599. *Synthetical Applications of Activated Metal Catalysts. Part X.* The Desulphurisation of Thionaphtheno*[3,2-b]*thionaphthen.*

By G. M. Badger, N. Kowanko, and W. H. F. Sasse.

The desulphurisation of thionaphtheno[3,2-*b*]thionaphthen (I) under various conditions gave bibenzyl, *trans*-stilbene, and 2-phenylthionaphthen. No 1,2,3,4-tetraphenylcyclobutane could be obtained. The results are discussed with reference to the mechanism of desulphurisation.

THIONAPHTHENO[3,2-*b*]THIONAPHTHEN (I) was first isolated by Anschütz and Rhodius [1] as a by-product on distillation of acetylthiosalicyclic acid, and later by Baker *et al.*[2] on pyrolysis of thiosalicylic acid in tetralin in the presence of phosphorus pentoxide. Its structure was proved by desulphurisation with Raney nickel, which was reported [2] to yield bibenzyl and 1,2,3,4-tetraphenylcyclobutane (II). Ghaisas and Tilak [3] have since synthesised thionaphthenothionaphthen by an unambiguous method and confirmed its structure. The desulphurisation of thionaphthenothionaphthen is of interest for the mechanism of desulphurisation of thiophen derivatives and has now been investigated in detail. Under a variety of conditions, bibenzyl, *trans*-stilbene, and 2-phenylthionaphthen (III) have been isolated; but the reported formation of tetraphenylcyclobutane could not be confirmed.

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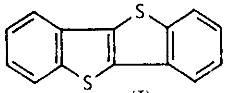
* Part IX, *J* 1960, 1658.

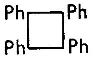
[1] Anschütz and Rhodius, *Ber.*, 1914, **47**, 2733.

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

[3] Ghaisas and Tilak, *J. Sci. Ind. Res.*, 1957, **16**, 345.

The desulphurisation of thionaphthenothionaphthen by the method of Baker *et al.*[2] gave bibenzyl in 91% yield, and no other product could be found. Use of W7 Raney nickel [4] in ethanol or in methanol similarly gave bibenzyl as the only product, in 63 and 64% yield; a W7 catalyst which had been aged for 3 months gave bibenzyl in 66% yield, and a catalyst aged for 18 months gave the same substance in 94·5% yield. The comparatively low yields of bibenzyl obtained with the most active catalysts are probably due to reduction


(I)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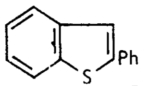
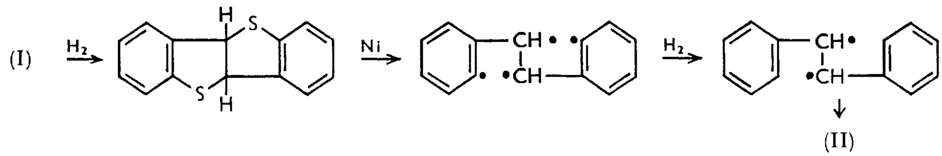

(III)

of bibenzyl to toluene (which, however, could not be detected with the quantities used; it has been observed in desulphurisation of 2,3,4,5-tetraphenylthiophen,[5] which gave some bibenzyl). When Raney cobalt was used, most of the thionaphthenothionaphthen was recovered unchanged, but some bibenzyl and *trans*-stilbene were obtained.

Poisoned and degassed nickel catalysts were also investigated in an attempt to increase the yield of unsaturated products. Although pyridine bases are known to be catalyst poisons,[6,7] 2,4,6-collidine did not inhibit the desulphurisation; but the C–C hydrogenolysis was prevented as bibenzyl was obtained in 98% yield. Desulphurisation with copper-poisoned Raney nickel [7] gave some unchanged material together with bibenzyl, 2-phenylthionaphthen, and a little *trans*-stilbene; and lead-poisoned Raney nickel similarly gave some unchanged material together with bibenzyl and 2-phenylthionaphthen. With a degassed W7-J Raney nickel,[8] at 200° in diethyl phthalate, bibenzyl was obtained in only 34% yield, the other products being 2-phenylthionaphthen (32%) and stilbene (17·5%).

