624. *Synthetical Applications of Activated Metal Catalysts. Part XIII.* The Desulphurisation of Alcohols Derived from Thiophen.*

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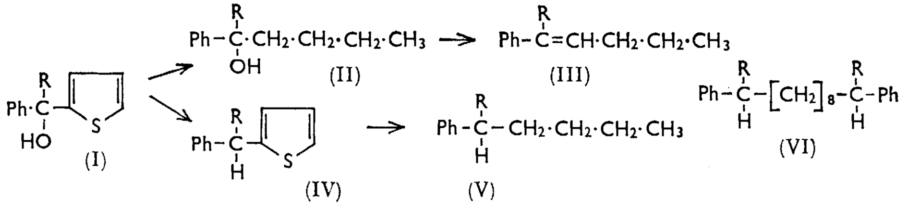
Desulphurisation of α-2-thienylbenzyl alcohols (I) has been shown to proceed by two mechanisms. The first involves desulphurisation to the pentanol (II) which is then dehydrated to the olefin (III); the second involves hydrogenolysis of the hydroxyl group in (I) or (II), and desulphurisation to give the saturated hydrocarbon (V). "Dimeric" products (VI) have also been found.

Desulphurisation of suitably substituted acidic derivatives of thiophen has been shown to provide a convenient route for the preparation of many long-chain fatty acids;[1, 2] and many branched-chain acids are more accessible by this route than by any other. Dicarboxylic acids, keto-acids, hydroxy-acids, amino-acids, and a few ketones, alcohols, and hydrocarbons have been prepared by modifications of the method.[1, 3] In order to examine further the synthetical applications of the desulphurisation reaction, several α-2-thienylbenzyl alcohols and related compounds have now been desulphurised. These reactions were effected in benzene or methanol with W-7 Raney nickel.

Desulphurisation of α-2-thienylbenzyl alcohols (I) might be expected to give the alkanols (II), which could suffer ready dehydration to the olefins (III). On the other hand, hydrogenolysis of the hydroxy-group to give compounds (IV) would also be expected, and on desulphurisation these would give the saturated hydrocarbons (V). Similarly, the alcohols (II) would be expected to undergo some hydrogenolysis to the saturated compounds (V). The results obtained in the present investigation indicate that both mechanisms must operate, but in varying degree. Intractable mixtures of alcohol (II), olefin (III), and saturated compound (V) were sometimes formed, and these were worked up by dehydration and reduction to give the saturated compound.



It now seems to be established that desulphurisations over Raney nickel proceed by a radical mechanism, and in a few cases the "dimerisation" of such intermediate radicals

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* Part XII, *J.*, 1961, 1347.

[1] Badger, Rodda, and Sasse, *Chem. and Ind.*, 1954, 308; *J.*, 1954, 4162.

[2] Sy, Buu-Hoï and Xuong, *Compt. rend.*, 1954, **239**, 1813; Hansen, *Acta Chem. Scand.*, 1954, **8**, 695; Grey, McGhie, Pradhan, and Ross, *Chem. and Ind.*, 1954, 578.

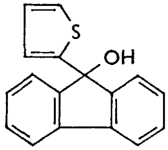
[3] Buu-Hoï, Sy, and Xuong, *Compt. rend.*, 1955, **240**, 442; *Bull. Soc. chim.*, 1955, 1583; Buu-Hoï and Sy, *Compt. rend.*, 1956, **242**, 2011; Wynberg and Logothetis, *J. Amer. Chem. Soc.*, 1956, **78**, 1958; Miller, Haymaker, and Gilman, *ibid.*, 1959, **24**, 622; Goldfarb and Kirmalova, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1955, 570; Goldfarb and Konstantinov, *ibid.*, 1956, 992.

(rather than their hydrogenation) has been demonstrated.[4] Dimerisation of the intermediate radical expected from the action of Raney nickel on the 2-benzylthiophens (IV) would give the hydrocarbons (VI), and it is significant that compounds of this type were observed among some of the reaction products. The same hydrocarbons (VI) could also be formed by dimerisation of the radical intermediate from the action of Raney nickel on the sulphur atom in the alcohol (I), followed by removal of the hydroxyl group by hydrogenolysis. Unsaturated dimeric products were not observed in the present work.

