767. Synthetic Applications of Activated Metal Catalysts. Part IV * The Formation of Dimeric Products during Desulphurisations.

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Desulphurisation of thiophen derivatives with W-7 Raney nickel has been shown to yield small amounts of dimeric products in addition to the expected monomeric compounds. The yield of dimeric product depends on the concentration of the thiophen derivative in the reaction mixture, the time of contact with the catalyst, and its hydrogen content. The results are discussed with reference to the mechanism of desulphurisation.

THE initial step in any desulphurisation with Raney nickel is, almost certainly, chemisorption of the sulphur atom to the catalyst.[1] It is generally supposed that this is followed by the fission of the carbon–sulphur bonds to give free radicals, which are hydrogenated to give the normal desulphurised product (route A).[2,3,4]

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* Part III, *J.*, 1957, 1652.

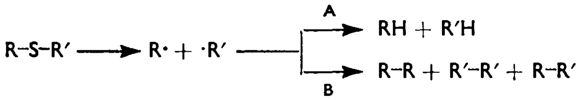
[1] Maxted, *Adv. Catalysis*, 1951, **3**, 129.

[2] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013.

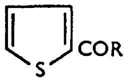
[3] Kenner, Lythgoe, and Todd, *J.*, 1948, 957.

[4] Baker, El-Nawawy, and Ollis, *J.*, 1952, 3163.

An alternative reaction (route B) is, however, possible.[2] In the desulphurisation of mercaptals and similar compounds with a nickel catalyst from which most of the chemisorbed hydrogen had been removed, Hauptmann and his co-workers [5] did observe a recombination of free radicals according to route B. Moreover, desulphurisation of 2-acetylthiophen (I; R = Me) with the very active W-6 and W-7 catalysts has been shown [6] to give some dodecane-2 : 11-dione (III; R = Me), presumably by route B, as well as the expected hexan-2-one (II; R = Me) by route A. This observation is consistent with the free-radical mechanism, as also is the work of Bonner.[7] As a further contribution to the study of the mechanism of desulphurisation, the amount of dimeric product (route B) formed from thiophen derivatives under different experimental conditions has been investigated.



(I)



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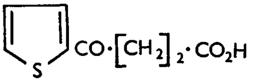

$CH_3\cdot[CH_2]_3\cdot COR$ (II)

$R\cdot CO\cdot[CH_2]_8\cdot COR$ (III)

$CH_3\cdot[CH_2]_3\cdot CH(OH)\cdot[CH_2]_2\cdot CO_2H$ (V)

$HO_2C\cdot[CH_2]_2\cdot CH(OH)\cdot[CH_2]_8\cdot CH(OH)\cdot[CH_2]_2\cdot CO_2H$ (VI)

Desulphurisation of 2-benzoylthiophen (I; R = Ph) has been found to give some 1 : 8-dibenzoyloctane (III; R = H) in addition to the expected valerophenone (II; R = Ph). With increasing concentration of benzoylthiophen in the reaction mixture the yield of the dimeric product (III) at first increased, and then decreased (see Table). The yield of dimeric product (III) was also dependent on the time of contact with the catalyst. When 2-benzoylthiophen was desulphurised by passage through a column packed with the nickel catalyst, so that the time of contact was relatively short, only a small yield of dimer was obtained. On the other hand, the yield of valerophenone was practically independent of both the concentration of benzoylthiophen in the reaction mixture and the time of contact. With a special deactivated catalyst, however, a reduced yield of valerophenone was obtained, but the yield of dibenzoyloctane was increased.

Similarly, in the desulphurisation of 2-acetylthiophen (cf. ref. 6), the yield of dodecane-2 : 11-dione at first increased with increasing concentration of acetylthiophen in the mixture, and then decreased. The desulphurisation of β-2-thenoylpropionic acid (IV) was somewhat more complex, but the amount of dimeric product was significantly greater when a deactivated catalyst was used. With W-7 Raney nickel, β-2-thenoylpropionic acid gave a compound which is presumably the dilactone of the dimeric product (VI) as well as the lactone of 4-hydroxyoctanoic acid (V). With the deactivated catalyst, however, the reduction of the keto-acid was incomplete. 4-Oxo-octanoic acid was obtained in addition to 4-hydroxyoctanoic lactone, and the only dimeric product isolated was 4 : 13-dioxohexadecane-1 : 16-dioic acid (?) identical with the acid previously obtained [6] by desulphurisation of β-(5-bromo-2-thenoyl)propionic acid.