It is generally accepted that the first step in desulphurisation of a thiophen derivative must be its chemisorption on the catalyst surface. This could occur (*a*) in a more or less perpendicular fashion, *via* the lone pair of electrons of the sulphur atom, or (*b*) flat, involving the π-electrons of the aromatic system.[9] The results of the desulphurisation of thionaphthenothionaphthen seem to provide information on this point. If the reported formation of 1,2,3,4-tetraphenylcyclobutane could have been confirmed it would follow that the desulphurisation probably occurs with the molecule flat on the catalyst surface, for the most feasible scheme for its formation would be as shown in the annexed sequence. However, no tetraphenylcyclobutane was obtained in the present work, though in several



experiments 2-phenylthionaphthen and *trans*-stilbene were isolated. This result lends support to the opposite view, namely, that the desulphurisation takes place in two stages and that the sulphur compound is chemisorbed in a more or less perpendicular fashion on the catalyst. It also suggests that the desulphurisation of thiophens proceeds by removal of the sulphur to give a diradical, with subsequent hydrogenation to the observed product. The alternative mechanism, namely, hydrogenation of the thiophen to the tetrahydro-stage and subsequent removal of the sulphur, seems to be excluded. Corson *et al.*[10] have already reported that the desulphurisation of 3-t-butylthionaphthen gives the expected

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[4] Billica and Adkins, *Org. Synth.*, Coll. Vol. III, p. 176.

[5] Badger, Christie, Pryke, and Sasse, *J.*, 1957, 4417.

[6] Maxted, *Adv. Catalysis*, 1951, **3**, 129; *J.*, 1948, 1093; Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

[7] Elsner and Paul, *J.*, 1953, 3156.

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

[9] Badger, *Austral. J. Sci.*, 1958, **21**, 45.

[10] Corson, Tiefenthal, Atwood, Heintzelman, and Reilly, *J. Org. Chem.*, 1956, **21**, 584.

(saturated) hydrocarbon together with 10% of the olefin that results from desulphurisation of the thionaphthen ring without hydrogenation. The isolation of *trans*-stilbene in the present work provides additional evidence that desulphurisation gives unsaturated intermediates which are subsequently hydrogenated.

EXPERIMENTAL

Thionaphtheno[3,2-b]*thionaphthen.*—The following method was simpler than that of Baker *et al.*[2] A mixture of thiosalicylic acid (25 g., B.D.H.), phosphorus pentoxide (40 g.), and tetralin (150 c.c.) was refluxed for 3 hr., the solvent decanted, and the residue extracted with boiling tetralin. The combined solutions were evaporated *in vacuo*, and the residue refluxed with potassium hydroxide (20 g.) in water (50 c.c.) and ethanol (100 c.c.) for 1 hr. After removal of the ethanol, water was added and the mixture extracted with benzene. After concentration and treatment with charcoal, the solid was collected and recrystallised from light petroleum (b. p. 80—100°) to give thionaphtheno[3,2-*b*]thionaphthen (1·6 g.), m. p. 214—216° (lit., 209—210°, 216°). A further 0·45 g. was obtained from the liquors. The m. p. was not depressed on admixture with an authentic specimen kindly supplied by Professor B. D. Tilak, and the two samples showed identical infrared spectra.

