

# THIOPHENES AND THIAPYRANS

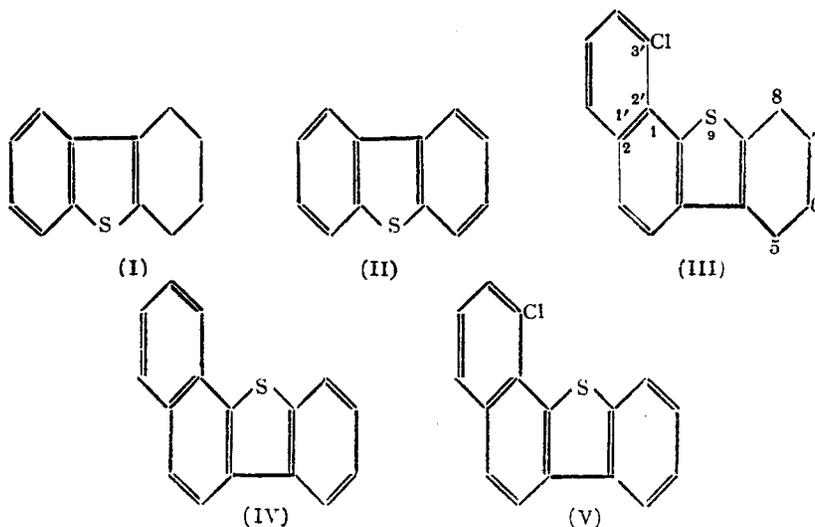
## Part IX. Studies in the Dehydrogenation of 1:2:3:4-Tetrahydrodibenzothiophene

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IN the new and general synthesis of dibenzothiophene (II) and its derivatives described recently by us, the final step involved dehydrogenation of 1:2:3:4-tetrahydrodibenzothiophene (I) and its derivatives with selenium at 300–20°. <sup>1,2</sup> Although the yield and the purity of the resulting dibenzothiophenes were good in most cases, in a few instances the yield was less satisfactory <sup>2</sup> and in the dehydrogenation of 1:2 (3'-chloro-2':1'-benzo)-5:6:7:8-tetrahydro-9-thiafluorene (III) the chlorine atom was eliminated during the dehydrogenation, with the formation of 1:2-benzo-9-thiafluorene (IV). In the case of substituted derivatives of (I), there was also the possibility of rearrangement and migration of the substituents during selenium dehydrogenation. Dehydrogenation of the model compound (I) has therefore, been exhaustively studied, with the view to arrive at the optimum conditions whereby the best yield of (II) is obtained under mild experimental conditions. Although dehydrogenation of the hydroaromatic and alicyclic compounds has been widely studied because of its importance in the elucidation of the constitution of natural products, systematic studies in the dehydrogenation of partially and fully reduced heterocyclic compounds, with the



possible exception of nitrogen heterocyclics, have not been reported in the literature. The results of the present study are, therefore, of interest not only in the synthesis of thiophene derivatives, but may also be applicable in the dehydrogenation of other heterocyclic compounds.

A brief survey of the different methods of dehydrogenations may be of interest because many of these have been employed in the present work and also because such a consolidated account does not appear to be accessible in the literature. The dehydrogenating agents may be roughly divided into the following four groups:—(1) metal and non-metal reagents, *e.g.*, sulphur and selenium, and platinum, palladium, nickel and copper-chromite catalysts. Whereas sulphur and selenium act by abstracting hydrogen as hydrogen sulphide or hydrogen selenide, the metals act catalytically; (2) quinones which act as hydrogen acceptors by being reduced to the hydroquinone derivatives; (3) halogens which are employed to halogenate the reduced compounds. The desired dehydrogenated product is then obtained by dehydrohalogenation of the intermediate halogeno derivative by treatment with a basic reagent. The intermediate halogeno derivative need not be isolated; (4) oxidizing agents like lead tetra-acetate and selenium dioxide. The first three methods are reviewed and the last method is not discussed as its use in the present work is precluded because of the susceptibility of the sulphur atom in the thiophene derivatives to oxidation.