Dimeric desulphurisation products were also obtained in small yield from other thiophen derivatives. Thus, desulphurisation of 2-propionylthiophen gave heptan-3-one and tetradecane-3 : 12-dione (?); thiophen-2-carboxylic acid (VII) gave *n*-valeric acid and

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[5] Hauptmann, Wladislaw, and Camargo, *Experientia*, 1948, **4**, 385; Hauptmann and Wladislaw, *J. Amer. Chem. Soc.*, 1950, **72**, 707, 710.

[6] Badger, Rodda, and Sasse, J., 1954, 4162.

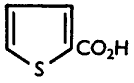
[7] Bonner, *J. Amer. Chem. Soc.*, 1952, **74**, 1034.

sebacic acid; and γ-2-thienylbutyric acid (VIII) gave octanoic acid and hexadecane-1 : 16-dioic acid. In several cases very small amounts of an additional by-product were noticed, but these were not obtained in sufficient quantity for identification. With 2-ethyl-5-heptanoylthiophen,[6] with γ-(5-alkyl-2-thienyl)butyric acids,[6] and with 2-acetyl-5-ethylthiophen, however, no dimeric product could be detected. It will be noted that these compounds have no free α-positions. Similarly, 3-acetylthionaphthen (IX) was desulphurised to 3-phenylbutan-2-one, and no dimeric product was obtained. The desulphurisation of dibenzothiophen gave diphenyl in 99% yield, and no side-products were observed.

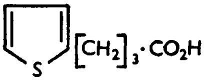
Desulphurisation of 2-benzoylthiophen.

Catalyst and remarks	Concn. of benzoylthiophen [a]	Yield of valerophenone (%) [b]	Yield of 1 : 8-dibenzoyloctane (%) [b]
W-7	1·33	58	3·8
W-7, added in portions	1·33	69	3·6
W-7	0·053	59	0·78
W-7	2·85	59	2·3
W-7, in column	—	60	0·97
Deactivated W-7	1·11	47	4·4

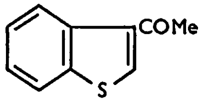
[a] Moles of 2-benzoylthiophen per l. of reaction mixture. For this purpose the volume of the catalyst (*ca.* 2 c.c./g. for fresh W-7) was deducted. [b] Based on the 2-benzoylthiophen consumed.



(VII)



(VIII)



(IX)

Discussion.—The results of the present work are consistent with the mechanism for the desulphurisation reaction which has been outlined above. The higher yields of dimeric product obtained with increasing concentration of thiophen derivative are not unexpected because under such conditions more molecules of the thiophen derivative will be chemisorbed per unit area of catalyst, and this will lead to a decrease in the mean distance between the free-radical intermediates. As the concentration is further increased, however, the yield of dimeric product is reduced. In these circumstances it is suggested that more molecules of thiophen derivative are adsorbed than can be desulphurised. The catalyst surface is " swamped," the interaction between the chemisorbed free radicals is hindered, and the rate of recombination is lowered.

No such concentration effects would be expected for the formation of the products arising by route A provided the reaction time is sufficient. The hydrogen content of the catalyst will, however, be a determining factor for this route. As the hydrogen content is decreased, route A would be expected to become less important, and the competing reaction (route B) more important. This has been confirmed, for greater yields of the dimeric products have been obtained by using deactivated catalysts.

In the desulphurisation of thiophen derivatives, the postulated intermediates must be diradicals with uncoupled electrons at positions 2 and 5 ($R-\overset{2}{\underset{\cdot}{C}}H=\overset{3}{C}H-\overset{4}{C}H=\overset{5}{\underset{\cdot}{C}}H\cdot$), and it is noteworthy that when recombination occurs it invariably involves the 5-position. Steric hindrance is evidently a factor here, making recombination at the substituted 2-position difficult or impossible. This suggests that the dimerisation must occur while the diene system is still adsorbed on the catalyst surface, for steric effects in solution would not be important unless the group R is very bulky. The failure of 2 : 5-disubstituted thiophens to give dimeric desulphurisation products is consistent with this interpretation.