Desulphurisations with Raney Nickel.—(i) *With* W7 *Raney nickel.* A mixture of thionaphthenothionaphthen (0·5 g.), W7 Raney nickel[4] (10 g.), and ethanol (85 c.c.) was refluxed for 3·5 hr., then filtered, and the nickel washed three times with boiling ethanol. Evaporation of the solvent and distillation of the residue gave an oil, b. p. 70°/0·05 mm. (0·236 g., 62·2%), which gave the infrared spectrum of bibenzyl. No high-boiling residue was observed. Gas–liquid chromatography on Celite–Apiezon L showed the presence of a small amount of impurity as a shoulder before the major peak. Chromatography of the product in light petroleum (b. p. $<40°$) on alumina gave bibenzyl, m. p. and mixed m. p. 51—52°. A similar experiment with methanol as solvent gave bibenzyl (0·239 g., 63%), m. p. and mixed m. p. 51—51·5°.

(ii) *With* W7 *Raney nickel aged for* 3 *months.* Desulphurisation was also effected, in ethanol, with a catalyst which had been kept at room temperature for 3 months under ethanol. Bibenzyl was obtained as an oil, b. p. 70°/0·05 mm. (0·247 g. from 0·5 g.; 65%), which failed to crystallise. It was identified by its infrared spectrum.

(iii) *With* W7 *Raney nickel aged for* 18 *months.* When the catalyst had been kept under aqueous methanol at 4—10° for 18 months and then washed twice by decantation with ethanol, desulphurisation of this naphthenothionaphthen (0·5 g.) in ethanol gave bibenzyl (oil), b. p. 60°/0·01 mm. (0·368 g., 94·5%) (correct infrared spectrum). Gas–liquid chromatography at 220° on a Celite–silicone column showed only one peak, with a retention time corresponding to bibenzyl.

(iv) *With* W7-J *Raney nickel at* 220°. A mixture of W7-J Raney nickel[8] (10 g.), diethyl phthalate (6 c.c.), and thionaphthenothionaphthen (1 g.) was heated at 200° for 2 hr. The product was extracted with ether (6 hr.), the extract dried and evaporated, and the residue refluxed with alcoholic potassium hydroxide for 8 hr. Water was added; most of the ethanol was removed by distillation, and the residue was again extracted with ether. Evaporation and distillation gave 5 fractions: (*a*) bibenzyl (0·240 g.; b. p. 70°/0·01 mm.; m. p. and mixed m. p. 52°); (*b*) a solid (0·109 g.; b. p. 100°/0·01 mm.; m. p. 95—100°); (*c*) a solid (0·069 g.; b. p. 120°/0·01 mm.; m. p. 135—140°); (*d*) a solid (0·216 g.; sublimed at 125/135°/0·01 mm.; m. p. 172°); and (*e*) a residue (0·037 g.; m. p. 172—173°). Fraction (*b*) was found by gas–liquid chromatography to consist of bibenzyl (0·018 g.) and stilbene (0·091 g.) (yields calculated from areas under peaks). The stilbene was identified by treating the fraction with bromine in carbon disulphide (dibromide, m. p. and mixed m. p. 237—240°). Fraction (*c*) recrystallised from ethanol to give 2-phenylthionaphthen (0·027 g.), m. p. and mixed m. p. 176°. The mother-liquors, after evaporation, were treated with bromine in carbon disulphide to give stilbene dibromide (0·075 g.; corresponding to 0·040 g. of stilbene), m. p. and mixed m. p. 237°. Recrystallisation of fraction (*d*) and of fraction (*e*) from ethanol gave 2-phenylthionaphthen, m. p. and mixed m. p. 175—176°. Total yields: bibenzyl, 34·2%; stilbene, 17·5%; 2-phenylthionaphthen, 32·0%.

(v) Desulphurisation of thionaphthenothionaphthen (0·44 g.) was also effected by the method of Baker *et al.*[2] with Raney nickel prepared according to Brown.[4] Working up gave bibenzyl (0·304 g., 91%) which failed to solidify but was identified by its infrared spectrum. No high-boiling residue was obtained.