Dehydrogenation by means of sulphur, selenium, and active forms of platinum and palladium has been discussed in a review by Plattner.<sup>3</sup> By the reaction with Raney nickel, preferably in presence of hydrogen acceptors such as benzene<sup>4</sup> or better cyclohexanone,<sup>5</sup> dehydrogenation of heterocyclic, alicyclic and hydroaromatic compounds have been carried out. When benzene is used as a hydrogen acceptor, the reaction is carried out under pressure at 275–370°, but when cyclohexanone is used, the reaction may be conducted in solvents at 70–150°. Vapour phase dehydrogenation has found commercial application in the dehydrogenation of terpenes, although the reaction may also be carried out in the liquid phase by use of sulphur or a copper-nickel formate catalyst.<sup>6</sup>

Chloranil, which was first introduced as a mild dehydrogenating agent for a few alicyclic and hydroaromatic compounds,<sup>7</sup> has recently been employed for the dehydrogenation of several hydroaromatic compounds such as tetralin which contain the group  $\text{—}\overset{|}{\text{CH}}\text{—}\overset{|}{\text{CH}}\text{—}$  adjacent to the aromatic nucleus.<sup>8</sup> By use of this reagent the dehydrogenation of reduced carbazole derivatives can be effected in good yields.<sup>9</sup>

Iodine and bromine [in the free form or in the form of N-bromosuccinimide (NBS)] have been employed in carrying out dehydrogenations. Iodine has been employed for the conversion of tetralin to naphthalene,<sup>10</sup> flavanones to flavones<sup>10</sup> and recently for the conversion of 1:2:3:4-tetrahydroanthraquinone to anthraquinone.<sup>12</sup> *l*-Menthone can be readily converted to thymol by bromination and subsequent elimination of hydrogen-bromide by treatment with quinoline.<sup>6</sup> The Wohl-Ziegler reaction<sup>13</sup> of bromination of olefines and aromatic and ketonic substances by means of NBS has been extended recently for effecting the dehydrogenation of tetralin<sup>14</sup> and of a 2:3-dihydrocoumarone derivative.<sup>15</sup> Dehydrogenation of tetralin is carried out by heating with the calculated quantity of NBS and a small amount of benzoyl peroxide in boiling carbon tetrachloride followed by addition of potassium acetate and acetic acid and continuing heating.<sup>11</sup> The reaction is thus carried out under mild conditions and is complete in one hour. 1:4-Dibromo-1:2:3:4-tetrahydronaphthalene, which is probably formed in the initial step, gives naphthalene by loss of two molecules of hydrogen bromide in the sodium acetate-acetic acid treatment. Whereas dehydrogenation with selenium or palladized carbon is carried out under drastic conditions, dehydrogenation with NBS is carried out under mild conditions, and the method promises to be of general application in compounds other than tetralin.

Most of the important dehydrogenating agents, discussed above, have been employed in the dehydrogenation of (I). The results are summarized in Table (I). Dehydrogenation with NBS was the mildest method employed and promises to be of particular value in the dehydrogenation of substituted derivatives of (I), containing functional groups such as methyl, methoxyl and halogen which are likely to suffer rearrangement or elimination under drastic conditions of dehydrogenation. Thus dehydrogenation of (III) with NBS, gave 1:2 (3'-chloro-2':1'-benzo)-9-thiafluorene (V), whereas dehydrogenation with selenium gave (IV). When the reaction product in the dehydrogenation of (III) with NBS was heated to remove residual carbon tetrachloride, considerable evolution of hydrogen bromide was noticed. In the dehydrogenation of (I) similar loss of hydrogen bromide was observed during vacuum distillation of the crude reaction product. It appears, therefore, that the dehydrobromination is not complete during the treatment with sodium acetate-acetic acid, but goes to completion during the heating involved in the isolation of the dehydrogenated product.

Dehydrogenation with selenium or palladized carbon, however, gave a clean product in high yield and even the crude substance obtained by solvent extraction was quite pure (m.p. 94–97°). Where the reduced dibenzothiophene

derivative is unlikely to undergo structural change, dehydrogenation by means of selenium or palladized carbon may be the methods of choice. The yield of (II) was slightly better when the dehydrogenation with palladized carbon was carried out in the presence of a very small amount of *p*-cymene (the reaction temperature remaining the same), than in the absence of a solvent. This may be due to the fact that unreacted (I) is brought into the reaction zone by the boiling solvent, whereas in the absence of a solvent, part of (I) gets mixed up with the sublimed product (II) and is thus removed from the reaction zone.