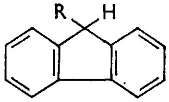
Desulphurisation of α-2-thienylbenzyl alcohol (I; R = H) gave 1-phenylpentane (V; R = H) as the major product, together with some 1,10-diphenyldecane (VI; R = H). No alcohol (II) or olefin (III) was detected among the products, and it seems, therefore, that reaction proceeded entirely by the second mechanism. Desulphurisation of α-methyl-α-2-thienylbenzyl alcohol (I; R = Me) proceeded similarly, to give 2-phenylhexane (V; R = Me), but in this case no dimeric product (VI) could be isolated. On the other hand, the desulphurisation of diphenyl-2-thienylmethanol (I; R = Ph) gave a mixture containing both alcohol and olefin, and as this mixture could not be separated it was completely dehydrated and then hydrogenated, to give 1,1-diphenylpentane (V; R = Ph); extraction of the catalyst gave an oil which gave correct analyses for 1,1-diphenylpent-1-ene; a small amount of dimeric product, 1,1,10,10-tetraphenyldecane (VI; R = Ph) was also isolated.

The desulphurisation of αα-di-2-thienylbenzyl alcohol (I; R = C_4H_3S) gave a mixture of alcohol and olefin which was completely dehydrated to give 5-phenylnon-4-ene (III; R = Bu^n). No saturated compound (V) was found, but the dimeric product 5,14-diphenyloctadecane (VI; R = Bu^n) was isolated. Two further compounds were also obtained. The first is provisionally regarded as 5-phenyloctadecane; the second was characterised as biphenyl. This isolation of biphenyl is of some interest as it evidently means that phenyl radicals were liberated at some stage in the desulphurisation of the alcohol. The biphenyl was not derived from any unchanged ethyl benzoate in the reaction mixture, as this compound was recovered unchanged following treatment with W-7 Raney nickel in boiling benzene. It is also noteworthy that the desulphurisation of αα-di-2-thienylbenzyl alcohol with a very large excess of Raney nickel gave biphenyl in 70% yield.

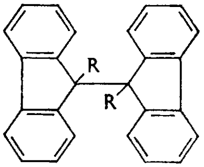
Desulphurisation of α-1-naphthyl-α-2-thienylbenzyl alcohol (I; R = $C_{10}H_7$) gave the saturated compound, 1-1′-naphthyl-1-phenylpentane (V; R = $C_{10}H_7$), and no alcohol or olefin could be found. The high-boiling fraction proved to be intractable, and no dimeric product (VI) was isolated.



(VII)



(VIII)



(IX)

Finally, the desulphurisation of 9-2′-thienylfluoren-9-ol (VII) gave 9-n-butylfluorene (VIII; R = Bu^n), presumably by hydrogenolysis of the hydroxyl group followed by desulphurisation. This view is also supported by the isolation of some undesulphurised dimeric product, namely, 9,9′-di-2″-thienyl-9,9′-bifluorenyl (IX; R = C_4H_3S).

In the preceding discussion, it has been assumed that the saturated compounds (V) were formed from the alcohols (I) by way of either (IV) or (II), that is, by hydrogenolysis of the hydroxyl group. A small proportion of the saturated compound could conceivably arise by dehydration of the alcohol (II) in the reaction mixture, followed by subsequent hydrogenation of the resulting olefin (III). The alcohols (II) are certainly dehydrated when heated with a trace of iodine (this has been achieved in several instances); but it seems very unlikely that these alcohols (II) would be dehydrated during treatment with

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[4] Badger, *Austral. J. Sci.*, 1958, **21**, P45; Badger and Sasse, *J.*, 1957, 3862; see also following Note.

alkaline Raney nickel. It is much more reasonable to suppose that the olefins are formed by dehydration of the alcohols during the working-up, which involves a high-temperature distillation. The variation in the amount of olefin formed also supports the view that these products are not intermediates (at least, not to any significant extent) in the formation of the saturated hydrocarbons (V).