Desulphurisation with Raney Cobalt.—A mixture of Raney cobalt (prepared from 33 g. of cobalt–aluminium alloy by the method for W7 Raney nickel [4]), thionaphthenothionaphthen (1 g.), and ethanol (50 c.c.) was refluxed for 5·5 hr. The cooled mixture was filtered and the residue continuously extracted with ethanol for 10 hr. and then with benzene for 12 hr. Evaporation of the benzene and recrystallisation of the residue from benzene–light petroleum gave unchanged thionaphthenothionaphthen (0·268 g.; m. p. 214—216°). The combined ethanol solutions were concentrated and cooled, to give a further quantity (0·535 g.) of unchanged sulphur-compound, m. p. 216°. The mother-liquors were diluted with water and extracted with benzene. (Examination by gas–liquid chromatography showed two peaks with retention times corresponding to bibenzyl and stilbene.) Evaporation of the benzene and distillation of the residue gave fractions, (*a*) bibenzyl (0·075 g.), m. p. and mixed m. p. 52°, (*b*) b. p. 150°/0·01 mm. (0·038 g.), m. p. 140—150°, and (*c*) a residue of thionaphthenothionaphthen (0·012 g.). After recrystallisation from ethanol, fraction (*b*) gave needles, m. p. 160°; but this m. p. was depressed by admixture with 1,2,3,4-tetraphenylcyclobutane. This was prepared by photodimerisation of stilbene [12] and had m. p. 163° (Found: C, 93·6; H, 6·9. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%). Treatment of fraction (*b*) with bromine in carbon disulphide gave stilbene dibromide, m. p. and mixed m. p. 237°. The mother-liquors yielded a small amount of unchanged thionaphthenothionaphthen. A m. p.–composition curve showed that m. p. 160° corresponds to a mixture of 60% of stilbene and 40% of thionaphthenothionaphthen.

Desulphurisations with Poisoned Raney Nickel.—(i) Thionaphthenothionaphthen (1 g.) was added to a mixture of W7 Raney nickel (10 g.), methanol (100 c.c.), and 2,4,6-collidine (4 g.) which had been stirred for 2 min. After refluxing for 4 hr. the mixture was worked up and gave bibenzyl (0·745 g., 98%), m. p. and mixed m. p. 52°. No other product was detected.

(ii) Raney nickel was prepared from nickel–aluminium alloy (20 g.) by the method for W7 catalyst except that the alloy was added as quickly as possible to the alkali at 100° and digested at this temperature for 20 min. After four decantations with water and one with ethanol the catalyst was added to a solution of neutral copper acetate (2 g.) in ethanol (120 c.c.) and the mixture stirred for 20 min. on the water-bath, then decanted twice with ethanol and used at once. Desulphurisation was effected by refluxing a mixture of thionaphthenothionaphthen (1 g.) and ethanol (100 c.c.) with the poisoned catalyst for 1 hr. Working up was complicated as part of the material was obtained as an inseparable mixture (m. p. *ca.* 165°) of thionaphthenothionaphthen and 2-phenylthionaphthen, the composition of which was determined by comparison of its ultraviolet spectrum with those of mixtures of known composition. Total yields: unchanged thionaphthenothionaphthen, 0·473 g., 47·3%; 2-phenylthionaphthen, 0·193 g., 22·1%; stilbene, 0·009 g., 1·2%; and bibenzyl, 0·175 g., 23·1%.

(iii) Raney nickel was prepared as in (ii) and added to a solution of hydrated lead acetate (3·8 g.) in water (100 c.c.), and the mixture stirred on the steam-bath for 20 min., washed by decantation twice with water and twice with ethanol, and used at once. Desulphurisation was effected by refluxing thionaphthenothionaphthen (1 g.) and ethanol (100 c.c.) with the poisoned catalyst for 3 hr. Working up gave unchanged thionaphthenothionaphthen (0·482 g., 48·2%), 2-phenylthionaphthen (0·146 g., 16·7%), and bibenzyl (0·204 g., 26·9%).

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[11] Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 353.

[12] Fulton, *Brit. J. Pharmacol.*, 1948, **3**, 75; Pailer and Müller, *Monatsh.*, 1948, **79**, 615.