As regards the efficacy of other dehydrogenation methods employed, the data summarized in Table I is self-explanatory and these methods have no advantage over the use of NBS, selenium or palladized carbon.

Attempts to dehydrogenate (I) by treatment with iodine in boiling alcohol and with Raney nickel in presence of cyclohexanone as hydrogen acceptor were unsuccessful.

#### EXPERIMENTAL

##### *Reagents employed*

1:2:3:4-Tetrahydrodibenzothiophene (I) was prepared according to our recent communication.<sup>1,2</sup>

##### *Dehydrogenating agents*

Sulphur:—B.D.H. reagent sublimed.

Selenium powder:—B.D.H. reagent.

Palladized carbon (30%):—Prepared from palladium tetrachloride according to Vogel.<sup>16</sup>

Chloranil:—m.p., 290°.

Iodine:—B.P. Quality.

N-Bromosuccinimide:—Prepared according to Shirley.<sup>17</sup> m.p., 172° (quick heating).

##### *Solvents*

Quinoline:—B.D.H. Synthetic.

*p*-Cymene:— B.D.H. MAR quality.

Nitrobenzene:—B.P. 210–12°.

Carbon tetrachloride:—B.D.H. Redistilled.

##### *Procedure*

Dehydrogenation of (I) is fully described in the comprehensive Table I. Dehydrogenation of (I) has been carried out according to the methods given

TABLE I  
Dehydrogenation of 1:2:3:4-tetrahydrodibenzothiophene (I)

| No. | Amount of (I) g. | Dehydrogenating agent, g. | Solvent and temperature                 | Reaction time, hours | Crude dibenzothiophene   |                           | Pure dibenzothiophene |  | Reference                      |                           |      |
|-----|------------------|---------------------------|---|----------------------|--|---------------------------|-----------------------|--|--------------------------------|---------------------------|------|
|     |                  |                           |   |                      | Isolation method   | Yield in g. and per cent. | M.P.                  | Purification method  |                                | Yield in g. and per cent. | M.P. |
| 1   | 1.900            | S, 0.7                    | 210–220°                                | 10                   | Ether  | 2.050                     | Oil                   | Fractionation, 140–50°/3 mm.   | 1.150<br>63%                   | 95–96°                    | 3    |
| 2   | 1.460            | S, 0.52                   | Quinoline<br>20 c.c.<br>boiling         | 2                    | Addition to dilute HCl and ether-extraction  | 1.372                     | Oil                   | (a) Fractionation<br>120–30°/0.5 mm.<br>(b) Above product triturated with <i>n</i> -hexane (2 c.c.) and solvent decanted off | 0.80<br>56%<br>0.48<br>33.5%   | 85–90°<br>93–95°          | 20   |
| 3   | 1.695            | Se, 1.65                  | 280–90°                                 | 18                   | Benzene  | 1.480<br>90%              | 94–96°                | Fractionation at<br>140–50°/1.5 mm.  | 1.465<br>88.5%                 | 95–96°                    | 21   |
| 4   | 0.810            | Pd-C<br>0.08              | 325°                                    | 7                    | Product sublimed during reaction   | 0.707<br>89%              | 93–97°                | Fractionation, 145–50°/2 mm.   | 0.633<br>80%                   | 94–97°                    | 16   |
| 5   | 1.480            | Pd-C<br>0.15              | <i>p</i> -cymene<br>(0.8 g.)<br>320°    | 13                   | Ether  | 1.367<br>94%              | 95–96°                |  |                                |                           | 22   |
| 6   | 1.210            | Chloranil<br>3.3          | <i>p</i> -xylene<br>20 c.c.<br>boiling  | 36                   | Dilution with H <sub>2</sub> O, extraction with benzene. Wash extract with 10% NaOH, H <sub>2</sub> O and remove solvent by steam-distillation | 1.290                     | Oil                   | (a) Fractionation,<br>135–45°/2 mm.<br>(b) Above product sublimed,<br>98–102°/2 mm.  | 0.880<br>74%<br>0.745<br>63%   | 83–85°<br>91–94°          | 7    |
| 7   | 1.475            | I, 4.1<br>AcONa,<br>2.65  | PhNO <sub>2</sub><br>20 c.c.<br>boiling | 5                    | PhNO <sub>2</sub> removed by steam-distillation  | 1.600                     | Oil                   | (a) Fractionation,<br>140–50°/2 mm.<br>(b) Above product triturated with <i>n</i> -hexane (3 c.c.)                           | 0.950<br>66%<br>0.450<br>31.5% | 89–93°<br>93–94°          | 12   |
| 8   | 1.736            | NBS<br>3.35               | CCl <sub>4</sub><br>50 c.c.<br>boiling  | 1                    | See ref. 14  | 1.2670                    | Oil                   | Fractionation,<br>145–50°/1.5 mm.  | 1.115<br>65.5%                 | 93–95°                    | 14   |