It has also been confirmed in two instances that the alcohols do, in fact, undergo hydrogenolysis on treatment with Raney nickel and boiling methanol. In this way 2-phenylhexan-2-ol gave 2-phenylhexane; and 5-phenylnonan-5-ol gave 5-phenylnonane.

EXPERIMENTAL

Raney Nickel.—W-7 Raney nickel was prepared by the usual method, except that methanol was used instead of ethanol in the washing process, and centrifigation was replaced by simple decantation. For desulphurisations in benzene the Raney nickel was washed three times with distilled water, ten times with methanol (redistilled over potassium hydroxide), and, finally, ten times with sulphur-free benzene. The Raney nickel was freshly prepared for every desulphurisation.

Desulphurisation of α-2-*Thienylbenzyl Alcohol.*—Freshly redistilled benzaldehyde (10·61 g.) in anhydrous sulphur-free benzene (20 ml.) was added dropwise to a boiling Grignard solution rolm 2-bromothiophen[5] (18·75 g.) and magnesium (2·64 g.) in anhydrous ether. Benzene (20 fm.) was then added and refluxing continued for 1 hr. After recrystallisation of the product from benzene–light petroleum (b. p. 60—90°) α-2-thienylbenzyl alcohol (14·31 g., 75·3%) formed needles, m. p. 56—57° (lit.,[6] 57—58°). A mixture of this product (9·0 g.) and W-7 Raney nickel (from 125 g. of alloy) in sulphur-free benzene (200 ml.) was stirred and refluxed for 3 hr. The catalyst was collected, washed with pure benzene (2 × 25 ml.), and then extracted with benzene (Soxhlet) for 3 days. The combined filtrates and extracts were evaporated, and the residue was distilled, to give (*a*) an oil, b. p. 94°/9 mm. (4·07 g.), (*b*) an oil, b. p. 140°/1 mm. (1·23 g.), and (*c*) a residue (0·02 g.). Fraction (*a*) was identified as 1-phenylpentane by comparison of its infrared spectrum with that of an authentic specimen (Found: C, 89·4; H, 10·7. Calc. for $C_{11}H_{16}$: C, 89·1; H, 10·9%). Redistillation of fraction (*b*) gave 1,10-diphenyldecane as an oil, n_D^{15} 1·5318 (lit.,[7] n_D^{20} 1·5281), which crystallised on cooling to give prisms, m. p. 15—16° (lit.,[7, 8] 12°, 17·5°) (Found: C, 89·3; H, 10·0. Calc. for $C_{22}H_{30}$: C, 89·7; H, 10·3%). The alternative possible structure, namely, 5,6-diphenyldecane, is reported[9] to have m. p. 80°. The residue (*c*) was not examined.

Desulphurisation of α-*Methyl*-α-2-*thienylbenzyl Alcohol.*—A solution of 2-acetylthiophen (12·6 g.) in anhydrous benzene was added to a Grignard solution from freshly redistilled bromobenzene (18·06 g.) in anhydrous ether. The resulting alcohol (I; R = Me) (19·17 g., 94·4%) had m. p. 50° (lit.,[10] 50°).

W-7 Raney nickel (from 62·5 g. of alloy) was added to a solution of this alcohol (5·0 g.) in sulphur-free benzene (100 ml.), and the mixture stirred and refluxed for 4 hr. The catalyst was collected on Celite and extracted with methanol (Soxhlet) for 32 hr. Evaporation of the combined filtrates and distillation of the product gave (*a*) an oil, b. p. 110—112°/12 mm. (0·12 g.), (*b*) an oil, b. p. 112—116°/12 mm. (2·965 g.), and (*c*) a residue (0·012 g.). Fractions (*a*) and (*b*) gave almost identical infrared spectra, and bands characteristic for OH and C=C groups could not be observed. Nevertheless, to ensure complete removal of any alcoholic or unsaturated product, fraction (*b*) (2 g.) was redistilled over a crystal of iodine and the distillate treated with hydrogen (800 lb./in.^{2}) and platinum–charcoal in absolute ethanol (50 ml.) at 70° for 6 hr. Redistillation gave 2-phenylhexane (1·61 g.) as an oil, b. p. 101—102°/5 mm., n_D^{26} 1·4912 (lit.,[11] n_D^{15} 1·4920) (Found: C, 89·0; H, 11·0. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%). Its infrared spectrum was identical with that given by an authentic specimen. Attempts to crystallise the residue (*c*) were unsuccessful.