Steric effects of this type have also been postulated [8] to explain the failure of 2 : 6-disubstituted pyridines to dimerise when heated with a deactivated Raney nickel catalyst.

Steric hindrance may also prevent the recombination of two free radicals from two molecules of 3-acetylthionaphthen, for no dimeric product was observed in this case. The inability of certain 3-substituted pyridines to undergo dimerisation over deactivated Raney nickel has been similarly explained.[8]

EXPERIMENTAL

Desulphurisation of 2-Benzoylthiophen.—(i) *In* 1·33M-*solution.* A solution of 2-benzoylthiophen (30 g.) in methanol (100 c.c.) was added all at once to W-7 Raney nickel (from 125 g. of alloy; and washed with methanol). After the strongly exothermic reaction had subsided, the mixture was refluxed for 5 hr. The catalyst was then separated and extracted (Soxhlet) with methanol for 24 hr. The combined methanolic solutions were evaporated and the residue was distilled to give fractions: (*a*) a colourless liquid (10 g.), b. p. 127—130°/17 mm.; (*b*) a pale green oil (10 g.), b. p. 94—94°/0·05 mm., which solidified to a colourless solid, m. p. 55—56°, alone or mixed with 2-benzoylthiophen; and (*c*) the residue (3·5 g.), which after recrystallisation from ethanol gave 1 : 8-dibenzoyloctane (0·65 g.) as colourless plates, m. p. 94—95° (Found: C, 82·1; H, 8·1; O, 10·2. Calc. for $C_{22}H_{26}O_2$: C, 81·95; H, 8·1; O, 9·9%) (Borsche *et al.*[9] report pale yellow leaflets, m. p. 91—92°). The dioxime crystallised from ethanol as colourless needles, m. p. 119—120° (Found: C, 75·4; H, 7·9; N, 7·55. Calc. for $C_{22}H_{28}O_2N_2$: C, 75·0; H, 8·0; N, 7·95%) (recorded m. p.s vary from 91—92° to 120—121°). Fraction (*a*) was characterised as *n*-valerophenone by its semicarbazone, m. p. 165—166° (lit., m. p. 166°), and by its 2 : 4-*dinitrophenylhydrazone*, which separated from chloroform as fine red needles, m. p. 152—153° (Found: C, 59·6; H, 5·25; O, 18·8. $C_{17}H_{18}O_4N_4$ requires C, 59·6; H, 5·3; O, 18·7%).

(ii) *In* 1·33M-*solution.* In a similar experiment the W-7 Raney nickel catalyst was added in portions during 1 hr., and refluxing continued for 2½ hr. Distillation gave fractions: (*a*) *n*-valerophenone (12·5 g.), b. p. 127—130°/17 mm.; (*b*) 2-benzoylthiophen (9 g.), b. p. 108—109°/0·1 mm.; (*c*) the residue (3 g.) from which 1 : 8-dibenzoyloctane (0·65 g.) was isolated.

(iii) *In* 0·053M-*solution.* The W-7 catalyst (from 80 g. of alloy) was added all at once to the benzoylthiophen (20 g.) in methanol (2000 c.c.), and the mixture refluxed for 17 hr. Working up as in method (i) gave *n*-valerophenone (6·8 g.), 2-benzoylthiophen (6·5 g.), and, from the residue (0·4 g.), 1 : 8-dibenzoyloctane (0·090 g.).

(iv) *In* 2·85M-*solution.* The W-7 catalyst (from 125 g. of alloy) was added all at once to benzoylthiophen (64·5 g.) in methanol (120 c.c.), and the mixture refluxed for 3 hr. Working up as before gave *n*-valerophenone (10 g.), 2-benzoylthiophen (45 g.), and 1 : 8-dibenzoyloxtane (0·39 g.).

(v) *In a column.* W-7 Raney nickel (from 125 g. of alloy; washed with methanol) was packed in a column (23 × 3½ cm.) with alternate beds (averaging 2 cm.) of sand. A saturated solution of the ketone (50 g.) in methanol was passed through the column under a nitrogen pressure of 10 lb./in.², considerable heat being generated as the front of the solution reached each band of catalyst; but the column had cooled to room temperature after 15 min. After 1 l. solution had been collected (1 hr.) the catalyst was extracted with boiling methanol. Working up in the usual way gave *n*-valerophenone (2·5 g.), 2-benzoylthiophen (45·15 g.), and 1 : 8-dibenzoyloctane (0·040 g.).

