a small amount of crystalline material which was identified as *phenylacetic acid*, m.p. and and mixed m.p. 75–76°.

12. *Reduction of benzyl mercaptan and di-p-tolyl sulfide.* To a 2-liter flask fitted with an adapter and condenser was added 20 g. of benzyl mercaptan, 500 cc. of 10% sodium hydroxide, and 40 cc. of ethyl alcohol. The mixture was heated to 50° and 40 g. of Raney alloy was added in the course of two to two and one-half hours with frequent and vigorous shaking. The reaction mixture was then heated for two hours and steam-distilled. The distillate was cooled, saturated with salt, and extracted with chloroform. The chloroform extract was dried overnight over calcium chloride; on distillation it yielded 9.2 g. of *toluene*. which was identified by boiling point and oxidation to benzoic acid. The steam-distillation residue was filtered, the residual nickel washed with hot water, and the combined filtrate and washings acidified to Congo Red paper with conc'd HCl. Exhaustive extraction of the acid solution with ether and evaporation of the ether left no residue.

Twenty-five grams of di-*p*-tolyl sulfide when reduced as described above yielded 13 g. of toluene, no alkali-soluble product being detected in the steam-distillation residue.

13. *Reduction of thiosalicylic acid.* To 10 g. of thiosalicylic acid in 300 cc. of 10% sodium hydroxide, there was added 20 g. of Raney alloy. The reduction was carried out as previously described. After filtration, the alkaline solution was acidified to Congo Red paper with HCl and repeatedly extracted with ether. The crude residue from the ether extracts gave 7.6 g. of a product which melted at 96–99° and did not couple with nitrodiazobenzene or give a color reaction with ferric chloride. After recrystallization from water, the product was identified as *benzoic acid*, m.p. and mixed m.p. 122–123°; N.E., 122; Found: 122.

14. *Reduction of p-thiocresol.* Twenty grams of *p*-thiocresol was reduced with 40 g. of alloy and 600 cc. of 10% sodium hydroxide. The reaction was carried out in a 2-liter flask with an adapter carrying a condenser. It was found desirable to add the alloy while the reaction mixture was kept below 40° in order to avoid loss of volatile reaction products. The alloy was placed in an Erlenmeyer flask which was attached to the adapter with Gooch rubber tubing (33). After all the alloy had been added, the reaction mixture was heated for 3–4 hours on the steam-bath with occasional shaking. The condenser was then set for downward distillation and the reaction mixture steam-distilled. From the steam-distillate was isolated 12 g. of *toluene*, b.p. 108–110°. The toluene was further identified by oxidation to benzoic acid, m.p. and mixed m.p. 121–122°. The steam-distillation residue was filtered, acidified, and extracted with ether. After evaporation of the ether a trace of material remained which did not give any reactions characteristic of a phenolic group and showed a negative qualitative sulfur test.

15. *Reduction of o-carboxyphenylthioglycolic acid.* *o*-Carboxyphenylthioglycolic acid was prepared from thiosalicylic acid and chloroacetic acid (32). Recrystallized from a mixture of alcohol and water, m.p. 212–214°; literature m.p. 210–211°.

Twenty grams of *o*-carboxyphenylthioglycolic acid was reduced in the usual manner with 100 g. of Raney alloy and 1500 cc. of 10% sodium hydroxide. After filtration, the alkaline solution was acidified, cooled, and filtered; yield 10.5 g., m.p. 121–122°, mixed m.p. with *benzoic acid* 122–123°; N.E., 122; Found: 123. In two experiments on the reduction of this compound, considerably less than the given amount of Raney alloy was used. In both of these experiments a large amount of the starting material was recovered along with 10–30% yields of benzoic acid. With the given amounts of alloy, none of the starting material was recovered, the crude reduction product giving a negative test for sulfur.