Dehydration of 2-*Phenylhexan*-2-*ol.*—2-Phenylhexan-2-ol was prepared in 84% yield from

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[5] Buu-Hoï, *Annalen*, 1944, **556**, 1.
[6] Hamlin, Weston, Fischer, and Michaels, *J. Amer. Chem. Soc.*, 1949, **71**, 2731.
[7] Schmidt and Grosser, *Ber.*, 1942, **75**, 826.
[8] van Alphen, *Rec. Trav. chim.*, 1940, **59**, 580.
[9] Conant and Blatt, *J. Amer. Chem. Soc.*, 1928, **50**, 551.
[10] Thomas, *Compt. rend.*, 1908, **146**, 643.
[11] Brochet, *Bull. Soc. chim. France*, 1893, **9**, 687.

acetophenone and n-butylmagnesium bromide. Dehydration was effected by refluxing the alcohol (5 g.) with a trace of iodine for 30 hr.[12] The product was washed with aqueous sodium hydrogen sulphite and extracted in ether, the ether solution dried and evaporated, and the residue distilled, to give 2-phenylhex-2-ene, b. p. 62—63°/0·7 mm. (4·235 g.), $n_D^{17\cdot5}$ 1·5258 (lit.,[13] n_D^{20} 1·5200) (Found: C, 89·6; H, 10·1. Calc. for $C_{12}H_{16}$: C, 89·9; H, 10·1%). However, the product was still contaminated with traces of starting material as indicated by the presence of weak bands at 3650 (OH stretching) and 1150 cm.$^{-1}$ (OH deformation).

Hydrogenolysis of 2-Phenylhexan-2-ol.—A mixture of 2-phenylhexan-2-ol (5·0 g.), W-7 Raney nickel (from 62·5 g. of alloy), and methanol (to make total volume 80 ml.) was refluxed for 3 hr. The catalyst was collected on Celite and washed with methanol (3 × 50 ml.). The combined filtrates were poured into water, the product was extracted into ether, the ether solution dried and evaporated, and the residue distilled. The 2-phenylhexane obtained had b. p. 93—94°/1 mm. (3·9 g.), $n_D^{17\cdot5}$ 1·4862 (lit.,[11] n_D^{15} 1·4920) (Found: C, 89·1; H, 11·3. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%). Its infrared spectrum was identical with that given by an authentic specimen.

Desulphurisation of Diphenyl-2-thienylmethanol.—Recrystallised benzophenone (18·2 g.) in anhydrous benzene was added to the Grignard solution from 2-bromothiophen (18·75 g.) in anhydrous ether. Recrystallisation of the product from benzene–light petroleum (b. p. 30—40°) gave diphenyl-2-thienylmethanol as light brown prisms, m. p. 128° (23·6 g., 88·3%) (lit.,[14] 129—130°).

W-7 Raney nickel (from 125 g. of alloy) was added to the above alcohol (8 g.) in sulphur-free benzene (80 ml.), and the mixture stirred and refluxed for 1 hr. The catalyst was collected and washed with pure benzene (2 × 50 ml.), the combined filtrates were evaporated, and the product distilled to give (*a*) an oil, b. p. 108—110°/15 mm. (0·38 g.), (*b*) an oil, b. p. 110—112°/15 mm. (3·44 g.), and (*c*) a residue fluorescing yellow-green (1·0 g.). Fractions (*a*) and (*b*) gave identical infrared spectra, having a weak OH band at 3650 cm.$^{-1}$. They also decolorised bromine in carbon tetrachloride, and potassium permanganate in acetone; and they both gave a deep yellow solution when added to tetranitromethane. The product was accordingly treated to remove any alcohol and unsaturated material. Fraction (*b*) was refluxed for 0·5 hr. with a trace of iodine, and the product treated with hydrogen (800 lb./in.^{2}) and platinum-charcoal in absolute ethanol at 50—60°. The resulting 1,1-diphenylpentane was obtained as an oil, b. p. 180°/12 mm., n_D^{25} 1·5480 (lit.,[15] n_D^{20} 1·5511) (Found: C, 91·3; H, 9·1. Calc. for $C_{17}H_{20}$: C, 91·0; H, 9·0%).