(vi) *In* 1·11M-*solution with deactivated catalyst.* An aqueous suspension of W-7 Raney nickel (from 80 g. of alloy) was heated at 90—95° with gentle stirring for 1 hr., then washed by decantation with methanol and added all at once to a solution of 2-benzoylthiophen (25 g.) in methanol (120 c.c.). After refluxing for 5 hr. the mixture was worked up and yielded *n*-valerophenone (4 g.), benzoylthiophen (15 g.), and 1 : 8-dibenzoyloctane (0·380 g.).

Desulphurisation of 2-Acetylthiophen.—(i) *In* 2M-*solution.* W-7 Raney nickel (from 125 g. of alloy) suspended in methanol was added all at once to 2-acetylthiophen (30 g.) in methanol, the total volume being 250 c.c., and the mixture refluxed for 5 hr. Distillation gave fractions:

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

[9] Borsche and Wollemann, *Ber.*, 1911, **44**, 3186.

(*a*) a colourless oil (16·5 g.), b. p. 110—115°/25 mm., 2-acetylthiophen [2 : 4-dinitrophenylhydrazone, m. p. 244° (lit., m. p. 245°)]; (*b*) a yellow oil (1 g.), b. p. 160°/25 mm.; and (*c*) a pale yellow solid (1 g.), b. p. 160—170°/25 mm. Fractions (*b*) and (*c*) were combined and recrystallised from light petroleum (b. p. $<$40°) at −70°, to yield dodecane-2 : 11-dione (0·270 g.) as colourless plates, m. p. and mixed m. p. 63—64·5°, and a further quantity (0·1 g.) of less pure material, m. p. 55—60°.

(ii) *In* 0·08M-*solution.* W-7 Raney nickel (from 125 g. of alloy) was added to 2-acetylthiophen (20 g.) in methanol (2000 c.c.). Distillation gave fractions: (*a*) hexan-2-one (0·87 g.), b. p. 57°/22 mm. [2 : 4-dinitrophenylhydrazone, m. p. 105° (lit., m. p. 104—105°)]; (*b*) 2-acetylthiophen (6·5 g.), b. p. 100—105°/22 mm.; (*c*) a pale yellow oil (0·83 g.), b. p. 160—170°/22 mm.; and (*d*) the residue (1 g.). Recrystallisation of the fraction (*c*) gave dodecane-2 : 11-dione (0·035 g.), m. p. 61—63°; but no pure product could be isolated from the residue.

(iii) *In* 18·5M-*solution.* A solution of 2-acetylthiophen (117 g.) in methanol (50 c.c.) was refluxed with W-7 Raney nickel (from 125 g. of alloy) for 22 hr. Working up in the usual way gave hexan-2-one (3 g.), 2-acetylthiophen (96 g.), and dodecane-2 : 11-dione (0·26 g.).

Desulphurisation of 2-*Propionylthiophen.*—A mixture of 2-propionylthiophen (27 g.) and W-7 Raney nickel (from 125 g. alloy) in ethanol (total volume 500 c.c.) was refluxed for 5 hr. Distillation of the product gave fractions: (*a*) heptan-3-one (4·4 g.), b. p. 66°/30 mm. [semicarbazone, m. p. 101—103° (lit., m. p. 102°); 2 : 4-*dinitrophenylhydrazone*, orange needles, m. p. 104—105° (from ethanol) (Found: C, 52·95; H, 6·1; O, 21·6. $C_{13}H_{18}O_4N_4$ requires C, 53·34; H, 6·2; O, 21·87)]; (*b*) 2-propionylthiophen (20 g.), b. p. 119°/29 mm., n^{20} 1·5538 (lit., n^{20} 1·5540); and (*c*) a pale yellow solid (0·5 g.), b. p. 100—120°/0·1 mm. After purification by chromatography in light petroleum (b. p. 40—100°) on alumina, fraction (*c*) yielded *tetradecane*-3 : 12-*dione* (?) (0·066 g.) as colourless plates, m. p. 78° (from hexane) (Found: C, 74·6; H, 11·7; O, 13·8. $C_{14}H_{26}O_2$ requires C, 74·3; H, 11·6; O, 14·1%).