16. *Preparation and reduction of 3-methyl-6-benzylmercaptophenylglyoxylic acid.* To 1.78 g. (0.01 mole) of 5-methylthianaphthenequinone dissolved in 10 cc. of 20% potassium hydroxide and 10 cc. of alcohol there was added 3.5 g. of benzyl chloride. The reaction mixture became warm and within a few minutes was completely colorless. It was heated for ten minutes on the steam-bath, cooled, and extracted with ether. The aqueous solution was freed from ether, cooled, and acidified, yielding 2.6 g. of a yellow crystalline solid, m.p. 136–139°. Recrystallized from ethyl alcohol, m.p. 138.5–139.5°.

Anal. Calc'd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93.

Found: C, 67.24; H, 4.96.

Five grams of the thioether was reduced in the usual manner with 15 g. of Raney alloy in 250 cc. of 10% sodium hydroxide. The reaction mixture was worked up in the usual manner; the residue from the ether extraction, after recrystallization from benzene-petroleum ether, gave 2.5 g. of colorless needles melting at 94–96°. A second recrystallization raised the melting point to 95–96°; N.E., 166; Found: 165.4. Mixed melting point with *m-methylmandelic acid* of experiment 8 showed no depression.

17. *Reduction of α-phenylmercapto-p-hydroxycinnamic acid.* Twenty grams of the cinnamic acid (12) was reduced with 50 g. of Raney alloy in 1000 cc. of 10% sodium hydroxide. The reduction was run under an efficient reflux condenser. After the reduction was complete, the solution was steam-distilled. From the steam-distillate *benzene* was isolated and identified by boiling point. The alkaline solution was filtered from the nickel, acidified to Congo Red with hydrochloric acid and exhaustively extracted with ether. The ether residue amounted to 10 g. and showed characteristic reactions for a hydroxyl and a carboxyl group. The residue was dissolved in ether and the ether solution extracted with sodium bicarbonate. The sodium bicarbonate solution on acidification and extraction with ether yielded a solid product which was identified as *β-(p-hydroxyphenyl)propionic acid*, m.p. and mixed m.p. 127–128°; N.E., 166; Found: N.E., 166.5.

18. *Reduction of α-phenylmercapto-β-(p-hydroxyphenyl)propionic acid.* Twenty grams of this acid (12) was reduced in exactly the same manner as described for the corresponding cinnamic acid. The steam-distillate yielded *benzene*, identified by b.p. and the steam-distillation residue, after acidification and extraction with ether, gave 8.9 g. of *β-(p-hydroxyphenyl)propionic acid*, m.p. and mixed m.p. 127–128°.

19. *Reduction of α-phenoxy-p-hydroxycinnamic acid.* Twenty-five grams of this acid (12) was reduced with 35 g. of Raney alloy in 700 cc. of 10% sodium hydroxide. After filtration of the nickel, the filtrate was added slowly to ice-cold hydrochloric acid. The acidified solution was thoroughly extracted with ether, the ether extracts combined, and then extracted with 5% sodium bicarbonate. The ether extracts on evaporation gave 1.2 g. of *phenol* identified by the m.p. of the aryloxy derivative, m.p. 98–99°. Mixed m.p. with an authentic sample of *phenoxyacetic acid* showed no depression.

The sodium bicarbonate extract was freed of ether, filtered through Supercel, and acidified. Upon extraction with ether and removal of the ether, a 6.4 g. residue was obtained which was identified as *β-(p-hydroxyphenyl)propionic acid;* m.p. and mixed m.p. 126.5–127°.

20. *Reduction of α-phenoxy-β-(p-hydroxyphenyl)propionic acid.* Twenty-five grams of this acid (12) was treated as described for the corresponding cinnamic acid. On acidification of the reduction filtrate, 14.6 g. of the starting material was obtained, m.p. and mixed m.p. 166–167°. The acidified filtrate was then extracted with ether and 1.6 g. of *β-(p-hydroxyphenyl)propionic acid* was obtained along with small amounts of *phenol.*

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SUMMARY

Organic sulfur compounds are hydrogenolyzed by the action of a nickel-aluminum alloy and aqueous alkali. In general, the reaction proceeds smoothly and good yields of desulfurized products are obtained.

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