in the references listed in the table with only minor alterations. The progress of the dehydrogenation was followed in experiments 4 and 5 by the measurement of hydrogen evolved.

Distillation temperatures refer to bath temperatures.

M.P. of dibenzothiophene cited in literature<sup>21, 23</sup>:—95–96° and 99°.

*Apparatus.*—Experiment 4 was carried out in the modified sublimation apparatus described by Vogel,<sup>16</sup> experiments 1, 2, 3, 7 were carried out in a R.B. Quickfit flask fitted with an air condenser and in experiments 6 and 8 a reflux condenser was used. Experiment 5 was conducted in an apparatus similar to that described by Linstead,<sup>18</sup> but in the present case a reflux condenser is also employed.

#### *Dehydrogenation of (III) with Selenium*

A mixture of (III) (1.2 g.) and selenium (0.81 g.) was heated at 300–20° for 14 hours. After cooling, the reaction mixture was extracted with benzene. Removal of benzene gave a brownish red powder (0.8 g., yield 87%) which on sublimation at 160–80°/3 mm. gave shining colourless plates (0.79 g., yield 77%), m.p. 185–86°, which were halogen-free. The m.p. rose to 186–87° by recrystallization from *n*-hexane (Found: C, 81.7; H, 4.5. C<sub>16</sub>H<sub>10</sub>S requires C, 82.1; H, 4.3%). The m.p. of the pure product was not depressed by admixture with a sample of pure (IV), m.p. 184–85°, prepared by a different route.<sup>19</sup>

#### *Dehydrogenation of (III) with NBS*

A mixture of (III) (250 mg.), NBS (335 mg.), benzoyl peroxide (10 mg.) and carbon tetrachloride (15 c.c.) was refluxed for 30 minutes. Potassium acetate (3 g.) and glacial acetic acid (1 c.c.) were added and heating continued for another 30 minutes. The reaction mixture was poured into cold dilute aqueous sodium hydroxide and ether extracted. The ether extract was washed, dried and solvent removed. When the residual solvent was being removed, evolution of hydrogen bromide occurred. The product on sublimation at 170–80°/0.8 mm., gave a pale yellow substance (168 mg.) m.p. 135–40°, which on two crystallizations from *n*-hexane-benzene, gave (V) as colourless needles, m.p. 147–8° (Found: C, 71.5; H 3.4. C<sub>16</sub>H<sub>9</sub>ClS requires C, 71.5; H, 3.3%). *sym*-Trinitrobenzene derivative gave orange needles from benzene, m.p. 171–72° (Found: N, 9.4. C<sub>22</sub>H<sub>12</sub>ClN<sub>3</sub>O<sub>6</sub>S requires N, 8.7%).

#### SUMMARY

The dehydrogenation of 1:2:3:4-tetrahydrodibenzothiophene (I) was studied by using various dehydrogenating agents in order to prepare dibenzothiophene (II) in optimum yield under mild conditions. Dehydrogenation

by means of selenium or palladised carbon gave good yields of (II), but the reaction was carried out at high temperatures ( $> 275^\circ$ ). By employing N-bromosuccinimide, the dehydrogenation could be carried out in a facile manner at lower temperatures ( $76^\circ$ ). These results are of value in the synthesis of derivatives of (II). Thus, whereas dehydrogenation of the chlorotetrahydrobenzothiafluorene (III) by treatment with selenium gave the benzothiafluorene (IV) by simultaneous dehydrogenation and dechlorination, dehydrogenation with N-bromosuccinimide gave the chlorine-containing benzothiafluorene (V).

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