Desulphurisation of 2-*Acetyl*-5-*ethylthiophen.*—W-7 Raney nickel (from 125 g. of alloy) was added all at once to a solution of 2-acetyl-5-ethylthiophen (24 g.) in methanol (100 c.c.). After refluxing for 7 hr. the product gave fractions: (*a*) octan-2-one (8·5 g.), b. p. 79°/23 mm. [semicarbazone, m. p. 122° (lit., m. p. 122—123°); *p*-nitrophenylhydrazone, m. p. 92—93° (lit., m. p. 92—93°)]; (*b*) 2-acetyl-5-ethylthiophen (9 g.), b. p. 125°/24 mm. [2 : 4-dinitrophenylhydrazone, m. p. 192—194° (lit., m. p. 194—194·5°)]; and (*c*) the residue (0·15 g.) from which a little 2-acetyl-5-ethylthiophen (0·09 g.) was isolated as its 2 : 4-dinitrophenylhydrazone, m. p. 192—194°.

Desulphurisation of 3-*Acetylthionaphthen.*—The desulphurisation of the ketone (30 g.) with W-7 Raney nickel (from 125 g. of alloy) was carried out as for acetylethylthiophen. Distillation of the product gave: (*a*) 3-phenylbutan-2-one (15·5 g.), b. p. 111°/23 mm. [semicarbazone, m. p. 171° (lit., m. p. 172—173°); 2 : 4-*dinitrophenylhydrazone*, orange prisms, m. p. 175—176° (chloroform–ethanol) (Found: C, 58·3; H, 4·9; O, 19·4. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9; O, 19·5%)]; (*b*) a pale green oil (1·5 g.), b. p. 150°/24 mm.; and (*c*) a pale green oil (8·5 g.), b. p. 98°/0·1 mm.; and (*d*) the residue (0·45 g.). Fraction (*c*) readily solidified and was identified as 3-acetylthionaphthen. No pure material could be isolated from the residue.

Desulphurisation of Dibenzothiophen.—A mixture of W-7 Raney nickel (from 65 g. of alloy), and dibenzothiophen (12 g.) in ethanol (total volume 100 c.c.) was refluxed for 5 hr. The catalyst was collected, washed repeatedly with hot ethanol, the combined solutions evaporated and the product distilled, to give diphenyl (9·85 g., 98%), m. p. and mixed m. p. 70°. No residue was obtained from the distillation.

Desulphurisation of γ-2-*Thienylbutyric Acid.*—W-7 Raney nickel (from 125 g. of alloy) was added all at once to an aqueous solution of γ-2-thienylbutyric acid (20 g.) and sodium carbonate (2 g.), the total volume being 300 c.c. After 2 hours' stirring at 90—95° in an open beaker the volume was 190 c.c. The mixture was slowly added to excess of hydrochloric acid under a condenser, and the resulting solution continuously extracted with ether. Distillation of the product gave: (*a*) *n*-octanoic acid (11·5 g.), b. p. 165—170°/22 mm. [*p*-bromophenacyl ester, m. p. 67° (lit., m. p. 67°)]; (*b*) γ-2-thienylbutyric acid (3 g.), b. p. 127—130°/0·6 mm. [*p*-bromophenacyl ester, m. p. 56·5—57·5° (lit., m. p. 58—59°)]; and (*c*) the residue (1 g.). The residue was taken up in aqueous sodium carbonate (charcoal), reprecipitated, recrystallised from ether, sublimed at 200°/23 mm., and recrystallised from concentrated nitric acid. Hexadecane-1 : 16-dioic acid (0·05 g.) was obtained as plates, m. p. 123—124° (lit., 124°) (Found: C, 67·4; H, 10·6; O, 22·2. Calc. for $C_{16}H_{30}O_4$: C, 67·1; H, 10·6; O, 23·35%).