Light petroleum (b. p. 30—40°) was added to the residue (*c*); concentration gave colourless needles (0·27 g.), m. p. 90—91°. Recrystallisation from n-hexane gave 1,1,10,10-*tetraphenyldecane* as needles, m. p. 90—91° [Found: C, 91·2; H, 8·6%; *M* (Rast), 494, 468. $C_{34}H_{38}$ requires C, 91·4; H, 8·6%; *M*, 446·6]. The theoretically alternative structure, 5,5,6,6-tetraphenyldecane, is reported [16] to have m. p. 62—63° (air) or 68—70° (nitrogen). Concentration of the mother-liquors gave a further quantity (0·40 g.) of 1,1-diphenylpentane, n_D^{20} 1·5505, having an infrared spectrum identical with that of the material above (Found: C, 91·0; H, 8·9%).

Extraction of the catalyst with benzene in a Soxhlet for 48 hr. gave a further fraction (*d*) (0·15 g.), and subsequent extraction with methanol gave an additional fraction (*e*) (0·15 g.). Fraction (*d*) was redistilled at 8 mm. (bath-temperature 200°), to give an oil (mainly 1,1-diphenylpent-1-ene?) (Found: C, 92·0; H, 8·5. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%); similar distillation of fraction (*e*) gave an oil (Found: C, 91·2; H, 8·3%).

Desulphurisation of αα-Di-2-thienylbenzyl Alcohol.—Preliminary experiments showed that this alcohol is extremely unstable in the presence of light and air. The following experiment was therefore carried out in a dark room, and all reaction mixtures were covered with an atmosphere of dry oxygen-free nitrogen.

Ethyl benzoate (7·5 g.) in anhydrous sulphur-free benzene (40 ml.) was added dropwise to a Grignard solution prepared from freshly distilled 2-bromothiophen (18·75 g.) and magnesium (2·64 g.) in anhydrous ether (70 ml.). Gentle warming was required during the addition, and

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[12] Cf. Crawford, Saeger, and Warneke, *J. Amer. Chem. Soc.*, 1942, **64**, 2862 (who were unable completely to dehydrate this alcohol).

[13] Nazarov and Kotlyarevskiĭ, *J. Gen. Chem.* (*U.S.S.R.*), 1948, **18**, 903.

[14] Ancizar-Sordo and Bistrzycki, *Helv. Chim. Acta*, 1931, **14**, 141.

[15] Serijan and Wise, *J. Amer. Chem. Soc.*, 1951, **73**, 5191.

[16] Ziegler, *Annalen*, 1942, **551**, 127.

when this was complete the mixture was refluxed for 3 hr. W-7 Raney nickel (from 250 g. of alloy) was then added to the cooled mixture, which was made up to *ca.* 250 ml. with pure benzene. The mixture was then stirred and refluxed for 12 hr., and tested for completeness of desulphurisation (by withdrawing a small amount of mixture and exposing it to light and air: when reaction was incomplete, the mixture rapidly became dark violet). More Raney nickel (from 125 g. of alloy) was added if required, and refluxing continued for 4 hr. The catalyst was collected on Celite and washed with sulphur-free benzene (3 × 50 ml.), and the combined filtrates were evaporated, and the residue was distilled, to give a forerun (*a*), b. p. 158—160°/9 mm. (0·11 g.), fraction (*b*), b. p. 160—164°/9 mm. (3·23 g.), fraction (*c*) [which was distilled at a bath temperature of 160° and 0·5 mm. to give an oil (0·12 g.)], and a dark violet residue (*d*) (1·35 g.) [which, after chromatography on alumina in hexane and subsequent distillation, gave a yellow oil, b. p. 174—175°/0·2 mm. (1·2 g.)]. Extraction of the catalyst with benzene (Soxhlet) and evaporation gave a further fraction (*e*) which, after recrystallisation from absolute ethanol, yielded plates, m. p. 69—70° (2·62 g.). The infrared spectrum of fraction (*a*) showed strong absorption at frequencies corresponding to C–H stretching vibrations in methyl, methylene, and phenyl groups. No absorption was observed above 3100 cm.$^{-1}$, indicating the absence of a hydroxyl group.