Desulphurisation of Thiophen-2-carboxylic Acid.—This carboxylic acid (10 g.) was desulphurised with W-7 Raney nickel (from 125 g. of alloy) in aqueous sodium carbonate (total volume 250 c.c.) as described for γ-2-thienylbutyric acid. After 2½ hr. the catalyst was filtered off and washed with hot aqueous sodium carbonate. The combined filtrates were made up to 400 c.c. with concentrated hydrochloric acid and set aside overnight. The solid which separated (0·39 g.; m. p. 126—128°) recrystallised from concentrated nitric acid, giving sebacic acid, m. p. and mixed m. p. 132°. The filtrate was then combined with the solution obtained by treatment of the catalyst with hydrochloric acid, and the mixture extracted continuously with ether. Evaporation and distillation gave a colourless oil (5·7 g.), b. p. 94°/23 mm., which gave a *p*-bromophenacyl ester, m. p. 62—63° alone or admixed with a specimen from *n*-valeric acid. No pure substance could be isolated from the residue (1 g.) from the distillation.

Desulphurisation of β-2-Thenoylpropionic Acid.—(i) *In* 0·2M-*solution.* W-7 Raney nickel (from 125 g. of alloy) was added all at once to an aqueous solution of β-2-thenoylpropionic acid (10 g.) and sodium carbonate (3 g.), the total volume being 400 c.c. After 2 hours' stirring at 90—95° in an open beaker, the mixture was gradually added to excess of hydrochloric acid under a condenser. The product, recovered by means of ether and distilled, gave 4-hexanolactone (6·2 g.), b. p. 132—134°/22 mm., n^{25} 1·4420 (lit., b. p. 127°/16 mm., n^{25} 1·4420) [phenylhydrazide, m. p. 107—108° (lit., m. p. 108—108·5°)]. Repeated recrystallisation of the distillation residue (1 g.) from benzene–light petroleum at −70° gave (?) 4 : 13-*dihydroxyhexadecane*-1 : 16-*dioic dilactone* (0·150 g.) as leaflets, m. p. 86—88° (Found: C, 68·1; H, 9·25; O, 22·8. $C_{16}H_{26}O_4$ requires C, 68·05; H, 9·3; O, 22·7%). It was insoluble in dilute aqueous sodium carbonate and in cold aqueous sodium hydroxide, but dissolved in the latter on warming and was reprecipitated unchanged with mineral acid. It was chromatographed in benzene on " neutral " alumina with little loss. In the infrared spectrum (Nujol mull, calcium fluoride prism) it gave a single strong absorption band at 5·69 μ.

(ii) *In* 0·0445M-*solution.* The reaction as above was repeated except that the initial volume was 1350 c.c., and the time of heating 6½ hr. Working up as before gave the lactone (5·5 g.), b. p. 132—134°/22 mm., and a fraction (0·5 g.), b. p. 140—160°/22 mm., which was partly soluble in cold aqueous sodium hydrogen carbonate solution and appeared to be a mixture of the lactone and 4-oxo-octanoic acid. The residue from the distillation gave the dilactone (0·04 g.) identical with the material described above.

(iii) *In* 0·029M-*solution, with deactivated catalyst.* β-2-Thenoylpropionic acid (10 g.) in aqueous sodium carbonate (3 g. of carbonate) was added to an aqueous suspension of W-7 catalyst (from 125 g. of alloy) which had been heated at 90—95° for 1 hr., the total volume of the mixture being 2 l. After 3 hours' heating at 90—95° with stirring, the catalyst was filtered off and washed with hot aqueous sodium carbonate. Acidification with concentrated hydrochloric acid, followed by strong cooling, gave a colourless precipitate (0·36 g.) which was collected and recrystallised from ethanol. The resulting 4 : 13-dioxohexadecanedioic acid (?) formed prisms, m. p. 152—153°, alone or mixed with the specimen previously obtained,[6] and was readily soluble in aqueous sodium hydrogen carbonate.

The filtrate was combined with the solution obtained by treating the catalyst with excess of hydrochloric acid, and the mixture extracted continuously with ether. Distillation of the product gave fractions: (*a*) 4-hexanolactone (4·5 g.), b. p. 131—133°/22 mm., n^{25} 1·4420; (*b*) a colourless oil (1·3 g.), b. p. 140—155°/22 mm., largely insoluble in aqueous sodium carbonate; (*c*) a colourless solid (1·25 g.), b. p. 160—165°/22 mm., which crystallised from hexane and had m. p. 53—54° alone or mixed with 4-oxo-octanoic acid; and (*d*) the residue (1 g.) from which no crystals could be isolated.

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