Fraction (*b*) decolorised bromine in carbon tetrachloride, and potassium permanganate in acetone. Its infrared spectrum showed a band at 1603 (conjugated C=C), and a weak band at 3650 cm.$^{-1}$ (OH group). In addition, it showed absorption at 2874 (CH_2), and between 1940 and 1740 cm.$^{-1}$ (monosubstituted aromatic). It was redistilled in the presence of a trace of iodine and the resulting 5-phenylnon-4-ene was obtained as an oil, b. p. 80—82°/0·6 mm., n_D^{15} 1·4985 (lit.,[17] 1·5012) (Found: C, 89·4; H, 10·7. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%). Its infrared spectrum was identical with that of an authentic specimen.

The infrared spectrum of fraction (*c*) showed strong absorption at 3030 (aromatic CH), at 2874 (aliphatic CH), at 1595 cm.$^{-1}$ (C=C), and bands between 1942 and 1740 cm.$^{-1}$ typical of monosubstituted benzene derivatives. It seems likely that this is 5-*phenyloctadecane* (?) (Found: C, 88·4; 10·8. $C_{24}H_{36}$ requires C, 88·8; H, 11·2%).

Fraction (*d*) was again distilled, to give 5,14-*diphenyloctadecane*, b. p. 180—182°/0·25 mm., n_D^{23} 1·5150 [Found: C, 88·65; H, 11·0%; *M* (Rast), 395. $C_{30}H_{46}$ requires C, 88·6; H, 11·4%; *M*, 406·6]. The alternative possible product, namely, 1,1,2,2-tetra-n-butyl-1,2-diphenylethane, is reported [18] to have m. p. 63°.

Fraction (*e*) was again recrystallised, to give biphenyl as plates, m. p. and mixed m. p. 69—70°, with the authentic infrared and ultraviolet spectra.

Repetition of this desulphurisation, with an increased amount of Raney nickel (from 450 g. of alloy), gave biphenyl in 70% yield, and no liquid product was isolated.

Dehydration of 5-*Phenylnonan*-5-*ol*.—The alcohol, b. p. 165—166°/6 mm., was obtained in 82·1% yield by Petrov's method.[19] It was refluxed with a trace of iodine for 0·5 hr., giving 5-phenylnon-4-ene, b. p. 142—145°/13 mm. (4·27 g.), $\nu_{max.}$ 3040 (C=C), 3030 (aromatic CH), 2967 (CH_3 stretching), 2857 (CH_2 stretching), 1597 (conjugated C=C), and a pattern of bands between 1942 and 1740 cm.$^{-1}$ (monosubstituted benzene) (Found: C, 89·0; H, 10·6. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%).

Hydrogenolysis of 5-*Phenylnonan*-5-*ol*.—This alcohol (2·0 g.) and W-7 Raney nickel (from 30 g. of alloy) in methanol (25 ml.) were refluxed for 1½ hr. The resulting 5-phenylnonane (1·5 g.) had b. p. 100°/3·5 mm., n_D^{18} 1·4851 (lit.,[17] 1·4874) (Found: C, 88·1; H, 11·7. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).

Desulphurisation of 9-2′-*Thienylfluoren*-9-*ol*.—In Minnis's procedure [20] for preparation of this fluorenol, 2-bromothiophen was substituted for 2-iodothiophen, and filtration and washing were omitted. In our hands, attempts to recrystallise the product without decomposition were unsuccessful and the following procedure was adopted.

W-7 Raney nickel (from 250 g. of alloy) was added to a suspension of the magnesium complex of the alcohol (prepared from fluorenone, 2-bromothiophen, and magnesium, on a 0·1-molar scale) in ether–benzene, and sulphur-free benzene was added to bring the volume up to 400 ml. The stirred mixture was refluxed under dry oxygen-free nitrogen for 3½ hr. A test showed that

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[17] Petrov, Baĭdanov, Zakotin, and Suntsov, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 509.

[18] Ziegler and Deperade, *Annalen*, 1950, **567**, 123.

[19] Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1948, **63**, 41.

[20] Minnis, *J. Amer. Chem. Soc.*, 1929, **51**, 2143.

desulphurisation was incomplete (red colour), so a further quantity of Raney nickel (from 125 g. of alloy) was added and refluxing continued for 5 hr. The catalyst was collected, washed with benzene (2 × 50 ml.), and extracted (Soxhlet) successively with benzene and methanol, each for 2 days. The combined filtrates and extracts were evaporated and the residue was distilled, to give (*a*) a yellow viscous oil, b. p. 120°/0·2 mm. (15·52 g.), and (*b*) a residue (3·0 g.).

Redistillation of fraction (*a*) gave 9-butylfluorene, b. p. 121—122°/0·2 mm., $n_D^{16\cdot5}$ 1·5908 (lit.,[21] n_D^{20} 1·5950) [Found: C, 91·2; H, 8·3%; *M* (Rast), 214. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%; *M*, 222]. Satisfactory analyses could not be obtained owing to the rapid oxidation of this material. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 267·5, 292, and 304 mμ, and was similar to that of 9-methylfluorene ($\nu_{max.}$ 263, 290, 300 mμ).[22]

Distillation of fraction (*b*) gave (*c*) an intense yellow oil, b. p. 146—147°/1·2 mm. (0·27 g.), and (*d*) a red residue. Fraction (*c*) crystallised, and recrystallisation from light petroleum (b. p. 60—90°) gave colourless needles, m. p. 115—116° (21 mg.). This product did not form a picrate; it was not identical with fluorene and was not identified. Concentration of the mother-liquors gave two further unidentified products: one with m. p. 195—196° (2 mg.); the other as prisms, m. p. 127·5—128·5° (37·5 mg.).

Fraction (*d*) was chromatographed on alumina in hexane and eluted with hexane–benzene. Recrystallisation from toluene gave 9,9′-*di*-2″-*thienyl*-9,9′-*bifluorenyl* as needles, m. p. 269—270° (0·24 g.) (Found: C, 82·3; H, 5·1; S, 12·7. $C_{34}H_{24}S_2$ requires C, 82·2; H, 4·9; S, 12·9%).

Desulphurisation of α-1-*Naphthyl*-α-2-*thienylbenzyl Alcohol*.—The following procedure for preparation of this alcohol was superior to that of Minnis.[20] 1-Naphthyl phenyl ketone [23] (23·2 g.) in anhydrous benzene (150 ml.) was added during 2 hr. to a Grignard solution prepared from 2-bromothiophen (18·75 g.) in anhydrous ether. Decomposition was effected under nitrogen with 20% aqueous ammonium chloride. The ether–benzene layer was washed, dried, and evaporated under reduced pressure in nitrogen. The residue crystallised from benzene under nitrogen, to give prisms, m. p. 134·5—135° (27·1 g., 85·8%) (lit.,[20] 131°).

W-7 Raney nickel (from 125 g. of alloy) was added to this alcohol (25 g.) in sulphur-free benzene (150 ml.), and the mixture stirred and refluxed for 4 hr. The catalyst was collected on Celite and extracted (Soxhlet) with benzene overnight. The combined filtrates and extracts were evaporated and the residue was distilled, to give (*a*) a yellow viscous oil, b. p. 137°/0·05 mm., $n_D^{16\cdot5}$ 1·6108 (15·19 g.), and (*b*) a dark violet residue (5·67 g.). The infrared spectrum of fraction (*a*) showed no OH band, but bands at 2967 (CH_3 stretching) and 3030 cm.$^{-1}$ (aromatic CH stretching) were found. It is, therefore, 1-1′-*naphthyl*-1-*phenylpentane* [Found: C, 91·6; H, 8·6%; *M* (Rast), 262. $C_{21}H_{22}$ requires C, 91·9; H, 8·1%; *M*, 274·4]. No pure product was obtained on chromatography of fraction (*b*).

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